INTRODUCTION

Forests are exposed to a variety of chemical and physical stresses (Bruck et al., 1989; Cowling, 1989; Aneja et al., 1990a, b; 1991, 1992; Saxena and Lin, 1990; Claiborn and Aneja, 1991; Kim and Aneja, 1992a, b; Aneja and Kim, 1993; Aneja, 1993) known to be injurious to some species of trees (Prinz, 1987; Klein and Perkins, 1988). At many high-elevation locations in the northern and southern Appalachians, spruce–fir forests have recently shown marked losses of foliar biomass, decreases in growth, and mortality (Johnson, 1983; Johnson and Siccama, 1983; Adams et al., 1985; McLaughlin, 1985; Schütt and Cowling, 1985; Bruck and Robarge, 1988). These changes in forest condition have led to the suspicion that stresses induced by airborne chemicals may be adding to the natural insect, fungal, cold, drought, and nutritional stresses under which these forests grow (Woodman and Cowling, 1987; Bruck, 1989).

Air pollution stress to a forest or vegetative ecosystem occurs whenever forest trees are exposed to toxic concentrations of gases, such as ozone, sulfur dioxide, hydrogen peroxide, fluoride, or when trees are exposed to accumulation of toxic chemicals in soil (Heck et al., 1986). Convincing data exist for vegetative injury caused by ozone (Winner et al., 1989). Damage to crops in the United States of America from ozone alone has been estimated to be $2–5 billion annually (Heck et al., 1988).

The specific sources of pollutants deposited at any given site are largely unknown, but are generally acknowledged to be due to the widespread use of coal, oil, and motor fuels in North America. Under a national program entitled "Mountain Cloud Chemistry/Forest Exposure Study" (MCCP) funded by the U.S. Environmental Protection Agency (EPA), the chemical and physical climate at five sites in the eastern United States of America was monitored from the period of 1986 to 1990 (Aneja et al., 1991; Aneja and Li, 1992; Li and Aneja, 1992). Mt Mitchell, North Carolina, is the southernmost site of this network. In addition, at the Mt Mitchell site, atmospheric photo-
chemical oxidants nitric acid (HNO₃), ozone (O₃), and hydrogen peroxide (H₂O₂) were monitored in ambient air.

All three photochemical oxidant species, HNO₃, O₃, and H₂O₂ are generated in the atmosphere via a complex series of reactions involving NO₂ and volatile organic compounds (VOCs) in the presence of sunlight. All three species are strong oxidizing agents and play important roles in atmospheric photochemistry, and in the aqueous phase chemistry of precipitation acidification. A simplified ozone formation scheme (Liu et al., 1987) is shown as follows:

\[ \text{NMHC} + \text{OH} + \text{O}_3 \rightarrow \text{RO}_2 \]  
\[ \text{RO}_2 + \text{NO} + \text{O}_2 \rightarrow \text{NO}_2 + \text{HO}_2 + \text{CARB} \]  
\[ \text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH} \]  
\[ \text{NO}_2 + \text{hv} \rightarrow \text{O}(1D) + \text{O}_2 \]  
\[ \text{O}(1D) + \text{H}_2\text{O} \rightarrow 2 \text{OH} \]  
\[ \text{OH} + \text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{HO}_2 \]  
\[ \text{HO}_2 + \text{HO}_2 + \text{M} \rightarrow \text{H}_3\text{O}_2 + \text{O}_2 + \text{M} \]

where CARB stands for carbonyl compounds. Hydrogen peroxide is formed in the atmosphere by the self-combination of hydroperoxyl radical (HO₂). Hydroperoxy radical is formed predominantly from the reaction of hydroxyl radical with carbon monoxide (as shown below) or with hydrocarbons (as shown above). The major source of hydroxyl radical in the clean atmosphere is the photolysis of ozone followed by reaction of the electronically excited oxygen atom with water vapor

\[ \text{O}_3 + \text{hv} \rightarrow \text{O}(1D) + \text{O}_2 \]  
\[ \text{O}(1D) + \text{H}_2\text{O} \rightarrow 2 \text{OH} \]  
\[ \text{OH} + \text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{HO}_2 \]  
\[ \text{HO}_2 + \text{HO}_2 + \text{M} \rightarrow \text{H}_3\text{O}_2 + \text{O}_2 + \text{M}. \]

