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OZONE CASE STUDIES AT HIGH ELEVATION IN THE EASTERN UNITED STATES

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ABSTRACT

A network of five high elevation sites ($\geq$ 1000 m, MSL) in the eastern U.S. measured ozone, NO_x, and meteorological parameters as part of the U.S. Environmental Protection Agency's Mountain Cloud Chemistry Program (MCCP) from May through October in 1986, 1987, and 1988. Analysis of the data showed that high ozone episodes ($\geq$ 70 ppbv) at the MCCP sites occurred frequently during June and July, and were strongly correlated to synoptic scale meteorological features. A comprehensive statistical analysis was performed on the data set to investigate the relationship between ozone and meteorology. Two major ozone episodes in 1988, each lasting greater than 3 days were examined in detail. The maximum one hour average ozone concentration was ~160 ppbv recorded at a southern site, Whitetop Mountain. Back trajectory analysis, at 850 mb, indicated that most MCCP sites were influenced by upwind urban and industrial source areas during high ozone episodes. Other meteorological parameters, such as temperature, and relative humidity also affect the ozone formation during the two episodes. The concentrations of NO_x were higher during the ozone episodes, reflecting the photochemical production of ozone in the regional scale.

Keywords: Ozone, photochemical episodes, high elevation

1. INTRODUCTION

It is generally recognized that photochemical oxidants, such as ozone, play an important role in damage to plants, and may be responsible in part, for the observed forest decline at high elevations in the Eastern United States (Woodman and Cowling, 1987) and central Europe (Schütt and Cowling, 1985). Since 1986, the MCCP has been monitoring ozone levels at five high altitude sites ($\geq$ 1000 m MSL) in the eastern United States between 35° N to 45° N , in which damage to ecosystems is apparent (Bruck et al., 1989). Similarly, ozone concentrations have been measured in the rural and Alpine sites in Europe (Feister and Warmbt, 1987; Volz and Kley, 1988; Janach, 1989).

In evaluating the effects of ozone on vegetation, it is now suggested by some that episodes with high ozone concentrations may be more important than chronic low concentration exposures (Heck et al., 1966; U.S. Environmental Protection Agency, 1986; Lefohn and Pinkerton, 1988). The frequency of high ozone episodes is controlled by meteorology, and influenced by anthropogenic emissions of NO_x and hydrocarbons (Logan, 1989). At high elevation locales, above the nocturnal inversion layer, ozone concentration begins to display either no discernible diurnal cycle or as elevation increases, a reversed diurnal cycle (nighttime maximum) (Aneja et al., 1991, 1994). A lack of nocturnal ozone depletion may result in prolonged periods of high ozone concentrations under certain meteorological regimes.

Most investigations of ozone episodes in the U.S. suggest that elevated ozone concentrations occurring in the summer months in the eastern part of the country are associated with slow-moving and persistent high pressure

systems (Wolff et al., 1977; 1979; 1980; 1982; 1987; Vukovich et al., 1977; Wight et al., 1978; Wolff and Lioy, 1980; Aneja et al. 1990, 1991, 1994). Heggested and Bennett (1984) and Aneja et al. (1992) also pointed out that high ozone episodes in the eastern United States may be accompanied by high ambient temperatures, high intensities of solar radiation, low relative humidities, and absence of precipitation. Such meteorological conditions are ideal for photochemical formation of ozone.

The concentration of pollutants, the duration of episodes and the length of time between episodes are important factors in assessing the adverse impact of pollution on the biosphere (Lefohn and Jones, 1986). The objectives of this paper are to: analyze meteorological conditions associated with the ozone episodes at high elevation sites in the eastern U.S.; perform an observational based analysis utilizing multivariate statistical methods to investigate the relationship between ozone concentration and meteorology; explore source - receptor relationships based on back trajectory analyses during the ozone episodes; and explore the relation between ozone and nitrogen oxides at one of these locations.

2. MCCP SITE DESCRIPTION AND MEASUREMENT METHODS

The Mountain Cloud Chemistry Program (MCCP) consists of five high-elevation sampling sites in the eastern United States: Whiteface Mountain, NY; Mt. Moosilauke, NH; Shenandoah Park, VA; Whitetop Mountain, VA; Mt. Mitchell, NC; and one low elevation sampling site, Howland, ME. Figure 1 illustrates the location of the MCCP sites.

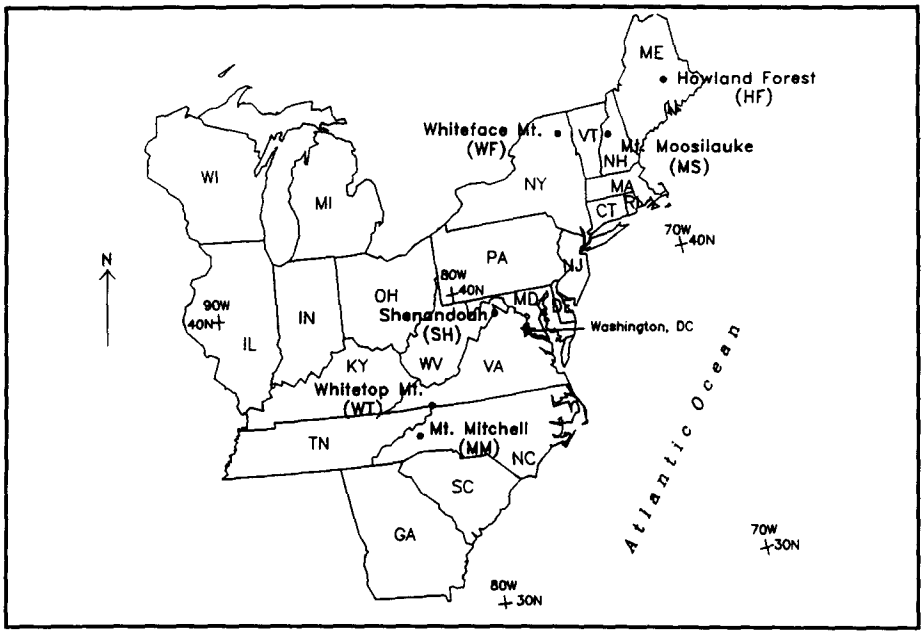

Figure 1: Map of eastern United States showing the locations of MCCP sites. HF - Howland, Maine; MS - Mt. Moosilauke, New Hampshire; WF - Whiteface Mountain, New York; SH - Shenandoah Park, Virginia; WT - Whitetop Mountain, Virginia; MM - Mt. Mitchell, North Carolina.

The northern-most high elevation site in the network is Whiteface Mountain (WF), New York (44°23'N, 73°59' W) located in the northeastern Adirondack Mountains in New York, at an elevation of 1483 m. Mt. Moosilauke (MS), New Hampshire (43°59'N, 71°48'W), is one of the most southern peaks of the White Mountains at an elevation of ~1000 m. The forest composition ranges from mixed hardwoods at lower elevations to spruce-fir (about 10% spruce) at mid-elevations, and pure balsam fir at high elevations.

The Shenandoah (SH), Virginia site (38°72'N, 78°20'W) is in the Shaver Hollow Watershed, located in the north-central sector of the Shenandoah National Park at an elevation of 1040 m. The tower location is representative of the surrounding deciduous forest canopy. The Whitetop Mountain (WT) site (36°38'N, 81°36'W) is located in the Mt. Rogers National Recreation Area of the Jefferson National Forest in southwestern Virginia, 6 km southwest of Mt. Rogers, the highest peak in Virginia. The TVA Whitetop Mountain summit research station (at 1689 m) straddles the main ridgeline of the Appalachian range. The southernmost MCCP site is located at Mt. Gibbs in Mt. Mitchell State Park (MM), North Carolina (35°44'N, 82°16'W), at an elevation of 1950 m. The site is ~1.5 km southwest of Mt. Mitchell, which is the highest peak in the eastern US (2038 m MSL). The summit is covered with Fraser fir, and the region from 1500 m to 1800 m is an ecosystem composed of mixed fir and spruce.

