

# 4

## **Environmental Concentrations, Patterns, and Exposure Estimates**

### **4.1 Introduction**

The effects of ozone ( $O_3$ ) on humans, animals, and vegetation have received extensive examination and are discussed elsewhere in this document. As indicated in the previous  $O_3$  criteria document (U.S. Environmental Protection Agency, 1986), most of the human and welfare effects research has focused on evaluating those impacts on health or vegetation of exposure to  $O_3$  that simulate ambient  $O_3$  exposures (e.g., matching the occurrence of hourly average concentrations or more prolonged times of exposure). This information on concentrations obtained from extensive monitoring in the United States can be useful both for linking anthropogenic emissions of  $O_3$  precursors with the protection of health and welfare (i.e., determining compliance with air standards) and for augmenting exposure assessment and epidemiology studies. The major emphasis in this chapter, however, will be on characterizing and summarizing the extensive  $O_3$ -monitoring data collected under ambient conditions. Although most of the  $O_3$  air quality data summarized were gathered for compliance and enforcement purposes, the hourly averaged  $O_3$  information can be used for determining patterns and trends and as inputs to exposure and health assessments (e.g., U.S. Environmental Protection Agency, 1992a; Lefohn et al., 1990a). In the sections that follow, the hourly averaged ambient  $O_3$  data have been summarized in different ways to reflect the interests of those who wish to know more about the potential for  $O_3$  to affect humans and the environment. This chapter is not an exposure assessment for ambient  $O_3$ ; rather, this chapter elucidates the features of  $O_3$  concentration patterns and exposure possibilities.

Trend patterns for  $O_3$  over several periods of time are described in Section 4.2. The trends for  $O_3$  have been summarized by the U.S. Environmental Protection Agency (1994) for 1983 to 1993. In addition, trends analysis for specific regions of the United States have been performed by several investigators. In some cases, attempts have been made to adjust for meteorological variation. In Section 4.3, the hourly averaged concentration information from several monitoring networks has been characterized for urban and rural areas. The diurnal variation (Section 4.4) occurring at urban and rural locations, as well as seasonal patterns, also are described. Specific focus is provided on  $O_3$  monitoring sites that experience low maximum hourly average concentrations because these locations form the "basis for comparison" for  $O_3$  concentrations and exposures. In Section 4.5, the seasonal patterns of hourly average concentrations are discussed. The hourly average concentration information is used in Section 4.6 to compare the spatial variations that occur in urban areas with those in nonurban areas, as well as with those in high-elevation locations. For

comparing indoor to outdoor O<sub>3</sub> exposures or concentrations, information is provided in Section 4.7 on the latest data on indoor/outdoor (I/O) ratios. Section 4.8 describes efforts to estimate both human and vegetation exposure to O<sub>3</sub>. Examples are provided on how both fixed-site monitoring information and human exposure models are used to estimate risks associated with O<sub>3</sub> exposure. A short discussion is provided on the importance of hourly average concentrations, which are used in human health and vegetation experiments that simulate "real world" exposures.

As indicated in the previous O<sub>3</sub> criteria document (U.S. Environmental Protection Agency, 1986), O<sub>3</sub> is the only photochemical oxidant other than nitrogen dioxide (NO<sub>2</sub>) that is routinely monitored and for which a comprehensive aerometric database exists. Data for peroxyacetyl nitrate (PAN) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) have been obtained only as part of special research investigations. Consequently, no data on nationwide patterns of occurrence are available for these non-O<sub>3</sub> oxidants; nor are extensive data available on the correlations of levels and patterns of these oxidants with those of O<sub>3</sub>. Sections 4.9 and 4.10 summarize the available data for these other oxidants. Section 4.11 describes the co-occurrence patterns of O<sub>3</sub> with NO<sub>2</sub>; sulfur dioxide (SO<sub>2</sub>); and acidic aerosols, precipitation, and cloudwater.

#### **4.1.1 Characterizing Ambient Ozone Concentrations**

It is important to distinguish among concentration, exposure, and dose when using air quality data to assess human health and vegetation effects. For this document, the following definitions apply:

1. The "concentration" of a specific air pollutant is the amount of that material per unit volume of air. Air pollution monitors measure pollutant concentrations, which may or may not provide accurate exposure estimates.
2. The term "exposure" is defined as the concentration of a pollutant encountered by the subject (animal, human, or plant) for a duration of time. Exposure implies that such an encounter leads to intake (i.e., through the respiratory tract or stomata).
3. The term "dose" is defined as that mass of pollutant delivered to an inner target. This term has numerous quantitative descriptions (e.g., micrograms of O<sub>3</sub> per square centimeter of lung epithelium per minute), so the context of the use of this term within the document must be considered. Human dosimetry is discussed in Chapter 8.

The dose incurred by an organism (e.g., plant, animal, or human) is a more complicated measure involving the concentration, the exposure duration, and the concurrent state of the organism's susceptibility. These distinctions become important because the concentration of an airborne contaminant that is measured in an empty room or at a stationary outdoor monitor is not in fact an exposure. A measured concentration functions as an alternative to an exposure only to the degree to which it represents concentrations actually experienced by individuals.

Concentrations of airborne contaminants for vegetation are considered to represent an exposure when a plant is subjected to them over a specified time period. As indicated in Chapter 5 (see Section 5.5), dose has been defined historically by air pollution vegetation researchers as ambient air quality concentration multiplied by time (O'Gara, 1922). However, a more rigorous definition was required. Runeckles (1974) introduced the concept of "effective dose" as the amount or concentration of pollutant that is adsorbed by vegetation, in

contrast to that which is present in the ambient air. Fowler and Cape (1982) developed this concept further and proposed that the "pollutant adsorbed dose" be defined in units of grams per square meter (of ground or leaf area) and could be obtained as the product of concentration, time, and stomatal (or canopy) conductance for the gas in question. Taylor et al. (1982) suggested internal flux (milligrams per square meter per hour) as a measure of the dose to which plants respond. In this chapter, dose will be taken to signify, for the purposes of vegetation, that amount of pollutant absorbed by the plant.

In order to characterize the specific doses responsible for affecting human health and vegetation, there has to be a linkage between exposure and actual dose. Unfortunately, it is difficult to predict this relationship, even with the available models. For example, the sensitivity of vegetation to O<sub>3</sub> as a function of time of day, period of growth, or edaphic conditions can determine the severity of response. For example, high O<sub>3</sub> concentrations may cause minimum injury or damage to plants, whereas more moderate O<sub>3</sub> concentrations may cause a greater degree of injury or damage (Showman, 1991). Because not enough is known to quantify the links between exposure and dosage, and routine monitoring for O<sub>3</sub> is summarized as hourly average concentrations (i.e., potential exposure), most of the information provided in this chapter is characterized in terms of concentration and exposure.

As indicated in Chapter 5, for many years, air pollution specialists have explored alternative mathematical approaches for summarizing ambient air quality information in biologically meaningful forms that can serve as alternatives for characterizing dose.

For vegetation, as indicated in Chapter 5 (Section 5.5), extensive research has focused on identifying indicators of concentration and duration (exposure) that are firmly founded on biological principles. Many of these indicators have been based on research results indicating that the magnitude of vegetation responses to air pollution is determined more as a function of the magnitude of the concentration than of the length of the exposure (U.S. Environmental Protection Agency, 1992b). Short-term (1- to 8-h), high O<sub>3</sub> concentrations (>0.1 ppm) have been identified by many researchers as being more important than long-term, low O<sub>3</sub> concentrations for induction of visible injury to vegetation (see Chapter 5 for further discussion).

Long-term, average concentrations were used initially as an exposure indicator to describe O<sub>3</sub> concentrations over time when assessing vegetation effects (Heck et al., 1982). Based on the view presented in the previous criteria document (U.S. Environmental Protection Agency, 1986) that higher concentrations of O<sub>3</sub> should be given more weight than lower concentrations (see Section 5.5 for further details), the following specific concerns about the use of a long-term average to summarize exposures of O<sub>3</sub> began appearing in the literature: the use of a long-term average failed to consider the impact of peak concentrations and of duration; a large number of hourly data sets within the commonly used 7-h window (0900 to 1559 hours), although diversely distributed and implying potentially diverse exposure potentials, were characterized by the same 7-h seasonal mean; and high hourly average concentrations (e.g., values greater than 0.1 ppm) occurred outside of a fixed 7-h window.

In summarizing the hourly average concentrations in this chapter, specific attention is given to the relevance of the exposure indicators used. For example, for human health considerations, concentration (or exposure) indicators such as the daily maximum 1-h average concentrations, as well as the number of daily maximum 4-h or 8-h average concentrations, are used to characterize information in the population-oriented locations. For vegetation, several different types of exposure indicators are used. For example, much of the National Crop Loss Assessment Network (NCLAN) exposure information is summarized in terms of

the 7-h average concentrations. However, because peak-weighted, cumulative indicators (i.e., exposure parameters that sum the products of hourly average concentrations multiplied by time over an exposure period) have shown considerable promise in relating exposure and vegetation response (see Section 5.5), several exposure indicators that use either a threshold or a sigmoidal weighting scheme are discussed in this chapter to provide insight concerning the O<sub>3</sub> exposures that are experienced at a select number of rural monitoring sites in the United States. The peak-weighted, cumulative exposure indicators used in this chapter are SUM06 and SUM08 (the sums of all hourly average concentrations equal to or greater than 0.06 and 0.08 ppm, respectively) and W126 (the sum of the hourly average concentrations that have been weighted according to a sigmoid function [see Lefohn and Runeckles, 1987] that theoretically is based on a hypothetical vegetation response).

The exposure indicators used for human health considerations are in concentration units (i.e., parts per million), whereas the indicators used for vegetation are in both parts per million (e.g., 7-h seasonal average concentrations) and parts per million per hour (e.g., SUM06, SUM08, W126). The magnitude of the peak-weighted, cumulative indicators at specific sites can be compared with those values experienced at areas that experience low hourly average maximum concentrations. In some cases, to provide more detailed information about the distribution patterns for a specific O<sub>3</sub> exposure regime, the percentile distribution of the hourly average concentrations (in parts per million) is given. For further clarification of the determination and rationale for the exposure indicators that are used for assessing human health and vegetation effects, the reader is encouraged to read Chapters 5 (Section 5.5) and 7.

#### **4.1.2 The Identification and Use of Existing Ambient Ozone Data**

Information is readily available from the database supported by a network of monitoring stations that were established to determine compliance with the National Ambient Air Quality Standards (NAAQS) for O<sub>3</sub>. Most of the data presented in this chapter were obtained from data stored in the U.S. Environmental Protection Agency's (EPA's) computerized Aerometric Information Retrieval System (AIRS) and were collected after 1978. As pointed out in the previous criteria document for O<sub>3</sub> and other photochemical oxidants (U.S. Environmental Protection Agency, 1986), there was some difficulty in interpreting the O<sub>3</sub> data obtained at most sites across the United States prior to 1979 because of calibration problems.

In the United States, O<sub>3</sub> hourly average concentrations are monitored routinely through the National Air Monitoring Network, consisting of three types of sites. The National Air Monitoring Station (NAMS) sites are located in areas where the concentrations of O<sub>3</sub> and subsequent potential human exposures are expected to be high. Criteria for these sites have been established by regulation to meet uniform standards of siting, quality assurance, equivalent analytical methodology, sampling intervals, and instrument selection to assure consistency among the reporting agencies. For O<sub>3</sub>, NAMS sites are located only in urban areas with populations exceeding 200,000. The other two types of sites are State and Local Air Monitoring Stations and Special Purpose Monitors, which meet the same rigid criteria for the NAMS sites but may be located in areas that do not necessarily experience high concentrations in populated areas.

For O<sub>3</sub>, the reporting interval is 1 h, with the instruments operating continuously and producing an integrated hourly average measurement. In many cases, EPA summarizes

air quality data by an O<sub>3</sub> "season". Table 4-1 summarizes the O<sub>3</sub> season for the District of Columbia and each of the states in the United States.

**Table 4-1. Ozone Monitoring Season by State**

State	Begin	End	State	Begin	End
Alabama	March	November	Montana	June	September
Alaska	April	October	Nebraska	April	October
Arizona	January	December	Nevada	January	December
Arkansas	March	November	New Hampshire	April	October
California	January	December	New Jersey	April	October
Colorado	March	September	New Mexico	January	December
Connecticut	April	October	New York	April	October
Delaware	April	October	North Carolina	April	October
D.C.	April	October	North Dakota	May	September
Florida	January	December	Ohio	April	October
Georgia	March	November	Oklahoma	March	November
Hawaii	January	December	Oregon	April	October
Idaho	April	October	Pennsylvania	April	October
Illinois	April	October	Rhode Island	April	October
Indiana	April	October	South Carolina	April	October
Iowa	April	October	South Dakota	June	September
Kansas	April	October	Tennessee	April	October
Kentucky	April	October	Texas <sup>a</sup>	January	December
Louisiana	January	December	Texas <sup>b</sup>	March	October
Maine	April	October	Utah	May	September
Maryland	April	October	Vermont	April	October
Massachusetts	April	October	Virginia	April	October
Michigan	April	October	Washington	April	October
Minnesota	April	October	West Virginia	April	October
Mississippi	March	November	Wisconsin	April	October
Missouri	April	October	Wyoming	April	October

<sup>a</sup>Air Quality Control Region (AQCR) Numbers 4, 5, 7, 10, and 11.

<sup>b</sup>AQCR Numbers 1, 2, 3, 6, 8, 9, and 12.

Source: Code of Federal Regulations (1991).

In this chapter, data are analyzed for the purpose of providing focus on specific issues of exposure-response relationships that are considered in the later effects chapters. The analyses proceed from a national picture of peak annual averages in Metropolitan Statistical Areas (MSAs), through national 10- and 3-year trends, to characteristic seasonal and diurnal patterns at selected stations, and then a brief examination of the incidence of episodic 1-h levels. Although there are O<sub>3</sub> data collected from monitoring stations not listed in AIRS, the major source of information was derived from ambient air concentrations from monitoring sites operated by the State and local air pollution agencies who report their data to AIRS. Because meteorology affects the identification of trends, methodologies that adjust for meteorology are described below.

To obtain a better understanding of the potential effect of ambient O<sub>3</sub> concentrations on human health and vegetation, hourly average concentration information was summarized for urban versus rural (forested and agricultural) areas in the United States. A land use characterization of "rural" does not imply that any specific location is isolated from anthropogenic influences. For example, Logan (1989) has noted that hourly average O<sub>3</sub> concentrations above 0.08 ppm are common in rural areas of the eastern United States in spring and summer, but are unusual in remote western sites. Consequently, for the purposes of comparing exposure regimes that may be characteristic of clean locations in the United States with those that are urban influenced (i.e., located in either urban or rural locations), this chapter characterizes data collected from those stations whose locations appear to be isolated from large-scale anthropogenic influences.

Long-term (multiyear) patterns and trends are available only from stationary ambient monitors; data on indoor concentrations are collected predominantly in selected settings during comparatively short-term studies. Data from the indoor and outdoor environments are reviewed here separately.

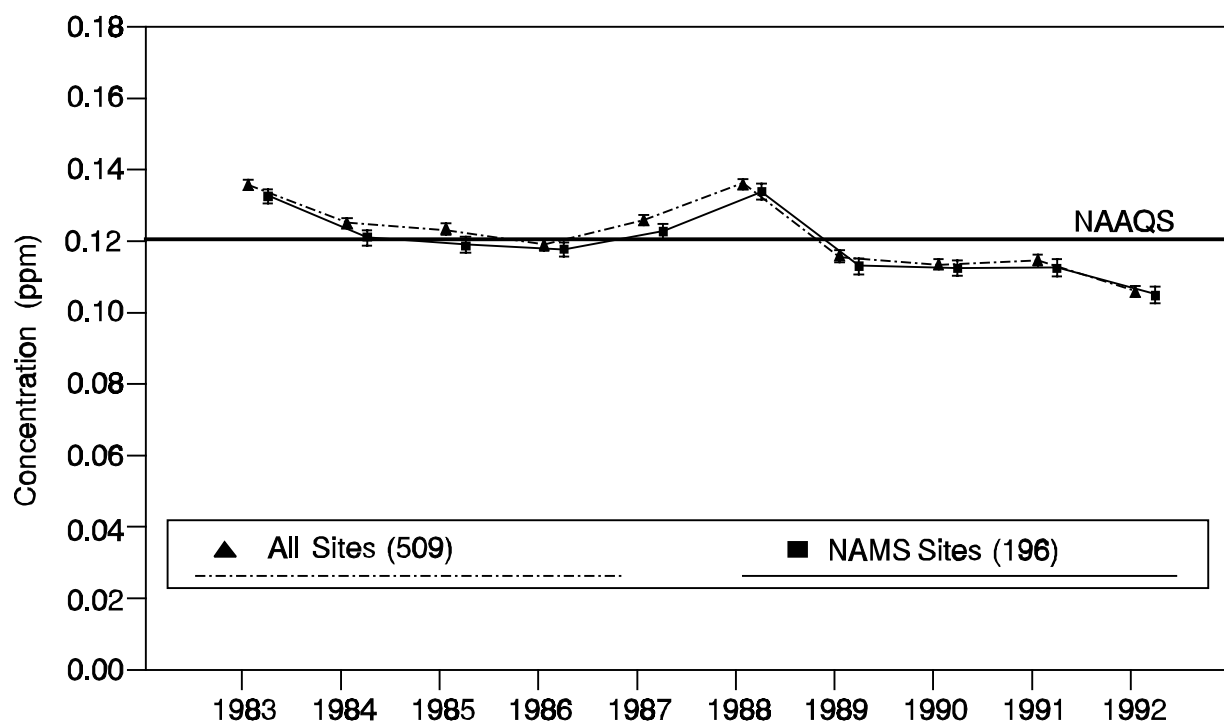
## 4.2 Trends in Ambient Ozone Concentrations

Ozone concentrations and, thus, exposure change from year to year. High O<sub>3</sub> levels occurred in 1983 and 1988 in some areas of the United States. These levels more than likely were attributable, in part, to hot, dry, stagnant conditions. However, O<sub>3</sub> levels in 1992 were the lowest of the 1983 to 1992 period (U.S. Environmental Protection Agency, 1993). These low levels may have been due to meteorological conditions that were less favorable for O<sub>3</sub> formation and to recently implemented control measures. Nationally, the summer of 1992 was the third coolest summer on record (U.S. Environmental Protection Agency, 1993). The U.S. Environmental Protection Agency (1993) has reported a 21% improvement in O<sub>3</sub> levels between 1983 and 1992, which, in part, may be attributed to relatively high O<sub>3</sub> levels in 1983, compared to the low O<sub>3</sub> exposure years from the period 1989 through 1992. However, new statistical techniques accounting for meteorological influences have been used by EPA and they appear to suggest an improvement (independent of meteorological considerations) of 10% for the 10-year period, 1983 to 1992 (U.S. Environmental Protection Agency, 1993).

The EPA summarizes trends for the NAAQS for the most current 3- and 10-year periods. In order to be included in the 10-year trend analysis in the annual *National Air Quality and Emissions Trend Report* (U.S. Environmental Protection Agency, 1993), a

station must report valid data for at least 8 of the last 10 years. A companion analysis of the most recent 3 years requires valid data in all 3 years. Analysis in the above report covers the periods 1983 to 1992 and 1990 to 1992, respectively; 509 sites met the 10-year period criteria, and 672 sites are included in the 1990 to 1992 database. The NAMS sites comprise 196 of the long-term trends sites and 222 of the sites in the 3-year database.

Figure 4-1 displays the 10-year composite average trend for the second highest daily maximum hourly average concentration during the O<sub>3</sub> season for the 509 trend sites and the subset of 196 NAMS sites. The 1992 composite average for the 509 trend sites is 21% lower than the 1983 average and 20% lower for the subset of 196 NAMS sites. The 1992 value is the lowest composite average of the past 10 years (U.S. Environmental Protection Agency, 1993). The 1992 composite average is significantly less than all the previous nine years, 1983 to 1991. As discussed in U.S. Environmental Protection Agency (1992a), the relatively high O<sub>3</sub> concentrations in 1983 and 1988 likely were attributable in part to hot, dry stagnant conditions in some areas of the country that were especially conducive to O<sub>3</sub> formation.



**Figure 4-1. National trend in the composite average of the second highest maximum 1-h ozone concentration at both National Air Monitoring Stations (NAMS) and all sites with 95% confidence intervals, 1983 to 1992.**

Source: U.S. Environmental Protection Agency (1993).

From 1991 to 1992, the composite mean of the second highest daily maximum 1-h O<sub>3</sub> concentrations decreased 7% at the 672 sites and 6% at the subset of 222 NAMS sites.

Also, from 1991 to 1992, the composite average of the number of estimated instances of  $O_3$  exceeding the standard decreased by 23% at the 672 sites, and by 19% at the 222 NAMS sites. Nationwide volatile organic compound (VOC) emissions decreased 3% from 1991 to 1992 (U.S. Environmental Protection Agency, 1993).

The composite average of the second daily maximum concentrations decreased in 8 of the 10 EPA regions from 1991 to 1992, and remained unchanged in Region VII. Except for Region VII, the 1992 regional composite means are lower than the corresponding 1990 levels. Although meteorological conditions in the east during 1993 were more conducive to  $O_3$  formation than those in 1992, the composite mean level for 1993 was the second lowest composite average for the decade (1984 to 1993) (U.S. Environmental Protection Agency, 1994).

Investigators have explored methods for investigating techniques for adjusting  $O_3$  trends for meteorological influences (Stoeckenius and Hudischewskyj, 1990; Wakim, 1990; Shively, 1991; Korsog and Wolff, 1991; Lloyd et al., 1989; Davidson, 1993; Cox and Chu, 1993). Stoeckenius and Hudischewskyj (1990) used a classification method to group days into categories according to the magnitude of  $O_3$  and the similarity of meteorological conditions within each defined group. Adjusted  $O_3$  statistics for each year were computed from the meteorologically grouped data, and the yearly frequency of occurrence of each group relative to its long-term frequency was described. Wakim (1990) used standard regression analysis to quantify the effect of daily meteorology on  $O_3$ . Adjusted  $O_3$  statistics were calculated by adding the expected  $O_3$  statistic for a year with typical meteorology to the average of the regression residuals obtained for the adjusted year. Shively (1991) described a model in which the frequency of exceedance of various  $O_3$  thresholds was modeled as a nonhomogeneous Poisson process where the parameter is a function of time and meteorological variables. Kolaz and Swinford (1990) categorized  $O_3$  days as "conductive" or "nonconductive", based on selected meteorological conditions within the Chicago, IL, area. Within these categories, the meteorological intensity of days conducive to daily exceedances of the NAAQS for  $O_3$  was calculated and used to establish long-term trends in the annual exceedance rate.

Cox and Chu (1993) modeled the daily maximum  $O_3$  concentration using a Weibull distribution with fixed-shape and scale parameters, the logarithm of which varies as a linear function of several meteorological variables and a yearly index. The authors tested for a statistically significant trend term to determine if an underlying meteorologically adjusted trend could be detected. Overall, the measured and modeled predicted percentiles tracked closely in the northern latitudes but performed less adequately in southern coastal and desert areas. The results suggested that meteorologically adjusted upper percentiles of the distribution of daily maximum 1-h  $O_3$  are decreasing in most urban areas over the period 1981 through 1991. The median rate of change was  $-1.1\%$  per year, indicating that  $O_3$  levels have decreased approximately 11% over this time period. The authors reported that trends estimated by ignoring the meteorological component appear to underestimate the rate of improvement in  $O_3$  primarily because of the uneven year-to-year distribution of meteorological conditions favorable to  $O_3$  formation.

Lefohn et al. (1993a) focused on a potentially useful method for identifying monitoring sites whose improvement in the level of  $O_3$  concentrations may be attributed more to the implementation of abatement control strategies than meteorological changes. As has been pointed out previously, meteorology plays an important role in affecting the  $O_3$  concentrations that are contained in the tail of the 1-h distributions, as indicated by the

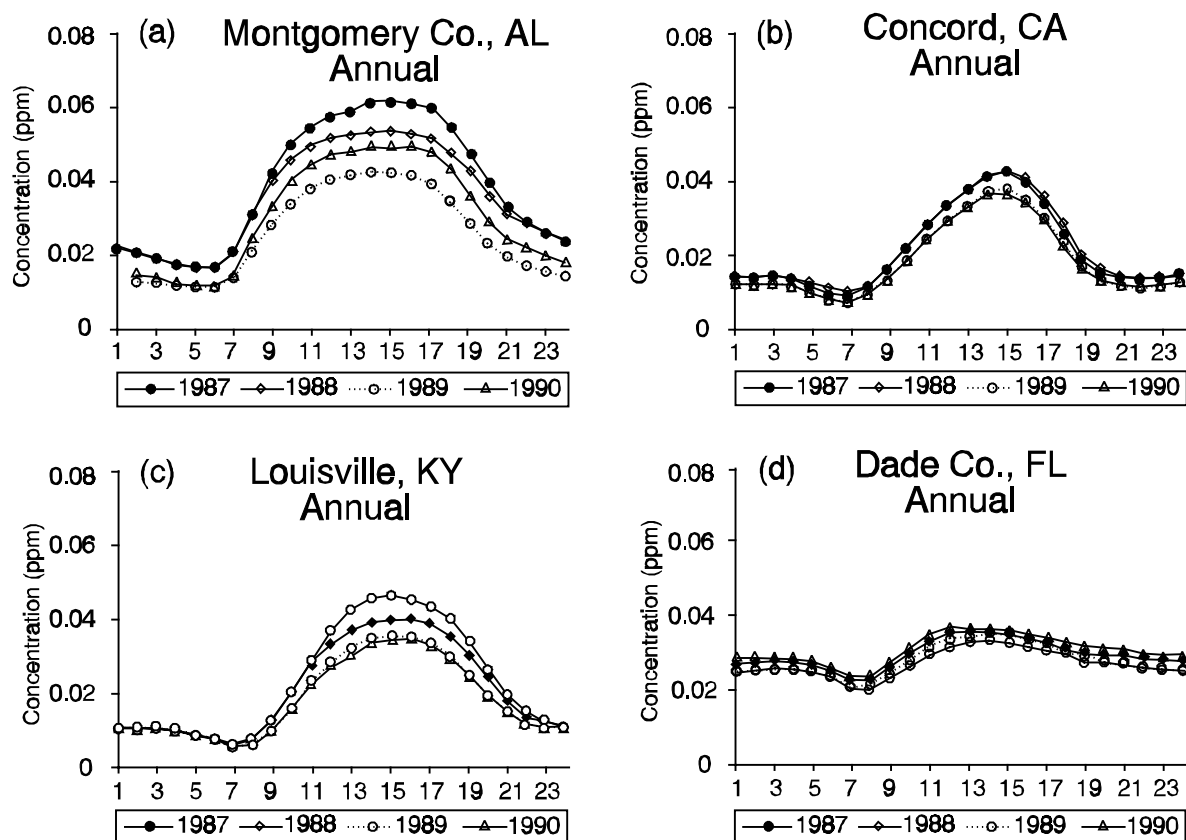


successful predictive application of the exponential-tail model to distributions (California Air Resources Board, 1992). Because meteorology plays such an important role in affecting the tail of the 1-h distribution at a specific site, changes in "attainment" status are not expected to affect changes in the entire distribution pattern and, thus, the average diurnal pattern. Lefohn et al. (1993b) investigated the change in the annual average diurnal pattern as changes in O<sub>3</sub> levels occurred. The authors reported that, although the amplitude of the diurnal patterns changed, there was little evidence for consistent changes in the shape of the annual diurnal patterns (Figure 4-2). In a follow-up to this analysis, Lefohn et al. (1993a) reported that 25 of the 36 sites that changed compliance status across years showed no statistically significant change in the shape of the average diurnal profile (averaged by O<sub>3</sub> season). In addition, the authors reported that for 71% (10 of 14) of the sites in Southern California and Dallas-Fort Worth, TX, that showed improvement in O<sub>3</sub> levels (i.e., reductions in the number of exceedances over the years), but still remained in "nonattainment," a statistically significant change in the shape of the seasonally averaged diurnal profile occurred (e.g., Figure 4-3). Thus, the authors noted that, for the Southern California and Dallas-Fort Worth sites, changes were observed in the seasonally averaged diurnal profiles, whereas for the sites moving between attainment and nonattainment status, such a change in shape generally was not observed. Lefohn et al. (1993a) pointed out that it was possible that meteorology played a more important role in affecting attainment status than did changes in emission levels.

