

associated with the observations by Logan (1989) that rural O₃ in the eastern United States in the spring and summer is severely impacted by anthropogenic and possibly natural emissions of NO_x and hydrocarbons, and that O₃ episodes occur when the weather is particularly conducive to photochemical formation of O₃. Meagher et al. (1987) reported for rural O₃ sites in the southeastern United States that the daily maximum 1-h average concentration was found to peak during the summer months. Taylor and Norby (1985) reported that, in the Shenandoah National Park, the probability of a day occurring in which a 1-h mean O₃ concentration was >0.08 ppm was the same during the months of May, June, and July, whereas the probability was nearly 40% less in August. The probability of an episode during each of the remaining months of the growing season was <5%. The month of July experienced both the highest frequency of episodes and the highest mean duration of exposure events.

Aneja and Li (1992) reported that the maximum monthly ozone levels occurred in either the spring or the summer (May to August), and the minimum occurred in the fall (September and October). The timing of the maximum monthly values differed across sites and years. However, in 1988, an exceptionally high O₃ concentration year, for almost all of the five sites, June was the month in which the highest monthly average concentration occurred. This was the month in which the greatest number of O₃ episodes occurred in the eastern United States.

4.5.3 Seasonal Pattern Comparisons with Sites Experiencing Low Exposures

Lefohn et al. (1990a) have characterized the O₃ concentrations that occurred at several sites in the United States that experience low maximum hourly average concentrations. The Theodore Roosevelt National Park site experienced its maximum in July for 1984 and 1985 and in May for 1986. Of the three western national forest sites evaluated by Lefohn et al. (1990a), only Apache National Forest experienced its maximum monthly mean concentration in the spring. The Apache National Forest site was above mean nocturnal inversion height, and no decrease of concentrations occurred during the evening hours. This site also experienced the highest hourly maximum concentration, as well as the highest W126 O₃ exposures. The Custer and Ochoco national forest sites experienced most of their maximum monthly mean concentrations in the summer. The White River Oil Shale site in Colorado experienced its maximum monthly mean during the spring and summer months.

The W126 sigmoidal weighting function index was also used to identify the month of highest O₃ exposure. A somewhat more variable pattern was observed than when the maximum monthly average concentration was used. For some sites, the winter/spring pattern was represented; for others, it was not. In some cases, the highest W126 exposures occurred earlier in the year than was indicated by the maximum monthly concentration. For example, in 1979, the Custer National Forest site experienced its highest W126 exposure in April, although the maximum monthly mean occurred in August. In 1980, the reverse occurred.

There was no consistent pattern for those sites located in the continental United States. The Theodore Roosevelt and Ochoco national park sites, the Custer National Forest site, and the White River Oil Shale site experienced their maximum O₃ exposures during the spring and summer months. The sites experiencing their highest O₃ exposures in the fall-to-spring period did not necessarily experience the lowest O₃ exposures.

4.6 Spatial Variations in Ozone Concentrations

4.6.1 Urban-Nonurban Area Concentration Differences

Diurnal concentration data presented earlier indicate that peak O₃ concentrations can occur later in the day in rural areas than in urban, with the distances downwind from urban centers generally determining how much later the peaks occur. Meagher et al. (1987) reported that for five rural sites in the Tennessee Valley region of the southeastern United States, O₃ levels were found to equal or exceed urban values for the same region. Data presented in the 1978 criteria document demonstrated that peak concentrations of O₃ in rural areas generally are lower than those in urban areas, but that average concentrations in rural areas are comparable to or even higher than those in urban areas (U.S. Environmental Protection Agency, 1978). Reagan (1984) noted that O₃ concentrations measured near population-oriented areas were depressed in comparison with data collected in more isolated areas. As noted earlier, urban O₃ values are often depressed because of titration by NO (Stasiuk and Coffey, 1974). In reviewing the NCLAN's use of kriging to estimate the 7-h seasonal average O₃ levels, Lefohn et al. (1987a) found that the 7-h values derived from kriging for sites located in rural areas tended to be lower than the actual values because of the effect of using data from urban areas to estimate rural values. In addition to the occurrence of higher average concentrations and occasionally higher peak concentrations of O₃ in nonurban than in urban areas, it is well documented that O₃ persists longer in nonurban than in urban areas (Coffey et al., 1977; Wolff et al., 1977; Isaksen et al., 1978). The absence of chemical scavengers appears to be the main reason.

4.6.2 Concentrations Experienced at High-Elevation Sites

The distributions of hourly average concentrations experienced at high-elevation cities are similar to those experienced in low-elevation cities. For example, the distribution of hourly average concentrations for several O₃ sites located in Denver were similar to distributions observed at many low-elevation sites in the United States. However, as will be discussed in Section 4.6.3, for assessing the possible impacts of O₃ at high-elevation sites, the use of absolute concentrations (e.g., in units of micrograms per cubic meter) instead of mixing ratios (e.g., parts per million) may be an important consideration.

Lefohn et al. (1990b) summarized the characterization of gaseous exposures at rural sites in 1986 and 1987 at several MCCP high-elevation sites. Aneja and Li (1992) have summarized the ozone concentrations for 1986 to 1988. Table 4-14 summarizes the sites characterized by Lefohn et al. (1990b). Table 4-15 summarizes the concentrations and exposures that occurred at several of the sites for the period 1987 to 1988. In 1987, the 7- and 12-h seasonal means were similar at the Whiteface Mountain WF1 and WF3 sites (Figure 4-24a). The 7-h mean values were 0.0449 and 0.0444 ppm, respectively, and the 12-h mean values were 0.0454 and 0.0444 ppm, respectively. Note that, in some cases, the 12-h mean was slightly higher than the 7-h mean value. This resulted when the 7-h mean period (0900 to 1559 hours) did not capture the period of the day when the highest hourly mean O₃ concentrations were experienced. A similar observation was made, using the 1987

Table 4-14. Description of Mountain Cloud Chemistry Program Sites^a

Site	Elevation (m)	Latitude			Longitude		
Howland Forest (HF1), ME	65	45°	11'		68°	46'	
Mt. Moosilauke (MS1), NH	1,000	43°	59'	18"	71°	48'	28"
Whiteface Mountain (WF1), NY	1,483	44°	23'	26"	73°	51'	34"
Shenandoah NP (SH1), VA	1,015	38°	37'	12"	78°	20'	48"
Shenandoah NP (SH2), VA	716	38°	37'	30"	78°	21'	13"
Shenandoah NP (SH3), VA	524	38°	37'	45"	78°	21'	28"
Whitetop Mountain (WT1), VA	1,689	36°	38'	20"	81°	36'	21"
Mt. Mitchell (MM1), NC	2,006	35°	44'	15"	82°	17'	15"
Mt. Mitchell (MM2), NC	1,760	35°	45'		82°	15'	

^aSee Appendix A for abbreviations and acronyms.

data, for the MCCP Shenandoah National Park sites. The 7- and 12-h seasonal means were similar for the SH1 and SH2 sites (Figure 4-24b). Based on cumulative indices, the Whiteface Mountain summit (1,483-m) site (WF1) experienced a higher exposure than the WF3 (1,026-m) site (Figure 4-24c). Both the sum of the concentrations ≥ 0.07 ppm (SUM07) and the number of hourly concentrations ≥ 0.07 ppm were higher at the WF1 site than at the WF3 site. The site at the base of the mountain (WF4) experienced the lowest exposure of the three O₃ sites. Among the MCCP Shenandoah National Park sites, the SH2 site experienced marginally higher O₃ exposures, based on the index that sums all of the hourly average concentrations (i.e., referred to as "total dose" in the figure) and sigmoidal values, than the high-elevation site (SH1; Figure 4-24d). The reverse was true for the sums of the concentrations ≥ 0.07 ppm and the number of hourly concentrations ≥ 0.07 ppm.

When the Big Meadows, Dickey Ridge, and Sawmill Run, Shenandoah National Park, data for 1983 to 1987 were compared, it again was found that the 7- and 12-h seasonal means were insensitive to the different O₃ exposure patterns. A better resolution of the differences was observed when the cumulative indices were used (Figure 4-25). There was no evidence that the highest elevation, Big Meadows, site consistently had experienced higher O₃ exposures than the other sites. In 2 of the 5 years, the highest elevation site experienced lower exposures than the Dickey Ridge and Sawmill Run sites, based on the sum of all concentration or sigmoidal indices. For 4 of the 5 years, the SUM07 index yielded the same result.

Taylor et al. (1992) indicate that the forests they monitored experienced differences in O₃ exposure. The principal spatial factors underlying this variation were elevation, proximity to anthropogenic sources of oxidant precursors, regional-scale meteorological conditions, and airshed dynamics between the lower free troposphere and the surface boundary layer. Table 4-16 summarizes the exposure values for the 10 EPRI Integrated Forest Study sites located in North America.

Table 4-15. Seasonal (April to October) Percentiles, SUM06, SUM08, and W126 Values for the Mountain Cloud Chemistry Program Sites^a

Site	Elev. (m)	Year	Min.	10	30	50	70	90	95	99	Max	No. Obs.	SUM06	SUM08	W126
Howland Forest, ME (HF1)	65	1987	0.000	0.013	0.021	0.028	0.035	0.046	0.052	0.065	0.076	4,766	5.9	0.0	7.7
		1988	0.000	0.012	0.021	0.028	0.036	0.047	0.054	0.076	0.106	4,786	10.9	2.9	11.6
Mt. Moosilauke, NH (MS1)	1,000	1987	0.006	0.027	0.036	0.045	0.053	0.065	0.074	0.086	0.102	4,077	45.0	9.5	40.1
		1988	0.010	0.026	0.033	0.043	0.055	0.076	0.087	0.113	0.127	2,835	51.9	21.2	43.4
Whiteface Mountain, NY (WF1) (36-031-0002)	1,483	1987	0.011	0.029	0.037	0.046	0.053	0.067	0.074	0.087	0.104	4,704	62.0	12.2	49.5
		1988	0.014	0.025	0.033	0.043	0.056	0.078	0.089	0.110	0.135	4,673	65.8	40.8	56.5
Whiteface Mountain, NY (WF3)	1,026	1987	0.010	0.025	0.033	0.039	0.047	0.064	0.075	0.091	0.117	4,755	45.4	14.4	40.3
Whiteface Mountain, NY (WF4)	604	1987	0.000	0.011	0.023	0.031	0.041	0.056	0.065	0.081	0.117	4,463	23.8	5.1	21.3
Mt. Mitchell, NC (MM1)	2,006	1987	0.008	0.034	0.044	0.051	0.058	0.067	0.074	0.085	0.105	3,539	59.4	7.8	46.5
		1988	0.011	0.038	0.054	0.065	0.075	0.095	0.106	0.126	0.145	2,989	145.1	69.7	116.6
		1989	0.010	0.038	0.047	0.054	0.059	0.068	0.072	0.081	0.147	2,788	54.8	3.5	40.7
		1992	0.005	0.036	0.043	0.048	0.053	0.063	0.069	0.081	0.096	3,971	37.8	4.4	36.7
Mt. Mitchell, NC (MM2)	1,760	1987	0.017	0.032	0.042	0.049	0.056	0.067	0.073	0.083	0.096	3,118	47.0	5.1	37.4
		1988	0.009	0.029	0.041	0.050	0.060	0.080	0.092	0.110	0.162	2,992	68.7	28.1	57.7
Shenandoah Park, VA (SH1)	1,015	1987	0.000	0.023	0.036	0.044	0.054	0.069	0.076	0.085	0.135	3,636	54.2	8.5	42.0
		1988	0.006	0.024	0.036	0.047	0.058	0.077	0.087	0.103	0.140	3,959	80.9	29.6	67.2
Shenandoah Park, VA (SH2)	716	1987 ^b	0.003	0.027	0.040	0.049	0.059	0.071	0.077	0.086	0.145	2,908	55.7	7.8	41.8
													55.8		
Shenandoah Park, VA (SH3)	524	1987	0.000	0.018	0.029	0.037	0.047	0.061	0.068	0.080	0.108	3,030	23.1	2.6	19.2
		1988	0.006	0.020	0.031	0.040	0.051	0.067	0.076	0.097	0.135	4,278	52.3	15.6	44.2
Whitetop Mountain, VA (WT1)	1,689	1987	0.011	0.038	0.051	0.059	0.066	0.078	0.085	0.096	0.111	4,326	147.7	32.4	105.7
		1988	0.000	0.030	0.046	0.058	0.068	0.084	0.094	0.119	0.163	3,788	133.8	51.0	102.8

^aSee Appendix A for abbreviations and acronyms.

^bCalculations based on a May to September season.

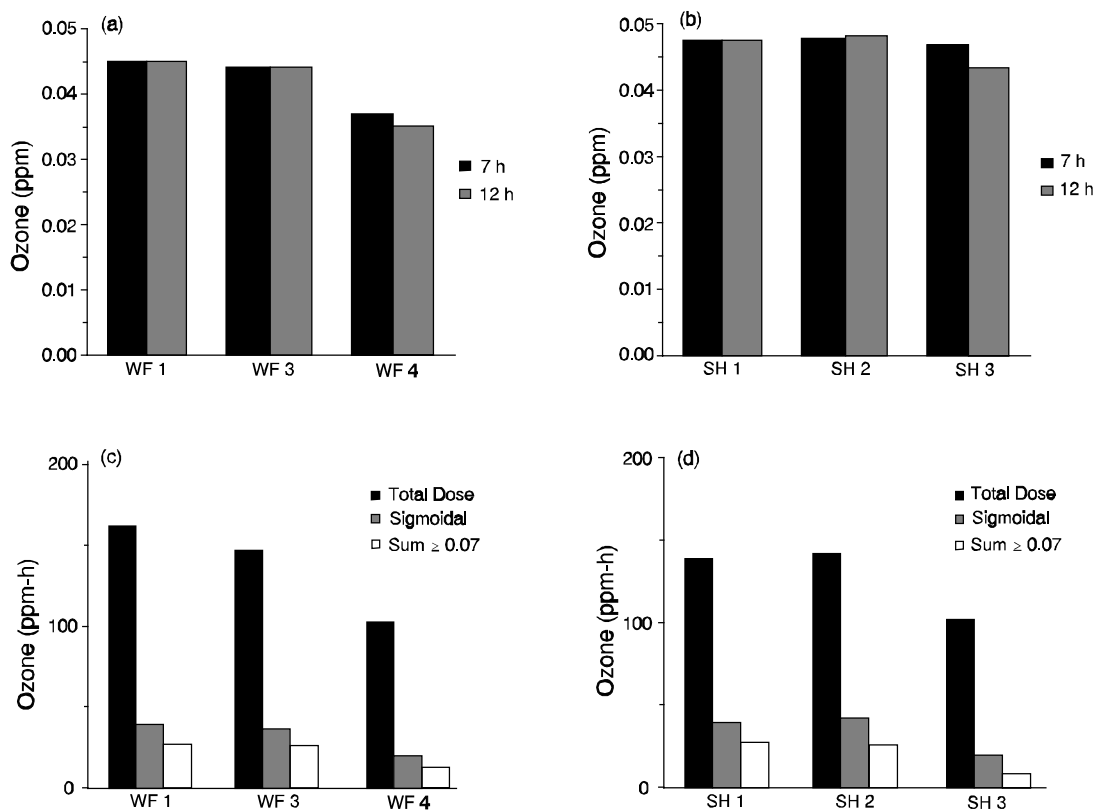


Figure 4-24. *Seven- and 12-h means at (a) Whiteface Mountain and (b) Shenandoah National Park for May to September 1987 and integrated exposures at (c) Whiteface Mountain and (d) Shenandoah National Park for May to September 1987.*

Source: Lefohn et al. (1990b).

