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Ozone in Rural Areas of the United States

JENNIFER A. LOGAN

Department of Earth and Planetary Sciences and Division of Applied Sciences, Harvard University Cambridge, Massachusetts

I present the results of an analysis of ozone data from rural locations in the United States. Ozone concentrations above 80 ppb are common in the east in spring and summer, but they are unusual in the west, and ozone shows considerably more day-to-day variability in the east. Variations in ozone levels are highly correlated over distances of several hundred kilometers in the east, indicating that high values are associated with episodes of large spatial scale, >600,000 km^2. There were 10 and seven such episodes in 1978 and 1979 respectively, between the months of April and September; they persisted for 3–4 days, on average, with a range of 2–8 days, and were most common in June. Daily maximum ozone values exceeded 90 ppb at over half the sites during these episodes and were often greater than 120 ppb at one or more sites. An analysis of the meteorology for each episode shows that they occurred preferentially in the presence of weak, slow-moving, and persistent high-pressure systems. Two episodes that occurred outside the summer half of the year were associated with unseasonably warm weather; only one episode, in March 1978, appeared to reflect a major stratospheric intrusion. Concentrations of NO_x at rural locations in the east are frequently high enough (>1 ppb) to permit significant photochemical formation of ozone. It is clear that rural ozone in the east in spring and summer is severely impacted by anthropogenic emissions of NO_x and hydrocarbons, and that ozone episodes occur when the weather is particularly conducive to photochemical formation of ozone. Ozone episodes were present on 23% of days in May–August in the east in 1978–1979. The effect of these pollution episodes on vegetation cannot be assessed with current information on dose-response characteristics, which is based primarily on exposure of crops to a given level of ozone for 7 hours a day. The results presented here may be used to design studies that account for the periodic exposure of vegetation to high values of ozone for several consecutive days.

1. INTRODUCTION

It has been recognized for some time that widespread air pollution episodes occur each summer, both in the eastern United States and in Europe. These episodes are characterized by the persistence of high concentrations of ozone (>80 ppb) for several days over areas exceeding 500,000 km^2 [e.g., *Cox et al.*, 1975; *Research Triangle Institute*, 1975; *Decker et al.*, 1976; *Vukovich et al.*, 1977; *Wolff et al.*, 1977; *Guicherit and van Dop*, 1977; *Wolff and Lioy*, 1980]. They are generally associated with slow-moving high-pressure systems, when meteorological conditions are particularly conducive to photochemical formation of ozone, with warm temperatures, clear skies, and low wind speeds that allow accumulation of pollutants such as ozone. Analysis of ozone and meteorological data from the northeastern United States shows that high values of ozone are strongly associated with warm temperatures and high surface pressure and are more weakly associated with wind speed and direction [e.g., *Research Triangle Institute*, 1975; *Clark and Karl*, 1982].

Model studies of photochemical production of ozone in rural areas suggest that ozone may increase by as much as 30 ppb per day under sunny summertime conditions and that concentrations can easily reach 100 ppb in the boundary layer during a 2- to 4-day stagnation event [*Trainer et al.*, 1987; *Sillman*, 1987; *S. Sillman et al.*, A regional scale model for ozone in the United States with subgrid representation of urban and power plant plumes, submitted to the *Journal of Geophysical Research*, 1988]. Production of ozone is sensitive to concentrations of its precursors, NO_x (=NO + NO_2) and hydrocarbons, and adequate concentrations of both are required to produce elevated concentrations of ozone in rural air. The requirement for hydrocarbons depends on the reactivity of the particular species; for a typical anthropogenic mix, about 50 ppb C is needed to generate 30 ppb ozone in 1 day [*Sillman*, 1987], while for isoprene, a more reactive biogenic species, about 5 ppb C will suffice [*Trainer et al.*, 1987]; about 1 ppb of NO_x is required in either case. Exploratory data from rural locations in the eastern United States suggests that these conditions are met frequently, as discussed further below.

Elevated concentrations of ozone are thought to be responsible for most of the crop damage caused by air pollution in the United States [e.g., *Heck et al.*, 1982] and may be contributing to the observed decline of forests in Europe and the eastern United States [*Skarby and Sellden*, 1984; *Woodman and Cowling*, 1987]. Estimates of the reduction in yield of agricultural crops in the United States have been based on studies in which crops were exposed to a variety of levels of ozone for 7 hours each day (0900–1559 LT), and on data for the average value of ozone for these hours between May and September [e.g., *Heck et al.*, 1984]. (Note that in this paper LT refers to local standard time, not adjusted for daylight savings time.) There are several problems associated with these estimates. First, most of the ozone data were from urban areas; a recent study shows that use of urban data in this context may lead to an underestimate of rural values by as much as 30% [*Lefohn et al.*, 1987*b*]. Second, the 7-hour period chosen does not overlap completely with the hours that ozone is highest in rural areas, as shown below. Third, a long-term seasonal average may not be the appropriate measure of ozone to use for assessing effects on vegetation. Several studies, reviewed recently by *Lefohn and Runeckles* [1987] and by the *Environmental Protection Agency* (*EPA*) [1986], emphasize that exposure of agricultural crops to short periods of high ozone may be more damaging than

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TABLE 1. Ozone Data Used in the Analysis

Station Number	Station Location	Time Period
	SURE Sites	
1	Montague, Massachusetts	Aug. 1, 1977 to Dec. 31, 1979
2	Scranton, Pennsylvania	Aug. 1, 1977 to Dec. 31, 1979
3	Indian River, Delaware	Aug. 1, 1977 to Dec. 31, 1979
4	Duncan Falls, Ohio	Aug. 1, 1977 to Dec. 31, 1979
5	Rockport, Indiana	Aug. 1, 1977 to Dec. 31, 1979
6	Giles County, Tennessee	Aug. 1, 1977 to Dec. 31, 1979
7	Fort Wayne, Indiana	Aug. 1, 1977 to Dec. 31, 1979
8	Research Triangle Park, North Carolina	Aug. 1, 1977 to Dec. 31, 1979
9	Lewisburg, West Virginia	Aug. 1, 1977 to Dec. 31, 1979
	NAPBN Sites	
10	Green Mountain National Forest, Vermont	Jan. 1, 1979 to Sept. 30, 1982
11	Croatan National Forest, North Carolina	Jan. 1, 1979 to Dec. 31, 1982
12	Chequamegon National Forest, Wisconsin	Jan. 1, 1979 to Sept. 30, 1982
13	Mark Twain National Forest, Missouri	Jan. 1, 1979 to Dec. 31, 1982
14	Kistachie National Forest, Louisiana	Jan. 1, 1979 to Oct. 4, 1982
15	Custer National Forest, Montana	Jan. 1, 1979 to Dec. 31, 1982
16	Apache National Forest, Arizona	Jan. 1, 1980 to Dec. 31, 1983
17	Ochoco National Forest, Oregon	Jan. 1, 1980 to Dec. 31, 1983
18	Whiteface Mountain, New York	Aug. 1, 1973 to Nov. 30, 1983

long-term exposures to lower concentrations for equivalent doses (dose = concentration × time of exposure). The same may hold true for tree seedlings [*Hogsett et al.*, 1985]. Vegetation may also be more sensitive to ozone at particular times in its annual growth cycle. Ozone data available in the literature do not provide adequate information on the variability of ozone in rural areas during the growing season, or on the patterns of occurrence of high values to which vegetation appears to be most susceptible.

Most analyses of data from rural sites in North America have focused either on seasonal and diurnal behavior and frequency distributions [e.g., *Research Triangle Institute*, 1975; *Decker et al.*, 1976; *Singh et al.*, 1978; *Evans et al.*, 1983; *Evans*, 1985; *Pratt et al.*, 1983; *Fehsenfeld et al.*, 1983; *Logan*, 1985; *Mukammal et al.*, 1985; *Angle and Sandhu*, 1986; *Lefohn and Mohnen*, 1986; *Lefohn et al.*, 1987*a*; *Meagher et al.*, 1987], or on case studies of individual ozone episodes [e.g., *Research Triangle Institute*, 1975; *Vukovich et al.*, 1977, 1985; *Wolff et al.*, 1977; *Wolff and Lioy*, 1980]. *Decker et al.* [1976] provided an excellent account of pioneering field studies of rural ozone, focusing on the association between elevated ozone and the passage of stagnant high-pressure systems. This study emphasizes the variability of ozone concentrations and examines ozone episodes from a climatological perspective. I discuss frequency distributions of ozone and NO_x at rural sites in the United States and examine spatial correlation patterns of ozone among the various sites. I present an analysis of the patterns of occurrence of ozone episodes east of the Mississippi in 1978 and 1979 and discuss the frequency of ozone episodes, their duration and spatial scale, and the associated meteorology; a preliminary account was given by *Logan* [1988]. Implications of these results are discussed in section 3, and conclusions are summarized in section 4.

2. Data and Analysis

2.1. *Sources of Data*

The data discussed here were obtained in two measurement programs, the Sulfate Regional Experiment (SURE) and its continuation as the Eastern Regional Air Quality Study (ERAQS), which consisted of nine stations operated from August 1977 to December 1979 [*Mueller and Watson*, 1982; *Mueller and Hidy*, 1983], and the National Air Pollution Background Network (NAPBN), run by the Environmental Protection Agency (EPA) in cooperation with the U.S. Forest Service, which consisted of another nine stations operated from the late 1970s to 1983 [*Evans et al.*, 1983; *Evans*, 1985]. The stations and time periods used in this study are given in Table 1. These programs both employed chemiluminescence ozone analyzers; they overlapped only in 1979. The data are given hourly, with resolution of 1 ppb (SURE) or 5 ppb (NAPBN). I used also ozone data obtained concurrently at Whiteface Mountain, New York [*Mohnen et al.*, 1977; *Lefohn and Mohnen*, 1986]. All of the measurements employed in this analysis were obtained at well-characterized rural sites, although some of the sites in the east were unavoidably subject to local pollution, particularly Research Triangle Park, North Carolina. The SURE sites are located in the most populated and industrialized part of the eastern United States, while the eastern NAPBN sites

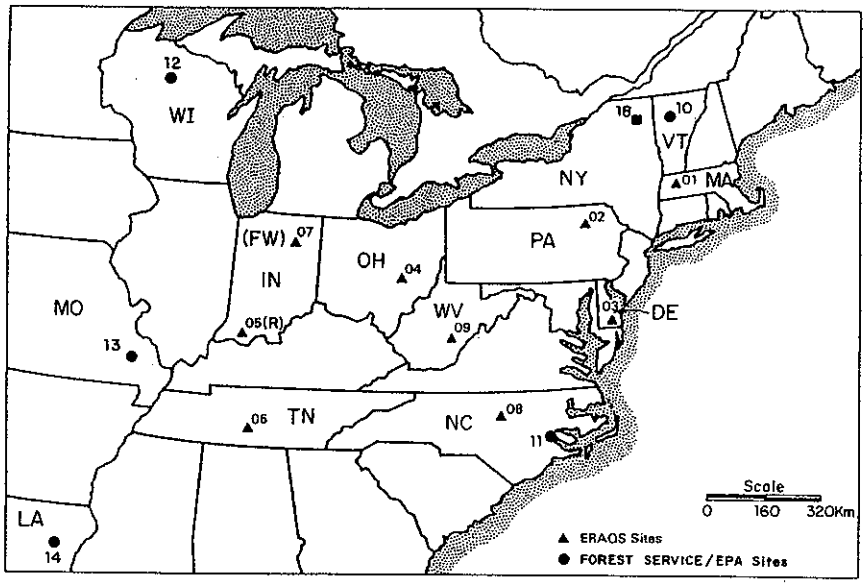

Fig. 1. Locations of ozone measurement stations in the eastern United States. Circles show the sites of the National Air Pollution Background Network [*Evans et al.*, 1983]; triangles show the SURE sites [*Mueller and Hidy*, 1983]. The square shows Whiteface Mountain, New York [*Mohnen et al., 1977*].

are on the periphery of this region, as shown in Figure 1. All SURE data are given in Eastern Standard Time.

Nitrogen oxides were also measured at the SURE sites, using a commercial chemiluminescence device with a hot molybdenum converter (300°–350°C) [*Mueller and Hidy*, 1983]. This type of instrument suffers from two problems. First, its lower limit of detection is 2 ppb; second, the conversion device is not specific to NO_2. It responds to PAN (peroxyacetyl nitrate), alkyl nitrates, and nitric acid [*Winer et al.*, 1974; *Joseph and Spicer*, 1978; *Fehsenfeld et al.*, 1987]. It is likely, however, that HNO_3 was lost on the inlet lines to the instrument [*Goldan et al.*, 1983]. Recent measurements at a rural eastern site show that NO, NO_2, PAN, HNO_3, and particulate nitrate account for over 90% of NO_y (the total of all oxidized nitrogen species), suggesting that alkyl nitrates are a small component of NO_y [*Parrish et al.*, 1986]. Hence it is likely that the SURE instrument provided a measurement that is approximately equal to (NO + NO_2 + PAN), referred to below as NO_x^*, following *Fehsenfeld et al.* [1988]. The data are given hourly, with resolution of 1 ppb.

