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Ozone in the urban southeastern United States

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Ozone measurements (daily maximum values) from the Aerometric Information Retrieval System database are analyzed for selected sites, during 1980 to 1988, in southeastern USA. Frequency distributions, for most sites during most years, show a typical bell-shaped curve with the higher frequency around the yearly daily maximum ozone mean of about 100 to about 110 $\mu g\ m^{-3}$ (50–55 ppbv). Abnormal years in ozone concentration may skew the distribution as the mean shifts. A correlation of daily maximum ozone concentrations above 140 $\mu g\ m^{-3}$ (70 ppbv) between sites shows a division between the sites in the northern portion of the region and those in the southern portion of the region. Variations in ozone levels are well correlated over distances of several hundred kilometers, suggesting that high values are associated with synoptic scale episodes. An ozone exposure analysis also shows higher ozone exposures (250–300 ppm days) in the northerly sites as compared to the southerly sites (150–170 ppm days).

INTRODUCTION

Atmospheric photochemical oxidants comprise a class of highly reactive chemical compounds (ozone, hydrogen peroxide, peroxyacetyl nitrate, etc.) produced within the Earth's atmosphere. In the upper atmosphere, ozone, the most abundant photochemical oxidant, protects life from the harmful effects of ultraviolet (UV) radiation from the sun. Paradoxically, near the Earth's surface, there is an increasing body of literature suggesting that photochemical air pollutants adversely affect human health, vegetation and welfare (Heck *et al.*, 1983; Guderian *et al.*, 1985). There is a growing concern, especially in the USA (Mohnen & Cowling, 1988) and western Europe (Skarley & Sellden, 1984), that the forest declines may be caused, in part, by an increase of tropospheric ozone.

Analyses of various databases of ground-level ozone measurements for the past few decades show that the tropospheric ozone concentrations have steadily increased (Logan, 1985; Walker, 1985; Oltmans & Komhyr, 1986; Volz & Kley, 1988). Comparing recent ozone measurements with those made at the Montsouris laboratory in Paris during 1876 and 1910, Volz & Kley (1988) suggest that ground-level ozone concentrations in mid-latitudes have more than doubled in the past 100 years (i.e. increased from *c.* 20 to *c.* 45 $\mu g\ m^{-3}$).

High summertime concentrations of atmospheric ozone in the urban and rural regions of the USA are increasingly becoming recognized as a major environmental problem. There is increasing evidence that the ozone National Ambient Air Quality Standard (NAAQS) is not meeting with success, even after a decade of the control program (Abelson, 1988; Chameides *et al.*, 1988; Lindsay *et al.*, 1989).

While most regions of the USA occasionally observe high surface ozone concentrations, probably no large region of the country experiences more pervasive high ozone levels than the southeast USA, where *c.* 40% of the nation's nonattainment areas are found.

These aspects of ozone in the urban southeast USA, plus some of the factors which might lead to elevated ozone levels, are discussed in this paper.

DATA AND THEIR ANALYSIS

Sources of data

Ozone data for this study were acquired from the US Environmental Protection Agency (EPA) Aerometric Information Retrieval System (AIRS) database. For ozone, this database contained both hourly averaged measurements and hourly averaged daily maximum readings from approximately 200 sites across the USA. The daily maximum data were used from selected sites in the southeast US region for the years 1980–88 (Fig. 1.)

All the ozone data were collected by using the chemiluminescence analyzer, and the basic calibration pro-

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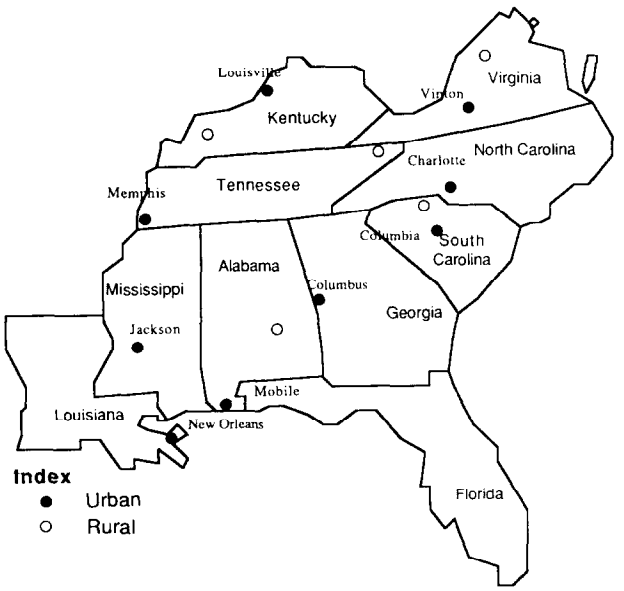