Nitric acid in the gas phase is formed during the day by reaction between the hydroxyl radical and nitrogen dioxide

\[ \text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3. \]

A number of observers have demonstrated that atmospheric photochemical oxidants, in general, are formed near urban and industrial areas with high levels of anthropogenic sources, and the long-range transport of these oxidants and their precursors from these regions may contribute to elevated oxidant levels in downwind rural areas (Vukovich et al., 1977; Cadle et al., 1982; Wolff et al., 1982). Since the lifetime in the troposphere of nitric acid is \( \approx 10-20 \text{ d} \) (Finlayson-Pitts and Pitts, 1986), ozone is \( \approx 30-60 \text{ d} \) (Logan, 1985; Hough and Derwent, 1990), and gaseous hydrogen peroxide is \( \approx 10-30 \text{ d} \) (Finlayson-Pitts and Pitts, 1986), it is possible for these oxidants to be transported long distances to remote forest areas.

In this paper we present the results of trends and analysis of HNO₃, and compare and contrast it to the temporal variability in the gas-phase status of ozone (Aneja et al., 1991), and hydrogen peroxide (Claiborn and Aneja, 1991) at a high-elevation site (\( \approx 2006 \text{ m m.s.l.} \)) near Mt Mitchell State Park in North Carolina (35°44′N, 82°17′W) during the late spring, summer, and autumn (May–September) of 1986–1990. We examine the underlying phenomena, and provide a comparison with seasonal distribution of selected recent ozone data, based on monthly average values.

**EXPERIMENTAL**

The Mt Mitchell research observatory consists of two sites. The main station (Site 1) is near the summit of Mt Gibbs, at an elevation \( \approx 2006 \text{ m m.s.l.} \) located about 2.5 km southwest of the Mt Mitchell. The second site (Site 2) is located at an elevation of \( \approx 1760 \text{ m m.s.l.} \) on Commissary Ridge, located \( \approx 1 \text{ km} \) on the southeast shoulder of Mt Mitchell.

Measurements of gaseous nitric acid were made at Site 1 during May–August of 1988 and 1989 using an annular denuder technique (Possanzini et al., 1986, Murthy, 1990). Three annular denuder tubes coated with NaCl, Na₂CO₃, and citric acid, respectively, were used in series to collect the acidic gases (HNO₃, H₂O₂, and SO₂), followed by a filter pack to collect particulate nitrates. The inlet to the annular denuder system consists of a coarse particle preseparator which is a Teflon-coated glass impactor (Possanzini, 1986). The impactor is designed with a very short cylindrical inlet to the impaction surface to prevent large particles and rain drops from entering the annular denuder system. Nitric acid was removed exclusively from other acids in the first denuder coated with NaCl. Samples were generally collected over a 24-h period, although limited sampling was conducted over shorter time periods of 12, 8, or 4 h (Murthy, 1990).

The level of detection for HNO₃, for this instrument is 0.05 \( \mu \text{g m}^{-3} \), with a precision of 3% in the range of 0.5–3 \( \mu \text{g m}^{-3} \). Field and laboratory blanks were prepared and analysed for background values. The analytical quality control (QC) solutions for nitrate (NO₃) were provided by the U.S. Environmental Protection Agency (EPA) and were run on the ion chromatograph after every five samples. The concentrations of the QC samples were chosen to be representative of those found in the ambient samples.

Ozone was measured using an ultra-violet absorption technique (Thermo Electron Corporation Ozone Analyser model 49). The level of detection for this instrument is 2 ppbv. The quality assurance protocols included weekly zero and span checks, and multipoint calibrations were conducted at least twice during the measurement period.

Ambient, gas-phase hydrogen peroxide was measured using the continuous fluorometric technique based on the horseradish peroxidase method (Laszrus et al., 1986) periodically during the latter portion of the growing season (July–September) of 1988 at the high-elevation site (Site 1) at Mt Mitchell, NC (Claiborn and Aneja, 1991). The dual channel analyser measures total peroxides on one channel, and by specific enzymatic destruction of hydrogen peroxide, organic peroxides only on the second channel, and has a lower detection limit of 0.1 ppbv. Gas-phase total and organic peroxide data were recorded on a chart recorder and extracted manually as 12-min averages. These data were then consolidated into hourly averages. The hydrogen peroxide analyser was calibrated at least once daily, and calibration solutions were checked weekly. Baseline checks were performed automatically, usually several times per day.

