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Ozone Climatology at High Elevations in the Southern Appalachians

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Ozone measurements are reported for two high-elevation sites located in the Mt. Mitchell State Park in North Carolina (site 1 on Mt. Gibbs, ~2006 m, and site 2 on Commissary Ridge, ~1760 m). These measurements are also compared to those from a nearby, low-elevation site (Fairview, ~850 m). The measurements were made from May through September during the years 1986 and 1988 and from May through October during 1987, at sites 1 and 2. Measurements were also made from May through September 1989 at site 1 only. During the monitoring season at site 1 the mean ozone concentrations were 50, 51, 66, and 52 ppbv for 1986, 1987, 1988, and 1989 field seasons, respectively, while at site 2 the mean ozone concentrations were 49, 49 and 52 ppbv for 1986, 1987, and 1988. (It has been shown that exposure to ozone concentrations of ≥50 ppbv is sufficient to cause damage to certain species of vegetation.) The daily maximum, 1-hour average, and 24-hour average concentrations were found to be greatest during summer months (late May through early July), with lower concentrations during fall (August and September), suggesting a correlation with the seasonal photochemical cycle. It is suggested that excess hydrocarbons released during budbreak may contribute to the seasonal signal in the ozone data. During the 1988 monitoring season there were three periods of very high ozone levels (>80 ppbv) which lasted over 100 hours. During these long episodes there were 48 hours during which ozone concentrations exceeded the current National Ambient Air Quality Standard (NAAQS) of 0.12 ppmv. High hourly averaged SO_2 (~25 ppbv) and NO_x (~11 ppbv) levels were also found during these episodes. Meteorological analyses show an association between periods of high ozone concentrations and synoptic-scale patterns. Such high gaseous pollutant concentrations were not observed during the previous two field seasons. Also, no exceedances of the NAAQS were observed during the field season of 1989. No discernible diurnal cycle in the ozone concentrations was observed at site 2; however, a reversed diurnal cycle (nighttime maximum) was evident at site 1. Also, average ozone concentrations increased from lower elevations to higher elevations. Evidence suggests that the relationship between the mountaintop and the height of the mixing layer, coupled with horizontal transport of ozone in the lower troposphere, may be important in explaining the nocturnal maximum at site 1 and the observed altitudinal gradient in ozone.

INTRODUCTION

During the past two decades, ozone has been characterized in the ambient environment [*Liu et al.*, 1980; *Levy et al.*, 1985; *Logan*, 1985; *Lefohn and Mohnen*, 1986; *Lefohn and Pinkerton*, 1988; *Hough and Derwent*, 1990], in urban areas [*Chameides et al.*, 1988; *Lindsay et al.*, 1989], and in rural areas [*Meagher et al.*, 1987; *Trainer et al.*, 1987; *Logan*, 1988]. In general, these measurements have been limited to lower elevations. Less extensive research has been undertaken on the behavior of ozone in alpine environments in the United States [*Samson*, 1978; *Wolff et al.*, 1987; *Aneja et al.*, 1990*a*].

Since 1986 the Mountain Cloud Chemistry Program (MCCP), funded by the U.S. Environmental Protection Agency (EPA), has been monitoring ozone levels at five high-altitude locations in the eastern United States. The southernmost of these locations is the North Carolina State University Climatological Observatory, located in the Mt. Mitchell State Park, North Carolina. Mt. Mitchell is the highest mountain in the United States east of the Mississippi River (~2038 m mean sea level (msl)); therefore this site provides a unique observatory for monitoring the chemical and physical climate in an alpine environment.

Red spruce and Fraser fir are the dominant tree species above ~1500 m msl in the alpine environment of the southern Appalachian Mountains. These trees have shown signs of decline in recent years [*Bruck et al.*, 1989], and air pollution has been suggested as playing a role in this decline. For example, *Reich and Amundson* [1985] and *Mohnen and Cowling* [1988] have reported that ozone exposure to 50 ppbv or more is sufficient to cause damage to certain species of vegetation. The extent of air pollution at Mt. Mitchell has recently been investigated [*Saxena et al.*, 1989; *Aneja et al.*, 1990*b*]. The concentration of pollutants, the duration of exposure, and the length of time between exposures are important factors in assessing the adverse impact of pollution on the biosphere. These aspects of ozone behavior at the Mt. Mitchell State Park, plus some of the factors which might lead to elevated ozone levels at this "remote" site, are characterized in this paper.

EXPERIMENT

The Mt. Mitchell observatory consists of two subsites. The highest station (site 1) is near the summit of Mt. Gibbs, at an elevation of ~2006 m (Figure 1). The second site is located at an elevation of ~1760 m on Commissary Ridge, which is 2.5 miles (1 mile = 1.6 km) northeast of site 1, on the southeast shoulder of Mt. Mitchell. We report results from these two high-elevation sites. These results are also compared to a third, low-elevation site, located nearby (Fairview, ~850 m). Concentrations are reported in parts per billion by volume (ppbv) so that all measurements are independent of barometric pressure and therefore independent of elevation.

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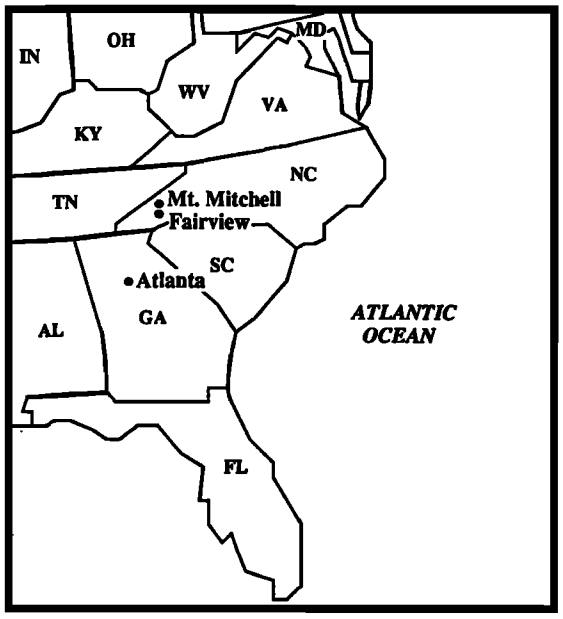

Fig. 1*a*. Map of southeastern United States showing the location of Mt. Mitchell and Fairview, North Carolina.

At each of the two high-elevation sites, instrumented towers were installed to collect meteorological, cloud microphysics, cloudwater, and gas-phase chemical data. Ozone measurements, based on ultraviolet absorption, were made with a Thermo Electron Corporation Ozone Analyzer (model 49). The level of detection for this instrument is 2 ppbv with an accuracy of ±20 ppbv for ozone values greater than 20 ppbv and ±4 ppbv for ozone values in the range of 0–20 ppbv. The precision of this instrument is ±20% for values in the range of 25–35 ppbv. Sulfur dioxide was measured with a Thermo Electron Corporation Analyzer (model 43). For the sulfur dioxide measurements the level of detection for the instrument is 0.6 ppbv with an accuracy of ±20% for SO_2 values in the range of 18–22 ppbv and a precision of ±5 ppbv for values in the range of 10–22 ppbv. Oxides of nitrogen were measured with a Monitor Lab Model 8440 Analyzer, for which the level of detection is 2 ppbv. The accuracy and precision of the NO_x instrument are identical to those of the SO_2 analyzer.

The analyzers were factory calibrated at the beginning of each field season. The quality assurance protocols included weekly zero and span checks, and multipoint calibrations were conducted at least twice during the measurement period. All calibrations were based on the National Bureau of Standards traceable reference standard. Data were stored as 15-min averages in a Campbell Scientific Model 21XL data logger.

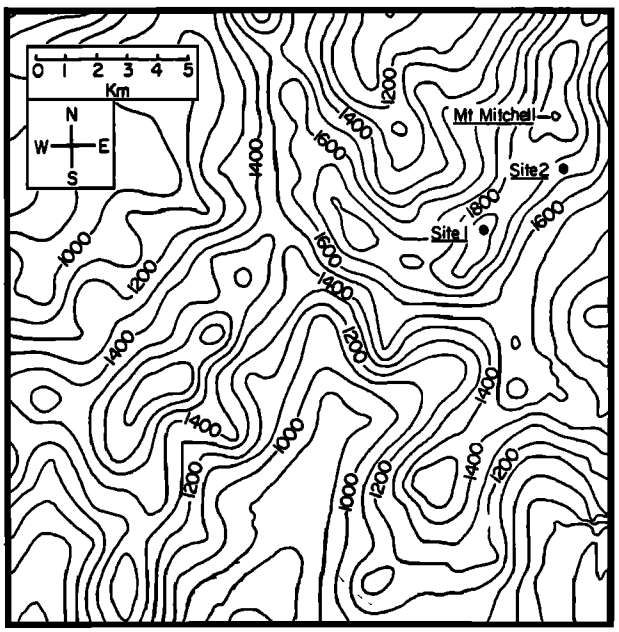

Fig. 1*b*. Topographical map of Mt. Mitchell area showing locations of site 1 and site 2.

RESULTS

Seasonal and Interseasonal Ozone Variations

Beginning in 1986, hourly averaged ozone concentrations were monitored continuously from May through September. The minimum and maximum concentrations for site 1 and site 2 are summarized in Table 1. Observed ozone levels were higher in 1988 than in 1989 or the previous two years at both sites (at the 99% significance level). Maximum ozone levels noted at site 2 were 80 ppbv during October 1986, 111 ppbv during July 1987, and 134 ppbv during July 1988. At site 1 the maximum values observed were 111 ppbv during June 1986, 103 ppbv during August 1987, 151 ppbv during July 1988, and 92 ppbv during July 1989.