Fig. 1. Selected urban (●) and rural (○) sites from the AIRS database representing the southeastern region of the USA.

cedure involved UV photometry. This calibration technique has been used for all the EPA ozone data.

Due to data handling limitations, and our particular interest in high concentrations, only daily maximum ozone concentrations collected from 1980 to 1988 were used in the study, instead of hourly averages. Lindsay *et al.* (1989) have also used the daily maximum ozone concentration data in their analysis of Atlanta ozone. Walker (1985) indicated, after examining various statistics in trend analysis, that the use of the daily maximum statistic has a fair amount of robustness. A robust statistic is one which is relatively insensitive to changes in a small number of values in the basic data set. Conversely, a nonrobust statistic is sensitive to changes in just a small fraction of the data set, i.e. it is unstable or erratic. In general, the more bits of data directly contributing to the statistic, the more robust it will be.

Meteorological surface data were obtained from the National Climatic Data Center, Asheville, to represent meteorology as near as possible to the selected ozone monitoring sites.

In order to capture the spatial representation of the Southeast US region, 14 sites were chosen (Fig. 1). Table 1 shows the selected rural sites (R) and their distances from the nearest urban centers, and Table 2 gives the urban (U) selected sites and their corresponding city populations.

Table 1. Selected rural sites in southeast US region and their distances from nearest urban center with a population

Rural sites (R)	Approx. distance from	Urban center
Chester Co., SC	50 km	Charlotte, NC
Sullivan Co., TN	120 km	Knoxville, TN
Augusta Co., VA	135 km	Richmond, VA
Muhlenberg Co., KY	40 km	Owensboro, KY
Montgomery Co., AL	40 km	Montgomery, AL

Table. 2. Urban sites selected to represent the southeastern US region and their corresponding populations (National Geographic Society, 1983, *Atlas of the World*)

Urban center (U)	Population
Louisville, KY	298000
Vinton (Roanoke) VA	100000
Memphis, TN	646000
Charlotte, NC	314000
Columbia, SC	99000
Columbus, GA	169000
Jackson, MS	203000
Mobile, AL	200000
New Orleans, LA	557000

The criteria for site selection were at least seven years of data for both urban and rural sites and all years having ≥200 days of data. Rural site selection, from the AIRS database, was difficult, since monitoring sites were located in strategic positions, in and outside of urban centers, to sense urban plumes and target those centers not meeting the compliance of 120 ppbv (240 $\mu g\ m^{-3}$). In this study, a site was considered rural

