

# Characterization of Ozone at High Elevation in the Eastern United States: Trends, Seasonal Variations, and Exposure

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Ozone measurements at five high-elevation ( $\geq 1000$  m msl) Mountain Cloud Chemistry Program (MCCP) sites in the eastern United States for the period from May to October 1986-1988 have been analyzed. In order to characterize and compare the exposure to ozone at these sites, several ozone exposure indices are used. The sum of all hourly mean ozone concentrations equal to or greater than 0.07 ppm (SUM07) for 1988 indicates a north-south gradient in ozone exposure: Southeastern sites (Mount Mitchell, North Carolina, 105 parts per million-hours (ppm-h), Whitetop Mountain, Virginia, 85.7 ppm-h, Shenandoah Park, Virginia, 51.6 ppm-h); Northeastern sites (Whiteface Mountain, New York, 49.2 ppm-h, Mount Moosilauke, New Hampshire, 34.2 ppm-h). This shows that forest areas in the southeastern high-elevation sites experienced higher ozone exposure than their northeastern counterparts during the hot and dry 1988 measurement season. Ozone episodes (concentrations greater than 70 ppbv lasting 8 hours or more) were more frequent during the summer months at all sites. This suggests a correlation with the seasonal photochemical cycle and perhaps with local biogenic hydrocarbon emissions. Seasonal analysis suggests that ozone maximum occurs during spring coincident with spring maximum at Mauna Loa, Hawaii and at Alpine stations in Europe, suggestive of an underlying hemispheric phenomena. A reversed diurnal cycle (nighttime maximum) pattern was also observed from May to October at all the five high-elevation sites. Back trajectory analysis, during high-ozone episodes, indicates that most MCCP sites were influenced by urban and industrial sources from the midwestern region of the United States, suggesting large-scale transport patterns.

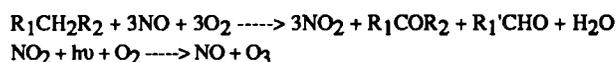
## 1. INTRODUCTION

High-elevation red spruce (*Picea rubens* Sarg.) and Fraser fir (*Abies fraseri* (Pursh.) Poir.) forests in the eastern United States from Maine to North Carolina have shown signs of damage and decline during the past two decades. The trend of decline and dieback of forests is increasingly apparent [Cowling, 1989; Bruck *et al.*, 1989] in the high-elevation forests of the Appalachians. Forest health is influenced by many stress factors e.g., rainfall patterns, high winds, insects, diseases, temperature and competition, [Woodman and Cowling, 1987; Klein and Perkins, 1988], and air pollution is considered to be one of the stress factors being evaluated as a cause of the observed forest decline [Saxena, *et al.*, 1989; Aneja *et al.*, 1990a, b; Claiborn and Aneja, 1991]. In recent years there has been increasing concern in the possible impact of atmospheric acidity [Jacobson *et al.*, 1990] and photochemical oxidants [Winner *et al.*, 1989; Garner *et al.*, 1989] on montane forested ecosystems.

The atmospheric inputs to the forest trees can be through the dry, wet, and cloud deposition processes. Ozone, the most prevalent photochemical oxidant, is thought to be the most important toxic air pollutant affecting forests [Woodman and Cowling, 1987]. However, only recently, ozone characterization at high elevation is beginning to be explored [Fehsenfeld *et al.*, 1983; Janach, 1989], especially in the eastern United States [Aneja *et al.*, 1989, 1991].

As a photochemical air pollutant, ozone is initially generated in the troposphere in the presence of sunlight from the photochemical reactions between ozone precursors nitrogen oxides ( $\text{NO}_x$ ), and nonmethane hydrocarbons (NMHC). Based on the absorption characteristics of the major atmospheric pollutants,  $\text{NO}_2$  is the most efficient

absorber of the fraction of the Sun's UV radiation between 290 and 380 nm [Leighton, 1961]. Thus based on a complex set of photochemical reactions now identified, a general net mechanism for ozone production in the troposphere from the oxidation of a straight-chain alkane (for example) is as follows [Warneck, 1988]:



where,  $\text{R}_1$  and  $\text{R}_2$  are suitable alkyl group, and  $\text{R}_1'$  is an alkyl group containing one carbon atom less than  $\text{R}_1$ . The above net reactions convert one molecule of n-alkane into one molecule of ketone and aldehyde each, and it oxidizes three molecules of NO to  $\text{NO}_2$ . The subsequent photodissociation of  $\text{NO}_2$  is the source of ozone. The complex chemical sequence of reactions is initiated by OH radical which is regenerated so that it can continue the chain reaction.

A number of observers have demonstrated that ozone, in general, is formed near urban and industrial areas with high levels of anthropogenic sources, and the long-range transport of ozone and its precursors from those regions within a high-pressure system may contribute to elevated ozone levels in downwind rural areas [Wolff *et al.*, 1977, 1982; Vukovich *et al.*, 1977; Wolff and Lioy, 1980]. Since the lifetime of ozone in the troposphere is between ~ 1 month [Logan, 1985] and ~ 2 months [Hough and Derwent, 1990], it is possible for ozone to be transported long distances to remote forest areas [Kelly *et al.*, 1984]. On the other hand, the local natural sources may also affect air quality in the forest areas.

Researchers in the past believed that natural hydrocarbons made little contribution to ozone formation in comparison with anthropogenic sources [Abelson, 1988]; however, Chameides *et al.* [1988] have shown that reactive hydrocarbons are also emitted in significant quantities by natural processes. A recent report showed that rural ozone levels were found to equal or exceed urban values for the same

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region [Meagher *et al.*, 1987]. It is now shown that forest trees produce NMHC and that their emission rates depend on the solar intensity, temperature, and other parameters. Consequently, high-ozone levels observed in rural areas may be attributed to both transport of ozone and/or its precursors from urban or industrial areas and photochemical formation from local natural sources.

The atmospheric processes underlying the ozone formation have been characterized for a long time [Liu *et al.*, 1980; Levy *et al.*, 1985; Trainer *et al.*, 1987; Liu *et al.*, 1987; Lindsay *et al.*, 1989]; however, the majority of published ozone data has been limited to lower-elevation sites [Logan, 1989; Aneja *et al.*, 1992]. There are few data on record for ozone behavior in high-elevation environments in the eastern United States [Aneja *et al.*, 1989; 1991] with the exception of measurements at Whiteface Mountain summit, before the inception of the Mountain Cloud Chemistry Program (MCCP) sponsored by U.S. Environmental Protection Agency [Mohnen and Cowling, 1988].

Since 1986, the MCCP has been monitoring ozone levels at five high-altitude locations ( $\geq 1000$  m msl) in the eastern United States selected from 35°N to 45°N to be representatives of the geographic and meteorological variability in this large region. One low-elevation site (Howland, Maine) has been augmented to allow for the evaluation of the impact of elevational gradients.

Red spruce and Fraser fir are the dominant tree species in the five high-elevation monitoring sites. These trees have shown signs of decline in recent years. The concentration of pollutants, the duration of episode, and the length of time between episodes are among the important factors in assessing the adverse impact of pollution on the biosphere. The objectives of this paper are to extend Aneja *et al.* [1991] findings to allow for a regional analysis at high elevations to (1) determine the frequency distribution of ozone and characterize its exposure, (2) determine the north-south gradients of ozone levels based on observations made at five high-elevation MCCP sites in the eastern United States; and (3) study the regional ozone climatology at high elevations in the eastern United States.

## 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, New York; Mount Moosilauke, New Hampshire; Shenandoah Park, Virginia; Whitetop Mountain, Virginia; Mount Mitchell, North Carolina; and one low-elevation sampling site, Howland, Maine (Table 1). Figure 1 illustrates the location of the MCCP sites.

TABLE 1 Description of the MCCP Sites

Site	Elevation, m	Latitude	Longitude
Howland Forest (HF1), Me.	65	45°13'N	68°43'W
Whiteface Mountain (WF1), N. Y.	1483	44°23'N	73°59'W
Mt. Moosilauke (MS1), N. H.	1000	43°59'N	71°48'W
Shenandoah Park (SH1), Va.	1040	38°72'N	78°20'W
Whitetop Mountain (WT1), Va.	1689	36°38'N	81°36'W
Mt. Mitchell (MM1), N. C.	2006	35°44'N	82°16'W

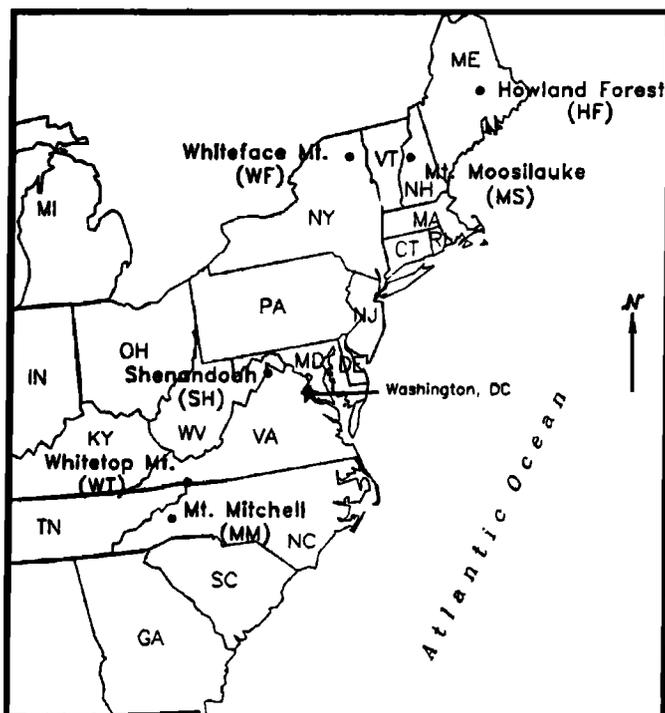


Fig. 1. Map of eastern United States showing the locations of MCCP sites: Howland, Maine (HF); Mount Moosilauke, New Hampshire (MS); Whiteface Mountain, New York (WF); Shenandoah Park, Virginia (SH); Whitetop Mountain, Virginia (WT); and Mt. Mitchell, North Carolina (MM).