Historically, the long-term O<sub>3</sub> trends in the United States characterized by EPA have emphasized air quality statistics that are closely related to the NAAQS. A report by the National Academy of Sciences (NAS) (National Research Council, 1991) stated that the principal measure currently used to assess O<sub>3</sub> trends is highly sensitive to meteorological fluctuations and is not a reliable measure of progress in reducing O<sub>3</sub> over several years for a given area. The NAS report recommended that "more statistically robust methods be developed to assist in tracking progress in reducing ozone." The NAS report also points out that most of the trends analyses are developed from violations of standards based on lower concentration cutoffs or using percentile distributions. Because of the interest by EPA in tracking trends in the quality of the air that people breathe when outdoors, most of the above measures have some association with the existing NAAQS, in the form of either threshold violations or O<sub>3</sub> concentrations.

Several of the alternative examples provided in the NAS report were described previously by Curran and Frank (1991). Several of the examples mentioned in the NAS report involved threshold violations: the number of days on which the maximum O<sub>3</sub> concentration was above 0.12 ppm (Jones et al., 1989; Kolaz and Swinford, 1990; Wakim, 1990); the number of times during the year that the daily summary statistics exceeded 0.080 or 0.105 ppm (Stoeckenius, 1991), or the number of days in California when the O<sub>3</sub> concentration exceeded 0.2 ppm (Zeldin et al., 1991). Several other O<sub>3</sub> concentration measures are described in this report.

As an alternative to the way in which EPA historically has implemented its trends analysis, U.S. Environmental Protection Agency (1992a) used percentiles in the range of the 50th percentile (or median) to the 95th percentile. The U.S. Environmental Protection Agency (1992a) reported that the pattern for the 10-year trends (1982 to 1991), using the various alternative O<sub>3</sub> summary statistics, were somewhat similar. There was a tendency for the curves to become flatter in the lower percentiles. The peak years of 1983 and 1988 were still evident in the trend lines for each indicator. The increase of 8% recorded in the annual

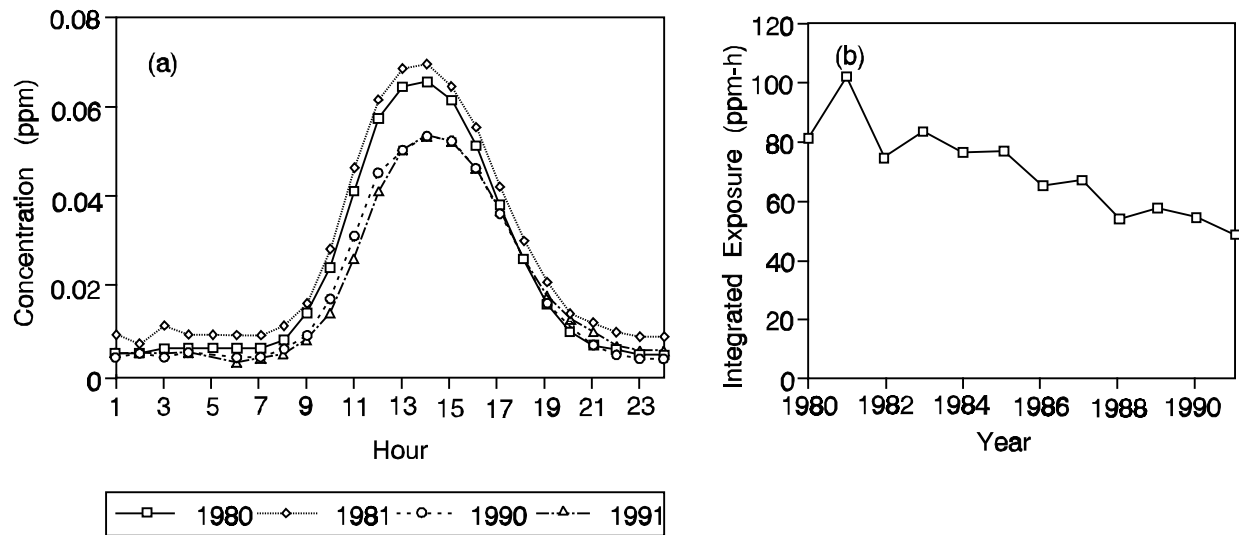


**Figure 4-2.** *The annually averaged composite diurnal curves for the following sites that changed from nonattainment to attainment status: (a) Montgomery County, AL; (b) Concord, CA; (c) Louisville, KY; and (d) Dade County, FL; for the period 1987 to 1990. The darkened curve in each figure identified the year in which the greatest number of daily maximum 4-h average concentrations  $\geq 0.08$  ppm occurred.*

Source: Lefohn et al. (1993b).

second-highest daily maximum 1-h concentration from 1987 to 1988 also was seen in the 95th and 90th percentile concentrations. The lower percentile indicators had smaller increases of 3 to 4%. The percent change between 1982 and 1991 for each of the summary statistics follows: annual daily maximum 1-h concentration, -11%; annual second daily maximum 1-h concentration, -8%; 95th percentile of the daily maximum 1-h concentrations, -5%; 90th percentile, -4%; 70th percentile, -1%; 50th percentile, or median of the daily maximum 1-h concentrations, +1%; and the annual mean of the daily maximum 1-h concentrations, -1%.

Besides EPA, additional investigators have assessed trends at several locations in the United States (e.g., Kuntasai and Chang, 1987; Gallopoulos et al., 1988; Korsog and Wolff, 1991; Lloyd et al., 1989; Rao et al., 1992; Davidson, 1993). For example, Kuntasai and Chang (1987) performed a basin-wide air quality trend analysis for the South Coast Air



**Figure 4-3.** A summary of the (a) seasonal (January to December) averaged composite ozone diurnal curve and (b) integrated exposure W126 index for the Los Angeles, CA, site for the period 1980 to 1991.

Source: Lefohn et al. (1993a).

Basin of California using multistation composite daily maximum 1-h average ambient concentrations for the third quarter from 1968 to 1985. Basin-wide ambient  $O_3$  concentrations appeared to show downward trends for the period 1970 to 1985, but because of high fluctuations, it was difficult to delineate trends for shorter periods. The meteorology-adjusted  $O_3$  showed a more consistent downward trend than did unadjusted  $O_3$ . Korsog and Wolff (1991) examined trends from 1973 to 1983 at eight major population centers in the northeastern United States, using a robust statistical method. The 75th percentile was used by the authors in determining trends. The data were collected over a 3-mo (June through August) period. The surface temperature and upper air temperature variables were found to be the best predictors of  $O_3$  behavior. Two regression procedures were performed to remove the variability of meteorological conditions conducive to high  $O_3$  (i.e.,  $O_3$  concentrations  $>0.08$  ppm). The results of the analysis showed that there had been a decrease of a few ppb on a yearly basis for the majority of the sites investigated by the authors.

Lloyd et al. (1989) investigated the improvement in  $O_3$  air quality from 1976 to 1987 in the South Coast Air Basin. The authors reported that when the trend in total exceedance hours of a consistent set of basin air monitoring stations was considered, the improvement over the period of investigation was substantial. The authors reported that the number of station hours at or above the Stage I Episode Level (0.2 ppm, 1-h average) had decreased by about two-thirds over the period 1976 to 1987. Davidson (1993) reported on the number of days on which  $O_3$  concentrations at one or more stations in the South Coast Air Basin exceeded the federal standard and the number of days reaching Stage I episode levels, for the months of May through October in the years 1976 to 1991. The author reported that the number of basin days exceeding the federal standard declined at an average annual rate of

2.27 days/year over the period. In addition, the number of basin days with Stage I episodes declined at an average annual rate of 4.70 days/year over the period 1976 to 1991. Rao et al. (1992) demonstrated the use of some statistical methods for examining trends in ambient O<sub>3</sub> air quality downwind of major urban areas. The authors examined daily maximum 1-h O<sub>3</sub> concentrations measured over New Jersey, metropolitan New York City, and Connecticut for the period 1980 to 1989. The analyses indicated that although there has been an improvement in O<sub>3</sub> air quality downwind of New York City, there has been little change in O<sub>3</sub> levels upwind of New York City during this 10-year period.

Lefohn and Runeckles (1987) proposed a sigmoidal weighting function that was used in developing a cumulative integrated exposure index (W126):

$$w_i = \frac{1}{[1 + M \times \exp^{(-A \times c_i)}]}, \quad (4-1)$$

where:  $w_i$  = weighting factor for concentration  $i$ ,  
 $M$  and  $A$  are positive arbitrary constants, and  
 $c_i$  = concentration  $i$ .

Lefohn et al. (1988b) reported the use of the sigmoidally weighted index with constants,  $M$  and  $A$ , 4,403 and 126 ppm<sup>-1</sup>, respectively. The authors referred to the index as W126. The values were subjectively determined to develop a weighting function that (1) included hourly average concentrations as low as 0.04 ppm, (2) had an inflection point near 0.065 ppm, and (3) had an equal weighting of one for hourly average concentrations at approximately 0.10 ppm and above. To determine the value of the index, the sigmoidal weighting function at  $c_i$  was multiplied by the hourly average concentration,  $c_i$ , and summed over all relevant hours. The index included the lower, less biologically effective concentrations in the integrated exposure summation. The weighting function has been used to describe the relationship between O<sub>3</sub> exposure and vegetation response (e.g., Lefohn et al., 1988b, 1992a).

Lefohn and Shadwick (1991), using the W126 sigmoidally weighted exposure index, assessed trends in O<sub>3</sub> exposures at rural sites in the United States over 5- and 10-year periods (1984 to 1988 and 1979 to 1988, respectively) for forestry and agricultural regions of the United States. Although the statistical analysis did not explore the effects on trends of the lower O<sub>3</sub> exposure period 1989 to 1992, the analysis did reflect the effect of the higher O<sub>3</sub> exposure years (1983 and 1988). The hot, dry summer of 1988 was associated with the highest O<sub>3</sub> exposures in both the forest and agricultural regions of the eastern United States. To compare the exposure index values across years, a correction for missing data was applied for each pollutant. The corrections were determined for each site on a monthly basis. The Kendall's K statistic (Mann-Kendall test) was used to identify linear trends. Estimates of the rate of change (slope) for the index were calculated. Table 4-2 summarizes the results of the analysis. For sites distributed by forestry regions, there were more positive than negative slope estimates for the 5-year analysis of sites in the southern, midwestern, and Mid-Atlantic regions. For the 10-year analysis, the above was true except for the Mid-Atlantic seasonal analysis, where there was one positive and one negative significant trend. In the southern region, 38% of the sites showed significant trends. For the sites in

**Table 4-2. Summary by Forestry and Agricultural Regions for**

### Ozone Trends Using the W126 Exposure Parameter Accumulated on a Seasonal Basis<sup>a</sup>

Forestry							
Region	5-Year Trends				10-Year Trends		
	Not Significant <sup>b</sup>		Significant		Not Significant		Significant
			–	+			–      +
South	53	(16)	0	14	13	1	7
Midwest	38	(1)	0	7	20	1	6
West	10	(0)	0	3	4	2	1
Pacific Northwest	4	(2)	0	0	2	0	0
Plains	3	(0)	0	0	2	0	0
Northeast	14	(0)	1	0	7	1	1
Mid-Atlantic	12	(0)	0	3	4	1	1
Rocky Mountains	5	(2)	0	1	2	0	1
All	139	(21)	1	28	54	6	17

Agricultural							
Region	5-Year Trends				10-Year Trends		
	Not Significant <sup>b</sup>		Significant		Not Significant		Significant
			–	+			–      +
Pacific	14	(2)	0	3	6	2	1
Mountain	5	(2)	0	1	2	0	1
Northern Plains	3	(0)	0	0	2	0	0
Lake States	10	(0)	0	1	5	0	1
Corn Belt	20	(1)	0	3	11	1	2
Northeast	26	(0)	1	3	11	2	2
Appalachian	27	(9)	0	14	8	0	8
Southeast	16	(5)	0	1	4	1	0
Delta State	9	(0)	0	2	4	0	1
Southeastern Plains	9	(2)	0	0	1	0	1
All	139	(21)	1	28	54	6	17

<sup>a</sup>See Appendix A for abbreviations and acronyms.

<sup>b</sup>Numbers in parentheses in the "Not Significant" column under "5-Year Trends" are the number of sites with exactly 3 years of data.

Source: Lefohn and Shadwick (1991).

the northeastern region, few sites showed a significant trend. There were considerably fewer sites in the remaining regions than in the four forestry regions above. Hence, for these regions, no significance was assigned to the differences in the number of negative and positive slope estimates in the tables. Similar to the results reported for the forestry regions, most of the sites in the agricultural regions showed no O<sub>3</sub> trends. However, in the Appalachian agricultural region, as many as 50% of the sites showed a pronounced indication of a trend. A predominance of positive significant trends for both the 5- and 10-year analyses was observed. In the other agricultural regions, there were approximately an equal number of positive and negative significant 5- and 10-year trends. The O<sub>3</sub> results produced patterns that were not pronounced enough to draw more than tentative conclusions for the 10-year analysis. For the 5-year analysis, there was still not a strong indication of an O<sub>3</sub> trend. However, when significant trends were observed, they were almost always positive. This can be attributed to eastern O<sub>3</sub> levels that were generally higher in 1988 than in previous years.

## **4.3 Surface Ozone Concentrations**

### **4.3.1 Introduction**

Ozone is measured at levels above the minimum detectable level at all monitoring locations in the world (Lefohn et al., 1990a). As discussed earlier in Chapter 3, the concept of a "natural" background of O<sub>3</sub> is complex. Concentrations of background O<sub>3</sub> can vary with temperature, wind speed and direction, vertical motion, geographic location including latitude and altitude, and season of the year. This background O<sub>3</sub> can be attributed the following sources: (1) downward transport of stratospheric O<sub>3</sub> through the free troposphere to near ground level; (2) in situ O<sub>3</sub> production from methane emitted from swamps and wetlands reacting with natural NO<sub>x</sub> emitted from soils, lightning strikes, and from downward transport of NO from the stratosphere into the troposphere; and (3) in situ production of O<sub>3</sub> from the reactions of biogenic VOCs with natural NO<sub>x</sub> (National Research Council, 1991). A fourth source to be considered is the O<sub>3</sub> production resulting from long range transport of O<sub>3</sub> from distant pollutant sources (see Chapter 3).

The occasional occurrence of stratospheric injection of O<sub>3</sub>, at specific times and in certain locations, is accepted and may be responsible for some of the rare occurrences of elevated levels that have been observed at some high- and low-elevation remote sites. A summer season average contribution of approximately 5 to 10 ppb for surface-level O<sub>3</sub> concentration from stratospheric intrusion has been estimated (Altshuller, 1989).

For purposes of comparing how O<sub>3</sub> levels have changed over time, it would be interesting to know how current levels compare to previous, historical natural background levels. However, estimations of background O<sub>3</sub> concentrations are difficult to make. The definition of background and the use of O<sub>3</sub> measurements are subject to much uncertainty. It is difficult, if not impossible, to determine whether any geographic location on earth is free from human influence (Finlayson-Pitts and Pitts, 1986). The natural precursor emissions can be responsible for the production of the O<sub>3</sub> concentrations observed at remote sites (Chameides et al., 1988; Zimmerman, 1979; Trainer et al., 1987). Citing indirect evidence for the possible importance of natural emissions, Lindsay et al. (1989) have emphasized that additional research is required to assess the role that natural hydrocarbons might play in urban and regional O<sub>3</sub> episodes.

It is possible for urban emissions, as well as O<sub>3</sub> produced from urban area emissions, to be transported to more rural downwind locations. This can result in elevated O<sub>3</sub> concentrations at considerable distances from urban centers (Wolff et al., 1977; Husar et al., 1977; Wight et al., 1978; Vukovich et al., 1977; Wolff and Lioy, 1980; Pratt et al. 1983; Logan, 1985; Altshuller, 1986; U.S. Environmental Protection Agency, 1986; Kelly et al., 1986; Pinkerton and Lefohn, 1986; Lefohn et al., 1987a; Logan, 1989; Lefohn and Lucier, 1991; Taylor and Hanson, 1992). For example, on over 40% of the 98 days that the maximum 1-h O<sub>3</sub> concentrations exceeded 0.12 ppm, the highest value was measured downwind of St. Louis at one of the rural sites, which was located approximately 50 km from downtown St. Louis (Altshuller, 1986). Urban O<sub>3</sub> concentration values often are depressed because of titration by NO<sub>x</sub> (Stasiuk and Coffey, 1974). Reagan (1984) and Lefohn et al. (1987a) have observed this phenomenon where O<sub>3</sub> concentrations at center-city sites were lower than some rural locations. Because of the absence of chemical scavenging, O<sub>3</sub> tends to persist longer in nonurban than in urban areas (U.S. Environmental Protection Agency, 1986; Coffey et al., 1977; Wolff et al., 1977; Isaksen et al., 1978).

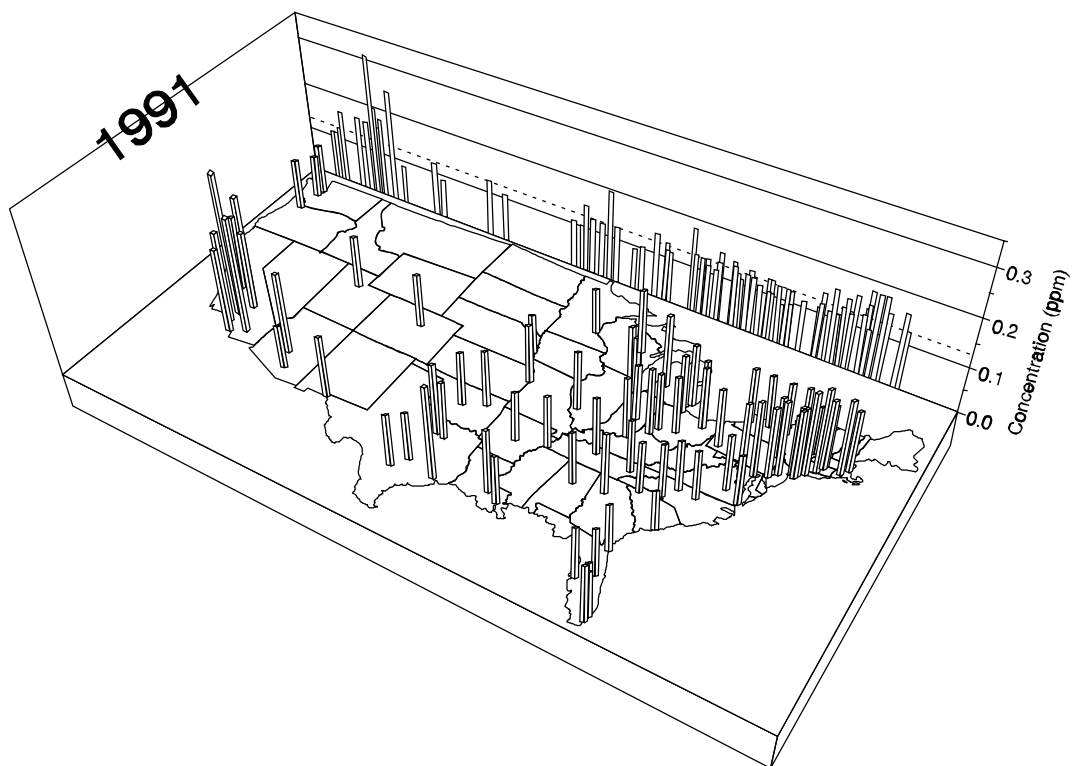
The distribution of O<sub>3</sub> or its precursors at a rural site near an urban source is affected by wind direction (i.e., whether the rural site is located up- or downwind from the source) (Kelly et al., 1986; Lindsay and Chameides, 1988). Thus, it may be difficult to apply land-use designations to the generalization of exposure regimes that may be experienced in urban versus rural areas. Because of this, it is difficult to identify a set of unique O<sub>3</sub> distribution patterns that adequately describe the hourly average concentrations experienced at monitoring sites in rural locations (Lefohn et al., 1991).

#### **4.3.2 Urban Area Concentrations**

Figure 4-4 shows the highest second daily maximum 1-h average O<sub>3</sub> concentrations in 1991 across the United States. The highest second daily maximum 1-h O<sub>3</sub> concentrations by MSA for the years 1989 to 1991 are summarized in Table 4-3. The highest O<sub>3</sub> concentrations are observed in Southern California, but high levels of O<sub>3</sub> also occur in the Texas Gulf Coast, the Northeast Corridor, and other heavily populated regions of the United States, but with a much lower frequency.

Lefohn (1992a) reported that, for many urban sites that experience high second daily maximum 1-h average values (i.e., >0.125 ppm), most are associated with only a few episodes. Monitoring sites in polluted regions tend to experience frequent hourly average O<sub>3</sub> concentrations at or near minimum detectable levels. The percentile summary information for some of these sites shows that, although some of the highest hourly average concentrations occur at these locations, their occurrence is infrequent (Table 4-4). For example, O<sub>3</sub> monitoring sites at Delmar, CA; Stratford and Madison, CT; Baton Rouge, LA; Bayonne, NJ; New York City and Babylon, NY; Harris County, TX; and Bayside, WI, exhibit maximum hourly average concentrations above 0.125 ppm; however, only 1% of the hourly average concentrations generally exceed 0.100 ppm. Although for human health considerations, the occurrence of a second daily maximum hourly average concentration >0.125 ppm is important, Table 4-4 illustrates that, for most of the sites listed (except for several sites in California), such high hourly average concentrations occur less than 1% of the time and are associated with occasional episodes.

As indicated in Section 4.1, interest has been expressed in characterizing O<sub>3</sub> exposure regimes for sites experiencing daily maximum 8-h concentrations above specific



**Figure 4-4. United States map of the highest second daily maximum 1-h average ozone concentration by Metropolitan Statistical Area, 1991.**

Source: U.S. Environmental Protection Agency (1992a).

thresholds (e.g., 0.08 or 0.10 ppm). Table 4-5 summarizes the highest second daily maximum 8-h average  $O_3$  concentrations by MSA for the years 1989 to 1991. The data have been reported for the  $O_3$  season as summarized in Table 4-1. In some cases, high concentrations occur in the fall and winter periods as well as in the summertime. Analyses documented the occurrence, at some sites, of multihour periods within a day of  $O_3$  at levels of potential health effects. Although most of these analyses were made using monitoring data collected from sites in or near nonattainment areas, the analysis of Berglund et al. (1988) showed that at five sites, two in New York state, two in rural California, and one in rural Oklahoma, an alternative  $O_3$  standard of an 8-h average of 0.10 ppm would be exceeded even though the existing 1-h standard would not be. Berglund et al. (1988) described the occurrence at these five sites (none of which was in or near a nonattainment area) of  $O_3$  concentrations showing only moderate peaks but exhibiting multihour levels above 0.10 ppm. Lefohn et al. (1993b) identified those areas in the United States for the period 1987 to 1989 where more than one occurrence of an 8-h daily maximum average concentration of 0.08 ppm was experienced, but an hourly average concentration equal to or greater than 0.12 ppm never occurred.

A follow-up to the points made above is whether an improvement in  $O_3$  levels may produce distributions of 1-h  $O_3$  that result in a broader diurnal profile than those seen in



**Table 4-3. The Highest Second Daily Maximum One-Hour Ozone Concentration (ppm) by Metropolitan Statistical Area (MSA) for the Years 1989 to 1991**

MSA	1989	1990	1991	MSA	1989	1990	1991
Akron, OH	0.14	0.11	0.13	Decatur, IL	0.09	0.09	0.10
Albany-Schenectady-Troy, NY	0.10	0.11	0.10	Denver, CO	0.11	0.11	0.11
Albuquerque, NM	0.10	0.10	0.09	Des Moines, IA	0.08	0.07	0.07
Allentown-Bethlehem, PA-NJ	0.10	0.11	0.12	Detroit, MI	0.14	0.12	0.13
Altoona, PA	0.10	0.10	0.11	Duluth, MN-WI	0.06		
Anaheim-Santa Ana, CA	0.24	0.21	0.20	Eau Claire, WI		0.06	
Anderson, IN	0.10			El Paso, TX	0.14	0.14	0.13
Anderson, SC			0.09	Elmira, NY	0.09	0.10	0.10
Ann Arbor, MI	0.10	0.09	0.11	Erie, PA	0.12	0.10	0.11
Appleton-Oshkosh-Neenah, WI	0.10	0.08	0.09	Eugene-Springfield, OR	0.08	0.09	0.09
Asheville, NC	0.08	0.09	0.08	Evansville, IN-KY	0.12	0.11	0.12
Atlanta, GA	0.12	0.15	0.13	Fayetteville, NC	0.11	0.10	0.10
Atlantic City, NJ	0.12	0.16	0.14	Flint, MI	0.10	0.10	0.10
Augusta, GA-SC	0.10	0.11	0.10	Fort Collins, CO	0.09	0.10	0.09
Aurora-Elgin, IL	0.11	0.09	0.13	Ft. Lauderdale-Hollywood-Pompano, FL	0.12	0.10	0.10
Austin, TX	0.11	0.11	0.10	Fort Myers-Cape Coral, FL	0.10	0.08	0.08
Bakersfield, CA	0.16	0.16	0.16	Fort Wayne, IN	0.12	0.09	0.10
Baltimore, MD	0.13	0.14	0.16	Fort Worth-Arlington, TX	0.13	0.14	0.15
Baton Rouge, LA	0.16	0.18	0.14	Fresno, CA	0.15	0.15	0.16
Beaumont-Port Arthur, TX	0.15	0.15	0.13	Galveston-Texas City, TX	0.14	0.15	0.15
Beaver County, PA	0.10	0.10	0.11	Gary-Hammond, IN	0.11	0.12	0.12
Bellingham, WA	0.05	0.08	0.07	Grand Rapids, MI	0.13	0.14	0.15
Benton Harbor, MI			0.12	Greeley, CO	0.10	0.11	0.10
Bergen-Passaic, NJ	0.12	0.13	0.14	Green Bay, WI	0.09	0.09	0.10
Billings, MT	0.08			Greensboro-Winston Salem-High Point, NC	0.10	0.12	0.11
Birmingham, AL	0.12	0.13	0.11	Greenville-Spartanburg, SC	0.10	0.11	0.11
Boston, MA	0.12	0.11	0.13	Hamilton-Middletown, OH	0.11	0.13	0.12
Boulder-Longmont, CO	0.11	0.10	0.10	Harrisburg-Lebanon-Carlisle, PA	0.11	0.12	0.11
Bradenton, FL	0.10	0.10	0.10	Hartford, CT	0.14	0.15	0.15
Brazoria, TX		0.15	0.13	Hickory, NC		0.09	
Bridgeport-Milford, CT	0.18	0.16	0.15	Honolulu, HI	0.05	0.05	0.05
Brockton, MA	0.13	0.12	0.15	Houma-Thibodaux, LA	0.11	0.12	0.10
Buffalo, NY	0.11	0.11	0.11	Houston, TX	0.23	0.22	0.20
Canton, OH	0.12	0.11	0.12	Huntington-Ashland, WV-KY-OH	0.12	0.14	0.14
Cedar Rapids, IA	0.08	0.07	0.08	Huntsville, AL	0.09	0.09	0.11
Champaign-Urbana-Rantoul, IL	0.09	0.09	0.08	Indianapolis, IN	0.12	0.11	0.11
Charleston, SC	0.09	0.10	0.09	Iowa City, IA	0.09	0.09	0.06
Charleston, WV	0.10	0.12	0.12	Jackson, MS	0.09	0.10	0.09
Charlotte-Gastonia-Rock Hill, NC-SC	0.13	0.12	0.12	Jacksonville, FL	0.11	0.11	0.10
Chattanooga, TN-GA	0.11	0.12	0.10	Jamestown-Dunkirk, NY		0.08	0.10
Chicago, IL	0.12	0.11	0.13	Janesville-Beloit, WI	0.12	0.09	0.11
Chico, CA	0.10	0.12	0.09	Jersey City, NJ	0.12	0.18	0.14
Cincinnati, OH-KY-IN	0.12	0.15	0.14	Johnson City-Kingsport-Bristol, TN-WV	0.11	0.12	0.12
Cleveland, OH	0.12	0.12	0.13	Johnstown, PA	0.10	0.10	0.11
Colorado Springs, CO	0.09	0.09	0.09	Joliet, IL	0.10	0.09	0.12
Columbia, SC	0.10	0.11	0.11	Kalamazoo, MI			0.08
Columbus, GA-AL	0.09	0.11	0.10	Kansas City, MO-KS	0.11	0.11	0.12
Columbus, OH	0.11	0.11	0.12	Kenosha, WI	0.13	0.11	0.15
Corpus Christi, TX	0.10	0.10	0.11	Knoxville, TN	0.10	0.12	0.11
Cumberland, MD-WV		0.09	0.10	Lafayette, LA	0.10	0.11	0.08
Dallas, TX	0.13	0.14	0.12	Lafayette, IN	0.09	0.10	
Danbury, CT	0.13	0.15	0.14	Lake Charles, LA	0.13	0.13	0.12
Davenport-Rock Island-Moline, IA-IL	0.11	0.10	0.10	Lake County, IL	0.13	0.10	0.12
Dayton-Springfield, OH	0.15	0.12	0.12	Lancaster, PA	0.10	0.10	0.12