4.6.3 Other Spatial Variations in Ozone Concentrations

Despite relative intraregional homogeneity, evidence exists for intracity variations in concentrations that are pertinent to potential exposures of human populations and to the assessment of actual exposures sustained in epidemiologic studies. Two illustrative pieces of data are presented in this section: (1) a case of relative homogeneity in a city with a population under 500,000 (New Haven, CT) and (2) a case of relative inhomogeneity of concentrations in a city of greater than 9 million population (New York City).

As described in the previous version of the criteria document (U.S. Environmental Protection Agency, 1986), the percentiles of the hourly average concentrations for a New Haven site and two other monitoring stations that were operating at the time in the same county, one in Derby, 9 mi west of New Haven, and one in Hamden, 6 mi north of New Haven, generally are similar. Table 4-17 shows the monitoring data and time of the maximum hourly concentrations by quarter at these three sites.

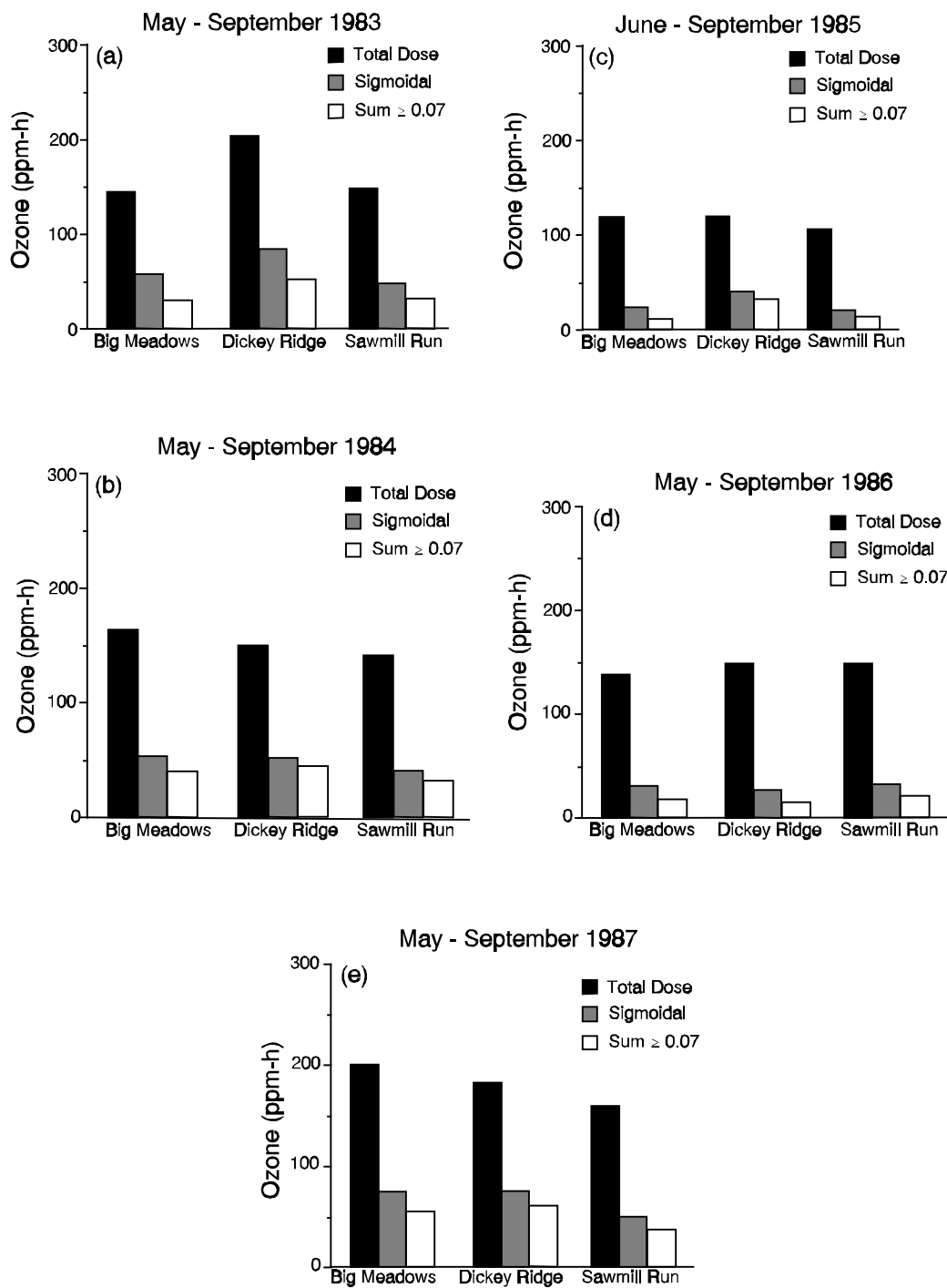


Figure 4-25. Integrated exposures for three non-Mountain Cloud Chemistry Program Shenandoah National Park sites, 1983 to 1987.

Source: Lefohn et al. (1990b).

Table 4-16. Summary Statistics for 11 Integrated Forest Study Sites^a

Site	Year	Quarter	24-h (ppb)	12-h (ppb)	7-h (ppb)	1-h Max (ppb)	SUM06 (ppm-h)	SUM08 (ppm-h)
HIGH ELEVATION SITES								
Whiteface Mountain, NY	1987	2	42	43	42	104	13.2	2.5
	1987	3	45	44	43	114	30.1	11.8
	1988	2	49	50	49	131	33.5	13.9
	1988	3	44	43	43	119	22.6	10.4
Great Smoky Mountain NP	1987	2	54	52	49	99	57.1	10.9
	1987	3	53	51	49	95	34.3	8.8
	1988	2	71	70	68	119	126.3	61.2
	1988	3	59	57	55	120	74.7	22.2
Coweeta Hydrologic Lab, NC	1987	2	50	48	47	85	32.4	2.6
	1987	3	47	44	42	95	24.1	2.4
	1988	2	61	59	59	104	81.6	18.5
	1988	3	57	54	51	100	63.6	19.8
LOW ELEVATION SITES								
Huntington Forest, NY	1987	2	36	42	42	88	9.8	0.9
	1987	3	24	32	33	76	5.4	0.2
	1988	2	40	46	46	106	19.2	6.1
	1988	3	37	46	48	91	18.6	2.7
Howland, MA	1987	2	34	39	39	69	1.9	0.0
	1987	3	26	32	31	76	3.8	0.0
	1988	2	36	41	41	90	8.1	2.9
	1988	3	24	30	30	71	1.7	0.0
Oak Ridge, TN	1987	2	42	53	50	112	39.5	13.5
	1987	3	29	44	41	105	24.3	9.0
	1988	2	40	57	58	104	26.4	9.8
	1988	3	32	47	51	122	19.7	7.7

Table 4-16 (cont'd). Summary Statistics for 11 Integrated Forest Study Sites^a

Site	Year	Quarter	24-h (ppb)	12-h (ppb)	7-h (ppb)	1-h Max (ppb)	SUM06 (ppm-h)	SUM08 (ppm-h)
LOW ELEVATION SITES (cont'd)								
Thompson Forest, WA	1987	2	36	43	41	103	10.7	3.6
	1987	3	30	36	34	94	10.3	2.1
	1988	2	32	39	37	103	8.1	2.3
	1988	3	32	39	36	140	13.5	6.7
B.F. Grant Forest, GA	1987	2	32	46	48	99	26.1	5.1
	1987	3	33	52	54	102	31.3	10.3
	1988	2	47	63	64	127	53.1	21.9
	1988	3	32	47	48	116	24.1	7.4
Gainesville, FL	1987	2	42	53	50	^b ^b	^b ^b	^b ^b
	1987	3	29	44	41	84	23.4	0.5
	1988	2	35	48	51	70	1.9	0.1
	1988	3	20	29	30			
Duke Forest, NC	1987	2	38	48	52	100	29.2 ^b	7.8 ^b
	1987	3	52	59	50	124	^b	^b
	1988	2	54	69	75	115	52.9	23.4
	1988	3	38	51	54	141		
Nordmoen, Norway	1987	2	32	40	41	75	2.4	0.0
	1987	3	14	18	20	32	0.0	0.0
	1988	2	22	28	29	53	0.0	0.0
	1988	3	11	15	16	30	0.0	0.0

^aSee Appendix A for abbreviations and acronyms.^bData were insufficient to calculate statistic.

Source: Adapted from Taylor et al. (1992).

**Table 4-17. Quarterly Maximum One-Hour Ozone Values at Sites in
and Around New Haven, Connecticut, 1976
(Chemiluminescence Method, Hourly Values in ppm)**

	Quarter of Year			
	1	2	3	4
New Haven, CT				
No. measurements	10	1,964	2,079	66
Max 1-h, ppm	0.045	0.274	0.235	0.066
Time of day	1100 hours	1400 hours	1400 hours	1000 hours
Date	March 29	June 24	August 12	October 3
Derby, CT				
No. measurements	11	2,140	2,187	1,360
Max 1-h, ppm	0.015	0.280	0.290	0.060
Time of day	2300 hours	1400 hours	1400 hours	1900 hours
Date	March 31	June 24	August 12	December 20
Hamden, CT				
No. measurements	56	2,065	1,446	286
Max 1-h, ppm	0.050	0.240	0.240	0.065
Time of day	2400 hours	1500 hours	1300 hours	1500 hours
Date	March 29	June 24	July 20	October 7

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

The source of much of the O₃ experienced in the New Haven area is the greater New York area (e.g., Wolff et al., 1975; Cleveland et al., 1976a,b). An urban plume transported over the distance from New York City to New Haven would tend to be relatively well-mixed and uniform, such that intracity variations in New Haven probably would be minimal.

As indicated in the previous version of the criteria document (U.S. Environmental Protection Agency, 1986), intracity differences in O₃ concentrations also have been reported by Kelly et al. (1986) for a 1981 study in Detroit, MI. Ozone concentrations were measured for about 3 mo at 16 sites in the metropolitan Detroit area and in nearby Ontario, Canada. Values at 15 sites were correlated with those at a site adjacent to the Detroit Science Center, about 3 km north of the central business district in Detroit. In general, the correlation decreased as distance from the Science Center site increased; and, in general, the actual concentrations increased with distance from that site toward the north-northeast. The highest O₃ concentrations were recorded at sites about 10 to 70 km north-northeast of the urban core. At greater distances or in other directions, O₃ maxima decreased.

Chicago is an example where O₃ concentrations increase as the distance from the inner city increases. Figure 4-26 shows, for a number of O₃ monitoring sites, the number of days in 1991 that the maximum hourly average concentration was greater than 0.1 ppm. The greatest number of exceedances of the daily maximum 1-h concentration of 0.1 ppm was to the north of the city.

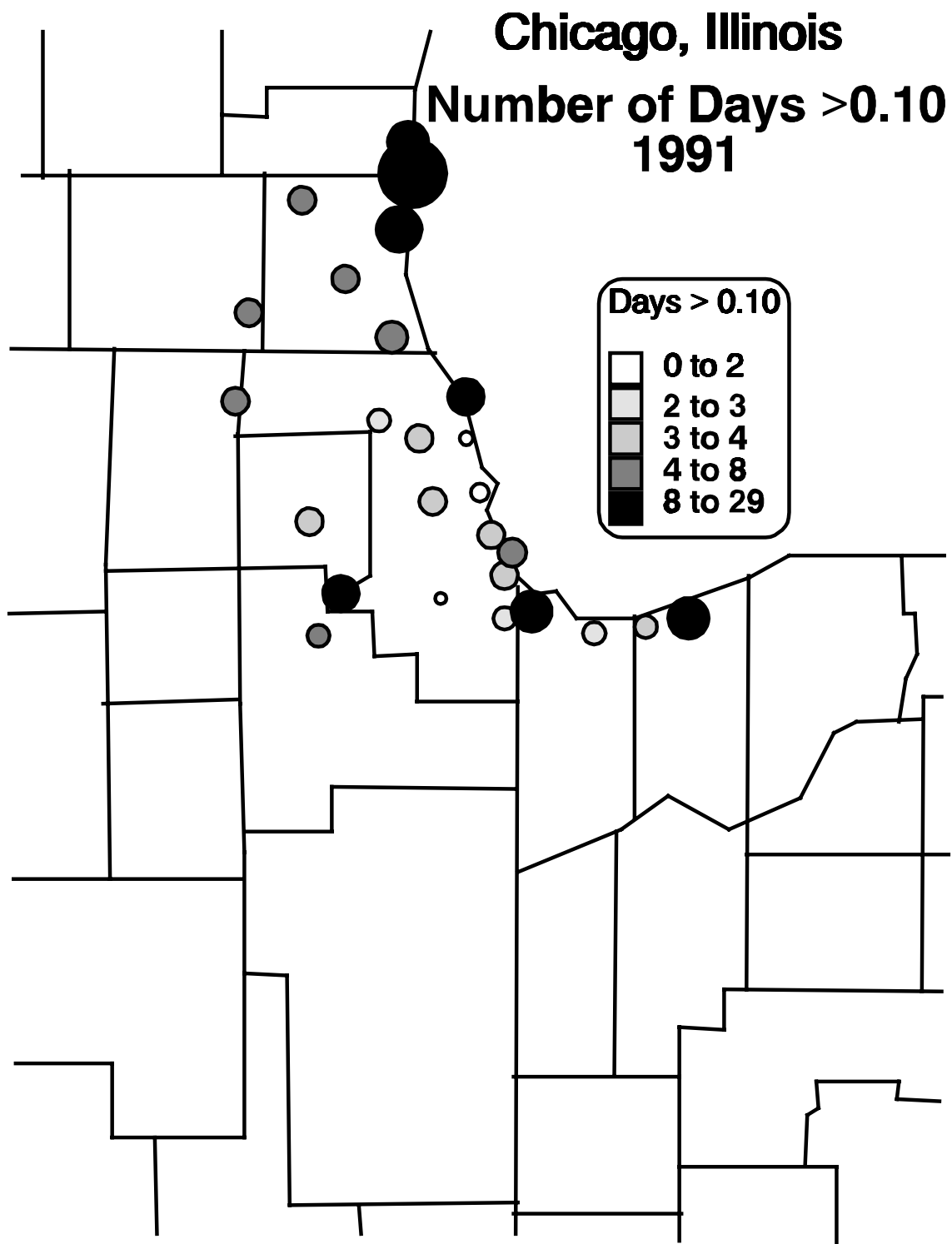


Figure 4-26. Number of days in 1991 for which the maximum hourly average ozone concentration was greater than 0.1 ppm at Chicago, IL.