The low elevation site is in the Howland Forest (HF), Maine (45°13'N, 68°43'W). It is located at 65 m elevation between Howland and Edinburg, Maine, 35 km north of Bangor. The forest is spruce with some balsam fir, hemlock, and white pine.

A meteorological tower was located at each site to provide measurements above the forest canopy. Parameters monitored included wind speed and direction, solar radiation, relative humidity, air temperature and barometric pressure. Ozone measurements, based on an ultraviolet absorption technique, were made with a Thermo Electron Corporation Ozone Analyzer (Model 49). The level of detection for this instrument is 2 ppbv; with an accuracy objective of ± 20% for ozone values greater than 20 ppbv, and ± 4 ppbv for ozone values in the range of 0 to 20 ppbv. The precision of this instrument is ± 20 % for values in the range of 25 to 35 ppbv. Oxides of nitrogen were measured with a Monitor Labs Model 8448 Analyzer, for which the level of detection is 2 ppbv with an accuracy objective of ± 20 % for NO_2 values in the range of 18-22 ppbv, and a precision of ± 5 ppbv for values in the range of 10 to 22 ppbv. This instrument has two major limitations. First, its detection limit is 2 ppbv; second, the instrument has an interference response to PAN (peroxyacetyl nitrate) (Fehsenfeld et al., 1987). Therefore, the measurements made are probably the concentration of NOx + PAN. The quality assurance protocols included, in general, weekly zero and span checks. Multipoint calibrations were conducted twice each monitoring season during the measurement period. All calibrations were based on the National Institute of Science and Technology traceable reference standard. All these data were stored as 1-hour averages in a Campbell Scientific Model 21XL datalogger.

3. RESULTS AND DISCUSSION

For the purposes of this study, ozone concentration ≥ 70 ppbv is defined as an "ozone event" and ozone concentrations ≥ 70 ppbv lasting over 8 h are defined as a "high ozone episode". Ozone concentrations ≥ 70 ppbv corresponds to mean ±2 σ for most of the sites during the period 0800 - 2000 EST. Table 1 and Table 2 present a summary of ozone episodes , at the five high elevation MCCP sites, from May through October during 1987 and 1988 respectively. Tables 3 and 4 provide the summary of monthly averaged meteorological data at the MCCP sites during the 1987 and 1988 field seasons respectively.

Table 1. Number and duration of ozone episodes at the five high elevation MCCP Sites from May to October during 1987.

Site	Month	Number of Episodes	Max. Duration of Episodes (hrs)	Max. Conc. During the Episodes (ppb)	No. of Episodes Lasting Over Three Days
MS1	May	3	25	98	0
	Jun	2	32	102	0
	Jul	2	19	96	0
	Aug	2	51	102	0
	Sep	1	8	79	0
	Oct	0	0	--	0
WF1	May	4	17	98	0
	Jun	2	24	94	0
	Jul	2	24	104	0
	Aug	1	93	97	1
	Sep	1	8	89	0
	Oct	0	0	--	0
SH1	May	2	43	86	0
	Jun	5	16	94	0
	Jul	4	22	99	0
	Aug	1	11	84	0
	Sep	1	31	--	0
	Oct	0	0	--	0
WT1	May	3	67	99	0
	Jun	8	77	107	1
	Jul	5	141	124	1
	Aug	4	80	107	2
	Sep	5	58	96	0
	Oct	3	28	95	0
MM1	May	0	0	--	0
	Jun	3	56	93	0
	Jul	2	9	90	0
	Aug	3	31	105	0
	Sep	0	0	--	0
	Oct	0	0	--	0

Table 2. Number and duration of ozone episodes at the five high elevation MCCP Sites from May to October during 1988.

Site	Month	Number of Episodes	Max. Duration of Episodes (hrs)	Max. Conc. During the Episodes (ppb)	No. of Episodes Lasting Over Three Days
MS1	May	0	0	--	0
	Jun	3	73	127	1
	Jul	4	91	117	1
	Aug	4	28	94	0
	Sep	2	10	82	0
	Oct	0	0	--	0
WF1	May	0	0	--	0
	Jun	3	89	135	1
	Jul	4	122	133	1
	Aug	5	45	109	1
	Sep	2	43	94	0
	Oct	0	0	0	0
SH1	May	2	107	110	1
	Jun	5	75	135	1
	Jul	4	123	140	1
	Aug	2	39	97	0
	Sep	0	0	--	0
	Oct	0	0	--	0
WT1	May	5	128	113	1
	Jun	9	98	121	3
	Jul	5	121	163	1
	Aug	4	24	102	0
	Sep	0	0	--	0
	Oct	0	0	--	0
MM1	May	5	165	118	1
	Jun	7	153	123	3
	Jul	4	108	151	1
	Aug	5	26	107	0
	Sep	2	11	85	0
	Oct	0	0	--	0

Table 3. Summary of monthly averaged meteorological data at five high elevation MCCP sites, from May to October, 1987.

Site	Month	Temp. (°C)	Rel. Hum. (%)	Tot. Precip. (mm)	Wind Speed (m/s)	Solar Rad. (W/m^2)	Pressure (mb)
MS1	May	9.9	66.2	30.2	4.6	227	908
	Jun	14.1	77.4	163.8	4.7	197	905
	Jul	18.1*	80.9*	--	3.4*	210	909*
	Aug	14.7	77.3	128.5	4.1	209	908
	Sep	10.9	84.6	141	4.7	126	907
	Oct	4.8	76.7	46.7	5.3	110	905
WF1	May	15.8	86.1	0	12.8	190	850
	Jun	11.1	80.8	40.9	9.3	190	846
	Jul	13.3	85.5	66.8	8.2	203	849
	Aug	11.5	80.1	23.4	7.6	184	855
	Sep	6.2*	89.8*	3	10.4*	101*	853*
	Oct	-0.5	82.9	1.1	8.9*	92.1	849
SH1	May	15.1	64.6	154.2	4.1	230	906
	Jun	19.4	68.2	91.4	4.1	259	904
	Jul	21.8*	69.9*	49	3.7	240	906
	Aug	20.3	69.4	40.6	4.2	228	906
	Sep	16.7	75.2*	266	4.4	155	905
	Oct	8.2	59.3	30.5	5.3	167	905
WT1	May	12.5	81.2	93.1	2.3	226	836
	Jun	14.4	85.2	153	2.5	228	836
	Jul	16.5	82.3	66.1	1.9	235	838
	Aug	15.9	85.6	57.7	3.1	194	838
	Sep	13.4	87.3	85.1	3.6	151	836
	Oct	4.7*	65.2*	23.6*	3.1	175	824
MM1	May	12.8	90.2	79.2	4.2	163	810
	Jun	13.3	84.4	145	6.5	231	809
	Jul	15.1	84.4	51.3	5.3	--	811
	Aug	14.6	88.1	47.2	6.5	--	810
	Sep	10.3	90.8	307	6.6	--	807
	Oct	4.8	60.7	3.3	7.4	--	805

-- No Data * Data Recovery < 50%

Table 4. Summary of monthly averaged meteorological data at five high elevation MCCP sites, from May to October, 1988.

