Measurements of Atmospheric Hydrogen Peroxide in the Gas Phase and in Cloud Water at Mt. Mitchell, North Carolina

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Measurements of atmospheric hydrogen peroxide in the gas phase were made during four intensive observation periods at the Mt. Mitchell State Park, North Carolina, during the growing season (May through September) of 1988. Cloud water hydrogen peroxide was measured during the entire field season of 1988 and during the late summer and fall of 1987 (August and October). Cloud water concentrations were found to be similar to those reported from another high-elevation location in the southeastern United States. Cloud water samples collected during these periods showed a wide range of levels (~ 0 - 219 $\mu M/L$) and average values of 38 $\mu M/L$ and 44 $\mu M/L$ for the entire sampling seasons of 1988 and 1987, respectively. Significant seasonal variation was noted both in 1987 and 1988, with cloud water levels of hydrogen peroxide much higher in the summer than in the fall. Gas-phase hydrogen peroxide levels ranged from the detection limit (0.1 ppbv) to above 4 ppbv. Gas-phase hydrogen peroxide demonstrated a nighttime maximum in the summer but not in the fall. The measurements taken in the fall were significantly lower than those taken during the summer, possibly due at least in part to seasonal variation. Atmospheric hydrogen peroxide levels were found to be increasing during stagnating high-pressure systems and were found to correspond to the back trajectory of the air mass with the highest concentrations corresponding to continental air masses. The hydrogen peroxide concentration was also found to be affected by radical formation from ozone and by loss processes such as wet and dry deposition.

INTRODUCTION

Atmospheric hydrogen peroxide plays an important role in the aqueous phase chemistry of precipitation acidification, particularly in the summer. It may be the primary oxidant involved in the production of aqueous phase sulfuric acid in cloud water when the pH is less than 4.5 [Penkett *et al.*, 1979; Martin and Damschen, 1981; Kunen *et al.*, 1983; Lee *et al.*, 1986; Lind *et al.*, 1987]. Like ozone, hydrogen peroxide is a strong oxidizing agent. Ozone has been shown to cause damage to vegetation, the cost of which is estimated to be $1-5 billion per year in crop loss alone, in the United States [Heck *et al.*, 1988]. Other photochemical oxidants such as hydrogen peroxide also may contribute to damage to vegetation. The results of one study, conducted on Norway spruce, suggest that hydrogen peroxide-containing mist can cause foliar damage [Masuch *et al.*, 1986]. In another study, simultaneous exposure to gaseous hydrogen peroxide, ozone, and sulfur dioxide was observed to enhance respiration in red spruce [Ennis *et al.*, 1990]. Since hydrogen peroxide is formed from the combination of hydroperoxyl radicals when the atmospheric level of NO_x is low such that NO does not compete for consumption of HO_2, significant atmospheric levels might be expected in the remote, southeastern regions of the United States, where there is an abundance of warm temperatures and sunshine and presumably low levels of atmospheric NO_x. This may be of particular significance to the mountainous areas in the southeastern United States, where acid deposition and air pollution are thought to contribute to the forest decline in the Appalachians [Woodman and Cowling, 1987; Bruck *et al.*, 1989].

Methods for measuring atmospheric gas-phase hydrogen peroxide have been hampered until recently by artifact formation during sampling and analysis [Zika and Saltzman, 1982; ten Brink *et al.*, 1984] and by interferences from other species such as SO_2 and O_3 [Heikes *et al.*, 1982]. More recently developed methods of measurement have attempted to address these problems [Dasgupta *et al.*, 1986; Lazrus *et al.*, 1986; Slemr *et al.*, 1986; Tanner *et al.*, 1986; Hartkamp and Bachhausen, 1987; Sakugawa and Kaplan, 1987], and now a body of data documenting ambient concentrations of hydrogen peroxide is growing, based on both aircraft-borne measurements [Heikes *et al.*, 1987; Boatman *et al.*, 1989; Daum, 1990; Daum *et al.*, 1990] and ground-level measurements [Slemr *et al.*, 1986; Tanner *et al.*, 1986; Olszyna *et al.*, 1988; Sakugawa and Kaplan, 1989].

Tropospheric gas-phase concentrations recently reported in the literature have ranged from below the level of detection (LOD), which is generally of the order of 0.1 ppbv, to nearly 7 ppbv [Heikes *et al.*, 1987; Boatman *et al.*, 1989; Daum *et al.*, 1990]. Levels as high as 9 ppbv have been reported for the stratosphere [Chance and Traub, 1987].