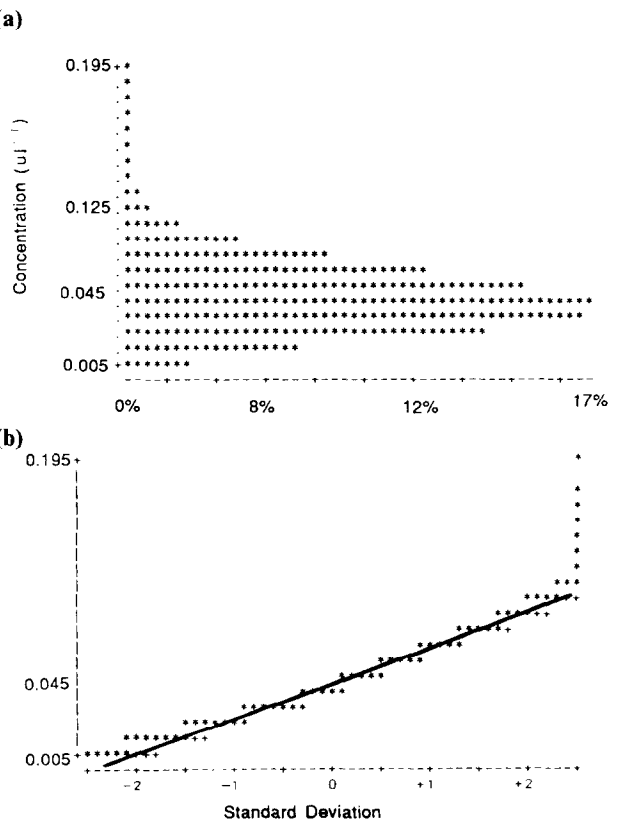

Fig. 2. (a) Frequency distribution of the pooled daily maximum ozone data (b) Normality plot of empirical quantiles (+) with quantiles of standard normal data calculated from the data's mean and standard deviation.

if it was located greater than or equal to 40 km from an urban center. A couple of rural sites are >100 km from urban centers.

Frequency distribution and seasonal behavior of ozone

All the ozone daily maximum data were pooled and checked for normality before any statistical analysis was performed. Using the Statistical Analysis Systems (SAS) univariate procedure, Fig. 2 was produced as a visual normality check for the data examined. Figure 2(a) is a frequency distribution for the data showing some skewness, but it still may be considered nearly normal. Figure 2(b) is a normal probability or quantile–quantile plot obtained by the univariate procedure. The empirical quantiles are plotted against the quantiles of a standard normal distribution. The vertical coordinate is the daily maximum concentration, and the horizontal coordinate is a standard normal quantile. The solid line provides a reference straight line that is drawn, using the sample mean and standard deviation. The asterisks (*) mark data values, and if the data are from a normal distribution, they should tend to fall along the reference lines. Again, Fig. 2(b) indicates that data normality is a valid assumption.

Typical frequency (%) distributions from most sites in the region have a bell-shaped curve with the highest frequencies around the background concentration, *c.* 120 μg m^{-3} (Fig. 3). In abnormal ozone years, this larger frequency can shift towards higher or lower concentrations from year to year, resulting in skewness in the ozone frequency distribution, as was the case for the Louisville, KY, site during 1983 (Fig. 4), when a maximum value of ~380 μg m^{-3} was recorded.

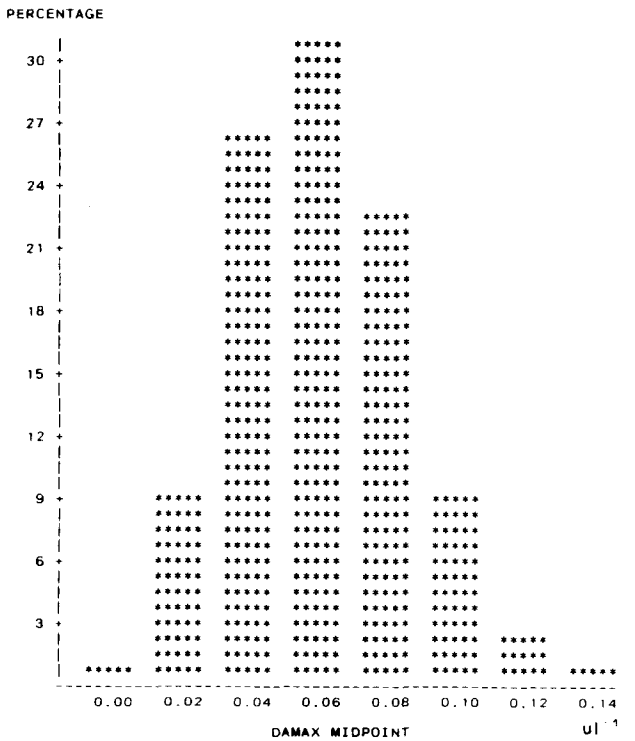

Fig.3. Typical bell-shaped frequency distribution observed in all sites most years in the region: SC(U), 1980.