Concentrations of O₃ vary with altitude and with latitude. Although a number of reports contain data on O₃ concentrations at high altitudes (e.g., Coffey et al., 1977; Reiter, 1977b; Singh et al., 1977; Evans et al., 1985; Lefohn and Jones, 1986), fewer reports are available that present data for different elevations in the same locality. There appears to be no consistent conclusion concerning the relationship between O₃ exposure and elevation.

Wolff et al. (1987) reported, for a short-term study at High Point Mountain in northwestern New Jersey, that both the daily maximum and midday O₃ concentrations were similar at different altitudes, but that the O₃ exposures increased with elevation. Wolff et al. (1987) conducted a study of the effects of altitude on O₃ concentrations at three sites located at three separate elevations on High Point Mountain in northwestern New Jersey. Data for several days indicate that in mid-July, when atmospheric mixing was good, vertical profiles were nearly constant, with concentrations increasing only slightly with elevation. Likewise, the daily O₃ maxima were similar at different elevations. At night, however, O₃ concentrations were nearly zero in the valley (i.e., the lowest-elevation site) and increased with elevation. Comparison of the O₃ exposures at the three sites (number of hours >0.08 ppm) showed that greater cumulative exposures were sustained at the higher elevations. Comparable data from an urban area (Bayonne) about 80 km southeast of High Point Mountain showed that the cumulative exposures were higher at all three of the mountain sites than in the urban area (Wolff et al., 1987). The investigators concluded from their concentration and meteorological data that elevated, mountainous sites in the eastern United States may be expected to be exposed to higher O₃ concentrations than valley sites throughout the year.

Winner et al. (1989) reported that, for three Shenandoah National Park sites (i.e., Big Meadows, Dickey Ridge, and Sawmill Run), the 24-h monthly mean O₃ concentrations tended to increase with elevation, but that the number of elevated hourly occurrences equal to or above selected thresholds did not. The authors reported that the highest elevation site (Big Meadows) experienced a smaller number of concentrations at or below the minimum detectable level than did the other two sites. The larger number of hourly average concentrations that occurred at or below the minimum detectable level at both Dickey Ridge and Sawmill Run resulted in lower 24-h averages at these sites.

Lefohn et al. (1990b), characterizing the O₃ exposures at several high-elevation sites, reported that, based on cumulative indices, the Whiteface Mountain summit site (WF1) experienced a slightly higher exposure than the lower elevation Whiteface Mountain (WF3) site. The site at the base of Whiteface Mountain (WF4) experienced the lowest exposure of the three O₃ sites. Among the MCCP Shenandoah National Park sites, the SH2 site experienced higher O₃ exposures than the high-elevation site (SH1). The "total dose" (correctly referred to as the sum of all hourly average concentrations) and sigmoidal (W126) indices were slightly higher at the SH2 than at the SH1 site. The data capture at the two sites for the 5-mo period was similar. However, the sum of the concentrations ≥0.07 ppm and the number of hourly concentrations ≥0.07 ppm were slightly higher at the SH1 than at the SH2 site. For the Whiteface Mountain sites, both the sum of the concentrations ≥0.07 ppm (SUM07) and the number of hourly concentrations ≥0.07 ppm were higher at the WF1 site than at the WF3 site.

When the Big Meadows, Dickey Ridge, and Sawmill Run, Shenandoah National Park, data for 1983 to 1987 were compared, a higher resolution of the differences among the regimes was observed when the cumulative indices were used. No specific trend could be identified that showed the highest elevation site, Big Meadows, had consistently experienced

higher O₃ exposures than the lower elevation sites. In 2 of the 5 years, the highest elevation site experienced lower exposures than the Dickey Ridge and Sawmill Run sites, based on the sum of all concentrations or sigmoidal indices. For 4 of the 5 years, the SUM07 index yielded the same result.

An important issue for assessing possible impacts of O₃ at high-elevation sites that requires further attention is the use of mixing ratios (e.g., parts per million) instead of absolute concentration (e.g., in units of micrograms per cubic meter) to describe O₃ concentration. In most cases, mixing ratios or mole fractions are used to describe O₃ concentrations. Lefohn et al. (1990b) have pointed out that the manner in which concentration is reported may be important when assessing the potential impacts of air pollution on high-elevation forests. Concentration varies as a function of altitude. Although the change in concentration is small when the elevational difference between sea level and the monitoring site is small, it becomes substantial at high-elevation sites. Given the same part-per-million value experienced at both a high- and low-elevation site, the absolute concentrations (i.e., micrograms per cubic meter) at the two elevations will be different. Because both O₃ and ambient air are gases, changes in pressure directly affect their volume. According to Boyle's law, if the temperature of a gas is held constant, the volume occupied by the gas varies inversely with the pressure (i.e., as pressure decreases, volume increases). This pressure effect must be considered when measuring absolute pollutant concentrations. At any given sampling location, normal atmospheric pressure variations have very little effect on air pollutant measurements. However, when mass/volume units of concentration are used and pollutant concentrations measured at significantly different altitudes are compared, pressure (and, hence, volume) adjustments are necessary. In practice, the summit site at Whiteface Mountain had a slightly higher O₃ exposure than the two low-elevation sites (Lefohn et al., 1991). However, at Shenandoah National Park sites, the higher elevation site experienced lower exposures than lower elevation sites in some years.

These exposure considerations are trivial at low-elevation sites. However, when one compares exposure-effects results obtained at high-elevation sites with those from low-elevation sites, the differences may become significant (Lefohn et al., 1990b). In particular, assuming that the sensitivity of the biological target is identical at both low and high elevations, some adjustment will be necessary when attempting to link experimental data obtained at low-elevation sites with air quality data monitored at the high-elevation stations.

4.7 Indoor Ozone Concentrations

Most people in the United States spend a large proportion of their time indoors. A knowledge of actual exposures of populations to indoor levels of O₃ is essential for the interpretation and use of results associated with epidemiological studies. However, essentially all routine air pollution monitoring is done on outdoor air. Until the early 1970s, very little was known about the O₃ concentrations experienced inside buildings. The ratio of the indoor/outdoor (I/O) O₃ concentrations is a parameter that has been widely used for studying the indoor and outdoor relationships, sources, and exposure patterns of O₃. However, the database on this subject is not large, and a wide range of I/O O₃ concentration relationships can be found in the literature. The only significant source of O₃ in indoor residential air is infiltration of outdoor O₃, with ventilation rates affecting the flow of air between indoor and outdoor (Zhang and Liou, 1994).

Reported I/O values for O_3 are highly variable (U.S. Environmental Protection Agency, 1986) and range from <0.1 to 0.8 for various indoor environments and ventilation rates (Weschler et al., 1989). Unfortunately, the number of experiments and kinds of structures examined to date provide only limited data for use in modeling indoor exposures. Data were summarized by Yocom (1982) describing studies of indoor-outdoor gradients in buildings and residences for either O_3 or photochemical oxidant. The results were highly variable. A relatively large number of factors can affect the difference in O_3 concentrations between the inside of a structure and the outside air. In general, outside air infiltration or exchange rates, interior air circulation rates, and interior surface composition (e.g., rugs, draperies, furniture, walls) affect the balance between replenishment and decomposition of O_3 within buildings (U.S. Environmental Protection Agency, 1986). Although indoor concentrations of O_3 will almost invariably be less than outdoors, the fact that people spend more time indoors than outdoors may result in greater overall indoor exposures.

Cass et al. (1991) have discussed the importance of protecting works of art from damage due to O_3 . Experiments show that the fading of artists' pigments in the presence of O_3 is directly related to the product of concentration times duration of exposure. Druzik et al. (1990) reported that, in a survey of 11 museums, galleries, historical houses, and libraries in Southern California, facilities with a high air exchange with the outdoors and no pollutant removal system have indoor O_3 concentrations more than two-thirds those of outdoor concentrations. The author reported that museums with conventional air-conditioning systems showed indoor O_3 concentrations about 30 to 40% of those outside, whereas museums with no forced ventilation system, where slow air infiltration provides the only means of air exchange, have indoor O_3 levels typically 10 to 20% of those outdoors. Several other studies have been reported in the literature and Table 4-18 lists the I/O ratios reported from these efforts as well as those from earlier years.

Automobiles and other vehicles constitute another indoor environment in which people may spend appreciable amounts of time. As with buildings, the mode of ventilation and cooling helps determine the inside concentrations. The U.S. Environmental Protection Agency (1986) describes studies for the I/O ratios. In one study reported by Contant et al. (1985), the I/O ratios from 49 measurements inside vehicles were 0.44 for the mean, 0.33 for the median, and 0.56 for maximum concentrations measured. Chan et al. (1991) reported an I/O ratio of 0.20 for median in-vehicle concentrations (0.011 ppm) and time-matched fixed-site measurements (0.051 ppm).

At present, there are no long-term monitoring data on indoor air pollutant concentrations comparable to the concentration data available for outdoor locations. Thus, for estimates of the exposure of building or vehicle occupants to O_3 and other photochemical oxidants, it is necessary to rely on extrapolations of very limited I/O data.

4.8 Estimating Exposure to Ozone

4.8.1 Introduction

Human exposure represents the joint occurrence of an individual being located at point (x,y,z) during time t , with the simultaneous presence of an air pollutant at concentration $C_{x,y,z}(t)$ (U.S. Environmental Protection Agency, 1991). Consequently, an individual's exposure to an air pollutant is a function of location as well as time. If a volume at a location can be defined such that air pollutant concentrations within it are homogeneous yet

Table 4-18. Summary of Reported Indoor-Outdoor Ozone Ratios

Structure	Indoor-Outdoor Ratio	Reference
Hospital	0.67 ^a	Thompson (1971)
Residence (with evaporative cooler)	0.60 ^a	Thompson et al. (1973)
Office (air-conditioned; 100% outside air intake)	0.80 ± 0.10	Sabersky et al. (1973)
(air-conditioned; 70% outside air intake)	0.65 ± 0.10	Sabersky et al. (1973)
Office	0.66 0.54	Shair and Heitner (1974) Shair and Heitner (1974)
Office/Lab	0.62	Hales et al. (1974)
Residence	0.70	Sabersky et al. (1973)
Residence	0.50-0.70	Moschandreas et al. (1978)
Two offices	0.30	Moschandreas et al. (1978)
Residence (gas stoves)	0.19	Moschandreas et al. (1981)
(all electric)	0.20	
Office	0.29	Moschandreas et al. (1978)
School room	0.19 (max concentration)	Berk et al. (1980)
Residence	0.10-0.25	Berk et al. (1981)
Residences (1 each) (air-conditioned)	0.00-0.09	Stock et al. (1983)
(100% outside air; no air-conditioning)	1.00	
Residences (12) (air-conditioned)	0.21 (mean concentration) 0.12 (med. concentration) 0.59 (max concentration)	Contant et al. (1985)
Residences (41)	0.30	Lebowitz et al. (1984)
Residences (6) (window open)	0.59 ± 0.16	Zhang and Liou (1994)
(window closed)	0.26 ± 0.12	
(air-conditioning)	0.28 ± 0.12	
Art gallery	0.50	Shaver et al. (1983)
Art gallery (three modes of ventilation in each 24-h period: recirculation, mixture of recirculated and outside air, and 100% outside air)	0.70 ± 0.10 (mean concentration)	Davies et al. (1984)
Museums	<0.10	Shaver et al. (1983)

Table 4-18 (cont'd). Summary of Reported Indoor-Outdoor Ozone Ratios

Structure	Indoor-Outdoor Ratio	Reference
Museum	0.45	Nazaroff and Cass (1986)
Museums		Druzik et al. (1990)
(with high air exchange, but no air-conditioning)	0.69-0.84 (1 h) 0.50-0.87 (8 h)	
(with no air-conditioning and with low air exchange rate)	0.10-0.59 (1 h) 0.10-0.58 (8 h)	
(with natural convection-induced air-exchange system)	0.33-0.49 (1 h) 0.28-0.40 (8 h)	
(with conventional air-conditioning system but with no activated carbon air filtration)	0.24-0.40 (1 h) 0.25-0.41 (8 h)	
(with activated carbon air-filtration system)	0.03-0.37 (1 h) 0.03-0.31 (8 h)	

^aMeasured as total oxidants.

potentially different from other locations, the volume may be considered a "microenvironment" (Duan, 1982). Microenvironments may be aggregated by location (i.e., indoor or outdoor) or activity performed at a location (i.e., residential, commercial) to form microenvironment types. Also, activity has two major dimensions: location and exertion. Various microenvironments can have different levels of ventilation that will significantly influence the delivered dose.

Air Quality Criteria for Carbon Monoxide (U.S. Environmental Protection Agency, 1991) discusses the difference between individual and population exposures. The document notes that Sexton and Ryan (1988) define the pollutant concentrations experienced by a specific individual during normal daily activities as "personal" or "individual" exposures. A personal exposure depends on the air pollutant concentrations that are present in the location through which the person moves, as well as on the time spent at each location. Because time-activity patterns can vary substantially from person to person, individual exposures exhibit wide variability (U.S. Environmental Protection Agency, 1991). Thus, although it is a relatively straightforward procedure to measure any one person's exposure, many such measurements may be needed to quantify exposures for a defined group. The daily activities of a person in time and space define the individual's activity pattern. Accurate estimates of air pollution exposure generally require that an exposure model account for the activity patterns of the population of interest.

From a public health perspective, it is important to determine the "population exposure", which is the aggregate exposure for a specified group of people (e.g., a community or an identified occupational cohort). Because exposures are likely to vary substantially between individuals, specification of the distribution of personal exposures within a

population, including the average value and the associated variance, is often the focus of exposure assessment studies.

In many cases, the upper tail of the distribution, which represents those individuals exposed to the highest concentrations, is frequently of special interest because the determination of the number of individuals who experience elevated pollutant levels can be critical for health risk assessments. This is especially true for pollutants for which the relationship between dose and response is highly nonlinear. Runeckles and Bates (1991) have pointed out the importance of peak concentrations in eliciting adverse human effects. As indicated in Section 4.1, results using controlled human exposures have shown the possible importance of concentration in relation to duration of exposure and inhalation rate. The implication of the importance of concentration can be translated into the conclusion that the simple definition of exposure (i.e., equal to concentration multiplied by time) may be too simplified.

Several human exposure models have been developed for most cases, because it is not possible to estimate population exposure solely from fixed-station data. Some of these models include information on human activity patterns (i.e., the microenvironments people visit and the time they spend there). These models also contain submodels depicting the sources and concentrations likely to be found in each microenvironment, including indoor, outdoor, and in-transit settings.