At Whiteface, Whitetop, and Mount Mitchell the main sites are located on the summit of mountains, while the main sites at Shenandoah and Moosilauke are along a ridge line. Additionally, sub-sites such as those at Whiteface, Shenandoah Park, and Mount Mitchell are located along the slope of the same mountain.

The northernmost high-elevation site in the network is Whiteface Mountain (WF) (44°23'N, 73°59'W) located in the northeastern Adirondack Mountains in New York, at an elevation of 1483 m. The summit is above the tree line, providing access to regional airflow (site 1). The Whiteface Mountain-Lake Placid Turn sampling site (site 2) is located at 1245 m, adjacent to a balsam fir canopy. A meteorological tower has been installed for routine monitoring.

Mount Moosilauke (MS), New Hampshire (43°59'N, 71°48'W), is one of the most southern peaks of the White Mountains. It is located about 50 km southwest of Mount Washington (1917 m) and about 10 km northeast of the United States Forest Service Hubbard Brook Experimental Forest and Watershed. The forest composition ranges from mixed hardwoods at lower elevations to spruce-fir (about 10% spruce) at midelevations, and pure balsam fir at high elevations. The meteorological station MCCP site at Mount Moosilauke is at ~ 1000 m and is partially shielded from the prevailing westerly winds.

The Shenandoah Park (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. The meteorological towers were erected at three sites in the watershed: site 1 at 1040 m, site 2 at 716 m, and site 3 at 524 m. The tower locations are representative of the surrounding deciduous forest canopy.

The Whitetop Mountain (WT) site (36°38'N, 81°36'W) is located in the Mount Rogers National Recreation Area of the Jefferson National Forest in southwestern Virginia, 6 km southwest of Mount Rogers, the highest peak in Virginia. The Tennessee Valley Authority Whitetop Mountain summit research station (at 1689 m) straddles the main ridge line of the Appalachian range, strategically located to intercept air flow from several directions. In addition to the summit station, other subsites have been established.

The southernmost MCCP site is located at Mount Gibbs in Mount Mitchell State Park (MM), North Carolina (35°44'N, 82°16'W), 1 mile southwest of Mount Mitchell, which is the highest peak in the eastern United States (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. A 16.5-m meteorological tower is installed near Mount Gibbs at 1950 m (site 1); additional gas sampling is also performed at 1775 m (site 2).

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 miles north of Bangor. The forest is spruce with lesser numbers of balsam fir, hemlock, and white pine. A second site is located 2 km west of the first at an elevation of 60 m in an extended spruce-fir stand.

Each of the locations had a meteorological walk-up tower to provide measurements above the forest canopy. The meteorological sensors were mounted on the top of the tower to detect the meteorological parameters such as wind speed and direction, solar radiation, relative humidity, air temperature, and barometric pressure. Ozone measurements, based on ultraviolet absorption technique, were made with a thermo electron corporation ozone analyzer (model 49). The level of detection for this instrument is 2 parts per billion by volume (ppbv), with an accuracy 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 25-35 ppbv. Oxides of nitrogen were measured with a monitor lab model 8448 analyzer, for which the level of detection is 2 ppbv with an accuracy of ± 20% for NO<sub>2</sub> values in the range of 18-22 ppbv, and a precision of ± 5 ppbv for values in the range of 10-22 ppbv. The quality assurance protocols included, in general, weekly zero and span checks. Multipoint calibrations were conducted twice during the measurement

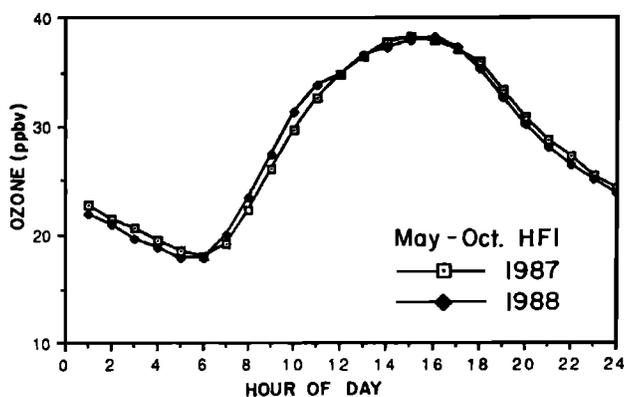


Fig. 2. Mean diurnal variation of ozone concentration from May to October in 1987 and 1988 at the low-elevation Howland Forest (Maine) site.

period. All these data were stored as 1-hour averages in a campbell scientific model 21XL datalogger. All calibrations were based on the National Institute of Science and Technology traceable reference standard.

Although there are some sites monitoring ozone throughout the year (e.g., Whiteface Mountain, New York), we mainly consider the data collected during May through October because elevated ozone concentrations or ozone episodes occurred mostly during this period, and most MCCP sites conducted ozone sampling only during the growing season. For some sites, ozone monitoring ended in late September [e.g., Whitetop Mountain, 1988; Mount Mitchell, 1988]. In 1986 there were limited data collected at Mount

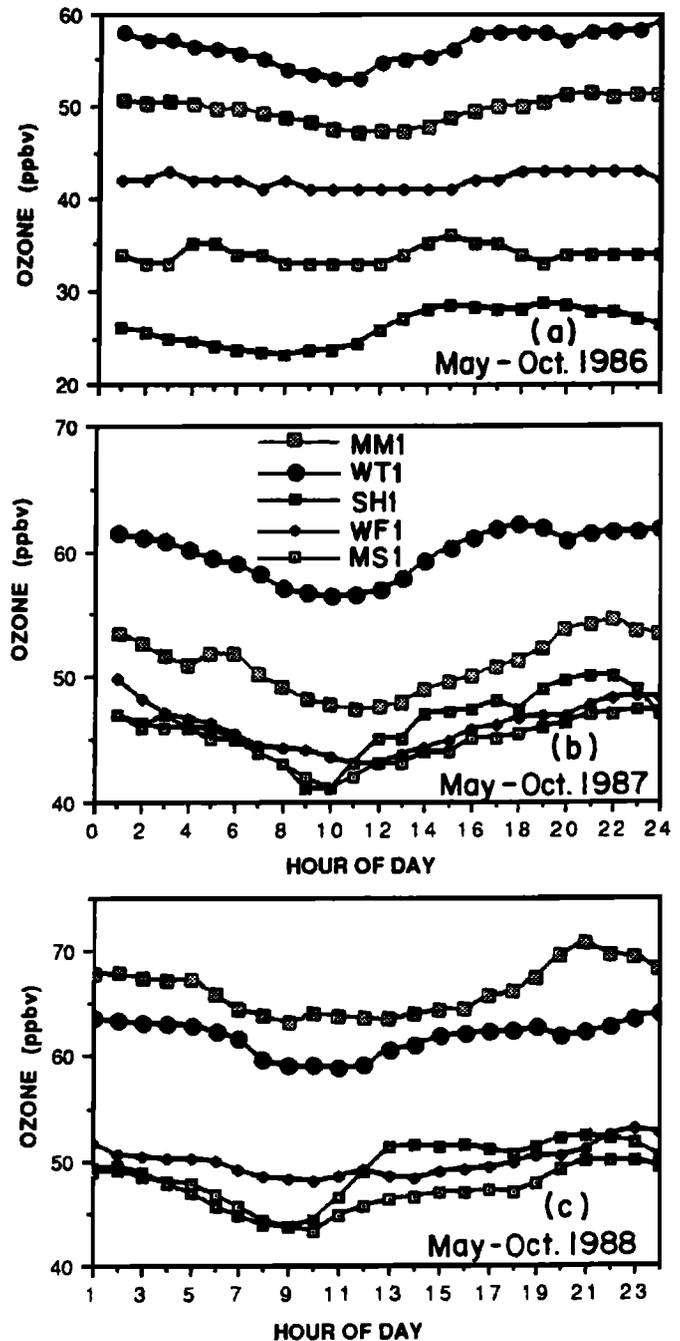


Fig. 3. Mean diurnal variation of ozone concentration at five high-elevation MCCP sites from May to October in (a) 1986, (b) 1987 and (c) 1988.

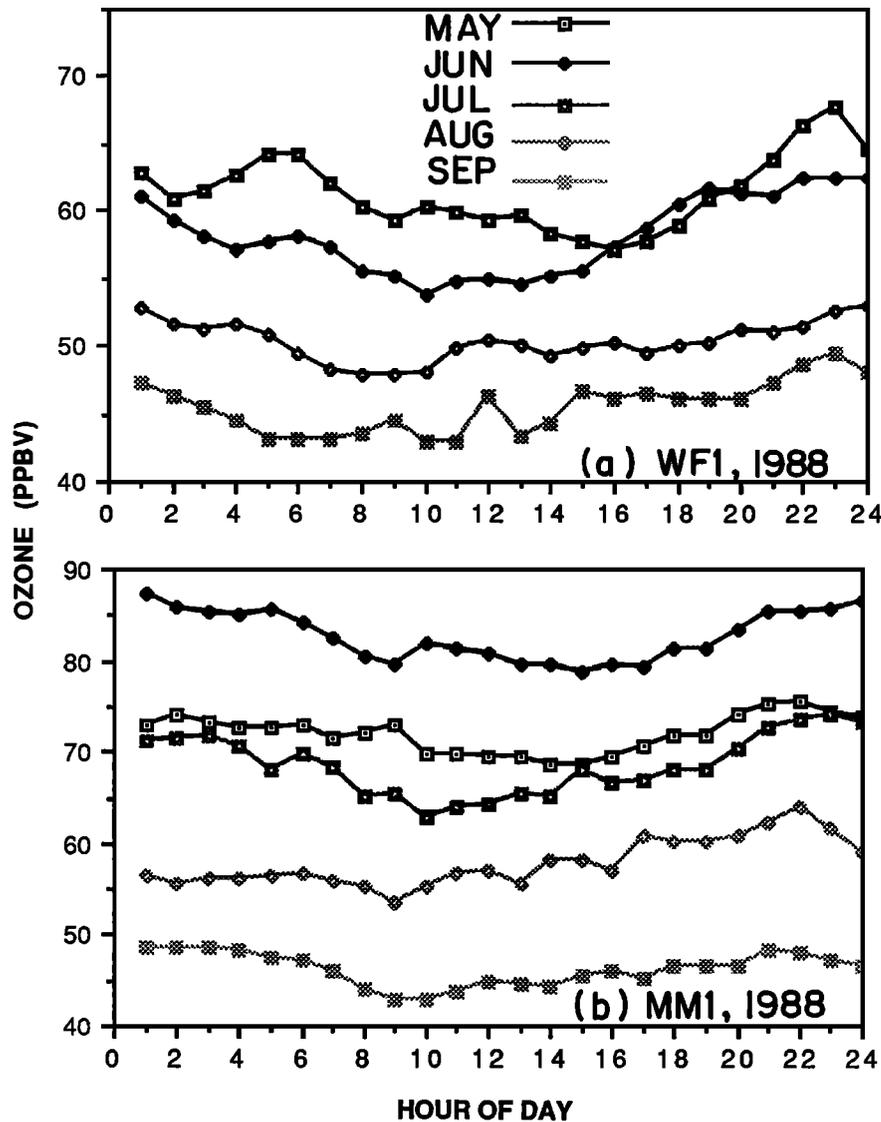


Fig. 4. Mean diurnal variation of ozone concentration at (a) Mount Mitchell, (North Carolina) site 1 and (b) Whiteface Mountain, (New York) by month (May to October 1988).