**Table 4-3 (cont'd). The Highest Second Daily Maximum One-Hour  
Ozone Concentration (ppm) by Metropolitan Statistical  
Area (MSA) for the Years 1989 to 1991**

MSA	1989	1990	1991	MSA	1989	1990	1991
Lansing-East Lansing, MI	0.10	0.10	0.11	Portland, OR-WA	0.09	0.15	0.11
Las Cruces, NM	0.11	0.10	0.10	Portsmouth-Dover-Rochester, NH-ME	0.11	0.10	0.13
Las Vegas, NV	0.11	0.11	0.09	Poughkeepsie, NY	0.08	0.12	0.13
Lawrence-Haverhill, MA-NH	0.12	0.10	0.13	Providence, RI	0.13	0.14	0.16
Lexington-Fayette, KY	0.11	0.11	0.10	Provo-Orem, UT	0.11	0.09	0.08
Lima, OH	0.10	0.10	0.10	Racine, WI	0.14	0.11	0.14
Lincoln, NE	0.06	0.07	0.07	Raleigh-Durham, NC	0.11	0.12	0.11
Little Rock-North Little Rock, AR	0.09	0.10	0.10	Reading, PA	0.11	0.11	0.12
Longview-Marshall, TX	0.10	0.13	0.11	Redding, CA	0.09	0.09	0.08
Lorain-Elyria, OH	0.12	0.09	0.10	Reno, NV	0.10	0.14	0.09
Los Angeles-Long Beach, CA	0.33	0.27	0.31	Richmond-Petersburg, VA	0.11	0.12	0.12
Louisville, KY-IN	0.11	0.13	0.13	Riverside-San Bernardino, CA	0.28	0.30	0.25
Lynchburg, VA		0.10	0.09	Roanoke, VA	0.10	0.09	0.10
Madison, WI	0.10	0.08	0.11	Rochester, NY	0.11	0.11	0.11
Manchester, NH	0.10	0.10	0.10	Rockford, IL	0.10	0.09	0.09
Medford, OR	0.09	0.10	0.07	Sacramento, CA	0.14	0.16	0.16
Melbourne-Titusville-Palm Bay, FL	0.10	0.09	0.09	St. Louis, MO-IL	0.13	0.13	0.12
Memphis, TN-AR-MS	0.12	0.12	0.11	Salinas-Seaside-Monterey, CA	0.11	0.09	0.09
Miami-Hialeah, FL	0.12	0.11	0.12	Salt Lake City-Ogden, UT	0.15	0.12	0.11
Middlesex-Somerset-Hunterdon, NJ	0.13	0.15	0.13	San Antonio, TX	0.11	0.10	0.11
Middletown, CT	0.17	0.16	0.17	San Diego, CA	0.19	0.17	0.18
Milwaukee, WI	0.15	0.13	0.18	San Francisco, CA	0.09	0.06	0.07
Minneapolis-St. Paul, MN-WI	0.10	0.10	0.09	San Jose, CA	0.13	0.12	0.12
Mobile, AL	0.10	0.11	0.09	San Juan, PR	0.06	0.07	0.08
Modesto, CA	0.13	0.12	0.11	Santa Barbara-Santa Maria-Lompoc, CA	0.16	0.13	0.10
Monmouth-Ocean, NJ	0.14	0.14	0.15	Santa Cruz, CA	0.08	0.08	0.10
Montgomery, AL	0.08	0.10	0.09	Santa Fe, NM	0.05	0.08	0.08
Muskegon, MI	0.14	0.13	0.15	Santa Rosa-Petaluma, CA	0.10	0.08	0.10
Nashua, NH	0.09	0.10	0.11	Sarasota, FL	0.10	0.10	0.10
Nashville, TN	0.14	0.13	0.12	Scranton-Wilkes-Barre, PA	0.11	0.11	0.13
Nassau-Suffolk, NY	0.15	0.14	0.18	Seattle, WA	0.09	0.13	0.11
New Bedford, MA	0.12	0.13	0.13	Sharon, PA	0.11	0.10	0.11
New Haven-Meriden, CT	0.15	0.16	0.18	Sheboygan, WI	0.11	0.11	0.16
New London-Norwich, CT-RI	0.14	0.16	0.14	Shreveport, LA	0.12	0.12	0.11
New Orleans, LA	0.11	0.11	0.11	South Bend-Mishawaka, IN	0.10	0.10	0.11
New York, NY	0.13	0.16	0.18	Spokane, WA		0.07	0.08
Newark, NJ	0.13	0.13	0.14	Springfield, IL	0.11	0.10	0.10
Niagara Falls, NY	0.10	0.10	0.10	Springfield, MO	0.09	0.08	0.08
Norfolk-Virginia Beach-Newport News, VA	0.10	0.11	0.11	Springfield, MA	0.13	0.12	0.13
Oakland, CA	0.13	0.12	0.12	Stamford, CT	0.16	0.14	0.15
Oklahoma City, OK	0.11	0.11	0.11	Steubenville-Weirton, OH-WV	0.11	0.09	0.12
Omaha, NE-IA	0.10	0.08	0.08	Stockton, CA	0.11	0.12	0.11
Orlando, FL	0.11	0.12	0.10	Syracuse, NY	0.10	0.11	0.11
Owensboro, KY	0.10	0.11	0.09	Tacoma, WA	0.09	0.13	0.09
Oxnard-Ventura, CA	0.17	0.15	0.16	Tallahassee, FL	0.07		0.05
Parkerburg-Marietta, WV-OH	0.12	0.11	0.12	Tampa-St. Petersburg-Clearwater, FL	0.10	0.11	0.11
Pascagoula, MS	0.10	0.11	0.10	Terre Haute, IN	0.11	0.11	0.10
Pensacola, FL	0.09	0.12	0.11	Toledo, OH	0.11	0.10	0.12
Peoria, IL	0.11	0.09	0.10	Trenton, NJ	0.14	0.14	0.15
Philadelphia, PA-NJ	0.16	0.14	0.16	Tucson, AZ	0.10	0.10	0.09
Phoenix, AZ	0.11	0.14	0.12	Tulsa, OK	0.12	0.12	0.12
Pittsburgh, PA	0.13	0.11	0.12	Utica-Rome, NY	0.09	0.10	0.10
Pittsfield, MA	0.09	0.11	0.10	Vallejo-Fairfield-Napa, CA	0.11	0.10	0.11
Portland, ME	0.13	0.13	0.14	Vancouver, WA	0.09	0.11	0.10

**Table 4-3 (cont'd). The Highest Second Daily Maximum One-Hour  
Ozone Concentration (ppm) by Metropolitan Statistical  
Area (MSA) for the Years 1989 to 1991**

MSA	1989	1990	1991	MSA	1989	1990	1991
Victoria, TX	0.10	0.07	0.10	Wilmington, DE-NJ-MD	0.13	0.14	0.15
Vineland-Millville-Bridgeton, NJ	0.13	0.13	0.12	Wilmington, NC		0.09	
Visalia-Tulare-Porterville, CA	0.15	0.14	0.12	Worcester, MA	0.10	0.12	0.14
Washington, DC-MD-VA	0.13	0.13	0.14	York, PA	0.10	0.12	0.11
W. Palm Beach-Boca Raton-Delray, FL	0.11	0.09	0.09	Youngstown-Warren, OH	0.11	0.10	0.12
Wheeling, WV-OH	0.11	0.11	0.11	Yuba City, CA	0.01	0.09	0.10
Wichita, KS	0.09	0.10	0.10	Yuma, AZ		0.09	0.09
Williamsport, PA	0.08	0.09	0.10				

high-oxidant urban areas where O<sub>3</sub> regimes contain hourly average concentrations with sharper peaks. The result would be an increase in the number of exceedances of daily maximum 8-h average concentrations  $\geq 0.08$  ppm, when compared to those sites experiencing sharper peaks. Lefohn et al. (1993b), using aerometric data at specific sites, observed how O<sub>3</sub> concentrations change when the sites change compliance status. One of the parameters examined was 4-h daily maxima. The number of exceedances for a specific daily maximum average concentration tended to decrease as fewer exceedances of the current 1-h standard were observed at a given site. The number of occurrences of the daily maximum 4-h average concentration  $\geq 0.08$  ppm and the number of exceedances of the current form of the standard had a positive, weak correlation ( $r = 0.51$ ). Lefohn et al. (1993a,b) reported few changes in the shape of the average diurnal patterns as sites changed attainment status; this may have explained why Lefohn et al. (1993b) could not find evidence that the number of occurrences of the daily maximum 4-h average concentration  $\geq 0.08$  ppm increased when the sites experienced few high hourly average concentrations.

There has been considerable interest in possibly substituting one index for another when attempting to relate O<sub>3</sub> exposure with an effect. For example, using O<sub>3</sub> ambient air quality data, McCurdy (1988) compared the number of exceedances of 0.12 ppm and the number of occurrences of the daily maximum 8-h average concentrations  $\geq 0.08$  ppm and reported that a positive correlation ( $r = 0.79$ ) existed between the second-highest 1-h daily maximum in a year and the expected number of days with an 8-h daily maximum average concentration  $> 0.08$  ppm O<sub>3</sub>. In this case, the predictive strength of using one O<sub>3</sub> exposure index to predict another is not strong.

Similar to analysis performed by McCurdy (1988), all of the hourly averaged data from rural agricultural and forested sites in the AIRS database were summarized into maximum 3-mo SUM06, second highest daily maximum hourly average concentration, and second highest daily maximum 8-h average concentration exposure indices per year for the period 1980 to 1991. For the rural agricultural sites, the correlation coefficients between the 3-mo SUM06 and the second highest daily maximum hourly average concentration and the second highest daily maximum 8-h average concentration were 0.650 and 0.739, respectively (Figure 4-5). For the rural forested sites, the correlation coefficients between the 3-mo SUM06 and the second highest daily maximum hourly average concentration and the second highest daily maximum 8-h average concentration were 0.585 and 0.683, respectively (Figure 4-6).

**Table 4-4. Summary of Percentiles of Hourly Average Concentrations (ppm)  
for the April-to-October Period<sup>a</sup>**

AIRS Site	Name	Year	Min.	10	30	50	70	90	95	99	Max	Number of Observations
060370016	Glendora, CA	1989	0.000	0.000	0.020	0.030	0.060	0.120	0.150	0.220	0.340	4,874
		1990	0.000	0.000	0.010	0.030	0.050	0.110	0.140	0.200	0.290	4,888
		1991	0.000	0.000	0.010	0.020	0.050	0.100	0.140	0.200	0.320	4,907
060595001	La Habra, CA	1989	0.000	0.000	0.010	0.030	0.040	0.070	0.090	0.140	0.260	4,875
		1990	0.000	0.000	0.010	0.020	0.040	0.070	0.090	0.140	0.210	4,887
		1991	0.000	0.000	0.010	0.020	0.040	0.070	0.090	0.130	0.210	4,899
060710005	San Bernardino County, CA	1989	0.000	0.020	0.050	0.060	0.090	0.140	0.160	0.200	0.270	4,871
		1990	0.000	0.020	0.040	0.060	0.080	0.120	0.150	0.180	0.330	4,899
		1991	0.000	0.020	0.040	0.060	0.080	0.120	0.140	0.190	0.270	4,905
060731001	Del Mar, CA	1989	0.000	0.020	0.040	0.040	0.050	0.070	0.080	0.120	0.250	4,814
		1990	0.000	0.020	0.030	0.040	0.050	0.060	0.070	0.100	0.170	5,060
		1991	0.000	0.020	0.040	0.050	0.050	0.060	0.070	0.100	0.150	5,017
090013007	Stratford, CT	1989	0.001	0.008	0.024	0.036	0.046	0.064	0.077	0.115	0.202	4,673
		1990	0.001	0.010	0.023	0.033	0.044	0.059	0.068	0.100	0.176	3,853
		1991	0.000	0.007	0.019	0.030	0.042	0.060	0.074	0.110	0.157	4,794
090093002	Madison, CT	1989	0.001	0.008	0.022	0.033	0.043	0.059	0.070	0.103	0.149	4,272
		1990	0.000	0.008	0.023	0.033	0.043	0.063	0.075	0.107	0.197	4,477
		1991	0.000	0.007	0.023	0.034	0.045	0.065	0.082	0.123	0.193	4,814
220330003	Baton Rouge, LA	1989	0.000	0.001	0.009	0.021	0.034	0.059	0.069	0.094	0.168	4,964
		1990	0.000	0.000	0.011	0.023	0.038	0.063	0.079	0.109	0.187	5,000
		1991	0.000	0.002	0.010	0.020	0.031	0.054	0.067	0.092	0.134	4,905
340170006	Bayonne, NJ	1989	0.001	0.001	0.008	0.021	0.036	0.059	0.074	0.099	0.147	4,815
		1990	0.001	0.001	0.009	0.022	0.036	0.058	0.073	0.106	0.185	4,939
		1991	0.001	0.002	0.011	0.024	0.038	0.065	0.082	0.110	0.167	4,943
360610063	New York, NY	1989	0.000	0.015	0.028	0.040	0.051	0.073	0.086	0.110	0.134	4,825
		1990	0.000	0.014	0.029	0.039	0.051	0.074	0.090	0.116	0.175	4,707
		1991	0.002	0.015	0.029	0.041	0.056	0.082	0.096	0.123	0.177	4,910
361030002	Babylon, NY	1989	0.001	0.004	0.015	0.027	0.039	0.060	0.073	0.101	0.156	4,407
		1990	0.000	0.006	0.017	0.027	0.040	0.060	0.075	0.105	0.146	4,876
		1991	0.001	0.005	0.018	0.030	0.044	0.067	0.081	0.111	0.217	4,873

**Table 4-4 (cont'd). Summary of Percentiles of Hourly Average Concentrations (ppm)  
for the April-to-October Period<sup>a</sup>**

AIRS Site	Name	Year	Min.	10	30	50	70	90	95	99	Max	Number of Observations
482010024	Harris County, TX	1989	0.000	0.000	0.010	0.020	0.030	0.060	0.070	0.110	0.230	4,728
		1990	0.000	0.000	0.010	0.020	0.040	0.070	0.090	0.130	0.220	4,274
		1991	0.000	0.000	0.000	0.020	0.030	0.060	0.080	0.110	0.170	4,322
550790085	Bayside, WI	1989	0.002	0.006	0.024	0.035	0.046	0.066	0.077	0.101	0.151	4,376
		1990	0.002	0.009	0.025	0.034	0.044	0.061	0.071	0.094	0.130	4,395
		1991	0.002	0.008	0.025	0.035	0.047	0.070	0.081	0.113	0.189	4,303

<sup>a</sup>See Appendix A for abbreviations and acronyms.

**Table 4-5. The Highest Second Daily Maximum Eight-Hour  
Average Ozone Concentration (ppm) by Metropolitan Statistical  
Area (MSA) for the Years 1989 to 1991**

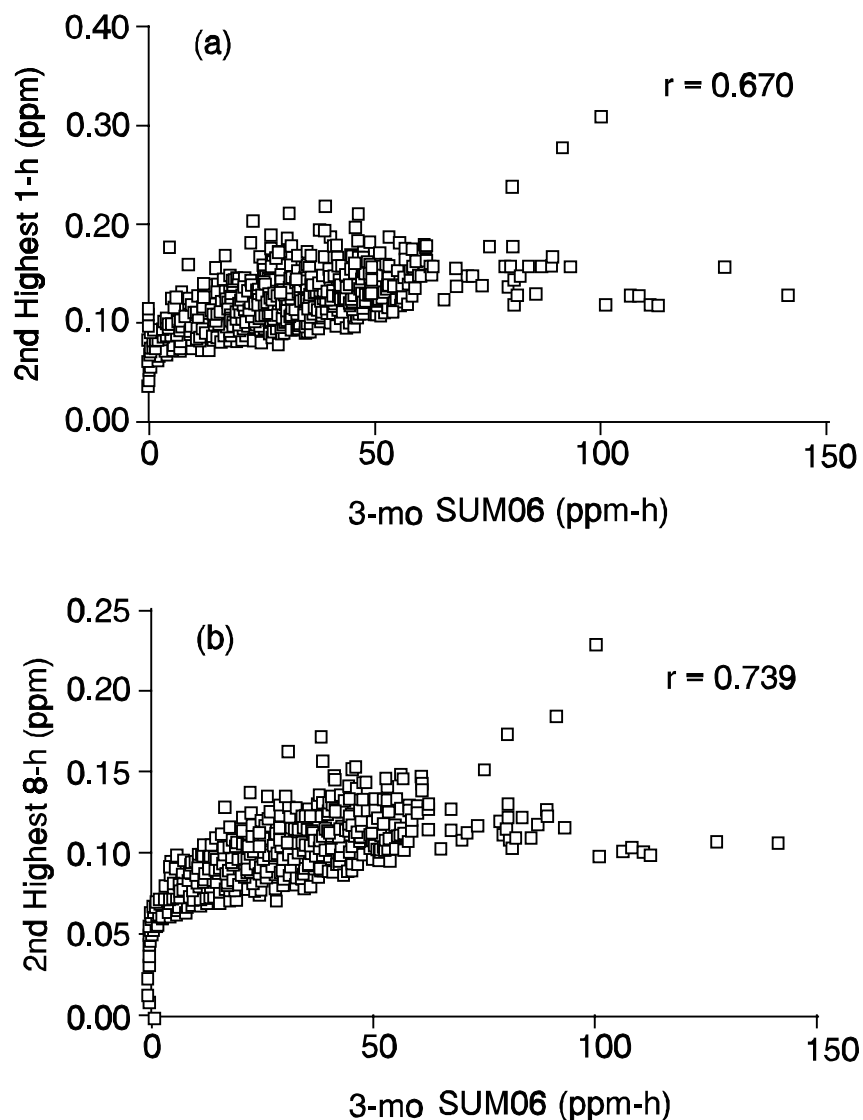
MSA	1989	1990	1991	MSA	1989	1990	1991
Akron, OH	0.109	0.097	0.102	Davenport-Rock Island-Moline, IA-IL	0.102	0.071	0.086
Albany-Schenectady-Troy, NY	0.087	0.091	0.089	Dayton-Springfield, OH	0.122	0.096	0.107
Albuquerque, NM	0.078	0.089	0.077	Decatur, IL	0.084	0.077	0.087
Alexandria, LA	0.077	0.076	0.074	Denver, CO	0.089	0.086	0.080
Allentown-Bethlehem, PA-NJ	0.091	0.098	0.112	Des Moines, IA	0.073	0.051	0.056
Altoona, PA	0.077	0.090	0.094	Detroit, MI	0.103	0.091	0.111
Anaheim-Santa Ana, CA	0.146	0.135	0.110	Duluth, MN-WI	0.073	0.051	
Anderson, IN	0.084			Eau Claire, WI		0.049	
Anderson, SC			0.081	El Paso, TX	0.083	0.087	0.080
Ann Arbor, MI	0.093	0.087	0.096	Elmira, NY	0.075	0.080	0.094
Appleton-Oshkosh-Neenah, WI	0.091	0.078	0.082	Eric, PA	0.092	0.088	0.093
Asheville, NC	0.083	0.074	0.064	Eugene-Springfield, OR	0.061	0.077	0.070
Atlanta, GA	0.096	0.125	0.102	Evansville, IN-KY	0.097	0.094	0.107
Atlantic City, NJ	0.104	0.135	0.112	Fayetteville, NC	0.089	0.088	0.085
Augusta, GA-SC	0.078	0.092	0.081	Flint, MI	0.093	0.086	0.090
Aurora-Elgin, IL	0.088	0.077	0.100	Fort Collins, CO	0.076	0.076	0.077
Austin, TX	0.099	0.103	0.084	Ft. Lauderdale-Hollywood-Pompano, FL	0.089	0.078	0.064
Bakersfield, CA	0.124	0.120	0.118	Fort Myers-Cape Coral, FL	0.084	0.070	0.062
Baltimore, MD	0.103	0.111	0.127	Fort Wayne, IN	0.105	0.091	0.096
Baton Rouge, LA	0.095	0.134	0.100	Fort Worth-Arlington, TX	0.098	0.116	0.116
Beaumont-Port Arthur, TX	0.110	0.100	0.101	Fresno, CA	0.116	0.105	0.119
Beaver County, PA	0.095	0.085	0.095	Galveston-Texas City, TX	0.102	0.096	0.094
Bellingham, WA	0.038	0.068	0.059	Gary-Hammond, IN	0.102	0.122	0.101
Benton Harbor, MI			0.098	Grand Rapids, MI	0.119	0.107	0.124
Bergen-Passaic, NJ	0.093	0.097	0.106	Greeley, CO	0.080	0.080	0.081
Billings, MT	0.56			Green Bay, WI	0.095	0.074	0.079
Biloxi-Gulfport, TX			0.089	Greensboro-Winston Salem-High Point, NC	0.083	0.100	0.087
Birmingham, AL	0.088	0.105	0.088	Greenville-Spartanburg, SC	0.088	0.091	0.085
Bismark, ND	0.086	0.062	0.061	Hamilton-Middletown, OH	0.095	0.111	0.105
Bloomington-Normal, IL	0.081	0.071	0.095	Harrisburg-Lebanon-Carlisle, PA	0.091	0.108	0.100
Boston, MA	0.109	0.105	0.118	Hartford, CT	0.114	0.109	0.112
Boulder-Longmont, CO	0.082	0.084	0.083	Hickory, NC		0.080	
Bradenton, FL	0.086	0.075	0.074	Honolulu, HI	0.020	0.037	0.042
Brazoria, TX		0.101	0.107	Houma-Thibodaux, LA	0.082	0.084	0.077
Bridgeport-Milford, CT	0.139	0.114	0.121	Houston, TX	0.121	0.141	0.115
Brockton, MA	0.110	0.106	0.107	Huntington-Ashland, WV-KY-OH	0.102	0.109	0.124
Buffalo, NY	0.085	0.096	0.097	Huntsville, AL	0.072	0.080	0.082
Canton, OH	0.098	0.098	0.099	Indianapolis, IN	0.097	0.099	0.100
Carson City, NV	0.070			Iowa City, IA	0.078	0.084	0.060
Cedar Rapids, IA	0.078	0.057	0.066	Jackson, MS	0.086	0.083	0.075
Champaign-Urbana-Rantoul, IL	0.084	0.080	0.077	Jacksonville, FL	0.090	0.084	0.077
Charleston, SC	0.094	0.084	0.074	Jamestown-Dunkirk, NY		0.068	0.082
Charleston, WV	0.087	0.083	0.099	Janesville-Beloit, WI	0.097	0.081	0.090
Charlotte-Gastonia-Rock Hill, NC-SC	0.089	0.100	0.094	Jersey City, NJ	0.105	0.128	0.117
Charlottesville, VA	0.076	0.089	0.091	Johnson City-Kingsport-Bristol, TN-WV	0.083	0.100	0.080
Chattanooga, TN-GA	0.091	0.094	0.083	Johnstown, PA	0.082	0.090	0.099
Chicago, IL	0.101	0.084	0.106	Joliet, IL	0.082	0.070	0.091
Chico, CA	0.081	0.083	0.074	Kalamazoo, MI			0.071
Cincinnati, OH-KY-IN	0.106	0.119	0.115	Kansas City, MO-KS	0.090	0.089	0.089
Cleveland, OH	0.099	0.096	0.101	Kenosha, WI	0.113	0.093	0.118
Colorado Springs, CO	0.072	0.065	0.068	Knoxville, TN	0.088	0.105	0.091
Columbia, SC	0.079	0.094	0.083	Lafayette, LA	0.080	0.086	0.075
Columbus, GA-AL	0.068	0.075	0.083	Lafayette, IN	0.077	0.092	0.090
Columbus, OH	0.097	0.098	0.112	Lake Charles, LA	0.088	0.084	0.096
Corpus Christi, TX	0.083	0.085	0.075	Lake County, IL	0.092	0.082	0.102
Cumberland, MD-WV		0.070	0.076	Lancaster, PA	0.085	0.089	0.096
Dallas, TX	0.101	0.115	0.095	Lansing-East Lansing, MI	0.093	0.083	0.087
Danbury, CT	0.098	0.105	0.116	Las Cruces, NM	0.074	0.082	0.074

**Table 4-5 (cont'd). The Highest Second Daily Maximum  
Eight-Hour Average Ozone Concentration (ppm) by Metropolitan  
Statistical Area (MSA) for the Years 1989 to 1991**