2.2. *Behavior of Ozone at Individual Sites*

The seasonal distributions of monthly average and monthly maximum concentrations of ozone at the sites in Table 1 have been reported elsewhere [*Mohnen et al.*, 1977; *Logan*, 1985, 1988]. Concentrations are highest in spring and summer, and average concentrations are similar at all the sites, about 35–50 ppb. Monthly maximum concentrations (that is, the monthly average of the daily maximum values) at the SURE sites in the east in summer are considerably higher, however, than at sites in the west, 60–85 ppb versus 45–60 ppb. The higher maxima in the east are not reflected in the daily average values because the diurnal variation of ozone is much more pronounced at the eastern sites, with lower minima compensating for higher maxima, as shown in Figure 2. Average daily profiles show a broad maximum from about noon until about 1800 LT (or later, in a few cases) at all the eastern sites, except for the peak of Whiteface

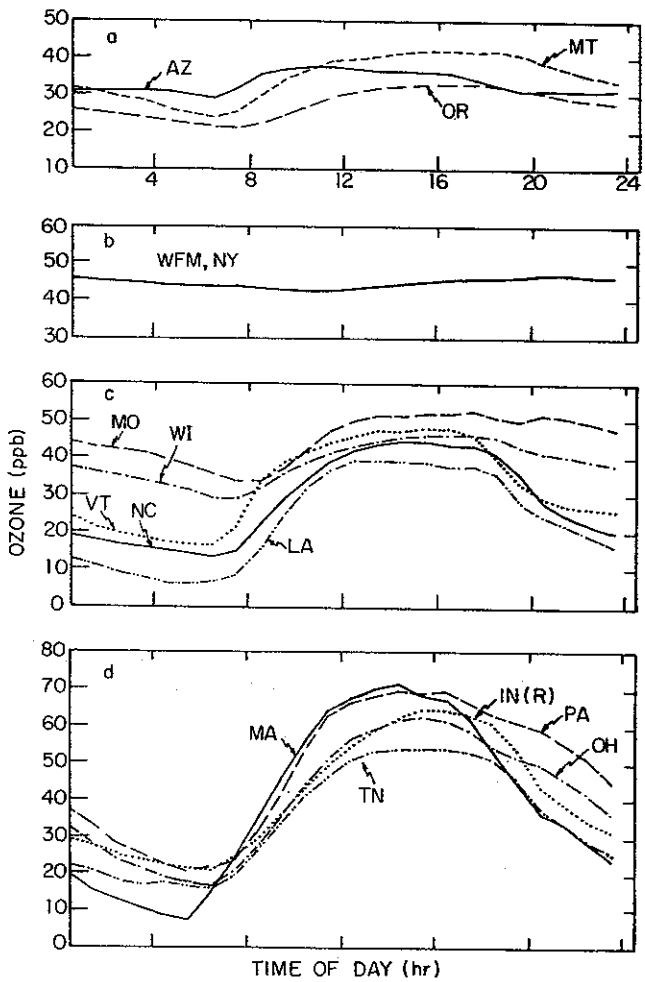

Fig. 2. Diurnal behavior of ozone at rural sites in the United States in July. (*a*) Results for the western NAPBN sites; (*b*) Whiteface Mountain; (*c*) eastern NAPBN sites; and (*d*) selected SURE sites. Sites are identified by the state in which they are located (see Table 1 and Figure 1).

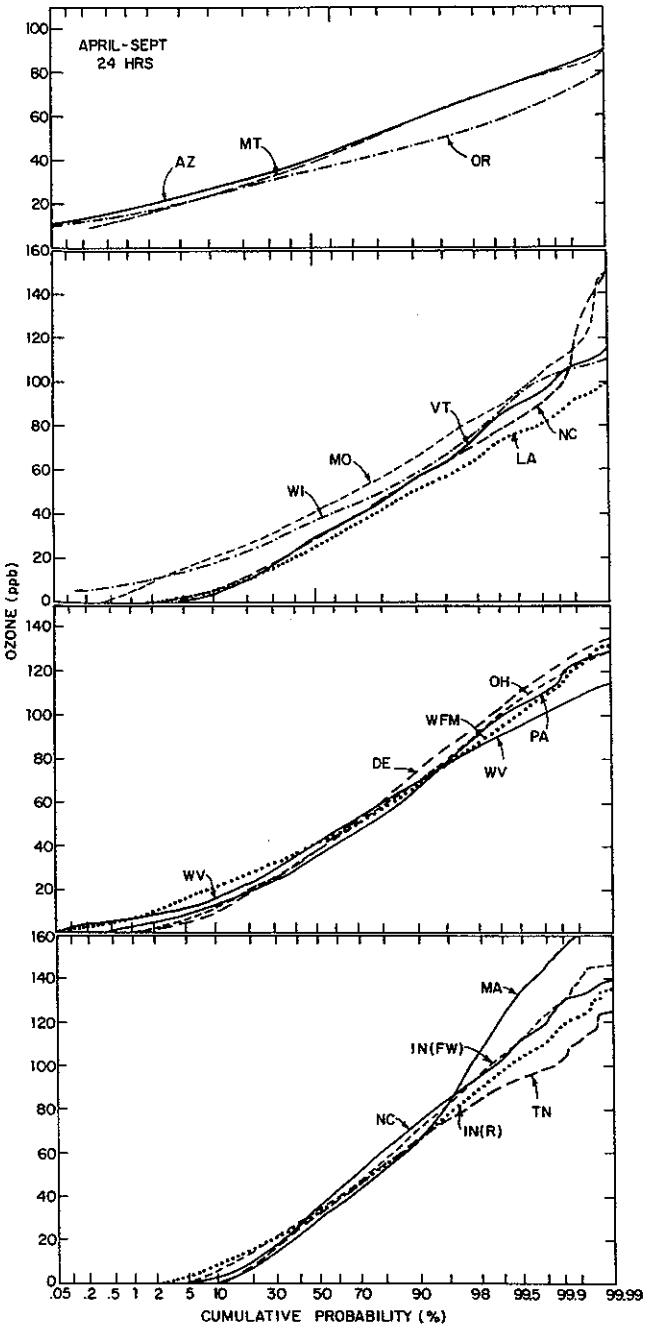

Fig. 3. Cumulative probability distributions for ozone from April 1 to September 30, from 0000–2300 LT. (Top panel) Results for the western NAPBN sites, (second panel) the eastern NAPBN sites, and (bottom two panels) the SURE sites and Whiteface Mountain. Sites are identified by the state in which they are located (see Table 1 and Figure 1); the time period included in the analysis is given in Table 1. Results are plotted on probability paper, such that normally distributed data define a straight line.

Mountain (WFM) at 1500 m where there is little diurnal variation, and highest values are found near midnight [*Mohnen et al.*, 1977]. Such behavior is characteristic of mountain stations located above the nocturnal inversion, which isolates the site from the effects of surface deposition [e.g., *Worth et al.*, 1967; *Angle and Sandhu*, 1986]. Figure 2 shows that maximum concentrations are higher at the SURE sites than at the NAPBN sites in the east; the latter are situated in more remote or coastal locations (see Figure 1). Maximum concentrations are lower still at the western NAPBN sites, which are in the most remote locations. *Decker et al.* [1976] noted previously that maximum ozone values at a remote western site were lower than at three rural sites in the midwest and east.

Figure 3 shows the cumulative frequency distributions for all sites from April 1 to September 30. Median values of ozone are similar at the sites, ~30–40 ppb, but high values occur much more often at the eastern sites than at those in the west. Ozone almost never (probability <0.5%) exceeds 80 ppb at the three western sites (top panel), while values over above 80 ppb occur between 3 and 8% of the time at the SURE sites and WFM (lower two panels) and at the NAPBN site in Missouri (site 13); values over 80 ppb are less common at the other eastern NAPBN sites that are in more remote locations (sites 10, 11, 12, and 14, Figure 1). This is illustrated further in Figure 4, which shows the number of days ozone exceeded 80 ppb and the 98%th percentile value of ozone for the eastern sites in 1979; these range from 22 to 54 days and from 80 to 103 ppb, respectively at the SURE sites and WFM, and from 5 to 39 days and 70 to 90 ppb at the NAPBN sites. The number of days that ozone exceeded 120 ppb, the National Ambient Air Quality Standard, is much smaller, 0–12 in 1979, as shown in Table 2; there were more days with high ozone in 1978 than in 1979, as discussed further below. Figure 4 and Table 2 suggest that the highest ozone values are experienced by sites that are influenced by major metropolitan and industrial sources of pollution, those in northern Indiana, Pennsylvania, Massachusetts, and Delaware. Figures 3 and 4 show that ozone values at Whiteface Mountain, a site once thought to be relatively free from the influence of pollution [*Mohnen et al.*, 1977], are typical of other rural locations in the eastern United States.

The distribution of ozone each month is shown for selected sites in Figure 5. The box plots give the 10th, 25th, 50th, 75th and 90th percentile values of ozone, and the maximum and minimum value for each month from 0800 to 1959 LT. This period is currently being used for exposure studies [e.g., *Shafer et al.*, 1987]; it was selected for the best overlap between the time of day when ozone is highest and when vegetation is photosynthetically active. The choice of a particular 12-hour period is rather arbitrary, since the diurnal behavior of ozone is not uniform at different locations, as shown in Figure 2. The panels for Massachusetts and Indiana, representing more polluted locations, show that concentrations are highest and most variable in late spring and early summer. Ozone is above 80 ppb about 25% of the time during the selected hours in June; median values are about 55–60 ppb for May, June, and July. The site at Whiteface Mountain, New York, appears to have lower ozone compared to the other eastern sites, but this merely reflects the different diurnal pattern at this site discussed earlier; maximum values occur outside the hours shown here, and high values are as common as at the other eastern sites (see Figure 3). Results from Wisconsin, a more remote eastern site, show a late spring maximum, with median values of 50 ppb and lower variability. Ozone is highest in late spring and summer at the remote western sites and displays less variability than at any of the eastern sites. Median values are lowest in Oregon, 40 ppb in summer.

Time series of daily maximum values of ozone in 1979 are shown in Figure 6 for 1979. The sites in the east show considerably more variability and significantly higher values

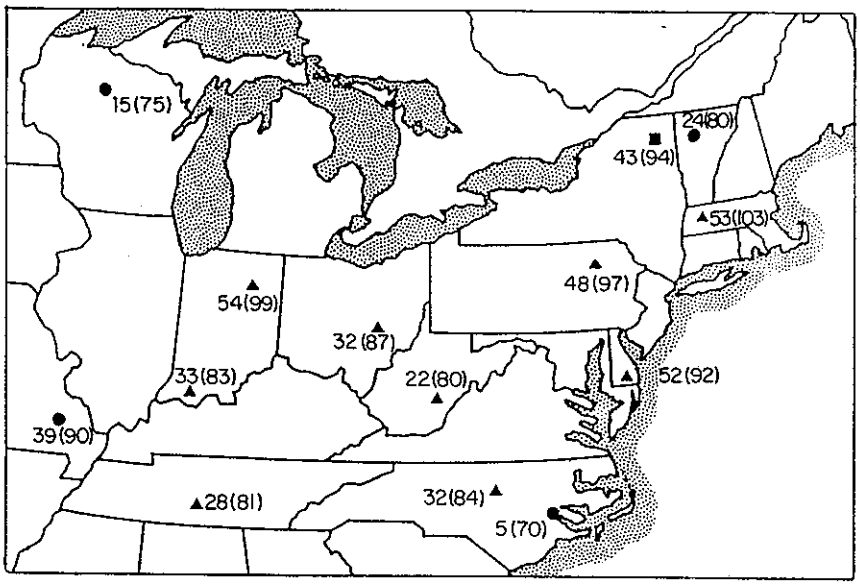

Fig. 4. Map of the number of days that ozone exceeded 80 ppb in 1979 at rural sites in the eastern United States. The 98th percentile value for ozone (in ppb) from April 1 to September 30, 1979, is also given for each site, in parentheses.

between May and August. Ozone exceeded 80 ppb on 26% of the days in these 4 months at the SURE sites and WFM in 1979 and on 39% of the days in 1978. The high values tend to occur in periods of a few days duration. Inspection of Figure 6*a*, which shows sites located within ~300 km of each other, suggests that high (and low) values tend to occur concurrently at these four sites in the northeast. Daily increases are as high as 50 ppb at the Massachusetts site, but they are generally smaller at the other eastern locations. The sites in the west (Figure 6*c*) show considerably less day-to-day variation in ozone and few values above 70 ppb, except at the Arizona site, located at 2500 m, which shows occasional values up to 90 ppb. The pattern at the Wisconsin site is intermediate between the eastern and western sites.

2.3. *Correlations of Ozone Between Sites*

An analysis was performed to evaluate whether ozone values at various sites were correlated with each other, as suggested by the data shown in Figure 6*a*. The focus was on ozone values in the afternoon, when ozone is usually at a maximum, and on the summer season, May 1 to September 30. Inspection of autocorrelograms for each hour of the day at individual sites (that is, autocorrelations of 0100 with 0100, 0200 with 0200, etc., for time lags of 0–30 days) showed that a similar pattern was found for all hours from 1000 to 1500; it was decided therefore to represent each day by a 6-hour average, 1000–1559. A typical time series and its autocorrelogram are shown in Figures 7 and 8. The half-

TABLE 2. Number of Days Ozone Exceeded 80 and 120 ppb in 1978 and 1979

Station Location	1978		1979	
	$O_3 > 80$	$O_3 > 120$	$O_3 > 80$	$O_3 > 120$
Montague, Massachusetts	48	16	53	12
Scranton, Pennsylvania	28*	1	48	3
Indian River, Delaware	79	2	52	2
Duncan Falls, Ohio	52*	6	32	0
Rockport, Indiana	69	6	33	0
Giles County, Tennessee	52*	0	28	1
Fort Wayne, Indiana	53*	5	54	3
Research Triangle Park, North Carolina	112	8	32	1
Lewisburg, West Virginia	64	0	22*	0
Green Mountain National Forest, Vermont	...	...	24*	0
Croatan National Forest, North Carolina	...	...	5	0
Chequamegon National Forest, Wisconsin	...	...	15	0
Mark Twain National Forest, Missouri	...	...	39	2
Kistachie National Forest, Louisiana	...	...	5*	0
Custer National Forest, Montana	...	...	0	0
Whiteface Mountain, New York	58	2	43	4

These numbers given represent lower limits to the total number of days in each category, as data were unavailable for some days.

*Data were missing for more than 20% of days from May 1 to September 30.