Site	Month	Temp. (°C)	Rel. Hum. (%)	Tot. Precip. (mm)	Wind Speed (m/s)	Solar Rad. (W/m^2)	Pressure (mb)
MS1	May	--	--	--	--	--	--
	Jun	14.1*	61.6*	26.4	4.9*	260*	904
	Jul	18.9	74.9	68.8*	3.3	226	910
	Aug	17.1	82.6	140	4.1	225	909
	Sep	10.8	79.3	51.8	5	152	909
	Oct	4.2	86.1	9.1	4.6	65.9	908
WF1	May	11.7	67.5	--	9.9	247	848
	Jun	7.3*	72.1*	--	9.7*	248*	844
	Jul	14.6*	81.6*	--	7.6	175*	849
	Aug	12.8	89.1	--	8.9	159	847
	Sep	6.6	83.1*	--	10.7	130	845
	Oct	-0.2	91.7	--	7.8	46.7	842
SH1	May	13.7	72.1	218	4.2	220	903
	Jun	17.4	66.2	41.1	4.3	265	905
	Jul	21.6	69.1	66.5	3.6	234	908
	Aug	21.1	72.7	74.9	4.1	219	907
	Sep	14.9	79.3	66.1	3.9	181	908
	Oct	6.4	64.3	5.8	4.8	145	904
WT1	May	9.9	67.8	78.2	2.8	247	833
	Jun	14.1	69.1	63.5	2.2	292	836
	Jul	16.6	75.9	103	2.5	231	839
	Aug	16.8	81.1	95.8	2.9	217	838
	Sep	12.5	91.2	143	3.3	148	837
	Oct	2.9	71.4*	83.1	--	149	831
MM1	May	10.8	71.4	26.9	5.6	301*	806
	Jun	13.6	73.3	36.8	5.8	356	809
	Jul	14.8	84.2	96.8	5.5	317*	811
	Aug	15.2*	88.1*	105*	5.6*	286*	810*
	Sep	12.1*	88.5*	145*	6.5*	270*	809*
	Oct	--	--	--	--	--	--

-- No Data * Data Recovery < 50%

During the 1987 field season at the northern sites, there were 12 episodes at (MS1), Mt. Moosilauke, NH; and 10 at (WF1), Whiteface Mountain, NY, lasting 8 to 93 hours. The maximum ozone concentrations were 102 ppbv at MS1 and 104 ppbv at WF1. At the southern sites, there were 13 episodes at (SH1), Shenandoah Park, VA; 28 at (WT1), Whitetop Mountain, VA, and 11 at (MM1), Mt. Mitchell, NC, lasting from 9 to 141 hours. The maximum one hour averaged ozone concentrations were 99 ppbv at SH1, 124 ppbv at WT1 and 105 ppbv at MM1. Most ozone episodes occurred in late May, June and July. Table 3 suggests these months had lower mean wind speeds, higher temperatures, lower relative humidities and higher solar radiation than August, September and October, for most sites.

The 1988 season in the Eastern U.S. was characterized by above normal temperatures, and below normal cloud cover and precipitation. These conditions were most notable during June and July (Table 4). Temperatures were well above normal in July for most of the eastern half of the U.S. (Mohnen et al, 1990). In 1988 there were also more frequent occurrences of ozone levels above 70 ppbv than 1987. The duration of the high ozone concentrations was also greater during the 1988 field season (> 50 ppbv 76% of the time, and > 120 ppbv 1.6% of the time). Analysis (Curran, 1989) suggests that the U.S. national average for ozone concentration was 14% higher in the summer of 1988 than the average for 1987.

There were 13 episodes at MS1, and 14 at WF1 (Table 2). The maximum ozone levels were 127 ppbv at MS1, and 135 ppbv at WF1 during those episodes. For the southern sites, there were 13 episodes at SH1; 23 at WT1; and 23 at MM1. The maximum hourly ozone concentrations were 140 ppbv at SH1, 164 ppbv at WT1, and 151 ppbv at MM1. The highest ozone concentrations at all the sites are observed during the first half of the summer, with lower concentrations and lowest episodes observed during September and October. At the Northern Sites (WF1 and MS1) ozone levels tend to decrease from May to October with the maximum monthly averaged value in May (or June if data are not available in May), while at the Southern Sites (SH1, WT1, and MM1) the ozone concentrations were increasing from late spring to the maximum monthly average in early summer and then decreasing through September and October.

Several studies (Vukovich et al; 1977; Wolff et al., 1977, 1979, 1980; Wolff and Lioy, 1980) have shown that as a clean high pressure Canadian air mass moves over the midwestern and eastern United States, it becomes a polluted air mass. High pressure areas characterized by slow movement, subsidence inversions, and minimal cloudiness are conducive to ozone formation. These synoptic scale conditions may persist for several days in the summertime over the eastern U.S.

Two such situations, where elevated and persistent ozone concentrations were, recorded at the MCCP high elevation sites, are analyzed here. The episodes examined occurred during (a) June 13 - 18, 1988; and (b) July 4 - 11, 1988. Synoptic features, air flow patterns and trajectories were examined at the 850 mb pressure level (~1.5 km above MSL) because the five monitoring sites are close to this level and 850 millibar (mb) data are readily available.
(a) The June 13 - 18, 1988 Episode: By the morning of the June 13, a high pressure system, which moved out of Canada through the Mid-west to the Southeast, prevailed over West Virginia, Virginia, North Carolina and Kentucky. Under the influence of this high pressure system, ozone concentrations increased in the afternoon associated with the increase of pressure at all five sites [Figure 2 (a) and Figure 3 (a) - (e)], although the northern sites were located at the border between the high pressure and a weak trough in the Northeast at 1200 VCT (0800 EST). At the beginning of the event, relative humidities were below 60% at Whiteface Mountain, Mt. Moosilauke and Shenandoah Park, and below 70% at Mt. Mitchell. During June 13 - 15, the high pressure system became stationary over the southeast and the Gulf States. Wind speeds were less than 6 m/s at the southern sites, however, they were relatively higher at the northern sites especially at Whiteface Mountain. The daytime maximum temperatures were higher than that of non-event day at all sites. Whiteface Mountain experienced the maximum

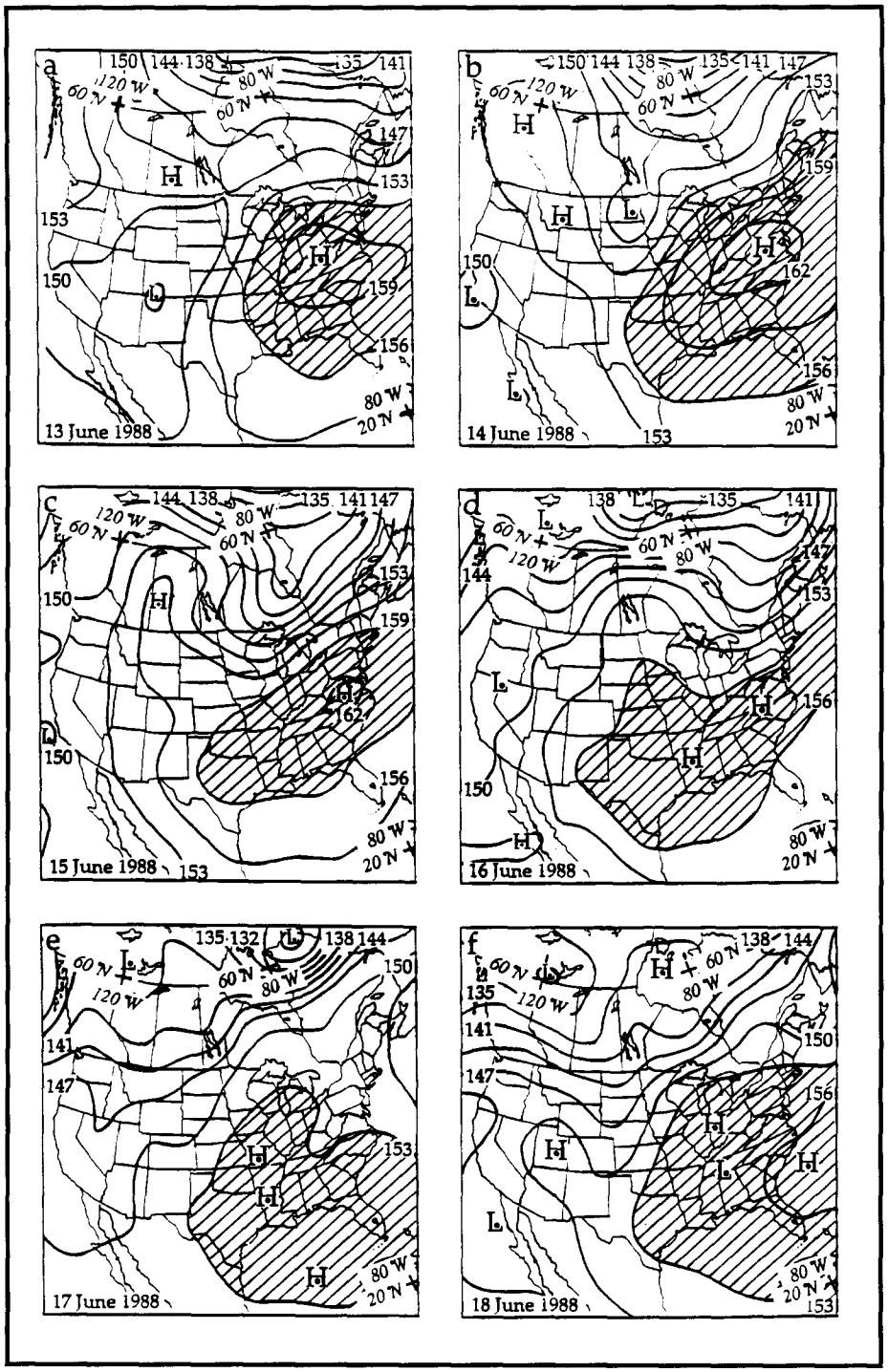

Figure 2: Height decameter (dm) of the 850 millibar (mb) level at 1200 UTC for the period June 13-18, 1988. The shaded areas indicate the high pressure systems (H).