Moosilauke and Shenandoah Park, and most data collected during the summer in 1986 were missing for every site except for Whitetop Mountain. Therefore most discussions here will mainly focus on data collected during 1987 and 1988.

### 3. RESULTS AND DISCUSSION

#### 3.1. Diurnal Ozone Variations

To understand the role of photochemistry in the elevated forest atmosphere, the diurnal behavior of ozone was studied. It is recorded in the literature that most ozone monitoring sites at low elevation, influenced by local sources (in particular, sources of oxides of nitrogen), show an afternoon maximum diurnal pattern, influenced by these local urban sources. *Lefohn and Mohnen* [1986] pointed out that the highest ozone hourly mean concentration occurs between 1000 and 1859 hours for sites under the influence of local urban sources. Nitrogen oxides may act as a sink in the urban areas, especially during the night. *Meagher et al.*, [1987] monitored rural ozone level at five lower-elevation

sites in the southeastern United States from 1977 to 1983. Data from their stations exhibited midafternoon maxima and early morning minima. Another example of such a large diurnal signal is shown in Figure 2 for the Howland Forest, Maine (~ 65 m) during 1987 and 1988. Inspection of Figure 2 indicates that the ozone minimum, on average (~ 18 ppbv) occurred about 500 or 600 EST, in the early morning before the sunrise, and the maximum (~ 38 ppbv) was in the afternoon at about 1600 EST. Ozone levels were continually increasing rapidly after sunrise to the maximum value and dropped rapidly to very low values during the nighttime period. Nighttime ozone losses were related to the surface deposition and the presence of local sources of nitrogen oxide. After the morning surface heating generates the convective boundary layer, the vertical mixing processes in the boundary layer transport the upper air with higher ozone levels to the surface at lower elevations. This mixing is important for increasing ozone levels at lower elevations such as Howland Forest. Ozone precursor emissions after sunrise may also contribute to the ozone rise in the morning through midafternoon.

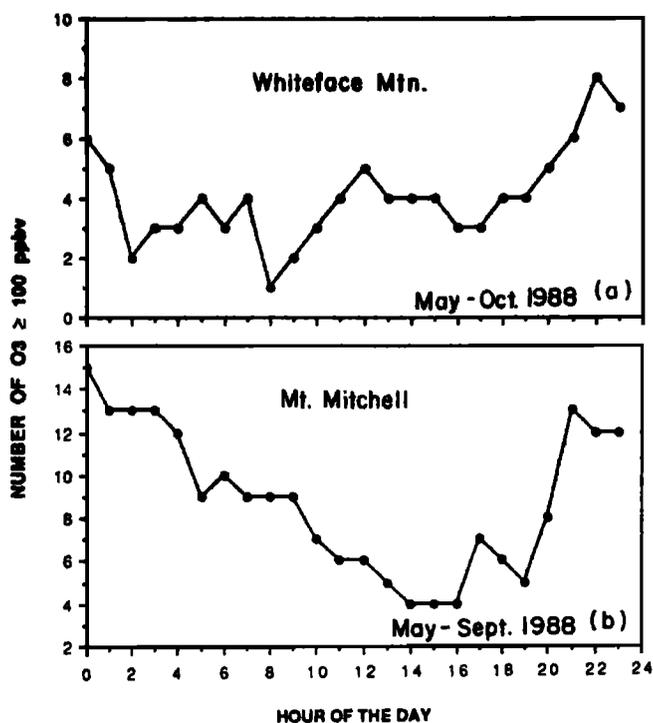


Fig. 5. Mean diurnal variation of ozone episodes (Ozone concentration  $\geq 100$  ppbv) during 1988 at (a) Whiteface Mountain and (b) Mount Mitchell.

However, we find a tendency in the diurnal variations to be reversed (i.e. ozone maxima occurred at night) and was reduced during the daytime at all the five high-elevation sites (Figure 3). For the two northern high-elevation sites, the average daytime value for the entire field season in 1987 was 44 ppbv at MSI compared to an average nighttime value of 46 ppbv (~ 4.5% higher), and the average daytime value was 49 ppbv at WF1 in 1987 compared to an average nighttime value of 51 ppbv (~ 4% higher). Among the southern sites the average daytime value was 49 ppbv in 1987 at MM1 compared to an average nighttime value of 53 ppbv (~ 8% higher). The difference between the daytime and nighttime average concentrations were found to be statistically significant (t statistic) at the 95% level for both 1987 and 1988. Figure 3 illustrates the mean diurnal patterns from May to October in 1986, 1987, and 1988 at five high-elevation sites. The ozone maximum occurred between 1800 and 2400 EST, while the minimum was observed between 900 and 1200 EST. In general, the ozone concentration decreased in the early morning and increased through the afternoon. The concentrations at sunrise were almost equal to the concentrations at sunset with the exception of those at SH1. This behavior was found in all seasons during the time ozone was monitored. Figure 4, for example, shows a tendency for the reverse diurnal pattern in every month during the field season at MM1 in 1988. It is interesting to note that the ozone concentration at SH1 rapidly increased after the minimum value occurred in the late morning and remained at a constant level or gradually increased throughout the afternoon when unstable conditions resulted in good vertical mixing (Figure 3). The trend reflected the photochemical formation of ozone from the limited ozone precursors at this remote site. A similar phenomenon was also observed at the other high-elevation MCCP sites.

During episodes lasting 4-6 days, ozone concentrations  $\geq 100$  ppbv were most frequently observed at night (Figure 5). Previous studies [Aneja, *et al.*, 1991] have shown that most of ozone episodes began in the late evening and early morning at Mount Mitchell in 1988. The number of hours during which ozone concentration  $\geq 80$  ppbv were observed at night was almost twice those observed during the daytime. The reverse diurnal variation of ozone was also frequently observed during the episode at other high-elevation stations when the air was in a stagnation condition under the high-pressure system. Figure 6 illustrates the ozone variation at five high-elevation sites on a particular day during the July 4-11, 1988 episode.

The July 4-11, 1988 ozone episode is examined further in an effort to explore the source-receptor relationship based on back trajectory analysis at 850 mbars. 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 Mount 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 6. Mount Moosilauke had a peak ozone concentration of 116 ppbv at 600 EST July 6, and the next day a peak ozone concentration of 129 ppbv occurred at Whiteface Mountain at 500 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 of 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. By the morning of July 8 a maximum ozone concentration of 163 ppbv occurred at 500 EST at Whitetop Mountain. The maximum 1-hour averaged ozone concentration at Mount Mitchell with 151 ppbv recorded at 500 EST in the morning of July 9. Ozone concentration  $\geq 120$  ppbv lasted 36 hours at Whitetop Mountain and 46 hours at Mount Mitchell, associated with higher temperature (~ 20°C), lower wind speed ( $\leq 8$  m/s), and dry conditions (~ 70%) during this episode. By July 10 the high-pressure system became weakened and moved eastward off the Atlantic coast. Ozone concentrations, dropped below 70 ppbv at all the sites on July 11.

Back trajectories (Figure 7) when ozone maxima occurred during this episode show that the high-ozone days ( $\geq 100$  ppbv) at the northern sites associated with west flow pattern, while the high-ozone days ( $\geq 120$  ppbv) at southern sites associated with north or northwest flow pattern. Air mass sampled at Whitetop Mountain and Mount Mitchell sites passed through upper Ohio Valley and with shorter 72-hour airflow distances. These two facts may represent the conditions conducive to produce ozone concentrations greater than 120 ppbv.

In general, the observed episodes of 1988 coincided with air stagnation events in the high-pressure system. Other similar meteorological conditions around peak ozone concentrations were observed. Temperatures were generally

4°C warmer during the episodes than a typical nonevent day, and relative humidities were less than 70% while wind speeds were generally  $\leq 8$  m/s except for that at Whiteface Mountain site. All of these were conducive to the photochemical formation of ozone during daytime hours.

The relationship between ozone concentrations and wind direction at the five sites was further investigated (Figure 8). These figures show that ozone concentrations are highest when the local wind direction is from the southwest (between 225° and 270°) at northern sites; while the ozone concentrations are highest when the local wind direction was from the north to northwest (between 270° and 360°) at Mount Mitchell. This is further evidence that sources of ozone and/or ozone precursors exist to the northwest of

Mount Mitchell and southwest of Mount Moosilauke and Whiteface Mountain. However, if those specific wind regimes preferentially occur at night, the high-ozone values may be due to nocturnal subsidence. To address this issue, Aneja *et al.* [1991] studied the relation of daytime and nighttime ozone concentration versus wind direction measured at Mount Mitchell separately. Their results indicate that ozone concentrations both during the day and at night were higher when the wind direction is between 270° and 360°, supporting the suggestion that air parcels were exposed to high-ozone or ozone precursor sources as it moves over the midwestern states.