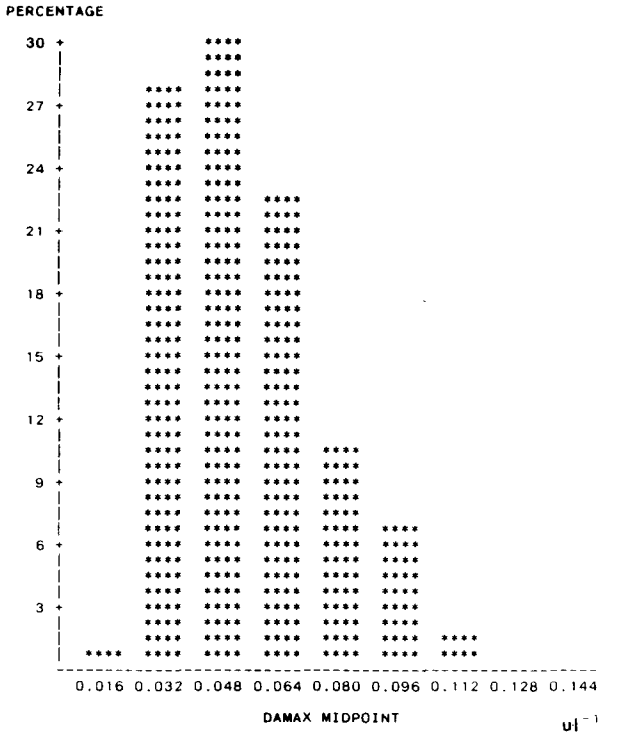

Fig. 4. Skewed frequency distribution: KY(U), 1984.

Ozone concentrations are highest in spring and summer (Fig. 5). These correlate well with solar radiation (Dogniaux, 1970) and with air-stagnation events (Korshover, 1976). The trend is usually a steady increase in ozone concentration from the start of the year to the summer months, followed by a tapering off through autumn and winter. The seasonal peaks in concentration occur in summer (June 1–Aug. 15), without significant differences between urban and rural sites (Table 3).

However, not all sites or all years fit into the same trend. Seasonal distributions at a few sites are more individual. For example, Jackson, MS, in 1987 shows small fluctuations around a background concentration and no exceedances of the 124 ppb (250 μg m^{-3}) standard. New Orleans, LA, on the other hand, has an early spring peak followed by lower concentrations in the summer with another peak again in the autumn. The city is located near the coast of the Gulf of Mexico on the Mississippi River delta, where local meteorology, such as summertime afternoon thunderstorms, may serve to scavenge the ozone out of the troposphere.

Correlation of high ozone concentration between sites

An analysis was performed to test whether ozone values at various sites were correlated with each other.