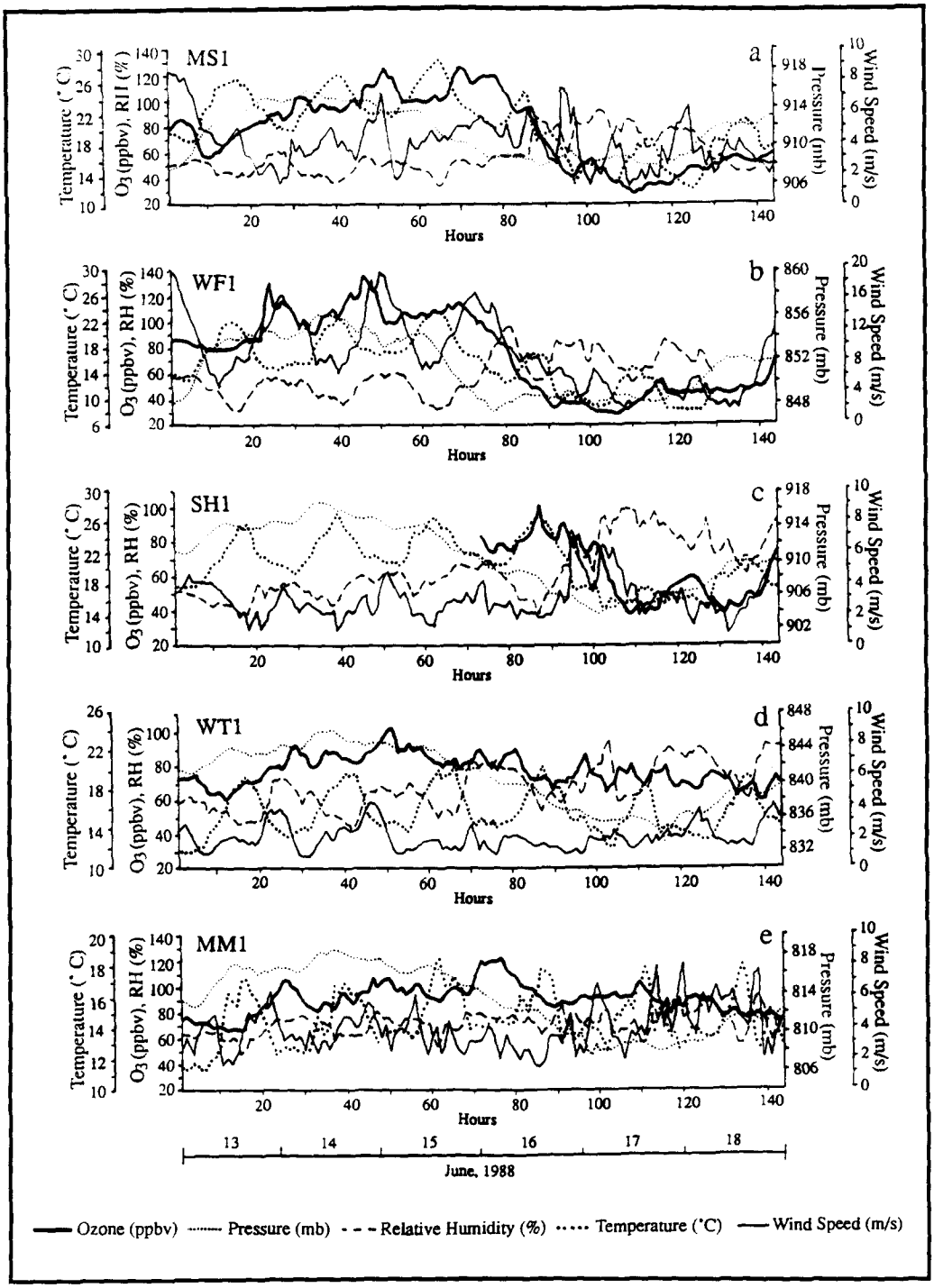

Figure 3: Hourly averaged ozone concentrations, ambient pressures, relative humidity, temperature and wind speed from June 13 - 18, 1988 at (a) Mt. Moosilauke, (b) Whiteface Mountain, (c) Shenandoah Park, (d) Whitetop Mountain, and (e) Mt. Mitchell.

ozone concentration (130 ppbv) in the early morning of June 15 (Figure 3). Apparently, the pressure measured at all the sites began to decline in the afternoon of June 15. Coincident with this decline, however, ozone levels reached the maximum value of 127 ppbv at 2100 EST of June 15 at Mt. Moosilauke, and 123 ppbv at 0400 EST of June 16 at Mt. Mitchell. The northern sites were influenced by a trough in the morning, consequently, the ozone concentration declined to ~ 40 ppbv at Mt. Moosilauke and Whiteface Mountain. At the same time, the high pressure system still influenced the southern sites as shown in Figure 2 (d). On June 17 and 18, the high pressure system weakened and the ozone concentration dropped below 70 ppbv in the morning of June 17th at Shenandoah Park, and were around 70 ppbv at Whitetop Mountain and Mt. Mitchell on June 18th. During this episode, ozone concentrations ≥ 70 ppbv lasted 73 hours at Mt. Moosilauke, 89 hours at Whiteface Mountain, 98 hours at Whitetop Mountain, and 129 hours at Mt. Mitchell. The ozone data are not available at Shenandoah during June 13 - 15.

Back trajectories (72 hrs.) at 850 mb, when ozone maxima occurred during this episode, are given in Figure 4. Air mass sampled at the northern sites passed through the midwestern states, which are believed to be high NO_x emission areas (Saeger et al., 1989), to the sites with longer mean displacements due to the high wind speeds. This may suggest that the role of transport of high ozone concentration and/or its precursors to the sites may have been more significant than that of mesoscale ozone production. However, very short 72 hour air flow distances were observed at Whitetop Mountain and Mt. Mitchell sites. It is noted from Figure 2 that Whitetop and Mt. Mitchell were close to the high pressure center. The air mass was stagnant for 3-5 days in this region. Therefore, high ozone concentration (≥ 120 ppbv) sampled at the southern sites perhaps reflects largely the role of mesoscale

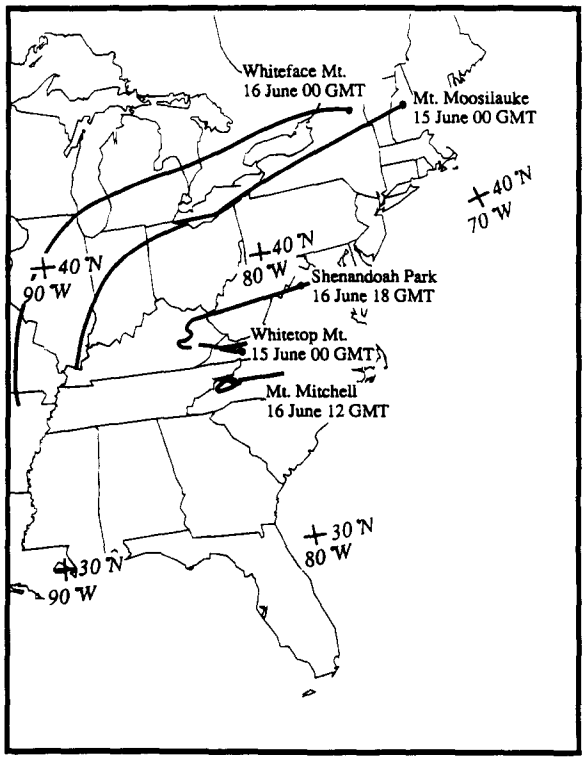

Figure 4: 72 hour back trajectory analysis during June 13 - 18, 1988 at Mt. Moosilauke; Whiteface Mountain; Shenandoah Park; Whitetop Mountain; and Mt. Mitchell.

photochemical production during the formation of this episode. However, other transport and production mechanisms for ozone cannot be ruled out.

