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TRENDS, SEASONAL VARIATIONS, AND ANALYSIS OF HIGH-ELEVATION SURFACE NITRIC ACID, OZONE, AND HYDROGEN PEROXIDE

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Abstract—Atmospheric photochemical oxidants nitric acid, ozone, and hydrogen peroxide were monitored in ambient air at Mt Mitchell State Park, North Carolina. Ozone measurements made from May to September during 1986–1990 are reported for two high-elevation sites (Site 1 on Mt Gibbs, approximately 2006 m; and Site 2 on Commissary Ridge, approximately 1760 m). These measurements are also compared to those from a nearby, low-elevation site (Fairview, approximately 830 m). Average ozone concentrations increased from lower to higher elevations. Meteorological analysis shows an association between periods of high ozone concentrations and synoptic-scale patterns. 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. Gas-phase hydrogen peroxide and nitric acid concentration were measured at Site 1 during 1988 and 1989, and typically range from 0 to 4 ppbv, and 0–2 ppbv, respectively. Seasonal analysis shows that the ozone maximum occurs during spring coincident with the spring maximum at Whiteface Mountain, NY, Mauna Loa in Hawaii, and at Alpine stations in Europe, suggesting that ozone production is a hemispheric rather than local phenomenon and that the underlying phenomenon affects perhaps the entire Northern Hemisphere. The diurnal cycle of gaseous hydrogen peroxide was similar to the high-elevation ozone signal, while gaseous nitric acid concentration peaked during the day. This apparent discrepancy in the diurnal cycle between the three atmospheric photochemical oxidants at high elevation may be due to a difference in the behavior of the altitudinal gradients of those oxidants resulting from a combination of photochemistry, meteorology and dynamic processes.

Key word index: Nitric acid, ozone, hydrogen peroxide, photochemical oxidants, high elevation.

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-

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chemical oxidants nitric acid (HNO_3), ozone (O_3), and hydrogen peroxide (H_2O_2) were monitored in ambient air.

All three photochemical oxidant species, HNO_3, O_3, and H_2O_2 are generated in the atmosphere via a complex series of reactions involving NO_x 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:

$$NMHC + OH + O_2 \longrightarrow RO_2 \quad (1)$$

$$RO_2 + NO + O_2 \longrightarrow NO_2 + HO_2 + CARB \quad (2)$$

$$HO_2 + NO \longrightarrow NO_2 + OH \quad (3)$$

$$NO_2 + h\nu + O_2 \longrightarrow NO + O_3 \quad (4)$$

where CARB stands for carbonyl compounds. Hydrogen peroxide is formed in the atmosphere by the self-combination of hydroperoxyl radical (HO_2). Hydroperoxyl 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

$$O_3 + h\nu \longrightarrow O(^1D) + O_2 \quad (5)$$

$$O(^1D) + H_2O \longrightarrow 2\ OH \quad (6)$$

$$OH + CO + O_2 \longrightarrow CO_2 + HO_2 \quad (7)$$

$$HO_2 + HO_2 + M \longrightarrow H_2O_2 + O_2 + M. \quad (8)$$

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

$$OH + NO_2 \longrightarrow HNO_3. \quad (9)$$

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 ~10–20 d (Finlayson-Pitts and Pitts, 1986), ozone is ~30–60 d (Logan, 1985; Hough and Derwent, 1990), and gaseous hydrogen peroxide is ~10–30 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 HNO_3, 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 (~2006 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 subsites. The main station (Site 1) is near the summit of Mt Gibbs, at an elevation ~2006 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 ~1760 m m.s.l. on Commissary Ridge, located ~1 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.*, 1983; Murthy, 1990). Three annular denuder tubes coated with NaCl, Na_2CO_3, and citric acid, respectively, were used in series to collect the acidic gases (HNO_3, HNO_2, and SO_2), 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, 1983). 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 HNO_3 for this instrument is $0.05\ \mu g\,m^{-3}$, with a precision of 3% in the range of $0.5–3\ \mu g\,m^{-3}$. Field and laboratory blanks were prepared and analysed for background values. The analytical quality control (QC) solutions for nitrate (NO_3^-) 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 (Lazrus *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 $0.05–5.62\ \mu g\,m^{-3}$ with a mean of

$1.14 \pm 0.96\ \mu g\ m^{-3}$ for 1988, and $1.40 \pm 0.59\ \mu g\ m^{-3}$ 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–$2.7\ \mu g\ m^{-3}$), and Shaw *et al.* (1982) for RTP, NC ($1.5\ \mu g\ m^{-3}$); and higher than the mean value ($0.43\ \mu g\ m^{-3}$) 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 HNO_3 concentrations higher than the nighttime levels (95% statistically significant level; *t*-statistic).