Tables 2 and 3 summarize the SO_2 and NO_x data for site 1. Sulfur dioxide concentrations ranged from less than 0.6 ppbv to as high as 24 ppbv (observed in May 1988). Total oxides of nitrogen NO_x ranged from less than 2 ppbv to ~11 ppbv (also observed in May 1988). The frequency distribution of SO_2 and NO_x is given in Figures 2 and 3. It suggests that at least for NO_x, most of the data collected are below the detection limit of the instrument. Moreover, as pointed out by *Fehsenfeld et al.* [1987], the NO_x instrument used is subject to interferences from peroxyacetyl nitrate (PAN) and other nitrogen compounds. At high concentrations (>10 ppbv) these interferences are probably not significant, but at the lower end of the detection limit (~2 ppbv) these interferences can be quite significant.

During the first three field seasons (1986–1988) the highest monthly mean ozone concentration (at the 99% confidence level) at site 1 was observed during June (Figure 4*a*). In 1989 the highest monthly mean ozone level at site 1 was observed during May. The lowest monthly mean concentrations were observed in October 1987 and in September 1988 and 1989 (Figure 4*a*). A similar trend was noted at site 2 (Figure 4*b*), although the monthly mean ozone concentration peaked in August during 1987 (measurements were not recorded for site 2 in 1989).

The daily averaged ozone concentrations, solar radiation and, temperature at site 1 for 1987 (Figure 5) and 1988 (Figure 6) show a seasonal trend as well, as represented by the best fit curve illustrated in each figure (for each case, linear and second-order relationships were considered). The seasonal trend is clearer in 1988 than in 1987. Also, in 1988 the maximum occurs around Julian day 142 (May 21), whereas in 1987 the maximum occurs later in the summer,

TABLE 1. Summary of Minimum, Maximum, and Mean Values for Ozone Levels at Mt. Mitchell, Sites 1 and 2 for Growing Seasons of 1986–1989

Year	Site	May	June	July	August	September	October
1986	MM1*		54/111		23/94	27/75	18/71
			(74.3)		(45.0)	(47.6)	(39.6)
1987	MM1	24.5/73.4	23.7/93.1	11.3/96.4	23.4/103	15.3/77.1	10.9/74.3
		(50.2)	(57.5)	(50.1)	(54.1)	(46.4)	(45.8)
1988	MM1	42.5/116	36.1/123	30.0/151	22.8/114	11.5/84.3	
		(72.0)	(82.8)	(68.7)	(57.4)	(46.7)	
1989	MM1	37.7/79.4	25.5/90.5	8.1/92.1	28.0/77.4	25.5/70.2	
		(61.4)	(52.3)	(53.6)	(51.1)	(45.6)	
1986	MM2†				28/69	22/67	24/80
					(46.0)	(45.7)	(44.3)
1987	MM2	18.0/94.4	17.2/91.5	17.9/111	22.2/96.9	17.0/77.6	
		(49.5)	(49.5)	(49.3)	(53.8)	(43.9)	
1988	MM2	36.7/105	24.3/108	18.7/134	14.3/92.1	9.3/64.2	
		(59.6)	(67.6)	(55.1)	(50.0)	(35.2)	

Concentrations are in parts per billion by volume, and values are for hourly averaged data. Mean values are in parentheses. Data were collected in October during 1986 and 1987 only.
*MM1, Mt. Mitchell site 1, ~2000 m msl.
†MM2, Mt. Mitchell site 2, ~1760 m msl.

around Julian day 183 (July 1). In each year the highest ozone concentrations are observed during the early portion of summer, with lower concentrations observed during September and October.

The most frequent ozone level shifted from between 40–50 ppbv in 1986 to 50–60 ppbv in 1987 and to 60–70 ppbv in 1988 (Figures 7*a*, 7*b*, and 7*c*). Our data show that the seasonally averaged ozone concentration was 32% higher in 1988 than in 1986 and 29% higher in 1988 than in 1987.

In 1988 there were also more frequent occurrences of ozone levels above 100 ppbv. 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). 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. The average ozone level for the summer of 1988 at site 1 was higher than that for the summer of 1989 as well. In 1989 the ozone level did not exceed 100 ppbv at Mt. Mitchell during the field season (mid-May through mid-September).

The seasonal trend in the ozone concentrations observed at Mt. Mitchell agrees with that noted by *Meagher et al.* [1987] and *Logan* [1985], who reported a summer maximum in ozone over most of the United States for latitudes ranging between 35° and 45°N. In 1988 the maximum seemed to occur much earlier (in May) compared to 1987, during which the maximum occurred around July 1. An early summer maximum, pronounced in 1988, has also been observed for other sites in the southeastern United States [*Lavery and Edgerton*, 1990].

Episodic Ozone Variations

During the early part of the summer of 1988, several high-ozone episodes, associated with synoptic high-pressure systems, were observed. An example of such an episode during early July 1988 is illustrated by the curves for ozone concentration, solar radiation, and temperature in Figure 8. For the purposes of this paper, ozone concentrations of >80 ppbv are defined as "high-ozone episodes" [*Logan*, 1985] (e.g., see Figure 8*a*). Table 4 presents a summary of ozone episodes from May through September of 1988. Periods during which hourly averaged ozone concentrations were >80 ppbv and >100 ppbv were especially frequent and of longer duration during June and July 1988. Ozone levels of >80 ppbv were measured over 50% of the time during June 1988.

In general, high-ozone episodes occurred during the passage of synoptic high pressure, which results in the following conditions: (1) low wind speed (<5 m/s), (2) warm temperature (daily maximum of >25°C at site 1), and (3) low relative humidity (<60%). These conditions are conducive to the photochemical formation of ozone during the daytime hours. Temperatures on episodic days on average were 3°C warmer than those on nonepisodic days, while wind speeds were generally light.

TABLE 2. Hourly SO_2 Concentrations (ppbv) at Mt. Mitchell Site 1, 1987–1989

	May	June	July	August	September	October	Total
1987							
Maximum	3.3	12.2	2.9	···	1.8	···	12.2
Mean ± s.d.	0.9 ± 0.5	2.2 ± 1.9	0.7 ± 0.6	···	0.2 ± 0.4	···	1.4 ± 1.5
1988							
Maximum	24.2	13.4	16.3	4.6	12.5	···	24.2
Mean ± s.d.	2.8 ± 2.2	3.6 ± 2.0	3.3 ± 2.3	2.9 ± 0.7	2.0 ± 1.1	···	3.0 ± 1.9
1989							
Maximum	19.8	4.8	5.8	7.8	7.2	···	19.8
Mean ± s.d.	3.7 ± 6.9	0.18 ± 0.5	0.3 ± 0.7	1.6 ± 0.9	2.1 ± 0.7	···	1.3 ± 3.0

TABLE 3. Hourly NO_x Concentrations (ppbv) at Mt. Mitchell Site 1, 1987 and 1988

	May	June	July	August	September	October	Total
1987							
Maximum	2.5	4.9	7.4	3.7	3.9	7.2	7.4
Mean ± s.d.	1.1 ± 0.7	0.4 ± 0.8	1.3 ± 0.8	1.0 ± 0.6	0.9 ± 0.7	1.5 ± 1.2	1.1 ± 0.8
1988							
Maximum	10.6	6.2	9.1	10.7	6.9	···	10.7
Mean ± s.d.	1.9 ± 1.4	1.5 ± 0.9	1.6 ± 1.7	0.9 ± 1.1	1.6 ± 0.9	···	1.6 ± 1.3

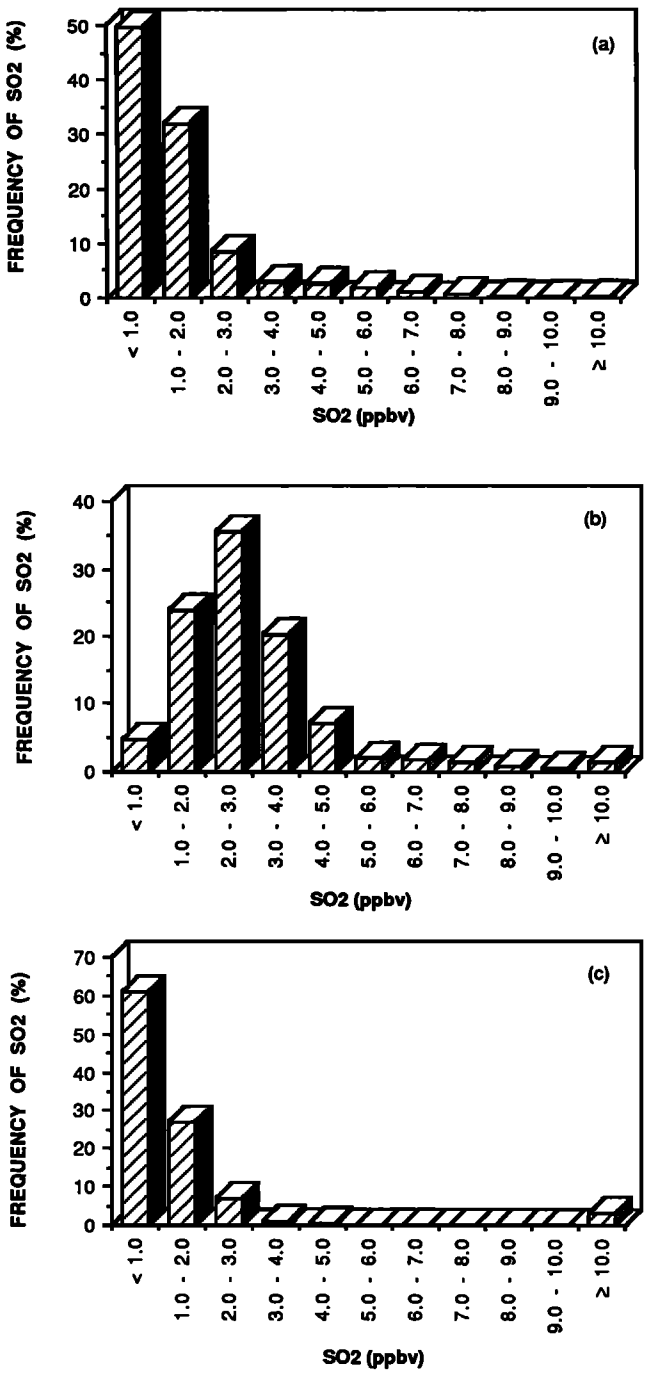

Fig. 2. Frequency distribution of sulfur dioxide (SO_2) concentrations monitored at site 1 from May to September (*a*) in 1987, (*b*) in 1988, and (*c*) in 1989.