(b) The July 4 - 11, 1988 Episode: The synoptic pressure pattern, (Figure 5); and hourly averaged ozone concentrations, site pressure, relative humidity, temperature and wind speed during this episode are illustrated in Figures 6. Relative humidity and temperature data are not available at Whiteface Mountain between July 7-11. Unlike previous episodes, a high pressure system moved from the Northeast to the Southeast on July 4 so that the northern sites first experienced the ozone episodes. Ozone concentrations were recorded above 70 ppbv in the evening at Mt. Moosilauke and Whiteface Mountain while the ozone levels at the southern sites were below 70 ppbv. As the high pressure system moved southward, ozone concentrations measured at southern sites were above 70 ppbv in the evening of July 5. The high pressure system became stationary and covered most of the eastern United States during July 6 - 8 as shown in Figure 5. Mt. Moosilauke had a peak ozone concentration of 116 ppbv at 0600 EST July 6, and the next day a peak ozone concentration of 129 ppbv occurred at Whiteface Mountain at 0500 EST. Ozone levels in excess of 100 ppbv were dominant at the southern sites from July 7 - 9 during the development of the high pressure system. Ozone concentration $\geq$ 120 ppbv lasted 11 hours with a 140 ppbv maximum value at 2300 EST of July 7 at Shenandoah Park. Air mass containing high ozone transported from north to south by anticyclonic circulation present over the eastern United States and the buildup of ozone within the high pressure system continued (Figure 6). By the morning of July 8, a maximum ozone concentration of 163 ppbv occurred at 0500 EST at Whitetop Mountain. The maximum one hour averaged ozone concentration at Mt. Mitchell of 151 ppbv occurred at 0500 EST on the morning of July 9. Ozone concentration $\geq$ 120 ppbv lasted 36 hours at Whitetop Mountain, and 46 hours at Mt. Mitchell (Figure 7) in conjunction with higher temperature (~ 20°C), lower wind speed ($\leq$ 8 m/s), and dry condition (~ 70%)during this episode (Figure 6). By July 10 the high pressure system weakened and moved eastward off the Atlantic coast. Ozone concentrations, dropped below 70 ppbv at all the sites on July 11.

Back trajectories (Figure 8) during this episode shows that the high ozone days ($\geq$ 100 ppbv) at the northern sites were associated with westerly flow, while the high ozone days ($\geq$ 120 ppbv) at southern sites were associated with north or northwest flow pattern. Air mass sampled at Whitetop Mountain and Mt. Mitchell sites passed through upper Ohio Valley, and with shorter (~72-hour) air flow distances. These conditions are conducive to the production of ozone concentrations greater than 120 ppbv.

In general, these two episodes in 1988 were associated with slow moving high pressure systems. During these episodes, temperatures were about 4°C warmer during the episodes than a typical non-event day, relative humidities were less than 70 %, while wind speeds were generally $\leq$ 8 m/s except for that at the Whiteface Mountain site. These conditions were conducive to the photochemical formation of ozone during daytime hours.

A statistical analysis was performed to investigate the relationship between ozone and other meteorological variables for the case studies. Table 5 is a correlation matrix obtained from hourly averaged day time (0800 - 2000 EST) values of ozone, barometric pressure, temperature, relative humidity, solar radiation and wind speed for the period, May-October, 1988. The results indicate that ozone increases with rising temperature, solar radiation and higher pressure. Ozone was also found to be negatively correlated to relative humidity and wind speed. The positive correlation of ozone with temperature and solar radiation has been known for some time. The negative correlation of ozone with relative humidity and wind speed can be explained by the scavenging and/or deposition of ozone at higher relative humidities and low wind speeds, which are generally suggestive of stagnant conditions (Liu et al., 1980; Kelly et al., 1984; Levy et al., 1985).

Low wind speed, warm temperature and low relative humidity conditions, which are generally associated with the passage of a synoptic high pressure system, result in high ozone concentrations as these conditions are

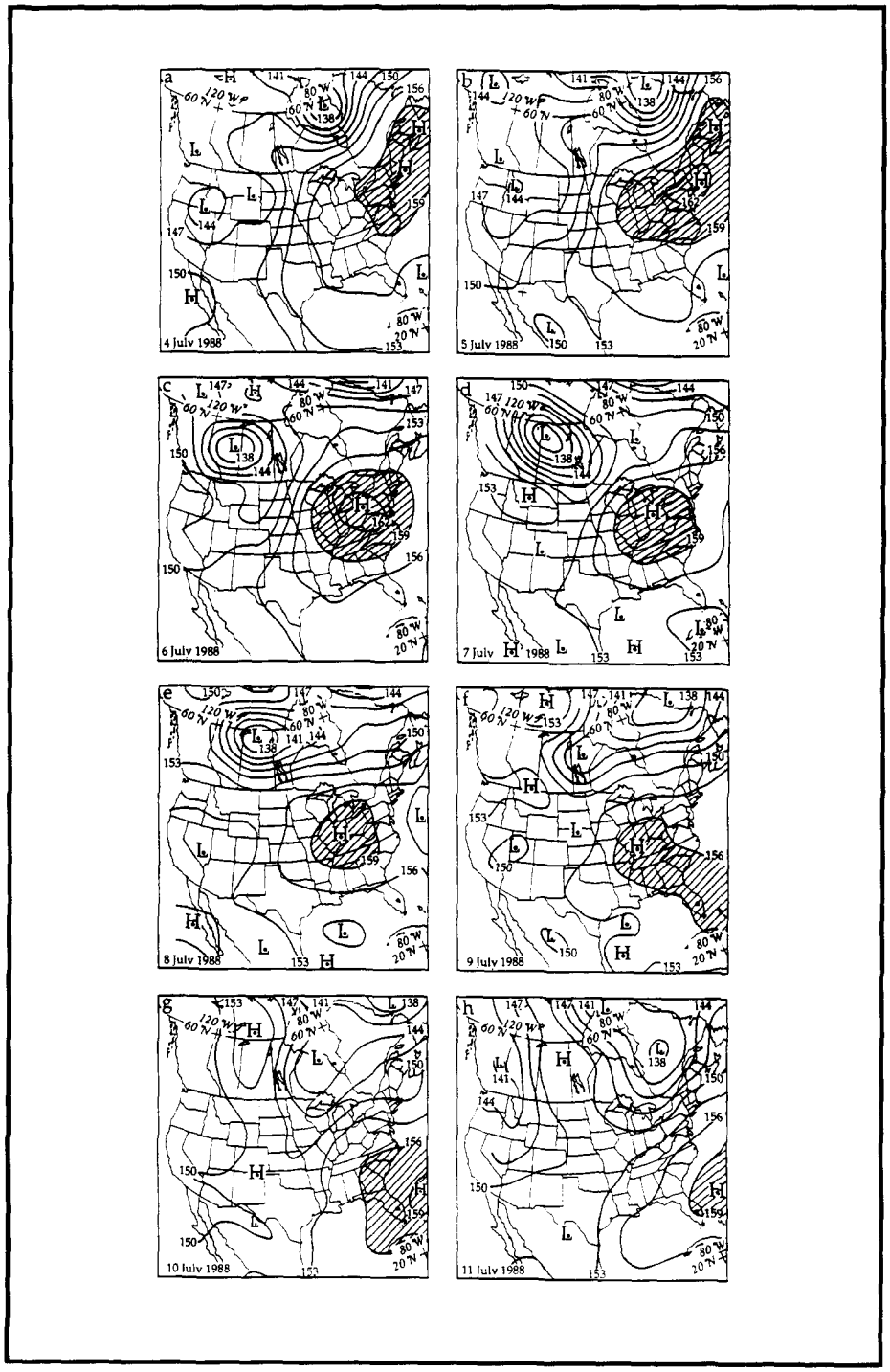

Figure 5: Height decameter (dm) of the 850 millibar (mb) level at 1200 UTC for the period July 4-11, 1988. The shaded areas indicate the high pressure systems (H).

