P2.6

CHARACTERIZATION OF SURFACE OZONE CONCENTRATIONS IN THE UNITED STATES

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The distribution, and spatial and temporal variability of surface ozone (O_3) reported into EPA's air quality system (AQS) are characterized. The data were collected in a variety of environments ranging from urban to relatively clean continental background in the continental U.S. Emphasis is placed on the 1-h and 8-h average daily maxima, although 24-h average values are well correlated with these metrics. This was done because the 1-h and 8-h averages are most closely linked to adverse health effects. Only sites with data capture rate of 75% or better for the appropriate averaging period and only data that were not flagged because of quality control issues were included in the analysis. Ozone is monitored during specified "ozone seasons", during which monitoring is mandatory. The lengths of these seasons vary across the U.S. In the Northeast, it ranges typically from April to October and in many southwestern states it extends all year round. The maximum number of stations record data from May to September and so this time frame is used in the analyses, although it should be noted that there are a number of instances of high ozone concentrations at other times of the year.

The distribution of mean daily 1-h maximum, 8-h maximum and 24-h average O_3 concentrations for May to September from 2000 to 2004 is shown in Table 1. CMSAs Consolidated Metropolitan Statistical Areas) as defined by the U.S. Census Bureau, basically refer to urban and their suburbs. If the data are further pooled into individual CMSAs, then a very narrow spread in the daily 8-h maximum concentrations is found. In this case, in only 5% of CMSAs is the daily 8-h maximum O_3 concentration above 57 ppb. This result suggests that there is a good deal of spatial variability of O_3 within urban/suburban areas. This raises the possibility of exposure misclassification in air pollution-health outcome studies.

Table 1. Summary of Percentiles of Data Pooled Across Monitoring Sites for May to September 2000-2004. Concentrations[1] are in ppb.

			Percentiles										
Pooled Group/ Avg. Time	**Number of Values**	**Mean**	**1**	**5**	**10**	**25**	**30**	**50**	**70**	**75**	**90**	**95**	**99**
Daily 1-h Maximum Concentrations													
Monitors in CMSAs[2]	367,121	58	20	29	34	44	46	56	66	70	84	94	116
Monitors not in CMSAs	323,891	55	20	28	33	43	45	54	64	67	79	87	104
8-h Daily Maximum Concentrations													
Monitors in CMSAs	367,029	50	16	23	28	37	40	49	58	61	73	81	98
Monitors not in CMSAs	323,815	49	16	23	28	37	39	48	57	59	70	77	91
24-h Average Concentrations													
Monitors in CMSAs	367,121	33	10	15	18	24	26	32	39	41	50	56	68
Monitors not in CMSAs	323,891	34	10	15	18	25	27	33	39	41	50	56	68

[1] Following common usage, mixing ratios or mole fractions are referred to as concentrations.
[2] CMSA = Consolidated Metropolitan Statistical Area

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1. Diurnal Variability in Ozone Concentrations

Diurnal variations in O_3 are controlled by a number of factors that differ from city to city, resulting in interurban differences across the U.S. In general, the maximum daily maximum1-h average O_3 occurs in mid afternoon as shown in Figure 1. However, it can be seen that rather high values can be found at any time of day or night. Occurrences of high ozone either at night or early in the morning likely result from transport of ozone rich air from above the planetary boundary layer.

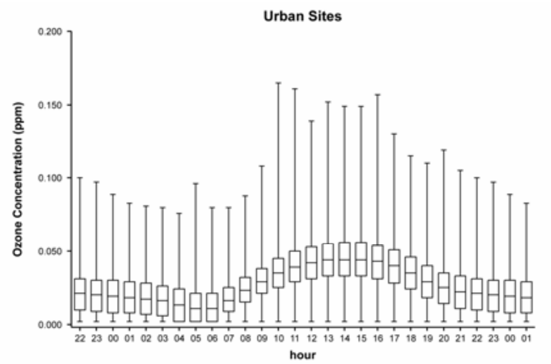

Figure 1. Composite, nationwide diurnal variability in hourly averaged O_3 in urban areas. Values shown are averages from April to October 2000 to 2004. Boxes define the interquartile range and the whiskers, the minima and maxima.