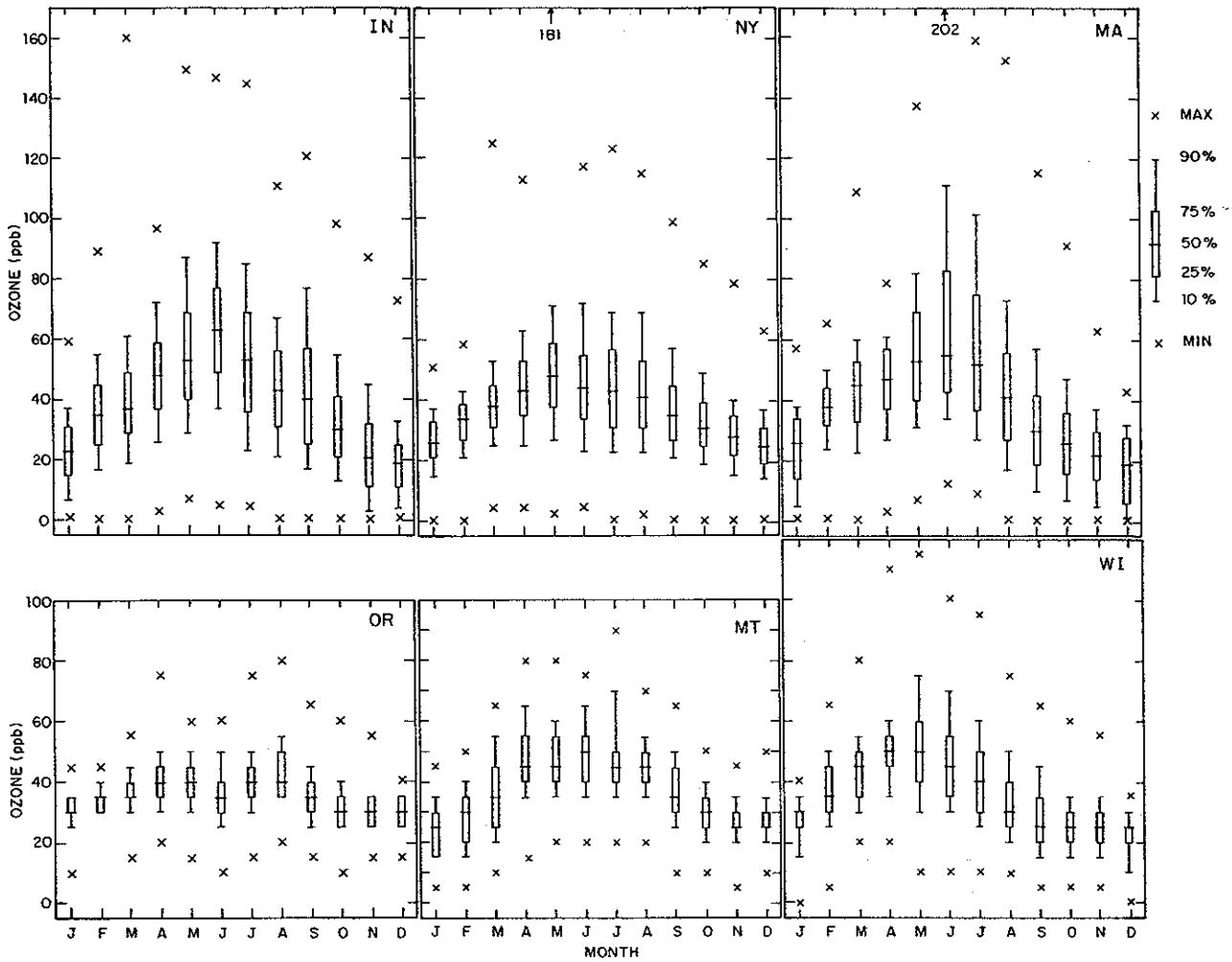

Fig. 5. Box graphs of the seasonal distribution of ozone at rural sites in the United States. The results for Indiana (IN) are for the combined measurements at the two sites in that state. Results are shown for the time period in Table 1, for the hours 0800–1959 LT. The five horizontal lines for each month show, from bottom to top, the 10th, 25th, 50th, 75th, and 90th percentiles of ozone values reported for that month for the selected hours; the crosses show the minimum and maximum values.

width of the autocorrelogram peak is ~2 days for this site, which is typical of the eastern sites.

The autocorrelation coefficient for ozone at a given site for time lag k (in days), r_k, is defined here as

$$r_k = \sum_{t=1}^{N-k} (x_t - \bar{x})(x_{t+k} - \bar{x}) \left[\sum_{t=1}^{N} (x_t - \bar{x})^2 \right]^{-1}$$

and the cross-correlation coefficient for ozone at a pair of sites for time lag k, cc_k, is

$$cc_k = \sum_{t=1}^{N-k} (x_t - \bar{x})(y_{t+k} - \bar{y}) \left[\left[\sum_{t=1}^{N} (x_t - \bar{x})^2 (y_t - \bar{y})^2 \right]^{1/2} \right]^{-1}$$

where x_i is the 6-hour average value of ozone for day i of the time series at the first site, y_i is the equivalent value at the second site, N is the number of days with concurrent measurements at both sites, and $\bar{x}$ is the mean value of x_i for the N days. For N observations of two independent normally distributed variables, approximate 95% confidence intervals for cc_k are $\pm 2/\sqrt{N}$ [*Chatfield*, 1984]; that is, correlation coefficients that fall outside these limits are significantly different from zero at the 5% level. Since daily average values of ozone are not independent but are correlated with the value on the preceding day (see Figure 8), the number of independent observations is $\approx N/2$. The 95% confidence intervals for cc_k, defined as $\pm 2/\sqrt{N/2}$, are between 0.25 and 0.34 for N in the range 70–133; this is a conservative estimate of the confidence intervals.

Figure 9 shows cross correlograms, cc_k plotted versus time lag k, for three pairs of sites separated by 200 km (Massachusetts and New York), 310 km (Ohio and Indiana) and 1070 km (Massachusetts and Indiana). The presence of a strong central peak shows that ozone is significantly correlated at each pair of sites; the correlation coefficient of the central peak is referred to as cc_k(max). The peaks at the closest two stations are coincident (top panel), while the peak at the more easterly site lags that at the westerly site by 0–1 day for the other two pairs. The full width at half height of the peaks is 3–4 days.

Cross-correlation coefficients cc_k(max) for pairs of sites in the eastern United States are shown in the top panels of

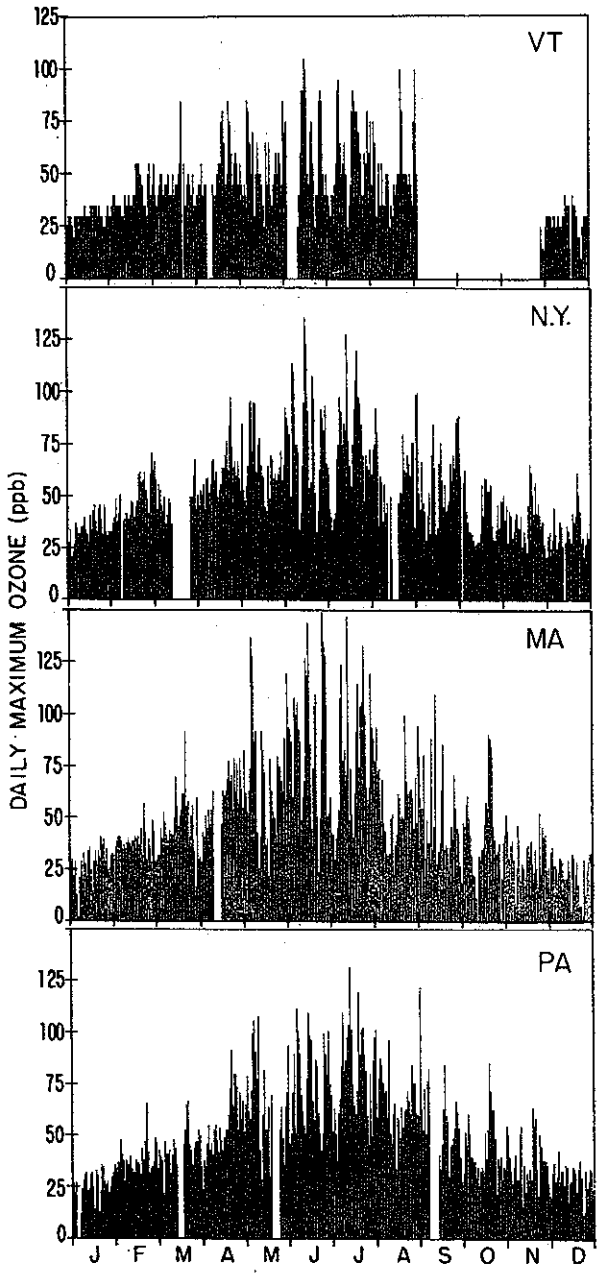

Fig. 6*a*. Time series of daily maximum values of ozone at rural sites in the northeastern United States in 1979.

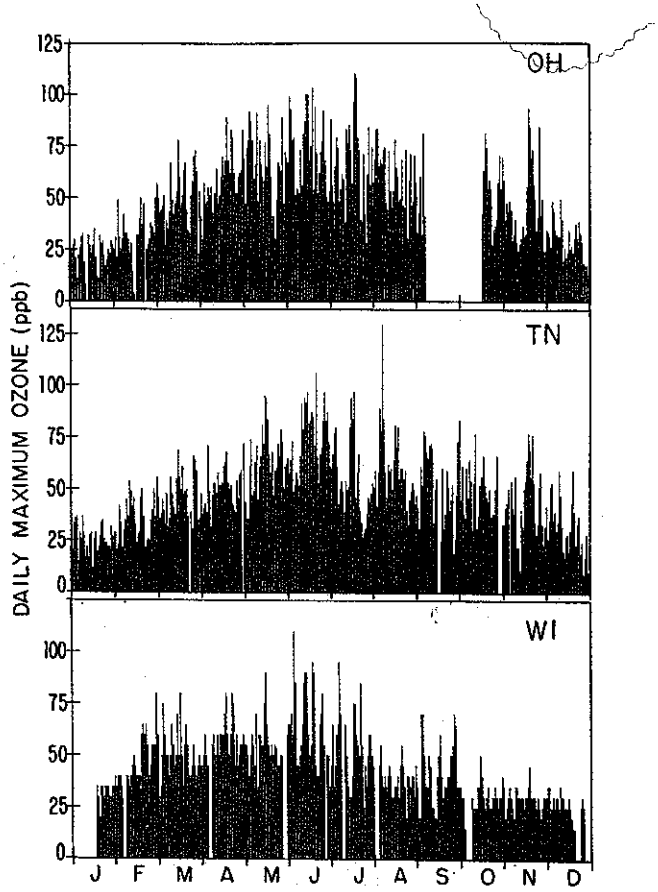

Fig. 6*b*. Time series of daily maximum values of ozone at rural sites in the central and eastern United States in 1979.

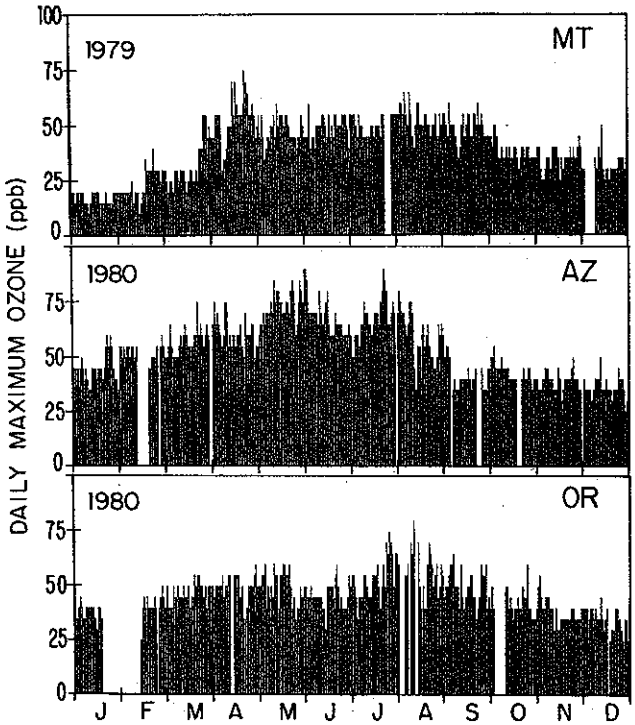

Fig. 6*c*. Time series of daily maximum values of ozone at rural sites in the western United States in 1979 (Montana) and 1980 (Arizona and Oregon).

Figures 10 and 11 for 1978 and 1979, respectively. Results are given only if cc_k(max) exceeds 0.4; these are all statistically significant according to the criterion described above. The lower panel gives the time lag of the central peak; a positive value shows that ozone at the easterly site lags that at the westerly site. Note that results for site 2 in Pennsylvania may not be representative in 1978 because data were lacking for half the study period. Correlation coefficients cc_k(max) are plotted as a function of the distance between the stations in Figure 12. There is significant correlation between ozone at most locations separated by less than 600 km and even for some locations separated by as much as 1000 km in an east–west direction. The low correlation coefficients for sites separated by less than 400 km are associated with north–south transects on the east coast. It appears that ozone is highly correlated for stations located in

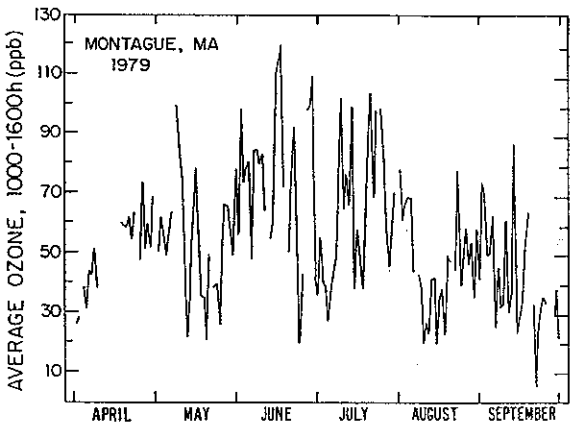

Fig. 7. Time series of 6-hour (1000–1559 LT) daily mean values for ozone at Montague, Massachusetts, for April 1 to September 30, 1979.

the southern portion of the region and for those in the north and northeast, but not between stations in the northeast and mid-Atlantic region. This pattern appears to be related to typical synoptic weather patterns, as discussed below. No significant correlations were found between the site in Louisiana and the other sites in Figure 11.