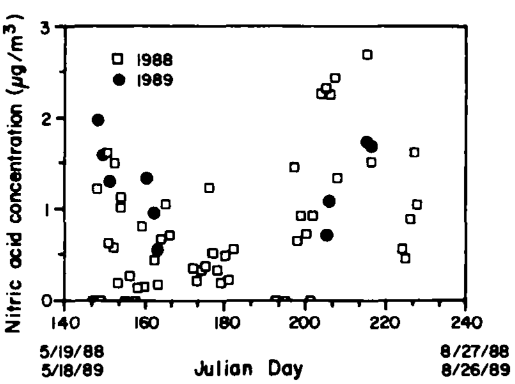

Fig. 1. Gaseous nitric acid concentration time series based on 24 h measurements for 1988 and 1989, at Mt Mitchell, NC, research observatory, Site 1, 2006 m m.s.l.

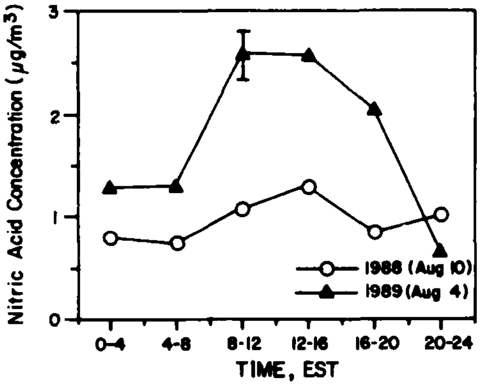

Fig. 2. Gaseous nitric acid diurnal variation, at Mt Mitchell, NC, research observatory, Site 1, 2006 m m.s.l.

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)

Year	Site	May	June	July	August	September	October
1986	MM1		54/111 (74.3)		23/94 (45.0)	27/75 (47.6)	18/71 (39.6)
1987	MM1	24.5/73.4 (50.2)	23.7/93.1 (57.5)	11.3/96.4 (50.1)	23.4/103 (54.1)	15.3/77.1 (46.4)	10.9/74.3 (45.8)
1988	MM1	42.5/116 (72.0)	36.1/123 (82.8)	30.0/151 (68.7)	22.8/114 (57.4)	11.5/84.3 (46.7)	
1989	MM1	37.7/79.4 (61.4)	25.5/90.5 (52.3)	8.1/92.1 (53.6)	28.0/77.4 (51.1)	25.5/70.2 (45.6)	
1990	MM1	14.3/92.6 (57.8)	33.0/99.1 (62.2)	26.1/128.3 (58.2)	39.8/88.2 (61.7)	22.8/95.9 (59.4)	
1986	MM2				28/69 (46.0)	22/67 (45.7)	24/80 (44.3)
1987	MM2	18.0/94.4 (49.5)	17.2/91.5 (49.5)	17.9/111 (49.3)	22.2/96.9 (53.8)	17.0/77.6 (43.9)	
1988	MM2	36.7/105 (59.6)	24.3/108 (67.6)	18.7/134 (55.1)	14.3/92.1 (50.0)	9.3/64.2 (35.2)	