Since there is no photochemical formation of ozone at night, it is interesting to explore the physical and chemical

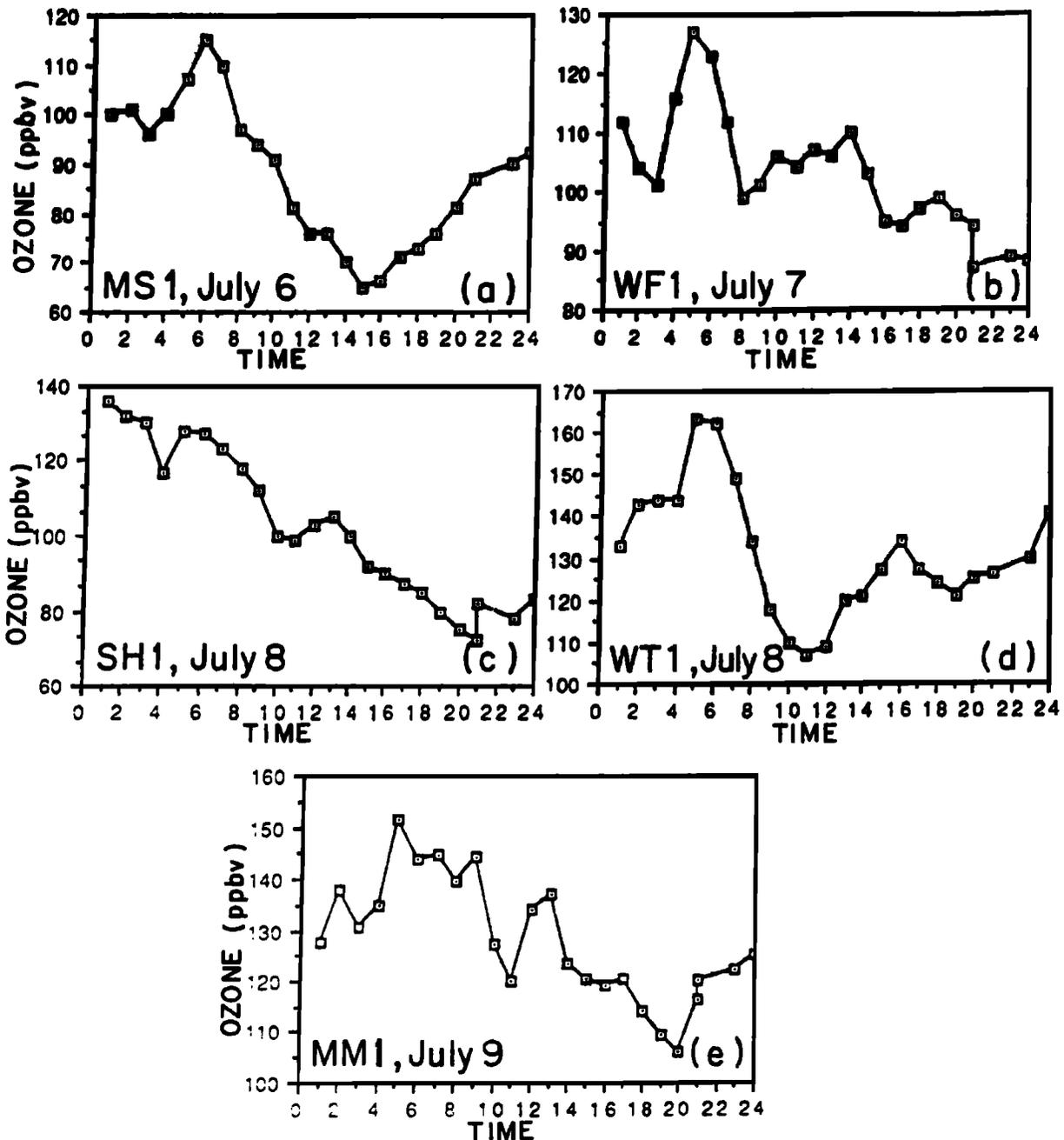


Fig. 6. Hourly averaged ozone concentrations during specific episode day at five MCCC sites in 1988. (a) Mount Moosilauke, July

6, (b) Whiteface Mountain, July 7, (c) Shenandoah Park, July 8, (d) Whitetop Mountain, July 8, and (e) Mount Mitchell, July 9.

dynamics which contribute to this nighttime maximum pattern. It is known that a low-elevation site (e.g., Howland Forest) below the nocturnal inversion layer experiences a greater destruction of ozone at night because of greater surface availability for deposition. However, mountainous sites above the nocturnal inversion layer do not experience the same depletion due to insufficient surface area and the absence of mixing which would dilute the ozone-rich air above the inversion layer with the ozone-depleted air below the inversion layer during the day [Wolff *et al.*, 1987]. Thus mechanisms potentially affecting the ozone concentration at Mount Mitchell would include (1) chemical kinetics, including photochemical formation of ozone or, to a lesser extent, photochemical decomposition; (2) the destruction of ozone near the ground due to deposition; (3) convective mixing of ozone from below and entrainment from above as the boundary layer grows, and (4) advection of higher concentrations of ozone in the free atmosphere when the mountaintop is above the nocturnal boundary layer (enhanced

by subsidence in regions of synoptic scale high pressure). Another process which could potentially lead to a noticeable increase in the ozone level at times other than those expected caused by the photochemical cycles is through stratospheric-tropospheric exchange including intrusions [Singh *et al.*, 1980]. Based on our knowledge of the photochemistry of ozone production, we expect to find maximum ozone levels when solar radiation is at its maximum, or midday, and midsummer (late in June).

In addition, the levels of nitric oxide (a sink for ozone during the night) seldom exceeded the limit of detection for the instrument (~ 2 ppbv) since there are nearly no urban sources in the vicinity of mountainous areas, and the road up the mountain had very little vehicular traffic (with NO emissions). This may be another reason for the reverse diurnal variation observed at five MCCP high-elevation sites. Preliminary analysis suggests that there appears to be no elevated point sources in the vicinity of (< 50 km) of most of these sites. However, during ozone episode conditions, point

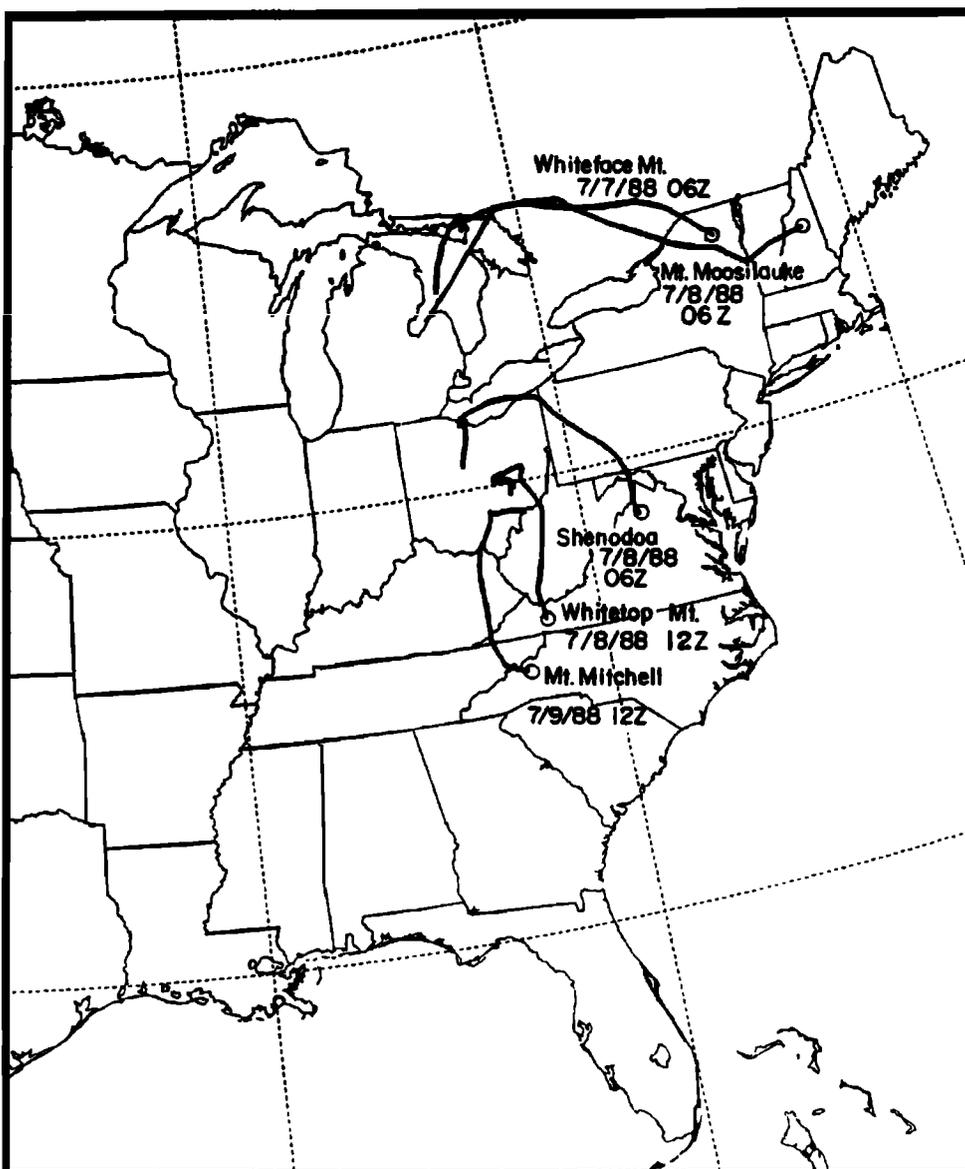
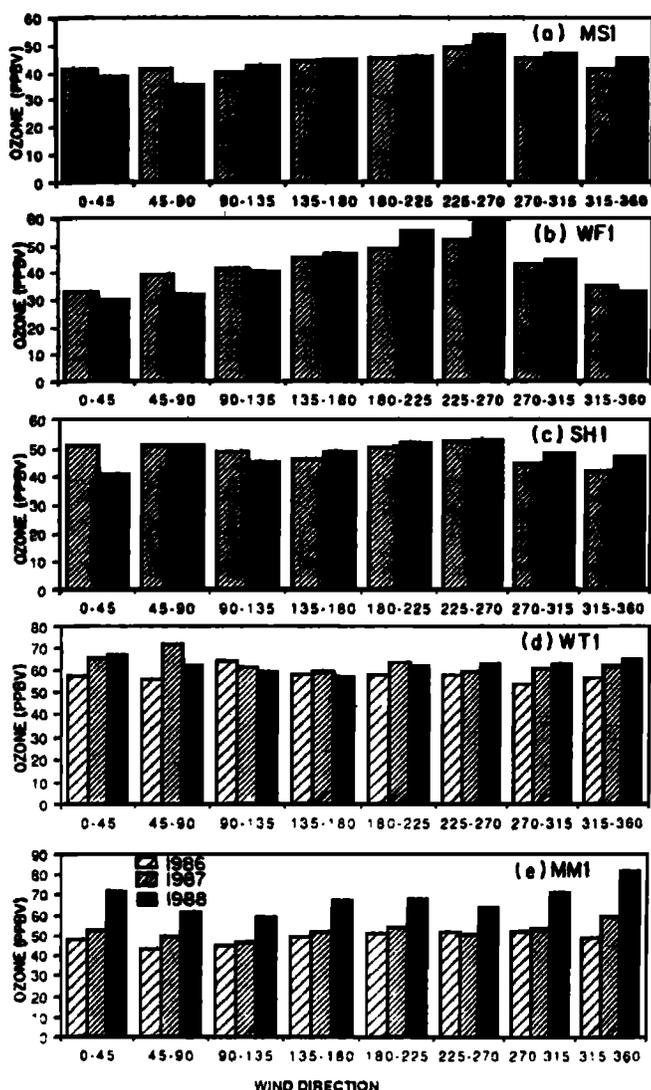