2.4. *Analysis of Ozone Episodes*

The spatial correlation analysis suggests that high values of ozone in the eastern United States tend to occur concurrently, or within 1–2 days of each other, at stations separated by several hundred kilometers. Here this analysis is extended, by selecting criteria to define the occurrence of an ozone episode in the region and examining the characteristics of these episodes.

Measurements of ozone are available for the nine SURE sites and for Whiteface Mountain in 1978 and 1979. An ozone episode is defined as the simultaneous occurrence of the average value of ozone from 1000 to 1559 LT exceeding 70 ppb at four or more of these 10 sites for 2 or more consecutive days; an episode-day is defined as the 6-hour average value of ozone exceeding 70 ppb at a single site. Most episode-days occurred during periods that also met the criterion for an ozone episode [*Logan*, 1988]. Figure 7 shows that the choice of 70 ppb should select periods when ozone was high. The upper quartile of the 6-hour averages exceeded 70 ppb at these 10 sites during April 1 to September 30, while the mean was ~55 ppb.

The number of sites exceeding 70 ppb (6-hour average) on each day from May 1 to September 30 is given in Figure 13 for 1978 and 1979; April is not included because there was only one episode, on March 31 and April 1, 1978, during these 2 years. Episodes outside the summer half of the year are discussed below. Figure 13 shows that there were 10 episodes in 1978 (including the one in early April) and seven in 1979, lasting from 2 to 8 days, with a median duration of 3–4 days. Dates of the episodes are given in Table 3. Episodes were most common in May, June, and July, and occurred with a median separation of 7 days in these months. The criterion used here to define an episode may slightly underestimate the total number, since the fraction of sites reporting data was 0.75 in 1978 and 0.86 in 1979; two sites provided no data for most of June 1978.

The selection of criteria for definition of an ozone episode is somewhat arbitrary, particularly in terms of the ozone concentration. I examined therefore the effect of an alternative definition, the simultaneous occurrence of the daily maximum value of ozone exceeding 80 ppb at four or more stations for 2 or more consecutive days. A similar definition was used independently in a study of ozone episodes in Europe [*Grennfelt et al.*, 1987]. The 17 periods classified as episodes with the first definition (a 6-hour average value of ozone >70 ppb) were also classified as episodes with the second definition, although their starting and ending dates sometimes varied by a day; in addition, there were five more "episodes" in 1978 and four more in 1979. The extra "episodes" were shorter (2–4 days), and of much smaller spatial scale, 300–600 km in an east-west direction; the daily maximum values were also smaller. It appears therefore that the original definition selects the appropriate periods as ozone episodes of large spatial scale.

Maps displaying the daily maximum values of ozone for 1 day during each episode are given in Figures 14 and 15 for 1978 and 1979, respectively; the SURE data are supplemented by the NAPBN data where possible, mostly in 1979. Daily maximum values were over 90 ppb for more than half the sites during each episode, and the National Ambient Air Quality Standard, 120 ppb, was exceeded at one or more sites for 13 of the 17 episodes (but not necessarily for the day illustrated in the figures). Aircraft measurements made during one episode (July 19–20, 1978) showed that ozone exceeded 100 ppb throughout most of the boundary layer [*Mueller and Hidy*, 1983]. Figures 14 and 15 also include information on the meteorological situation: (1) tracks of anticyclones, published monthly by the *National Oceanic and Atmospheric Association* (*NOAA*) [1978, 1979]; (2) locations of highs and fronts for days when anticyclones were not identified on the NOAA summaries, taken from daily weather maps [*National Weather Service*, 1978, 1979]; and (3) areas which experienced an air stagnation event according to the definition of *Korshover* [1976] (see also

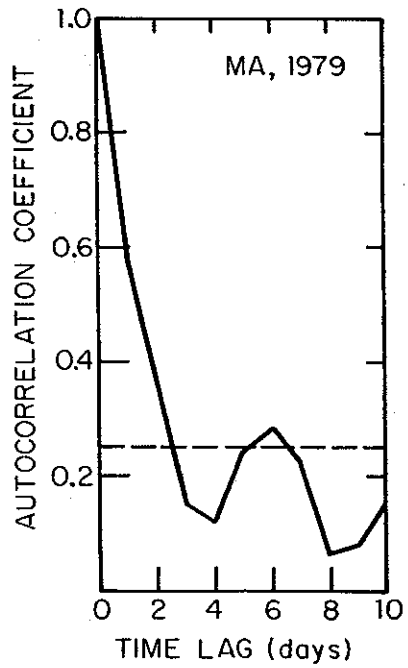

Fig. 8. The autocorrelogram for ozone from May 1 to September 30, 1979, for the time series shown in Figure 7.

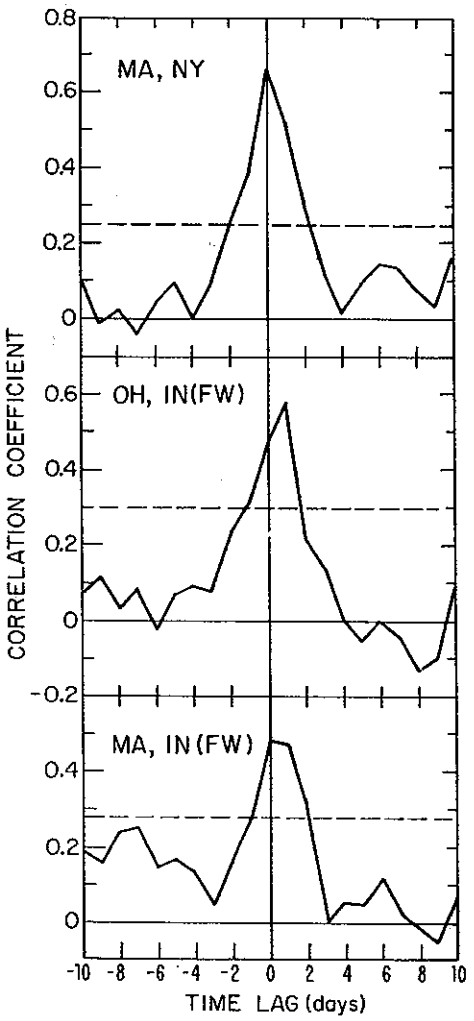

Fig. 9. Time-lagged correlation coefficients for 6-hour daily mean values of ozone at pairs of sites in the eastern United States. Values below the dashed line are not statistically significant (see text). Results are shown for May 1 to September 30, 1979. The sites in the top panel are separated by 200 km, those in the middle panel by 310 km, and those in the lower panel by 1070 km.

Korshover and Angell [1982]), areas where the surface geostrophic wind is less than 8 m s^{-1} for at least 4 days (corresponding to a surface wind less than 4 m s^{-1}); areas with any precipitation, fronts, or winds at 500 mbar exceeding ~13 m s^{-1} are excluded.

The spatial scale of the episodes shown in Figures 14 and 15 exceeds 1000 km in an east–west direction; some episodes exceed 1600 km (see Table 3). Most are at least 600 km in extent, north–south. Half of the episodes occurred during air-stagnation events, as defined by *Korshover* [1976]. This is a restrictive criterion for the type of meteorological conditions favorable for ozone production [cf. *Altshuller*, 1978]. Most episodes (13 of 17) occurred during the passage of an anticyclone across the eastern United States; two occurred the day after an anticyclone dissipated over the region, and for one of these an anticyclone formed off the east coast, while for the other a warm front crossed the region [*National Weather Service*, 1978, 1979]. The remaining two episodes occurred when the eastern United States was under the influence of high pressure, according to the daily weather maps, even though anticyclones were not identified in the NOAA monthly summaries (see Table 3).

While most ozone episodes were associated with tracks of anticyclones, the converse was not true. I examined the characteristics of the 34 anticyclones that moved through the region (shown in Figure 14) in 1978 and 1979, between May and August [*NOAA*, 1978, 1979]. All four of those that persisted for 4 or more days were associated with ozone episodes, as were five of the 10 that lasted for 3 days, but only six of the 20 that lasted for 2 days. In a few cases, more than one anticyclone occurred concurrently with an ozone episode. Of the anticyclones that lasted 3 or more days, the median pressure for those associated with episodes was 1022 mbar, while it was 1028 mbar for those that were not; the average surface pressure for these months is 1016 mbar (data for 1931–1960; *NOAA* [1968]).

The analysis of anticyclones shows that ozone episodes occur preferentially in the presence of weak, slow-moving, and persistent high-pressure systems, as they migrate from west to east, or from northwest to southeast, across the eastern half of the United States. The area influenced by these systems is substantial [*National Weather Service*, 1978, 1979]. These facts account for the high degree of correlation between ozone at sites separated by large east–west distances and for ozone at the eastern site lagging that at the western site by 1–2 days. The evolution of two major episodes, illustrating this pattern, is given by *Logan* [1988]. The results shown here, derived from 2 years of data, strengthen the conclusions of case studies of individual episodes that first showed a strong association between high ozone and the passage of high-pressure systems [e.g., *Cox et al.*, 1975; *Research Triangle Institute*, 1975; *Decker et al.*, 1976; *Vukovich et al.*, 1977; *Wolff et al.*, 1977; *Guicherit and van Dop*, 1977; *Wolff and Lioy*, 1980]. It has been argued, based on these earlier studies, that the highest ozone concentrations are usually found on the trailing side of the center of the high [*Ripperton et al.*, 1977]. This appears to be the case in somewhat less than half the cases shown here. *Vukovich and Fishman* [1986] analyzed the influence of the paths of anticyclones across the United States on concentrations of ozone in July and August of 1977–1981. They found that the spatial pattern of ozone in the eastern United States in a given month was influenced strongly by the passage of high-pressure systems. The results shown here suggests that the pattern of precursor emissions, in addition to the meteorological situation, influences the concentrations of ozone during an episode. Emissions of NO_x and hydrocarbons are highest between Illinois and New Jersey [e.g., *Middleton*, 1987], the location of most of the episodes in 1978 and 1979.

There were several episodes in which values of ozone were high in the northeast states (Massachusetts and New York), but low in the southeast (Delaware and North Carolina), and vice versa. Inspection of the daily weather maps shows that low values occur in the southeast when it is under the influence of clean air masses from the Atlantic (for example, June 16, 1979, and July 20, 1979), while the low values are found in the northeast states when they receive clean air from northern Canada (for example, June 24, 1978, and August 8, 1979). These influences account for the low correlation coefficients discussed above between ozone at stations in the two areas.

Most ozone episodes in 1978 coincided with sulfate episodes of large spatial scale (>1000 km) [*Mueller and Hidy*,

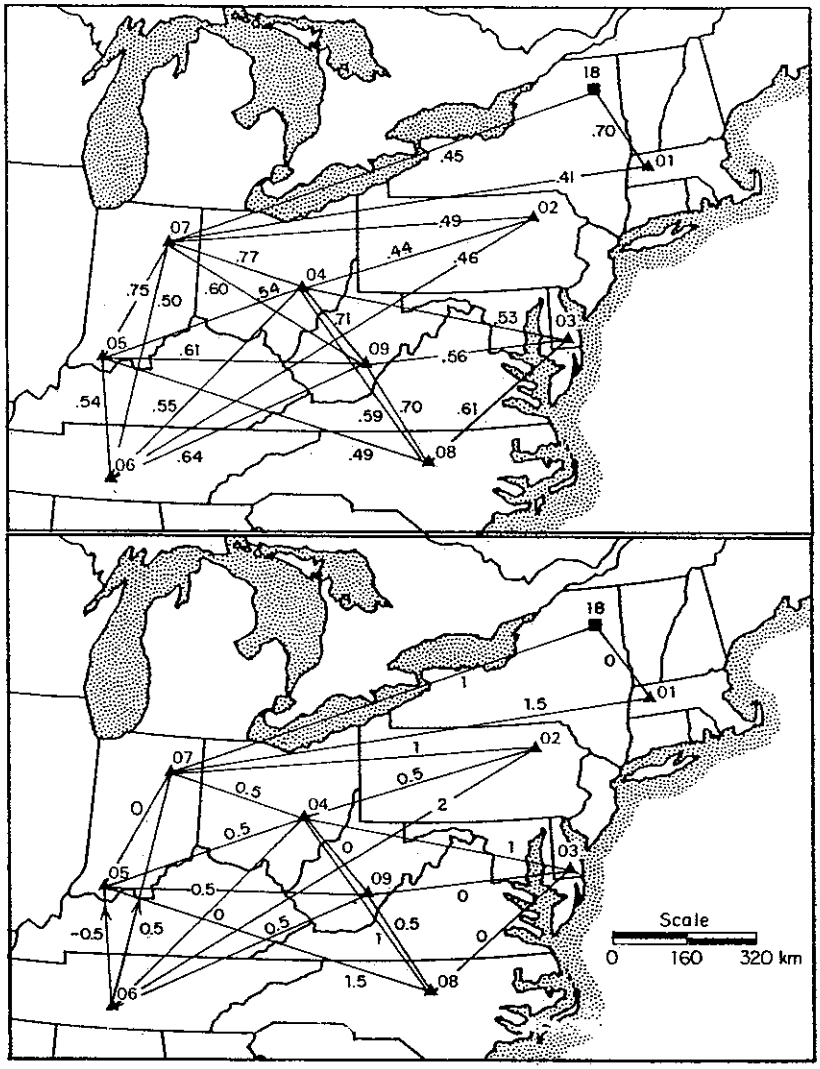

Fig. 10. (Top) Cross-correlation coefficients for ozone at pairs of sites in the eastern United States in 1978. Results are shown if the value of cc_k for the central peak, cc_k(max), exceeds 0.4, for all possible pairs among the SURE sites and WFM. (Bottom) Time in days by which the eastern site lags the western site. Further details are given in the text.