The daily maximum 8-h O_3 concentration generally occurs between 10 a.m. and 6 p.m., as shown in Figure 2. Again, there are a number of cases where the highest values occur either early in the morning or at night.

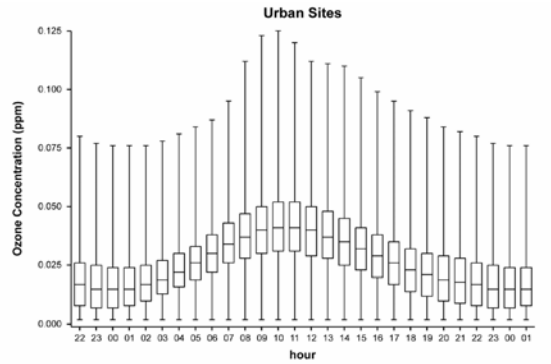

Figure 2. Composite, nationwide diurnal variability in 8-h average O_3 in urban areas. Values shown are averages from April to October 2000 to 2004. Boxes define the interquartile range and the whiskers, the minima and maxima. The hour refers to the start of the 8-h averaging period.

The diurnal behavior of O_3 in twelve selected U.S. urban areas is shown in Figure 3 a-l. These areas were chosen because these areas have the highest ozone levels in the U.S. and assessments of health risks associated with exceedences of the ozone National Ambient Air Quality Standard are performed in these areas.. Of special note is the diurnal pattern of ozone in Houston, Texas. As can be seen from Figure 3j, very high values (~200 ppbv) were found in mid-morning. These short period spikes in O_3 are associated with massive, transient emissions of highly reactive VOCs (HRVOCs) such as ethylene and propylene from petrochemical production and refining in the area surrounding the Houston Ship Channel. Such “emission events” often occur in close proximity to NOx sources, enhancing their ozone formation potential. Slow, rotating sea-breeze winds trap these emissions, allowing them to build up to high levels. These factors result in very rapid formation of concentrated ozone plumes, or Transient High Ozone Events (THOEs), in marked contrast to the more typical situation elsewhere in which emissions and ozone are more evenly distributed, and ozone builds up more slowly (Olaguer et al., 2006). The association of THOEs with HRVOCs has been confirmed by many investigators (see e.g., Ryerson et al.) from the 2000 Texas Air Quality Study (TexAQS 2000).

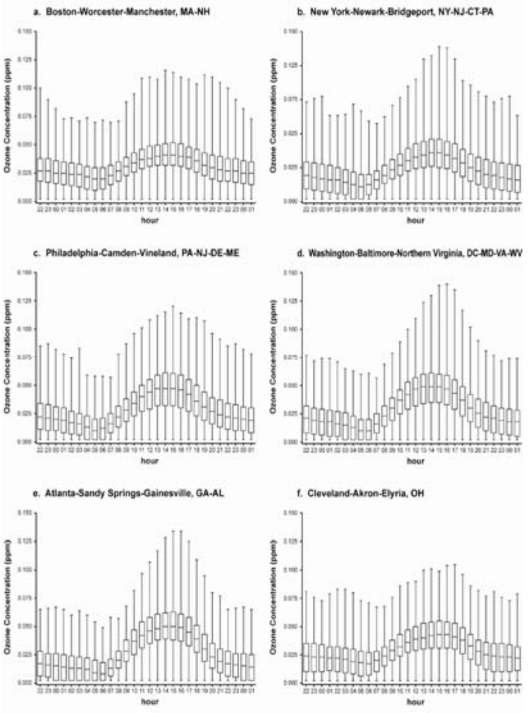

Figure 3a-f. Diurnal variability in hourly averaged O_3 in selected urban areas. Values shown are averages from April to October 2000-2004. Boxes define the interquartile range and the whiskers, the minima and maxima.