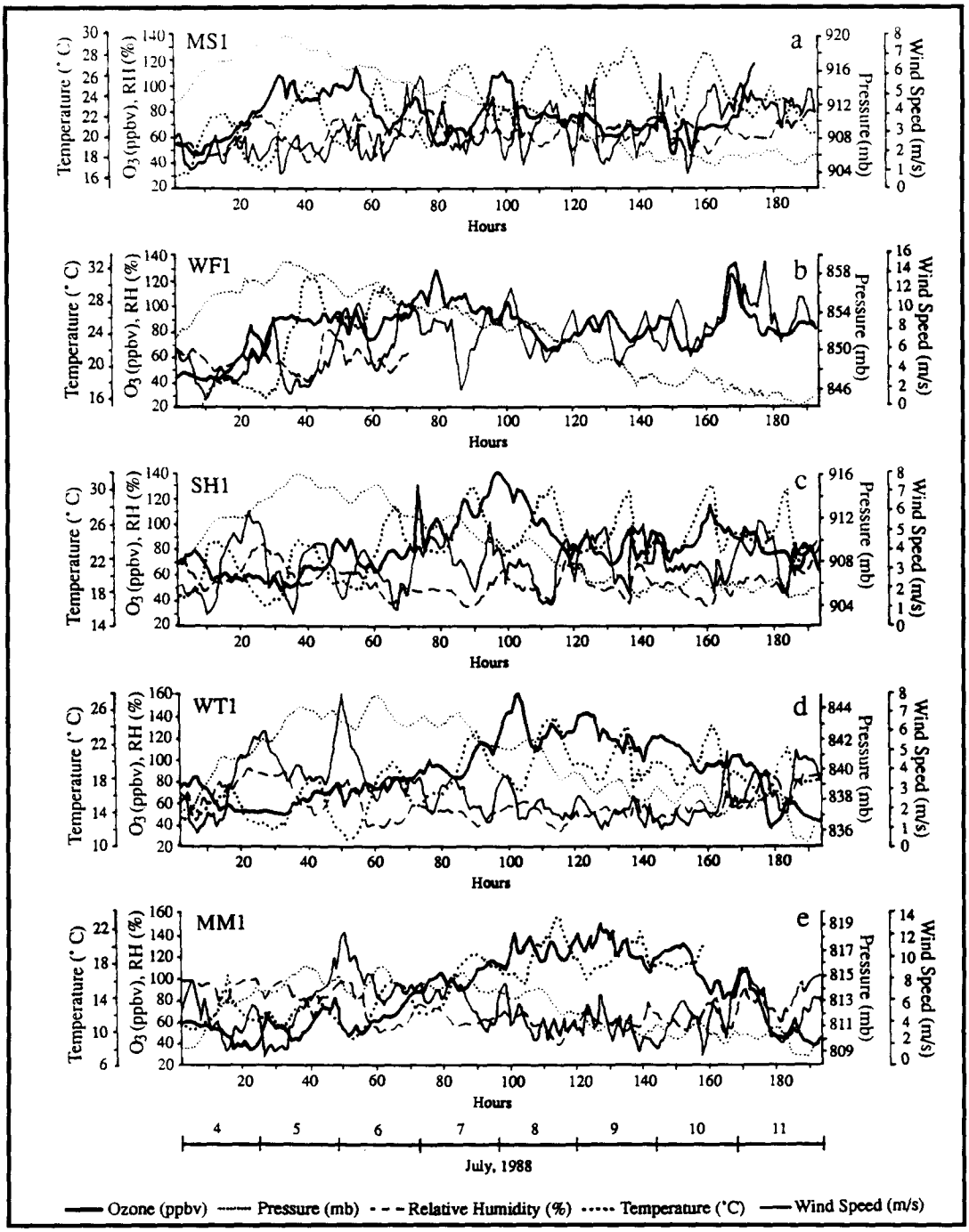

Figure 6: Hourly averaged ozone concentrations, ambient pressures, relative humidity, temperature and wind speed from July 4 - 11, 1988 at (a) Mt. Moosilauke, (b) Whiteface Mountain, (c) Shenandoah Park, (d) Whitetop Mountain, and (e) Mt. Mitchell.

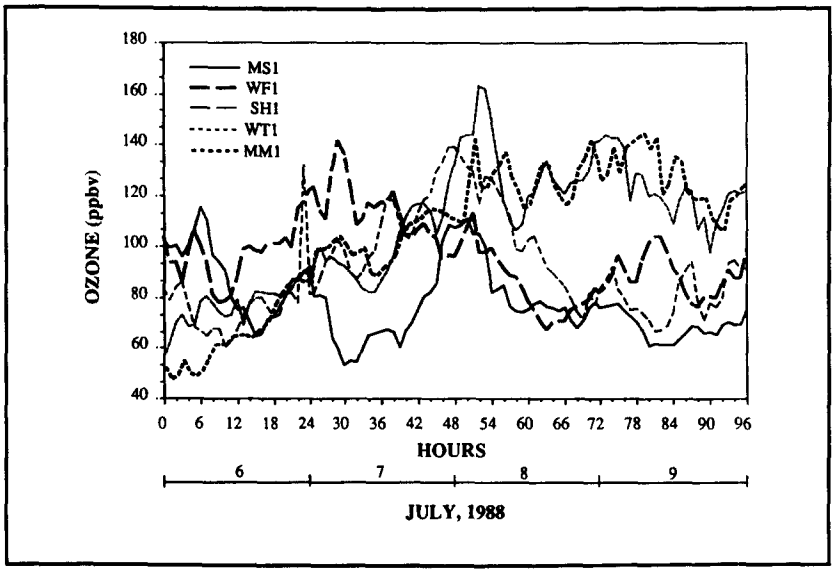

Figure 7: Hourly averaged ozone concentrations for the episode days at the five MCCP sites during July 6-9, 1988.

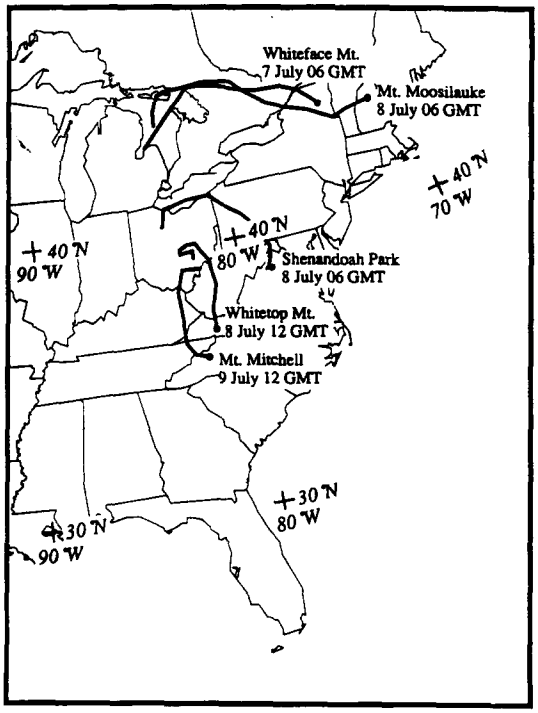

Figure 8: 72 hour back trajectory analysis during July 4 - 11, 1988 at Mt. Moosilauke; Whiteface Mountain; Shenandoah Park; Whitetop Mountain; and Mt. Mitchell.

conducive to the photochemical formation of ozone during the day time hours (Aneja et al., 1991). This has been found to be the case in our study also. At all the five high elevation sites ozone events were found to be accompanied by higher than average pressure, solar radiation, and temperature; and lower than average relative humidity and wind speed (Table 6). The difference in the mean values of pressure, temperature, solar radiation, relative humidity and wind speed were found to be significant at all the five high elevation sites (t-test) at the 95% confidence level for the data set corresponding to ozone events and ozone non-events hourly averaged values.