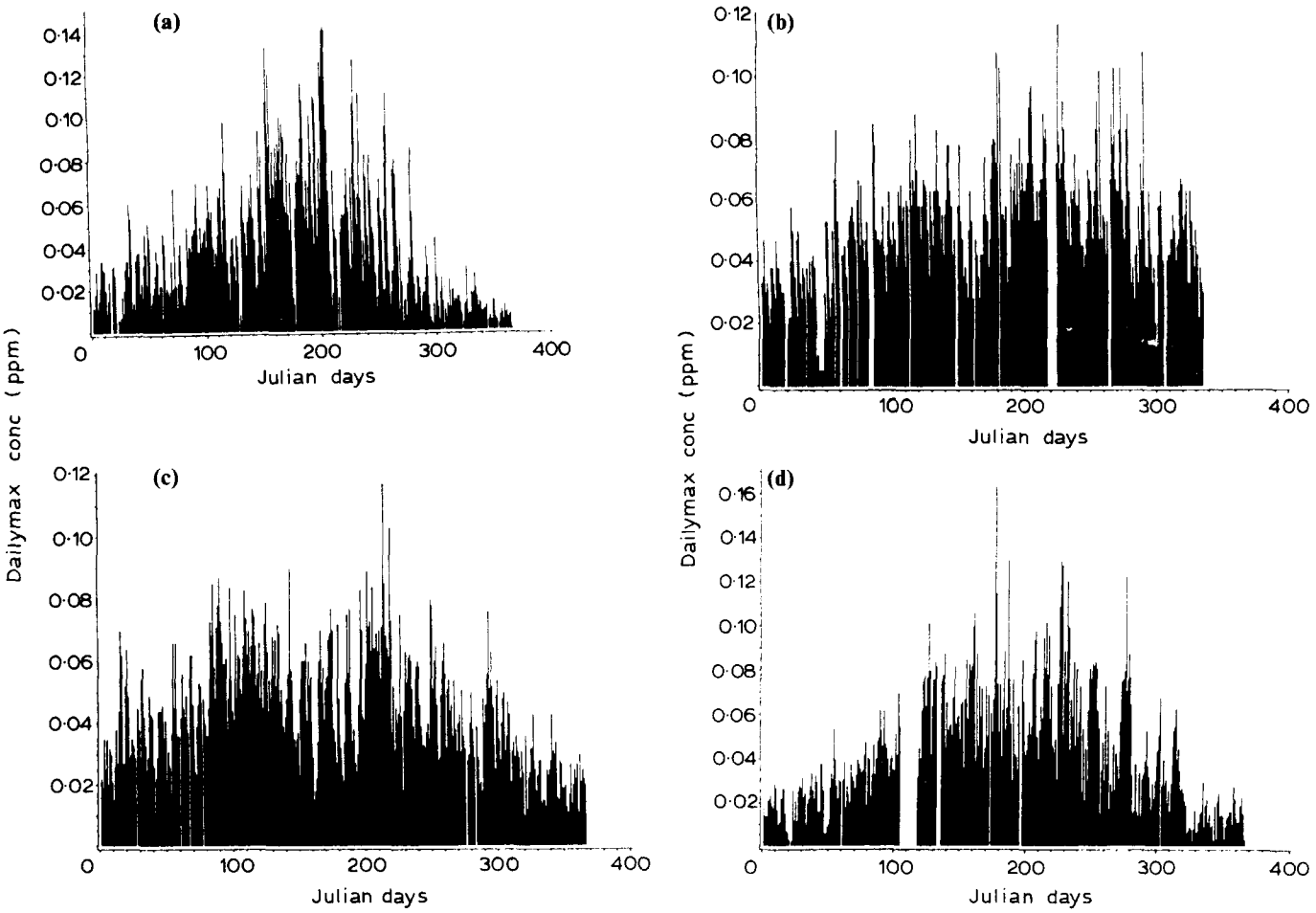

Fig. 5. Typical seasonal distribution of dailymax ozone for (a) SC(R) 1981; (b) KY(U) 1985; (c) MS(U) 1981; (d) (LA(U) 1986.

Table 4 is a regional matrix representing ozone correlations between all possible pairs of urban sites, as percentages of time that the given pair was ≥140 $\mu g\ m^{-3}$ simultaneously, for all 9 years. Since the calculations were over a long time span, those sites indicating percentages ≥25% were regarded as significant. The 25% criterion was arbitrarily used to bring out those pairs of sites that have higher daily maximum ozone correlations from less significant ones. For example, the North Carolina site (NC(U)) had high ozone concentrations concurrently with the South Carolina (SC(U)) site 35% of the time, and with the Alabama (AL(U)) site 28% of the time.

Table 3. Daily maximum ozone concentration averages (mean values) during May–October and annually

Site	May-Oct (nl litre^{-1})	Annual (nl litre^{-1})
URBAN		
KY	59·8	45·4
VA	60·4	49·7
TN	55·8	50·2
NC	65·1	52·4
SC	59·0	50·7
GA	55·5	53·2
MS	54·5	50·8
AL	52·1	50·7
LA	49·5	44·3
RURAL		
KY	58·9	54·1
TN	50·8	44·7
SC	64·6	54·4

Figure 6 shows the significant pairs as connected by a line in the southeastern region. At first glance, there are differences in the amounts and combinations of ozone concentrations from those sites in the northern portion of the region (SC(U), NC(U), TN(U), KY(U) and VA(U)) from those in the southern portion of the region (MS(U), AL(U) and GA(U)). While there appears to be a better correlation (*c.*25%) among the northern pairs of sites, there is little correlation between the southern sites themselves, or any evidence that the northern and southern sites in the region are behaving similarly when daily maximum concentrations are above 140 $\mu g\ m^{-3}$.