There were three particularly long ozone episodes, lasting over 100 hours, during June and July 1988. The first episode began at 1700 EST on June 13, 1988, and lasted 111 hours. On five occasions during this episode, ozone concentrations of >100 ppbv persisted for periods ranging from 2 to 13 hours. The maximum ozone concentration of 122 ppbv occurred at 0400 EST on June 16. The second episode started at 2000 EST on June 23 and ended on June 26, 1988. Ozone levels exceeding 100 ppbv and lasting 2–10 hours were observed on four occasions. During the third long episode (Figure 8) a maximum ozone concentration of 150

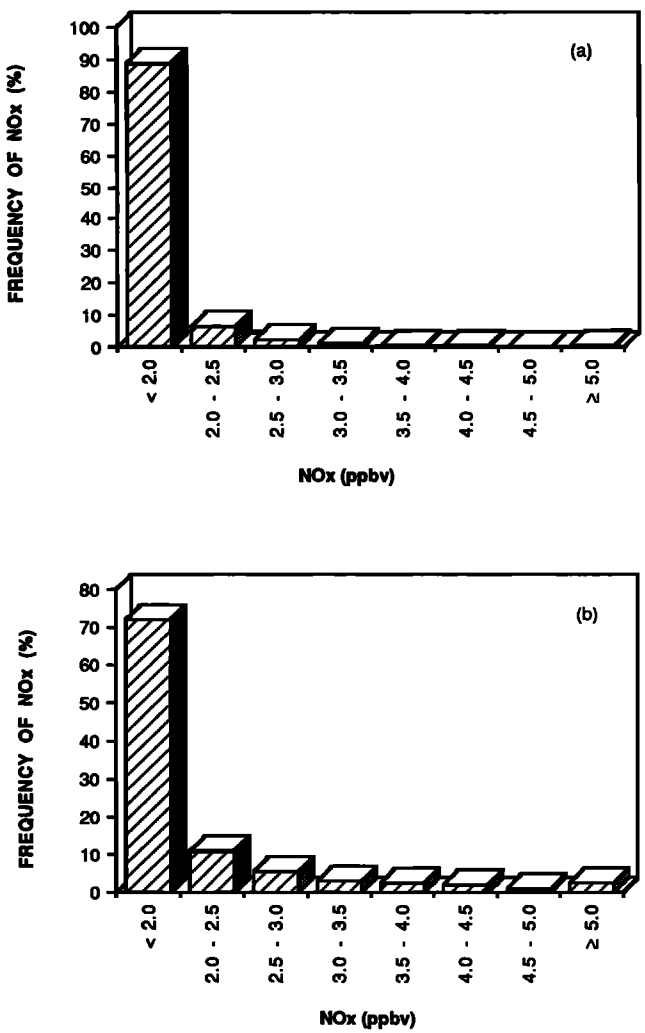

Fig. 3. Frequency distribution of total oxides of nitrogen (NO_x) concentrations monitored at site 1 (*a*) from May to October 1987 and (*b*) from May to September 1988.

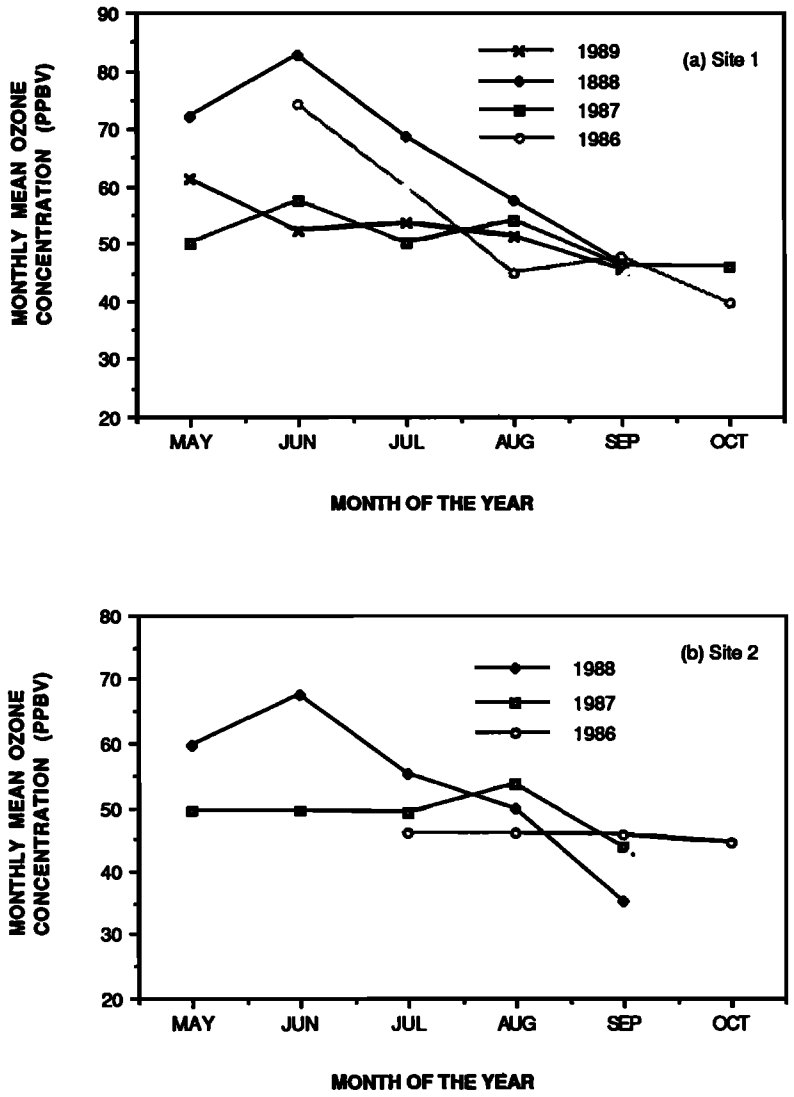

Fig. 4. Monthly mean ozone concentration at (*a*) site 1 and (*b*) site 2.

ppbv was observed at 0500 EST on July 9. This episode lasted 106 hours, starting at 1900 EST on July 6, 1988, and ending at 0400 EST on July 11, 1988. Two periods with ozone concentrations of >100 ppbv occurred during this episode and lasted for 69 and 3 hours. All three of the prolonged episodes began in the evening and ended before morning, with peak concentrations occurring during the night.

Ozone episodes during 1987 are summarized in Table 5. Most observations of ozone levels of >80 ppbv were observed during June 1987, reflecting the seasonal pattern seen during 1988. The longest episode lasted 18 hours, from 1100 EST on June 6 to 0400 EST on June 7, 1987. Ozone concentrations exceeding 100 ppbv occurred on only one occasion, August 9, 1987.

The relationship between ozone episodes and synoptic weather was particularly evident during the 1988 field season (Figure 9). A cyclical variation in ozone concentration was observed (Figure 9*a*), with approximately 10 peaks of ozone concentration of >100 ppbv. When synoptic weather patterns were analyzed for this period, it was found that increasing ozone concentrations preferentially occurred on the east (leading) side of ridges of high pressure, with northwest winds at 850 mbar (H and NW in Figure 9*a*), while sharp decreases in ozone concentrations occurred with pressure trough or cold-frontal passages (T and CF in Figure 9*a*). An example of an 850-mbar height and temperature analysis for a period of rapid ozone increase at site 1, during which northwest winds were observed, is given in Figure 9*b*.

Diurnal Ozone Variations

Meagher et al. [1987] monitored rural ozone levels at five lower-elevation sites in the southeastern United States for various periods since 1977. Data from their stations exhibited midafternoon maxima and early morning minima typical of most diurnal ozone patterns seen at lower-elevation sites. Amplitudes of these cycles were influenced by local urban sources, and nighttime ozone losses were related to deposition and the presence of local sources of nitrogen oxides. An example of such a large diurnal signal is shown in Figure 10 for Fairview (~850 m), North Carolina, located about 35 km south of Mt. Mitchell. For contrast the cumulative diurnal signal for site 1 and site 2 are also shown in Figure 10. Note