Fig. 7. Seventy-Two hour back trajectory analysis at 850 mbar during July 4-11, 1988 at Mount Moosilauke (MSI), Whiteface

Mountain (WFI), Sheandoah Park (SHI), Whitetop Mountain (WTI), and Mount Mitchell (MMI).



sources > 50 km no doubt will have an influence in providing ozone and/or its precursors to these sites as illustrated by back trajectory analysis earlier.

The relative importance of vertical transport of ozone, the horizontal advection, and chemical kinetics in the enhancement of nocturnal ozone is open to some debate. In order to resolve the role of transport and chemical kinetics in ozone climatology, simultaneous measurements of vertical profiles of ozone and its precursors, as well as profiles of meteorological parameters, such as wind speed and temperature, are needed at a few representative locations for an extended period.

### 3.2. Seasonal Variations

Hourly averaged ozone concentrations were monitored continuously from May to October at the five high-elevation sites since 1986. The maximum and mean concentrations for those sites by month are summarized in Table 2. The data are not available during the spring or summer month at MS1, SH1, and WF1 in 1986.

The monthly mean ozone concentrations measured at the five sites from May to October in 1986 to 1988 are also shown in Table 2 and Figure 9. The record of ozone at these sites is characterized by similar seasonal variations. The maximum monthly mean ozone level occurs in either the spring or the summer (May-August), and the minimum occurs in the fall (September and October), but they differ in their relative levels. This seasonal variation pattern at these sites agrees with that noted by *Aneja et al.* [1991]. *Logan* [1985] also reported that a summer maximum extending through July or August was found over most of the low-elevation United

Fig. 8. Ozone concentration versus wind direction at (a) Mount Moosilauke, (b) Whiteface Mountain, (c) Shenandoah Park, (d) Whitetop Mountain, and (e) Mount Mitchell.

TABLE 2. Summary of Monthly Maximum and Mean Values for Ozone Levels at MCCP Sites From May to October in 1986, 1987, and 1988

Year	May	June	July	August	September	October
<b>MS1</b>						
1986	...	...	...	...	...	61.0/33.9
1987	97.7/53.6	102/49.9	95.6/47.6	102/45.7	79.0/35.7	50.3/29.1
1988	...	127/57.0	117/58.0	94.0/46.6	82.0/39.1	68.0/36.0
<b>WF1</b>						
1986	...	...	85.0/44.1	86.0/47.5	79.0/40.5	57.3/34.9
1987	102/52.5	94.0/51.9	104/46.9	97.0/45.3	89.0/38.9	73.0/40.1
1988	...	135/58.1	133/61.4	109/50.3	108/45.6	72.0/36.0
<b>SH1</b>						
1986	...	...	...	...	43.0/24.0	49.0/27.7
1987	88.0/47.7	93.6/51.2	92.3/51.0	98.5/52.5	99.2/44.8	71.0/32.0
1988	110/62.5	135/59.2	140/61.1	124/52.5	73.0/39.7	59.0/31.2
<b>WT1</b>						
1986	98.0/57.9	120/62.8	110/61.2	103/57.5	76.0/47.5	65.0/41.6
1987	99.0/62.2	111/63.3	124/62.0	107/65.6	98.0/56.1	95.0/49.2
1988	105/63.6	121/74.6	163/67.1	103/53.7	74.0/44.5	...
<b>MM1</b>						
1986	...	111/74.3	...	94.0/45.0	75.0/47.6	71.0/39.6
1987	73.4/50.2	93.1/57.5	96.4/50.1	103/54.1	77.1/46.4	74.3/45.8
1988	116/72.0	123/82.8	151/68.7	114/57.4	84.3/46.7	...

Concentrations are in ppbv, and values are for hourly averaged data.

States from 35°N to 45°N. Moreover, Janach [1989] suggests that the spring ozone peak seems to affect the entire northern hemisphere, based on measurements at Alpine stations in Europe and Mauna Loa, Hawaii.

The seasonal trends from daily-averaged ozone concentrations for 1988 are shown in Figure 10. Daily-averaged solar radiation and temperature are also presented in Figure 10. The curves show a seasonal trend as represented by the best fit curve illustrated in each figure (for each case, linear and second-order relationships were considered). In each year the highest ozone concentrations at all those sites are observed during the first half of summer, with lower concentrations observed during September and October. At the Northern sites (MS1 and WF1) 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 the ozone concentration were increasing from late spring to the maximum monthly average in early summer and then decreasing through September and October.

There are at least four factors that may contribute to the observed seasonal variation: (1) It is known that ozone concentration is correlated with solar radiation and temperature; (2) the observed spring maximum in tropospheric ozone at northeastern sites may reflect upper tropospheric/stratospheric exchange since stratosphere-troposphere exchange is most effective during this period [Logan, 1985]; (3) excess local NO<sub>x</sub> and natural hydrocarbon emissions may occur during late spring and summer [Aneja et

al., 1991]; and (4) occurrence of enhanced anthropogenic activity [Liu et al., 1987].

Overall, possible sources of ozone in the troposphere are from photochemical formation (in situ and/or in-transit) and stratospheric intrusion. Tropospheric and stratospheric exchange may contribute to the background tropospheric ozone levels (30-50 ppbv in high-elevation sites in the eastern United States). It is observed by some investigators [Johnson and Viezee, 1981] that ozone values during spring were generally higher than those measured during the fall in the stratosphere, suggesting that the observed spring maximum at northern sites may also be due to the vertical exchange at a time of maximum ozone concentration in the stratosphere. On the other hand, the photochemical

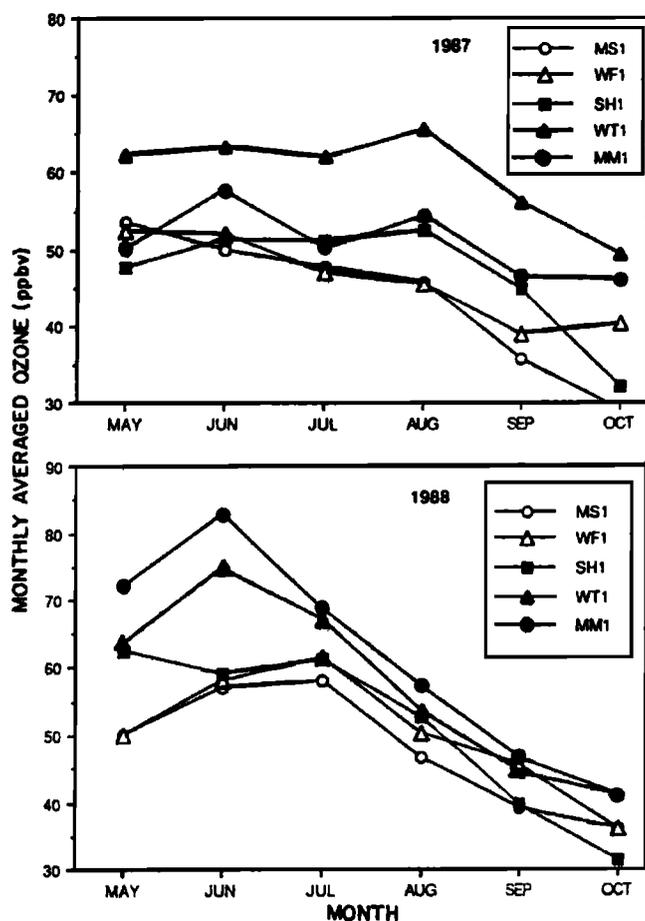


Fig. 9. Monthly averaged ozone concentration.