Ozone correlations (percentage of time) are plotted as a function of the distance between the sites (Fig. 7). There is significant correlation between high ozone values at most locations separated by as much as *c.* 400 km and even between some locations separated by as much as 800 km. In a similar analysis, Logan (1989)

Table 4. Regional matrix describing percentage of concurrent ozone concentrations ≥ 140 μg m^{-3} between the nine urban sites

	KY(U)	V(U)	TN(U)	NC(U)	SC(U)	GA(U)	MS(U)	AL(U)	LA(U)
KY(U)	—	27	37	27	22	18	25	18	13
VA(U)	—	—	21	28	21	17	13	13	14
TN(U)	—	—	—	19	16	20	25	17	17
NC(U)	—	—	—	—	35	22	27	19	17
SC(U)	—	—	—	—	—	17	19	20	12
GA(U)	—	—	—	—	—	—	16	18	18
MS(U)	—	—	—	—	—	—	—	23	21
AL(U)	—	—	—	—	—	—	—	—	26
LA(U)	—	—	—	—	—	—	—	—	—

found high correlation between rural sites in the north-eastern USA separated by as much as 1000 km. This strongly suggests patterns perhaps related to typical synoptic high pressure patterns, where ozone and its precursors are transported over the region. However, in-situ production of ozone cannot be neglected since it is clearly shown there is a north–south separation of ozone correlation between the sites. In a typical summer, high pressure stagnation (wind speed ≤ 4 m s^{-1}) ozone production is more dependent on the availability of precursors present at a particular location (Logan, 1989; Korshover, 1976). This may be the reason for higher ozone concentrations in the more populous states of North Carolina, Tennessee, Kentucky and Virginia.

Ozone exposure

Ozone exposure is calculated, based on sum of all days maximum ozone concentrations equal to or greater than 140 μg m^{-3}, 'sum of season dose' (ppm days). This exposure index combines the concentration and occurrence for high ozone levels. Figure 8 illustrates the ozone dose at the sites for the years 1982–86, during which time a maximum number of sites had overlapping years of ozone concentrations recorded. This is not an attempt to calculate the damage done to either plants or humans during this period, but simply to show the differences in exposure between the selected sites in the region. Inspection of Fig. 6 shows

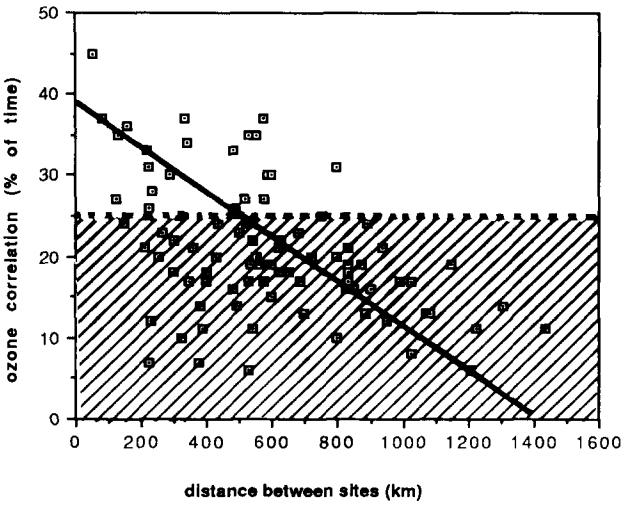

Fig. 7. Correlation of high ozone concentration at pairs of sites as a function of distance between the sites.