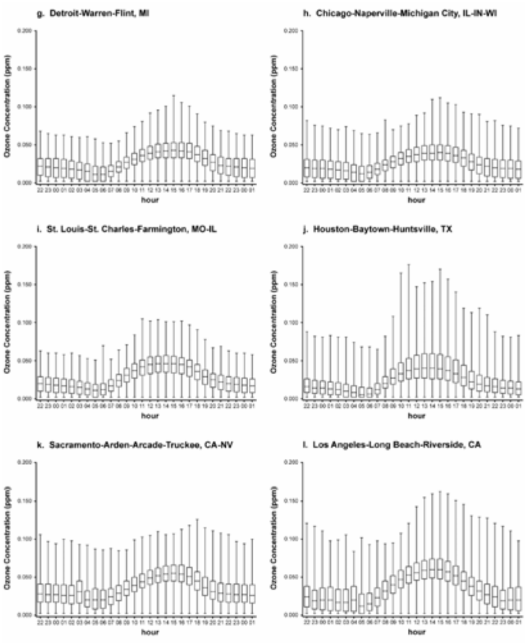

Figure 3g-l. Diurnal variability in hourly averaged O_3 in selected urban areas. Values shown are averages from April to October 2000-2004. Boxes define the interquartile range and the whiskers, the minima and maxima.

Proper assessment of local ozone production and transport in Houston must focus on two distinct features associated with the sea breeze. First, there is the slow wind rotation that traps pollutants locally. The second important feature is the occurrence of stalled sea breeze fronts. Stalled fronts result in stagnant zones at the boundary of converging air masses, which not only allow ozone and precursors to build up at the surface, but also uplift them to create "walls" of pollution, as observed during TexAQS 2000. This pollution can be transported by fast winds aloft, and later entrained back to the surface (Banta et al., 2005).

Composite diurnal patterns of O_3 are shown in Figure 4 for 1-h average O_3 and Figure 5 for 8-h average O_3 at CASTNET sites. CASTNET sites are located in rural areas and are meant to be representative of a much larger area than are the urban monitoring sites. As can be seen from a comparison of Figures 4 and 5 with 1 and 2, diurnal patterns of O_3 are smoother and shallower than at the urban sites. Maxima in 1-h average O_3 also tend to occur in the afternoon. However, highest concentrations observed during any particular hour at night at CASTNET sites (~130 ppbv) are higher than those observed in urban areas. In addition, daily 1-h maxima at CASTNET sites have exceed 150 ppbv on a number of occasions. There are a number of causes for the different behavior of O_3 between the urban/suburban and rural monitoring sites. Many of the CASTNET sites are located far enough downwind of major sources of O_3 precursors so that maximum photochemical production of O_3 has occurred. In addition, there is a lack of titration of O_3 by NO emitted by traffic at urban locations. It is somewhat ironic that some of the lowest mean O_3 concentrations are found near downtown Los Angeles. Of course, some of the highest are found well downwind of Los Angeles. Since many of the CASTNET sites are elevated above sea level, they are more likely to be influenced by stratospheric intrusions and by transport above the planetary boundary layer.

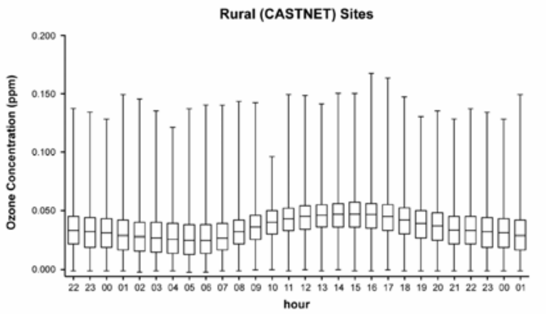

Figure 4. Composite diurnal variability in hourly O_3 concentrations observed at CASTNET sites. Values shown are averages from April to October 2000-2004. Boxes define the interquartile range and the whiskers, the minima and maxima.

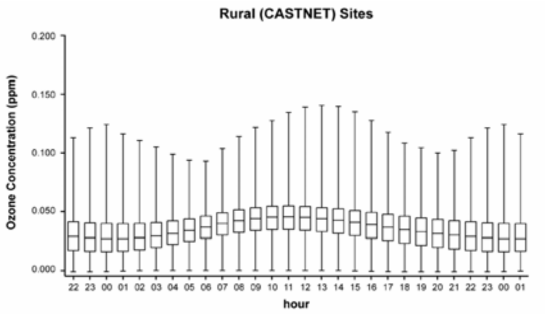

Figure 5. Composite diurnal variability in 8-h average O_3 concentrations observed at CASTNET sites. Values shown are averages from April to October 2000-2004. Boxes define the interquartile range and the whiskers, the minima and maxima.