MSA	1989	1990	1991	MSA	1989	1990	1991
Las Vegas, NV	0.084	0.082	0.075	Provo-Orem, UT	0.094	0.070	0.071
Lawrence-Haverhill, MA-NH	0.104	0.077	0.106	Racine, WI	0.110	0.090	0.118
Lewiston-Auburn, ME	0.089	0.090	0.101	Raleigh-Durham, NC	0.099	0.094	0.091
Lexington-Fayette, KY	0.097	0.097	0.088	Reading, PA	0.095	0.101	0.109
Lima, OH	0.088	0.086	0.091	Redding, CA	0.080	0.100	0.093
Lincoln, NE	0.057	0.060	0.060	Reno, NV	0.081	0.109	0.075
Little Rock-North Little Rock, AR	0.077	0.083	0.089	Richmond-Petersburg, VA	0.094	0.101	0.097
Longview-Marshall, TX	0.076	0.089	0.086	Riverside-San Bernardino, CA	0.196	0.193	0.189
Lorain-Elyria, OH	0.096	0.082	0.091	Roanoke, VA	0.077	0.075	0.078
Los Angeles-Long Beach, CA	0.188	0.170	0.178	Rochester, NY	0.094	0.097	0.103
Louisville, KY-IN	0.096	0.093	0.119	Rockford, IL	0.085	0.073	0.081
Lynchburg, VA		0.083	0.079	Sacramento, CA	0.105	0.125	0.124
Madison, WI	0.089	0.079	0.089	St. Louis, MO-IL	0.105	0.098	0.107
Manchester, NH	0.084	0.098	0.087	Salinas-Seaside-Monterey, CA	0.082	0.074	0.071
Medford, OR	0.063	0.076	0.055	Salt Lake City-Ogden, UT	0.114	0.086	0.086
Melbourne-Titusville-Palm Bay, FL	0.082	0.082	0.069	San Antonio, TX	0.100	0.080	0.085
Memphis, TN-AR-MS	0.099	0.100	0.093	San Diego, CA	0.139	0.135	0.128
Miami-Hialeah, FL	0.087	0.076	0.072	San Francisco, CA	0.064	0.056	0.054
Middlesex-Somerset-Hunterdon, NJ	0.108	0.111	0.111	San Jose, CA	0.094	0.075	0.086
Middletown, CT	0.119	0.117	0.125	San Juan, PR	0.043	0.042	0.044
Milwaukee, WI	0.115	0.100	0.118	Santa Barbara-Santa Maria-Lompoc, CA	0.129	0.129	0.075
Minneapolis-St. Paul, MN-WI	0.090	0.077	0.079	Santa Cruz, CA	0.066	0.058	0.067
Mobile, AL	0.079	0.098	0.062	Santa Fe, NM	0.049	0.069	0.076
Modesto, CA	0.101	0.106	0.091	Santa Rosa-Petaluma, CA	0.083	0.061	0.076
Monmouth-Ocean, NJ	0.118	0.107	0.122	Sarasota, FL	0.085	0.083	0.080
Montgomery, AL	0.066	0.081	0.071	Scranton-Wilkes-Barre, PA	0.088	0.096	0.111
Muskegon, MI	0.139	0.100	0.119	Seattle, WA	0.078	0.099	0.087
Nashua, NH	0.072	0.095	0.110	Sharon, PA	0.098	0.095	0.094
Nashville, TN	0.093	0.102	0.107	Sheboygan, WI	0.103	0.088	0.103
Nassau-Suffolk, NY	0.099	0.115	0.121	Shreveport, LA	0.098	0.102	0.087
New Bedford, MA	0.104	0.101	0.106	South Bend-Mishawaka, IN	0.089	0.089	0.093
New Haven-Meriden, CT	0.108	0.122	0.128	Spokane, WA		0.060	0.060
New London-Norwich, CT-RI	0.128	0.127	0.115	Springfield, IL	0.085	0.082	0.087
New Orleans, LA	0.075	0.086	0.079	Springfield, MO	0.075	0.061	0.069
New York, NY	0.111	0.119	0.133	Springfield, MA	0.123	0.113	0.117
Newark, NJ	0.108	0.107	0.119	Stamford, CT	0.113	0.112	0.115
Niagara Falls, NY	0.082	0.092	0.095	Steubenville-Weirton, OH-WV	0.094	0.075	0.098
Norfolk-Virginia Beach-Newport News, VA	0.089	0.095	0.089	Stockton, CA	0.086	0.093	0.090
Oakland, CA	0.091	0.091	0.083	Syracuse, NY	0.090	0.093	0.098
Oklahoma City, OK	0.089	0.090	0.089	Tacoma, WA	0.077	0.094	0.077
Omaha, NE-IA	0.075	0.075	0.073	Tallahassee, FL	0.072		
Orlando, FL	0.096	0.082	0.075	Tampa-St. Petersburg-Clearwater, FL	0.088	0.085	0.083
Owensboro, KY	0.096	0.104	0.077	Terre Haute, IN	0.087	0.095	0.089
Oxnard-Ventura, CA	0.147	0.119	0.129	Toledo, OH	0.093	0.084	0.107
Parkersburg-Marietta, WV-OH	0.094	0.088	0.104	Trenton, NJ	0.119	0.112	0.131
Pascagoula, MS	0.082	0.092	0.077	Tucson, AZ	0.074	0.084	0.080
Pensacola, FL	0.080	0.098	0.082	Tulsa, OK	0.093	0.094	0.097
Peoria, IL	0.087	0.075	0.088	Utica-Rome, NY	0.082	0.094	0.091
Philadelphia, PA-NJ	0.118	0.110	0.123	Vallejo-Fairfield-Napa, CA	0.076	0.074	0.078
Phoenix, AZ	0.086	0.096	0.094	Vancouver, WA	0.058	0.080	0.042
Pittsburgh, PA	0.107	0.100	0.106	Victoria, TX	0.093	0.056	0.086
Pittsfield, MA	0.075	0.094	0.095	Vineland-Millville-Bridgeton, NJ	0.122	0.106	0.108
Portland, ME	0.124	0.109	0.134	Visalia-Tulare-Porterville, CA	0.114	0.103	0.104
Portland, OR-WA	0.071	0.111	0.092	Washington, DC-MD-VA	0.106	0.110	0.114
Portsmouth-Dover-Rochester, NH-ME	0.107	0.086	0.123	W. Palm Beach-Boca Raton-Delray, FL	0.081	0.067	0.059
Poughkeepsie, NY	0.079	0.085	0.101	Wheeling, WV-OH	0.086	0.089	0.093
Providence, RI	0.107	0.112	0.127	Wichita, KS	0.079	0.089	0.081

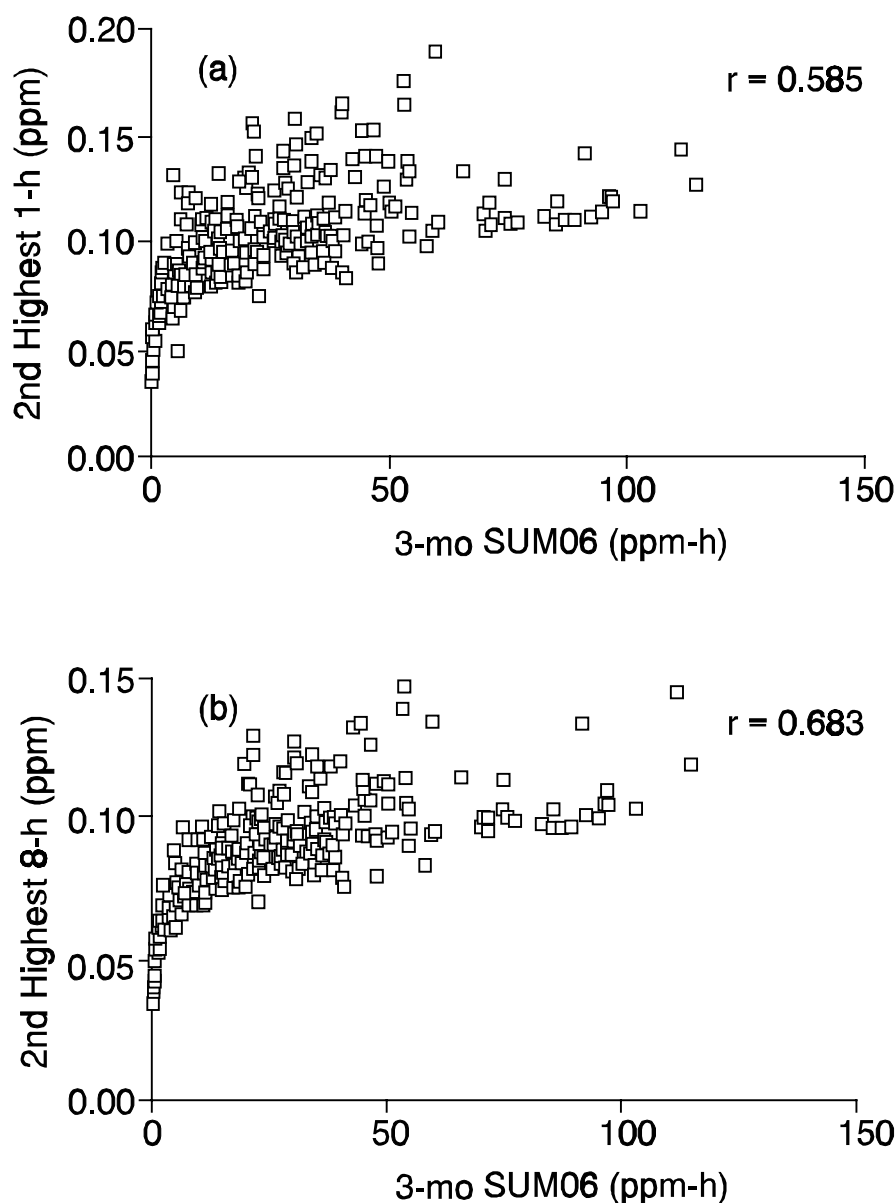
**Table 4-5 (cont'd). The Highest Second Daily Maximum Eight-Hour Average Ozone Concentration (ppm) by Metropolitan Statistical Area (MSA) for the Years 1989 to 1991**

MSA	1989	1990	1991	MSA	1989	1990	1991
Williamsport, PA	0.065	0.072	0.087	York, PA	0.091	0.108	0.103
Wilmington, DE-NJ-MD	0.105	0.110	0.118	Youngstown-Warren, OH	0.088	0.085	0.101
Wilmington, NC		0.086		Yuba City, CA	0.084	0.076	0.084
Worcester, MA	0.097	0.089	0.107	Yuma, AZ	0.080	0.075	0.070



**Figure 4-5.** *The relationship between (a) the second highest daily maximum hourly average ozone ( $O_3$ ) concentration and the maximum 3-mo SUM06 value and (b) the second highest daily maximum 8-h average  $O_3$  concentration and the maximum 3-mo SUM06 value for specific site years at rural agricultural sites for the 1980-to-1991 period.*





**Figure 4-6.** *The relationship between (a) the second highest daily maximum hourly average ozone ( $O_3$ ) concentration and the maximum 3-mo SUM06 value and (b) the second highest daily maximum 8-h average  $O_3$  concentration and the maximum 3-mo SUM06 value for specific site years at rural forested sites for the 1980-to-1991 period.*

One of the difficulties in attempting to use correlation analysis between indices for rationalizing the substitution of one exposure index for another to predicting an effect (e.g., SUM06 versus the second highest daily maximum hourly average concentration) is the introduction of the error associated with estimating levels of one index from another. Lefohn et al. (1989) have recommended that if a different exposure index (e.g., second highest daily maximum hourly average concentration) is to be compared to, for example, the SUM06 for

adequacy in predicting crop loss, then the focus should be on how well the two exposure indices predict crop loss using the effects model that is a function of the most relevant index, and not on how well the indices predict one another. Using data from both urban and rural O<sub>3</sub> monitoring sites in the midwestern United States that were located near agricultural or forested areas, Lefohn et al. (1989) reported a large amount of scatter between the second highest daily maximum hourly average concentration and the SUM06 indices. This large scatter indicated considerable uncertainty when attempting to predict a value for SUM06, given a specific second highest daily maximum hourly average concentration value. The authors reported that for a given second highest daily maximum hourly average concentration, the SUM06 values varied over a large range. Lefohn et al. (1989) concluded that such large uncertainty would introduce additional uncertainty when attempting to use the predicted exposure index to estimate an effect. The authors concluded that less error would be introduced if either of the two indices were used directly in the development of an exposure-response model.

As pointed out by the U.S. Environmental Protection Agency (1986), a familiar measure of O<sub>3</sub> air quality is the number or percentage of days on which some specific concentration is equalled or exceeded. This measure, however, does not shed light on one of the more important questions regarding the effects of O<sub>3</sub> on both people and plants: what is the possible significance of high concentrations lasting 1 h or longer and then recurring on 2 or more successive days?

The recurrence of high O<sub>3</sub> concentrations on consecutive days was examined in four cities (one site in each city) by the U.S. Environmental Protection Agency (1986). The numbers of multiday events were tallied by length of event (i.e., how many consecutive days) using data for the daylight hours (0600 to 2000 hours) in the second and third quarters of 1979 through 1981. These sites were selected because they included areas known to experience high O<sub>3</sub> concentrations (e.g., California), and because they represent different geographic regions of the country (west, southwest, and east).

Because of the importance of episodes and respites, the U.S. Environmental Protection Agency (1986) commented on the occurrences of the length of episodes and the time between episodes. The agency concluded that its analysis showed variations among sites in the lengths of episodes as well as the respite periods. In its discussion, the U.S. Environmental Protection Agency (1986) defined a day or series of days on which the daily 1-h maximum reached or exceeded the specified level as an "exposure"; the intervening day or days when that level was not reached was called a "respite". Four O<sub>3</sub> concentrations were selected: 0.06, 0.12, 0.18, and 0.24 ppm. At the Dallas site, for example, the value equalled or exceeded 0.06 ppm for more than 7 days in a row. The Pasadena site experienced 10 such exposures, but these 10 exposure events spanned 443 days; in Dallas, the 11 exposures involved only 168 days. At the lowest concentration ( $\geq 0.06$  ppm), the Dallas station recorded more short-term ( $\leq 7$  days) exposures (45) involving more days (159) than the Pasadena station (14 exposures over 45 days) because the daily 1-h maximum statistic in Pasadena remained above 0.06 ppm for such protracted periods. At concentrations  $\geq 0.12$  ppm, the lengthy exposures at the Pasadena site resolved into numerous shorter exposures, whereas in Dallas the exposures markedly dwindled in number and duration.

### 4.3.3 Nonurban Area Concentrations

#### 4.3.3.1 Sites That Experience Low Maximum Hourly Average Concentrations

It is important to establish reference points that can be used to describe the distribution of hourly average concentrations at monitoring sites experiencing low maximum concentrations. Doing so will make it possible to confirm that the hourly average concentrations in control chambers utilized for research experiments associated with human health and vegetation effects are similar to those experienced under ambient conditions. For example, there has been concern expressed that O<sub>3</sub> concentrations in charcoal-filtration chambers used by NCLAN did not simulate the levels in those areas of the United States that experience low maximum O<sub>3</sub> concentrations (see Chapter 5, Section 5.5). Heuss (1982) expressed concern that the O<sub>3</sub> levels in the charcoal-filtration chambers were lower than those at sites experiencing low maximum hourly average concentrations, and that the resulting agricultural loss estimates derived from the NCLAN models may have been too high.

Two possible approaches for establishing reference points have been discussed (Lefohn et al., 1990a). One method is to estimate, using mathematical models and historical data, unpolluted background levels prior to disturbance by human influence. However, there are difficulties with this approach. Background can be defined as the unpolluted conditions in preindustrial times (i.e., absolutely unpolluted air in which there was no human interference). Alternatively, a background also can be defined as the condition *currently* existing at any location that is presently free from human influence. However, almost all geographic locations on the earth have been impacted by human influences (e.g., Finlayson-Pitts and Pitts, 1986; Hong et al., 1994) (see Section 4.3.1).

It is unlikely that a single value or even a fixed range of O<sub>3</sub> background values can apply uniformly across North America or elsewhere in the northern or southern hemispheres. Any attempt to quantify the historical background is subject to much uncertainty for the following reasons:

1. Little is known with certainty about the nature of past unpolluted conditions.
2. Even if all anthropogenic emissions of O<sub>3</sub> precursors were eliminated, it is unlikely that O<sub>3</sub> in, for example, eastern North America, would return to preindustrial levels. Since preindustrial times, major land use changes have occurred. Because substantial amounts of natural emissions of O<sub>3</sub> precursors are derived from soils and vegetation, especially during the warmer months, it is probable that these land use changes have modified the emissions of O<sub>3</sub> precursors and, thus, changed the concentrations of O<sub>3</sub>.

Although not representing natural O<sub>3</sub> background, attempts have been made, using historical data, to estimate O<sub>3</sub> concentrations in the late 1800s and early 1900s. Model simulations and limited observations suggest that tropospheric O<sub>3</sub> has increased in the northern hemisphere since the preindustrial times and future increases may be possible (Bojkov, 1986; Volz and Kley, 1988; Thompson, 1992). However, several investigators have discussed the possible confounding influences that led to a great deal of uncertainty associated with characterizing the O<sub>3</sub> concentrations measured in the late 1800s and early 1900s (Lisac and Grubisic, 1991; Lefohn et al., 1992c; Cartalis and Varotsos, 1994). Using data collected over the past 30 years, consistent trends in tropospheric O<sub>3</sub> have not been observed across the

northern hemisphere (World Meteorological Organization/United Nations Environment Program, 1994). Using ozonesonde data, observations show that tropospheric O<sub>3</sub> has increased above some locations in the northern hemisphere. However, in the 1980s, the trends were variable and either small or nonexistent (Logan, 1994). European measurements at some surface sites indicate an increase in O<sub>3</sub> concentration since earlier this century. Because of the uncertainty associated with measurements taken in the late 1880s and early 1990s, it is difficult to compare O<sub>3</sub> concentration levels experienced in the United States with today's levels. However, it can be concluded that O<sub>3</sub> levels measured around 100 years ago were lower than the values observed today at most sites in the United States, and that consistently increasing trends in O<sub>3</sub> concentration measured at surface levels have not been observed annually at sites monitoring O<sub>3</sub> in the United States.

An alternative approach (adopted by Lefohn et al., 1990a, to establish reference points) is to examine O<sub>3</sub> hourly average concentration data from those monitoring sites in the world that experienced low maximum hourly average values. When data from these sites, including several in North America, were characterized, and the range of hourly average concentrations compared, it was found that the distributions of hourly average concentrations for sites with the lowest hourly average concentrations were similar. The authors believed the data from these sites could be used for establishing reference points that could be compared with more polluted areas.

Is it appropriate to use sites that experience the lowest hourly average concentrations in the United States today as reference levels, or should O<sub>3</sub> background levels that may have existed 100 years ago be used? Although it might be argued that all sites in the United States have been affected to such a level that today's values are not relevant because an increase in O<sub>3</sub> concentrations has occurred since the late 1800s, two key points argue against this line of reasoning. First, as indicated above, although O<sub>3</sub> levels have increased since the last century, consistent trends in tropospheric O<sub>3</sub> have not been observed across the northern hemisphere. Thus, at some monitoring sites, O<sub>3</sub> levels may not show increasing trends. Second, all the increases in background levels of O<sub>3</sub> may not necessarily be associated with changes in anthropogenic emissions. Since preindustrial times, major land use changes, resulting from human-induced activities, have occurred. Changes in natural emissions of O<sub>3</sub> precursors associated with soils and vegetation in the last 100 years may be associated with these land use changes, with the result that some of the increased levels in O<sub>3</sub> concentrations may be attributed to sources other than anthropogenic emissions. Thus, using historical data that contain large uncertainties in the estimation of O<sub>3</sub> concentrations as a reference point, may yield unrealistically low hourly average concentrations.

Based on a review of available data, the U.S. Environmental Protection Agency (1989) has indicated that a reasonable estimate of O<sub>3</sub> background concentration near sea level in the United States today, for an annual average, is from 0.020 to 0.035 ppm. This estimate included a 0.005- to 0.015-ppm contribution from stratospheric intrusions and a 0.01-ppm contribution from photochemically affected biogenic nonmethane hydrocarbons. In addition, the U.S. Environmental Protection Agency (1989) estimated that an additional 0.010 ppm is possible from the photochemical reaction of biogenic methane. A more conservative approach would be to associate the sum of O<sub>3</sub> concentrations from these two processes with the differences between 0.020 to 0.035 ppb and the stratospheric intrusion contribution.

For calculating annual average concentrations, the estimate made by the U.S. Environmental Protection Agency (1989) may be valid. Pratt et al. (1983), using data from low-elevation rural sites in Minnesota and North Dakota, reported that annual average

concentrations for an O<sub>3</sub> monitoring site in LaMoure County, ND (400 m), for 1978 through 1981, ranged from 0.030 to 0.035 ppm, whereas an O<sub>3</sub> monitoring site in Traverse County, MN (311 m), had a range of 0.029 to 0.035 ppm. Bower et al. (1989) reported that the remote northern Scotland site, Strath Vaich (270 m), had a 1987 to 1988 annual average O<sub>3</sub> concentration of 0.031 ppm.

The U.S. Environmental Protection Agency (1989) has estimated that background O<sub>3</sub> concentrations for a 1-h daily maximum at sea level in the United States during the summer are in the range of 0.03 to 0.05 ppm. However, the actual value may vary from site to site. Using measurements at a remote site in South Dakota, Kelly et al. (1982) estimated the background O<sub>3</sub> in air masses entering the midwestern and eastern United States to be 0.03 to 0.05 ppm. Lefohn and Foley (1992) reported that hourly average O<sub>3</sub> concentration data available for sites that experience low maximum hourly average values in the western United States indicate that, in almost all cases, the maximum hourly average concentrations were in the range of 0.060 to 0.075 ppm, and, at some of the sites, there were infrequent occurrences of hourly average concentrations below 0.02 ppm (i.e., lack of scavenging). These observations were similar to those reported for several O<sub>3</sub> monitoring sites experiencing low maximum hourly average O<sub>3</sub> concentrations for other locations in the world (Lefohn et al., 1990a; Pedersen and Lefohn, 1994).

Some vegetation researchers have used the seasonal average of the daily 7-h (0900 to 1559 hours) average as the exposure parameter in exposure-response models (Heck et al., 1982). For quantifying the effects of air pollution on crops and trees, some investigators have used controlled environment and field methods with charcoal-filtration systems (Olszyk et al., 1989). In both the design of the experiments and the analysis of the data, the 7-h (0900 to 1559 hours) seasonal mean reference point for O<sub>3</sub> was assumed to be 0.025 ppm. The 0.025 ppm concentration was used to estimate crop loss across the United States (Adams et al., 1985, 1989). For sites experiencing low maximum hourly average concentrations in the western United States, except for several years of O<sub>3</sub> measurements at Olympic National Park (Table 4-6), the 7-mo (April to October) average of the 7-h daily average concentrations ranged from 0.025 to 0.045 ppm (Altshuller and Lefohn, 1996).

Ozone hourly average concentrations were characterized at several sites located in both the western and south-central United States that experienced low maximum hourly average concentrations (Table 4-6). Redwood National Park, CA; Olympic National Park, WA; Glacier National Park, MT; Denali National Park, AK; Badlands, SD; Great Sand Dunes National Monument, CO; Theodore Roosevelt National Park, ND; and Quachita National Forest, AR, experienced no hourly average concentration  $\geq 0.08$  ppm for the period April to October (Altshuller and Lefohn, 1996). Except for 1988, the year in which Yellowstone National Park, WY, experienced a major forest fire, the Wyoming site experienced no hourly average concentrations  $\geq 0.08$  ppm. Logan (1989) has noted that O<sub>3</sub> hourly average concentrations above 0.08 ppm rarely are exceeded at remote western sites. In almost all cases for the above sites, the maximum hourly average concentration was  $\leq 0.075$  ppm. There have been some questions raised to whether the distributions experienced at those sites exhibiting low maximum hourly average concentrations in the western United States were representative of sites in the eastern and midwestern United States because of differences in biogenic precursors. The O<sub>3</sub> monitoring site in the

**Table 4-6. Seasonal (April to October) Percentile Distribution of Hourly  
Ozone Concentrations, Number of Hourly Mean Ozone Occurrences  $\geq 0.08$  and  $\geq 0.10$ ,  
Seasonal Seven-Hour Average Concentrations, W126, and SUM06 Values for Sites  
Experiencing Low Hourly Average Concentrations with Data Capture  $\geq 75\%$   
(Concentrations in ppm)<sup>a</sup>**

Location	Site/AIRS ID	Year	Min.	Percentiles							Max	No. of Obs.	Hours		Seasonal 7-h	W126 (ppm-h)	SUM06 (ppm-h)
				10	30	50	70	90	95	99			$\geq 0.08$	$\geq 0.10$			
Redwood, CA	Redwood NP 060150002	1988	0.002	0.011	0.018	0.023	0.029	0.038	0.041	0.046	0.060	4,825	0	0	0.026	1.8	0.1
		1989	0.000	0.010	0.017	0.022	0.027	0.034	0.038	0.042	0.047	4,624	0	0	0.024	1.0	0.0
		1990	0.000	0.011	0.018	0.023	0.028	0.035	0.038	0.043	0.053	4,742	0	0	0.025	1.2	0.0
		1991	0.001	0.012	0.019	0.025	0.031	0.038	0.041	0.045	0.054	4,666	0	0	0.027	1.7	0.0
		1992	0.000	0.010	0.017	0.021	0.026	0.035	0.039	0.045	0.055	4,679	0	0	0.023	1.1	0.0
		1993	0.000	0.010	0.017	0.022	0.027	0.035	0.038	0.042	0.054	4,666	0	0	0.025	1.1	0.0
Olympic, WA	Olympic NP 530090012	1982	0.000	0.000	0.010	0.010	0.020	0.030	0.030	0.040	0.060	4,704	0	0	0.020	7.4	0.1
		1984	0.000	0.000	0.010	0.010	0.020	0.020	0.020	0.030	0.050	4,872	0	0	0.015	1.6	0.0
		1986	0.000	0.000	0.010	0.020	0.020	0.040	0.040	0.040	0.060	4,776	0	0	0.025	13.7	0.1
		1989	0.000	0.003	0.010	0.015	0.022	0.030	0.035	0.046	0.065	4,220	0	0	0.021	0.7	0.1
		1990	0.000	0.005	0.012	0.018	0.023	0.030	0.034	0.043	0.064	4,584	0	0	0.022	0.8	0.3
		1991	0.000	0.006	0.014	0.019	0.024	0.033	0.036	0.044	0.056	4,677	0	0	0.025	0.9	0.0
		1993	0.000	0.004	0.010	0.016	0.021	0.029	0.034	0.041	0.064	4,595	0	0	0.022	0.7	0.3
Glacier, MT	Glacier NP 300298001	1989	0.000	0.003	0.015	0.026	0.036	0.046	0.050	0.058	0.067	4,770	0	0	0.036	5.9	1.8
		1990	0.000	0.003	0.014	0.026	0.035	0.044	0.047	0.052	0.066	5,092	0	0	0.036	4.1	1.3
		1991	0.000	0.001	0.014	0.027	0.036	0.046	0.049	0.056	0.062	5,060	0	0	0.036	5.3	0.7
		1992	0.000	0.001	0.013	0.025	0.033	0.043	0.048	0.055	0.077	4,909	0	0	0.033	4.1	1.0
Yellowstone, WY	Yellowstone NP 560391010	1988	0.002	0.020	0.029	0.037	0.044	0.054	0.058	0.070	0.098	4,257	17	0	0.043	14.0	8.9
		1989	0.002	0.018	0.027	0.036	0.044	0.052	0.057	0.063	0.071	4,079	0	0	0.042	11.0	6.7
		1990	0.000	0.015	0.023	0.029	0.036	0.043	0.046	0.053	0.061	4,663	0	0	0.034	3.8	0.5
		1991	0.004	0.020	0.030	0.037	0.042	0.048	0.051	0.057	0.064	4,453	0	0	0.042	7.7	1.2
		1992	0.001	0.018	0.029	0.036	0.042	0.051	0.056	0.064	0.075	4,384	0	0	0.042	10.7	6.3
		1993	0.000	0.018	0.028	0.036	0.042	0.047	0.050	0.054	0.060	4,399	0	0	0.041	6.5	0.2
	022900003	1990	0.003	0.017	0.024	0.029	0.034	0.040	0.043	0.048	0.050	3,978	0	0	0.030	2.1	0.0
		1991	0.005	0.018	0.024	0.028	0.034	0.041	0.043	0.047	0.057	4,809	0	0	0.030	2.7	0.0
		1992	0.003	0.016	0.023	0.028	0.034	0.044	0.047	0.050	0.054	4,800	0	0	0.031	3.7	0.0
		1993	0.002	0.017	0.023	0.028	0.033	0.041	0.043	0.048	0.055	4,773	0	0	0.030	2.6	0.0

**Table 4-6 (con't). Seasonal (April to October) Percentile Distribution of Hourly Ozone Concentrations, Number of Hourly Mean Ozone Occurrences  $\geq 0.08$  and  $\geq 0.10$ , Seasonal Seven-Hour Average Concentrations, W126, and SUM06 Values for Sites Experiencing Low Hourly Average Concentrations with Data Capture  $\geq 75\%$  (Concentrations in ppm)<sup>a</sup>**

Location	Site/AIRS ID	Year	Min.	Percentiles							Max	No. of Obs.	Hours		Seasonal 7-h	W126 (ppm-h)	SUM06 (ppm-h)
				10	30	50	70	90	95	99			$\geq 0.08$	$\geq 0.10$			
Badlands, SD	Badlands NP 460711010	1988	0.005	0.022	0.032	0.038	0.045	0.053	0.056	0.061	0.072	4,791	0	0	0.043	13.3	5.2
		1989	0.007	0.020	0.028	0.034	0.041	0.049	0.053	0.060	0.071	4,840	0	0	0.040	9.2	3.1
		1990	0.006	0.019	0.027	0.032	0.037	0.044	0.048	0.054	0.063	4,783	0	0	0.037	4.8	0.8
		1991	0.005	0.020	0.028	0.034	0.040	0.047	0.050	0.056	0.066	4,584	0	0	0.038	6.2	0.7
Great Sand Dunes, CO	Sand Dunes NM 080030002	1988	0.010	0.028	0.035	0.039	0.044	0.050	0.053	0.058	0.076	4,827	0	0	0.043	11.1	1.9
		1989	0.011	0.031	0.037	0.041	0.045	0.050	0.052	0.057	0.063	4,436	0	0	0.044	10.8	1.2
		1990	0.010	0.030	0.037	0.041	0.045	0.052	0.055	0.062	0.070	4,624	0	0	0.044	13.6	5.1
		1991	0.008	0.029	0.037	0.043	0.048	0.055	0.058	0.065	0.077	4,130	0	0	0.046	17.0	9.0
Theodore Roosevelt, ND, North Unit	Theodore Roosevelt NP 380530002	1984	0.000	0.017	0.025	0.032	0.039	0.047	0.050	0.059	0.068	4,923	0	0	0.038	7.0	2.8
		1985	0.000	0.019	0.026	0.032	0.038	0.046	0.049	0.054	0.061	4,211	0	0	0.038	5.0	0.1
		1986	0.004	0.017	0.027	0.033	0.039	0.047	0.050	0.056	0.062	4,332	0	0	0.039	5.5	0.4
		1989	0.004	0.023	0.032	0.039	0.045	0.054	0.058	0.065	0.073	4,206	0	0	0.046	14.2	11.0
		1992	0.005	0.019	0.027	0.033	0.039	0.047	0.050	0.056	0.063	4,332	0	0	0.040	6.1	0.8
		1993	0.004	0.018	0.025	0.031	0.037	0.045	0.048	0.055	0.064	4,281	0	0	0.038	4.6	0.7
Point Reyes, CA	Point Reyes NP 060410002	1989	0.007	0.021	0.026	0.031	0.036	0.042	0.045	0.058	0.080	4,577	1	0	0.033	4.8	2.5
		1990	0.006	0.017	0.022	0.025	0.029	0.036	0.040	0.046	0.063	4,856	0	0	0.028	1.8	0.4
		1991	0.006	0.019	0.025	0.030	0.034	0.040	0.043	0.048	0.072	4,588	0	0	0.031	3.0	0.6
		1992	0.007	0.018	0.024	0.028	0.033	0.041	0.045	0.050	0.066	4,794	0	0	0.031	3.0	0.3
Arches, UT	Arches NP 490190101	1989	0.000	0.031	0.040	0.045	0.050	0.057	0.059	0.065	0.084	4,260	2	0	0.048	21.2	12.6
		1990	0.000	0.020	0.025	0.028	0.031	0.036	0.039	0.045	0.056	4,639	0	0	0.030	1.7	0.0
Montgomery Co., AR	Quachita NF 050970001	1991	0.000	0.002	0.010	0.016	0.023	0.035	0.041	0.051	0.064	4,835	0	0	0.027	1.6	0.1
		1992	0.000	0.005	0.015	0.024	0.030	0.041	0.045	0.053	0.067	4,902	0	0	0.033	3.0	0.9
		1993	0.000	0.008	0.019	0.027	0.035	0.047	0.052	0.061	0.070	4,844	0	0	0.036	6.7	3.7

<sup>a</sup>See Appendix A for abbreviations and acronyms.