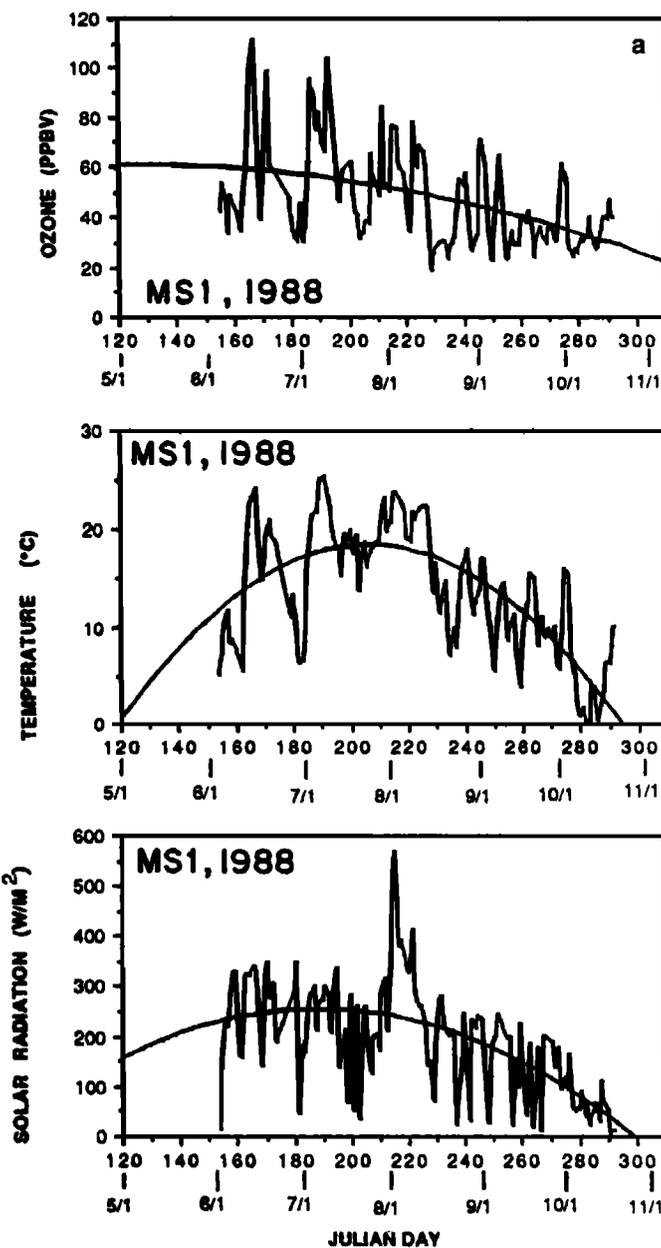


Fig. 10. Daily averaged ozone concentration, solar radiation, and temperature during 1988 at (a) Mount Moosilauke, (b) Whiteface Mountain, (c) Shenandoah Park, (d) Whitetop Mountain, and (e) Mount Mitchell. Regression curves shown in each panel are based on third-order polynomial regression analysis.

production of ozone requires hydrocarbons, NO<sub>x</sub>, and UV radiation. Aneja *et al.* [1991] suggested that budbreak may represent a biological stress (as in other plant species) which results in natural hydrocarbons being given off in excess amounts by conifers during growth period, thus contributing to the observed high average ozone concentrations during late spring and summer.

3.3. Frequency Distributions of Ozone Exposure

Numerous studies have focused on the selection of ozone exposure indices for the effect on forest decline [Lefohn and Benedict, 1985; Oshima, 1975; Pinkerton and Lefohn, 1987; Lefohn and Pinkerton, 1988; Mohnen *et al.*, 1990]. Since no specific parameters may be completely satisfactory for

describing the ozone exposure to its effects, several characterization statistics were used in this study, including: (1) maximum, minimum, and mean values of hourly averaged concentration for the entire growing season (May to October); (2) number of hours of occurrence of elevated ozone levels over 0.05 ppm, 0.07 ppm, 0.10 ppm, and 0.12 ppm; (3) frequency distribution of hourly averaged values for seasonal periods; and (4) sum of all hourly mean ozone concentrations equal to or greater than 0.07 ppm (SUM07).

It is now recognized that forest trees may be more sensitive to short-term, high-concentration ozone exposures than to long-term, low-concentration exposures [Heck *et al.*, 1966; Garner *et al.*, 1989]. The selection of the 0.05, 0.07, 0.10, and 0.12 ppm of ozone concentrations was based on most previously reported studies. Reich and Amundson

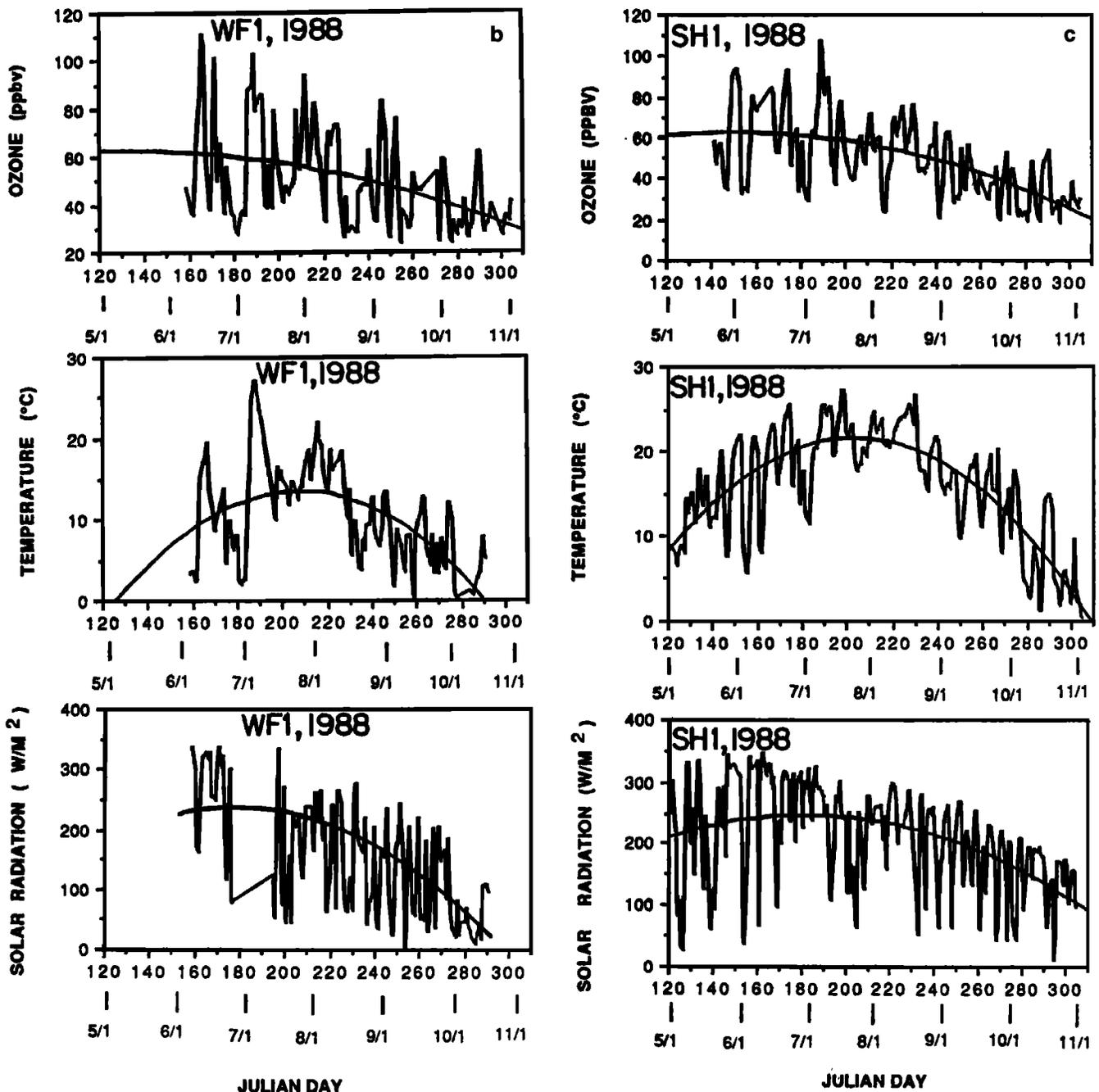


Fig. 10. (continued)

[1985], and *Garner et al.* [1989] reported that ozone exposure to 0.05 ppm or more is sufficient to cause damage to certain species of vegetation.

Hourly averaged ozone monitoring data at five stations from May to October during 1986 to 1988, minimum, maximum, and mean values, number of hours of occurrence of ozone levels over specific criteria; and number of data capture for the season are summarized in Table 2. The frequency distribution patterns for ozone concentration are illustrated in Figure 8. Of the five sites examined in this study, elevated ozone concentrations occurred at southern sites including Whitetop Mountain and Mount Mitchell. The Mount Moosilauke site experienced relatively low-ozone exposures during 1987 and 1988, while the moderate ozone

concentrations, in general, were recorded at Whiteface Mountain and Shenandoah Park.

We notice that ozone exposures based on mean values (Table 2) were higher at both Whitetop Mountain and Mount Mitchell, the two southern sites, when compared to the two northern sites, Whiteface and Mount Moosilauke. The highest mean ozone concentration was recorded at Mount Mitchell in 1988. The mean values may reflect the elevated levels of ozone exposures when hourly averaged ozone concentrations  $\geq 0.10$  ppm frequently occur as indicated by *Lefohn and Benedict* [1985]. However, using this index seems to ignore the duration of elevated ozone exposure. For example, different areas with different number of elevated ozone occurrences may have a similar mean value.