Methods for measuring hydrogen peroxide in precipitation samples have also been hampered by problems associated with decomposition of peroxides in the stored samples [Kok *et al.*, 1986], differentiation between hydrogen peroxide and other hydroperoxides [Lazrus *et al.*, 1985; Heikes, 1991], and interferences due to sulfur dioxide [Yoshizumi *et al.*, 1984; Lazrus *et al.*, 1985]. Hydrogen peroxide has been measured in rainwater [Kok, 1980; Zika *et al.*, 1982; Kelly *et al.*, 1985; Römer *et al.*, 1985; Olszyna *et al.*, 1988] and in cloud water either from aircraft [Daum *et al.*, 1984; Kelley *et al.*, 1985; Römer *et al.*, 1985], at mountainous site [Olszyna *et al.*, 1988; Lazrus *et al.*, 1985; Sakugawa and Kaplan 1989], or at ground level [Sakugawa and Kaplan, 1989]. Cloud water levels reported so far ranged from undetectable to as high as 247 $\mu M/L$, which was reported at Whitetop Mountain, Virginia [Olszyna *et al.*, 1988].

At Mt. Mitchell, North Carolina, sulfate ion has been found to be the predominant anion present in cloud water [Saxena *et al.*,

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1989; *Aneja et al.*, 1990]. The pH of cloud water at the site tends to range from 2.2 to 4.5 in the spring and summer and as high as 5.5 in the fall [*Saxena et al.*, 1989; *Aneja et al.*, 1990,1991a]. These observations, coupled with the pH dependency of the relative oxidation rates of sulfur dioxide by ozone, hydrogen peroxide, and oxygen, suggest that hydrogen peroxide might be an important contributor to the acidification of cloud water at Mt. Mitchell. Considering this factor and the possible damage due to direct exposure to hydrogen peroxide, atmospheric hydrogen peroxide may play a role in the decline observed in the Mt. Mitchell forests. For these reasons, gas-phase and cloud water concentrations of hydrogen peroxide were measured, in conjunction with other chemical, physical, and meteorological parameters, as part of the Mountain Cloud Chemistry Program (MCCP), a 4-year project to characterize the chemical and physical climatology at five high-elevation sites, and one low-elevation site, in the eastern United States. This paper summarizes the results of the hydrogen peroxide studies conducted during the growing seasons of 1987 and 1988 at Mt. Mitchell, North Carolina (Figure 1), the southernmost site of the MCCP network, and discusses those factors that affect the hydrogen peroxide climate at this location.

EXPERIMENT

Atmospheric monitoring and cloud water collection were conducted at Mt. Mitchell, North Carolina, during the growing season (approximately May through September) of 1988 as part of the Mountain Cloud Chemistry Program, sponsored by the U.S. Environmental Protection Agency (EPA). As well as being the southernmost site and the site with the highest elevation in the MCCP network, Mt. Mitchell also has the distinction of being the highest point east of the Mississippi River in the United States. The Mt. Mitchell research site, which was established in 1986, actually consists of two subsites (Figure 1): one is located at Mt. Gibbs (site 1), on the same ridge as Mt. Mitchell, at an elevation of approximately 2006 m (above mean sea level, msl); and the second (site 2) is located approximately 4 km away on Commissary Ridge (the southeast shoulder of Mt. Mitchell) at an elevation of approximately 1760 m (msl).