4.8.2 Fixed-Site Monitoring Information Used To Estimate Population and

Vegetation Exposure

Based on the information provided in earlier sections in this chapter, fixed-site monitors alone cannot accurately depict population exposures for most cases, because indoor and in-transit concentrations of O_3 may be significantly different from ambient O_3 concentrations, and ambient outdoor concentrations of O_3 that people come in contact with may vary significantly from O_3 concentrations measured at fixed-site monitors. Fixed-site monitors measure concentrations of pollutants in ambient air. Ambient air as noted by the U.S. Environmental Protection Agency (1991) is defined in the *U.S. Code of Federal Regulations* (1991) as air that is "external to buildings, to which the general public has access." But the nature of modern urban lifestyles in many countries, including the United States, is that people spend an average of over 20 h per day indoors (Meyer, 1983). Reviews of studies summarized in Section 4.7 show that indoor O_3 concentration measurements vary significantly from simultaneous measurements in ambient air. The difference between indoor and outdoor air quality and the amount of time people spend indoors reinforce the conclusion that using ambient air quality measurements alone does not provide accurate estimates of population exposure in most cases.

It is assumed that exposure for vegetation is the same as the concentration information provided at fixed monitors in the field (see Sections 5.5 and 5.6). In some cases, because of foliar scavenging and height differences between the vegetation canopy and the pollutant monitor, the measured concentration is not equivalent to the vegetation exposure.

A subgroup, children attending summer camp, has been studied by several investigators to evaluate the influence of ambient air pollution on respiratory health and function. Because children are predominantly outdoors and relatively active while at camp, they provide a unique opportunity to examine the relationships between respiratory health and

function and concurrent air pollution levels. Children may be at potentially increased risk from air pollution by virtue of their lifestyle patterns, which often involve several hours of outdoor exercise, regardless of air quality, during daylight hours.

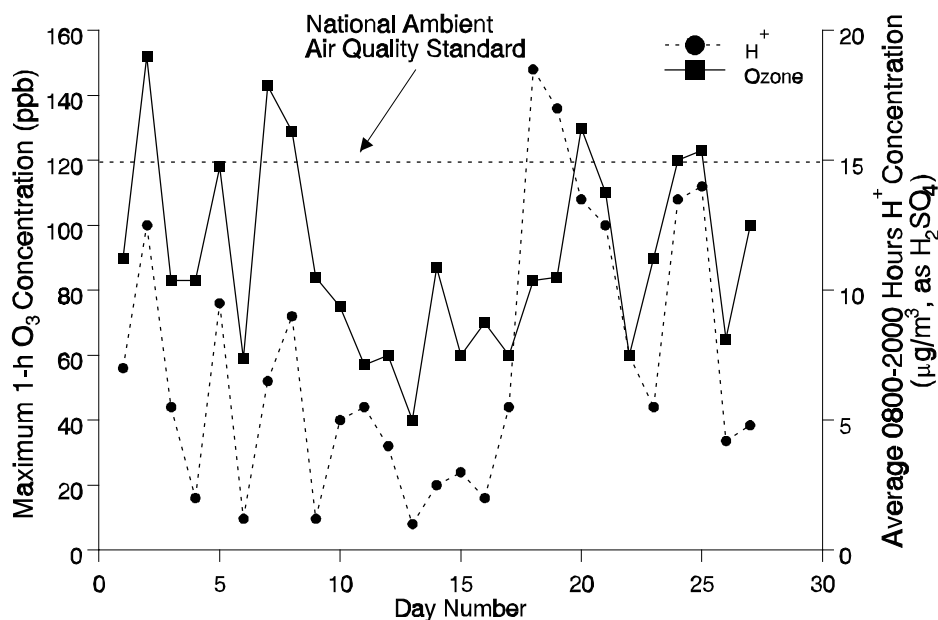
For campers, attempts have been made to estimate human exposure to O₃ using types of activity patterns (Mage et al., 1985; Paul et al., 1987). Mage et al. (1985) developed an objective approach to estimate the dose delivered to the lung of a 12-year-old camper by using pulmonary minute volume associated with a specific activity, the fractional penetration beyond the trachea, and infiltration of ozone indoors. Lioy and Dyba (1989) have applied the parameters used by Mage et al. (1985) to predict the delivered O₃ dose over a 4-day episodic period. The schedule of a hypothetical camper was matched to the actual O₃ concentrations, and the predicted doses were estimated.

Several studies involving children attending summer camp have been summarized in Chapter 7. In one study, Avol et al. (1990) reported that O₃ levels at a Southern California summer camp, located 190 km southeast of Los Angeles, CA, rose gradually throughout each day, displaying a "broad peak" between 1000 and 2000 hours each day. Daily maxima typically occurred in late afternoon (1500 to 1700 hours); subsequently, concentrations gradually declined to overnight O₃ levels of 0.025 to 0.050 ppm. Spektor et al. (1991) investigated the pulmonary function of 46 healthy children on at least 7 days for each child during a 4-week period at a northwestern New Jersey residential summer camp in 1988. The daily levels of 1-h peak O₃ and the 12-h average hydrogen ion (H⁺) concentrations are shown in Figure 4-27. On 5 of these days, the current NAAQS of 0.12 ppm was exceeded. The maximum hourly concentration attained during the study was 0.15 ppm. The year 1984 was a milder O₃ exposure year and Figure 4-28 summarizes the maximal 1-h O₃ concentrations at Fairview Lake during a 1984 study period (Spektor et al., 1988).

4.8.3 Personal Monitors

A personal exposure profile can be identified by using a personal exposure monitor. McCurdy (1994) has described the development of personal exposure monitors by several companies. However, few data are available describing personal exposures for individuals using these monitors. An example of a pilot study using a personal exposure monitor was described for assessing O₃ exposure in 23 children by Liu et al. (1993). The accuracy of the monitor was within 20% of the actual value. The authors collected indoor, outdoor, and personal O₃ concentration data as well as time-activity data in State College, PA. Results from the pilot study demonstrated that fixed-site ambient measurements may not adequately represent individual exposures. Outdoor O₃ concentrations showed substantial spatial variation between rural and residential regions. In addition, Liu et al. (1993) reported that models based on time-weighted indoor and outdoor concentrations explained only 40% of the variability in personal exposures. When the model used included observations for only those participants who spent the majority of their day in or near their homes, an R² of 0.76 resulted when estimates were regressed on measured personal exposures. The authors concluded that contributions from diverse indoor and outdoor microenvironments should be considered to estimate personal O₃ exposure accurately. From these results, it is clear that additional data are needed to better quantify the O₃ exposures to which populations are exposed.

Figure 4-27. *Maximum 1-h ozone (O₃) concentrations (in parts per billion) and average 0800 to 2000 hours strong acid concentrations (expressed as micrograms per*



cubic meter of sulfuric acid [H₂SO₄] for each day that pulmonary function data were collected at Fairview Lake camp in 1988. The correlation coefficient between O₃ and the hydrogen ion (H⁺) was 0.56.

Source: Spektor et al. (1991).

4.8.4 Population Exposure Models

McCurdy (1994) has reviewed the current status of human exposure modeling. The author describes two distinct types of O₃ exposure models: (1) those that focus narrowly on predicting indoor O₃ levels and (2) those that focus on predicting O₃ exposures on a community-wide basis. The models that predict indoor O₃ levels have been described by Sabersky et al. (1973), Shair and Heitner (1974), Nazaroff and Cass (1986), and Hayes (1989, 1991). McCurdy (1994) discusses four distinct models that predict O₃ exposure on a community-wide basis. These models and their distinguishing features are:

1. pNEM/O₃ based on the National Air Quality Standards Exposure Model (NEM) series of models (Paul et al., 1987; Johnson et al., 1990; McCurdy et al., 1991).
 - Uses mass-balance approach and seasonal considerations for I/O ratio estimation.
 - Variables affecting indoor exposure obtained by Monte Carlo sampling from empirical distributions of measured data.

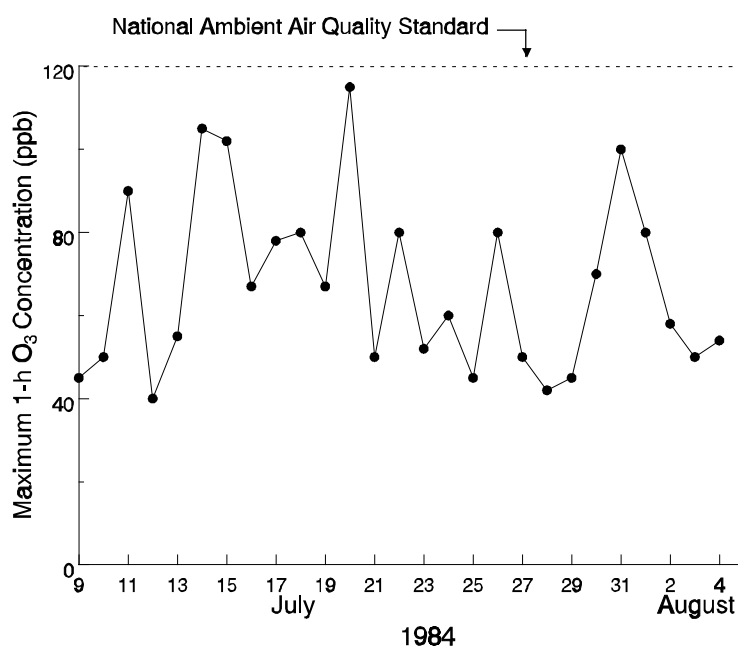


Figure 4-28. Maximal 1-h ozone concentrations at Fairview Lake during the study period.

Source: Spektor et al. (1988).

2. Systems Applications International (SAI)/NEM (Hayes et al., 1984; Hayes and Lundberg, 1985; Austin et al., 1986; Hayes et al., 1988; Hayes and Rosenbaum, 1988).
 - More districts and microenvironments and more detailed mass-balance model than pNEM/O₃.
 - Human activity data outdated and inflexible.
3. Regional Human Exposure Model (REHEX) (Lurmann and Colome, 1991; Winer et al., 1989; Lurmann et al., 1989; Lurmann et al., 1990).
 - More detailed geographic resolution than NEM.
 - Uses California-specific activity data and emphasizes in-transit and outdoor microenvironments.
4. Event probability exposure model (EPEM) (Johnson et al., 1992).
 - Estimates probability that a randomly selected person will experience a particular exposure regime.
 - Lacks multiday continuity.

McCurdy (1994) points out that all four models are related to the NEM. The NEM is an EPA exposure model developed in the 1980s (Biller et al., 1981). Outdoor air quality data are obtained from monitoring or modeling data. In most applications of NEM, fixed-site monitoring data are used. The hourly average values are transformed by a suitable relationship so that they better represent air quality outside of the various microenvironments of interest. McCurdy (1994) points out that the important point of the NEM spatial dimension is that people can be assigned to a monitor using U.S. census data. In addition,

community trips can be assigned among the districts, grid cells, or neighborhood types using census data. Thus, the NEM model simulates the movement of people through space for work-trip purposes. Interested readers are referred to McCurdy (1994) for further discussion of the pNEM model.

4.8.5 Concentration and Exposures Used in Research Experiments

It is important to adequately characterize the exposure patterns that result in vegetation and human health effects. Hourly average concentrations used in many of the high treatment experimental studies did not necessarily mimic those concentrations observed under ambient conditions. Although the ramifications of this observation on the effects observed are not clear, it was pointed out that the highest treatments used in many of the open-top chamber experiments were bimodal in the distribution of the hourly average concentrations. In other experiments designed to assess the effects of O₃ on vegetation, constant concentration (i.e., square wave) exposures were implemented. As has been discussed in earlier sections of this chapter, hourly average concentrations change by the hour and square wave exposure regimes do not normally occur under ambient conditions. In addition to the exposures used at the highest treatment levels, there is concern that the hourly average concentrations used in the control treatments may be lower than those experienced at isolated sites in the United States or in other parts of the world. Although the ramifications of using such exposure regimes are unclear, there is some concern that the use of atypically low control levels may result in an overestimation of vegetation yield losses when used as the baseline for evaluating the effects of treatments at higher concentrations (Lefohn and Foley, 1992).

For assessing the human health effects of O₃ exposure, a series of studies has explored prolonged 6.6-h O₃ exposures at low levels (i.e., 0.08 to 0.12 ppm) (Horstman et al., 1990). McDonnell et al. (1991), using similar hourly average concentration regimes, have confirmed the findings reported by Horstman et al. (1990). All the research investigations using 6.6-h durations have applied constant concentrations during the exposure period. If, as indicated in the introduction of this chapter, concentration is more important than duration and ventilation rate, different human health effects may occur as a result of different exposure regimes that have identical 6.6-h average concentrations. Because of this, it is important to explore the different types of exposure regimes that occur under ambient conditions during an 8-h episode.

Lefohn and Foley (1993) reported on an analysis of hourly average data for O₃ monitoring sites that never experienced an exceedance of an hourly average concentration ≥ 0.12 ppm and that experienced 8-h daily maximum average concentrations >0.08 ppm. For those monitoring sites that met the above two criteria, they identified the number of times the 8-h daily maximum average concentration exceeded 0.08 ppm during the monitoring year. For the period 1987 to 1989, there were 925 exposure regimes identified from 166 site-years of data that met the above criteria. The data were then organized into the following seven categories:

- I. The occurrence of 8-h daily maximum averages >0.08 ppm and <0.09 ppm;
- II. The occurrence of 8-h daily maximum averages >0.08 ppm but ≤ 0.082 ppm, which contained only hourly average concentrations >0.08 ppm but ≥ 0.082 ppm;
- III. 8-h daily maximum averages >0.08 ppm, which contained hourly average concentrations <0.09 ppm;

- IV. 8-h daily maximum averages >0.08 ppm and <0.09 ppm, which contained at least one hourly average concentration ≥ 0.09 ppm but <0.10 ppm;
- V. 8-h daily maximum averages >0.08 ppm and <0.09 ppm, which contained at least one hourly average concentration ≥ 0.10 ppm;
- VI. 8-h daily maximum averages <0.08 ppm, which contained at least one hourly average concentration ≥ 0.09 ppm but <0.10 ppm; and
- VII. 8-h daily maximum averages <0.08 ppm, which contained at least one hourly average concentration ≥ 0.10 ppm.

Figure 4-29 summarizes the results of the analysis. The results indicated that there was a poor relationship between the value of the 8-h daily maximum average concentration and the frequency of occurrence of hourly average concentrations within specific ranges (e.g., between 0.09 and 0.10 ppm). In no case could the authors identify a monitoring site that experienced the square-wave type of exposure that was described in Category II (i.e., the occurrence of 8-h daily maximum averages >0.08 ppm but ≤ 0.082 ppm). Lefohn and Foley (1993) concluded that the square wave exposures used in the 6.6-h human health effects experiments were not found under ambient conditions. The authors identified 453 additional exposure regimes, where the 8-h daily maximum average was <0.08 ppm but experienced maximum hourly average concentrations ≥ 0.09 ppm. Thus, if hourly average concentrations ≥ 0.08 ppm are of concern for affecting human health, there will be instances where occurrences above this threshold are evident, but the 8-h average value is below 0.08 ppm.