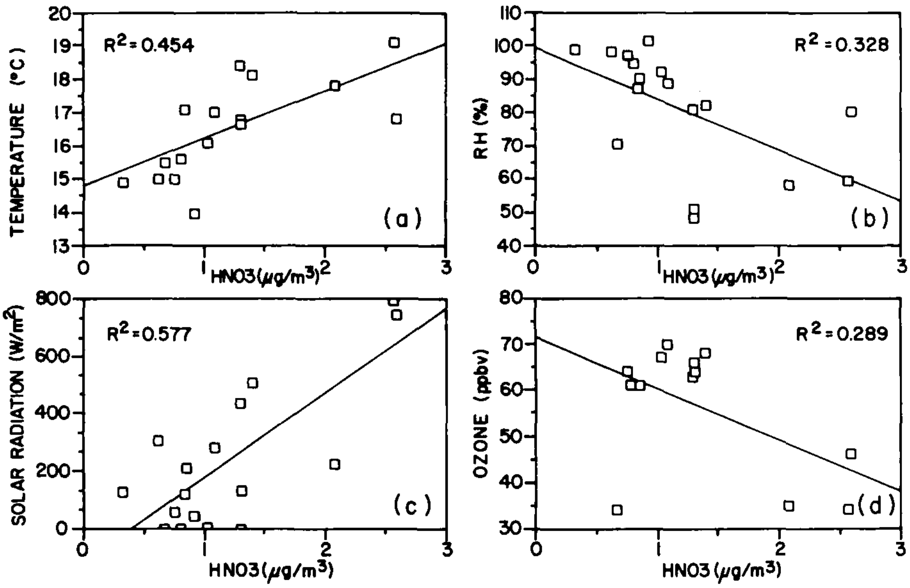

Fig. 3. Relationship between gaseous nitric acid, and physical and chemical meteorological variables, at Mt Mitchell, NC, research observatory, Site 1, 2006 m m.s.l.; (a) temperature vs gaseous nitric acid concentration; (b) relative humidity vs gaseous nitric acid concentration; (c) solar radiation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

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.

The rate constant for equation (9) is $1.1*10^{-11}$ $cm^3\,mole^{-1}\,s^{-1}$ (Finlayson-Pitts and Pitts, 1986). The average NO_2 concentration measured at Mt Mitchell was ~2.5 ppb. Thus, assuming a OH concentration of $5*10^6$ $molecule\,cm^{-3}$ 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 at Mt Mitchell is via the reaction of NO_2 and OH. Considerable levels of gaseous nitric acid were observed even during nights, though maximum concentrations always occurred at midday. The oxidation of NO_2 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 O_3 may also be present at Mt Mitchell, since ozone levels are higher during the night (Aneja *et al.*, 1991).

$$NO_2 + O_3 \longrightarrow NO_3 + O_2. \qquad (10)$$

NO_3 can also combine with the existing NO_2 to produce N_2O_5. Under high relative humidity conditions, N_2O_5 combines with water vapor in the atmosphere to generate nitric acid.

$$N_2O_5 + H_2O \longrightarrow HNO_3. \qquad (11)$$

Nighttime production of HNO_3 is expected to be low at Mt Mitchell due to the relatively low levels of NO_x.

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.

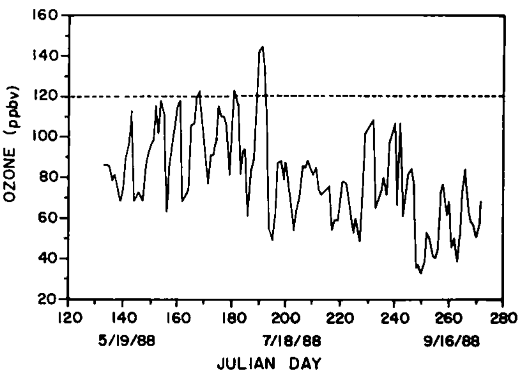

Fig. 4. Maximum hourly average ozone concentrations measured during 1988 at Mt Mitchell, NC, research observatory, Site 1, 2006 m m.s.l.

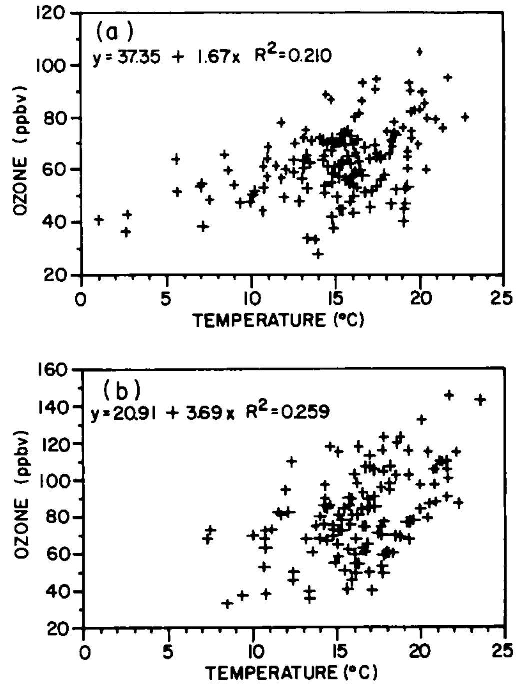

Fig. 5. Daily maximum ozone concentrations vs daily maximum temperature at Mt Mitchell, NC, research observatory, Site 1, 2006 m m.s.l.; (a) during 1987, (b) during 1988.