At both sites 1 and 2, meteorological and cloud microphysics parameters were measured from the top platform of a 16.5-m tower which placed the equipment above the forest canopy, which is composed of 6- to 7-m-tall Fraser fir and red spruce [*Saxena et al.*, 1989; *Aneja et al.*, 1990, 1991a]. During cloud events, bulk cloud water samples were collected hourly, using a passive collector also installed on the top of the tower at site 1 [*Kadlecek et al.*, 1983] and an active collector installed on the top of the tower at site 2 [*Jacob et al.*, 1985]. Cloud water samples taken at both sites 1 and 2 were analyzed for hydrogen peroxide in addition to a variety of other ionic species. Ozone measurements were made at both sites with a Thermo Electron Co. analyzer, model 49, based on ultraviolet absorption. The level of detection for the ozone analyzer is 2 ppbv. For ozone concentrations greater than 20 ppbv the accuracy is ± 20%, and for values in the range of 0-20 ppbv, the accuracy is ±4 ppbv. Oxides of nitrogen were measured at site 1 with a Monitor Lab model 8440 analyzer, based on chemiluminescence; however, levels were generally lower than the detection limit of the analyzer (~ 2 ppbv). Sulfur dioxide was measured at site 1 with a Thermo Electron Co. analyzer, model 43. The level of detection for the sulfur dioxide analyzer is 0.6 ppbv, the accuracy is ± 20% for SO₂ levels in the range of 18-22 ppbv, and the precision is ± 5 ppbv in the range
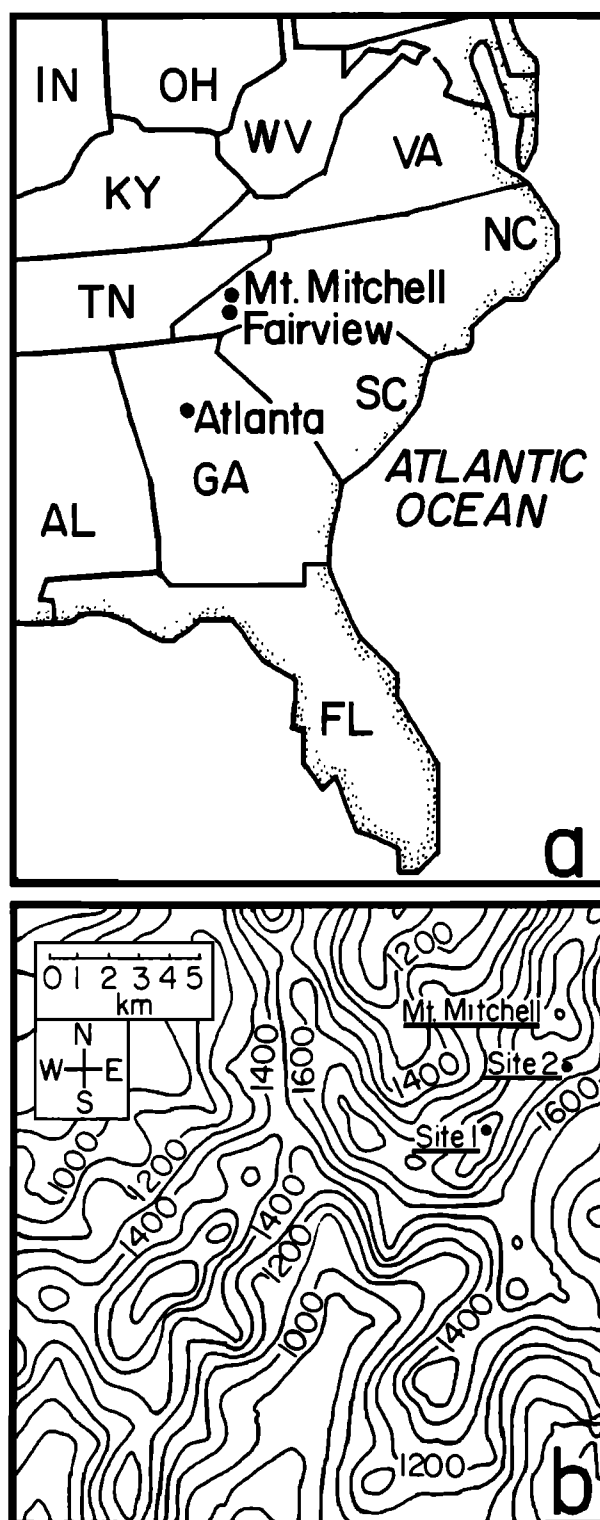

Fig. 1. (*a*) Map of southeastern United States showing the location of Mt. Mitchell. (*b*) Topographical map of the Mt. Mitchell area showing locations of sites 1 and 2.

of 10-22 ppbv. The quality assurance protocols for ozone, oxides of nitrogen, and sulfur dioxide measurements in general included zero and span checks weekly and multipoint calibrations two times during the measurement season. Calibrations for these analyzers were based on National Institute of Science and Technology (NIST) traceable reference standards. All gas-phase

instruments were housed in an instrument shack located below the meteorological tower, and the inlet manifold for the gas instruments, constructed of glass, was extended out of the building to a height of approximately 6-7 m above the forest floor, which placed the inlet for the instruments at the top of the forest canopy. This glass manifold was cleaned with acetone at the start of the season. Sample air was delivered from the manifold inside the instrument shelter to the sample inlet of each analyzer through 1/4 in. diameter PFA Teflon tubing. The instrument shelter was temperature controlled to above the ambient temperature at all times so that there was no condensation in sample lines. The residence times were 10 s in the glass manifold and 5 s in the Telfon sample line to the hydrogen peroxide analyzer.