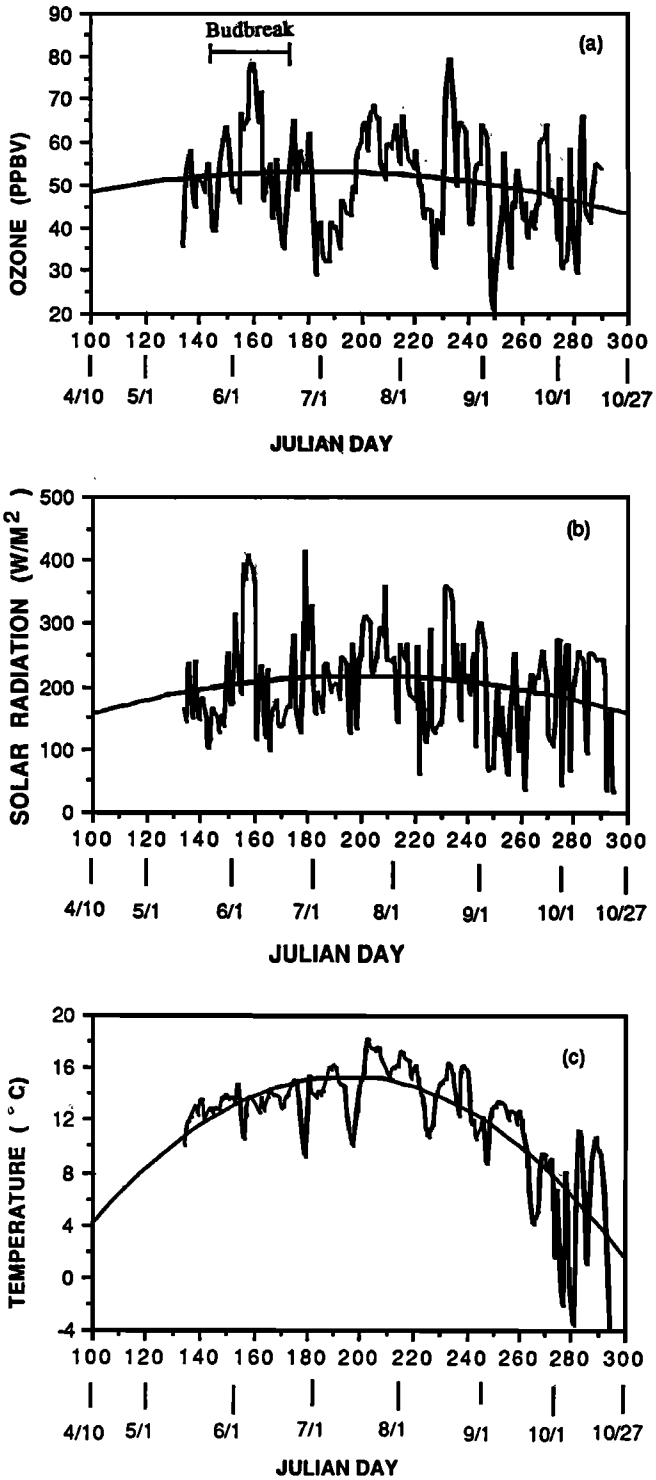

Fig. 5. Daily averaged (*a*) ozone concentration, (*b*) solar radiation, and (*c*) temperature at site 1 from May to October 1987. Regression curves shown in each panel are based on third-order polynomial regression analysis.

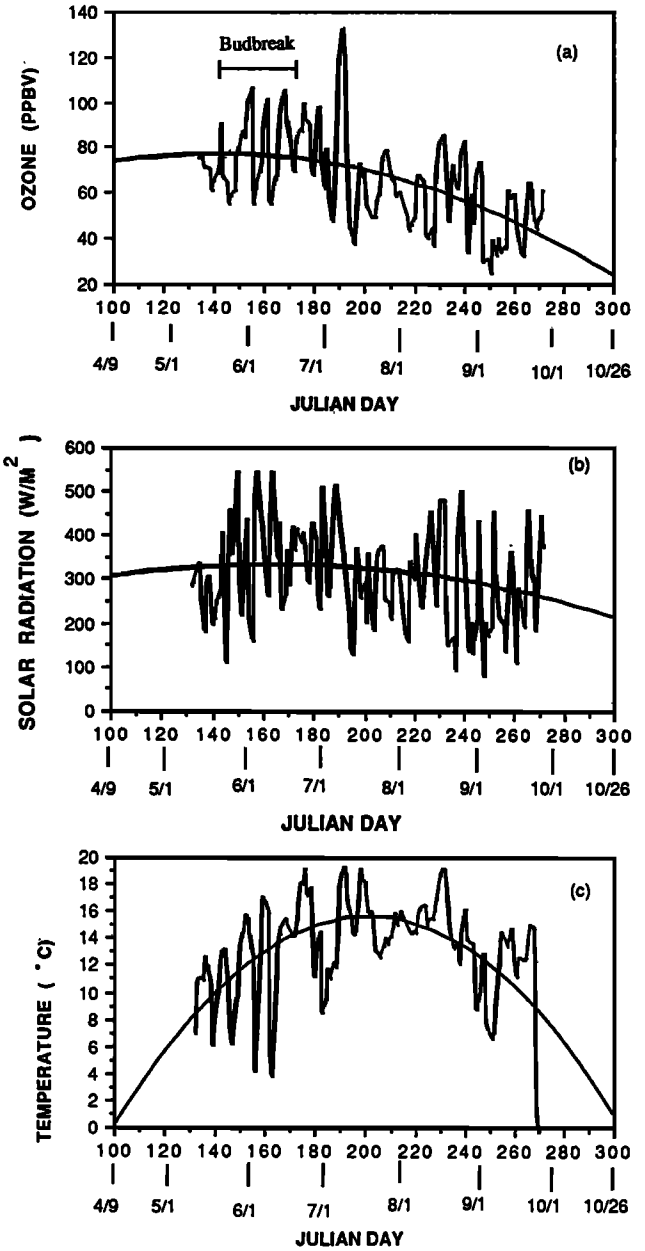

Fig. 6. Daily averaged (*a*) ozone concentration, (*b*) solar radiation, and (*c*) temperature at site 1 from May to September 1988. Regression curves shown in each panel are based on third-order polynomial regression analysis.

the high mean ozone concentration and the weak reverse diurnal signal at site 1 and the lack of diurnal signal and slightly lower concentration at site 2. The curves for Fairview and site 2 approach each other during the midafternoon, when vertical exchange and convective mixing in the boundary layer are greatest.

A reverse diurnal variation was noted at site 1 (summit station) for each of the first three field seasons (Figures 11*a* and 12*a*). The average daytime value for the entire field season was 49 ppbv in 1986 compared to an average nighttime value of 50 ppbv (~2% higher). The average daytime value was 49 ppbv in 1987 compared to an average nighttime value of 53 ppbv (8% higher). Similarly, in 1988 the average daytime value was 65 ppbv compared to the average nighttime value of 68 ppbv (~5% higher). The difference between the daytime and nighttime average concentrations was found to be statistically significant (*t* statistic) at the >95% level for 1986, 1987, and 1988. When daytime and nighttime values were compared on a month-by-month basis, the difference was statistically significant at the 99% confidence level. The ozone maximum occurred between 2000 and 2100 EST,

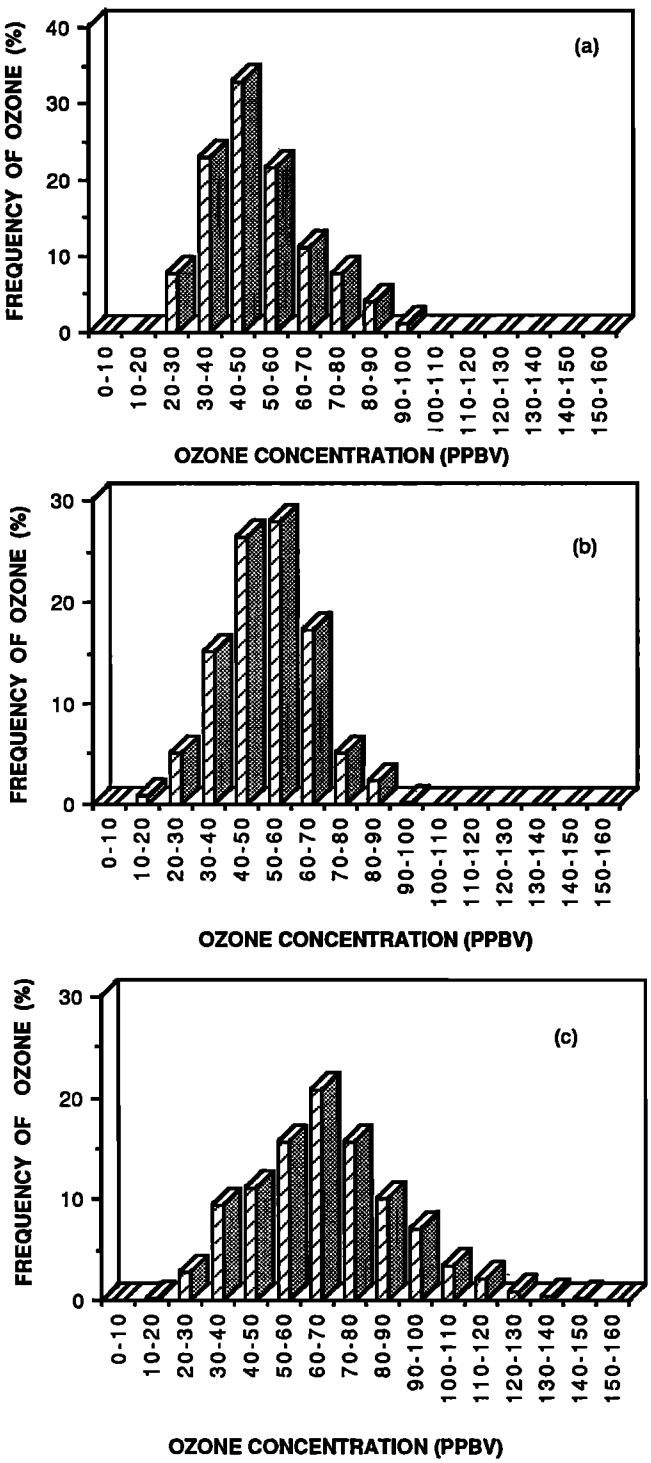

Fig. 7. Frequency distribution of ozone concentrations monitored at site 1 from May to September (*a*) in 1986, (*b*) in 1987, and (*c*) in 1988.

while the minimum was observed during midday. Significant diurnal variations in ozone concentration have not been observed at site 2 (Figures 11*b* and 12*b*).