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

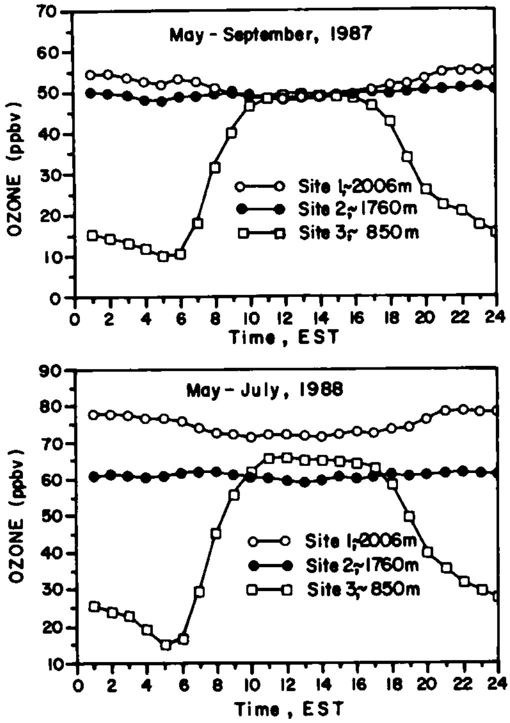

Fig. 6. The diurnal variation of ozone concentration for 1987 and 1988 (May–September) at Mt Mitchell, NC, Site 1, (2006 m m.s.l.); Site 2 (1760 m m.s.l.); and Fairview, North Carolina (850 m m.s.l.).

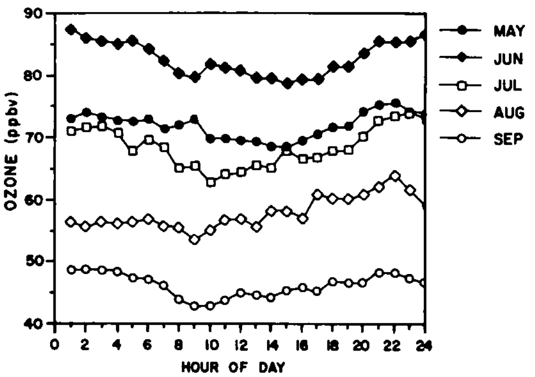

Fig. 7. Mean diurnal variation of ozone concentration from May to September 1988 at Mt Mitchell, NC, research observatory, Site 1, 2006 m m.s.l.

Rockies also demonstrated no diurnal ozone variation (Peake and Fong, 1990).

For more detailed comparisons, we have plotted (Fig. 8) monthly averaged values for seasonal distributions of selected recent data from various high elevation sites both in the Northern Hemisphere (Whiteface Mountain, NY, 1483 m; Davos, Alpine Valley, 1700 m; Mauna Loa, Hawaii, 3400 m) and the Southern Hemisphere (South Pole, 2800 m). We have also provided similar data for two low-elevation sites, i.e. Payerne, Switzerland, ~450 m (in the Northern Hemisphere); and Samoa, South Pacific, at sea level (in the Southern Hemisphere). Some of this data were obtained from Janach (1989). These observations are compared and contrasted with ozone measurements at Mt Mitchell, Site 1. Figure 8 illustrates higher ozone concentrations in the Northern Hemisphere than in the Southern Hemisphere by about a factor of 2. It also illustrates that the continental sites have higher ozone levels than the remote oceanic sites; and ozone concentrations increase from lower to higher elevation in the mountains (Janach, 1989; Aneja *et al.*, 1991).