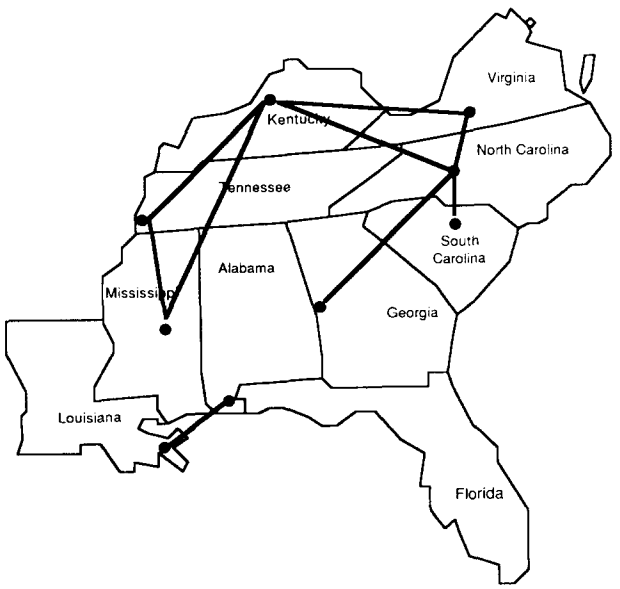

Fig. 6. Cross-correlation for ozone (≥140 μg m^{-3}) at pairs of urban sites in the southeast USA during 1980–88.

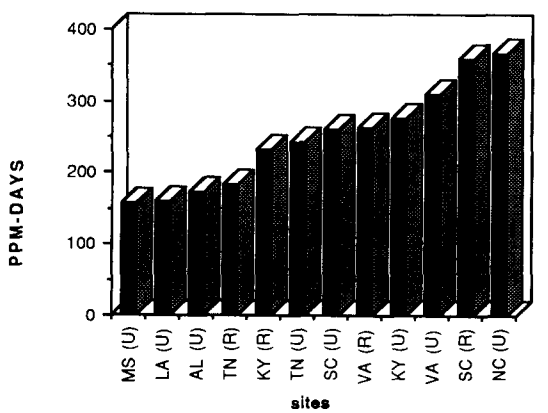

Fig. 8. Exposure (ppm-days) for selected sites in the region for the years 1982–86. Exposure was defined as the sum of all days (≥140 μg m^{-3}) at a particular site.

that the northerly sites (SC, NC, KY and VA) have higher ozone exposures, ranging from 250 to 300 ppm days, as compared to the southerly sites (MS, LA and AL), which have ozone exposures of 150 to 170 ppm days.

DISCUSSION

The ozone problem appears to be extensive in the southeast US region, especially in the urban environment. Daily maximum ozone values exceeded the NAAQS of 0·12 ppm (240 μg m^{-3}) at most of the sites during the past decade, reaching a high of 380 μg m^{-3} in 1983 in the Louisville, KY, site. While it was not ascertained how these high ozone levels were achieved, it is suggested that regional-scale transport of ozone and its precursors must play a role in the production of ozone levels greater than 140 μg m^{-3} and that local production, in general, is necessary, in addition to regional-scale transport, in order to consistently generate ozone levels greater than 240 μg m^{-3}.

The database for the ozone precursors is limited, but Logan (1989) has suggested that concentrations of NO_x in rural areas of the east are frequently high enough (>2 μg m^{-3}) to allow for photochemical ozone to form in significant concentrations during meteorologically favorable conditions. However, in urban areas, NO_x concentrations are much larger than 2μg m^{-3}.

The prevailing opinion has been that, usually and in most locations, ozone formation in the troposphere is hydrocarbon-limited. Based on two detailed hydrocarbon measurement studies for the eastern USA, the NMHC (nonmethane hydrocarbons) concentrations reported are 71 ppbv (as carbon) with a range of 37 to 224 ppbv (as carbon) near Columbus, OH (Vaughan *et al.*, 1982); and median values of NMHC at five sites in North Carolina were 40, 68, 73, 79 and 85 ppbv (as carbon) with a range of 32 to 132 ppbv (Seila *et al.*, 1984). Thus far, hydrocarbon emissions from anthropogenic sources have been the focus of ozone controls. However, Chameides *et al.* (1988), using model calculations, have called this control policy into question, since reactive hydrocarbons (e.g. isoprene) are also emitted in significant quantities, near urban areas in the Southeast USA, by natural processes. By taking into account natural hydrocarbon sources from trees, for the Atlanta metropolitan area, they showed that these natural emissions can significantly affect urban ozone levels. In order to resolve the role of transport and chemical kinetics, simultaneous measurements of ozone and its precursors, and of meteorological parameters are needed. This will provide important information on future planning of ozone control programs, and aid in the establishment and evaluation of regional air quality standards.

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