2. Seasonal Variability in Ozone Concentrations

Box plots showing composite diurnal variations in the same 12 urban areas discussed above are shown in Figures 6 a-l., but covering the period November to March. Although most attention is

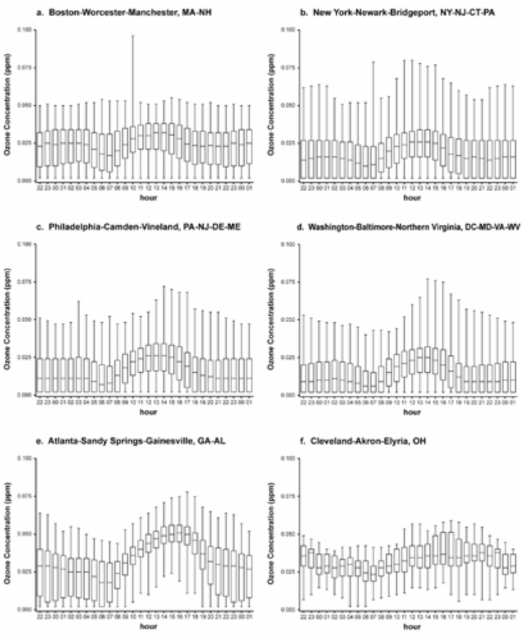

Figure 6a-f. Diurnal variability in 1-h average O_3 concentrations in EPA's 12 cities. Values shown represent averages from November through March 2000-2004. Boxes define the interquartile range and the whiskers, the minima and maxima.

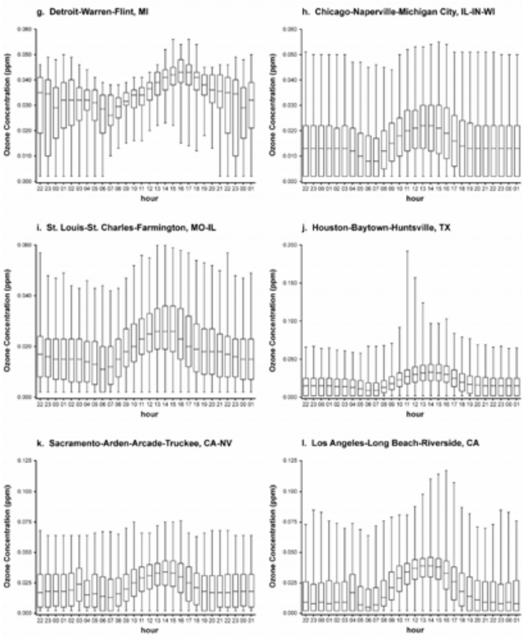

Figure 6g-l. Diurnal variability in 1-h average O_3 concentrations in EPA's 12 cities. Values shown represent averages from November through March 2000-2004. Boxes define the interquartile range and the whiskers, the minima and maxima.

given to ozone episodes occurring in the summer, and ozone is commonly thought of as a summer pollutant, there are a number of occasions on which high ozone values are found in other seasons.

These occurrences could be due to causes as diverse as stratospheric-tropospheric exchange (more likely in northern states) or photochemical activity (more likely in southern states). Data for O_3 at individual sites along with data fro other meteorological and chemical parameters must be examined to draw any conclusions about possible cause.

3. Year-to-year variability in Ozone Concentrations

The year-to-year variability in the mean daily maximum 8-h average O_3 concentrations are shown in Figure 7. Although there were sizable declines at the upper end of the O_3 distribution over the past 15 years, O_3 concentrations nearer the center of the distribution showed much smaller changes from 1990 to 2004. This finding is consistent with observations in Europe (Volz-Thomas et al., 2003). There were noticeable dips in 2003 and 2004 (Figure 7). The dips in mean O_3 levels were likely associated with cooler than normal conditions in the eastern U.S. (Levinson and Waple, 2004; Levinson, 2005), where most O_3 monitors are located. However, there might have also been some contribution from the NOx SIP Call implemented in 2003.