The maximum frequencies of hourly ozone concentration ranged between 0.03 and 0.04 ppm at the northern sites, and between 0.04 and 0.05 ppm at Shenandoah Park during 1987 and 1988. The most frequent ozone level shifted from between 0.04 and 0.05 ppm in 1987 to between 0.06 and

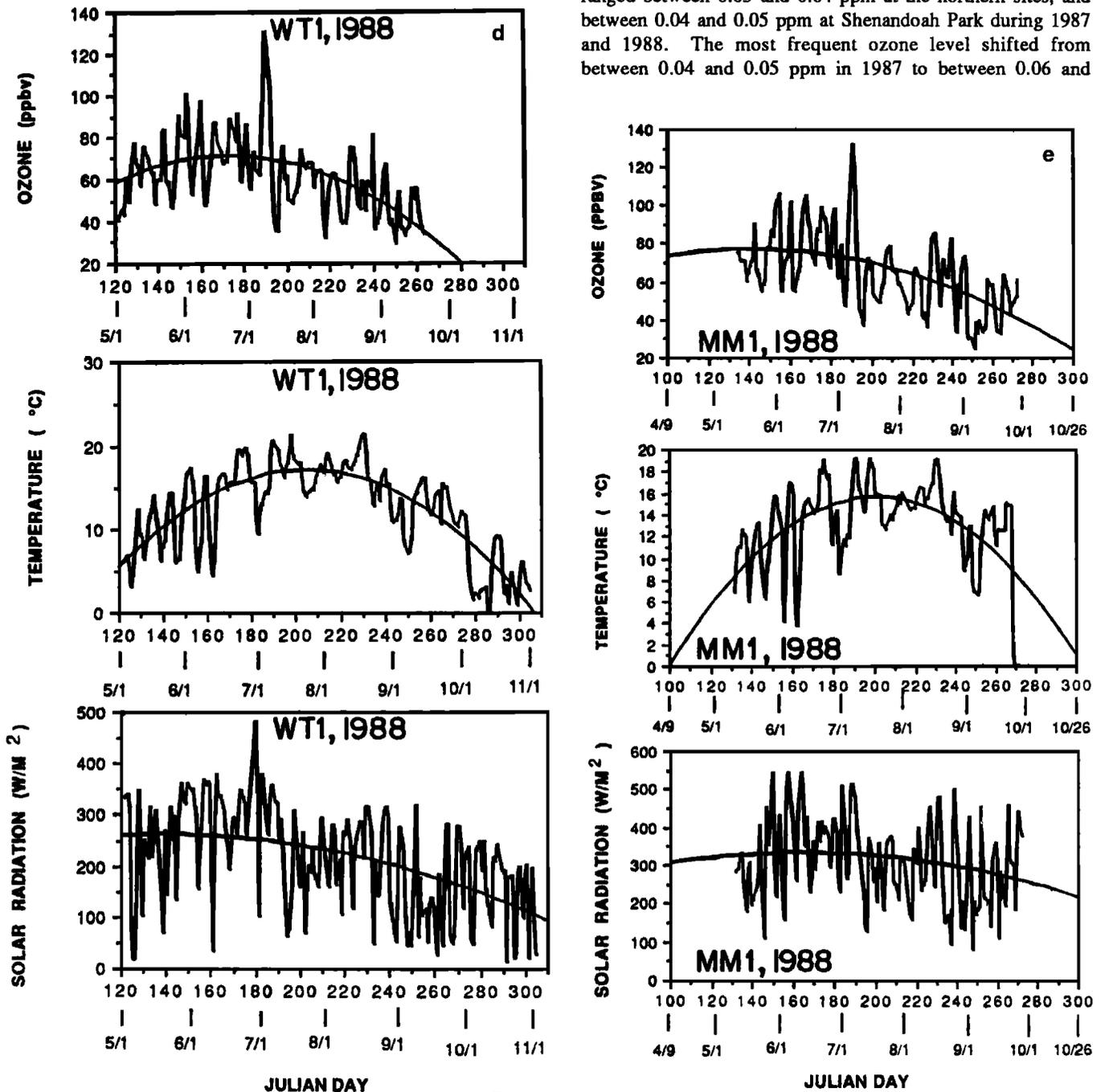
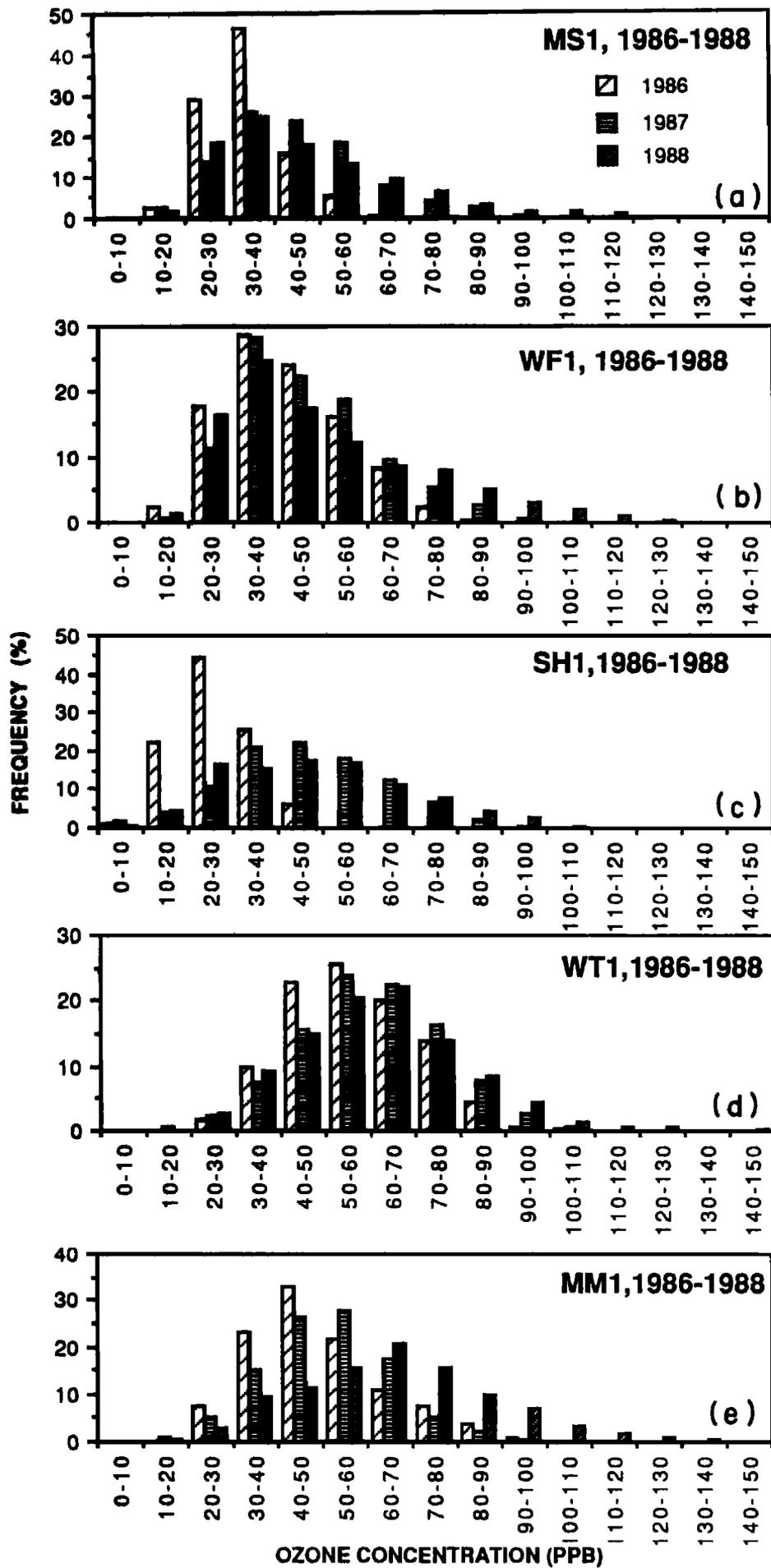


Fig. 10. (continued)



0.07 ppm in 1988 at both Whitetop Mountain and Mount Mitchell, the two southern sites. Hourly averaged ozone concentration equal to or greater than 0.05 ppm occurred more than 30% of the time at northern sites (MS1 and WF1) and more than 40% of the time at southern sites (SH1, WT1 and MM1) during 1987 and 1988. Preliminary 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. For the two southern most sites, Whitetop Mountain and Mount Mitchell, ozone levels were equal to or greater than 0.05 ppm 52%-76.7% of the time (1824-3210 hours), and there were few occurrences below 0.02 ppm (Figure 11). The ozone levels equal to or greater than 0.07 ppm ranged from 7.2 (MS1, 1987) to 19.1 (WF1, 1988) of the time at northern sites and 7.6 (MM1, 1987) to 40.3% (MM1, 1988) of the time at southern sites. In general, the Whitetop Mountain and Mount Mitchell sites experienced higher ozone concentrations. The maximum hourly mean ozone concentrations were 0.16 ppm at Whitetop and 0.15 ppm at Mount Mitchell in 1988. There were 7 hours (~ 0.25% of time) ozone concentrations equal to or greater than 0.12 ppm at Mount Moosilauke, and 14 hours (~ 0.47% of the time) at Whiteface Mountain in 1988. For the southern sites there were 16 hours (~ 0.43% of the time) ozone levels equal to or greater than 0.12 ppm at Shenandoah Park, 37 hours (~ 1.2% of the time) at Whitetop, and 48 hours (~ 1.6% of the time) at Mount Mitchell in 1988.

Figure 12 illustrates the values of the sum of all hourly mean ozone concentrations equal to or greater than 0.07 ppm during the growing season (SUM07, parts per million-hour (ppm-h)). The SUM07 is an exposure index that combines the concentration and occurrence for high ozone levels. The ozone exposures were between 20 and 27 ppm-h at Mount Moosilauke, Whiteface Mountain, Shenandoah Park, and Mount Mitchell sites in 1987. Compared to other sites, a much higher ozone exposure was recorded at Whitetop Mountain, with a SUM07 of 95.5 ppm-h. In 1988, the values of SUM07 continually increased from north to south. The highest ozone exposure over the 2-year period was 105 ppm-h experienced at Mount Mitchell during the 1988 monitoring season. In general, ozone levels were higher in the south than those in the north. Combining the ozone exposures for both 1987 and 1988, it is found that the sum of all hourly mean ozone concentrations equal to or greater than 0.07 ppm was 54.9, 76.4, 76.9, 181, and 126 ppm-h at Mount Moosilauke, Whiteface Mountain, Shenandoah Park, Whitetop Mountain, and Mount Mitchell, respectively, suggesting a north-south gradient in ozone exposure.