Aneja et al. (1991), have explored the relationship between ozone episodes and synoptic weather and have found that at the Mt. Mitchell Site (MM1), increasing ozone concentrations preferentially occurred on the leading edge of ridges of high pressure systems, while sharp decreases in ozone concentrations occurred with pressure troughs. In this study a comprehensive statistical analysis is performed to support the association between high ozone and high pressure systems (statistically significant (t statistic) at the > 95% level). Table 7 provides ozone events (O_3 conc. $\geq$ 70 ppbv) related to higher than average pressure conditions in the atmosphere for the measurement season. At all the five sites, ozone events were found to be often accompanied by higher than average pressure ~87% of the time at WF1, ~83% at MS1, ~76% at SH1, ~67% at WT1, and ~60% at MM1. The data set for ozone and pressure were then considered for only the two episodes (June 13-18 and July 4-11, 1988). An examination of Table 8 reveals that higher than average pressure for the season during the episode was found ~93% of the period at WF1, ~77% at MS1, ~83% at SH1, ~90% at WT1, and ~91% at MM1. Out of these periods, ozone events ($O_3 \geq 70$ ppbv) were observed ~74% of the times at WF1, ~73% at MS1, ~71% at SH1, ~81% at WT1, and ~72% at MM1. These results are similar to earlier findings of Vukovich et al. (1977) and Aneja et al. (1991) that higher ozone concentrations are accompanied by higher pressures.

It was also observed during the two episodes that ozone was negatively correlated to relative humidity r = -0.60, -0.56, -0.76, -0.64 and -0.60 respectively at the five sites WF1, MS1, SH1, WT1 and MM1 when only the day time (0800 to 2000) values were considered. Comparison of these results with the values in Table 5 indicates that the absolute values of 'r' is higher during the episodes. The positive correlations observed between ozone and temperature during the two episodes were also found to be higher (with the exceptions of sites at MS1 and WF1) when compared with values for the entire season in Table 5; suggesting that ozone formation was enhanced during the episodes by increasing temperature and decreasing relative humidity.

4. THE RELATION BETWEEN OZONE AND NITROGEN OXIDES

For determining the photochemistry activity within the local areas, nitrogen oxides (NO_x) were also measured at the Mt. Mitchell site using a photolysis/chemiluminescence detector. NO_x levels at remote locations in the eastern United States are frequently below 2 ppbv (Fehsenfeld, et al., 1988, Aneja et al., 1991), and it is generally believed that production of ozone is NO_x limited in rural areas (Liu et al., 1987). NO_x concentrations as well as ozone concentrations at Mt. Mitchell during the two episodes discussed above are given in Figures 9 and 10. Concentrations of NO_x below 2 ppbv were observed about 72% of time during May-September in 1988 at Mt. Mitchell (Aneja et al., 1991). However, NO_x levels during some high ozone episodes reached up to ~ 10 ppbv indicating the site to be dominated by anthropogenic NO_x sources during meteorological conditions favorable for contamination of the sampled air masses.

It is believed that NO_x can not be transported for a very long distance due to its short lifetime. However, the atmospheric NO_x levels in the rural and remote troposphere can be strongly influenced by PAN during the photochemical episodes. The longer lifetime of PAN in the colder regions can allow PAN to act as an effective

Table 5. Correlation matrices of ozone and meteorological variables for the five high elevation MCCP sites for hourly averaged day time (0800 - 2000 EST) values during May to October, 1988.

SITE = WF1

Variable	Ozone	Press.	Temp.	RH	SR	WS
Ozone	1.00					
Press.	0.45	1.00				
Temp.	0.72	0.53	1.00			
RH	-0.38	-0.38	-0.37	1.00		
SR	0.15	0.25	0.28	-0.55	1.00	
WS	-0.22	-0.30	-0.02	0.16	0.06	1.00

SITE = MS1

Variable	Ozone	Press.	Temp.	RH	SR	WS
Ozone	1.00					
Press.	0.25	1.00				
Temp.	0.67	0.29	1.00			
RH	-0.35	-0.20	-0.38	1.00		
SR	0.19	0.13	0.42	-0.59	1.00	
WS	-0.17	-0.50	-0.33	0.12	0.03	1.00

SITE = SH1

Variable	Ozone	Press.	Temp.	RH	SR	WS
Ozone	1.00					
Press.	0.18	1.00				
Temp.	0.70	0.31	1.00			
RH	-0.41	-0.20	-0.24	1.00		
SR	0.26	0.22	0.36	-0.50	1.00	
WS	-0.21	-0.36	-0.29	0.12	-0.17	1.00

SITE = WT1

Variable	Ozone	Press.	Temp.	RH	SR	WS
Ozone	1.00					
Press.	0.11	1.00				
Temp.	0.37	0.55	1.00			
RH	-0.59	-0.06	-0.27	1.00		
SR	0.29	0.20	0.31	-0.57	1.00	
WS	-0.20	-0.10	-0.21	0.30	-0.18	1.00

SITE = MM1

Variable	Ozone	Press.	Temp.	RH	SR	WS
Ozone	1.00					
Press.	0.03	1.00				
Temp.	0.34	0.52	1.00			
RH	-0.48	-0.05	-0.31	1.00		
SR	0.16	0.15	0.29	-0.49	1.00	
WS	0.05	-0.42	-0.35	0.35	-0.14	1.00

Table 6. Mean of hourly averaged values of ozone concentrations and meteorological variables at the five high elevation MCCP Sites for ozone events, ozone nonevents, and overall day time (0800 - 2000 EST) conditions during May-October 1988.

Site	Type	Ozone (ppbv)	Wind Speed (m/s)	Rel. Hum. (%)	Temp. (°C)	Pressure (mb)	Solar Rad. (W/m^2)
WF1	Event[a]	84.66	8.19	64.69	19.78	850.81	371.31
	Nonevent[b]	41.55	8.03	81.38	8.95	845.13	277.24
	Overall[c]	48.96	8.06	79.53	10.15	845.96	288.08
MS1	Event	83.96	3.73	62.88	23.11	912.10	387.25
	Nonevent	41.14	4.32	74.62	14.04	907.72	314.88
	Overall	46.12	3.98	73.26	14.98	908.17	322.42
SH1	Event	84.60	3.43	53.47	24.93	907.46	486.40
	Nonevent	42.54	3.91	68.82	15.87	905.76	361.60
	Overall	49.13	3.88	66.80	17.05	905.99	377.73
WT1	Event	83.59	2.25	59.0	17.85	837.59	512.13
	Nonevent	52.15	2.65	78.69	14.20	836.57	368.95
	Overall	61.00	2.50	73.43	15.13	836.87	403.90
MM1	Event	85.98	4.83	70.43	15.76	809.60	376.85
	Nonevent	52.44	5.36	82.37	13.80	809.30	326.57
	Overall	64.78	4.82	78.13	14.48	809.41	342.86

[a] Event = The data set sorted by $O_3 \geq 70$ ppbv and time 0800 - 2000 EST.

[b] Nonevent = The data set sorted by $O_3 \leq 70$ ppbv and time 0800 - 2000 EST.

[c] Overall = The entire data set for the time period 0800 - 2000 EST.

Table 7. Relationship of ozone events to higher than average pressure for the season at the five high elevation MCCP sites during May-October 1988.

Site	No. of Hourly Averaged Values for $O_3 \geq 70$ ppbv	No. of Hourly Averaged Values for $O_3 \geq 70$ ppbv and Pressure Above the Average Value for the Season May-October 1988
WF1	568	494
MS1	399	331
SH1	612	468
WT1	1005	674
MM1	1179	708

Table 8. Duration of high pressure and its relationship with ozone events ($O_3 \geq 70$ ppbv) during the two episodes (June 13-June 18 and July 4-July 11, 1988) at the five high elevation MCCP sites.