Quachita National Forest in Arkansas experienced distributions of hourly average concentrations similar to some of the western sites.

Evans et al. (1983) summarized O<sub>3</sub> hourly averaged data collected at eight stations located in eight national forests across the United States. The first three stations began operations in 1976 (Green Mountain National Forest, VT; Kisatchie National Forest, LA; and Custer National Forest, MT); the second three in 1978 (Chequamegon National Forest, WI; Mark Twain National Forest, MO; and Croatan National Forest, NC); and the last two in 1979 (Apache National Forest, AZ; and Ochoco National Forest, OR). For the period 1979 to 1983, hourly maximum average concentrations at the sites (Custer, Ochoco, and Apache national forests) were similar to the hourly average concentrations determined for six of the seven sites characterized by Lefohn and Foley (1992). In almost all cases, none of the sites experienced hourly average concentrations  $\geq 0.08$  ppm, and the maximum hourly average concentrations were in the range of 0.060 to 0.075 ppm. Table 4-7 summarizes the percentile distributions for the three national forest sites.

Several sites experiencing low maximum hourly average concentrations were characterized by Lefohn et al. (1990a), using various exposure indices. One of the indices used was W126 (see Section 4.1); the W126 values, calculated over an annual period, are provided in Table 4-8. The W126 values for Theodore Roosevelt National Park were in the range of 6.48 to 8.03 ppm-h. The maximum hourly average concentration reported at the site was 0.068 ppm. The W126 values at the Custer and Ochoco national forests sites ranged from 5.79 to 22.67 ppm-h. The maximum hourly average concentrations measured at each site were 0.075 and 0.080 ppm, respectively. The W126 values calculated for the Custer and Ochoco national forest sites showed greater variability from year to year than the values calculated for the South Pole, Barrow, and Theodore Roosevelt National Park sites.

As the W126 values increased, the magnitude of the year-to-year variability also increased. For 2 years of data, the W126 values calculated for the White River U-4 Oil Shale, UT, site were 19.98 and 32.10 ppm-h. The maximum hourly concentration recorded was 0.079 ppm. The W126 values calculated for the Apache National Forest site ranged from 10.24 to 81.39 ppm-h. The highest hourly average concentration was 0.090 ppm.

The 7-h (0900 to 1559 hours) average concentration has been used by vegetation researchers to characterize O<sub>3</sub> exposures experienced in plant chamber experiments (see Chapter 5). Because O<sub>3</sub> concentrations are highest during the warm-season months and, at many low-elevation sites, during daylight hours, the 7-mo seasonal, 7-h (0900 to 1559 hours) average concentration is higher than annual average values. Most remote sites outside North America experience seasonal 7-h averages of 0.025 ppm (Table 4-9) (Lefohn et al., 1990a). The seasonal average of the daily 7-h average values for the South Pole, Antarctica, range from 0.024 to 0.027 ppm. The values range from 0.022 to 0.026 ppm at Barrow, AK. In the continental United States and southern Canada, values range from approximately 0.028 to 0.050 ppm (Lefohn et al., 1990a). At an O<sub>3</sub> monitoring site at the Theodore Roosevelt National Park, the range of the 7-mo (April to October) average of the 7-h daily average concentrations was from 0.038 to 0.046 ppm (Table 4-6). These 7-mo seasonal averages appear to be representative of values that may occur at other sites located in the United States and other locations in the northern hemisphere. In earlier investigations, Lefohn (1984) reported 3-mo (June to August), 7-h averages of 0.048, 0.044, and 0.059 ppm at remote sites at Custer, Ochoco, and Apache national forests, respectively.



**Table 4-7. Seasonal (April to October) Percentile Distribution of Hourly Ozone Concentrations, Number of Hourly Mean Ozone Occurrences  $\geq 0.08$  and  $\geq 0.10$ , Seasonal Seven-Hour Average Concentrations, and W126 Values for Three "Clean" National Forest Sites with Data Capture  $\geq 75\%$  (Concentrations in ppm)<sup>a</sup>**

Site	AIRS ID	Year	Min.	10	30	Percentiles		90	95	99	Max	No. of Obs.	Hours		Seasonal 7-h (ppm)	W126 (ppm-h)
						50	70						$\geq 0.08$	$\geq 0.10$		
Custer NF, MT	300870101	1978	0.000	0.010	0.020	0.035	0.040	0.050	0.055	0.060	0.070	4,759	0	0	0.033	8.3
		1979	0.010	0.025	0.035	0.040	0.045	0.050	0.055	0.060	0.075	5,014	0	0	0.043	13.2
		1980	0.010	0.025	0.035	0.040	0.050	0.055	0.060	0.065	0.070	4,574	0	0	0.043	19.7
		1983	0.010	0.025	0.035	0.040	0.045	0.050	0.055	0.060	0.065	4,835	0	0	0.042	10.7
Ochoco NF, OR	410130111	1980	0.010	0.030	0.035	0.040	0.045	0.055	0.055	0.065	0.080	4,759	5	0	0.044	16.5
		1981	0.010	0.025	0.030	0.035	0.040	0.045	0.045	0.055	0.075	4,459	0	0	0.035	4.7
		1982	0.010	0.025	0.030	0.035	0.040	0.045	0.050	0.055	0.065	4,697	0	0	0.038	7.6
		1983	0.010	0.025	0.035	0.035	0.040	0.045	0.050	0.055	0.060	4,423	0	0	0.039	6.8
Apache NF, AZ	040110110	1981	0.010	0.025	0.030	0.035	0.040	0.045	0.050	0.055	0.065	4,806	0	0	0.039	7.6
		1982	0.015	0.030	0.040	0.045	0.050	0.055	0.060	0.065	0.075	4,714	0	0	0.047	21.9
		1983	0.004	0.025	0.035	0.040	0.045	0.055	0.055	0.065	0.070	4,788	0	0	0.042	14.6

<sup>a</sup>See Appendix A for abbreviations and acronyms.

**Table 4-8. The Value of the W126 Sigmoidal Exposure Parameter  
Calculated Over the Annual Period  
(Units in ppm-h)<sup>a</sup>**

Site	Elevation (m)	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987
South Pole, Antarctica	2,835					2.65	3.72	3.01	2.41	3.54	2.76	4.09	
Bitumount, Alberta, Canada	350				2.99								
Barrow, AK	11					2.60	2.60	3.15	2.36	2.79	2.03	2.46	3.69
Theodore Roosevelt NP, ND	727									8.03	6.69	6.48 <sup>b</sup>	
Custer NF, MT	1,006				14.08	22.67			12.18				
Ochoco NF, OR	1,364					19.54	5.79	9.10	8.02				
Birch Mountain, Alberta, Canada	850				19.73								
White River Oil Shale Project, UT	1,600							19.98	32.10				
Fortress Mountain, Alberta, Canada	2,103											25.04	83.89
Apache NF, AZ	2,424					81.39	10.24	27.18	17.48				
Mauna Loa, HI	3,397					27.48	45.68	33.68	48.90	19.18	32.66	24.48	
Whiteface Mountain, NY	1,483				86.50	68.30	33.75	32.03	37.82	42.94	41.36	32.07	58.33
Hohenpeissenberg, FRG	975	61.28	25.04	35.64	21.76	18.53	29.53	49.00	19.85	40.43			
American Samoa	82					0.28	0.24	0.25	0.28	0.30	0.26	0.30	0.32

<sup>a</sup>See Appendix A for abbreviations and acronyms.

<sup>b</sup>Collection did not occur during the months of October, November, and December.

Source: Lefohn et al. (1990a).

**Table 4-9. The Value of the Ozone Season (Seven-Month) Average of the Daily Seven-Hour (0900 to 1559 Hours) Concentration (ppm)<sup>a</sup>**

Site	Elevation (m)	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987
South Pole, Antarctica	2,835					0.025	0.027		0.026	0.027	0.024	0.025	
Bitumount, Alberta, Canada	350				0.028								
Barrow, AK	11					0.022	0.025	0.024	0.024	0.022	0.026	0.022	0.026
Theodore Roosevelt NP, ND	727									0.038	0.039	0.039 <sup>b</sup>	
Custer NF, MT	1,006				0.043	0.044			0.042				
Ochoco NF, OR	1,364					0.043	0.035	0.038	0.038				
Birch Mountain, Alberta, Canada	850				0.036								
White River Oil Shale Project, UT	1,600							0.045	0.045				
Fortress Mountain, Alberta, Canada	2,103											0.041	0.050
Apache NF, AZ	2,424					0.054	0.039	0.047	0.040				
Mauna Loa, HI	3,397					0.035	0.039	0.034	0.038	0.035	0.035	0.034	
Whiteface Mountain, NY	1,483				0.049	0.046	0.040	0.034	0.041	0.044	0.043	0.043	0.045
Hohenpeissenberg, FRG	975	0.047	0.040	0.044	0.040	0.037	0.043	0.047	0.040	0.043			
American Samoa	82					0.010	0.010	0.011	0.009	0.012	0.010	0.011	

<sup>a</sup>See Appendix A for abbreviations and acronyms.

<sup>b</sup>Collection did not occur during the months of October, November, and December.

Source: Lefohn et al. (1990a).

#### 4.3.3.2 Urban-Influenced Nonurban Areas

It is difficult to identify a set of unique O<sub>3</sub> distribution patterns that adequately describes the hourly average concentrations experienced at monitoring sites in nonurban locations because, as indicated earlier, many nonurban sites in the United States are influenced by local sources of pollution or long-range transport of O<sub>3</sub> or its precursors. Unlike the clean sites characterized by Lefohn and Jones (1986), Lefohn et al. (1990a), and Lefohn and Foley (1992), urban-influenced nonurban sites sometimes show frequent hourly average concentrations near the minimum detectable level, but almost always show occurrences of hourly average concentrations above 0.1 ppm. The frequent occurrence of hourly average concentrations near the minimum detectable level is indicative of scavenging processes (i.e., NO<sub>x</sub>); the presence of high hourly average concentrations can be attributable to the influence of either local generation or the long-range transport of O<sub>3</sub>. For example, Evans et al. (1983) reported that the Green Mountain (VT) and Mark Twain national forest (MO) sites were influenced by long-range transport of O<sub>3</sub>. The U.S. Environmental Protection Agency (1986) reported that the maximum hourly average concentrations at Green Mountain (for the period 1977 to 1981) and Mark Twain (for the period 1979 to 1983) were 0.145 and 0.155 ppm, respectively. Using hourly averaged data from the AIRS database for a select number of rural monitoring sites, Table 4-10 summarizes the percentiles of the hourly average O<sub>3</sub> concentrations, the number of occurrences of the hourly average concentration  $\geq 0.10$  ppm, and the 3-mo sum of all hourly average concentrations  $\geq 0.06$  ppm.

As part of a comprehensive air monitoring project sponsored by the Electric Power Research Institute (EPRI), O<sub>3</sub> measurements were made by the chemiluminescence method from 1977 through 1979 at nine "nonurban" Sulfate Regional Experiment (SURE) Program sites and Eastern Regional Air Quality Study sites in the eastern United States. On the basis of diurnal NO<sub>x</sub> patterns that indicated the influence of traffic emissions, five of the sites were classed as "suburban", and the other four were classed as "rural". The O<sub>3</sub> data from these nine stations are summarized in Table 4-11. The sites are influenced either by local sources or by transport of O<sub>3</sub> or its precursors. The maximum hourly average concentrations generally are higher than 0.125 ppm, and the occurrence of hourly average concentrations near minimum detectable levels indicates NO<sub>x</sub> scavenging processes.

As part of its effort to provide long-term estimates of dry acidic deposition across the United States, the National Dry Deposition Network (NDDN) operated more than 50 sites, which included 41 in the eastern United States and 9 in the western United States, that routinely recorded hourly average O<sub>3</sub> concentrations. Figure 4-7 shows the locations of the NDDN sites. Edgerton and Lavery (1992) have summarized the O<sub>3</sub> concentrations at some of the sites for the period 1988 to 1990. Table 4-12 summarizes the 7-h (0900 to 1559 hours) growing season average concentration (May to September) for selected sites in the Midwest and the East. Fifty-nine percent of the monitoring sites listed in the table have been classified as agricultural and 36% as forested; one site was classified as commercial. As noted by the U.S. Environmental Protection Agency (1992a), 1988 was an exceptionally high O<sub>3</sub> concentration year, when compared with 1989 and 1990. The number of hourly O<sub>3</sub> concentrations  $\geq 0.08$  ppm is presented in Table 4-12. Edgerton and Lavery (1992) have summarized O<sub>3</sub> hourly average concentration data for several sites using the cumulative

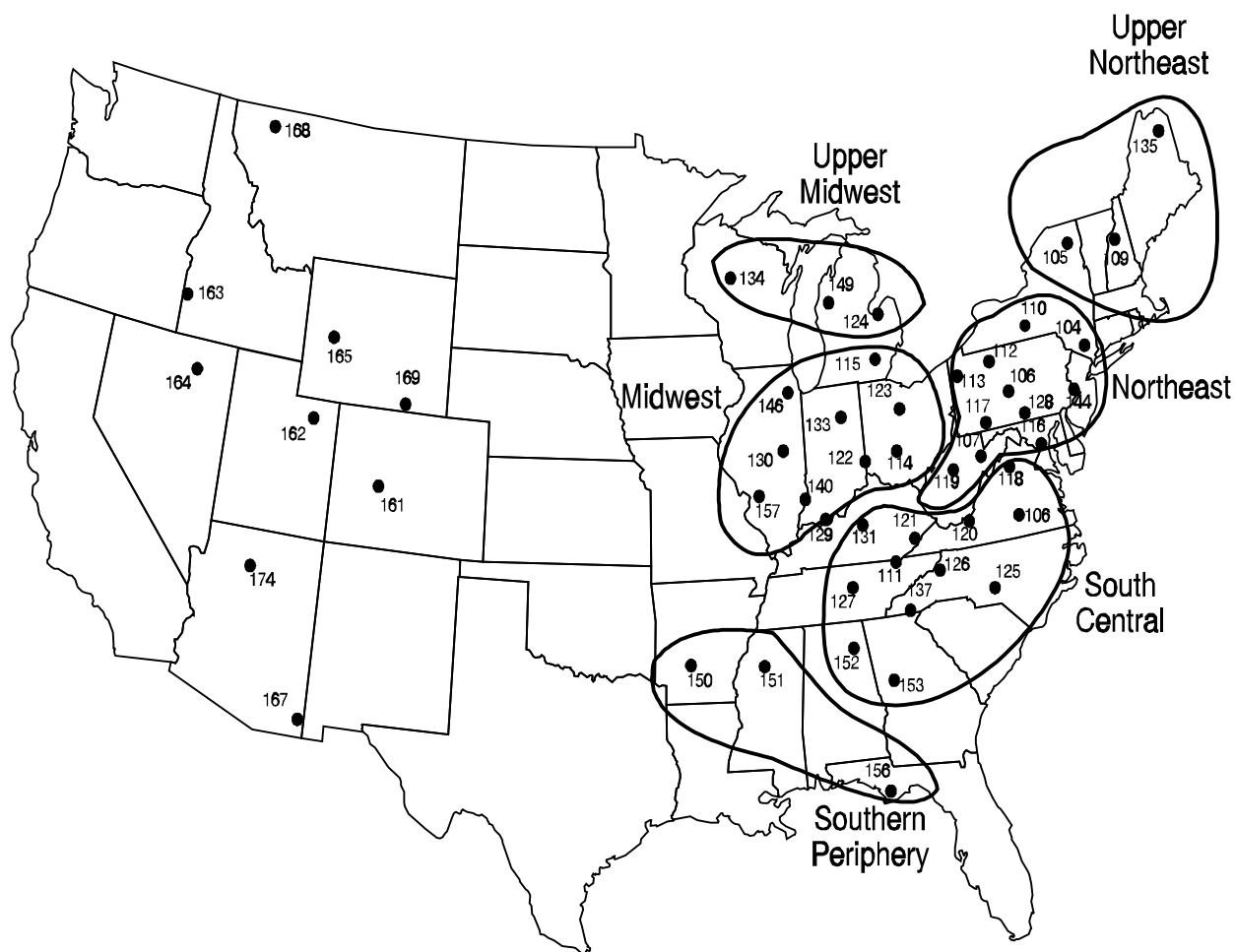
**Table 4-10. Summary of Percentiles, Number of Hourly Occurrences  $\geq 0.10$  ppm, and Three-Month SUM06 Values for Selected Rural Ozone Monitoring Sites in 1989 (April to October) (Concentrations in ppm)<sup>a</sup>**

AIRS Site	Name	Percentiles (ppm)									Number of	Number of	Max Uncorrected
		Min.	10	30	50	70	90	95	99	Max	Hourly Values	Occurrences $\geq 0.10$	3-mo SUM06 Value (ppm-h)
RURAL AGRICULTURAL													
170491001	Effingham County, IL	0.000	0.009	0.023	0.036	0.046	0.063	0.070	0.081	0.104	4,600	1	25.3
180970042	Indianapolis, IN	0.001	0.006	0.021	0.034	0.046	0.063	0.072	0.085	0.103	4,592	3	25.4
240030014	Anne Arundel, MD	0.000	0.006	0.021	0.032	0.045	0.064	0.073	0.090	0.120	4,360	10	25.5
310550032	Omaha, NE	0.002	0.021	0.030	0.037	0.047	0.062	0.067.0	0.075	0.098	4,160	0	24.9
420070003	New Brighton, PA	0.000	0.008	0.021	0.032	0.043	0.062	.070	0.087	0.102	5,055	4	29.4
510610002	Fauquier County, VA	0.000	0.009	0.021	0.033	0.045	0.061	0.069	0.084	0.122	5,050	5	24.6
RURAL FOREST													
060430004	Yosemite NP, CA	0.000	0.008	0.022	0.035	0.049	0.065	0.072	0.083	0.111	4,853	3	37.6
360310002	Essex County, NY	0.016	0.031	0.040	0.049	0.056	0.066	0.072	0.086	0.106	4,792	4	45.6
470090101	Smoky Mountain NP, TN	0.000	0.025	0.036	0.044	0.053	0.065	0.070	0.081	0.098	4,764	0	35.9
511870002	Shenandoah NP (Dickey Ridge), VA	0.004	0.027	0.037	0.045	0.054	0.065	0.071	0.082	0.100	4,454	1	33.5
RURAL OTHER													
040132004	Scottsdale, AZ	0.000	0.006	0.018	0.031	0.045	0.062	0.071	0.084	0.107	5,070	4	31.7
350431001	Sandoval County, NM	0.000	0.010	0.020	0.030	0.040	0.060	0.060	0.070	0.090	5,059	0	25.1
370810011	Guilford County, NC	0.004	0.010	0.023	0.034	0.046	0.063	0.070	0.083	0.113	4,853	2	27.7
371470099	Farmville, NC	0.000	0.010	0.023	0.034	0.044	0.062	0.070	0.083	0.100	4,833	2	26.4
550270001	Horicon, WI	0.002	0.019	0.029	0.037	0.047	0.062	0.070	0.088	0.111	4,142	11	24.6
551390007	Oshkosh, WI	0.002	0.016	0.028	0.038	0.048	0.063	0.070	0.084	0.121	4,206	3	27.9

<sup>a</sup>See Appendix A for abbreviations and acronyms.

**Table 4-11. Summary of Percentiles of Hourly Average Concentrations for Electric Power  
Research Institute Sulfate Regional Experiment (SURE) Program Sites/Eastern Regional Air  
Quality Study (ERAQS) Ozone Monitoring Sites  
(Units in ppm)**

SURE/ERAQS Name	Year	Min.	10	30	Percentiles		90	95	99	Max	Number of Observations
					50	70					
Montague, MA	1978	0.000	0.002	0.018	0.032	0.043	0.061	0.075	0.119	0.202	7,138
	1979	0.000	0.000	0.013	0.025	0.035	0.056	0.070	0.103	0.149	8,485
Scranton, PA	1978	0.000	0.015	0.031	0.040	0.048	0.062	0.073	0.094	0.126	5,461
	1979	0.000	0.011	0.022	0.030	0.040	0.061	0.074	0.097	0.132	8,313
Indian River, DE	1978	0.000	0.010	0.024	0.035	0.049	0.072	0.085	0.103	0.134	6,874
	1979	0.000	0.008	0.020	0.031	0.042	0.063	0.073	0.092	0.138	8,527
Duncan Falls, OH	1978	0.000	0.005	0.022	0.034	0.049	0.071	0.081	0.110	0.144	5,125
	1979	0.000	0.010	0.021	0.029	0.042	0.060	0.069	0.086	0.110	7,595
Rockport, IN	1978	0.000	0.008	0.021	0.032	0.044	0.066	0.078	0.101	0.145	6,849
	1979	0.000	0.008	0.019	0.028	0.038	0.055	0.064	0.083	0.104	8,391
Giles County, TN	1978	0.000	0.000	0.018	0.032	0.046	0.066	0.075	0.087	0.110	6,034
	1979	0.000	0.000	0.014	0.024	0.036	0.055	0.065	0.081	0.130	8,439
Roanoke, IN	1978	0.000	0.004	0.019	0.032	0.044	0.067	0.079	0.106	0.160	5,874
	1979	0.000	0.004	0.017	0.026	0.038	0.061	0.074	0.098	0.133	8,001
Research Triangle Park, NC	1978	0.000	0.001	0.017	0.032	0.049	0.076	0.087	0.108	0.142	7,081
	1979	0.000	0.001	0.012	0.024	0.037	0.058	0.068	0.084	0.131	8,652
Lewisburg, WV	1978	0.002	0.020	0.034	0.045	0.056	0.072	0.079	0.091	0.115	7,019
	1979	0.000	0.013	0.022	0.029	0.039	0.056	0.065	0.080	0.099	7,849



**Figure 4-7. The location of National Dry Deposition Network monitoring sites as of December 1990.**

Source: Edgerton and Lavery (1992).

integrated exposure index, W126, as proposed by Lefohn and Runeckles (1987). Based on evidence presented in the literature relating  $O_3$  exposure with agricultural yield reduction, the index was proposed as a way to weight the higher hourly average concentrations greater than the lower values. The data in the table illustrate the large differences in cumulative exposure between those that occurred in 1988 and those that were experienced in 1989 and 1990. The percentile of the hourly average concentrations is summarized in Table 4-13. Although several of the monitoring sites are located in fairly remote locations in the eastern United States (based on land use characterization) the maximum hourly average concentrations reflect the transport of  $O_3$  or its precursors into the area.

Taylor et al. (1992) have summarized the  $O_3$  concentrations that were experienced at 10 EPRI Integrated Forest Study sites in North America. The authors reported that in 1988 all sites experienced maximum hourly average concentrations  $\geq 0.08$  ppm. In almost all cases, the sites experienced multiple occurrences above 0.08 ppm. This implies that,

**Table 4-12. Seven-Hour Growing Season Mean, W126 Values, and Number of Hourly Ozone Concentrations  $\geq 80$  ppb for Selected Eastern National Dry Deposition Network Sites<sup>a</sup>**

Subregion	State	Site	Land Class <sup>b</sup>	7-h Mean (ppb)			W126 (ppm-h)			SUM06 (ppm-h)			SUM08 (ppm-h)		
				1988	1989	1990	1988	1989	1990	1988	1989	1990	1988	1989	1990
NORTHEAST															
Connecticut Hill	NY	110	RF	55.0	48.3	45.3	75.5	40.3	36.8	86.8	47.2	35.8	44.3	5.5	3.3
Washington’s Crossing	NJ	144	RA	—	52.8	52.4	—	46.0	43.7	—	52.1	48.4	—	21.2	21.3
Pennsylvania State University	PA	106	RA	59.0	46.0	51.0	63.5	25.4	42.7	65.6	28.1	45.0	32.3	5.0	11.6
Laurel Hill State Park	PA	117	RF	62.7	48.4	48.6	68.8	29.1	31.0	75.5	30.8	32.1	41.6	7.0	8.0
Beltsville	MD	116	RA	—	54.6	55.5	—	45.4	45.7	—	48.6	49.4	—	22.9	21.9
Cedar Creek State Park	WV	119	RA	59.8	44.9	48.2	50.4	19.6	24.3	56.3	19.0	23.2	27.0	4.1	6.5
UPPER NORTHEAST															
Whiteface Mountain	NY	105	RF	43.5	45.7	42.3	37.8	25.3	31.2	40.9	25.2	29.0	17.0	2.6	8.4
Ashland	ME	135	RA	—	37.9	35.3	—	9.1	8.7	—	5.4	5.8	—	0.6	0.8
MIDWEST															
Argonne National Lab	IL	146	RA	61.1	51.4	46.3	59.1	29.6	21.6	69.4	35.0	25.7	32.3	10.4	3.6
Vincennes	IN	140	RA	62.0	51.1	50.9	68.1	36.4	35.8	78.5	40.3	41.2	36.7	8.7	11.8
Oxford	OH	122	RA	65.3	53.5	51.7	91.8	48.4	46.4	103.2	55.3	51.7	56.8	15.8	17.2
UPPER MIDWEST															
Unionville	MI	124	RA	—	51.5	47.4	—	35.4	30.7	—	41.6	31.6	—	9.0	7.1
Perkinstown	WI	134	RA	—	44.2	38.8	—	19.0	11.6	—	18.3	7.6	—	0.2	0.0
SOUTH CENTRAL															
Sand Mountain	AL	152	RA	—	52.6	63.6	—	40.6	68.7	—	33.2	83.4	—	3.4	24.0
Georgia Station	GA	153	RA	—	48.1	62.6	—	28.1	69.7	—	21.8	77.7	—	4.6	28.4
Perryville	KY	129	RA	65.2	50.8	—	103.6	39.7	—	99.6	38.9	—	39.7	5.2	—
Research Triangle Park	NC	101	RC	62.3	50.8	—	62.3	31.7	—	71.0	35.5	—	20.5	6.6	—
Coweeta	NC	137	RF	55.6	41.0	47.9	44.3	16.1	21.3	—	—	—	—	—	—
Edgar Evins State Park	TN	127	RF	—	47.2	56.1	—	26.9	44.5	—	24.4	49.2	—	1.5	8.2
Horton Station	VA	120	RF	62.3	51.4	54.4	127.6	61.2	70.6	150.7	64.0	82.8	60.2	8.5	9.2
SOUTHERN PERIPHERY															
Caddo Valley	AR	150	RF	—	46.2	49.5	—	18.5	21.0	—	15.6	25.2	—	0.2	2.3
Sumatra	FL	156	RF	—	39.8	46.3	—	17.8	20.0	—	16.5	17.4	—	1.0	0.9

<sup>a</sup>See Appendix A abbreviations for and acronyms.