Most of the ozone episodes (>80 ppbv) discussed earlier began in the late evening and early morning. Ozone levels increased through the afternoon, and concentrations at sunrise were almost equal to those at sunset. During episodes lasting 4–6 days, ozone concentrations of >100 ppbv were most frequently observed at night. The number of hours during which levels of >80 ppbv were observed at night was almost twice that of those observed during the daytime (Figures 13*a* and 13*b*).

Elevational Gradients in Ozone

Altitudinal gradients in ozone concentration can be seen when ozone data for 1986 from site 1 (2006 m), site 2 (1760 m), and Fairview (850 m) are compared (Figure 10). The greatest ozone concentrations are observed at site 1 at all times during the day, with the next highest concentrations observed at site 2. The concentrations at Fairview were much lower (by ~20 ppbv) than the high-elevation sites during the 1986 field season.

In 1986, site 1 ozone levels were higher than those of site 2 at the 90% confidence level. In 1987, ozone concentrations at site 1 were slightly higher than those at site 2 (Figure 11) (at the 99% confidence level). Significant differences between the two sites were recorded in 1988, when the ozone concentration at site 1 was always greater than at site 2 at the 99% confidence level (Figure 11). These results agree with electrochemical sonde data that show ozone concentration increases with height in the troposphere [*Warneck*, 1988, and references therein]. For the 4-year period 1986–1989, ozone levels exceeded 0.12 ppm (the basis of the NAAQS for ozone) for 8 hours at site 2 compared to 35 hours at site 1. The ozone levels exceeded 100 ppbv for 77 hours at site 2 compared to 218 hours at site 1 during this same period. None of these exceedances of the NAAQS for ozone at site 1 were observed during the 1989 field season.

DISCUSSION

Mechanisms potentially affecting the ozone concentration at Mt. Mitchell would include (1) chemical kinetics including photochemical formation of ozone or, to a lesser extent, by 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 due to the photochemical cycle 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).

At Mt. Mitchell an early summer maximum is noted in the ozone level. There are three factors in particular that may contribute to this observed seasonal trend: (1) it is known that ozone concentration is correlated with solar radiation and temperature, (2) the observed spring maximum in tropospheric ozone at site 1 may reflect stratospheric exchange at a time of maximum ozone concentration in the stratosphere, and (3) we hypothesize that excess local natural hydrocarbon emissions related to budbreak may contribute to high ozone concentrations during late spring and early summer.

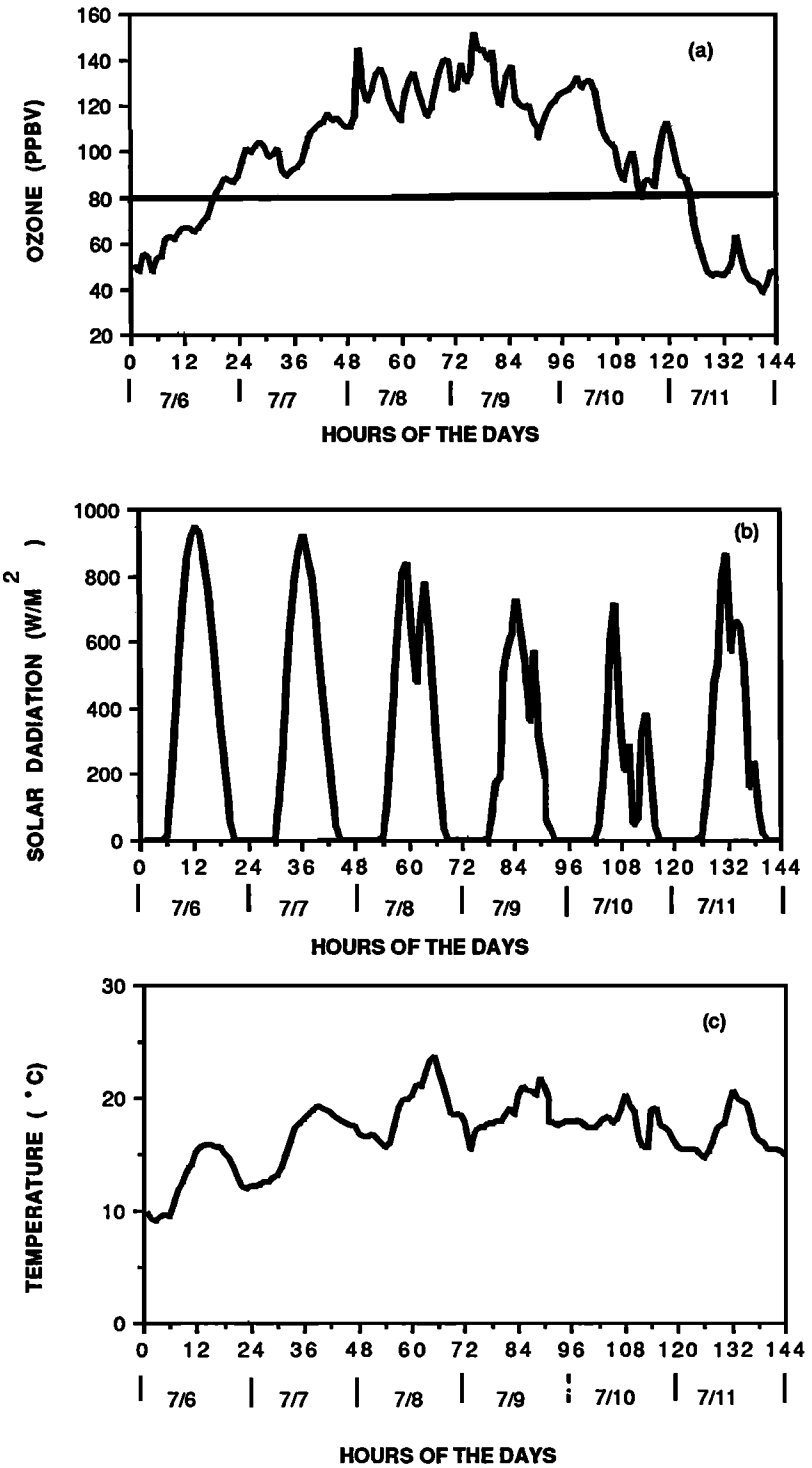

Fig. 8. Hourly averaged (*a*) ozone, (*b*) solar radiation, and (*c*) temperature during July 6–11, 1988, at site 1. The line at 80 ppbv in Figure 6*a* denotes a high ozone episode.

1. The maximum ozone concentrations observed for each field season were associated with high solar radiation (Figures 4, 5*b*, and 6*b*) and somewhat with high temperature (Figures 5*c* and 6*c*), consistent with the known correlation between solar radiation, temperature, and the formation of ozone. Results of a stepwise multiple regression analysis (parameters investigated were wind speed, temperature, relative humidity, solar radiation, and pressure) indicate that at the 95% confidence level, in 1987 ozone was significantly correlated to solar radiation ($r^2 = 0.22$). Adding temperature improved the correlation ($r^2 = 0.312$). Temperature shows a maximum value around Julian day 195, and maximum solar radiation around Julian day 201, while a maximum in the ozone level appears to occur around Julian day 183. A similar stepwise multiple regression analysis for 1988 showed that ozone was significantly correlated first nega-

TABLE 4. Number and Duration of Episodes at Mt. Mitchell Site 1 From May to September 1988

	May	June	July	August	September
Number of episodes	9	15	14	8	4
Maximum duration of episodes, hours	35	132	106	23	7
Average duration of episodes, hours	10	28	11	6	4
Total number of episodes lasting ≥20 hours	2	5	1	1	0
Total number of episodes lasting ≥100 hours	0	2	1	0	0

The ozone episodes are defined as when ozone concentration is greater than 80 ppbv.

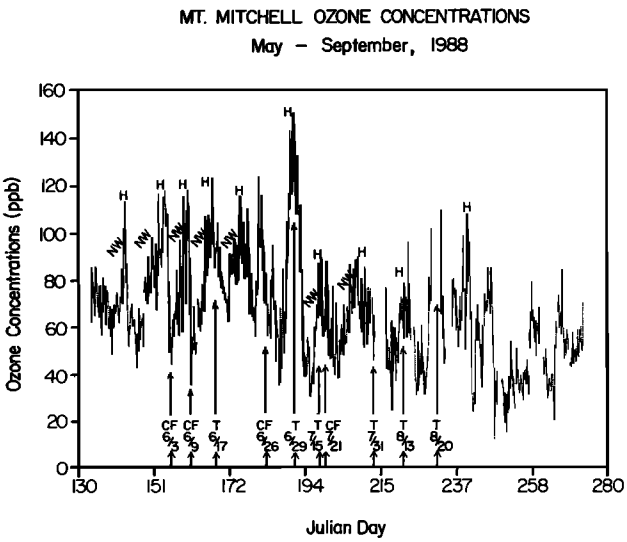

Fig. 9a. Ozone concentrations at site 1 from May to September 1988. NW refers to northwest winds at 850 mbar, CF refers to cold front passage, T refers to pressure trough passage, and H refers to high-pressure ridge at 850 mbar.

tively to relative humidity (r^2 = 0.30), then positively to temperature (r^2 = 0.416), and finally negatively correlated to pressure (r^2 = 0.438). The maximum in the ozone level appears to occur around Julian day 142.