1983], although only half the sulfate episodes were concurrent with ozone episodes, as defined above (see Figure 13). However, ozone exceeded 80 ppb at four or more stations during all but one sulfate episode between mid-May and mid-September. The sulfate events in the summer half of the year occurred when the eastern United States was influenced by high-pressure systems; a detailed analysis of the sulfate episodes is given by *Mueller and Hidy* [1983].

Ozone episodes do not occur exclusively in the summer half of the year. Two brief episodes occurred in October and November of 1978 (Figure 16). Daily maximum values of ozone were lower than those found during the summer episodes, with values exceeding 90 ppb at only 1–3 sites. High-pressure systems were located in the south of the region for both, and the weather was unseasonably warm; record high temperatures were recorded in New England during the October episode [*Wagner*, 1979] and in Michigan during the November episode [*Dickson*, 1979]. The character of the March episode was different; snow was found in the north of the region, and maximum temperatures were below 7°C [*National Weather Service*, 1978]. The meteorology during this period has been analyzed in detail by *Mukammal et al.* [1985], who ascribed high values of ozone in Ontario to a stratospheric intrusion event. The data in Figure 17 show that ozone values were high over a much larger region than identified by *Mukammal et al.* [1985] for as long as 3–4 days, and that daily maximum concentrations exceeded 120 ppb on 2 consecutive days. This was the only period of elevated ozone found in the study when the weather was not conducive to photochemical formation of ozone. It has been argued that stratospheric intrusions rarely manifest themselves in elevated concentrations of surface ozone over large areas [*Viezee et al.*, 1983], and this single case in 2 years would appear to support this conclusion.

2.5. *Nitrogen Oxides in the Eastern United States*

Measurements of NO_x^* at the SURE sites provide useful information regarding the distribution of NO_x in the eastern United States, even though the data have some serious limitations, as discussed in section 2.1. The seasonal distribution of NO_x^* is shown in Figure 18. Concentrations of NO_x^* are highest in winter and lowest in summer, with monthly

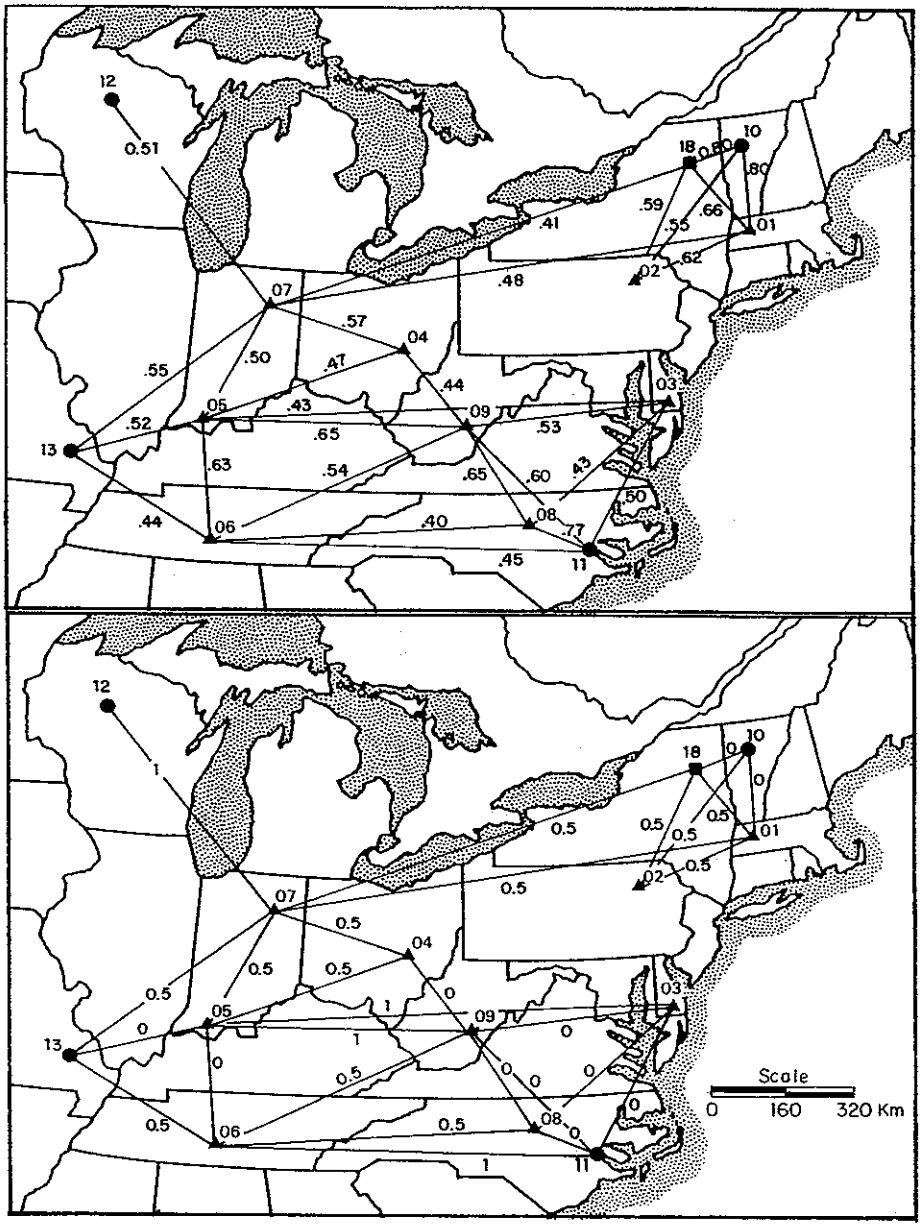

Fig. 11. (Top) Cross-correlation coefficients, cc_k(max), for ozone at pairs of sites in the eastern United States in 1979, and (bottom) time lags in days; see Figure 10 for details. In addition, correlations were calculated between each NAPBN site (numbers 10, 11, 12, 13 and 14 in Vermont, North Carolina, Wisconsin, Missouri, and Louisiana) and its nearest neighbors. The site in Louisiana was not correlated with any of the sites in the figure.

mean values in the range 4–10 ppb at six of the sites and 10–15 ppb at the other three, between April and September.

The diurnal variation of NO_x^* in summer is shown in Figure 19. Concentrations are highest from 0600 to 0900 LT, then they decrease rapidly and are almost constant from 1200 to 1800 LT, after which they increase again. There is often a secondary minimum before dawn. A similar diurnal pattern was found at Scotia, Pennsylvania, using much more sensitive instrumentation for NO_x and PAN, lending some confidence to the SURE results; *Parrish et al.* [1986] reported a morning maximum for (NO_x + PAN) of 5 ppb and an afternoon minimum of 2 ppb. *Trainer et al.* [1987] have argued that the sharp morning peak at Scotia coincides with the breakup of the morning inversion and reflects mixing of NO_x from above. This may be the case also for a few of the SURE sites that show a peak near 0900 LT, but for the others it is likely that the earlier peak at 0700 LT reflects nearby highway sources.

Parrish et al. [1986] reported that NO_x was much larger than PAN in the morning at Scotia, but concentrations of the two were similar, on average, in the afternoon, reflecting conversion of NO_x to PAN. If the same ratio held at the SURE sites, this would imply that average concentrations of NO_x in the afternoon were in the range 1–4 ppb. The median afternoon value of NO_x at Scotia was ~1.5 ppb [*Hubler et al.*, 1987].

Cumulative probabililty distributions for NO_x^* from 1200 to 1800 LT, for April 1 to September 30, are shown in Figure 20. The location with the lowest median value (<2 ppb, the lower limit of detection of the instrument) is in Delaware, near the east coast, and may receive marine air masses unpolluted by local sources; it occasionally experiences

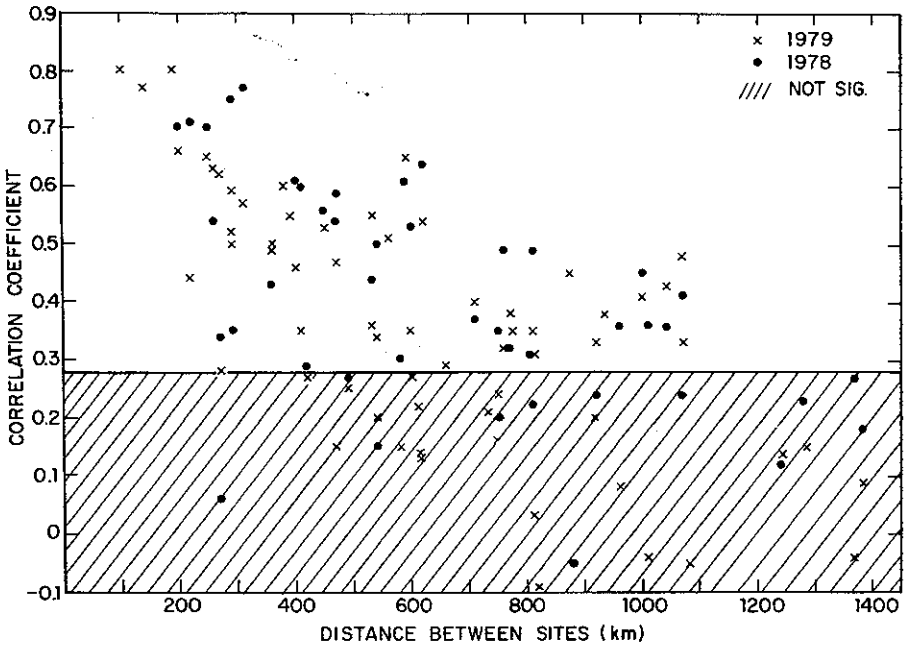

Fig. 12. Correlation coefficients, cc_k(max), for ozone at pairs of stations, as a function of distance between the stations. The shaded area shows coefficients that are not statistically significant (see text).

extremely high values because it is within 1 km of a power plant. It is unclear why NO_x^* at the site in northern Indiana is also extremely low, especially since there is a pronounced early morning peak, and the site is 2 km from a major highway. There are moderate-sized urban areas within 20 km of the two sites with largest median values, ~6 ppb (North Carolina and southern Indiana), and the remaining sites all have median values of 2–4 ppb NO_x^*. If half of the afternoon NO_x^* is PAN, the results in Figure 20 suggest that NO_x exceeds 1 ppb about 70% of the time at most eastern sites. Clearly, NO_x^* is extremely variable, with 98th percentile values in the range 11–25 ppb (excluding the Delaware site); this reflects the short lifetime of NO_x in summer (a few hours) and the difficulty of finding a site in the eastern United States removed from local sources such as highways.

2.6. *Relationship Between Ozone and NO_x^**

Buhr et al. [1986] reported that afternoon concentrations of ozone at Scotia increased from about 40 to 80 ppb, as NO_x increased from about 0.3 to 3 ppb, with most of the change occurring between 0.3 and 1 ppb; ozone was independent of NO_x above about 3 ppb. Ozone at the SURE sites appears to be independent of the concentration of NO_x^* for values exceeding 2 ppb, in general agreement with the Scotia results and with photochemical model calculations [*Liu et al.*, 1987; *Sillman et al.*, submitted manuscript, 1988]. There does not appear to be any difference in concentrations of NO_x^* during episode and nonepisode periods in summer, but this may be an artifact caused by the insensitivity of the SURE instruments to low values.

3. Discussion

3.1. *Representativeness of Ozone Data From 1978 and 1979*

The analysis of ozone episodes is based on only 2 years of data, and ozone is known to display considerable interannual variability. Five years of measurements made at the NAPBN sites on the periphery of the region suggest that 1979 was a typical year for ozone [*Evans*, 1985], while the continuation of measurements at the SURE site in Tennessee until 1984 suggest a similar conclusion for both 1978 and 1979 [*Meagher et al.*, 1987]. Data from Whiteface Mountain, however, show that ozone was higher in 1978 and 1979 than in any other year from 1974 to 1985 [*Lefohn and Mohnen*, 1986]. A recent study of ozone data in the same region as that considered here, but mainly from urban stations, for 1978–1983, suggests that ozone was higher than average in 1978 and also in 1979 in the north of the region, but lower than average in the south of the region [*Pinkerton and Lefohn*, 1987]. Maps showing monthly mean maximum values of ozone for July and August of 1977–1981 tend to support this conclusion [*Vukovich and Fishman*, 1986].