4.9 Concentrations of Peroxyacetyl Nitrates in Ambient Atmospheres

4.9.1 Introduction

The biological effects of PAN in human exposures, toxicological studies of animals, and plant response and yield have been considered previously (U.S. Environmental Protection Agency, 1986). Controlled human exposure studies involving O_3 and $O_3 + PAN$ are discussed elsewhere in this document (Chapter 7, Section 7.2.6.3). Some effects on respiratory parameters have been reported in one study, but not in others. However, the PAN concentrations used in these studies have been well above the maximum ambient concentrations usually experienced many years ago within the Los Angeles Basin (U.S. Environmental Protection Agency, 1986) and, more importantly, above the maximum ambient concentrations in the more recent measurements considered in this section.

The PANs are of importance as reservoirs for NO_2 as NO_x is depleted relative to VOCs in plumes moving downwind into less polluted areas (Chapter 3, Section 3.2.4). In performance evaluation of ozone air quality models, measured concentrations of PANs are useful in model evaluation (Chapter 3, Section 3.6.4.2).

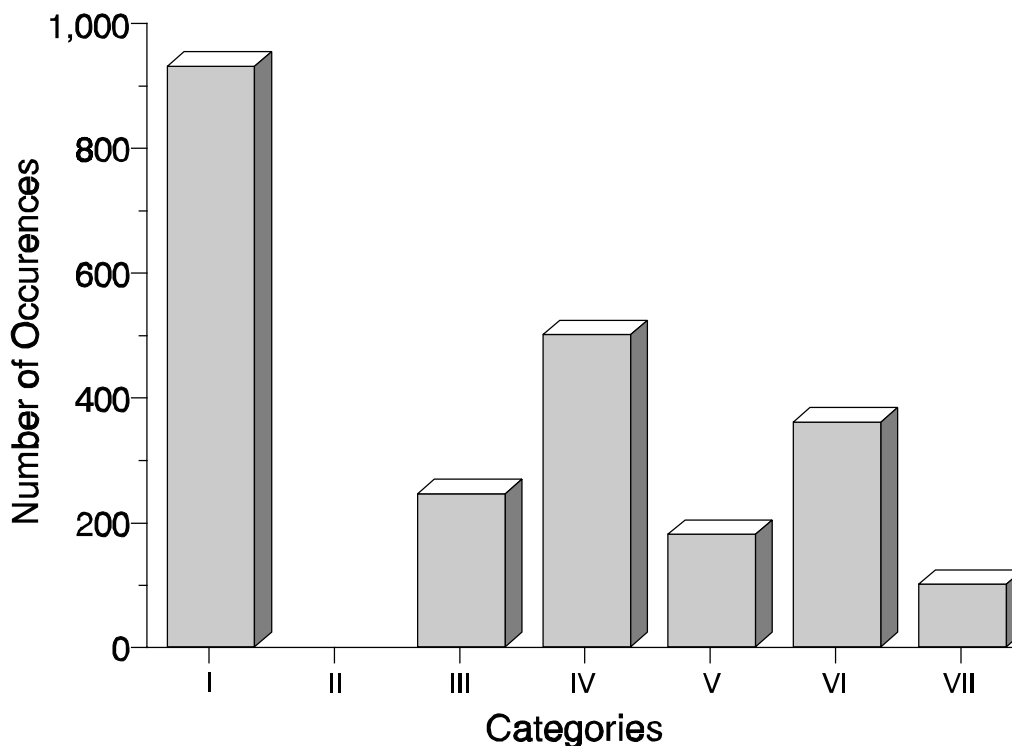


Figure 4-29. *The number of occurrences for each of the seven categories described in text.*

In the previous air quality criteria for O₃ and other photochemical oxidants (U.S. Environmental Protection Agency, 1986), extensive tabulations of PAN and peroxypropionyl nitrate (PPN, CH₃CH₂C(O)OONO₂) concentrations were given based on measurements made between 1965 and 1981 from references up to 1983. In the present work, references from 1983 to the present are used for measurements of PANs in urban and rural locations. The urban area measurements are from the United States, Canada, France, Greece, and Brazil. The use of measurements from abroad serve to illustrate or support certain U.S. results as well as to demonstrate the widespread presence of PANs in the atmosphere. These PAN measurements usually were of limited duration, and the results should not be assumed to be comparable to those obtained at the O₃ monitoring sites discussed earlier in this chapter (see also Section 4.10).

4.9.2 Urban Area Peroxyacetyl Nitrate Concentrations

For urban sites, the prior criteria document for ozone and other photochemical oxidants contains a number of tables tabulating measurements of PAN, PPN, and PPN to PAN and PAN to O₃ ratios (Altshuller, 1983; U.S. Environmental Protection Agency, 1986). Based on comparisons of PAN measurements in Los Angeles in 1980 with those made in the 1960s, it was uncertain whether PAN concentrations had decreased. In the Los Angeles area, the average and maximum PAN concentrations reported ranged from 1.6 to 31 ppb and from 6 to 214 ppb, respectively. The wide variations, at least in part, were associated with the range of years, different seasons, and differing average times among studies. On average, the

PPN to PAN ratios among studies in Los Angeles ranged from 0.15 to 0.20, whereas the PAN to O₃ ratios among studies ranged from 0.04 to 0.20. In the earlier PAN measurement results, studies conducted in the South Coast Air Basin predominated.

The average PAN concentrations measured in other cities usually were lower than in the Los Angeles area, whereas the maximum PAN concentrations overlapped with the lower end of range in Los Angeles. The PPN and PAN ratios in other cities ranged from 0.1 to 0.4, whereas the PAN to O₃ ratios were in the 0.01 to 0.05 range.

Seasonally, PAN to O₃ ratios tended to be somewhat higher in the winter. The diurnal characteristics of O₃ and of PAN were similar, but not identical.

The urban area measurement results are tabulated in Table 4-19. The earlier maximum PAN concentrations reported usually were substantially higher than those given in Table 4-19. A possible exception occurs for the Claremont, CA, results. Measurements of PAN and PPN were made in 1989 and 1990 at sites downwind of Los Angeles: Perrin, 90 km to the east-southeast, and Palm Springs, 120 km to the east (Grosjean and Williams, 1992). The concentrations of PAN and PPN were high, and the concentration maxima occurred during the evening hours, which was consistent with downwind transport from the Los Angeles area rather than from local sources.

In Southern California, the maximum PAN concentrations appear to be more evenly distributed spatially during the fall than during the summer (Williams and Grosjean, 1990). At coastal and central locations, the PAN maxima during the fall were comparable to those observed at inland locations during the summer.

As observed previously, PAN concentrations in other U.S. cities and in cities in other countries tend to be substantially lower than in Los Angeles and its surrounding urban areas (Table 4-19). An exception occurs for the measurements from Paris (Tsalkani et al., 1991). Maximum PAN concentrations in the 20 to 35 ppb range were observed.

In measurements made in 1992 in Atlanta, GA, at the Georgia Institute of Technology campus site, not only were PAN and PPN measured, but very occasionally peroxyacetylnitrate (MPAN, CH₂=C(CH₃)C(O)OONO₂) (a product of the atmospheric photooxidation of local biogenic sources of isoprene) was observed (Williams et al., 1993). Maximum diurnal concentrations of peroxyacyl nitrates and O₃ occur in late afternoon and early evening. The average MPAN concentration was 0.3 ppb, and the maximum value was 0.5 ppb and constituted about 15% of the concurrent PAN concentrations.

In a study in Rio de Janeiro performed to investigate the effects of the use of ethanol or ethanol-containing fuel on PAN concentrations, the maximum PAN concentration reached 5.4 ppb (Tanner et al., 1988). However, this maximum concentration is well below the maximum concentrations reported in and around Los Angeles, and it falls within the maximum PAN values reported for a number of other cities (Table 4-19).

4.9.3 Concentration of Peroxyacetyl Nitrate and Peroxypropionyl Nitrate in Rural Areas

Prior measurements of nonurban PAN and PPN concentrations and PAN to O₃ ratios are available (Altshuller, 1983; U.S. Environmental Protection Agency, 1986). At nonurban sites that are not impacted by urban plumes, PAN and PPN concentrations are

**Table 4-19. Summary of Measurements of Peroxyacetyl Nitrate
and Peroxypropionyl Nitrate in Urban Areas^a**

Site	Month/ Year	Number of Days Sampled	PAN Concentration (ppb)		PPN Concentration (ppb)		Reference
			Average/Mean	Max	Average/Mean	Max	
Long Beach, CA	6-12/1987	16	NA	16	NA	NA	Williams and Grosjean (1990)
Anaheim, CA	6-12/1987	14	NA	19	NA	NA	Williams and Grosjean (1990)
Los Angeles, CA	6-12/1987	16	NA	13	NA	NA	Williams and Grosjean (1990)
Burbank, CA	6-12/1987	16	NA	19	NA	NA	Williams and Grosjean (1990)
Azusa, CA	6-9/1987	11	NA	13	NA	NA	Williams and Grosjean (1990)
Claremont, CA	6-9/1987	10	NA	30	NA	NA	Williams and Grosjean (1990)
Perrin, CA	6/1989 to 6/1990	NA	1.6	9.1	NA	0.73	Grosjean and Williams (1992)
Palm Springs, CA	6/1989 to 6/1990	NA	1.6	7.6	NA	0.42	Grosjean and Williams (1992)
Downey, CA	2/1984	10	1.2	6.7	0.06	0.40	Singh and Salas (1989)
Boulder, CO	5, 6 and 8, 9/1987	12 45	0.63 0.59	2.0 3.8	0.08 0.07	0.3 0.6	Ridley et al. (1990)
Denver, CO	3/1984	9	0.64	2.0	0.02	0.09	Singh and Salas (1989)
Houston, TX	3/1984	9	0.75	7.9	0.045	0.54	Singh and Salas (1989)
Philadelphia, PA	4/1983	19	1.1	3.7	0.14	0.50	Singh and Salas (1989)
Staten Island, NY	4/1983	7	1.6	5.5	0.21	0.90	Singh and Salas (1989)
Atlanta, GA	7, 8/1992	36	0.71	2.9	0.14	0.37	Williams et al. (1993)
Edmonton, Alberta, Canada	12/1983 to 4/1984	66		7.5	NA	NA	Peake et al. (1988)
Calgary, Alberta, Canada	7/1981 to 2/1982	213	0.14	6.6	NA	NA	Peake and Sandhu (1983)
University of Calgary, Alberta, Canada	10/1980 to 8/1981	175	0.22	2.4	NA	NA	Peake and Sandhu (1983)
Simcoe, Ontario, Canada	6/1980 to 3/1981	191	1.3	5.6	NA	NA	Corkum et al. (1986)

**Table 4-19 (cont'd). Summary of Measurements of Peroxyacetyl Nitrate
and Peroxypropionyl Nitrate in Urban Areas^a**

Site	Month/ Year	Number of Days Sampled	PAN	Max	PPN	Max	Reference
			Concentration (ppb) Average/Mean		Concentration (ppb) Average/Mean		
Rio de Janeiro							
Vila Isabel	7/1985	8	NA	5.4	NA	1.0	Tanner et al. (1988)
PUC/RJ	7/1985	4	NA	3.3	NA	0.6	Tanner et al. (1988)
Athens, Greece	2-11/1985	113	NA	3.7	NA	NA	Tsani-Bazaca et al. (1988)
Paris, France	11/1985 to 11/1986	NA	1.1	20.5	NA	NA	Tsalkani et al. (1991)

^aSee Appendix A for abbreviations and acronyms.

much lower than those in urban areas. Average PAN concentrations ranged between 0.1 and 1.0 ppb, whereas the PAN to O₃ ratios were at or below 1.

Concentrations of PAN, PPN, and other peroxyacyl nitrates have been reported (Table 4-20) at Tanbark Flat, CA, 35 km northeast of Los Angeles, during 1989, 1990, and 1991 and at Franklin Canyon, CA, 25 km west of Los Angeles, during 1991 (Grosjean and Williams, 1992; Grosjean et al., 1993). As indicated by the results tabulated in Table 4-20, the concentrations were high at these mountain sites, the PPN to PAN ratios were relatively high, and the concentration maxima occurred during the afternoon hours. These concentration levels of PAN and PPN are attributed to downwind transport from the Los Angeles urban area. The MPAN was occasionally detected with average concentrations of 1.2 ppb at Tanbark Flat and 1.0 ppb at Franklin Canyon in 1991.

At Tanbark Flat, the O₃ and PAN diurnal concentration patterns were similar to those in upwind urban areas. The PAN to O₃ ratios at the O₃ maximum were as follows: 1989, 0.05; 1990, 0.08; 1991, 0.05; all the ratios are within the same range as at sites in urban areas in and around Los Angeles.

Additional measurements of PAN and PPN or other peroxyacyl nitrates are available over a period of years at Niwot Ridge, CO, just west of the Denver-Boulder area; at Point Arena, CA; and at a forest site, Scotia, PA (Ridley et al., 1990). The concentrations reported at all of these sites are much lower than the mountain sites in California. The Niwot Ridge site concentrations, which show the effects of easterly upslope flow of air parcels from Denver-Boulder, are still low compared to the sites downwind of the urban Los Angeles area (Table 4-20).

The PAN concentrations at the Scotia rural site in the eastern United States tend to be somewhat higher than the Niwot Ridge or Point Arena sites (Table 4-20). This difference may relate to higher regional precursor concentration levels.

4.10 Concentration and Patterns of Hydrogen Peroxide in the Ambient Atmosphere

Efforts to measure H₂O₂ began in the 1970s, but the early reports of H₂O₂ concentrations above 10 ppb and even 100 ppb appear to be in error because of the artifact H₂O₂ generated within the presence of O₃ (Chapter 3, Section 3.5.1.3). Subsequent measurements of H₂O₂ in the 1980s resulted in maximum H₂O₂ concentrations at or below 5 ppb and mean concentrations at or below 1 ppb (Sakugawa et al., 1990).

Studies comparing more recent methods for measuring H₂O₂, which were conducted in North Carolina, indicated differences among measurement methods in synthetic mixtures of H₂O₂, including possible interferences, and in the ambient atmosphere of up to about ±25% (Kleindienst et al., 1988). However, results from the same study from mixtures irradiated in a smog chamber produced larger differences among methods, especially for the luminol technique compared to the fluorescence technique and with tunable-diode laser absorption spectroscopy. Another comparison study conducted in California resulted in differences between methods for measuring H₂O₂ that varied by a factor or two (Lawson et al., 1988). In the measurements of H₂O₂ discussed below, the cryogenic fluorescence method or the scrubber-coil fluorescence method generally was used.