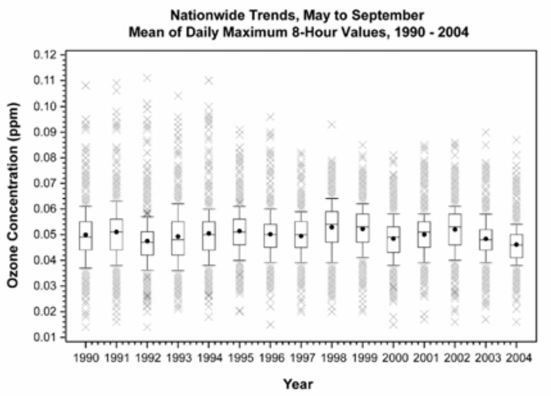

Figure 7. Year-to-year variability in nationwide mean daily maximum 8-h O_3 concentrations. The whiskers on the box plot represent the 10th and 90th percentile concentrations. The "X"s above and below the whiskers are the values that fall below and above the 10^{th} and 90^{th} percentile concentrations. The dots inside the box represent the mean, for the statistic, at all sites.

The NOx SIP Call established a NOx Budget Trading Program (NBP) to cap the emissions from electric generation units (EGU) and large industrial boilers at concentrations which would aid the states east of the Mississippi River in meeting their air quality goals.

The year-to-year variability in ozone at monitoring sites in national parks is shown in Figures 8 a-p. Sites at several national parks (Acadia in 1996, Joshua Tree in 1993, Mammoth Cave in 1996, Voyageurs in 1996 and Yellowstone in 1996) were moved. These moves often results in offsets in O_3 and this should be kept in mind when viewing Figures 8 a-p. Trends for these sites have also not been calculated in Table 2. As noted in (e.g.) The Ozone Report-Measuring Progress through 2003 (U.S. EPA, 2004), O_3 trends in national parks in the South and the East are similar to trends in nearby urban areas and reflect the regional nature of ozone pollution. For example, O_3 in Charleston, SC and Charlotte, NC tracks O_3 in nearby Cowpens NP and Cape Romaine NP in South Carolina; O_3 in Philadelphia, PA and Baltimore, MD tracks O_3 in Brigantine NWR in New Jersey; and O_3 in New York City and Hartford, CT tracks O_3 in Cape Cod NS. The situation is not as clear in the West, where some national parks are affected by local pollution sources (e.g., Lassen Volcanic and Yosemite National Parks) more than others.

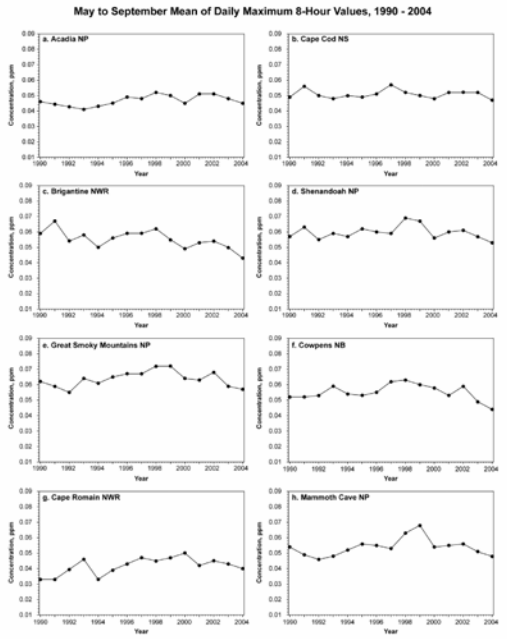

Figure 8a-h. Year-to-year variability in mean daily maximum 8-h O_3 concentrations at selected national park (NP), national wildlife refuge (NWR), and national monument (NM) sites.