Heggestad and Bennett [1984] pointed out that high-ozone episodes in the eastern United States are generally accompanied by high ambient temperatures, high solar radiation intensity, low relative humidities, and the absence of precipitation. The early portion of the 1988 field season was abnormally hot and dry in the southeastern Appalachian Mountains, as in many other portions of the country. During the early summer a strong upper level ridge over the central portion of the United States brought very dry conditions over the Appalachians and Ohio River Valley. As already discussed, several stagnating high-pressure systems were noted during the early part of the summer. Regional temperatures were well above normal in July and August for most of the eastern half of the United States.

At site 1 the mean solar radiation was 314 W/m^2, and the mean temperature was 13°C during the 1988 monitoring period, while the corresponding values were 167.1 W/m^2 and 11°C during the 1986 monitoring period and 203 W/m^2 and 13°C during the 1987 monitoring period. Therefore interseasonal variation in ozone concentration at Mt. Mitchell may reflect year-to-year climate fluctuations over the southeastern United States.

2. It has been noted that a phased seasonal variation exists between the background tropospheric ozone and the stratospheric ozone, and it has been speculated that the source of background ozone in the free troposphere is stratospheric exchange [*Singh et al.*, 1980]. The observed spring maximum in tropospheric ozone at site 1 may reflect the vertical exchange in the free troposphere at a time of maximum ozone concentration in the stratosphere.

3. Tree budbreak usually occurs at higher elevations in the Mt. Mitchell Park between May 15 and June 15 (Figures 5 and 6) [*White*, 1984; N. Nicholas, personal communication, 1989]. We hypothesize that excess local natural hydrocarbon emissions, related to budbreak or during the growth cycle of a tree, may contribute to high ozone concentrations during this time period. It is not well known how trees react to internal and external stresses in their emissions of nonmethane hydrocarbon compounds, although there is some evidence that suggests that these emissions may be in-

TABLE 5. Number and Duration of Episodes at Mt. Mitchell Site 1 from May to September 1987

	May	June	July	August	September
Number of episodes	0	9	3	13	0
Maximum duration of episodes, hours	0	18	4	12	0
Average duration of episodes, hours	0	9	3	3	0
Total number of episodes lasting ≥20 hours	0	0	0	0	0

The ozone episodes are defined as when ozone concentration is greater than 80 ppbv.

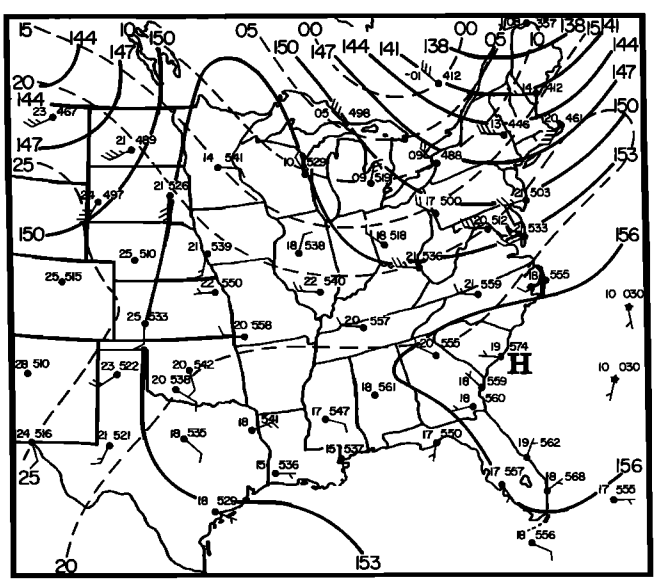

Fig. 9b. Height and temperature analysis at 850 mbar for 1200 UTC on June 23, 1988.

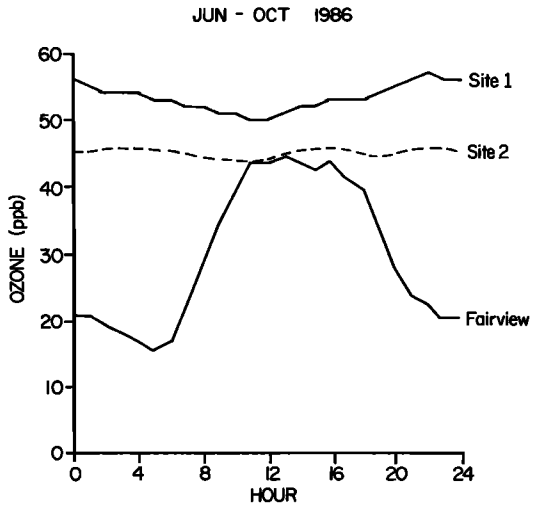

Fig. 10. The diurnal variation of ozone for 1986 at Fairview, North Carolina, site 1 and site 2.

creased during periods of stress or during certain periods in their growth cycle. For example, it is known that nonmethane hydrocarbons (NMHC) both known and unknown are produced in plants in response to environmental stresses [*Cracker*, 1971; *Tingey et al.*, 1976; *Unsworth*, 1984]. It is suggested that budbreak may represent a biological stress which may result in natural hydrocarbons being given off in excess amounts during growth period, thus contributing to the observed high average ozone concentrations during late spring and early summer. While rural regions are generally thought to be NO_x limited [*Liu et al.*, 1987], it has not been verified that the Mt. Mitchell area is always NO_x limited. Although there were some incidents of high NO_x levels observed at Mt. Mitchell (Table 3), simultaneous hydrocarbon measurements were not made, so that the instantaneous NMHC to NO_x ratio was unknown, and therefore we do not know whether the site was hydrocarbon limited during these periods. The roles of NO_x and of hydrocarbons, both anthropogenic and biogenic, in the ozone climatology at Mt.

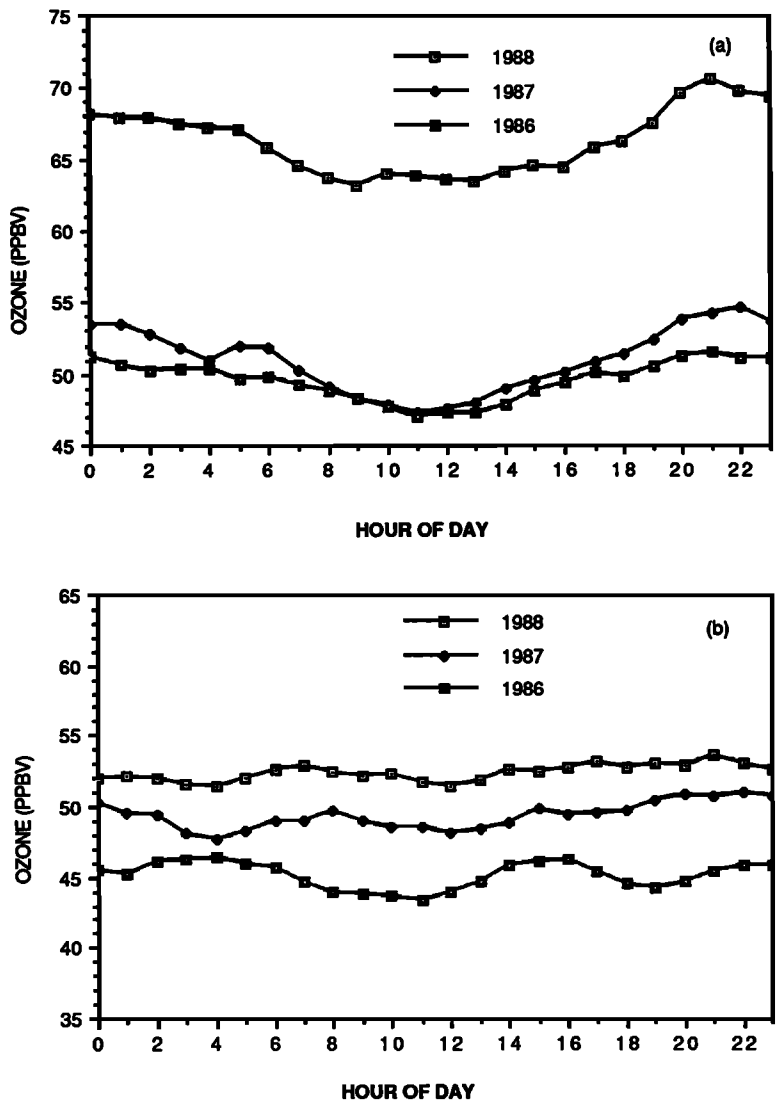

Fig. 11. Mean diurnal variation of ozone concentration from May to September 1986, 1987, and 1988 at (*a*) site 1 and (*b*) site 2.