**RESULTS**

Concentrations of gaseous nitric acid were found to be in the range of 0.05–5.62 \( \mu \text{g m}^{-3} \) with a mean of...
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1.14 ± 0.96 μg m⁻³ for 1988, and 1.40 ± 0.59 μg m⁻³ during the 1989 field season. The range of concentrations noted at Mt Mitchell are similar to those reported by Cadle (1985) for Warren, Michigan (1.0–2.7 μg m⁻³), and Shaw et al. (1982) for RTP, NC (1.5 μg m⁻³); and higher than the mean value (0.43 μg m⁻³) reported for eastern England (Harrison and Allen, 1990). Time series plots of the gaseous nitric acid concentrations in 1988 and 1989 show a bimodal variation, i.e. peaking in concentration during late spring and again in summer but decreasing during the fall (Fig. 1). A similar seasonal variation in nitric acid concentrations has been observed by other researchers (Cadle 1985; Meixner et al., 1985; Russell et al., 1985), although the reasons for this bimodal seasonal variation are still unclear.

Short-term measurements (4 h duration), made on two different days during the two years, show a diurnal trend in nitric acid concentration, with higher concentrations during the day. As can be seen from Fig. 2, the diurnal variation is more pronounced on 4 August 1989, while much less variation was noted on 10 August 1988. Hence, the diurnal variation can be more or less pronounced on a particular day, depending on the synoptic weather situation. Twelve-hour duration sampling for daytime and nighttime samples showed daytime HNO₃ concentrations higher than the nighttime levels (95% statistically significant level; t-statistic).

The minimum, mean, and maximum ozone concentrations for each month at Site 1 during May–September 1990 are summarized in Table 1, and are compared to growing season data for 1986–1989 at Sites 1 and 2 (Aneja et al., 1991). Maximum 1-h average 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 1-h average values observed were 111 ppbv during June 1986, 103 ppbv during August 1987, 151 ppbv during July 1988, 92 ppbv during July 1989, and 128 ppbv during July 1990. Ozone concentrations were higher in 1988 than in 1989 and 1990 or the previous two years at both sites.

During the field season of 1988, 273 hourly hydrogen peroxide measurements were recorded (Claiborn and Aneja, 1991). Gas-phase hydrogen peroxide at Mt Mitchell ranged from the level of detection (0.1 ppbv) to above 4 ppbv. In general, atmospheric hydrogen peroxide levels at Mt Mitchell State Park are comparable to, or higher than, values reported in the literature. At nearby Whitetop Mtn, VA (Olszyna et al., 1988), a maximum of 2.6 ppbv was reported in the summer of 1986, and a maximum of 0.57 ppbv in the fall. Values over 4 ppbv have been observed aloft, over the eastern United States of America (Heikes et al., 1987).

DISCUSSION

The measured nitric acid concentrations were compared with the corresponding meteorological (temperature, solar radiation, relative humidity, wind direction, cloudiness and precipitation) and ozone data to determine the generation and removal mechanisms for gaseous nitric acid. Statistical analysis of these meteorological variables and the 24 h integrated nitric acid values show low correlation coefficients ($r^2 < 0.2$), suggesting the integrated measurements not only depend on the formation pathways, but also on deposition and removal mechanisms such as precipitation and cloud interception. However, good correlations were observed when short-term nitric acid concentrations were correlated with the corresponding meteorological data. The relationship between nitric acid, temperature, relative humidity, solar radiation and ozone are shown in Fig. 3. The results indicate that nitric acid gas-phase concentrations are correlated to solar radiation ($r^2 = 0.57$), and to temperature ($r^2 = 0.45$). High concentrations of nitric acid were generally associated with low relative humidity ($r^2 = 0.33$) (Grosjean, 1983). A multiple regression of
Table 1. Summary of minimum, maximum, and (mean) values for ozone levels at Mt. Mitchell, Sites 1 (MM1, ~2006 m m.s.l.) and 2 (MM2, ~1760 m m.s.l.) for growing seasons of 1986–1990. Concentrations are in ppbv, and values are for hourly averages (note: data were collected in October during 1986 and 1987 only).