Photochemical formation of ozone is favored by particular meteorological conditions, so it is useful to compare climatological data for 1978 and 1979 with long-term averages. Monthly summaries published in each issue of *Monthly Weather Review* show that in 1978 August and September were somewhat warmer than usual, while in 1979 June and July were cooler than usual, and August and September were wetter than usual [see *Logan*, 1988]. The number of stagnation days east of the Rocky Mountains in June–August in 1978 and 1979 was the same as the average for 1976–1985 [*Korshover and Angell*, 1982; J. K. Angell, private communication, 1987] (see also *Logan* [1988]). There were, however, more stagnation days between May 1 and September 30 in the region in 1978, 26 compared with 21 in 1979. Four anticyclones spent 4–6 days crossing the region in 1978, while none lingered for more than 3 days in 1979. Given the warmer and drier weather in 1978, and the strong association shown above between ozone episodes and slow-moving anticyclones, it is not surprising that high values of ozone were more common in 1978 than in 1979. The climatological

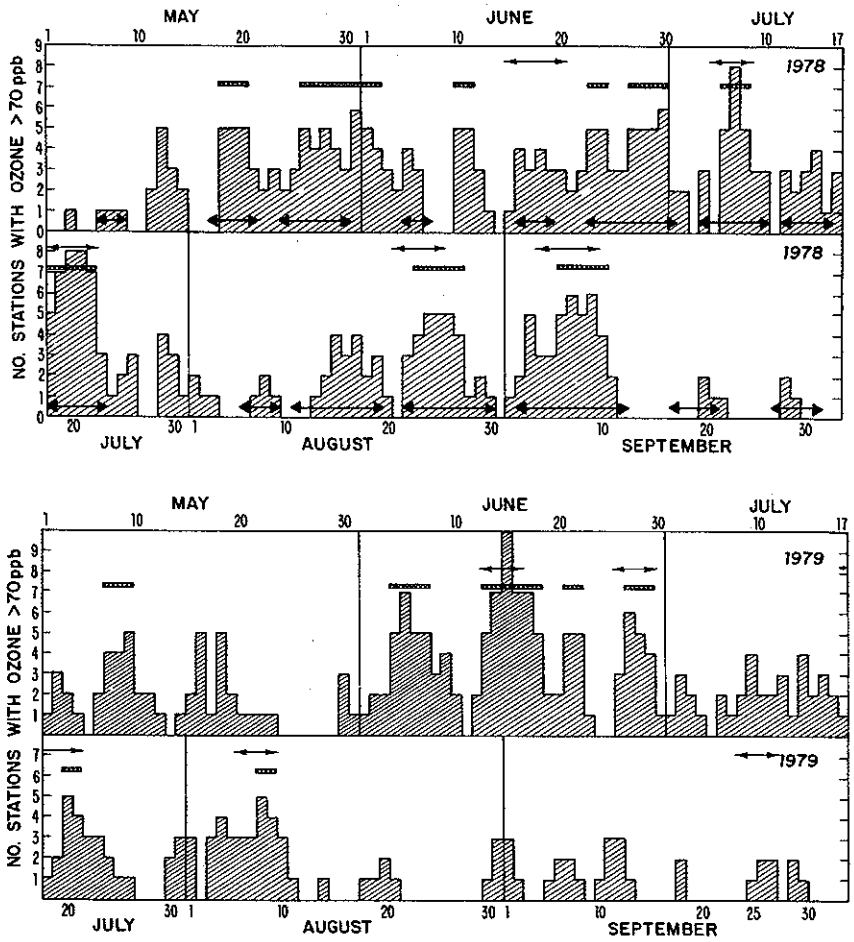

Fig. 13. Time series of the number of stations with a 6-hour mean value of ozone (1000–1600 LT) exceeding 70 ppb for 1978 and 1979. Results are shown for the nine SURE sites and Whiteface Mountain, New York (see Figure 1) for May 1 to September 30. The cross-hatched bars show the times of ozone episodes, defined by the criterion described in the text. Light arrows show the times of air stagnation events in the region, defined according to Korshover's criterion (see text). Heavy arrows in 1978 show the duration of sulfur events of large spatial scale (>1000 km), as defined by *Mueller and Hidy* [1983].

data do not, however, suggest that the weather in either year was particularly anomalous.

In summary, the ozone and meteorological data suggest that ozone in 1978 may have been higher than usual, and the frequency of episodes somewhat greater than usual, but the lack of long-term records for ozone in rural areas prevents a more quantitative assessment of this issue.

3.2. *Comparison With Ozone Data From Europe*

Comparison of the results shown here with studies of ozone episodes in western Europe [*Cox et al.*, 1975; *Guicherit and van Dop*, 1977; *Derwent et al.*, 1987; *Grennfelt et al.*, 1987] shows that maximum concentrations are similar, and episodes occur under the same type of meteorological conditions. There is some evidence, however, that elevated ozone values occur more frequently in the eastern United States. A recent study of ozone data from nine sites in West Germany for 1980–1984 shows that only one site regularly experienced concentrations above 80 ppb more often than Whiteface Mountain, New York [*Lefohn and Mohnen*, 1986]. The results in Figure 3 and Table 2 demonstrate that ozone values at Whiteface Mountain are typical of those in the eastern United States. Measurements at four British sites for about 10 years show that ozone exceeded 80 ppb on 7–12 days between April and September [*Derwent et al.*, 1987]; by comparison, ozone exceeded 80 ppb during these months on an average of 53 days in 1978 and 40 days in 1979 at the SURE sites and WFM (with a range of 21–97 days). Ozone exceeded 80 ppb on 50 days at a remote site in the Netherlands in 1976, a particularly favorable year meteorologically for ozone, but on only 4 days the following year [*Guicherit*, 1988]. Ozone was above 80 ppb on between 1 and 23 days at various sites in northwest Europe in 1985; there were six episodes (defined by a less stringent criterion, as discussed in section 2.4), and highest values were found to the south and east, in West Germany and Austria [*Grennfelt et al.*, 1987]. Preliminary measurements suggest that concentrations of NO_x^* in Europe are similar to or higher than those found at the SURE sites [*Grennfelt et al.*, 1987; *Reiter et al.*, 1987].

There are two factors that may contribute to differences in ozone in the eastern United States and northwest Europe, meteorology, and emissions of ozone precursors. The area of densest anthropogenic emissions of ozone precursors in the United States is about 10°–15° further south than in Europe, so that average summer temperatures and the flux of ultraviolet radiation are higher, favoring photochemical

TABLE 3. Ozone Episodes in 1978 and 1979

Dates	Number of Days	Stagnation Event	Anticyclone	Number of Days	Spatial Scale, km
		1978			
March 11–13	3	no	yes	2	1070
March 31 to April 1	2	no	yes	2	1070
May 18–20	3	no	yes	4	1400
May 26 to June 2	8	no	no*		1300
June 10–11	2	no	yes	3	1070
June 23–24	2	no	yes†	2	1070
June 27–30	4	no	yes	2	1070
July 6–8	3	yes	yes	4	1300
July 18–22	5	yes	no*		1300
Aug. 23–27	5	yes	yes	5	1300
Sept. 6–10	5	yes	yes	6	1300
Oct. 22–23	2	no	yes	3	1070
Nov. 5–6	2	yes	yes	2	1360
		1979			
May 7–9	3	no	no‡		1070
June 4–9	6	no	yes	3	1070
June 13–18	6	yes	yes	3	1600
June 21–22	2	no	no		1400
June 27–29	3	yes	yes†	2	1600
July 20–21	2	yes	yes	3	1600
Aug. 8–9	2	yes	yes†	2	1070

The columns give the dates of each ozone episode, as defined in the text; the length in days; the occurrence of a stagnation event, according to Korshover's criteria (see text); the occurrence of an anticyclone track east of the Mississippi on the days of the episode, as identified by *NOAA* [1978, 1979]); the number of days the anticyclone persisted in the region; and the spatial scale of the episode. Note that data were available for more sites covering a larger area in 1979.

*There was high pressure in the region, according to the daily weather maps.

†Two anticyclones influenced the region during the episode.

‡An anticyclone formed and stagnated for 2 days (May 7–8) off the east coast, just off the map on Figure 12.

formation of ozone; a detailed comparison of meteorology is beyond the scope of this study. Average emissions of NO_x are higher in Europe, because of higher population densities, and the average hydrocarbon to NO_x ratio appears to be similar to that in the United States; emission inventories for hydrocarbons in Europe are, however, poorly defined at present [*Selby*, 1987]. It is likely also that emissions of isoprene are higher in the eastern United States, because of the predominance of deciduous forests, and the higher summer temperatures. Isoprene is emitted only by certain types of vegetation, including deciduous trees; emission rates depend strongly on temperature and light intensity and are highest in the warm summer months [e.g., *Lamb et al.*, 1985, 1987]. Recent studies show that isoprene, in combination with anthropogenic sources of NO_x, may provide an important source of ozone in rural areas of the eastern United States [*Trainer et al.*, 1987].

3.3. *Requirements for an Ozone Episode*

There has been strong empirical evidence for over a decade relating pollution episodes in the industrialized continents to the passage of slow-moving high-pressure systems [e.g., *Research Triangle Institute*, 1975; *Decker et al.*, 1976]. There have been few definitive studies, however, of the mechanisms responsible for production of ozone in rural air. Direct transport of urban ozone, transport of precursors, NO_x and nonmethane hydrocarbons (NMHC), followed by photochemical production of ozone far downwind of the source region, oxidation of naturally occurring hydrocarbons, and stratospheric intrusions have all been implicated, as discussed in a recent review by *Altshuller* [1986]. The present study and many others suggest that input from the stratosphere is rarely responsible for ozone episodes. Evaluation of the relative roles of the remaining photochemical processes requires a detailed model for dynamics and photochemistry. Studies with simple photochemical models, however, have shown that ozone levels exceeding 90 ppb are to be expected in rural air during favorable meteorological conditions, given the prevailing concentrations of NO_x and hydrocarbons [*Trainer et al.*, 1987; *Sillman et al.*, submitted manuscript, 1988].

Model results suggest ozone may build up to 90 ppb (from an initial value of 40 ppb) in 3–4 days if afternoon NO_x concentrations exceed ~1 ppb and hydrocarbon concentrations are also sufficiently high (see below). The data shown in Figure 20 suggest that NO_x exceeds 1 ppb more than 70% of the time at six of the SURE sites and more than 40% of the time at the other three locations. This assumes that one half of the NO_x^* recorded by the SURE instrumentation in the afternoon is PAN, as discussed in section 2.5. The SURE sites appear to represent typical rural locations in the northeastern United States. Monthly mean values for NO_x^* in summer, 4–15 ppb, are similar to those reported by other investigators using similar instrumentation at several locations in the eastern United States. [*Research Triangle Institute*, 1975; *Decker et al.*, 1976; *Pratt et al.*, 1983; *Shaw and Paur*, 1983] and to the average value for NO_x found at Scotia using much more sensitive instrumentation, 3 ppb [*Fehsenfeld et al.*, 1988]. Lower concentrations have been reported for only one site in the east, Whiteface Mountain, where a

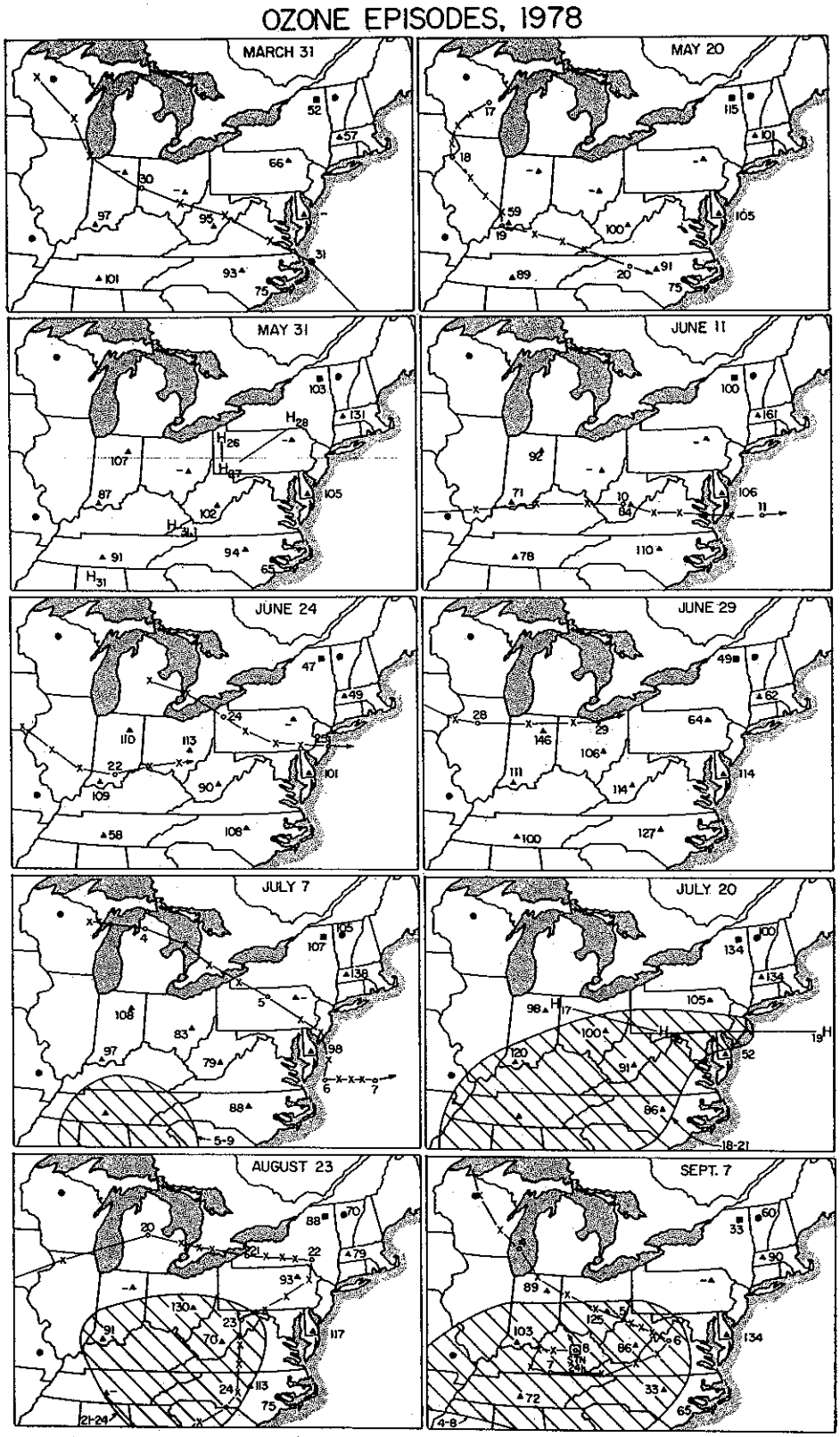

Fig. 14. Daily maximum values of ozone for 1 day during each episode occurring between April and September 1978. The track of the anticyclone (or anticyclones) associated with each event is shown by the open circles (position at 0700 LT on the indicated day), with the crosses showing the intervening positions every 6 hours [*NOAA*, 1978]. Additional highs (H), and fronts are taken from daily weather maps [*National Weather Service*, 1978], which give their positions at 0700 LT, some 8–10 hours earlier than the time of the daily ozone maximum. The area and dates of 4-day air stagnation events are shown by the cross-hatched area (J. K. Angell, private communication, 1987). Results are shown for the NAPBN sites when available, in addition to the SURE sites and Whiteface Mountain.