Gas-phase total peroxides and hydrogen peroxide measurements were taken at site 1 during four "intensives" scheduled throughout the field season of 1988. Gas-phase total and hydrogen peroxide data were recorded on a chart recorder and extracted manually as 12-min averages. These data were then consolidated into hourly averages. Gas-phase hydrogen peroxide was measured using the continuous, dual-channel fluorometric analyzer based on the horseradish peroxidase method [Lazrus et al., 1985]. The level of detection of the instrument is 0.1 ppbv. The hydrogen peroxide analyzer was calibrated once daily against aqueous phase standards which were also made up daily by serial dilutions of 3% H₂O₂ solution. The hydrogen peroxide stock solution was checked weekly by titration against KMnO₄ solutions, which in turn were titrated against a standard Na₂C₂O₄ solution. The uncertainty of these calibrations as described by the 95% confidence interval when all calibrations were considered was ±12% at the 1 ppbv level. When the calibrations for the fall intensive were considered separately, the uncertainty was ±10% for the fall and ±11% for the rest of the field season. Calibrations were not checked against gas-phase standards, so that possible errors propagating through the remainder of the system must also be estimated. Possible sources of measurement errors are introduced due to fluctuations in the reagent line flow rates, stripping efficiency of less than 100%, and high proportions of organic peroxides to hydrogen peroxide. We assume the collection efficiency is complete, since we operated the instrument within the recommended operating range of flow rates and reagent pH values. The measured standard deviation in the flow rate of the stripping solution line was 6.5%.

The dual-channel fluorometric analyzer measures total peroxides on one channel (Sp, following the nomenclature introduced by Heikes [1991]) and, by specific enzymatic destruction of hydrogen peroxide by catalase, organic peroxides and some residual hydrogen peroxide on the second channel (Sc). The hydrogen peroxide concentration is calculated from the residual fraction of hydrogen peroxide after reaction with catalase (α_0) and the ratio of the pseudo-first-order reaction rate constants, k_i/k_o (K) as follows [Heikes, 1991]:

$$[H_2O_2] = \frac{\alpha_o^K S_p - S_c}{\alpha_o^K - \alpha_o} \qquad (1)$$

where k_i is the pseudo-first-order reaction rate constant for the enzyme-catalyzed decomposition of the mixture of hydroperoxides collected by the analyzer and k_o is the pseudo-first-order reaction rate constant for the enzyme-catalyzed decomposition of hydrogen peroxide. The residual fraction was calculated during calibrations each time fresh reagent solutions were prepared. The residual fraction is a measure of the amount of hydrogen peroxide detected by the second channel, after the catalase enzyme is added, and is

calculated as the ratio of hydrogen peroxide detected after, to hydrogen peroxide detected before, catalase addition. This fraction varied from batch to batch and ranged from 0.1 to 0.3. Values for K used previously by other investigators have ranged from 1:52 to 1:14, and laboratory measurements have indicated ratios as high as 1:8 [Heikes, 1991]. As recommended by Heikes [1991], a value of 1:14 was assumed in order to allow for some mixture effects. This value is intermediate between 1:52 and 1:8 and is applied with an uncertainty of ± 15% at α_o = 0.2 and Sc/Sp = 0.6.

Cloud water hydrogen peroxide measurements were taken throughout the field seasons of 1988 and during August and October of 1987. Cloud water samples were collected hourly at both sites 1 and 2, "fixed" for total hydroperoxide according to the derivatization technique of Kok et al. [1986] in order to minimize losses due to decomposition, and immediately refrigerated. These samples were later sent to the Tennessee Valley Authority lab in Muscle Shoals, Alabama, where they were analyzed for hydrogen peroxide content using the enzyme fluorometric technique [Lazrus et al., 1986]. This method, along with the derivatization technique mentioned above, measures soluble organic peroxides (R₁OOH) as well as hydrogen peroxide. Although organic peroxides make up a significant portion of the total peroxides collected by the gas-phase analyzer at Mt. Mitchell, organic peroxides rarely exceeded 5% of the total peroxide signal for aqueous phase samples, and therefore the total peroxide signal is reported here as hydrogen peroxide. A limited number of samples (N = 42) were collected in 1987 during August and October. A larger data set (N = 252 for site 1; N = 32 for site 2) was collected in 1988.