<sup>b</sup>RA = Rural agricultural; RF = Rural forest; RC = Rural commercial; — = No data or insufficient data.

Source: Edgerton and Lavery (1992).



**Table 4-13. Summary of Percentiles for National Dry Deposition Network Monitoring Sites  
(Units in ppm)**

Site No.	Name	Year	Min.	10	30	Percentiles					Max	Number of Observations
						50	70	90	95	99		
RURAL AGRICULTURAL SITES												
106	Pennsylvania State University, PA	1988	0.000	0.013	0.026	0.036	0.049	0.073	0.086	0.114	0.143	4,716
		1989	0.000	0.010	0.022	0.033	0.043	0.059	0.066	0.082	0.104	5,089
		1990	0.000	0.015	0.027	0.038	0.048	0.065	0.074	0.090	0.120	5,056
116	Beltsville, MD	1989	0.002	0.003	0.014	0.029	0.044	0.068	0.081	0.096	0.131	5,062
		1990	0.000	0.001	0.015	0.027	0.041	0.067	0.080	0.103	0.137	4,597
119	Cedar Creek, WV	1988	0.000	0.008	0.017	0.029	0.044	0.069	0.082	0.108	0.134	4,938
		1989	0.001	0.006	0.013	0.024	0.037	0.056	0.065	0.082	0.172	5,044
		1990	0.001	0.007	0.014	0.024	0.038	0.057	0.067	0.085	0.116	5,025
122	Oxford, OH	1988	0.001	0.019	0.032	0.044	0.058	0.083	0.096	0.117	0.221	4,746
		1989	0.001	0.017	0.029	0.039	0.050	0.069	0.077	0.092	0.109	5,073
		1990	0.000	0.015	0.028	0.037	0.048	0.067	0.077	0.092	0.116	5,077
124	Unionville, MI	1989	0.003	0.021	0.031	0.038	0.047	0.063	0.071	0.086	0.113	5,041
		1990	0.004	0.020	0.029	0.036	0.044	0.061	0.069	0.084	0.105	5,065
129	Perryville, KY	1988	0.002	0.024	0.038	0.049	0.062	0.080	0.094	0.110	0.143	4,061
		1989	0.001	0.020	0.033	0.043	0.052	0.066	0.072	0.086	0.102	4,787
134	Perkinstown, WI	1989	0.007	0.023	0.032	0.038	0.046	0.057	0.062	0.071	0.085	5,029
		1990	0.006	0.020	0.028	0.035	0.041	0.050	0.056	0.065	0.074	5,063
135	Loring AFB/Ashland, ME	1989	0.002	0.017	0.026	0.032	0.039	0.049	0.055	0.063	0.103	5,067
		1990	0.002	0.014	0.023	0.029	0.036	0.046	0.051	0.068	0.088	5,080
140	Vincennes, IN	1988	0.000	0.007	0.024	0.036	0.052	0.076	0.089	0.104	0.120	4,908
		1989	0.000	0.009	0.025	0.036	0.047	0.064	0.072	0.085	0.112	5,065
		1990	0.000	0.009	0.025	0.035	0.045	0.062	0.073	0.089	0.110	5,084
144	Washington Crossing, NJ	1989	0.000	0.006	0.021	0.033	0.046	0.067	0.078	0.100	0.159	5,053
		1990	0.001	0.008	0.021	0.032	0.043	0.065	0.079	0.104	0.148	5,058
146	Argonne National Laboratory, IL	1988	0.000	0.004	0.019	0.032	0.046	0.073	0.085	0.103	0.146	5,037
		1989	0.000	0.005	0.019	0.029	0.041	0.061	0.070	0.088	0.126	5,055
		1990	0.000	0.004	0.017	0.028	0.039	0.057	0.065	0.077	0.097	5,033

**Table 4-13 (cont'd). Summary of Percentiles for National Dry Deposition Network Monitoring Sites  
(Units in ppm)**

Site No.	Name	Year	Min.	Percentiles							Max	Number of Observations
				10	30	50	70	90	95	99		
RURAL AGRICULTURAL SITES (cont'd)												
152	Sand Mountain, AL	1989	0.000	0.020	0.031	0.041	0.051	0.065	0.072	0.082	0.097	4,509
		1990	0.000	0.021	0.035	0.045	0.057	0.074	0.080	0.093	0.117	5,068
153	Georgia Station, GA	1989	0.002	0.014	0.025	0.034	0.045	0.062	0.069	0.082	0.118	3,540
		1990	0.002	0.021	0.034	0.044	0.056	0.073	0.084	0.102	0.144	4,814
RURAL FOREST SITES												
105	Whiteface Mountain, NY	1988	0.000	0.016	0.026	0.034	0.044	0.062	0.074	0.098	0.129	5,051
		1989	0.003	0.022	0.030	0.038	0.047	0.059	0.066	0.078	0.093	4,698
		1990	0.005	0.018	0.028	0.036	0.046	0.060	0.069	0.086	0.115	5,016
110	Ithaca, NY	1988	0.005	0.025	0.034	0.043	0.055	0.080	0.090	0.103	0.126	4,827
		1989	0.002	0.025	0.036	0.044	0.052	0.065	0.071	0.081	0.101	5,064
		1990	0.001	0.022	0.033	0.041	0.049	0.063	0.069	0.081	0.093	5,075
117	Laurel Hill, PA	1988	0.001	0.012	0.025	0.036	0.050	0.076	0.092	0.119	0.156	5,007
		1989	0.000	0.009	0.020	0.031	0.043	0.061	0.069	0.087	0.110	4,697
		1990	0.001	0.009	0.020	0.030	0.042	0.060	0.071	0.086	0.109	5,032
120	Horton Station, VA	1988	0.010	0.031	0.045	0.057	0.067	0.084	0.096	0.114	0.145	5,012
		1989	0.002	0.032	0.043	0.050	0.059	0.070	0.076	0.085	0.103	4,976
		1990	0.004	0.032	0.044	0.052	0.059	0.071	0.075	0.084	0.097	5,066
127	Edgar Evins State Park, TN	1989	0.000	0.017	0.028	0.037	0.047	0.062	0.067	0.077	0.090	5,060
		1990	0.001	0.019	0.032	0.041	0.052	0.067	0.073	0.085	0.109	5,027
137	Coweeta, NC	1988	0.001	0.010	0.022	0.034	0.047	0.065	0.072	0.094	0.145	4,182
		1989	0.001	0.007	0.016	0.025	0.037	0.055	0.061	0.071	0.094	4,275
		1990	0.000	0.008	0.018	0.029	0.043	0.059	0.064	0.072	0.085	5,046
150	Caddo Valley, AR	1989	0.002	0.005	0.016	0.028	0.041	0.057	0.063	0.075	0.102	5,046
		1990	0.002	0.004	0.015	0.029	0.041	0.057	0.065	0.077	0.094	5,078
156	Sumatra, FL	1989	0.001	0.012	0.022	0.030	0.040	0.057	0.065	0.075	0.098	4,700
		1990	0.000	0.011	0.023	0.033	0.043	0.057	0.063	0.072	0.118	4,444
RURAL COMMERCIAL SITE												
101	Research Triangle Park, NC	1988	0.000	0.004	0.020	0.035	0.050	0.072	0.084	0.111	0.137	5,030
		1989	0.000	0.004	0.019	0.030	0.042	0.063	0.071	0.083	0.121	4,893

although the sites were located in remote forested areas, the sites experienced elevated O<sub>3</sub> concentrations that were more than likely due to long-range transport of O<sub>3</sub> or its precursors.

Ozone concentrations on a seasonal basis in the Shenandoah National Park exhibit some features in common with both urban and rural areas. During some years, maximum hourly average concentrations exceed 0.12 ppm, although some sites in the park exhibit a lack of hourly average concentrations near minimum detectable level. Taylor and Norby (1985) have characterized O<sub>3</sub> episodes, which they defined as any day in which a 1-h mean O<sub>3</sub> concentration was >0.08 ppm. Based on a 4-year monitoring period in the park, the probability was 80% that any given episode during the growing season would last 2 or more days, whereas the probabilities of episodes lasting for periods greater than 3, 4, and 5 days were 30, 10, and 2%, respectively. Single-day O<sub>3</sub> episodes were infrequent. Taylor and Norby (1985) noted that, given the frequency of respites, there was a 50% probability that a second episode would occur within 2 weeks.

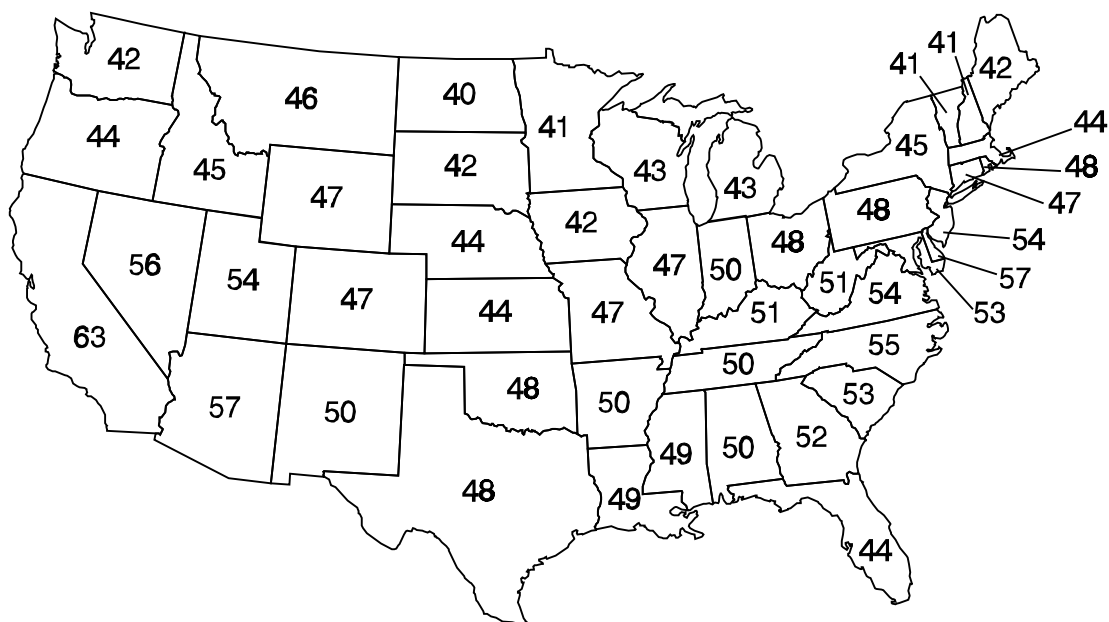
Because of a lack of air quality data collected at rural and remote locations, it has been necessary to use interpolation techniques to estimate O<sub>3</sub> exposures in nonurban areas. In the absence of actual O<sub>3</sub> data, interpolation techniques have been applied to the estimation of O<sub>3</sub> exposures across the United States (Reagan, 1984; Lefohn et al., 1987a; Knudsen and Lefohn, 1988). "Kriging", a mathematical interpolation technique, has been used to provide estimates of seasonal O<sub>3</sub> values for the NCLAN for 1978 through 1982 (May to September of each year) (Reagan, 1984). These values, along with updated values, coupled with exposure-response models were used to predict agriculturally related economic benefits anticipated by lower O<sub>3</sub> levels in the United States (Adams et al., 1985; Adams et al., 1989).

Kriging is a statistical tool developed by Matheron (1963) and named in honor of D.G. Krige. Although originally developed specifically for ore reserve estimation, kriging has been used for other spatial estimation applications, such as analyzing and modeling air quality data (Grivet, 1980; Faith and Sheshinski, 1979). At its simplest, kriging can be thought of as a way to interpolate spatial data much as an automatic contouring program would. In a more precise manner, kriging can be defined as a best, linear unbiased estimator of a spatial variable at a particular site or geographic area. Kriging assigns low weights to distant samples and vice versa, but also takes into account the relative position of the samples to each other and the site or area being estimated.

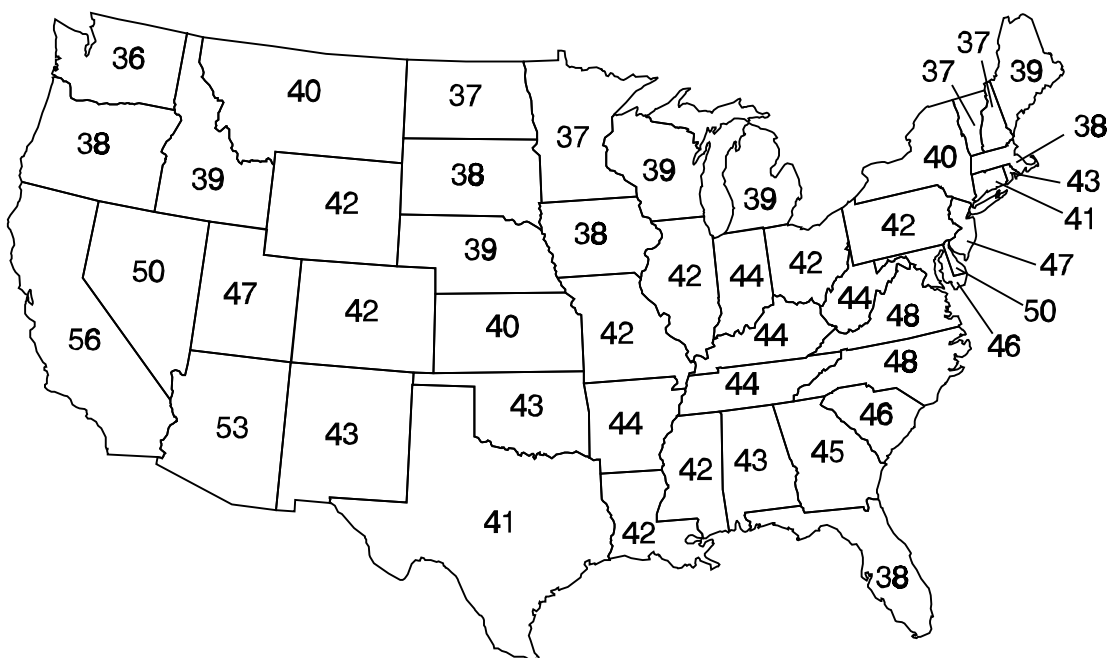
Figure 4-8 shows the average for the 1985 through 1987 period for the seasonal (April to October) average of the daily maximum 7- and 12-h values across the United States. The estimates made for the Rocky Mountain region had large uncertainties associated with them because of a lack of monitoring sites.

Because of the importance of the higher hourly average concentrations in eliciting injury and yield reduction for agricultural crops (U.S. Environmental Protection Agency, 1992b), kriging was used to predict O<sub>3</sub> exposures in the eastern United States. The sigmoidally weighted W126 exposure index was used as described earlier in this section. Lefohn et al. (1992b) used the W126 index in its kriging to characterize the O<sub>3</sub> exposures that occurred during the period 1985 to 1989. Figure 4-9 illustrates the integrated O<sub>3</sub> exposure for the 1988 and 1989 periods (data derived from work described in Lefohn et al., 1992b). Using the kriged data in the East, the 1988 exposures were the highest for the 5-year period, whereas 1989 exhibited the lowest exposures. The O<sub>3</sub> gradient pattern analyses described by Lefohn et al. (1992b) identified contiguous areas of persistent,

(a)

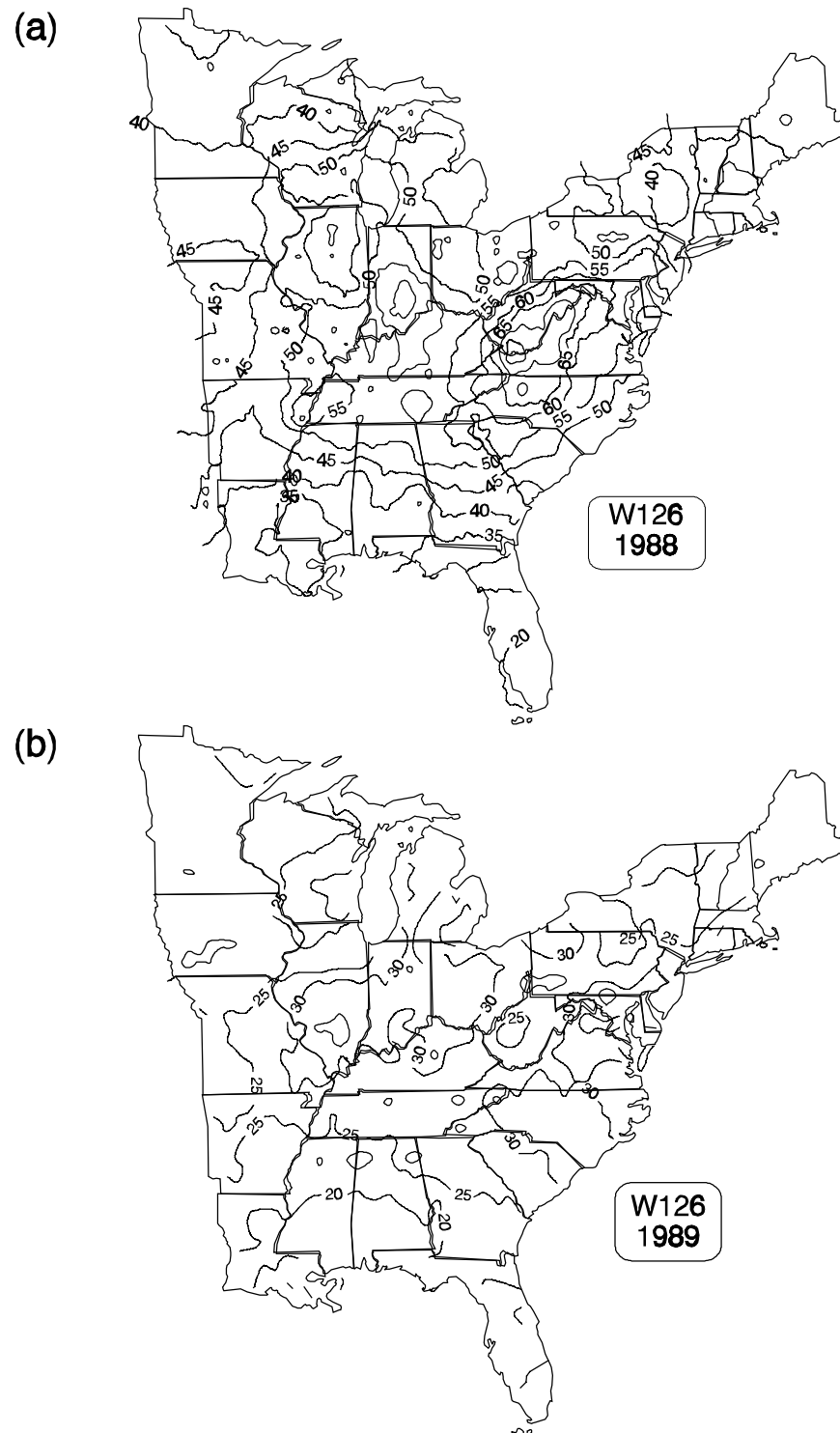


(b)



**Figure 4-8.** The kriged 1985 to 1986 maximum (a) 7-h and (b) 12-h average concentrations of ozone across the United States.

Source: Lefohn et al. (1991).



**Figure 4-9.** *The kriged estimates of the W126 integrated ozone exposure index for the eastern United States for (a) 1988 and (b) 1989.*

Source: Lefohn et al. (1992b).

relatively high seasonal O<sub>3</sub> values. The largest area extended from New Jersey south to northern Georgia and South Carolina. This area was roughly bounded on the west by the Appalachian Mountains. A second area, which exhibited persistent relatively high seasonal O<sub>3</sub> exposures, was centered over the Ohio River Valley in the region near the Kentucky-Indiana-Ohio borders. Relatively low O<sub>3</sub> exposures were found in Minnesota, Iowa, Wisconsin, Maine, Vermont, New Hampshire, and Florida. On a year-to-year basis, the analysis by Lefohn et al. (1992b) showed that regions that tended to be high for a specific year continued to experience O<sub>3</sub> exposures that were higher when compared to other regions.

## **4.4 Diurnal Variations in Ozone Concentrations**

### **4.4.1 Introduction**

By definition, diurnal variations are those that occur during a 24-h period. Diurnal patterns of O<sub>3</sub> may be expected to vary with location, depending on the balance among the many factors affecting O<sub>3</sub> formation, transport, and destruction. Although they vary with locality, diurnal patterns for O<sub>3</sub> typically show a rise in concentration from low (or levels near minimum detectable amounts) to an early afternoon peak. The 1978 criteria document (U.S. Environmental Protection Agency, 1978) ascribed the diurnal pattern of concentrations to three simultaneous processes: (1) downward transport of O<sub>3</sub> from layers aloft; (2) destruction of O<sub>3</sub> through contact with surfaces and through reaction with nitric oxide (NO) at ground level; and (3) in situ photochemical production of O<sub>3</sub> (U.S. Environmental Protection Agency, 1978; Coffey et al., 1977; Mohnen et al., 1977; Reiter, 1977a).

The form of an average diurnal pattern may provide information on sources, transport, and chemical formation and destruction effects at various sites (Lefohn, 1992b). Nontransport conditions will produce early afternoon peaks. However, long-range transport processes will influence the actual timing of a peak from afternoon to evening or early morning hours. Investigators have utilized diagrams that illustrate composite diurnal patterns as a means to describe qualitatively the differences in O<sub>3</sub> exposures between sites (Lefohn and Jones, 1986; Böhm et al., 1991). Although it might appear that composite diurnal pattern diagrams could be used to quantify the differences in O<sub>3</sub> exposures between sites, Lefohn et al. (1991) cautioned their use for this purpose. The average diurnal patterns are derived from long-term calculations of the hourly average concentrations, and the resulting diagram cannot identify adequately, at most sites, the presence of high hourly average concentrations and, thus, may not adequately distinguish O<sub>3</sub> exposure differences among sites. Logan (1989) noted that diurnal variation of O<sub>3</sub> did not reflect the presence of high hourly average concentrations.

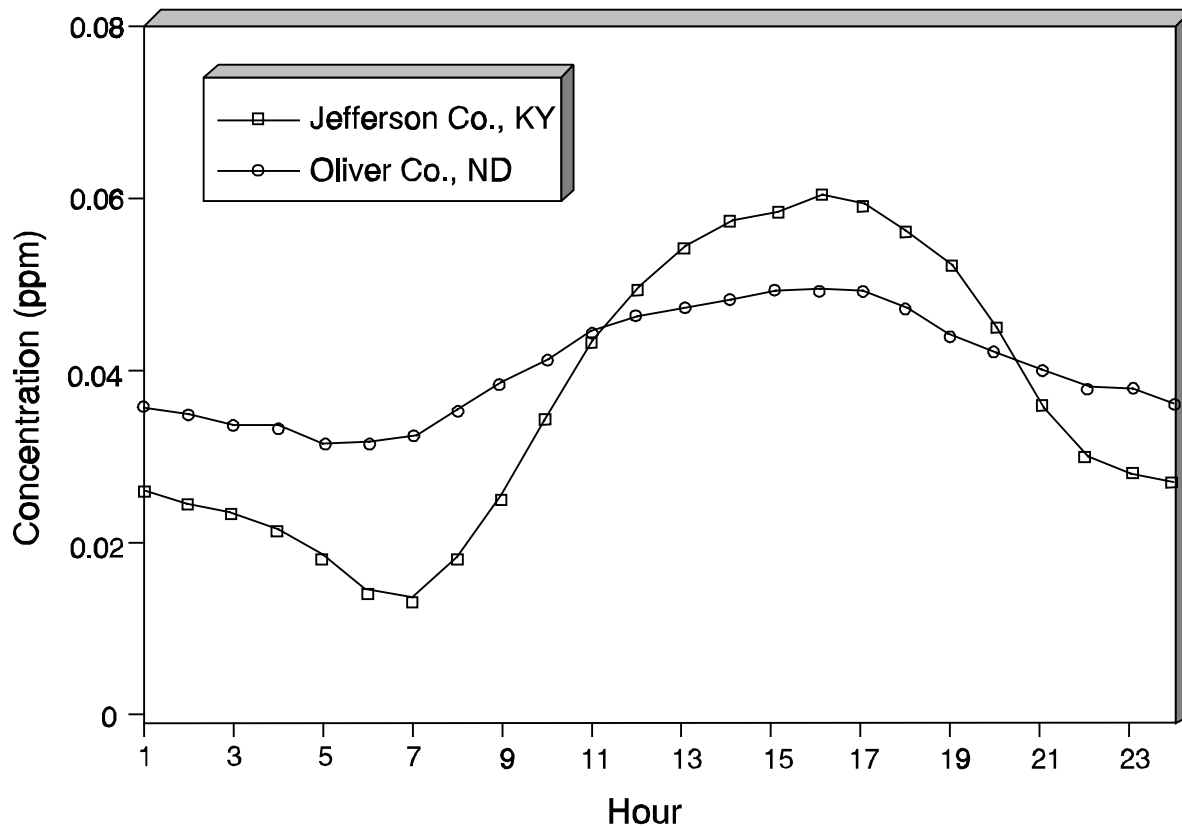
Unique families of diurnal average profiles exist, and it is possible to distinguish between two types of O<sub>3</sub> monitoring sites. A seasonal diurnal diagram provides the investigator with the opportunity to identify whether a specific O<sub>3</sub> monitoring site has more scavenging than any other site. Ozone is rapidly depleted near the surface below the nocturnal inversion layer (Berry, 1964). Mountainous sites, which are above the nocturnal inversion layer, do not necessarily experience this depletion (Stasiuk and Coffey, 1974). Taylor and Hanson (1992) reported similar findings using data from the Integrated Forest Study. For the low-elevation sites, the authors reported that intraday variability was most significant due to the pronounced daily amplitude in O<sub>3</sub> concentration between the predawn minimum and midafternoon-to-early evening maximum. The authors reported that the

interday variation was more significant in the high-elevation sites. Ozone trapped below the inversion layer is depleted by dry deposition and chemical reactions if other reactants are present in sufficient quantities (Kelly et al., 1984). Above the nocturnal inversion layer, dry deposition generally does not occur, and the concentration of O<sub>3</sub> scavengers generally is lower, so O<sub>3</sub> concentration remains fairly constant (Wolff et al., 1987). A flat diurnal pattern is usually interpreted as indicating a lack of efficient scavenging of O<sub>3</sub> or a lack of photochemical precursors, whereas a varying diurnal pattern is taken to indicate the opposite. With the composite diagrams alone, it is difficult to quantify the daily or long-term exposures of O<sub>3</sub>. For example, the diurnal patterns for two such sites are illustrated in Figure 4-10. The Jefferson County, KY, site is urban-influenced and experiences elevated levels of O<sub>3</sub> and NO<sub>x</sub>. The Oliver County, ND, site is fairly isolated from urban-influenced sources and hourly average O<sub>3</sub> concentrations are mostly below 0.09 ppm. The flat diurnal pattern observed for the Oliver County site is usually interpreted as indicating a lack of efficient scavenging of O<sub>3</sub> or a lack of photochemical precursors, whereas the varying diurnal pattern observed at the Jefferson County site may be interpreted to indicate the opposite. Logan (1989) has described the diurnal pattern for several rural sites in the United States (Figure 4-11) and noted that average daily profiles showed a broad maximum from about 1200 hours until about 1800 hours at all the eastern sites, except for the peak of Whiteface Mountain, NY. Logan (1989) noted that the maximum concentrations were higher at the SURE sites than at the Western National Air Pollution Background Network sites in the East, because the latter were situated in more remote or coastal locations.