Seasonal analysis of the Northern Hemisphere sites shows that the ozone maximum occurs during spring. It is interesting to note that the seasonal maximum in the Southern Hemisphere occurs during its fall. At these high-elevation sites in the Northern Hemisphere this may best be explained by photochemical ozone production and subsequent accumulation of ozone and its precursors during winter. The lifetimes of ozone and its precursors are enhanced during winter. Thus the above ozone production occurs over the region, as solar intensities and temperatures increase in spring, and the underlying transport process can spread ozone over the entire hemisphere. However, it is also possible that the springtime maximum is in part due to increased ozone flux due to stratospheric intrusion and its subsequent subsidence (Singh *et al.*, 1980; Janach, 1989).

Statistically significant seasonal variation in the ambient hydrogen peroxide level during 1988 was observed, with summertime levels of hydrogen peroxide (mean 0.76 ± 0.57 ppbv) significantly greater than those observed in the fall (mean 0.20 ± 0.26 ppbv). This seasonal trend is depicted in Fig. 9, which shows daily averaged values for hydrogen peroxide and for the organic peroxides measured by the technique for all days for which peroxides measurements were taken. Some of the highest values observed occurred during the spring intensive (Julian Day, JD, 160–170) during which period the site was under the influence of a high pressure system. During this period, high ozone levels were observed, as well.

Figure 10 shows the daily averaged dewpoint for the same days. It is interesting to note that, during a given intensive, the hydrogen peroxide and total peroxides concentrations appear to correlate with dewpoint, whereas this correlation is not apparent when the entire data set is considered. A positive correlation to water vapor content is expected. Perhydroxyl radical is predominantly formed from the reactions of hydroxyl radical with carbon monoxide (equation (7)) or with hydrocarbons (equations (1) and (2)). The major source of hydroxyl radical in clean atmospheres is the photolysis of ozone followed by reaction of the electronically excited oxygen atom with water vapor (equations (5) and (6)).

Nighttime hydrogen peroxide levels measured during the summer of 1988 (mean 0.95 ± 0.70 ppbv) were

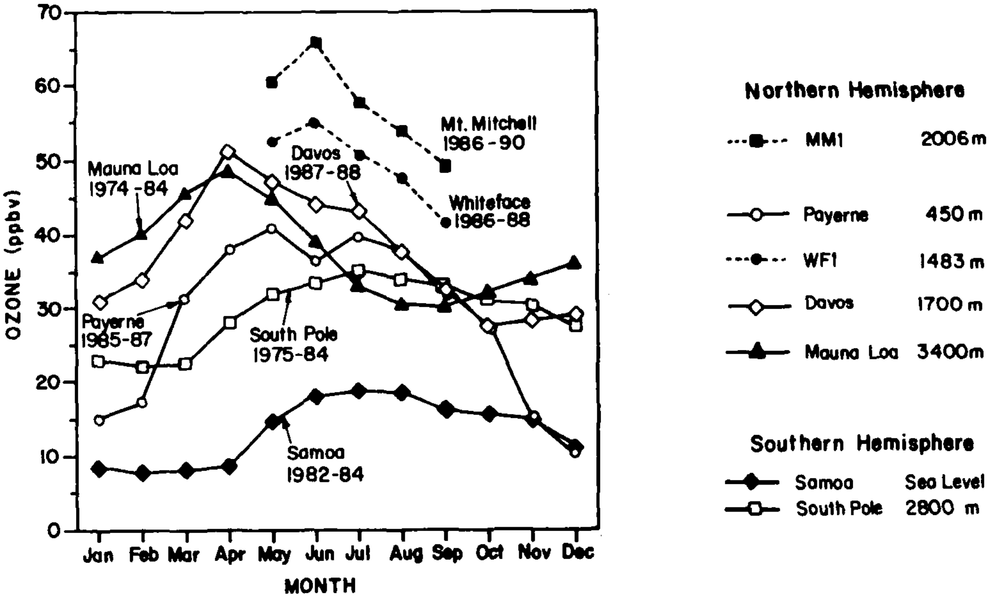

Fig. 8. Comparison of ozone distributions at high and low elevations in the North and South Hemispheres.