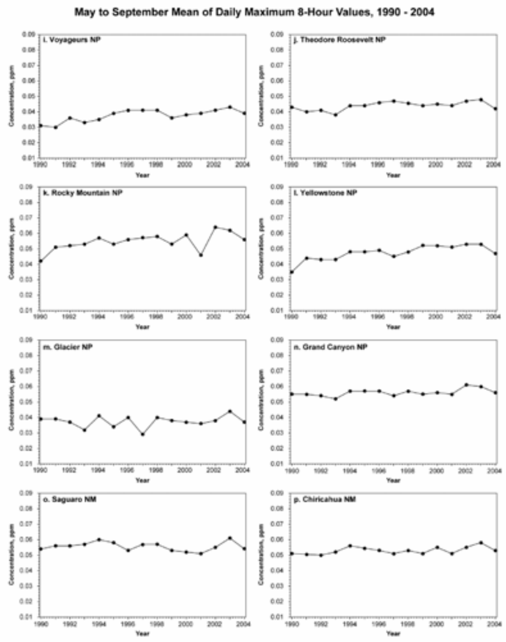

Figure 8i-p. Year-to-year variability in mean daily maximum 8-h O_3 concentrations at selected national park (NP), national wildlife refuge (NWR), and national monument (NM) sites.

Comparison of the calculated trends at national park sites with box plots of nationwide O_3 in Figure 7 shows that O_3 concentrations near the center of the distribution do not necessarily track those at the upper end. In addition, Table 2 shows that trends at several sites reversed direction in going from the 98th to 95th percentile values.

Disclaimer: This paper has been subjected to internal agency review, but the views expressed are the authors' own and do not reflect those of the U.S. EPA.

Table 2. Trends in Warm Season (May to September) Daily Maximum 8-h O_3 Concentrations at National Parks in the United States (1990 to 2004). Trends are given as ppb yr^{-1}.

	Mean		**95th %-ile**		**98th %-ile**	
Site	**trend**	**p–value**	**trend**	**p–value**	**trend**	**p–value**
Acadia NP (ME)[3]	—	—	—	—	—	—
Brigantine NWR (NJ)	-0.80[2]	0.014	-1.7[2]	0.004	-1.9[2]	0.003
Cape Cod NS (MA)	0	0.423	0	0.349	-0.5	0.19
Cape Romain NWR (SC)	0.7[1]	0.046	1.0[1]	0.01	1.0	0.07
Chiricahua NM (AZ)	0.22[1]	0.046	0.2	0.084	0.15	0.218
Cowpens NB (SC)	0	0.423	0.1	0.349	0.4	0.349
Denali NP (AK)	0.17	0.12	0.6[1]	0.01	0.6[1]	0.002
Glacier NP (MT)	0	0.5	0.1	0.349	0.27	0.19
Grand Canyon NP (AZ)	0.25	0.07	0	0.5	0.13	0.218
Great Smoky Mountains NP (NC-TN)	0.29	0.248	0.9	0.19	0.4	0.423
Joshua Tree NP (CA)[3]	—	—	—	—	—	—
Lassen Volcanic NP (CA)	0.25	0.141	0.2	0.19	0	0.5
Mammoth Cave NP (KY)[3]	—	—	—	—	—	—
Olympic NP (WA)	0.14	0.141	0.3[1]	0.037	0.2	0.19
Pinnacles NM (CA)	-0.1	0.218	-0.5	0.07	-0.56	0.057
Rocky Mountain NP (CO)	0.91[1]	0.004	1.0[1]	0.014	0.88	0.07
Saguaro NM (AZ)	-0.2	0.279	-0.3	0.19	-0.38	0.141
Sequoia/Kings Canyon NP (CA)	0.38	0.218	0	0.461	0	0.539
Shenandoah NP (VA)	0	0.461	-0.2	0.385	0.33	0.279
Theodore Roosevelt NP (ND)	0.38[1]	0.023	0.2	0.19	0.2	0.141
Voyageurs NP (MN)[3]	—	—	—	—	—	—
Yellowstone NP (WY)[3]	—	—	—	—	—	—

[1] Upward trend, significant at p = 0.05 level.
[2] Downward trend, significant at p = 0.05 level.
[3] Site moved. See text for details.

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