There is concern that the highest hourly average concentrations observed at rural agricultural and forested sites occur outside the most biologically active period of the day. To address this concern, a review of the hourly average data collected at all rural agricultural and forested sites in EPA's AIRS database for 1990 to 1992 was undertaken to evaluate the percentage of time hourly average concentrations  $\geq 0.1$  ppm occurred during the period 0900 to 1559 hours in comparison with the 24-h period. Each rural site for each of the 3 years that experienced a 3-mo SUMO6  $\geq 26.4$  ppm-h (see Chapter 5, Section 5.6 for more details concerning the use of a 3-mo SUMO6 exposure index) was characterized. It was found that 70% of the rural agricultural and forested sites used in the analysis experienced at least 50% of the occurrences  $\geq 0.1$  ppm during the period 0900 to 1559 hours when compared to the 24-h period (Figure 4-12). When O<sub>3</sub> monitoring sites in California were eliminated, approximately 73% of the remaining sites experienced at least 50% of the occurrences  $\geq 0.10$  ppm during the daylight 7-h period when compared with the 24-h period (Figure 4-13). Reviewing Figures 4-12 and 4-13, for most rural agricultural and forested sites that experience 3-mo SUMO6  $\geq 26.4$  ppm in the United States, most of the hourly average concentrations  $\geq 0.1$  ppm occur during the 0900 to 1559 hours period.

#### **4.4.2 Urban Area Diurnal Patterns**

The U.S. Environmental Protection Agency (1986) has discussed diurnal patterns for urban sites. Figure 4-14, reproduced from the previous document, shows the diurnal pattern of O<sub>3</sub> concentrations on July 13, 1979, in Philadelphia, PA. On this day a peak 1-h average concentration of 0.20 ppm, the highest for the month, was reached at 1400 hours, presumably as the result of meteorological factors, such as atmospheric mixing and local

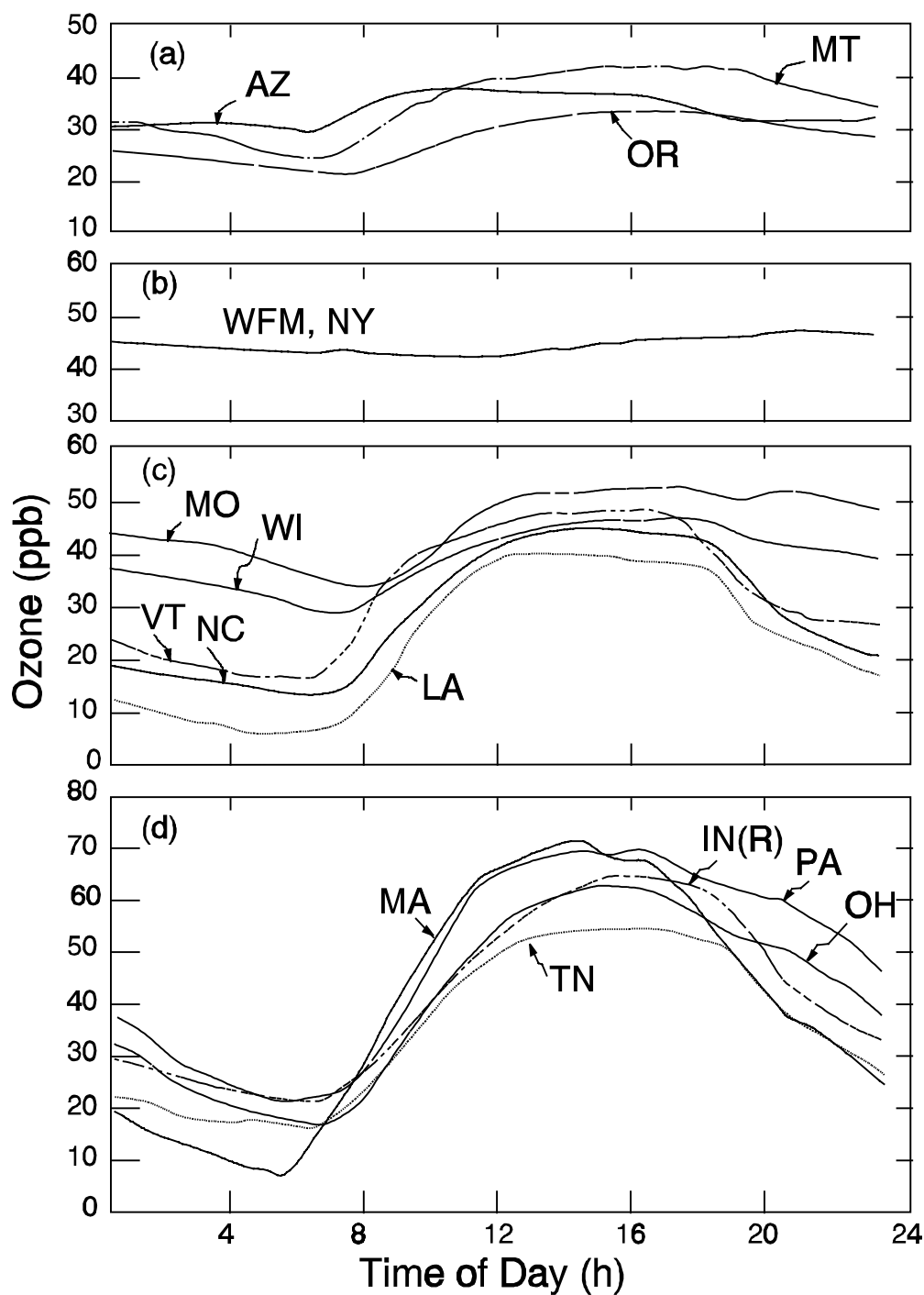


**Figure 4-10.** *The comparison of the seasonal diurnal patterns using 1988 data for Jefferson County, KY, and Oliver County, ND.*

photochemical processes. The severe depression of concentrations to below detection limits (less than 0.005 ppm) between 0300 and 0600 hours usually is explained as resulting from the scavenging of  $O_3$  by local  $NO$  emissions. In this regard, this station is typical of most urban locations.

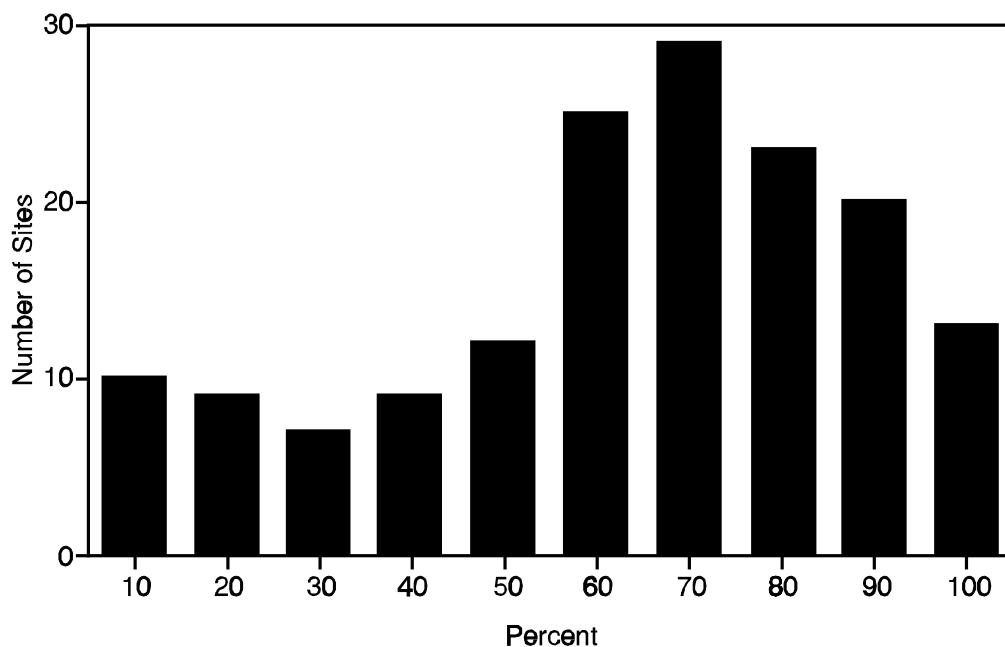
Diurnal profiles of  $O_3$  concentrations can vary from day to day at a specific site, however, because of changes in the various factors that influence concentrations. Composite diurnal data (that is, concentrations for each hour of the day averaged over multiple days or months) often differ markedly from the diurnal cycle shown by concentrations for a specific day. In Figures 4-15 through 4-17 (reproduced from the previous document), diurnal data for 2 consecutive days are compared with composite diurnal data (1-mo averages of hour-by-hour measurements) at three different kinds of sites: (1) center city-commercial (Washington, DC), (2) rural-near urban (St. Louis, MO), and (3) suburban-residential (Alton, IL). Several obvious points of interest present themselves in these figures: at some sites, at least, peaks can occur at virtually any hour of the day or night, but these peaks may not show up strongly in the longer term average data; some sites may be exposed to multiple peaks during a 24-h period; and disparities, some of them large, can exist between peaks (the diurnal data) and the 1-mo average (the composite diurnal data) of hourly  $O_3$  concentrations.



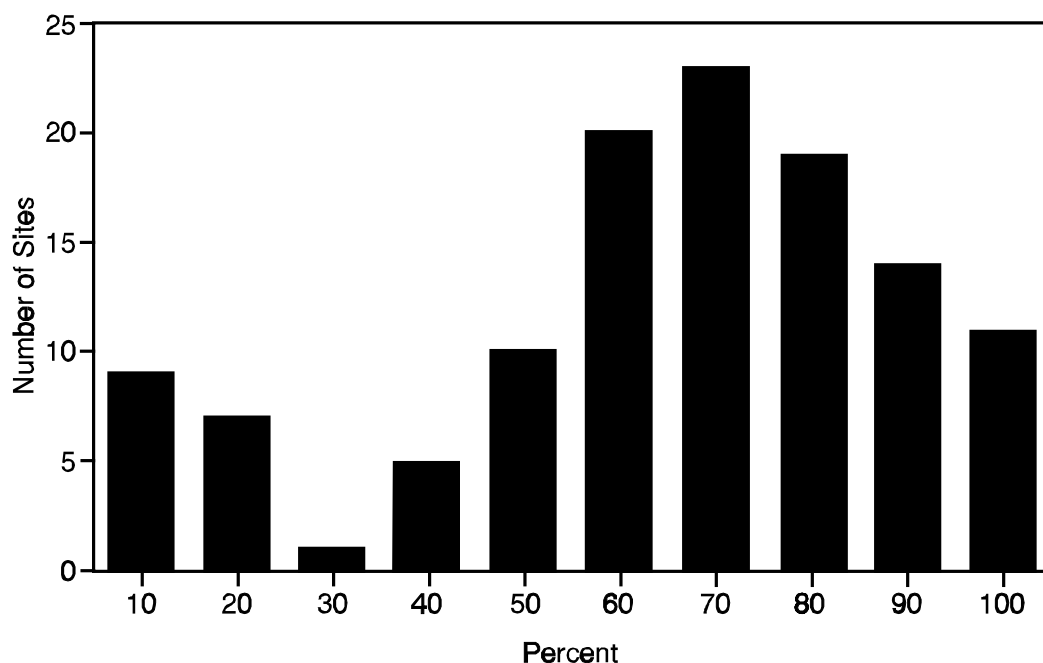


**Figure 4-11.** Diurnal behavior of ozone at rural sites in the United States in July. Sites are identified by the state in which they are located. (a) Western National Air Pollution Background Network (NAPBN); (b) Whiteface Mountain (WFM) located at 1.5 km above sea level; (c) eastern NAPBN sites; and (d) sites selected from the Electric Power Research Institute's Sulfate Regional Air Quality Study. IN(R) refers to Rockport.

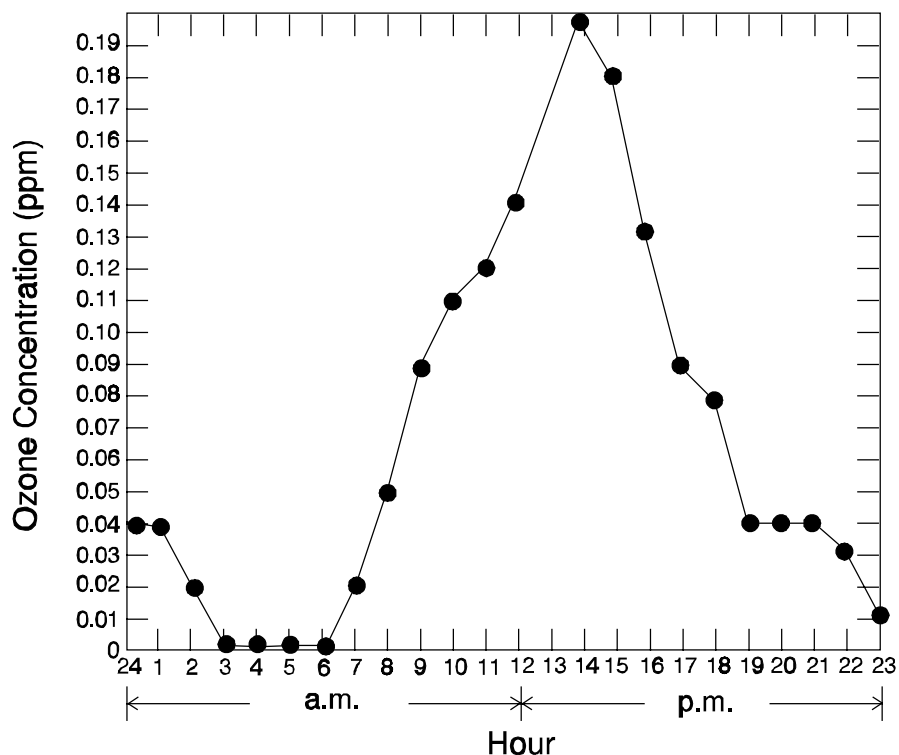
Source: Logan (1989).



**Figure 4-12.** *Percent of time hourly average concentrations  $\geq 0.1$  ppm occurred between 0900 and 1559 hours in comparison to 24-h period for all rural agricultural and forested sites with 3-mo SUM06  $\geq 26.4$  ppm-h.*



**Figure 4-13.** *Percent of time hourly average concentrations  $\geq 0.1$  ppm occurred between 0900 and 1559 hours in comparison to 24-h period for all non-California rural agricultural and forested sites with 3-mo SUM06  $\geq 26.4$  ppm-h.*

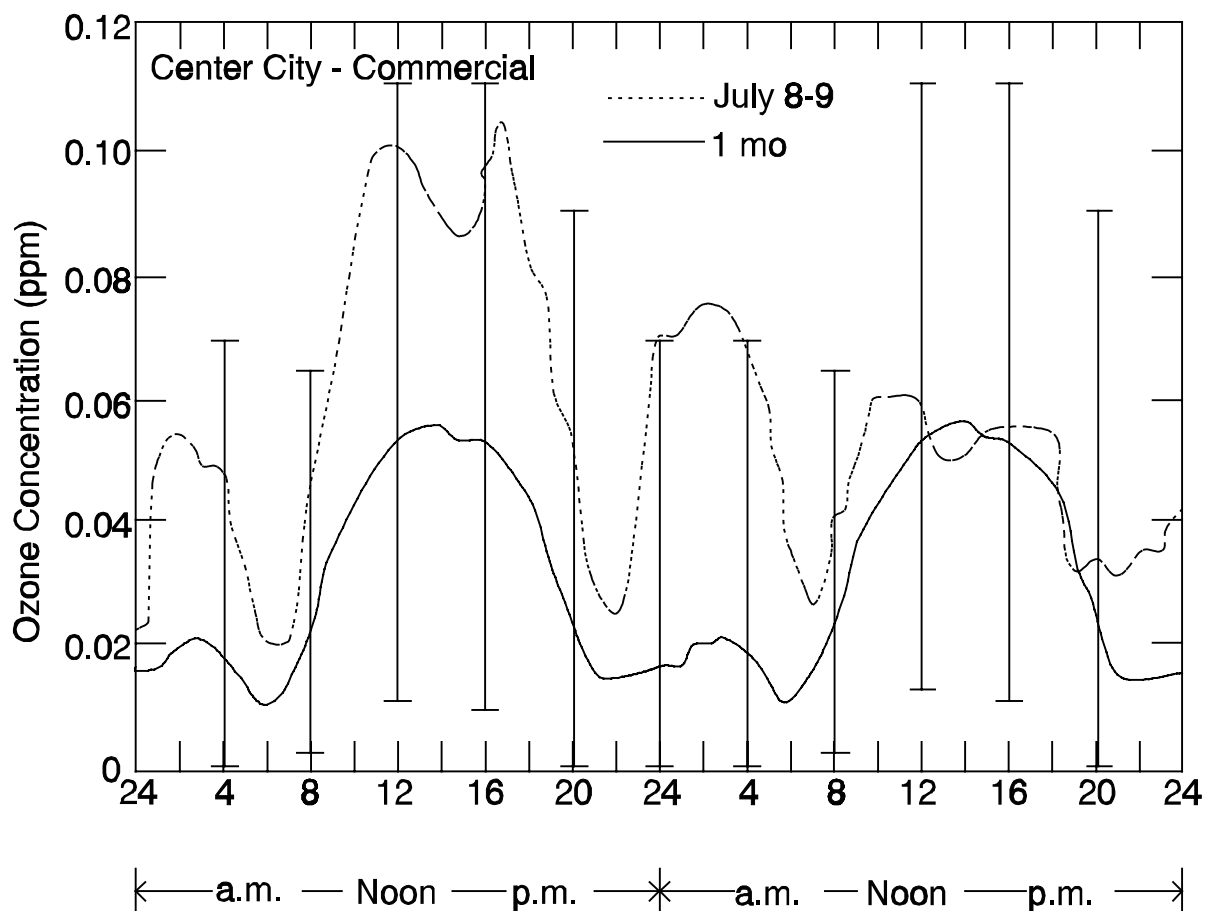


**Figure 4-14.** *Diurnal pattern of 1-h ozone concentrations on July 13, 1979, Philadelphia, PA.*

When diurnal or short-term composite diurnal  $O_3$  concentrations are compared with longer term composite diurnal  $O_3$  concentrations, the peaks are smoothed as the averaging period is lengthened. Figure 4-1 demonstrates the effects of lengthening the period of time over which values are averaged. This figure shows a composite diurnal pattern calculated on the basis of 3 mo. Although seasonal differences are observed, the comparison of 3-mo (Figure 4-18) with 1-mo composite diurnal concentrations (Figure 4-17) at the Alton, IL, site readily demonstrates the smoothing out of peak concentrations as the averaging period is lengthened. As indicated in the previous version of the document (U.S. Environmental Protection Agency, 1986), although this is an obvious and familiar result in the statistical treatment of monitoring data, it is highly pertinent to the protection of human health and welfare from the effects of  $O_3$ .

#### 4.4.3 Nonurban Area Diurnal Patterns

Nonurban areas only marginally affected by transported  $O_3$  usually have a flatter diurnal profile than sites located in urban areas. Nonurban  $O_3$  monitoring sites experience differing types of diurnal patterns (Böhm et al., 1991; Lefohn, 1992b). As indicated earlier,  $O_3$  concentrations at a specific location are influenced by local emissions and by long-range transport from both natural and anthropogenic sources. Thus, considerable variation of  $O_3$  exposures among sites characterized as agricultural or forested is found and there is no preference for maximum diurnal patterns to occur in either the second or third quarter.

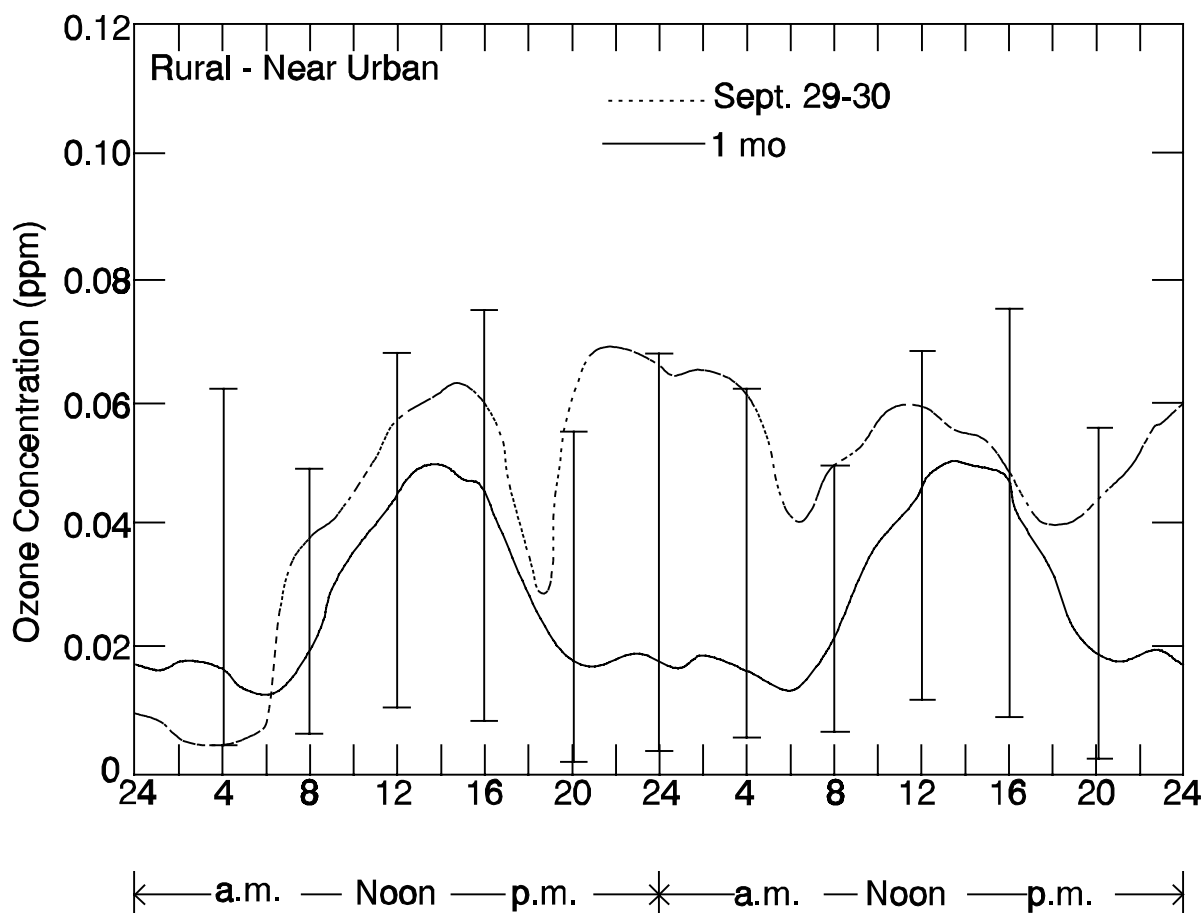


**Figure 4-15. Diurnal and 1-mo composite diurnal variations in ozone concentrations, Washington, DC, July 1981.**

Source: U.S. Environmental Protection Agency (1986).

The diurnal patterns for several agricultural sites have been characterized (U.S. Environmental Protection Agency, 1986). Figures 4-19 and 4-20 show some typical patterns of exposure. As discussed by U.S. Environmental Protection Agency (1986), the six sites, whose diurnal patterns are illustrated in Figure 4-18, represent counties with high soybean, wheat, or hay production. The figures show a distinct afternoon maximum with the lowest concentrations occurring in the early morning and evening hours. Quarterly composite diurnal patterns clearly show the division of the afternoon  $O_3$  concentrations into two seasonal patterns, the low, "winter" levels in the first and fourth quarters and the high, "summer" levels in the second and third quarters of the year.

Remote forested sites experience unique patterns of  $O_3$  concentrations (Evans et al., 1983; Lefohn, 1984). These sites tend to experience a weak diurnal pattern, with

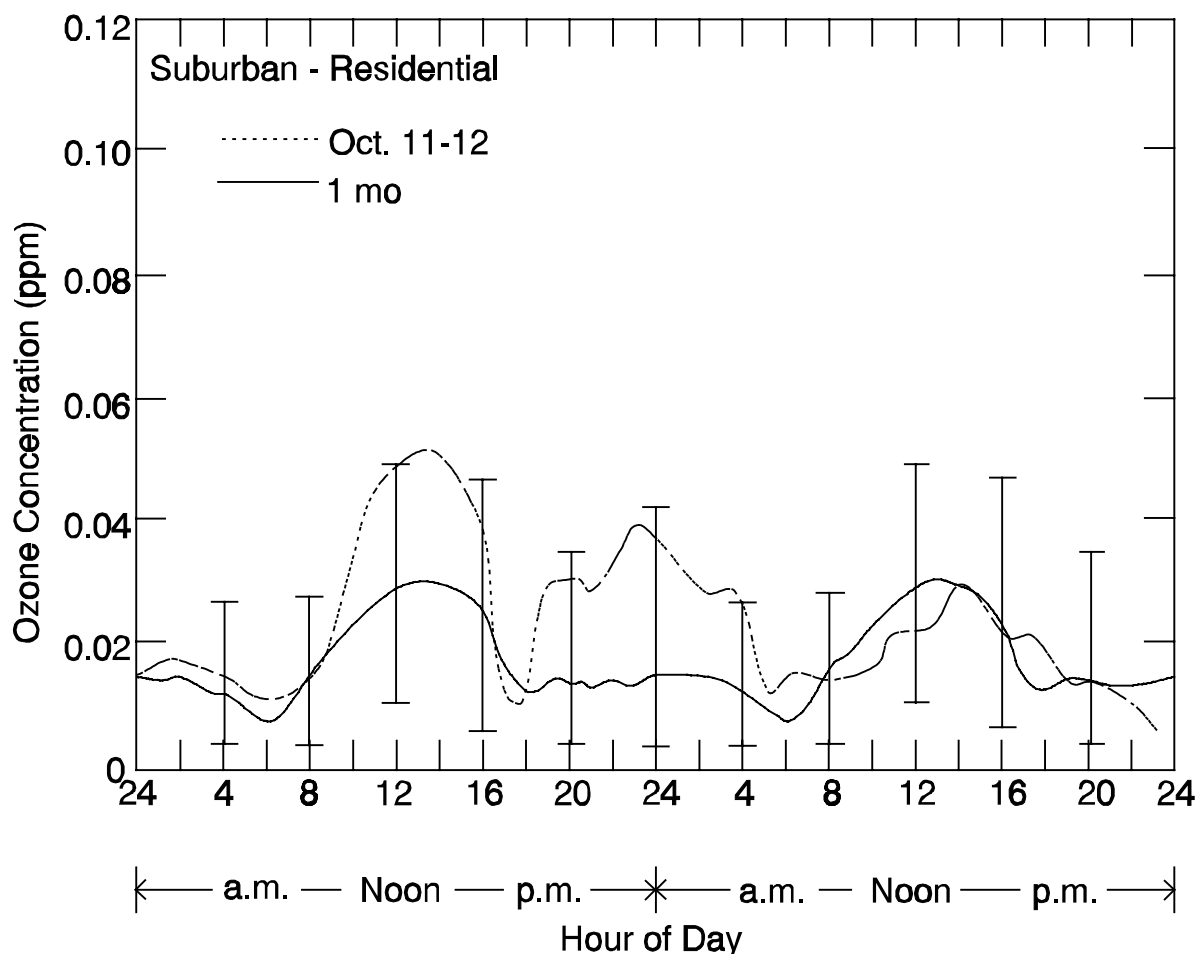


**Figure 4-16. Diurnal and 1-mo composite diurnal variations in ozone concentrations, St. Louis County, MO, September 1981.**

Source: U.S. Environmental Protection Agency (1986).

hourly average  $O_3$  concentrations that occur frequently in the range of 0.04 to 0.05 ppm. Figure 4-21 shows diurnal patterns for several sites in the NDDN network that are located in forested areas. Several of the NDDN sites analyzed by Edgerton and Lavery (1992) exhibit fairly flat average diurnal patterns. Such a pattern is based on average concentrations calculated over an extended period. On a daily basis, some variation in  $O_3$  concentration does occur from hour to hour, and, in some cases, high hourly average concentrations are experienced either during daytime or nighttime periods (Lefohn and Mohnen, 1986; Lefohn and Jones, 1986; Logan, 1989; Lefohn et al., 1990b; Taylor et al., 1992).