<table>
<thead>
<tr>
<th>Year</th>
<th>Site</th>
<th>May</th>
<th>June</th>
<th>July</th>
<th>August</th>
<th>September</th>
<th>October</th>
</tr>
</thead>
<tbody>
<tr>
<td>1986</td>
<td>MM1</td>
<td>54/111</td>
<td>(74.3)</td>
<td>23/94</td>
<td>27/75</td>
<td>18/71</td>
<td></td>
</tr>
<tr>
<td>1987</td>
<td>MM1</td>
<td>24.5/73.4</td>
<td>(50.2)</td>
<td>11.3/96.4</td>
<td>23.4/103</td>
<td>13.3/77.1</td>
<td>10.9/74.3</td>
</tr>
<tr>
<td>1988</td>
<td>MM1</td>
<td>42.5/116</td>
<td>(77.0)</td>
<td>30.0/151</td>
<td>22.8/114</td>
<td>11.5/84.3</td>
<td></td>
</tr>
<tr>
<td>1989</td>
<td>MM1</td>
<td>37.7/79.4</td>
<td>(61.4)</td>
<td>8.1/92.1</td>
<td>28.0/77.4</td>
<td>25.5/70.2</td>
<td></td>
</tr>
<tr>
<td>1990</td>
<td>MM1</td>
<td>14.3/92.6</td>
<td>(57.8)</td>
<td>26.1/128.3</td>
<td>39.8/88.2</td>
<td>22.8/95.9</td>
<td></td>
</tr>
<tr>
<td>1986</td>
<td>MM2</td>
<td>18.0/94.4</td>
<td>(49.5)</td>
<td>17.9/111</td>
<td>22.2/96.9</td>
<td>17.0/77.6</td>
<td></td>
</tr>
<tr>
<td>1987</td>
<td>MM2</td>
<td>36.7/105</td>
<td>(59.6)</td>
<td>18.7/134</td>
<td>143.9/21</td>
<td>9.3/64.2</td>
<td></td>
</tr>
<tr>
<td>1988</td>
<td>MM2</td>
<td>24.3/108</td>
<td>(67.6)</td>
<td>33.0/99.1</td>
<td>26.2/128.3</td>
<td>38.9/88.2</td>
<td>22.8/95.9</td>
</tr>
</tbody>
</table>

Fig. 3. Relationship between gaseous nitric acid, and physical and chemical meteorological variables, at Mt. Mitchell, NC, research observatory, Site 1, 2006 m m.s.l.; (a) temperature vs gaseous nitric acid concentration; (b) relative humidity vs gaseous nitric acid concentration; (c) solar radiation vs gaseous nitric acid concentration; and (d) ozone vs gaseous nitric acid concentration.

The rate constant for equation (9) is $1.1 \times 10^{-11}$ cm$^3$ mole$^{-1}$ s$^{-1}$ (Finlayson-Pitts and Pitts, 1986). The average NO$_2$ concentration measured at Mt. Mitchell was ~2.5 ppb. Thus, assuming a OH concentration of $5 \times 10^6$ molecule cm$^{-3}$ and using the above rate constant, the calculated production rate of HNO$_3$ is ~0.5 ppbv h$^{-1}$. This production rate is in agreement with the measured concentrations from shorter measurement runs (Fig. 2). From the above estimate, it appears that the major pathway for the production of nitric acid on the above variables suggests that ~60% of the total variation in the short-term nitric acid measurements can be explained by temperature, solar radiation and relative humidity. The correlation between the solar radiation and nitric acid suggests that the major pathway for the formation of nitric acid at Mt. Mitchell could be the oxidation of nitrogen dioxide via OH radicals (equation (9)). As the major pathway for the production of OH radicals is the photolysis of ozone and the subsequent reaction of O(1D) with water (equations (5) and (6)), the diurnal cycle in the nitric acid concentration observed could be a reflection of the diurnal cycle expected in the average OH radical concentrations.
of nitric acid at Mt Mitchell is via the reaction of NO₂ and OH. Considerable levels of gaseous nitric acid were observed even during nights, though maximum concentrations always occurred at midday. The oxidation of NO₂ by OH radicals does not occur during the night (no production of OH radicals). To account for the levels observed during night, an oxidation mechanism by O₃ may also be present at Mt Mitchell, since ozone levels are higher during the night (Aneja et al., 1991).

\[ \text{NO}_3 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2. \] (10)

NO₃ can also combine with the existing NO₂ to produce N₂O₅. Under high relative humidity conditions, N₂O₅ combines with water vapor in the atmosphere to generate nitric acid.