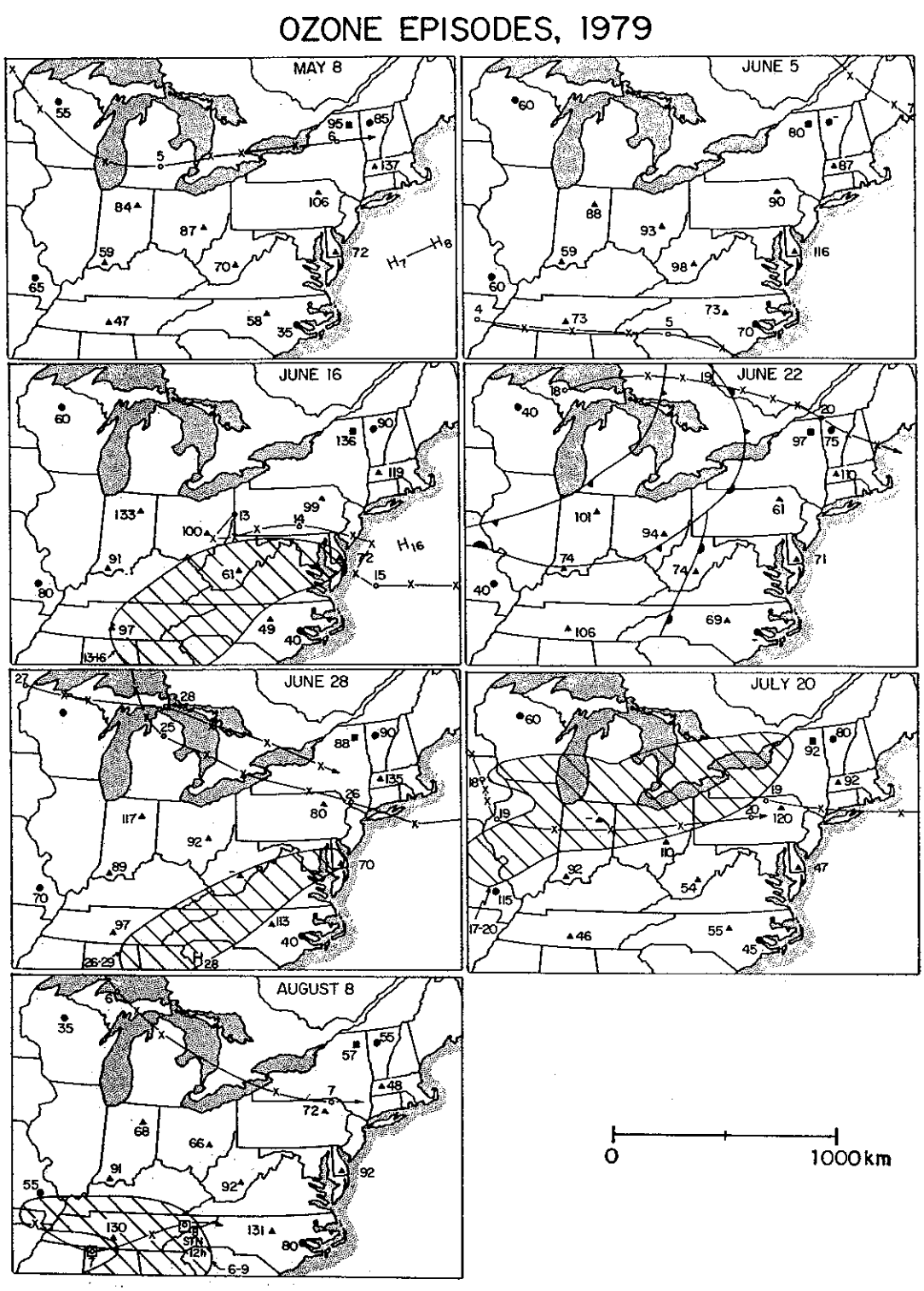

Fig. 15. Daily maximum values of ozone for 1 day during each episode in 1979. Further details are given in Figure 14.

median value of 1 ppb was recorded for NO_x^* in July 1982 [*Kelly et al.*, 1984]. It seems likely that afternoon concentrations of NO_x exceed 1 ppb much of the time at many rural locations in the eastern United States. By contrast, concentrations of NO_x at remote sites in the western United States appear to be much lower, with median values of 0.25 and 0.3 ppb reported for sites on the west coast and the Colorado mountains, respectively [*Fehsenfeld et al.*, 1988]. Large-scale ozone episodes do not occur in the west.

The amount of NMHC needed to generate ozone values above 90 ppb in the models discussed above depends on the reactivity of the specific hydrocarbons and on the concentration of NO_x. For a typical mix of anthropogenic hydrocarbons found in rural air about 25 ppb C is required for $NO_x \approx 1$ ppb, and about 15 ppb C is required for $NO_x \approx 2$ ppb (*Sillman et al.*, submitted manuscript, 1988). *Trainer et al.* [1987] have shown, based on field data, that ozone may reach 100 ppb in 2 days with afternoon $NO_x \approx 1$ ppb and

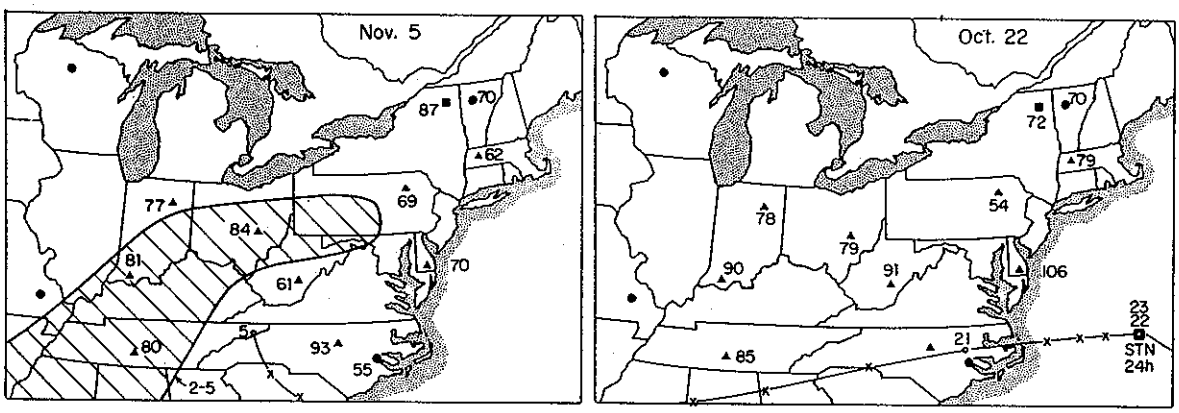

Fig. 16. Daily maximum values of ozone during two episodes in autumn 1978. Further details are given in Figure 14.

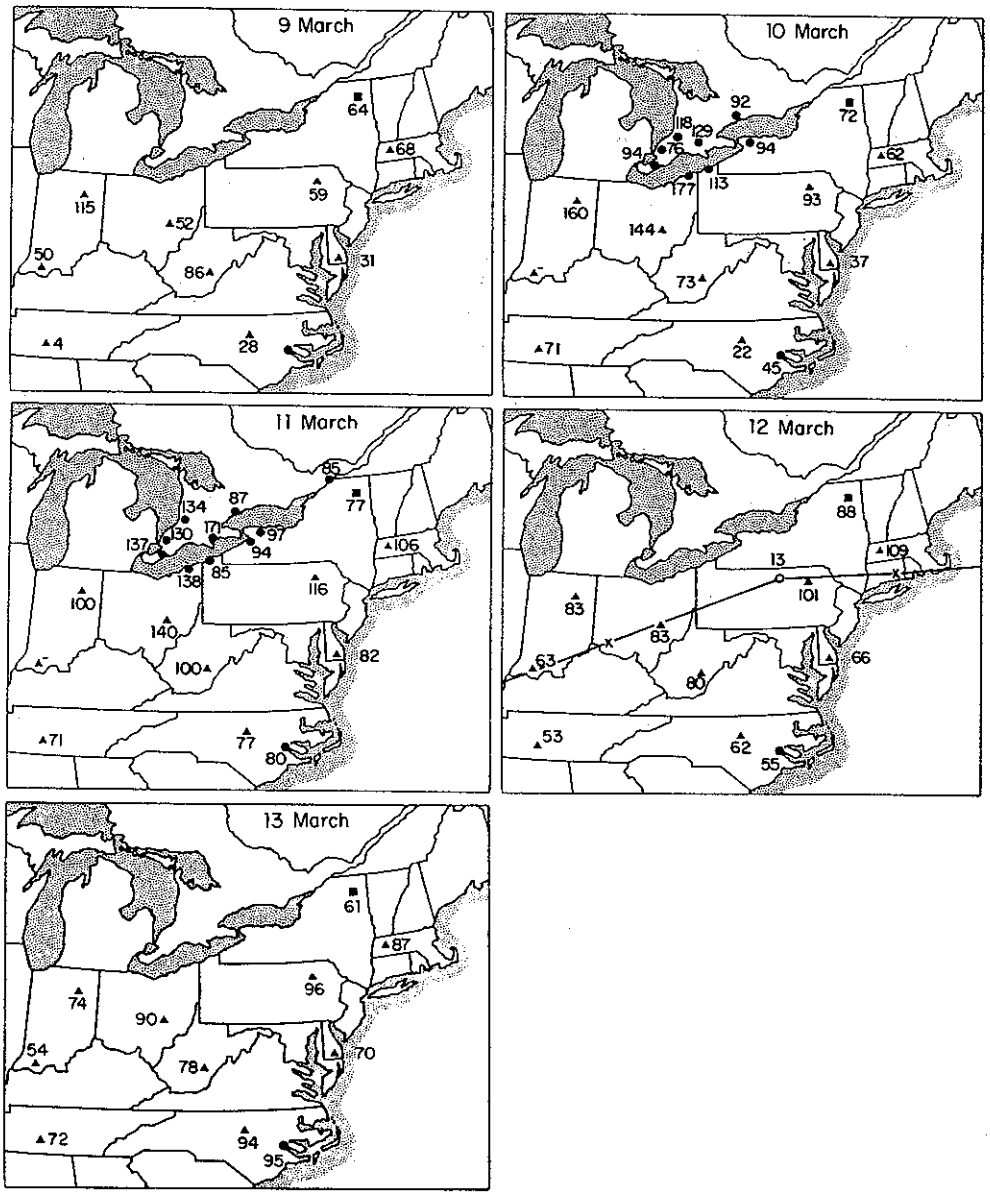

Fig. 17. Daily maximum values of ozone during the episode in March 1978. The figures are supplemented by measurements reported by *Mukammal et al.* [1985] for sites in Ontario and environs, on March 10 and 11 (solid circles).

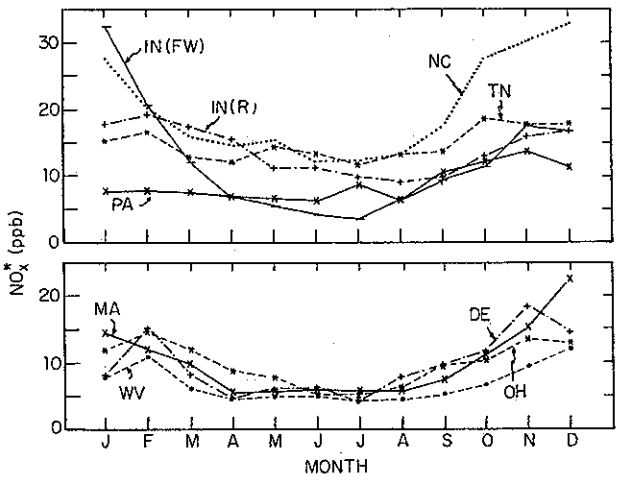

Fig. 18. Monthly mean values of NO_x^* at the SURE sites, for the dates given in Table 1. The curves are labeled by the state in which the site is located (see Table 1 and Figure 1).

isoprene ≈5 ppb. These approximate values are appropriate for sunny summer conditions at ~40°N.

Two studies of detailed hydrocarbon composition during a summer month are available for the eastern United States; these appear to represent two extremes, based on comparisons with other more fragmentary data sets. The first study took place at West Jefferson, 40 km from the city of Columbus, Ohio, as part of the 1980 PEPE/NEROS study [*Vaughan et al.*, 1982]. The median concentration of NMHC was 71 ppb C, with a range of 37–224 ppb C; however, all but two of the 19 samples were below 117 ppb C. Concentrations of isoprene were low, typically <2.0 ppb C (W. Lonnemann, Environmental Protection Agency, private communication, 1986). The second study took place in Scotia, Pennsylvania, concurrent with the NO_x measurements discussed earlier. Here average concentrations of anthropogenic NMHC were much lower, 25 ppb C, with a range of 8–48 ppb C [*Westberg et al.*, 1986]; isoprene concentrations were, however, much higher, with an average concentration at noon of 16 ppb C (H. Westberg, private communication, 1986). It should be noted that the site was located in a large clearing in the middle of a deciduous forest. Concentrations of NMHC appear to be lower only at sites with a coastal influence, for example, Maine, with a mean of 15 ppb C [*Sexton and Westberg*, 1984]. Median values of NMHC at five sites in North Carolina were 40, 68, 73, 79, and 85 ppb C, with a range of 32–132 ppb C [*Seila et al.*, 1984]; a higher median value was found at a site in the Smoky Mountains, Tennessee, 106 ppb C, with a range of 87–171 ppb C [*Arnts and Meeks*, 1981]. Average values reported for isoprene in the east range from 3.4–12 ppb C, with higher values found in the canopy of oak forests (see review by *Altshuller* [1983]). In summary, it appears that concentrations of anthropogenic NMHC are high enough to permit production of ozone values above 90 ppb at most locations in the northeast where measurements have been made, if adequate NO_x is available and suitable weather prevails. In addition, for locations near deciduous forests, concentrations of isoprene are also likely to be high enough during warm weather to permit significant formation of ozone. These conclusions are based on only a few studies, and better definition of the NMHC distribution in a variety of rural locations is required.