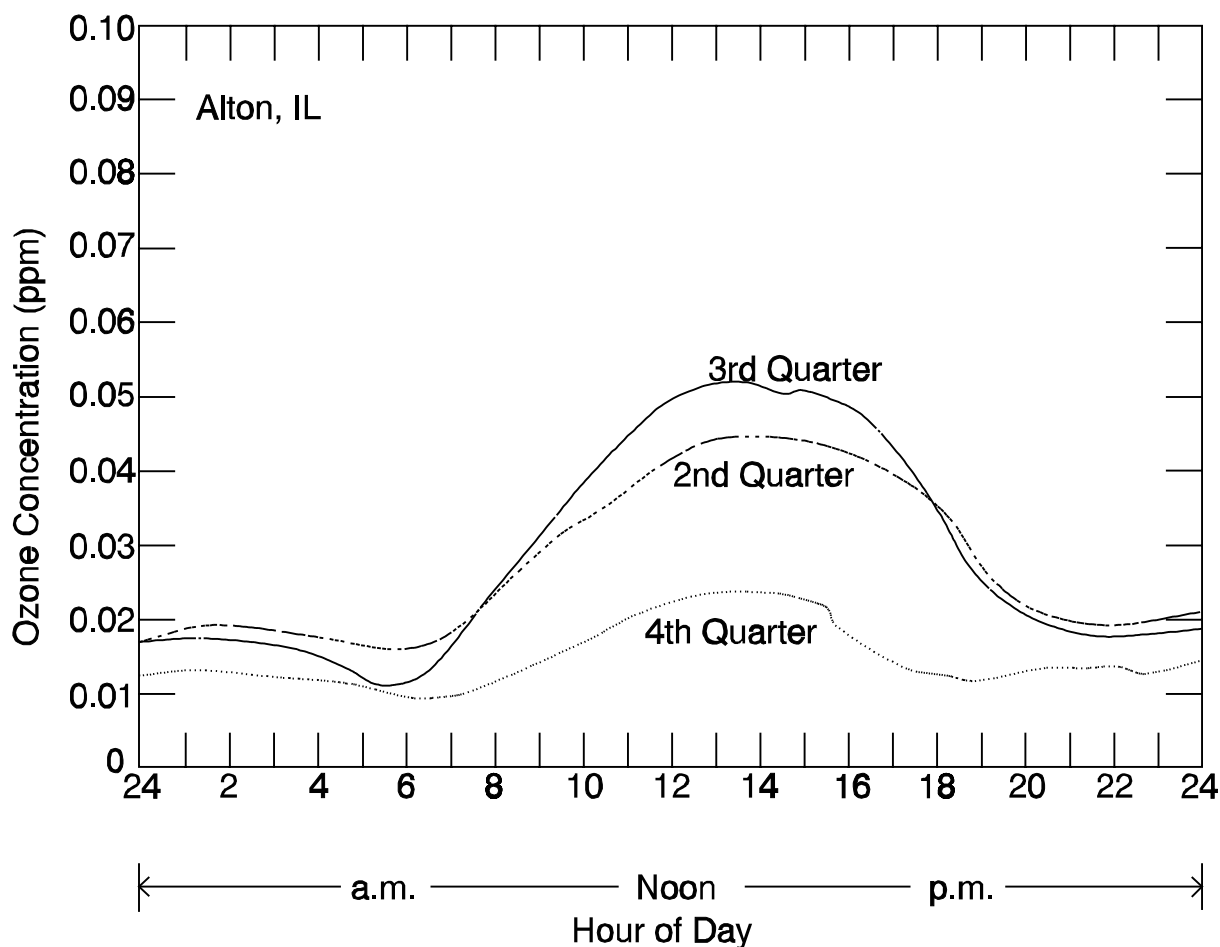
Lefohn et al. (1990b) characterized  $O_3$  concentrations at high-elevation monitoring sites. The authors reported that a fairly flat diurnal pattern for the Whiteface Mountain summit site (WF1) was observed (Figure 4-22a), with the maximum hourly average concentrations occurring in the late evening or early morning hours. A similar pattern was observed for the mid-elevation site at Whiteface Mountain (WF3). The site at the base of Whiteface Mountain (WF4) showed the typical diurnal pattern expected from sites that



**Figure 4-17.** *Diurnal and 1-mo composite diurnal variations in ozone concentrations, Alton, IL, October 1981 (fourth quarter).*

Source: U.S. Environmental Protection Agency (1986).

experience some degree of  $O_3$  scavenging. More variation in the diurnal pattern for the highest Shenandoah National Park sites occurred than for the higher elevation Whiteface Mountain sites, with the typical variation for urban-influenced sites in diurnal pattern at the lower elevation Shenandoah National Park site (Figure 4-22b). Aneja and Li (1992), in their analysis of the five high-elevation Mountain Cloud Chemistry Program (MCCP) sites (see Section 4.6.2 for site descriptions), noted the flat diurnal pattern typical of high-elevation sites that has been described previously in the literature. Aneja and Li (1992) noted that the peak of the diurnal patterns over the period May to October (1986 to 1988) for the five sites occurred between 1800 and 2400 hours, whereas the minimum was observed between 0900 and 1200 hours. However, it is important to note that, as indicated by Lefohn et al. (1990b), the flat diurnal pattern is not observed for all high-elevation sites.

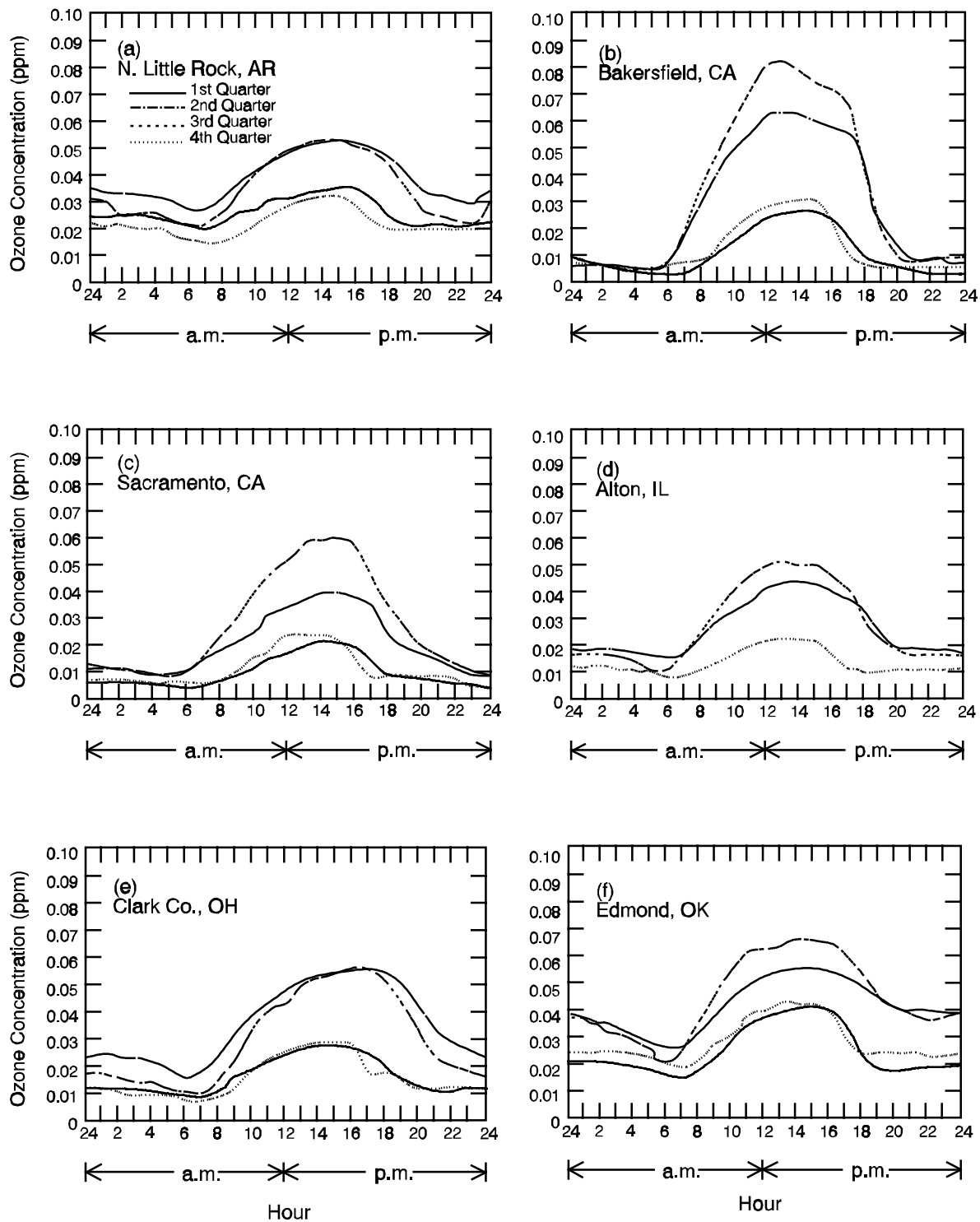


*Figure 4-18. Composite diurnal patterns of ozone concentrations by quarter, Alton, IL, 1981.*

## 4.5 Seasonal Patterns in Ozone Concentrations

### 4.5.1 Urban Area Seasonal Patterns

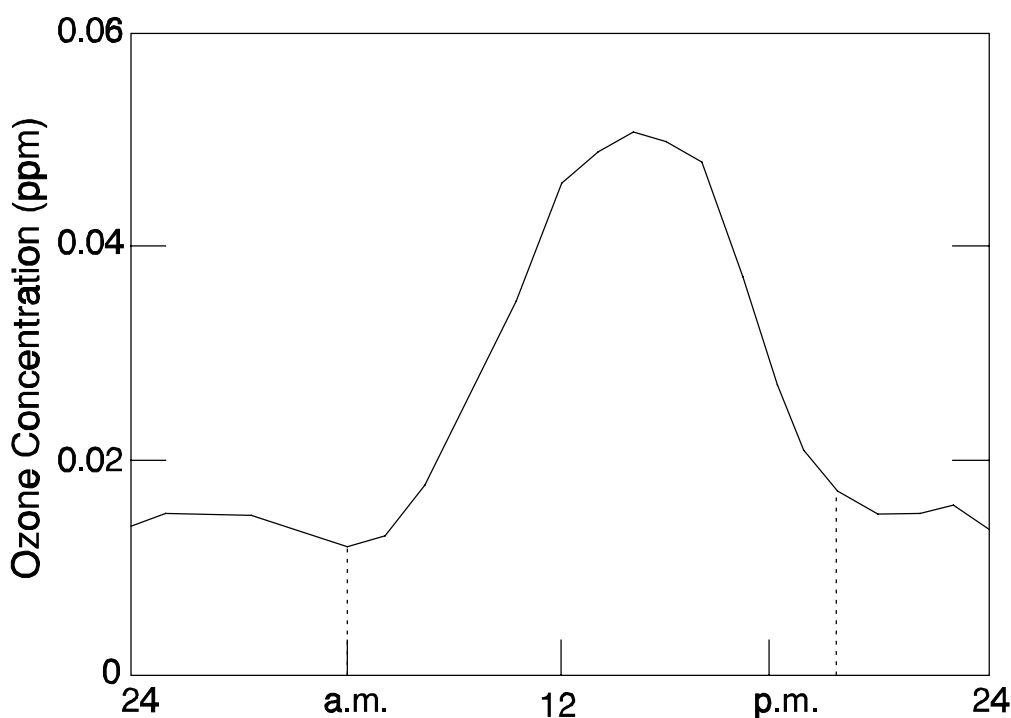
Seasonal variations in  $O_3$  concentrations in 1981 were described by the U.S. Environmental Protection Agency (1986). The current form of the standard focuses on the highest hourly average concentrations. The description that follows uses the highest hourly average concentration as an indication of exposure. Figure 4-23 shows the 1-mo averages and the single 1-h maximum concentrations within the month for eight sites across the nation. The data from most of these sites exhibit the expected pattern of high  $O_3$  in late spring or in summer and low levels in the winter. Data from Pomona, CA (Figure 4-23c), and Denver, CO (Figure 4-23d), show summer maxima. Tampa, FL, shows a late spring maximum but with concentrations in the fall (i.e., October) approaching those of spring (June) (Figure 4-23f). Dallas data also tend to be skewed toward higher spring concentrations; but note that November concentrations are also relatively high (Figure 4-23h). Because of seasonal humidity and storm tracks from year to year, the general weather conditions in a



**Figure 4-19. Quarterly composite diurnal patterns of ozone concentrations at selected sites representing potential for exposure of major crops, 1981.**

Source: U.S. Environmental Protection Agency (1986).





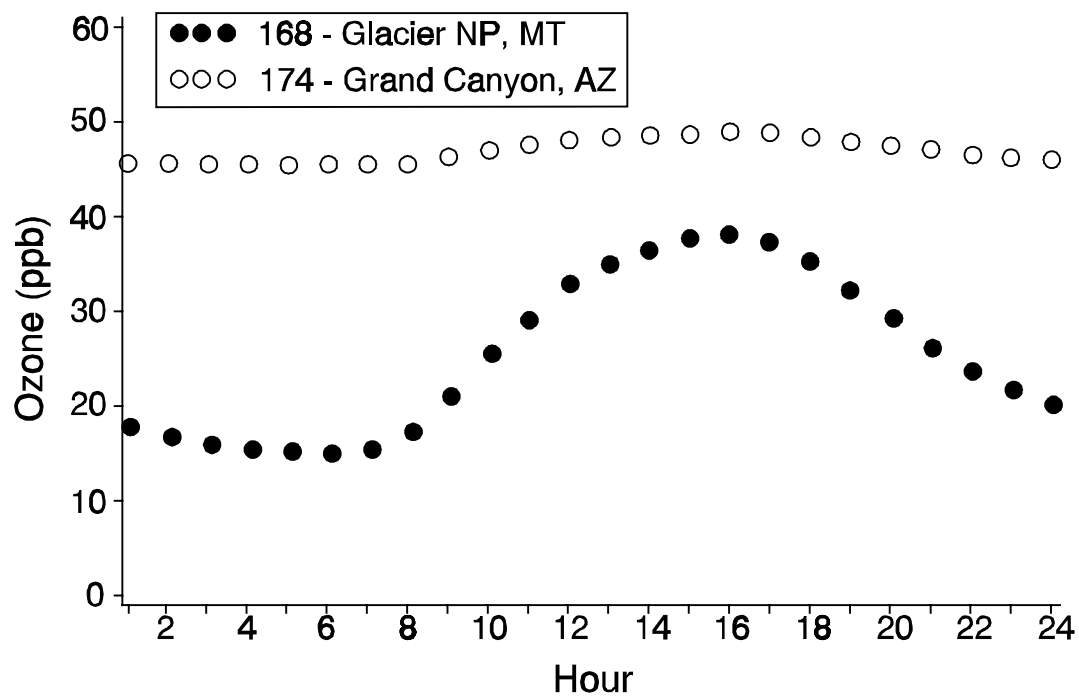
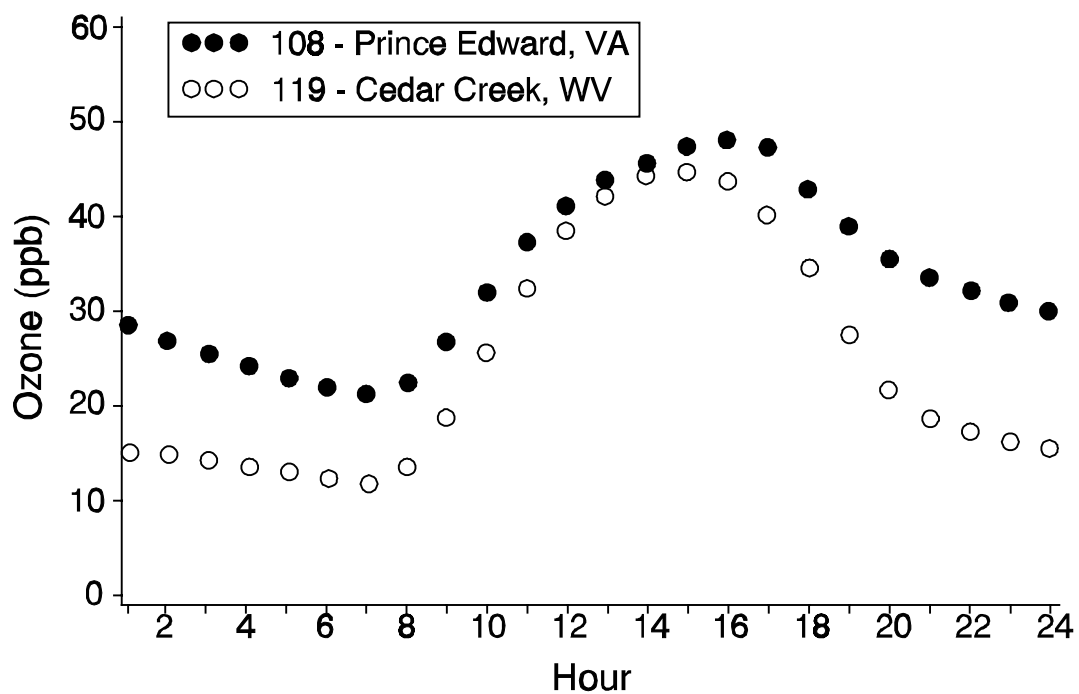
**Figure 4-20.** *Composite diurnal ozone pattern at a rural National Crop Loss Assessment Network site in Argonne, IL, August 6 through September 30, 1980.*

Source: U.S. Environmental Protection Agency (1986).

given year may be more favorable for the formation of  $O_3$  and other oxidants than during the prior or following year. For example, 1988 was a hot and dry year during which some of the highest  $O_3$  concentrations of the last decade occurred, whereas 1989 was a cold and wet year in which some of the lowest concentrations occurred (U.S. Environmental Protection Agency, 1992a).

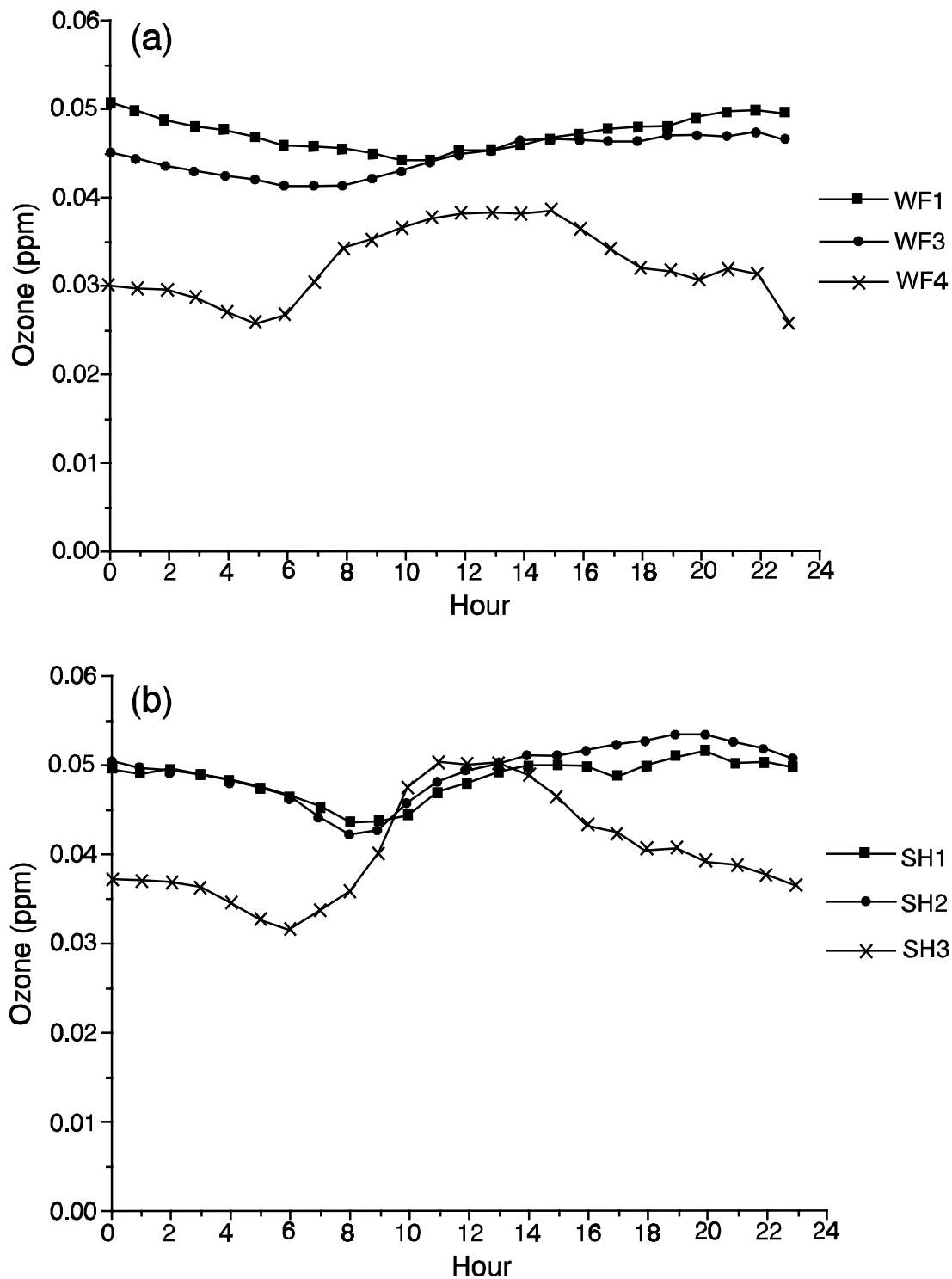
#### 4.5.2 Nonurban Area Seasonal Patterns

In the literature, several investigators have reported on the tendency for average  $O_3$  concentrations to be higher in the second versus the third quarter of the year for many isolated rural sites (Evans et al., 1983; Singh et al., 1978). This observation has been attributed either to stratospheric intrusions or to an increasing frequency of slow-moving, high-pressure systems that promote the formation of  $O_3$ . Lefohn et al. (1990a) reported that for several clean sites, the highest values of exposure indices occurred in the third quarter rather than in the second. The results of this analysis will be discussed in the Section 4.5.3. Taylor et al. (1992) reported that for 10 forest sites in North America, the temporal patterns of  $O_3$  on quarterly or annual periods exhibited less definitive patterns. Based on the exposure index selected, different patterns were reported. The different patterns may be



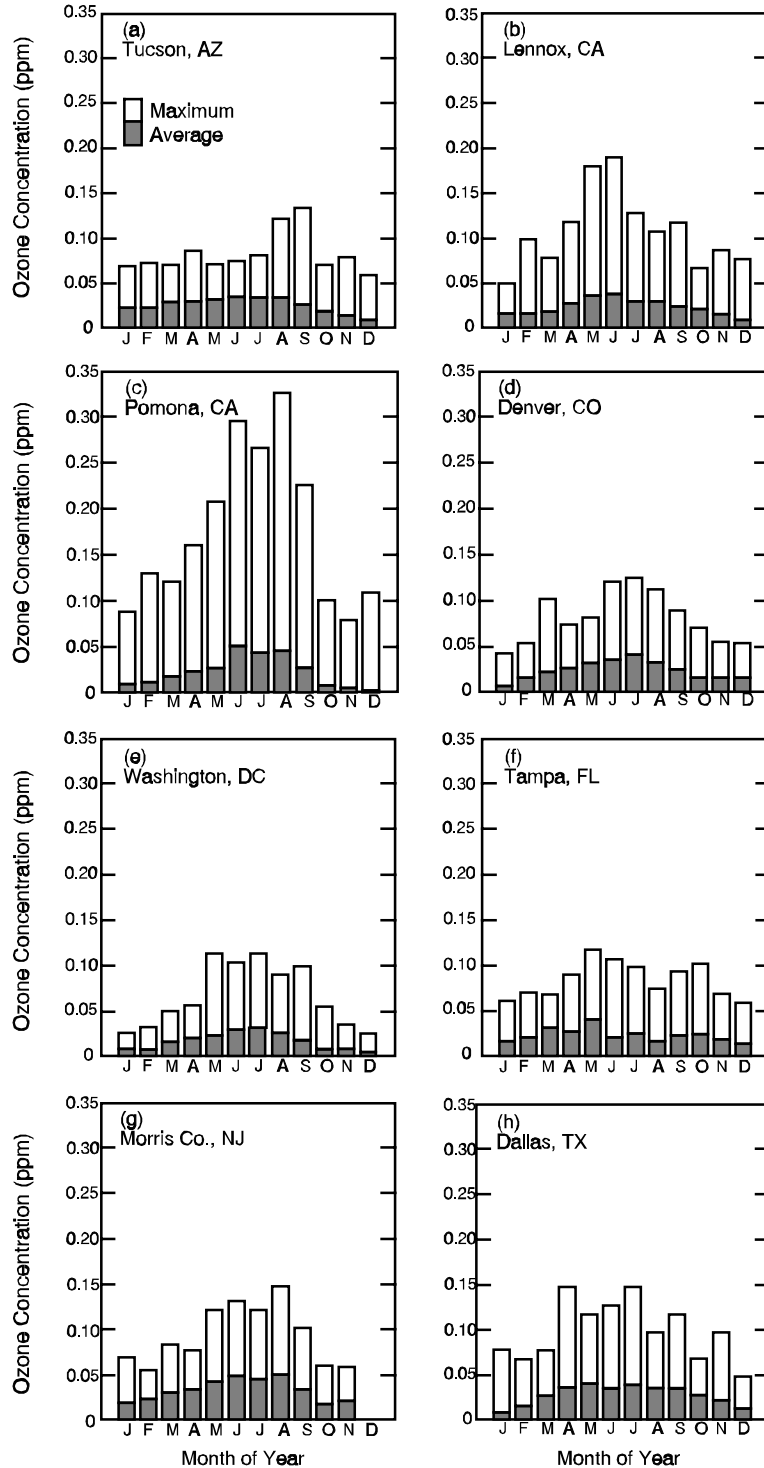
**Figure 4-21. Composite diurnal ozone pattern at selected National Dry Deposition Network sites.**

Source: Edgerton and Lavery (1992).



**Figure 4-22.** Composite diurnal pattern at (a) Whiteface Mountain, NY, and the (b) Mountain Cloud Chemistry Program Shenandoah National Park site for May to September 1987.

Source: Lefohn et al. (1990b).



**Figure 4-23.** Seasonal variations in ozone concentrations as indicated by monthly averages and the 1-h maximum in each month at selected sites, 1981.

Source: U.S. Environmental Protection Agency (1986).