In addition, it is noted from Table 3 and Figure 11 that the number of ozone concentrations  $\geq 0.07$  ppm and SUM07 recorded at Mount Mitchell in 1987 was less than those at Whiteface or Shenandoah Park, while the mean concentration was higher at Mount Mitchell (0.051 ppm) than at Whiteface Mountain (0.046 ppm) or Shenandoah Park (0.046 ppm). Furthermore, as shown in Table 3, there were a larger number of ozone concentrations  $\geq 0.05$  ppm at Mount Mitchell in 1987 than at the other two sites. This indicates that ozone

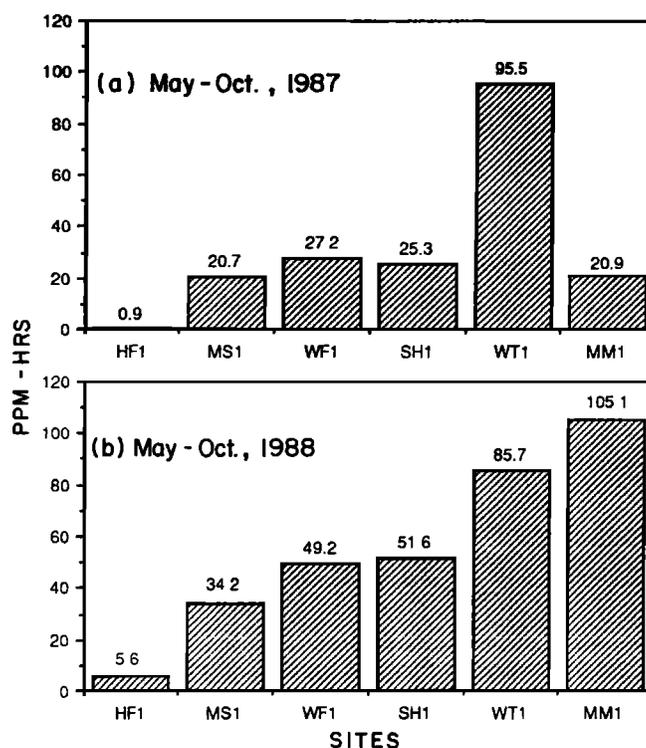


Fig. 12. Sum of all hourly mean ozone concentrations equal to or greater than 0.07 ppm sum of season exposure (ppm-h) by site in (a) 1987 and (b) 1988.

levels in the range of 0.05-0.07 ppm were more prevalent at Mount Mitchell in 1987. Such a distribution pattern increases the mean concentration at Mount Mitchell though the number of ozone levels  $\geq 0.07$  ppm was less.

There were at least 2 months of missing data in 1986 for all sites except for Whitetop Mountain. Thus the comparison with the data in 1987 and 1988 may not be appropriate. However, from 1986 to 1987, the data collected at Whitetop Mountain indicated a 7% increase in mean concentration and 550 more hours with ozone levels  $\geq 0.07$  ppm. It is observed that ozone increased from 1987 to 1988 at the five sites. For example, the mean values increased 3.3% (Whitetop) to 29% (Mount Mitchell). The number of hourly ozone concentrations  $\geq 0.10$  ppm and  $\geq 0.12$  ppm shows significant increase, which is believed to be due to the hot and dry weather condition during 1988. An exception existed at Whitetop Mountain where the SUM07, which neglects the ozone concentration below 0.07 ppm, shows slight decrease from 1987 to 1988. A possible explanation for this decrease is that the number of hourly ozone concentration  $\geq 0.07$  ppm and total number of valid data in 1987 were more than those in 1988 resulting in higher values of sum of season dose in 1987.

Based on the effect of ozone on plants, more realistic exposure parameters may be used for high-elevation forest areas. The sum of all hourly mean ozone concentrations equal to or greater than 0.07 ppm, combining both concentrations and length of exposure, may be an adequate parameter of ozone exposure. Although the peak ozone concentrations are clearly important in adverse effects on vegetation, the effects of ozone concentration below 0.07 ppm are uncertain. Therefore the level of minimum concentration for use in determining the sum of ozone concentrations should be studied.

Fig. 11. Frequency distribution of ozone concentrations monitored at MCCP sites from May to October, 1986-1988 at (a) Mount Moosilauke, (b) Whiteface Mountain, (c) Shenandoah Park, (d) Whitetop Mountain, and (e) Mount Mitchell.

TABLE 3. Summary of Hourly Averaged Ozone Data by Site and Year

Year	Number of Hours O <sub>3</sub> ≥ 0.05 ppmv	Number of Hours O <sub>3</sub> ≥ 0.07 ppmv	Number of Hours O <sub>3</sub> ≥ 0.10 ppmv	Number of Hours O <sub>3</sub> ≥ 0.12 ppmv	Number of Observations	Minimum (ppmv)	Maximum (ppmv)	Mean (ppmv)
1986	29 (5.8%)	0	0	<u>MSI</u> 0	500	0.01	0.061	0.034
1987	1210 (33.7%)	260 (7.2%)	2 (0.06%)	0	3594	0.006	0.102	0.045
1988	1050 (37.0%)	399 (14.1%)	75 (2.6%)	7 (0.25%)	2837	0.01	0.127	0.047
1986	724 (27.0%)	74 (2.8%)	0	<u>WFI</u> 0	2679	0.01	0.086	0.042
1987	1502 (37.2%)	345 (8.5%)	4 (0.1%)	0	4042	0.011	0.104	0.046
1988	1187 (40.0%)	568 (19.1%)	97 (3.3%)	14 (0.47%)	2973	0.014	0.135	0.05
1986	0	0	0	<u>SHI</u> 0	1258	0.006	0.049	0.026
1987	1373 (40.4%)	328 (9.7%)	0	0	3398	0.002	0.099	0.046
1988	1665 (45.0%)	612 (16.5%)	50 (1.35%)	16 (0.43%)	3700	0.006	0.14	0.049
1986	2150 (65.1%)	653 (20%)	11 (0.33%)	1 (0.03%)	3301	0.001	0.12	0.056
1987	3210 (74.0%)	1203 (27.7%)	33 (0.76%)	1 (0.02%)	4338	0.011	0.124	0.06
1988	2449 (73.2%)	1017 (30.4%)	109 (3.3%)	37 (1.1%)	3344	0.019	0.163	0.062
1986	978 (41.2%)	272 (11.4%)	5 (0.21%)	0	2371	0.018	0.111	0.049
1987	1824 (52.7%)	269 (7.6%)	1 (0.03%)	0	3539	0.008	0.105	0.051
1988	2269 (76.5%)	1204 (40.3%)	212 (7.0%)	48 (1.6%)	2986	0.011	0.151	0.066

Ozone data include minimum, maximum, seasonal mean ozone concentration and number of hours ozone concentration ≥ 0.05 ppmv, 0.07 ppmv, 0.10 ppmv, and 0.12 ppmv from May to October, 1986-1988.

## 4. SUMMARY AND CONCLUSIONS

The purpose of this study was to characterize ozone exposures and develop a climatology for ozone at high elevations over the eastern United States. Ozone measurements from five high-elevation sites were characterized from May to October during 1986-1988 by using different exposure indices. The results show that the selected high-elevation forest areas have been exposed to high-ozone concentrations. The maximum hourly averaged ozone concentrations during the 3-year period were 0.127 ppm at Mount Moosilauke, 0.135 ppm at Whiteface Mountain, 0.140 ppm at Shenandoah Park, 0.163 ppm at Whitetop Mountain and 0.151 ppm at Mount Mitchell. All these maximum values were observed in 1988. Over the 3-year monitoring period there were 7 hours of ozone concentrations equal to or greater than 0.12 ppm at Mount Moosilauke, 14 hours at Whiteface Mountain, 16 hours at Shenandoah Park, 29 hours at Whitetop Mountain, and 48 hours at Mount Mitchell. The sum of all hourly mean ozone concentrations equal to or greater than 0.07 ppm (SUM07), one of the indices for characterizing ozone exposure, was 54.9 ppm-h at Mount Moosilauke, 76.4 ppm-h at Whiteface Mountain, 76.9 ppm-h at Shenandoah Park, 181 ppm-h at Whitetop Mountain, and 126 ppm-h at Mount Mitchell during the same period. It is noted that using different indices may result in a different north-south gradient for ozone exposure. However, the lowest ozone level was observed at Mount Moosilauke, followed by Whiteface Mountain or Shenandoah Park, and the highest ozone level was recorded at Whitetop Mountain and Mount Mitchell, suggestive of a north-south gradient in ozone exposure. However, further measurements are needed to ascertain more fully this north-south gradient in ozone exposure.

Ozone levels exhibit seasonal variations similar to those observed previously at Alpine stations in Europe and Mauna Loa, Hawaii. Concentrations were significantly higher in late spring at the northern sites and in early to midsummer at the southern sites than those in fall. Higher ozone concentrations are associated with higher solar radiation and temperature and perhaps with the higher level of hydrocarbons emitted by natural sources during this time period.

Reverse diurnal patterns were observed in the ozone level at five high-elevation sites compared to lower-elevation sites (e.g., Howland Forest, Maine) and urban areas. The ozone maximum values occurred in late evening and on some occasions in early morning at the five mountain stations. It is suggested that this reverse diurnal pattern is attributable to a number of factors: (1) the destruction of ozone near the ground and mixing by turbulent diffusion in the mixing layer during the day, (2) a downslope wind regime and less chemical destruction during the night, and (3) surface contact at night when the mountainous monitoring sites are above the nocturnal inversion layer.

It is known that both long distance transport and photochemical reactions may contribute to elevated ozone exposure at high-elevation forest areas. In order to resolve the ozone problem and plan effective control strategies, it will be necessary to determine how much of the ozone increase observed in those mountain forest locations is due to transport from urban or industrial areas and how much ozone is produced photochemically from the local sources of

precursors. To deal with the problem, effort should begin with research to characterize sources of atmospheric NMHC compounds and low-level oxides of nitrogen compounds. The contribution to atmospheric ozone from natural hydrocarbons, though not well-understood, may be significant in some high-elevation rural areas. Therefore continued long-term monitoring of ozone and its precursors at the high-elevation forest areas may provide important information on the climatology of free tropospheric ozone and may offer a signal for enhanced anthropogenic and/or biogenic activity. This information will be critical to the future planning of ozone control programs.

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