**Table 4-20. Summary of Measurements of Peroxyacetyl Nitrate
and Peroxypropionyl Nitrate in Rural Areas^a**

Site	Month/ Year	Number of Days Sampled	PAN Concentration (ppb)		PPN Concentration (ppb)		Reference
			Average/Mean	Max	Average/Mean	Max	
Tanbark Flat, CA	8-10/1989	69	2.9	>16.1	0.75	5.1	Williams and Grosjean (1991)
	8,9/1990	34	4.8	22.0	0.76	4.3	Grosjean et al. (1993)
	8/1991	22	2.8	12.8	0.43	2.66	Grosjean et al. (1993)
Franklin Canyon, CA	9/1991	9	1.6	7.0	0.18	1.15	Grosjean et al. (1993)
Niwot Ridge, CO	7/1984	16	0.28	2.3	0.016	0.17	Singh and Salas (1989)
	6, 7/1984	23	≈0.25	NA	NA	NA	Fahey et al. (1986)
	8, 9/1984	21	≈0.25	NA	NA	NA	Fahey et al. (1986)
	6, 7/1987	46	0.81 ^(b) 0.21 ^(c)	3.2	0.08 ^(b) 0.01 ^(c)	0.45	Ridley et al. (1990)
Point Arena, CA	1/1984	14	0.12	1.1	0.005	0.07	Singh and Salas (1989)
	Spring 1985	NA	0.05	NA	NA	NA	Ridley (1991)
Scotia, PA	Summer 1986	NA	≈0.6	NA	NA	NA	Ridley (1991)
	6-8/1988	47	1.0	NA	NA	NA	Buhr et al. (1990)
Kananaskis Valley, Alberta, Canada	9/1979,	NA	≈0.5	2.3	NA	NA	Peake et al. (1983)
	4/1982,						
	6-8/1982						
Frijoles Mesa, NM	10/1987 to 1/1989	NA	0.26	1.9	NA	NA	Gaffney et al. (1993)

^aSee Appendix A for abbreviations and acronyms.

^bFlow from Boulder-Denver area.

^cFlow across the Rockies.

Based on interpretation of a compilation of H_2O_2 measurements made between 1984 and 1988 at a number of urban locations, at rural/remote locations, and on aircraft flights, it was concluded that the higher H_2O_2 concentrations were associated with the following measurement conditions: in afternoon hours, during summer months, at rural locations, and at lower latitudes (Sakugawa et al., 1990; Van Valin et al., 1987). The H_2O_2 concentrations increase from the surface to the top of the boundary layer (Daum et al., 1990). Available values for mean H_2O_2 concentrations at three U.S. locations were (1) at the summit of Whitetop Mountain, VA: summer, 0.80 ppb; winter, 0.15 ppb (Olszyna et al., 1988); (2) at the summit of Whiteface Mountain: 1986, 0.6 ppb; 1987, 0.8 ppb (Mohnen and Kadlec, 1989); and (3) at Westwood, CA: summer, ≈ 1.0 ppb; winter, 0.2 ppb (Sakugawa and Kaplan, 1989). At Westwood, the highest correlation with various parameters was found for solar radiation consistent with the higher H_2O_2 concentrations being observed in the afternoon during the late spring and early summer months (Sakugawa and Kaplan, 1989). In the same study, the average H_2O_2 concentrations were observed to increase from Westwood, near the coast in the Los Angeles Basin, to Duarte, inland; at Daggett in the Mohave Desert; and at Sky Mountain and Lake Gregory in the San Bernardino Mountains. The ratios of O_3 to H_2O_2 concentrations at these sites were ≥ 100 . In subsequent measurements, the same relationship in H_2O_2 concentrations between Westwood and the other California sites listed above was observed (Sakugawa and Kaplan, 1993). Unlike the results at several urban sites and other mountain sites, it was reported that the highest diurnal H_2O_2 concentrations at Lake Gregory in the San Bernardino Mountains were observed during the nighttime hours (Sakugawa and Kaplan, 1993).

4.11 Co-occurrence of Ozone

4.11.1 Introduction

There have been several attempts to characterize air pollutant mixtures (Lefohn and Tingey, 1984; Lefohn et al., 1987b). Pollutant combinations can occur at or above a threshold concentration either together or temporally separated from one another. For example, for characterizing the different types of co-occurrence patterns, Lefohn et al. (1987b) grouped air quality data within a 24-h period starting at 0000 hours and ending at 2359 hours. Patterns that showed air pollutant pairs appearing at the same hour of the day at concentrations equal to or greater than a minimum hourly mean value were defined as "simultaneous-only" daily co-occurrences. When pollutant pairs occurred at or above a minimum concentration during the 24-h period, without occurring during the same hour, a "sequential-only" co-occurrence was defined. During a 24-h period, if the pollutant pair occurred at or above the minimum level at the same hour of the day and at different hours during the period, the co-occurrence pattern was defined as "complex-sequential". A co-occurrence was not indicated if one pollutant exceeded the minimum concentration just before midnight and the other pollutant exceeded the minimum concentration just after midnight. As will be discussed below, studies of the joint occurrence of gaseous NO_2/O_3 and SO_2/O_3 reached two conclusions: (1) the co-occurrence of two-pollutant mixtures lasted only a few hours per episode, where an episode was defined by the threshold concentration used, and (2) the time between episodes is generally long (i.e., weeks, sometimes months) (Lefohn and Tingey, 1984; Lefohn et al., 1987b).

For exploring the co-occurrence of O₃ and other pollutants (e.g., acid precipitation, acidic cloudwater, and acidic sulfate aerosols), there are limited data available. In most cases, routine monitoring data are not available from which to draw general conclusions. However, published results are reviewed and summarized for the purpose of assessing an estimate of the possible importance of co-occurrence patterns of exposure.

4.11.2 Nitrogen Oxides

Ozone occurs frequently at concentrations ≥ 0.03 ppm at many rural and remote monitoring sites in the United States (Evans et al., 1983; Lefohn, 1984; Lefohn and Jones, 1986). Therefore, for many rural locations in the United States, the co-occurrence patterns observed by Lefohn and Tingey (1984) for O₃ and NO₂ were defined by the presence or absence of NO₂. As anticipated, Lefohn and Tingey (1984) reported that most of the sites analyzed experienced fewer than 10 co-occurrences (when both pollutants were present at an hourly average concentration ≥ 0.05 ppm). However, the authors did note that several urban monitoring sites in the South Coast Air Basin experienced more than 450 co-occurrences. The rural sites of Riverside, Fontana, and Rubidoux, CA, had more than 100 co-occurrences. Denver and San Jose, CA, also experienced more than 100 co-occurrences of O₃/NO₂. Lefohn and Tingey (1984) reported that for Rubidoux, because NO₂ concentration maxima tended to peak in the evenings or early morning, the co-occurrences were present at these times. For more moderate areas of the country, Lefohn et al. (1987b) reported that even with a threshold of 0.03 ppm O₃, the number of co-occurrences with NO₂ was small.

4.11.3 Sulfur Dioxide

Because elevated SO₂ concentrations are mostly associated with industrial activities (U.S. Environmental Protection Agency, 1992a), co-occurrence observations are usually associated with monitors located near these types of sources. Lefohn and Tingey (1984) reported that, for the rural and nonrural monitoring sites investigated, most sites experienced fewer than 10 co-occurrences of SO₂ and O₃. Only Rockport, IN, and Paradise No. 21 (KY) had more than 40 co-occurrences during the monitoring period (48 and 45, respectively). The monitors at these two sites were influenced by the local sources. The authors noted that at Fontana there were numerous O₃ episodes above 0.05 ppm, and there was a high probability that when the SO₂ hourly average concentrations rose above 0.05 ppm, both pollutants would be present at levels equal to or greater than 0.05 ppm.

Meagher et al. (1987) reported that several documented O₃ episodes at specific rural locations appeared to be associated with elevated SO₂ levels. The investigators defined the co-occurrence of O₃ and SO₂ to be when hourly mean concentrations were equal to or greater than 0.10 and 0.01 ppm, respectively. On reviewing the hourly mean O₃ and SO₂ data used by Lefohn et al. (1987b) in 1980 (using a threshold of 0.05 ppm for both pollutants), the Paradise No. 23 (KY); Giles County, TN; Murphy Hill (reported as Marshall County by Meagher et al., 1987), AL; and Saltillo (reported as Hardin Co. by Meagher et al., 1987), TN, sites experienced fewer than 7 days over a 153-day period for a co-occurrence of any form (i.e., simultaneous only, sequential, and complex co-occurrence). Thus, as reported by Lefohn et al. (1987b), the co-occurrence pattern of O₃ and SO₂ was infrequent.

The above discussion was based on the co-occurrence patterns associated with the presence or absence of hourly average concentrations of pollutant pairs. Taylor et al. (1992) have discussed the joint occurrence of O₃, nitrogen, and sulfur in forested areas using

cumulative exposures of O₃ with data on dry deposition of sulfur and nitrogen. The authors concluded in their study that the forest landscapes with the highest loadings of sulfur and nitrogen via dry deposition tended to be the same forests with the highest average O₃ concentrations and largest cumulative exposure. Although the authors concluded that the joint occurrences of multiple pollutants in forest landscapes were important, nothing was mentioned about the hourly co-occurrences of O₃ and SO₂ or O₃ and NO₂.

4.11.4 Acidic Sulfate Aerosols

Acid sulfates, which are usually composed of sulfuric acid (H₂SO₄), ammonium bisulfate, and ammonium sulfate, have been measured at a number of locations in North America. Acidic sulfate and neutralized species can accumulate and range in concentration from 0 to 50 µg/m³ at a specific location or a number of locations simultaneously (Lioy, 1989). For many summertime studies, peaks of H₂SO₄ or H⁺ appear to be associated with the presence of a slow-moving high pressure system (Lioy and Waldman, 1989). Acid sulfates are found primarily in the fine particle size range (<2.5 µm in diameter). Lioy (1989) reports that the acidic sulfate concentrations measured in the summertime can be found at 20 µg/m³ for over an hour and can be found at high concentrations of 10 to 20 µg/m³ for 6 to 24 h at one or more sites (Lioy, 1989). Acidic sulfate aerosol concentrations can occur at concentrations in the summertime above 10 µg/m³ for periods longer than 5 h (Lioy, 1989). As has been discussed earlier in this chapter, the highest O₃ exposures for sites affected by anthropogenically derived photooxidant precursors are expected to occur during the late spring and summer months. Thus, the potential for O₃ and acidic sulfate aerosols to co-occur at some locations in some form (i.e., simultaneously, sequentially, or complex-sequentially) is real. Our knowledge of the potential exposure of the co-occurrence of acidic sulfate aerosols and O₃ is limited because routine monitoring data for acidic aerosols are not available. Information on the co-occurrence patterns is limited to research studies and some of the results of these studies are provided in this section.

Spektor et al. (1991) investigated the effects of single- and multiday O₃ exposures on respiratory function in active normal children aged 8 to 14 years at a northwestern New Jersey residential summer camp in 1988. During the investigation, the authors measured daily levels of 1-h peak O₃ and the 12-h average H⁺ concentrations. On 7 days, the acid aerosol concentrations (reported as H₂SO₄) were higher than 10 µg/m³, reaching a 12-h maximum of 18.6 µg/m³. Figure 4-27 shows the relationship between daily maximum O₃ and daily 12-h average H⁺ concentrations. Thurston et al. (1992) reported occurrences in 1988 of maximum 24-h average concentrations of H⁺ as high as 18.7 µg/m³ (Buffalo, NY) and a maximum daily hourly average concentration of 0.164 ppm. Although lower than Buffalo, high O₃ or H⁺ values were reported by the investigators for Albany and White Plains, NY. It is unclear whether the O₃ or H⁺ maximum concentrations occurred simultaneously; however, it is clear that high concentrations could occur either sequentially, complex-sequentially, or simultaneously. Evidence exists in the literature indicating that hourly co-occurrences are experienced. Raizenne and Spengler (1989) described an episodic co-occurrence pattern in 1986 of high hourly averaged concentrations of O₃ and H₂SO₄ that occurred at a residential summer camp located on the north shore of Lake Erie, Ontario, (Figure 4-30). Thurston et al. (1994) conducted a study of ambient acidic aerosols in the Toronto, Ontario, metropolitan area in July and August of 1986, 1987, and 1988, and reported on the fine particle (aerodynamic equivalent diameter <2.5 µm) samples collected twice per day. The authors

reported that their results indicated that acidic aerosol episodes (i.e., $H^+ \geq 100 \text{ nmol/m}^3$) occurred routinely during the summer months and that H^+ peaks were correlated with sulfate (SO_4) episodes. Figure 4-31 illustrates the relationship among SO_4 , H^+ , and O_3 .