Site	Total Number of Hours of Data Capture During the Two Episodes	Total Number of Hours When the Pressure was Above Average*	Total Number of Hours when Both Ozone Concentrations ≥ 70 ppbv, and Pressure Being Above Average*
WF1	312	290	215
MS1	277	238	162
SH1	236	259	130
WT1	311	279	225
MM1	311	284	203

*Average is computed for the measurement season (May to October).

reservoir agent in transferring NO_x from source regions to the remote atmosphere (Fehsenfeld et al., 1988). This may be a possible reason for observed high NOx concentrations at Mt. Mitchell.

In general, during the two episodes at MM1, ozone concentration increased with increasing NO_x concentrations during the daytime hours at Mt. Mitchell (Figures 9 and 10), reflecting the photochemistry activities. NO_x levels generally decrease, with a few exceptions, during nighttime because nighttime chemistry may provide a significant sink for NO_x through the processes involving reactions of NO_3 and N_2O_5 (Parrish et al, 1986). However, the rate of ozone formation depends on the concentration of NMHC, as well as ratio of NMHC/NO_x in a non-linear manner. Ozone concentrations sometimes decreased with the increase of NO_x during the daytime. For example, when NO_x concentration reached to 4 ppbv at 12:00 EST on June 15, the ozone concentration dropped to below 90 ppbv (Figure 9).

5. SUMMARY AND CONCLUSIONS

Based on 850 mb pressure back trajectory analyses, it is found that high ozone concentrations at the MCCP sites are strongly correlated to passage of high pressure system and other meteorological conditions, including: solar radiation, temperature, wind speed, wind direction, and relative humidity. Ozone episodes, defined as concentrations equal to or greater than 70 ppbv lasting 8 hours or more, were more frequent and of longer duration during the summer months at all sites, especially in 1988. In general high ozone episodes occurred during the passage of synoptic high pressure system, associated with low wind speed (< 8m/s), warm temperature (~3°C higher than normal), and low relative humidity (< 70%). The air parcels in high pressure systems undergo stagnation, producing conditions favorable to ozone formation. It is noted that high ozone concentrations preferentially occurred with winds from west to southwest at Mt. Moosilauke and Whiteface Mountain (two northern sites), and with winds from west to northwest at Mt. Mitchell (a southern site), suggesting that higher ozone concentrations or ozone precursors are being transported to those sites from the mid-western states, with further corroboration provided by 72-hour back trajectory analysis.

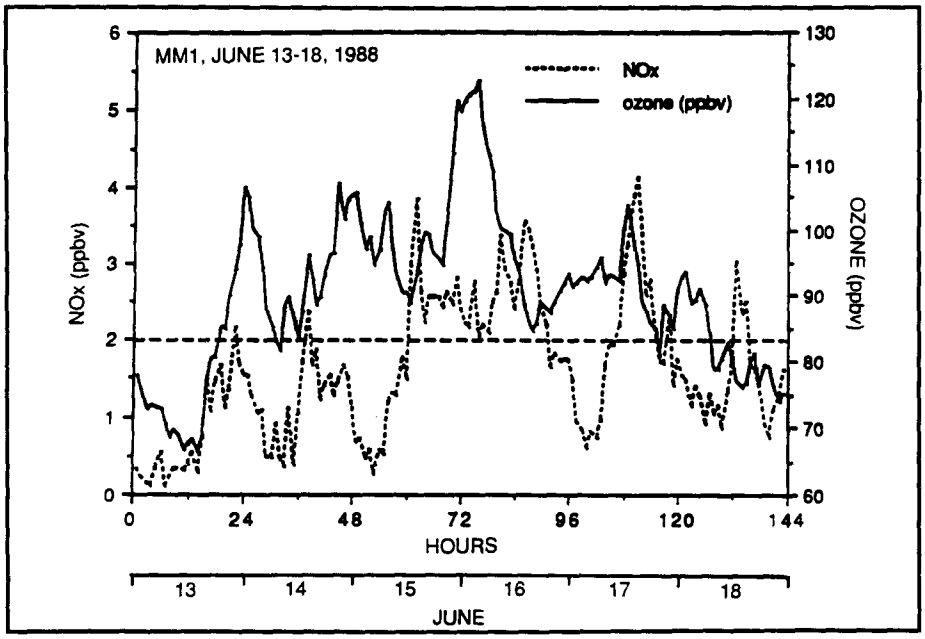

Figure 9: NO_X and Ozone concentration during June 13 - 18, 1988 at the Mt. Mitchell Site. The dotted horizontal line shows the detection limit for the NO_X instrument.

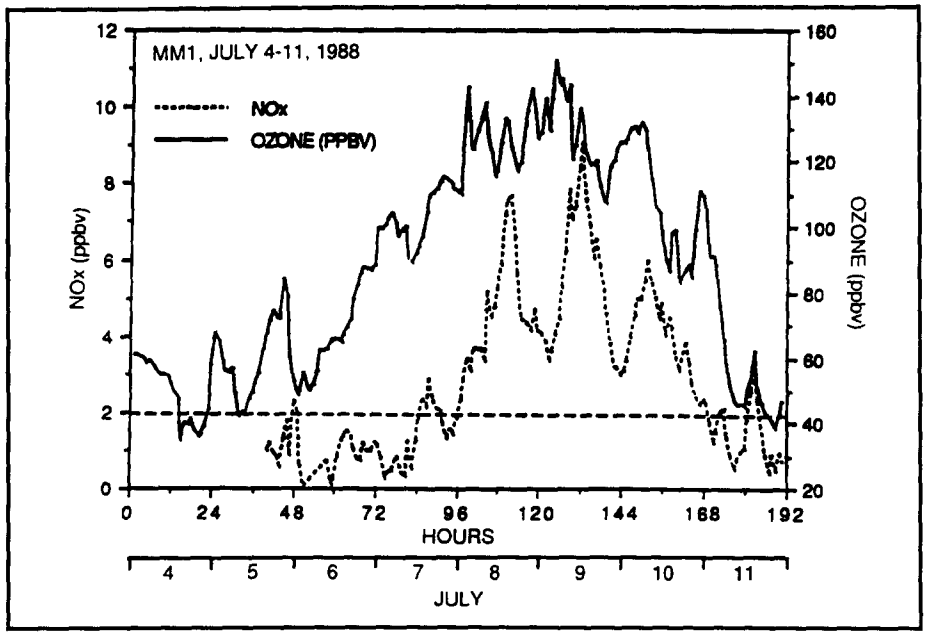

Figure 10: NO_X and Ozone concentration during July 4 - 11, 1988 at the Mt. Mitchell Site. The dotted horizontal line shows the detection limit for the NO_X instrument.

A statistical analysis performed on the data set revealed that the ozone events were accompanied by higher than average pressure, solar radiation, temperature and lower than average relative humidity and wind speed for the season which was found to be significant at the 95% level of confidence. It was also found that ozone events preferentially occurred when the pressure observed at the sites was higher than the average pressure for the season. During the episodes, ozone formation was found to be enhanced by increasing temperature and decreasing relative humidity.

The concentrations of NO_x were higher during the ozone episodes, reflecting the photochemical production of ozone on the regional scale. In general, ozone concentration increased with increasing NO_x concentrations during the daytime hours. However, ozone concentrations sometimes decreased with the increase of NO_x during the daytime at Mt. Mitchell.

An observational based statistical analysis provides an understanding of the physico-chemical processes in the atmosphere. In order to resolve the role of transport and chemical kinetics, simultaneous measurements of ozone and its precursors and meteorological parameters are needed. This will provide important information on future planning of ozone control programs, and in the establishment and evaluation of regional air quality standards.

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DISCLAIMER

The contents of this document do not necessarily reflect the views and policies of the Environmental Protection Agency, nor the views of all members of the Mountain Cloud Chemistry Consortia, nor does mention of trade names or commercial or non-commercial products constitute endorsement or recommendation for use.

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