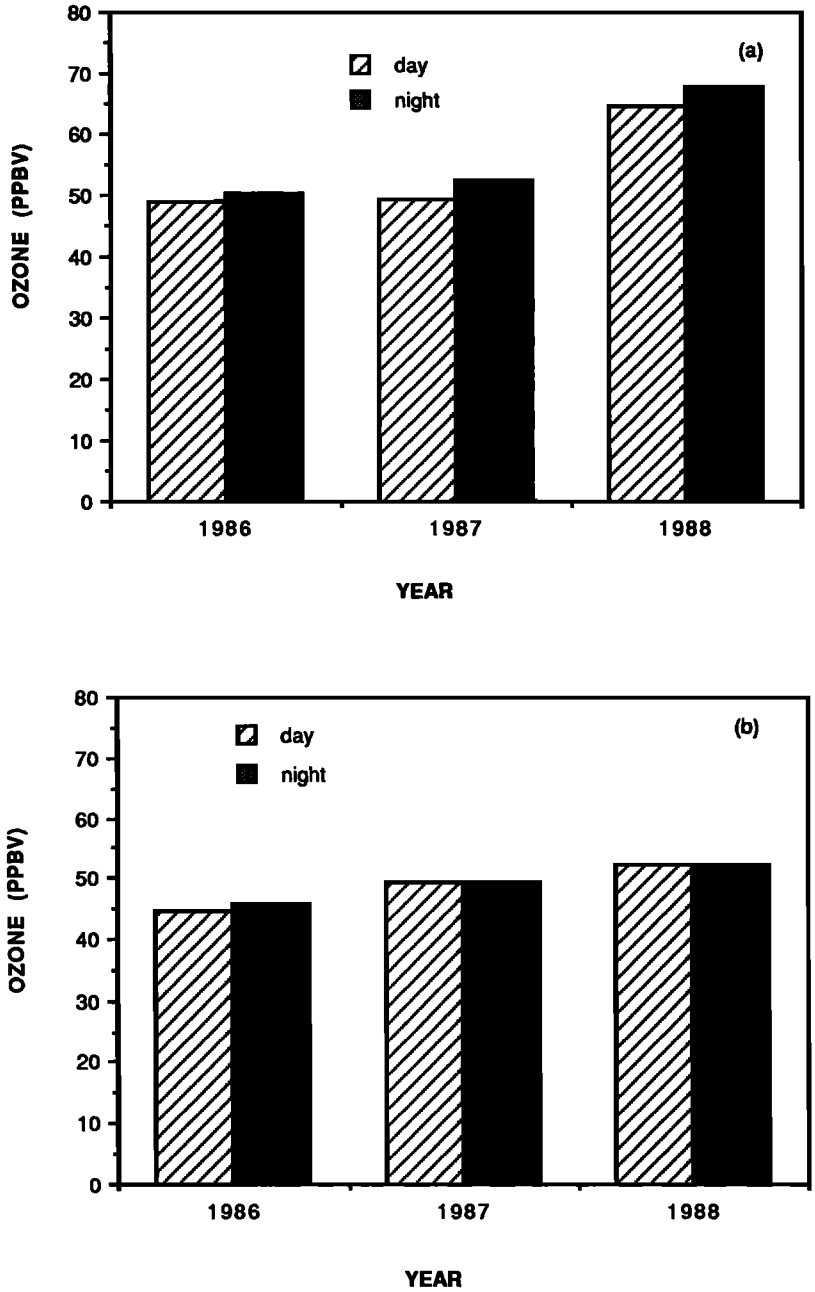

Fig. 12. Daytime and nighttime mean ozone concentrations for May to October 1987 and May to September 1986 and 1988 at (*a*) site 1 and (*b*) site 2. Daytime is defined as 0800–2000 LT.

Mitchell need to be explored further, and to do so would require simultaneous monitoring of speciated hydrocarbons and measuring of NO_x levels with a much lower level of detection than the current analyzers provide. Also, the seasonal dependency of biogenic hydrocarbon emissions, particularly the more reactive species such as isoprene and terpene, and including the effects of budbreak on these emissions, is an area which warrants further study.

Ozone episodes exceeding concentrations of 100 ppbv at Mt. Mitchell are coincident with the backside of high-pressure systems. Comparison of atmospheric pressure and ozone data from site 1 shows that the peak in ozone concentration occurs on the backside of centers of high pressure. These air parcels have the longest residence time in the high-pressure system. The high-pressure conditions are conducive to photochemical O_3 formation. The association between synoptic-scale high pressure and ozone has also been reported for other locations in the mid-Atlantic United States [*Vuckovich et al.*, 1977; *Wolff et al.*, 1987].

The relationship between ozone concentrations and wind direction at Mt. Mitchell was also investigated. Ozone concentrations are highest when the local wind direction is from the north to northwest (between 270° and 360°) at site 1 (Figure 14), suggesting that higher levels of ozone emissions and/or its precursors are transported to Mt. Mitchell from the Ohio River Valley located to the northwest. Preliminary back-trajectory analysis supports this hypothesis. Although the local wind indication is not necessarily expected to be a good indication of the source of the air mass to the mountaintop, good correlation between wind direction and the

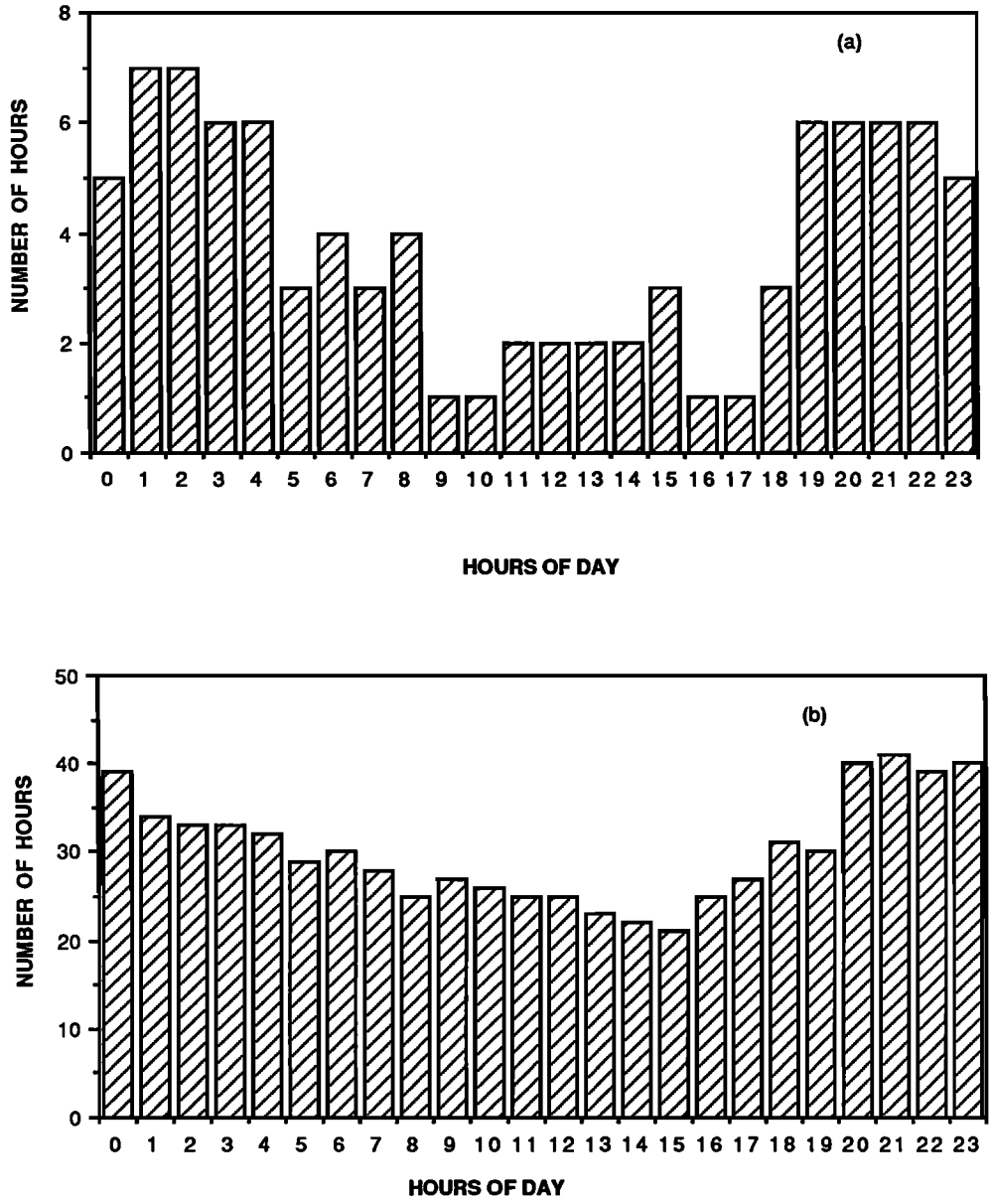

Fig. 13. Number of hours with ozone concentration of >80 ppbv at site 1 May to September in (*a*) 1987 and (*b*) 1988.

back trajectory has been observed at Mt. Mitchell, except when the air parcel approaches the mountain from the north-northeast. If northwest winds preferentially occur at night, the high ozone values may be due to nocturnal subsidence. To clarify this issue, nighttime and daytime ozone concentrations versus wind direction were plotted (Figure 15). The results indicate that ozone concentrations both during the day and at night were higher when the wind direction is from between 270° and 360°, supporting the suggestion that higher levels of ozone emissions and/or its precursors are transported to Mt. Mitchell from the northwest.

The typical diurnal ozone variation including a daytime maximum was not observed at either site 1 or site 2. The lack of a typical diurnal variation at the Mt. Mitchell sites does not come as a surprise. Ozone is relatively stable in the natural troposphere, and its lifetime is thought to be approximately 10 days [*Liu et al.*, 1980] and maybe as high as 50 or 60 days [*Hough and Derwent*, 1990]. Such an absence of daytime maximum ozone levels has been reported by other investigators as well. The diurnal variation of ozone as a function of NO_x levels was investigated at Niwot Ridge, Colorado [*Fehsenfeld et al.*, 1983], and at low levels of NO_x (0.1–0.3 ppbv) there was also an apparent lack of diurnal variation, although at higher levels (particularly above 0.6 ppbv) a daytime maximum was observed. At this same location there was little diurnal variation noted during midwinter. Ozone levels monitored at a remote mountain location in the Canadian Rockies also demonstrated no diurnal variation [*Peake and Fong*, 1990]. Ozone profiles from tethered balloon data in hilly terrain on the Swiss plateau also indicate that the largest typical diurnal variation (daytime maximum) occurred in the lowest elevations in the valley where, presumably, surface deposition processes were greatest [*Broder and Gygax*, 1985].