The measurements available at present for NO_x and NMHC suggest that ambient concentrations in much of the rural United States east of the Mississippi and north of Tennessee and North Carolina are sufficiently high that ozone episodes are to be expected, given favorable meteorological conditions. It is unfortunate that data for both these families of precursors are exceedingly sparse and were often obtained several years ago, with instrumentation that was nonspecific and insufficiently sensitive to detect the lower range of concentrations.

3.4. *Implications of Ozone Analysis for Human Health and for Vegetation*

The results presented in Figure 6 and Table 2 show that concentrations of O_3 in rural air are occasionally high enough to violate the National Ambient Air Quality Standard in the United States (120 ppb), designed to provide an adequate margin of safety to protect human health. A recent study has shown that exposure to ozone concentrations as low as 120 ppb for several hours may be harmful for exercising individuals [*Folinsbee et al.*, 1988]. Ozone exceeded 120 ppb on 0–4 days in 1978 and 0–8 days in 1979 at eight of the SURE sites and WFM; values above 120 ppb were found on 16 days in 1978 and 12 days in 1979 at the ninth SURE site, in western Massachusetts (see Table 2). This site is influenced by transport from the New York conurbation. Violations of the standard usually occur during ozone episodes of large spatial scale, when ozone remains high for several consecutive days. On these occasions, moderately polluted rural air is likely to affect urban ozone in downwind regions, and the regional nature of the problem leads to significant population exposure.

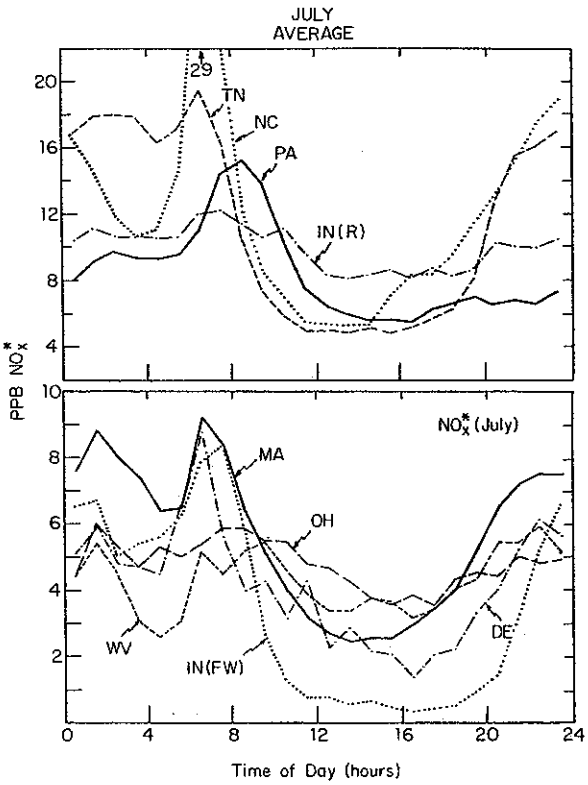

Fig. 19. Diurnal variation of NO_x^* in July at the SURE sites. See Figure 18 for further details.

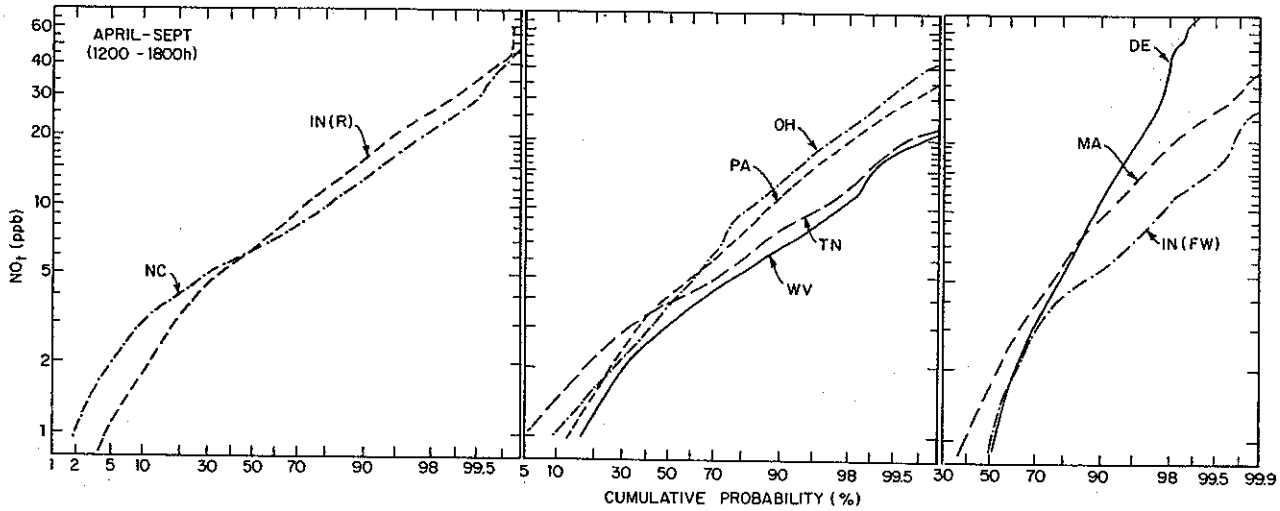

Fig. 20. Cumulative probability distributions for NO_x^* from April 1 to September 30, from 1200–1759 LT. The three panels are arranged in order of increasing median value of NO_x^*, from left to right. See Figure 18 for further details.

The effects of ozone on vegetation have been assessed primarily by exposing commercial crops to different ozone levels for 7 hours (0900–1600 LT) in open-top chambers in the field [*Heck et al.*, 1982, 1983, 1984]. The yield of many species decreases linearly as ozone increases from 25 ppb to over 100 ppb; yield reductions (relative to 25 ppb) of 0–10% were found for ozone levels of 40 ppb for five important crops, with losses of 8–27% for ozone levels of 65 ppb [*Heck et al.*, 1982].

Average concentrations of ozone (0900–1600 LT) are in the range 57–70 ppb in June (the seasonal maximum) and 38–51 ppb in September at the SURE sites in the eastern United States; values are lower for the coastal sites and for the more remote midwest and western sites, 37–50 ppb in June and 29–43 ppb in September (see Table 4). The results of *Heck et al.* [1982] imply that yields of commercial crops are reduced significantly by ozone in the east, with smaller reductions in the more remote midwest and west.

There is increasing evidence that current ozone levels in the east may have a deleterious influence on trees [*Woodman and Cowling*, 1987]. Ozone induces visible damage and is inferred to decrease growth in white pine in the eastern United States and Canada [e.g., *Hayes and Skelly*, 1977; *Benoit et al.*, 1982; *McLaughlin et al.*, 1982]. Tree seedlings

TABLE 4. Mean Values of Ozone (0900–1559 LT), and the Most Probable Time of Maximum Ozone

Station Location	June, ppb	Sept, ppb	Most Probable Time Of Maximum O_3,* LT
Montague, Massachusetts	68.4	37.5	1500
Scranton, Pennsylvania	57.1	38.6	1500 (0000)
Indian River, Delaware	69.8	44.9	1600
Duncan Falls, Ohio	61.5	49.7	1600
Rockport, Indiana	62.2	48.0	1500
Giles County, Tennessee	59.9	44.5	1600
Fort Wayne, Indiana	65.5	44.7	1600
Research Triangle Park, North Carolina	66.8	51.2	1400
Lewisburg, West Virginia	61.6	47.3	1600
Green Mountain National Forest, Vermont	46.5	33.3	1600 (2300)
Croatan National Forest, North Carolina	48.8	35.1	1500
Chequamegon National Forest, Wisconsin	45.7	29.2	1600 (2300)
Mark Twain National Forest, Missouri	49.1	43.0	2300 (1600)
Kistachie National Forest, Louisiana	39.3	40.0	1500
Custer National Forest, Montana	48.7	37.2	1500 (2300)
Apache National Forest, Arizona	50.2	36.8	2300†
Ochoco National Forest, Oregon	37.1	36.6	1500 (2300)
Whiteface Mountain, New York	44.6	36.3	0000

*The most probable time of occurrence of the daily maximum, from April 1 to September 30, for the years of data given in Table 1; the times are less well defined for the NABPN sites than for the SURE sites, as the former are given with resolution of 5 ppb and the latter with a resolution of 1 ppb. The number in parenthesis is the time of occurrence of any secondary maximum.

†This site has a very broad secondary maximum from 0900 to 1700 LT.

grow significantly taller when exposed to charcoal-filtered air, as opposted to ambient air, in the east [*Duchelle et al.*, 1982; *Shafer et al.*, 1987]. Exposure to ozone at concentrations typical of the eastern United States causes a reduction in net photosynthesis in oak, sugar maple, white pine, and poplar; the magnitude of the reduction was considerably less for most of the trees than for commercial crops, but the effects of ozone on trees may be compounded over many growing seasons [*Reich and Amundson*, 1985].

This analysis of ozone data should be useful for designing more realistic exposure studies for commercial crops and trees and for assessing damage caused by ozone. These studies should account for the observed diurnal behavior of ozone and for the periodic nature of exposure to high values. The 7-hour period used for crop studies is not the period of highest ozone, which occurs from about 1200 until 1800 LT or later at most of the eastern sites (see Figure 2 and Table 4). A 12-hour period (0800–2000 LT) has been used in some recent studies [e.g., *Shafer et al.*, 1987]. Neither a 7- or 12-hour seasonal average is an appropriate measure of exposure to ozone; such averages mask the differences in exposure to high values shown in Figures 3–6. The variability of ozone within a month and from month to month for 0800–2000 LT was given in Figure 5. Median concentrations were 55–60 ppb at the SURE sites in the east and 40–50 ppb at the western sites and in the more remote midwest locations, during the months of May to July; values exceeding 90 ppb can occur as much as 10% of the time during these hours at the more polluted sites. High values tend to occur during episodes, which recur several times each growing season, as discussed in section 2.4. While ozone is usually highest in midafternoon, the most probable time of occurrence of the daily maximum is near midnight at a few sites, with a secondary maximum in midafternoon; several other sites have a secondary maximum near midnight (see Table 4). The effect on vegetation of high levels of ozone at night does not appear to have been evaluated.

4. Summary and Conclusions

Ozone values in the eastern United States are highly correlated over several hundred kilometers, and high values tend to occur during episodes of large spatial scale, often >600,000 km^2. There were 10 and seven such episodes in 1978 and 1979, respectively, between the months of April and September; they persisted for 3–4 days, on average, with a range of 2–8 days, and were most common in June. Daily maximum ozone values exceeded 90 ppb at over half the sites during these episodes and often were greater than 120 ppb at one or more sites. Ozone episodes occurred preferentially in the presence of weak, slow-moving, and persistent high-pressure systems. A few episodes occurred outside the summer half of the year. In general, they occurred during unusually warm weather, and peak values for ozone were lower than in summer episodes. One particular episode in March 1978 may have reflected a stratospheric intrusion event. It appears that 1978 may have been a somewhat high year for ozone in the east, while 1979 may have been more typical, based on limited data comparisons. Ozone episodes of the scale described here appear to be more common in the eastern United States than in western Europe, again, based on limited data.

Ozone concentrations above 80 ppb are common in rural areas of the eastern United States in spring and summer, but they are unusual at remote western sites. Concentrations of NO_x in rural areas of the east are frequently high enough (>1 ppb) to permit significant photochemical formation of ozone during favorable weather conditions; NO_x is much lower in remote regions in the west.

High concentrations of ozone found over large regions of the eastern United States may contribute to the urban ozone problem [cf. *Coffey and Stasiuk*, 1975], as moderately polluted air moves into a city and receives fresh emissions of ozone precursors, leading to still higher values. Ozone in rural air exceeds the National Ambient Air Quality Standard a few days each year and may contribute significantly to high values found in metropolitan areas where most of the population resides.

Ozone episodes were present during a significant fraction of the growing season in the east in 1978 and 1979, on 23% of the days in May to August. The effect of these pollution episodes on vegetation cannot be assessed quantitatively with current information on dose-response characteristics [*Heck et al.*, 1984; *Lefohn and Runeckles*, 1987; *Lefohn et al.*, 1988]. The results presented here should aid in the design of studies that account for the periodic exposure of vegetation to high values of ozone for several consecutive days. The diurnal behavior of ozone varies considerably, with high values found at night at some locations. The effect of different diurnal patterns of exposure to ozone requires investigation.

Rural ozone in the eastern United States is impacted severely by anthropogenic emissions of NO_x and hydrocarbons. Several modeling studies are in progress, with the goals of enhancing understanding of this phenomena and devising appropriate control strategies for ozone [e.g., *Lamb*, 1983, 1986; *Liu et al.*, 1984]. The SURE program, designed almost 15 years ago for investigation of long-range transport of SO_2, has provided perhaps the most detailed long-term measurements for ozone and NO_x^*, yet it is woefully inadequate for testing details of these models. Ozone is no longer measured routinely at rural sites in the United States. A measurement program for ozone and its precursors, using the best available instrumentation, is urgently needed in the eastern United States to test these models and to improve our understanding of this serious environmental problem.

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J. A. Logan, Department of Earth and Planetary Sciences and Division of Applied Sciences, Harvard University, Pierce Hall, 29 Oxford Street, Cambridge, MA 02138.

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