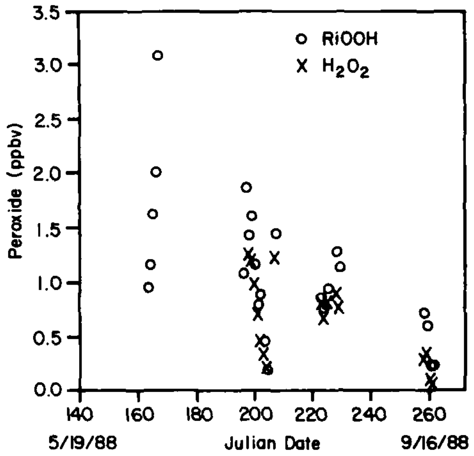

Fig. 9. Daily averaged values of total gaseous hydroperoxide (RiOOH) and gaseous H_2O_2 measured during the 1988 field season at Mt Mitchell, NC, research observatory, Site 1, 2006 m m.s.l.

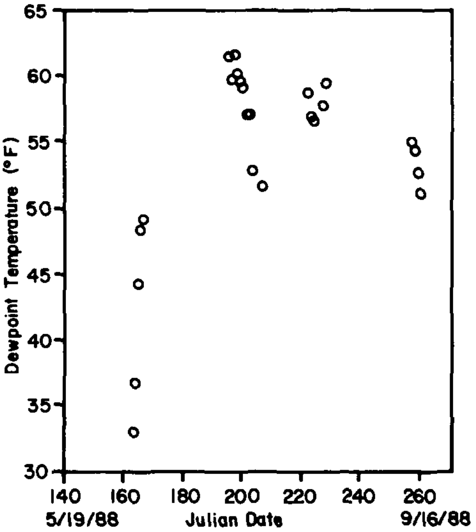

Fig. 10. Daily averaged dewpoint temperature for 1988 at Mt Mitchell, NC, research observatory, Site 1, 2006 m m.s.l.

significantly higher than daytime levels (mean 0.57 ± 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 ± 0.31 ppbv) were not found to be significantly higher than the daytime levels (mean 0.18 ± 0.16 ppbv).

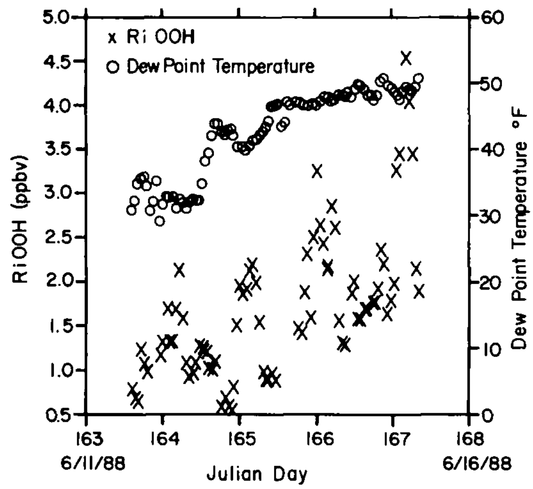

Fig. 11. Hourly averaged RiOOH vs dewpoint temperature for 1988 at Mt Mitchell, NC, research observatory, Site 1, 2006 m m.s.l.

SUMMARY AND CONCLUSIONS

The diurnal behavior of the three photochemical oxidant species, i.e. HNO_3, O_3, and H_2O_2 studied here shows an apparent anomaly. There is no nighttime formation of ozone and hydrogen peroxide yet they show a nighttime maxima in concentration at this high-elevation site, contrary to their diurnal behavior at low elevation. While the exact reason for this apparent anomolous 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 O_3 and H_2O_2 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 H_2O_2 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 H_2O_2 is confined to a shallow nocturnal boundary layer. Further, at night, the mountain top is exposed to ozone-rich and H_2O_2-rich and HNO_3-poor air in the free atmosphere with little destruction by surface. The result is higher ozone and H_2O_2 concentration detected at night at the mountain top. Thus O_3 and H_2O_2 show a reversed diurnal variation (i.e. nighttime maxima), and HNO_3 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 Hemispheric high-elevation sites. These maxim 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 (NO_x) and hydrocarbons associated with anthropogenic activity. However, the role of natural emissions cannot be ignored. The concentration of NO_x is a fundamental parameter affecting, ozone production (Trainer *et al.*, 1987) in these "remote" environments. In the continental locales, higher NO_x concentrations, acts as a catalyst to enhance ozone production, while in remote oceanic regions low NO_x concentrations and radicals consume ozone.

We have made simultaneous measurements of three photochemical oxidants, i.e. HNO_3, O_3, and H_2O_2 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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