The nocturnal maximum at site 1, however, was not

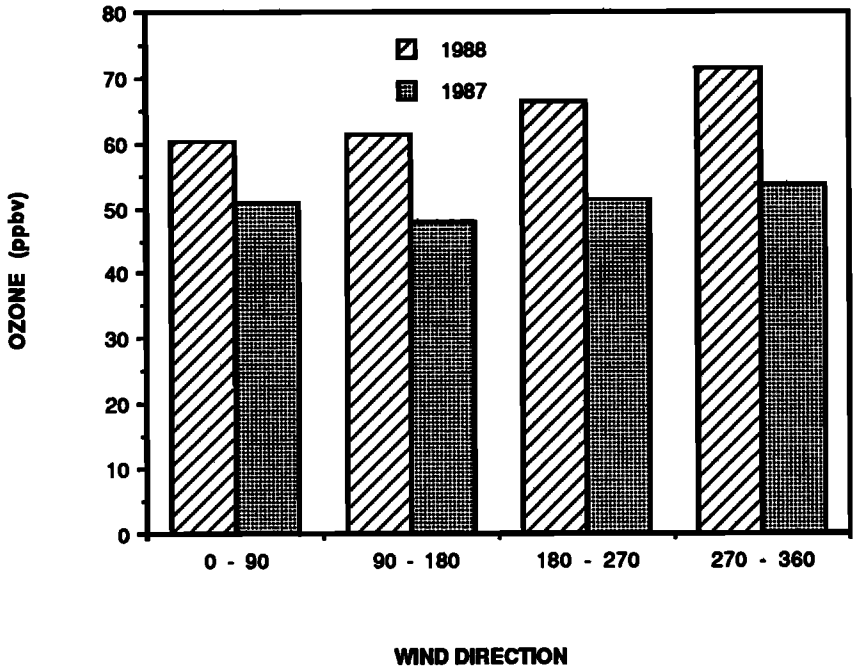

Fig. 14. Ozone concentration versus wind direction at site 1 from May to September 1987 and 1988.

expected. This reverse diurnal pattern in ozone concentrations observed at site 1 may be explained by the combined effects of several of the mechanisms mentioned in the beginning of this discussion section, including advective processes at night, high surface deposition processes in the mixed layer during the day, and the diurnal variation of the location of the mountaintop with respect to the convective boundary layer. Whether the nocturnal ozone maximum observed at site 1 is related to the residual layer left in the wake of the boundary layer collapse or is related to higher ozone concentrations in the free atmosphere is open to some debate.

Alternatively, higher ozone concentrations were found in a residual layer at night in a study on the transport of ozone and the role of convective processes over heterogeneous terrain in north Germany [*Jochum et al.*, 1989]. Vertical ozone profiles taken by aircraft-borne instruments show that daytime concentrations are constant with height in the mixed layer. At this time, ozone is being photochemically produced, while destruction of ozone is simultaneously being communicated throughout the mixed layer. At night, however, destruction of ozone is confined to a shallow surface layer, resulting in higher observed ozone concentrations in the residual layer than those observed during the daytime.

Vertical transport associated with downslope winds may also play a role in the nocturnal ozone maximum. In a study of the boundary layer structure above a valley in Switzerland, *Broder and Gygax* [1985] investigated the local diurnal variations in ozone concentrations and deposition and found that surface deposition is significant over hilly terrain and that at night ozone-rich air is brought to the surface by nocturnal downslope winds. A similar mechanism may be operating near Mt. Gibbs, acting to bring higher ozone concentration in the residual layer or from the free troposphere to the surface.

SUMMARY

The objective of the research presented in this paper is to develop a climatology for ozone at high elevations over the eastern United States in an attempt to assess its role in forest decline. It has been shown that exposure to ozone concentrations of ≥50 ppbv is sufficient to cause damage to certain species of vegetation. During the monitoring season at site 1, the mean ozone concentrations were approximately 50, 51, 66, and 52 ppbv for 1986, 1987, 1988, and 1989 field seasons, respectively. At site 2 the mean ozone concentrations were 49, 49, and 52 ppbv for 1986, 1987, and 1988 field seasons, respectively.

A pattern of seasonal variation is noted for both site 1 and site 2, with the maximum monthly mean ozone concentrations occurring during the early summer and minimum concentrations during the fall.

In this paper, periods with ozone concentrations of >80 ppbv are defined as "high-ozone episodes." Episodes during which hourly averaged ozone concentrations were >80 ppbv and >100 ppbv were especially frequent and of long duration during June and July 1988. A relationship between ozone episodes and synoptic weather patterns was found. In general, high-ozone episodes occurred during the passage of synoptic high pressure, with associated subsidence that produces conditions favorable for ozone formation. Increasing ozone concentrations preferentially occurred with northwest winds on the east side of high-pressure ridges (at 850 mbar), while sharp decreases in ozone concentrations occurred with cold-frontal or trough passages.

An elevational gradient in average ozone concentration was observed at Mt. Mitchell, with increasing ozone concentrations measured with increasing elevation. These findings are consistent with sounding data that show an increase in ozone concentration with height in the troposphere. Different diurnal variations of ozone concentration were observed at site 1, site 2, and the Fairview site. The diurnal pattern at Fairview displays a maximum concentration during the day, typical of low elevation and urban areas. The ozone concentrations at site 2 are relatively constant throughout the day, while ozone at site 1 experiences a

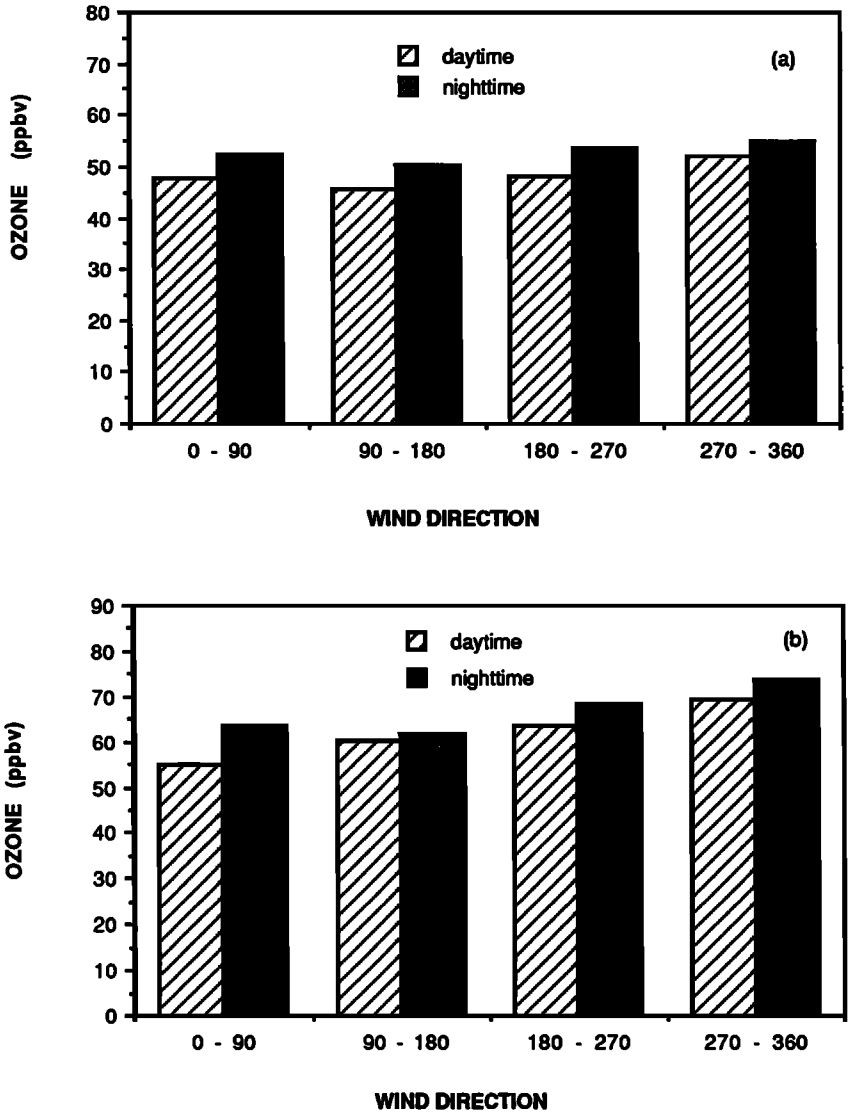

Fig. 15. Daytime and nighttime ozone concentrations versus wind direction at site 1 in (*a*) 1987 and (*b*) 1988.

reverse diurnal pattern with a nocturnal ozone maximum. In the absence of a known chemical mechanism which would explain the reversed diurnal cycle in the ozone at site 1, it is suggested that advective transport of ozone from the lower troposphere at night, when the nocturnal boundary layer is below the mountaintop, and possibly nocturnal downslope winds may explain the increased nocturnal ozone at site 1.

Since there are no urban sources in the vicinity of the Mt. Mitchell sites, levels of nitric oxide (a precursor chemical for formation of ozone) were often observed below the limit of detection for the instrument. Occasionally, however, levels above 2 ppbv and as high as 11 ppbv were observed. Levels as low as 30–50 pptv are adequate for ozone formation [*Janach*, 1989]. The contribution to atmospheric ozone from natural hydrocarbons is not well understood but may be significant in some rural areas. Therefore the role of local photochemical production in the ozone climatology at Mt. Mitchell is still undetermined.

Recent evidence [*Chameides et al.*, 1988] suggests that our strategies for photochemical oxidant control may be seriously flawed, especially in the southeastern United States. In order to resolve the role of transport and chemical kinetics in high-elevation ozone climatology, simultaneous soundings of ozone and measurements of its precursors and meteorological parameters are needed at a few representative locations for an extended period. Continued long-term monitoring of ozone and its precursors at Mt. Mitchell, North Carolina, will therefore provide important information on the climatology of free tropospheric ozone, information that will be critical to future planning of ozone control programs and in the establishment and evaluation of regional air quality standards.

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