\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow \text{HNO}_3. \] (11)

Nighttime production of HNO₃ is expected to be low at Mt Mitchell due to the relatively low levels of NO₂.

Maximum average hourly ozone concentrations above the forest canopy, measured in 1988, are shown in Fig. 4. There were 48 h of ozone concentration greater than 0.12 ppmv (the current National Ambient Air Quality Standard). Most high ozone episodes in 1988 occurred from late spring to midsummer (Fig. 4). Ozone episodes (hourly ozone concentration > 80 ppbv) frequently occurred in June and July of 1988. Ozone levels > 80 ppbv were measured over 50% of the time during June 1988 (Aneja et al., 1991).

It is found that high ozone concentrations were controlled by meteorological conditions also as observed for nitric acid earlier. The high ozone concentrations were detected on hot dry days with the passage of synoptic high-pressure systems. The relationship between daily maximum ozone concentrations and daily maximum temperature during 1987 and 1988 are shown in Fig. 5. The correlation coefficients \( r^2 \) were 0.21 and 0.26 for 1987 and 1988, respectively. Other meteorological conditions, such as the solar radiation, relative humidity, and wind speed also affect the ozone concentration. These meteorological conditions are conducive to the photochemical formation of ozone and responsible for the observed ozone seasonal variations at Mt Mitchell. Aneja et al. (1991) proposed that perhaps the higher levels of hydrocarbon emitted by natural sources during the late spring and early summer may also be responsible for the observed ozone pattern.

The mean diurnal signal for ozone during 1987 and 1988 is shown in Fig. 6. Note 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 typical diurnal ozone patterns seen at lower-elevation rural locations exhibit midafternoon maxima (Meagher et al., 1987). An example of such a diurnal signal is also shown in Fig. 6 for a lower-elevation site, Fairview (~850 m), North Carolina, located about 35 km south of Mt Mitchell (Aneja et al., 1991).

The monthly mean diurnal patterns for ozone at Site 1 from May to September in 1988 are shown in Fig. 7. Diurnal variations appeared to be weakly reversed (i.e. ozone maxima occurred at night) and reduced during the day at Site 1. These reversed diurnal patterns were observed in every month during the field season. Similar phenomena were noted by Lefohn and Mohnen (1986) at Whiteface Mountain in New York, where the ozone concentrations exhibited little change during the day. Ozone levels monitored at a remote mountain location in the Canadian
Fig. 6. The diurnal variation of ozone concentration for 1987 and 1988 (May–September) at Mt Mitchell, NC, Site 1, (2006 m a.s.l.); Site 2 (1760 m a.s.l.); and Fairview, North Carolina (850 m a.s.l.).

Fig. 7. Mean diurnal variation of ozone concentration from May to September 1988 at Mt Mitchell, NC, research observatory, Site 1, 2006 m a.s.l.

Figures 6 and 7 illustrate the diurnal variation and mean diurnal variation of ozone concentration, respectively, for 1987 and 1988 at Mt Mitchell, NC. The data show that ozone concentrations are highest during the late morning and early afternoon, with a minimum in the early morning and late evening.

Table 1 shows the seasonal distribution of ozone concentrations at Mt Mitchell, NC, Site 1, for the years 1987 and 1988. The table indicates that ozone concentrations are highest in the summer months and lowest in the winter months.

The diurnal variation of ozone concentration is shown in Figure 6 for the years 1987 and 1988. The data are presented for Site 1, 2006 m a.s.l.; Site 2, 1760 m a.s.l.; and Fairview, North Carolina, 850 m a.s.l.

Figures 7 and 8 illustrate the mean diurnal variation of ozone concentration and the seasonal distribution of ozone concentrations at Mt Mitchell, NC, Site 1, respectively. The data show that ozone concentrations are highest during the summer months and lowest during the winter months.

The seasonal distribution of ozone concentrations at Mt Mitchell, NC, Site 1, for the years 1987 and 1988 is shown in Figure 8. The data are presented for Site 1, 2006 m a.s.l.; Site 2, 1760 m a.s.l.; and Fairview, North Carolina, 850 m a.s.l.

The diurnal variation of ozone concentration is shown in Figure 9 for the years 1987 and 1988. The data are presented for Site 1, 2006 m a.s.l.; Site 2, 1760 m a.s.l.; and Fairview, North Carolina, 850 m a.s.l.