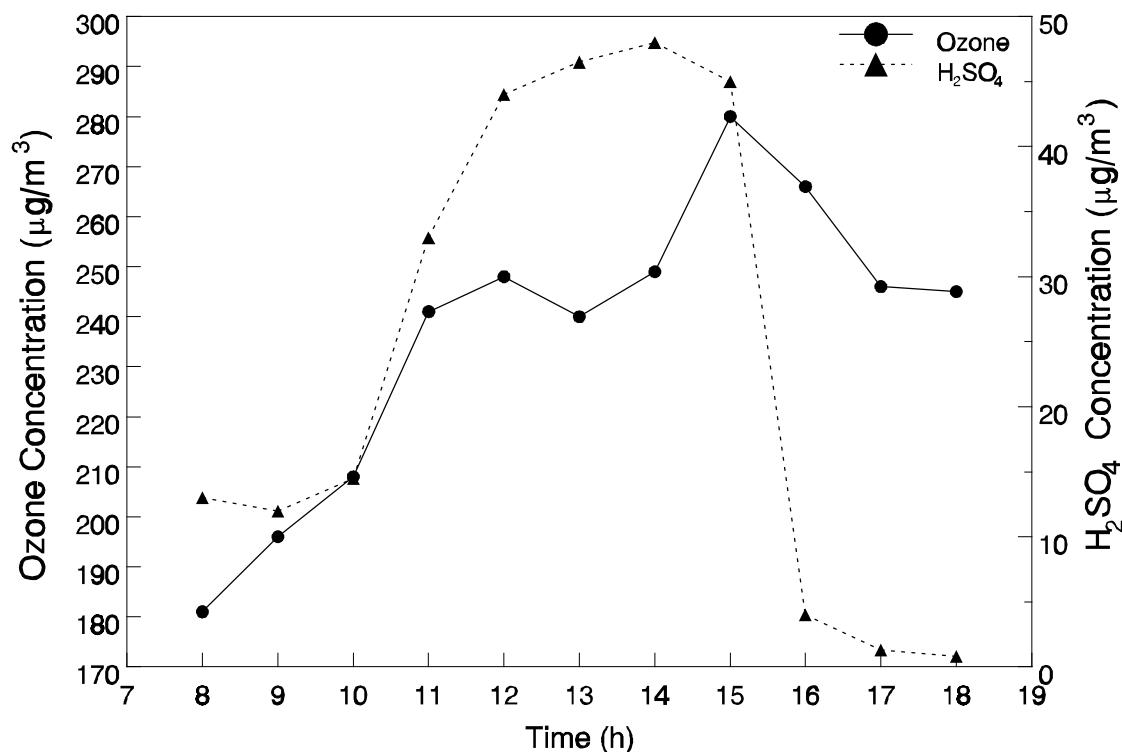


Figure 4-30. *The co-occurrence pattern of ozone and sulfuric acid (H_2SO_4) for July 25, 1986, at a summer camp on the north shore of Lake Erie, Ontario, Canada.*

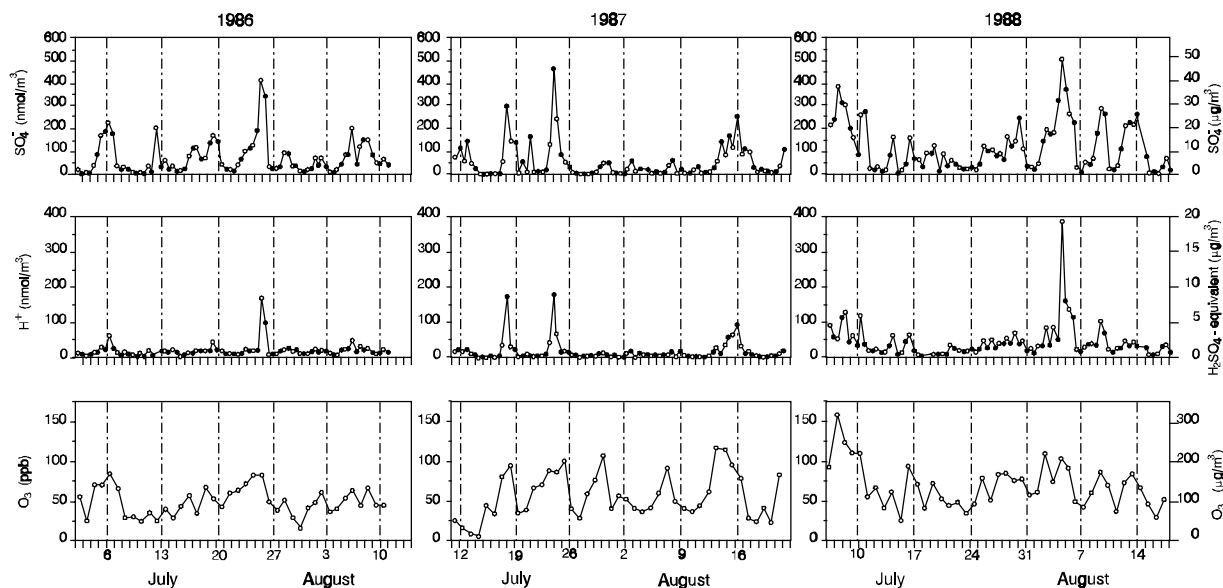
Source: Raizenne and Spengler (1989).

4.11.5 Acid Precipitation

Concern has been expressed about the possible effects on vegetation from co-occurring exposures of O_3 and acid precipitation (Prinz et al., 1985; National Acid Precipitation Assessment Program, 1987; Prinz and Krause, 1988). Little information has been published concerning the co-occurrence patterns associated with the joint distribution of O_3 and acidic deposition (i.e., H^+). Lefohn and Benedict (1983) reviewed EPA's SAROAD monitoring data for 1977 through 1980 and, using National Atmospheric Deposition Program (NADP) and EPRI wet deposition data, evaluated the frequency distribution of pH events for 34 NADP and 8 EPRI chemistry monitoring sites located across the United States. Unfortunately, there were few sites where O_3 and acidic deposition were comonitored.

Figure 4-31. *Sulfate (SO_4), hydrogen ion (H^+), and ozone (O_3) measured at Bredalbane Street (Site 3) in Toronto during July and August 1986, 1987, and 1988.*

Source: Thurston et al. (1994).



As a result, Lefohn and Benedict (1983) focused their attention on O_3 and acidic deposition monitoring sites that were closest to one another. In some cases, the sites were as far apart as 144 km. Using hourly O_3 monitoring data and weekly and event acidic deposition data from the NADP and EPRI databases, the authors identified specific locations where the hourly mean O_3 concentrations were ≥ 0.1 ppm and 20% of the wetfall daily or weekly samples were below pH 4.0. Elevated levels of O_3 were defined as hourly mean concentrations equal to or greater than 0.1 ppm. Although for many cases, experimental research results of acidic deposition on agricultural crops show few effects at pH levels above 3.5 (National Acid Precipitation Assessment Program, 1987), it was decided to use a pH threshold of 4.0 to take into consideration the possibility of synergistic effects of O_3 and acidic deposition.

Based on their analysis, Lefohn and Benedict (1983) reported five sites where there may be the potential for agricultural crops to experience additive, less than additive, or synergistic (i.e., greater than additive) effects from elevated O_3 and H^+ concentrations. The authors stated that they believed, based on the available data, the greatest potential for interaction between acid rain and O_3 concentrations in the United States, with possible effects on crop yields, may be in the most industrial areas (e.g., Ohio and Pennsylvania). However, they cautioned that, because no documented evidence existed to show that pollutant interaction had occurred under field growth conditions and ambient exposures, their conclusions should only be used as a guide for further research.

In their analysis, Lefohn and Benedict (1983) found no colocated sites. The authors rationalized that data from non-co-monitoring sites (i.e., O_3 and acidic deposition) could be used because O_3 exposures are regional in nature. However, work by Lefohn et al. (1988a) has shown that hourly mean O_3 concentrations vary from location to location within a region, and that cumulative indices, such as the percent of hourly mean concentrations ≥ 0.07 ppm, do not form a uniform pattern over a region. Thus, extrapolating hourly mean O_3 concentrations from known locations to other areas within a region may provide only qualitative indications of actual O_3 exposure patterns.

In the late 1970s and the 1980s, both the private sector and the government funded research efforts to better characterize gaseous air pollutant concentrations and wet deposition. The event-oriented wet deposition network, EPRI/Utility Acid Precipitation Study Program, and the weekly oriented sampling network, NADP, provided information that can be compared with hourly mean concentrations of O_3 collected at several comonitored locations. No attempt was made to include H^+ cloud deposition information. In some cases, for mountaintop locations (e.g., Clingman's Peak, Shenandoah, Whiteface Mountain, and Whitetop Mountain), the H^+ cloud water deposition is greater than the H^+ deposition in precipitation (Mohnen, 1989), and the co-occurrence patterns associated with O_3 and cloud deposition will be different than those patterns associated with O_3 and deposition in precipitation.

Smith and Lefohn (1991) explored the relationship between O_3 and H^+ in precipitation, using data from sites that monitored both O_3 and wet deposition simultaneously and within one minute latitude and longitude of each other. The authors reported that individual sites experienced years in which both H^+ deposition and total O_3 exposure were at least moderately high (i.e., annual H^+ deposition $\geq 0.5 \text{ kg ha}^{-1}$ and an annual O_3 cumulative, sigmoidally weighted exposure (W126) value $\geq 50 \text{ ppm-h}$). With data compiled from all sites, it was found that relatively acidic precipitation ($\text{pH} \leq 4.31$ on a weekly basis or $\text{pH} \leq 4.23$ on a daily basis) occurred together with relatively high O_3 levels (i.e., W126 values $\geq 0.66 \text{ ppm-h}$ for the same week or W126 values $\geq 0.18 \text{ ppm-h}$ immediately before or after a rainfall event) approximately 20% of the time, and highly acidic precipitation (i.e., $\text{pH} \leq 4.10$ on a weekly basis or $\text{pH} \leq 4.01$ on a daily basis) occurred together with a high O_3 level (i.e., W126 values $\geq 1.46 \text{ ppm-h}$ for the same week or W126 values $\geq 0.90 \text{ ppm-h}$ immediately before or after a rainfall event) approximately 6% of the time. Whether during the same week or before, during, or after a precipitation event, correlations between O_3 level and pH (or H^+ deposition) were weak to nonexistent. Sites most subject to relatively high levels of both hydrogen ion and O_3 were located in the eastern portion of the United States, often in mountainous areas.

4.11.6 Acid Cloudwater

In addition to the co-occurrence of O_3 and acid precipitation, results have been reported on the co-occurrence of O_3 and acidic cloudwater in high-elevation forests. Vong and Guttorp (1991) characterized the frequent O_3 -only and pH-only, single-pollutant episodes, as well as the simultaneous and sequential co-occurrences of O_3 and acidic cloudwater. The authors reported that both simultaneous and sequential co-occurrences were observed a few times each month above the cloud base. Episodes were classified by considering hourly O_3 average concentrations $\geq 0.07 \text{ ppm}$ and cloudwater events with $\text{pH} \leq 3.2$. The authors reported that simultaneous occurrences of O_3 and pH episodes occurred two to three times per month at two southern sites (Mitchell, NC, and Whitetop, VA) and the two northern sites (Whiteface Mountain, NY, and Moosilauke, NH) averaged one episode per month. No co-occurrences were observed at the central Appalachian site (Shenandoah, VA), due to a much lower cloud frequency. Vong and Guttorp (1991) reported that the simultaneous occurrences were usually of short duration (mean = 1.5 h/episode) and were followed by an O_3 -only episode. As would be expected, O_3 -only episodes were longer than co-occurrences and pH episodes, averaging an 8-h duration.

4.12 Summary

Ozone is a pervasive compound that is detected at all monitoring locations throughout the world. To obtain a better understanding of the potential for ambient O₃ exposures affecting human health and vegetation, hourly average concentration information is summarized for urban, rural forested, and rural agricultural areas in the United States.

The distribution of O₃ 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). It is difficult to apply land-use designations to the generalization of exposure regimes that may be experienced in urban versus rural areas, because the land use characterization of "rural" does not imply that a specific location is isolated from anthropogenic influences. Rather, the characterization implies only the current use of the land. Because it is possible for urban emissions, as well as O₃ produced from urban area emissions, to be transported to more rural downwind locations, elevated O₃ concentrations can occur at considerable distances from urban centers. Urban O₃ concentration values often are depressed because of titration by NO. Because of the absence of chemical scavenging, O₃ tends to persist longer in nonurban than in urban areas, and exposures may be higher in nonurban than in urban locations.

For vegetation, as indicated in Chapter 5 (Section 5.5), extensive research has focused on identifying exposure indices with a firm foundation on biological principles. Many of these exposure indices have been based on research results indicating that the magnitude of vegetation responses to air pollution is more an effect of the magnitude of the concentration than the length of the exposure. For O₃, the short-term (1- to 8-h), high concentration exposures (>0.1 ppm) have been identified by many researchers as being more important than long-term, low concentration exposures in producing visible injury to plants (see Chapter 5 for further discussion). Similarly, for human health considerations, results using controlled human exposures have shown the possible importance of concentration in relation to duration of exposure and inhalation rate.

In summarizing the hourly average concentrations in this chapter, specific attention is given to the relevance of the exposure indices used. For example, for human health considerations, concentration (or exposure) indices such as the daily maximum 1-h average concentrations, as well as the number of daily maximum 4- or 8-h average concentrations above a specified threshold, are used to characterize information in the population-oriented locations. For vegetation, several different types of exposure indices are used. Because much of the NCLAN exposure information is summarized in terms of 7-h average concentrations, this exposure index is used. However, because peak-weighted, cumulative indices (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 Chapter 5, Section 5.5), several exposure indices that use either a threshold or a sigmoidally weighted scheme are used in this chapter to provide insight concerning the O₃ exposures that are experienced at a select number of rural monitoring sites in the United States. The peak-weighted cumulative exposure indices such as SUM06, SUM08, and W126 are used.

Ozone hourly average concentrations have been recorded for many years by the State and local air pollution agencies who report their data to EPA. The 10-year (1983 to 1992) composite average trend for the second highest daily maximum hourly average concentration during the O₃ season for 509 trend sites and a subset of 196 NAMS sites,

shows that the 1992 composite average for the trend sites is 21% lower than the 1983 average and 20% lower for the subset of NAMS sites. The 1992 value is the lowest composite average of the past 10 years. The 1992 composite average is significantly less than all the previous 9 years, 1983 to 1991. The relatively high O₃ concentrations in 1983 and 1988 were attributable, in part, to hot, dry, stagnant conditions in some areas of the country that were especially conducive to O₃ formation.

From 1991 to 1992, the composite mean of the second highest daily maximum 1-h O₃ 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 exceedances of the O₃ standard decreased by 23% at the 672 sites, and 19% at the 222 NAMS sites. Nationwide 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 O₃ formation than those in 1992, the composite mean level for 1993 was the second lowest composite average for the decade (1984 to 1993).

Information is provided in this chapter on methods used for investigating techniques for adjusting O₃ trends for meteorological influences. Historically, the long-term O₃ trends in the United States characterized by EPA have emphasized air quality statistics that are closely related to the NAAQS. Information is provided on the use of alternative indices. Besides EPA, additional investigators have assessed trends at several locations in the United States, and information is provided for both urban and rural areas.

Interest has been expressed in characterizing O₃ exposure regimes for sites experiencing daily maximum 8-h concentrations above specific thresholds (e.g., 0.08 or 0.10 ppm). Documented evidence has been published showing the occurrence, at some sites, of multihour periods within a day of O₃ at levels of potential health effects. Although most of these analyses were made using monitoring data collected from sites in or near nonattainment areas, one analysis showed that at five sites, two in New York state, two in rural California, and one in rural Oklahoma, an alternative O₃ standard of an 8-h average of 0.10 ppm would be exceeded even though the existing 1-h standard would not be. The study indicated the occurrence at these five sites, none of which was in or near a nonattainment area, of O₃ concentrations showing only moderate peaks but showing multihour levels above 0.10 ppm.

An important question is whether an improvement in O₃ levels would produce distributions of 1-h O₃ concentrations that result in a broader diurnal profile than those seen in high-oxidant urban areas where O₃ 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 ≥ 0.08 ppm, when compared to those sites experiencing sharper peaks. One research effort observed, using aerometric data at specific sites, how O₃ 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 ≥ 0.08 ppm and the number of exceedances of the current form of the standard had a positive, weak correlation ($r = 0.51$). The investigators reported few changes in the shape of the average diurnal patterns as sites changed attainment status. The lack of a change

in shape may have explained why the investigators could not find evidence that the number of occurrences of the daily maximum 4-h average concentration ≥ 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_3 exposure with an effect. For example, using O_3 ambient air quality data, the number of exceedances of 0.125 ppm and the number of occurrences of the daily maximum 8-h average concentrations ≥ 0.08 ppm have been compared with the result 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_3 . However, there was not much predictive strength in using one O_3 exposure index to predict another. Similarly, the maximum 3-mo SUM06, second highest daily maximum hourly average concentration, and second highest daily maximum 8-h average concentration exposure indices were compared. For the rural agricultural and forest sites, the correlations among the indices were not strong.