The seasonal distribution of ozone concentrations at Mt Mitchell, NC, Site 1, for the years 1987 and 1988 is shown in Figure 10. The data are presented for Site 1, 2006 m a.s.l.; Site 2, 1760 m a.s.l.; and Fairview, North Carolina, 850 m a.s.l.

The diurnal variation of ozone concentration is shown in Figure 11 for the years 1987 and 1988. The data are presented for Site 1, 2006 m a.s.l.; Site 2, 1760 m a.s.l.; and Fairview, North Carolina, 850 m a.s.l.

The seasonal distribution of ozone concentrations at Mt Mitchell, NC, Site 1, for the years 1987 and 1988 is shown in Figure 12. The data are presented for Site 1, 2006 m a.s.l.; Site 2, 1760 m a.s.l.; and Fairview, North Carolina, 850 m a.s.l.

The diurnal variation of ozone concentration is shown in Figure 13 for the years 1987 and 1988. The data are presented for Site 1, 2006 m a.s.l.; Site 2, 1760 m a.s.l.; and Fairview, North Carolina, 850 m a.s.l.

Figure 14 shows the daily averaged dewpoint for the same days. The data show that the dewpoint is highest during the summer months and lowest during the winter months.

The diurnal variation of ozone concentration is shown in Figure 15 for the years 1987 and 1988. The data are presented for Site 1, 2006 m a.s.l.; Site 2, 1760 m a.s.l.; and Fairview, North Carolina, 850 m a.s.l.

The seasonal distribution of ozone concentrations at Mt Mitchell, NC, Site 1, for the years 1987 and 1988 is shown in Figure 16. The data are presented for Site 1, 2006 m a.s.l.; Site 2, 1760 m a.s.l.; and Fairview, North Carolina, 850 m a.s.l.

The diurnal variation of ozone concentration is shown in Figure 17 for the years 1987 and 1988. The data are presented for Site 1, 2006 m a.s.l.; Site 2, 1760 m a.s.l.; and Fairview, North Carolina, 850 m a.s.l.

The seasonal distribution of ozone concentrations at Mt Mitchell, NC, Site 1, for the years 1987 and 1988 is shown in Figure 18. The data are presented for Site 1, 2006 m a.s.l.; Site 2, 1760 m a.s.l.; and Fairview, North Carolina, 850 m a.s.l.

The diurnal variation of ozone concentration is shown in Figure 19 for the years 1987 and 1988. The data are presented for Site 1, 2006 m a.s.l.; Site 2, 1760 m a.s.l.; and Fairview, North Carolina, 850 m a.s.l.

The seasonal distribution of ozone concentrations at Mt Mitchell, NC, Site 1, for the years 1987 and 1988 is shown in Figure 20. The data are presented for Site 1, 2006 m a.s.l.; Site 2, 1760 m a.s.l.; and Fairview, North Carolina, 850 m a.s.l.

The diurnal variation of ozone concentration is shown in Figure 21 for the years 1987 and 1988. The data are presented for Site 1, 2006 m a.s.l.; Site 2, 1760 m a.s.l.; and Fairview, North Carolina, 850 m a.s.l.

The seasonal distribution of ozone concentrations at Mt Mitchell, NC, Site 1, for the years 1987 and 1988 is shown in Figure 22. The data are presented for Site 1, 2006 m a.s.l.; Site 2, 1760 m a.s.l.; and Fairview, North Carolina, 850 m a.s.l.

The diurnal variation of ozone concentration is shown in Figure 23 for the years 1987 and 1988. The data are presented for Site 1, 2006 m a.s.l.; Site 2, 1760 m a.s.l.; and Fairview, North Carolina, 850 m a.s.l.

The seasonal distribution of ozone concentrations at Mt Mitchell, NC, Site 1, for the years 1987 and 1988 is shown in Figure 24. The data are presented for Site 1, 2006 m a.s.l.; Site 2, 1760 m a.s.l.; and Fairview, North Carolina, 850 m a.s.l.
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Fig. 8. Comparison of ozone distributions at high and low elevations in the North and South Hemispheres.

Fig. 9. Daily averaged values of total gaseous hydroperoxide (ROOH) and gaseous H$_2$O$_2$ measured during the 1988 field season at Mt. Mitchell, NC, research observatory, Site 1, 2006 m a.s.l.

Fig. 10. Daily averaged dewpoint temperature for 1988 at Mt. Mitchell, NC, research observatory, Site 1, 2006 m a.s.l.

significantly higher than daytime levels (mean $0.57 \pm 0.28$ ppbv). During the summer, a significant difference between nighttime and daytime levels was observed for the total peroxides as well. This result was not expected, based on our current understanding of the photochemistry of hydrogen peroxide formation. The nighttime maximum in ambient hydrogen peroxide at Mt. Mitchell (Fig. 11) is very different from the typical diurnal pattern reported in the literature. For example, in southern California (Sakugawa and Kaplan, 1989), a daytime maximum hydrogen peroxide was observed in the early afternoon, corresponding to a minimum in the NO$_x$ and a maximum in the O$_3$, 1–3 h after the daily peak of solar radiation. Recently, however, nocturnal maxima in hydrogen peroxide have been observed at other mountaintop sites as well, at Mauna Loa (Heikes, 1989) and at Whitetop Mountain (Meagher, personal communication). The reversed diurnal trend observed at Mt. Mitchell during summer was not noted during the fall, where the nighttime levels (mean $0.21 \pm 0.31$ ppbv) were not found to be significantly higher than the daytime levels (mean $0.18 \pm 0.16$ ppbv).
considered reservoir species and observation has shown an apparent anomaly. There is no nighttime maxima in concentration at this high-elevation site, contrary to their diurnal behavior at low elevation. While the exact reason for this apparent anomalous behavior may not be known at this time the following explanation may provide some insight. Both ozone (Liu et al., 1987) and gaseous hydrogen peroxide (Heikes et al., 1987) are considered reservoir species and observation has shown that their concentration increases with altitude; on the other hand, model calculations suggest that the concentration of gaseous nitric acid decreases with altitude (Parrish et al., 1986; Trainer et al., 1991). Thus the observed nighttime maximum pattern for O₃ and H₂O₂ at Mt Mitchell may be explained by transport mechanisms which are related to the diurnal variation of mixing height. During the daytime, Mt Mitchell is in the surface layer, and upslope winds during the day transport air from lower levels in the mixed layer. The destruction of ozone and H₂O₂ is therefore communicated throughout the surface layer. At night, however, mountainous sites above the nocturnal boundary layer do not experience the same depletion due to the absence of mixing, and the destruction of ozone and H₂O₂ is confined to a shallow nocturnal boundary layer. Further, at night, the mountain top is exposed to ozone-rich and H₂O₂-rich and HNO₃-poor air in the free atmosphere with little destruction by surface. The result is higher ozone and H₂O₂ concentration detected at night at the mountain top. Thus O₃ and H₂O₂ show a reversed diurnal variation (i.e. nighttime maxima), and HNO₃ shows the maxima during the day due to photochemical formation.

Seasonal analysis for the three photochemical oxidants shows that the maximum for all three occurs during late spring. The trend in the ozone seasonal variation is nearly coincident with other Northern Hemisphere high-elevation sites. These maxima in oxidant concentrations are consistent with the enhancement in their and/or its precursor’s lifetimes during winter, and their subsequent accumulation and/or production from precursors to affect the entire Northern Hemisphere; or stratospheric exchange at a time of maximum photochemical oxidant concentrations during spring in the stratosphere (Janach, 1989). The reasons for the second seasonal nitric acid maxima at Mt Mitchell during fall remain unresolved.

The continental high-elevation sites have higher ozone concentrations than the remote oceanic sites. The main cause of this is attributed to increasing emissions of nitrogen oxides (NOₓ) and hydrocarbons associated with anthropogenic activity. However, the role of natural emissions cannot be ignored. The concentration of NOₓ is a fundamental parameter affecting ozone production (Trainer et al., 1987) in these "remote" environments. In the continental locales, higher NOₓ concentrations, acts as a catalyst to enhance ozone production, while in remote oceanic regions low NOₓ concentrations and radicals consume ozone.

We have made simultaneous measurements of three photochemical oxidants, i.e. HNO₃, O₃, and H₂O₂ at Mt Mitchell and attempted to provide a unified understanding of their behavior in the free troposphere. This behavior provides a signal which is characteristic of northern hemispheric chemical climatological changes. Such a signal may be very useful in interpreting changes in pollutant emissions brought about by amendments in the Clean Air Act.

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