One of the difficulties in attempting to use correlation analysis between indices for rationalizing the substitution of one exposure index for another for 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 those of another. Evidence has been presented in the literature for recommending 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. Less error would be introduced if either of the two indices were used directly in the development of an exposure-response model.

The EPA has indicated that a reasonable estimate, as an annual average, of O_3 background concentration near sea level in the United States today is from 0.020 to 0.035 ppm; this estimate included a 0.005 to 0.015 ppm contribution from the stratosphere. The EPA concluded that a reasonable estimate of natural O_3 background concentration for a 1-h daily maximum at sea level in the United States during the summer is on the order of 0.03 to 0.05 ppm. Reviewing data from sites that appear to be isolated from anthropogenic sources, it has been reported that, in almost all cases, none of the sites experienced hourly average concentrations ≥ 0.08 ppm and that the maximum hourly average concentrations were in the range of 0.060 to 0.075 ppm. Using data from these sites, in the continental United States, the 7-mo (April to October) average of the 7-h daily average concentrations range from approximately 0.025 to 0.045 ppm. At an O_3 monitoring site at the Theodore Roosevelt National Park, 7-mo (April to October) averages of the 7-h daily average concentrations of 0.038, 0.039, and 0.039 ppm, respectively, were experienced in 1984, 1985, and 1986. These 7-h seasonal averages appear to be representative of the 8-h daily average O_3 concentrations that may occur at other fairly clean sites in the United States and other locations in the northern hemisphere.

Diurnal variations are those that occur during a 24-h period. Diurnal patterns of O_3 may be expected to vary with location, depending on the balance among the many factors affecting O_3 formation, transport, and destruction. Although they vary with locality, diurnal patterns for O_3 typically show a rise in concentration from low levels or levels near minimum detectable amounts to an early afternoon peak. The diurnal pattern of concentrations can be ascribed to four simultaneous processes: (1) downward transport of O_3 from layers aloft,

(2) destruction of O_3 through contact with surfaces and through reaction with NO at ground level, (3) in situ photochemical production of O_3 , and (4) horizontal transport of O_3 and its precursors.

Although it might appear that composite diurnal pattern diagrams could be used to quantify the differences in O_3 exposures among sites, caution has been expressed in 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 adequately identify, at most sites, the presence of high hourly average concentrations; thus, they may not be adequate to distinguish O_3 exposure differences among sites. Unique families of diurnal average profiles exist, and it is possible to distinguish between two types of O_3 monitoring sites. A seasonal diurnal diagram provides the investigator with the opportunity to identify whether a specific O_3 monitoring site has more scavenging than any other site. For low-elevation sites, intraday variability is most significant due to the pronounced daily amplitude in O_3 concentration between the predawn minimum and midafternoon to early-evening maximum, whereas interday variation is more significant in the high-elevation sites.

Seasonal variations in O_3 concentrations in urban areas usually show the pattern of high O_3 in late spring or in summer and low levels in the winter. Because of temperature, relative humidity, and seasonal changes in storm tracks from year to year, the general weather conditions in a 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 in 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.

Several investigators have reported on the tendency for average O_3 concentrations to be higher in the second than in the third quarter of the year for many isolated rural sites. This observation has been attributed to either stratospheric intrusions or an increasing frequency of slow-moving, high-pressure systems that promote the formation of O_3 . However, for several clean rural sites, the highest exposures have occurred in the third quarter rather than in the second. For rural O_3 sites in the southeastern United States, the daily maximum 1-h average concentration was found to peak during the summer months. For sites located in rural areas, but not isolated from anthropogenic sources of pollution, the different patterns may be associated with anthropogenic emissions of NO_x and hydrocarbons.

Concentrations of O_3 vary with altitude and with latitude. There appears to be no generalizable conclusion concerning the relationship between O_3 exposure and elevation. The differences in exposure occur when one site is above the natural inversion and the other is not. An important issue for assessing possible impacts of O_3 at high-elevation sites that requires further attention is the use of mixing ratios (e.g., parts per million) instead of absolute concentration (e.g., in units of micrograms per cubic meter) to describe O_3 concentration. In most cases, mixing ratios, or mole fractions, are used to describe O_3 concentrations. The manner in which concentration is reported may be important when assessing the potential impacts of air pollution on high-elevation forests. Concentration varies as a function of altitude. Although the change in concentration is small when the elevational difference between sea level and the monitoring site is small, it becomes substantial at high-elevation sites. Given the same part-per-million value registering at both a high- and low-elevation site, the absolute concentrations (i.e., micrograms per cubic meter) at the two elevations will be different. Because both pollutants and ambient air are gases, changes in pressure directly affect their volume. This pressure effect must be considered when measuring absolute pollutant concentrations. Although these exposure considerations

are trivial at low-elevation sites, when one compares exposure-effects results obtained at high-elevation sites with those from low-elevation sites, the differences may become significant.

Most people in the United States spend a large proportion of their time indoors. Until the early 1970s, very little was known about the O₃ concentrations experienced inside buildings. Even to date, the database on this subject is not extensive, and a wide range of I/O O₃ concentration relationships can be found in the literature. Reported I/O values for O₃ are highly variable. A relatively large number of factors can affect the difference in O₃ concentrations between the inside of a structure and the outside air. In general, outside air infiltration or exchange rates, interior air circulation rates, and interior surface composition (e.g., rugs, draperies, furniture, walls) affect the balance between replenishment and decomposition of O₃ within buildings. The I/O O₃ concentration ratios generally fall in the range of 0.1 to 0.7, and indoor concentrations of O₃ will almost invariably be less than those outdoors.

It is important that accurate estimates of both human and vegetation exposure to O₃ be available for assessing the risks posed by the pollutant. Examples are provided on how both fixed-site monitoring information and human exposure models are used to estimate risks associated with O₃ exposure.

In many cases, the upper tail of the distribution, which represents those individuals exposed to the highest concentrations, often generates special interest because the determination of the number of individuals who experience elevated pollutant levels can be critical for health risk assessments. This is especially true for pollutants for which the relationship between dose and response is highly nonlinear.

Because it is not possible to estimate population exposure, in most cases, solely from fixed-station data, several human exposure models have been developed. Some of these models include information on human activity patterns (i.e., the microenvironments people visit and the times they spend there). These models also contain submodels depicting the sources and concentrations likely to be found in each microenvironment, including indoor, outdoor, and in-transit settings.

A subgroup that has been studied by several investigators to assess the influence of ambient air pollution on their respiratory health and function is children attending summer camp. Because children are predominantly outdoors and relatively active while at camp, they provide a unique opportunity to assess the relationships between respiratory health and function and concurrent air pollution levels. Examples are provided on the type of exposure patterns that children experience.

A personal exposure profile can be identified by using a personal exposure monitor. Few data are available for individuals using personal exposure monitors. Results from a pilot study demonstrated that fixed-site ambient measurements may not adequately represent individual exposures. Outdoor O₃ concentrations showed substantial spatial variation between rural and residential regions. The study showed that the use of fixed-site measurements could result in an error as high as 127%. In addition, the study showed that models based on time-weighted I/O concentrations explained only 40% of the variability in personal exposures. The investigators concluded that contributions from diverse indoor and outdoor microenvironments could estimate personal O₃ exposure accurately.

The field of human exposure modeling is relatively young, with the first rigorous exposure modeling analyses appearing in the mid-1970s and the theoretical constructs regarding human exposure to environmental pollution being published in the early 1980s. Two distinct types of O₃ exposure models exist: (1) those that focus narrowly on predicting

indoor O₃ levels and (2) those that focus on predicting O₃ exposures on a community-wide basis. The following four distinct models address the prediction of O₃ exposures on a community-wide basis: (1) pNEM/O₃, (2) SAI/NEM, (3) REHEX, and (4) EPEM. All four O₃ exposure models are derived from the NEM (NAAQS exposure model), which was first developed in the early 1980s. Most applications of NEM use fixed-site monitoring data, U.S. census data, and human-activity data. The calculations result in an estimate of the O₃ concentration experienced by an individual in each microenvironment that the person inhabits.

The hourly average concentrations used in many of the high-treatment experimental vegetation and human health effects studies did not necessarily simulate those concentrations observed under ambient conditions. Although the ramifications of this observation on the effects observed are not clear, it has been pointed out that the highest treatments used in many of the vegetation open-top chamber experiments were bimodal in the distribution of the hourly average concentrations. In other experiments designed to assess the effects of O₃ on vegetation, constant concentration (i.e., square wave) exposures were implemented. As discussed in earlier sections of this Chapter, square wave exposure regimes do not normally occur under ambient conditions. Similar square wave exposures have been used in human health effects studies. In addition to the exposures used at the highest treatment levels for vegetation experiments, there is concern that the hourly average concentrations used in the charcoal-filtered control treatments may be lower than those experienced at isolated sites in the United States and in other parts of the world. Although the ramifications of using such exposure regimes is unclear, there is some concern that the use of atypically low control levels may result in an overestimation of vegetation yield losses when used as the baseline for evaluating the effects of treatments at higher concentrations.

Published data on the concentrations of photochemical oxidants other than O₃ in ambient air are neither comprehensive nor abundant. A review of the data shows that PAN and PPN are the most abundant of the non-O₃ oxidants in ambient air in the United States, other than the inorganic nitrogenous oxidants such as NO₂ and possibly nitric acid. At least one study has reported that a higher homologue of the series, peroxybenzoyl nitrate (PBzN), like PAN, is a lachrymator. No unambiguous identification of PBzN in the ambient air of the United States has been made.

Given the information available on PAN, the concentrations of PAN that are of most concern are those to which vegetation could potentially be exposed, especially during daylight hours in agricultural areas. These are followed in importance by concentrations both indoors and outdoors, in urban and nonurban areas, to which human populations potentially could be exposed. Most of the available data on concentrations of PAN and PPN in ambient air are from urban areas. The levels to be found in nonurban areas will be highly dependent on the transport of PAN and PPN or their precursors from urban areas, because the concentrations of the NO_x precursors to these compounds are considerably lower in nonurban than in urban areas.

There have been several attempts to characterize air pollutant mixtures. Pollutant combinations can occur at or above a threshold concentration either together or temporally separated from one another. Studies of the joint occurrence of gaseous NO₂/O₃ and SO₂/O₃ have concluded that the co-occurrence of two-pollutant mixtures lasted only a few hours per episode, and that the time between episodes is generally long (i.e., weeks, sometimes months). Using hourly averaged data collected at rural sites for vegetation considerations, the periods of co-occurrence represent a small portion of the potential plant growing period. For human

ambient exposure considerations, the simultaneous co-occurrence of NO_2/O_3 was infrequent in most cases. However, for several sites located in the South Coast Air Basin, more than 450 simultaneous co-occurrences of each pollutant, at hourly average concentrations ≥ 0.05 ppm, were present. Although the focus of co-occurrence research has been on patterns associated with the presence or absence of hourly average concentrations of pollutant pairs, some researchers have discussed the joint occurrence of O_3 , nitrogen, and sulfur in forested areas, combining cumulative exposures of O_3 with data on dry deposition of sulfur and nitrogen. One study reported that several forest landscapes with the highest dry deposition loadings of sulfur and nitrogen tended to experience the highest average O_3 concentrations and the largest cumulative exposure. Although the investigators concluded that the joint occurrences of multiple pollutants in forest landscapes were important, nothing was mentioned about hourly co-occurrences of O_3 and SO_2 or O_3 and NO_2 .

Knowledge of the potential exposure of the co-occurrence of acidic sulfate aerosols and O_3 is limited because routine monitoring data for acidic aerosols are not available. Information on the co-occurrence patterns is limited to research studies; some of the results are provided in this chapter. Acid sulfates, which are composed of H_2SO_4 , ammonium bisulfate, and ammonium sulfate, have been measured at a number of locations in North America. Acidic sulfate and neutralized species can accumulate and range in concentration from 0 to $50 \mu\text{g}/\text{m}^3$ at a specific location or a number of locations simultaneously. For many summertime studies, peaks of H_2SO_4 or H^+ appear to be associated with the presence of a slow-moving high pressure system. Acid sulfates are found primarily in the fine particle size range ($< 2.5 \mu\text{m}$ in diameter). The acidic sulfate concentrations measured in the summertime can be found at $20 \mu\text{g}/\text{m}^3$ for over an hour and at high concentrations of 10 to $20 \mu\text{g}/\text{m}^3$ for 6 to 24 h at one or more sites. Acidic sulfate aerosol concentrations can occur at concentrations in the summertime above $10 \mu\text{g}/\text{m}^3$ for periods longer than 5 h. The highest O_3 exposures for sites affected by anthropogenically derived photooxidant precursors are expected to occur during the late spring and summer months. Thus, the potential for O_3 and acidic sulfate aerosols to co-occur at some locations in some form (i.e., simultaneously, sequentially, or complex-sequentially) is real and requires further characterization.

Concern has been expressed about the possible effects on vegetation from co-occurring exposures of O_3 and acid precipitation. One study explored the relationship between O_3 and H^+ in precipitation, using data from sites that monitored both O_3 and wet deposition simultaneously and within one minute latitude and longitude of each other. The investigators reported that individual sites experienced years in which both H^+ deposition and total O_3 exposure were at least moderately high (i.e., annual H^+ deposition $\geq 0.5 \text{ kg ha}^{-1}$ and an annual O_3 cumulative sigmoidally weighted exposure (W126) value $\geq 50 \text{ ppm-h}$). Based on data compiled from all sites, relatively acidic precipitation ($\text{pH} \leq 4.31$ on a weekly basis or $\text{pH} \leq 4.23$ on a daily basis) occurred together with relatively high O_3 levels (i.e., W126 values $\geq 0.66 \text{ ppm-h}$ for the same week or W126 values $\geq 0.18 \text{ ppm-h}$ immediately before or after a rainfall event) approximately 20% of the time, and highly acidic precipitation (i.e., $\text{pH} \leq 4.10$ on a weekly basis or $\text{pH} \leq 4.01$ on a daily basis) occurred together with a high O_3 level (i.e., W126 values $\geq 1.46 \text{ ppm-h}$ for the same week or W126 values $\geq 0.90 \text{ ppm-h}$ immediately before or after a rainfall event) approximately 6% of the time. Whether during the same week or before, during, or after a precipitation event, correlations between O_3 level and pH (or H^+ deposition) were weak to nonexistent. Sites most subject to relatively high levels of both H^+ and O_3 were located in the eastern portion of the United States, often in mountainous areas.

The co-occurrence of O₃ and acidic cloudwater in high-elevation forests has been characterized. The frequent O₃-only and pH-only, single-pollutant episodes, as well as the simultaneous and sequential co-occurrences of O₃ and acidic cloudwater, have been reported. Both simultaneous and sequential co-occurrences were observed a few times each month above the cloud base.

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