Baseline checks were performed automatically, usually several times per day. Statistical analyses were performed on a VAX computer, using RS-1 statistical software. Unless otherwise noted, statistical significance is assumed to be at the 99% confidence level

RESULTS

Gas Phase Hydrogen Peroxide

Because of early difficulties with the catalase enzyme, only the total peroxides channel was operational during the spring intensive (June and early portion of July 1988). Since this analytical method quantitatively collects only the lower molecular weight, soluble peroxides [Lazrus et al., 1986; Heikes, 1991], the total peroxides signal is not a true indication of the total organic peroxides content of the atmosphere. Nevertheless, the total peroxides signal should give at least a qualitative indication of the behavior of the soluble total peroxides; therefore these early measurements are also discussed in this paper. Hydrogen peroxide measurements were periodically made during the two summer intensives (July and August) and during the fall intensive (September).

Concentrations of gas-phase hydrogen peroxide measured during the two summer intensives of 1988 (mean 0.76±0.57 ppbv) were significantly greater than those observed during the fall intensive, during which generally cloudy conditions prevailed (mean 0.20±0.26 ppbv) (Table 1 and Figure 2). A similarly significant difference between concentrations in the summer and in the fall was observed in the total peroxides concentration as well, with the mean concentration of total peroxides collected by the analyzer during the summer intensives nearly 3.5 times that collected during the fall intensive. Although hydrogen peroxide was not measured during the spring intensive, the total peroxides

TABLE 1.　Summary of Values for Ambient, Gas-Phase Hydrogen Peroxide Levels at Mt. Mitchell Site 1 for Growing Season of 1988

Period	N	Mean	s.d.	Median	Minimum*	Maximum
1988	273	0.63	0.57	0.53	LOD	4.18
Days	130	0.48	0.30	0.43	LOD	1.24
Nights	143	0.76	0.71	0.66	LOD	4.18
Summer	208	0.76	0.57	0.68	LOD	4.18
Days	101	0.57	0.28	0.57	LOD	1.24
Nights	107	0.95	0.70	0.86	LOD	4.18
Fall	65	0.20	0.26	0.13	LOD	1.22
Days	29	0.18	0.16	0.16	LOD	0.68
Nights	36	0.21	0.31	0.10	LOD	1.22

Site 1 is located at ~2006 m msl.　Gas-phase concentrations are parts per billion by volume, and values are for 1-hour averaged data.
*LOD denotes detection level.

concentration measured during the spring intensive was 65% higher than the total peroxides concentration measured during the summer intensives.　Only a limited number of hourly measurements were made in June, however, and these were made during a stagnating high-pressure system, so it is unclear whether the high peroxide levels in June are due to seasonal variation or to the presence of this system.　Although the gas-phase data are limited, so that it is difficult to establish a seasonal trend on the basis of these data alone, the seasonal variations during the 1988 field season are more strongly suggested when both the gas-phase and cloud water hydrogen peroxide concentrations are examined in the discussion section.

Time plots (hourly averages) of gas-phase hydrogen peroxide and total peroxides concentrations measured during the four intensives are given in Figures 3-6.　Time plots of temperature, pressure, dew point, solar radiation, ozone, and sulfur dioxide elucidate the conditions present during these four intensive periods.　The spring intensive was characterized by a stagnating high-pressure system that occurred during the period of J.D. 165-170.　This intensive
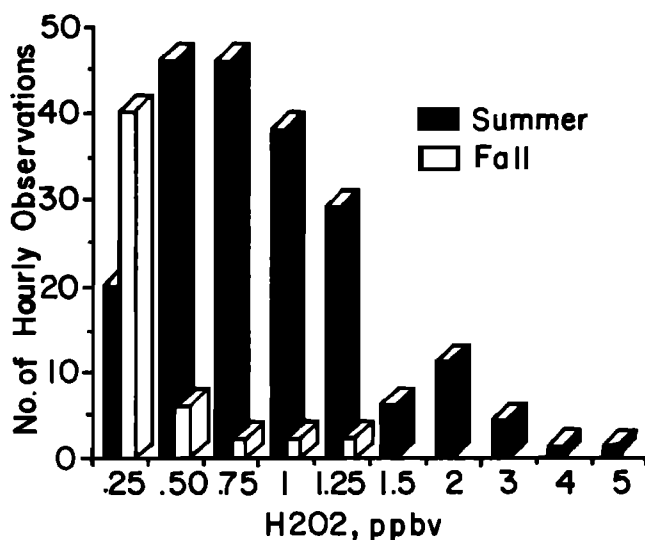

Fig. 2.　Frequency distribution of the summer (July and August intensives) and fall (September intensive) hourly averaged ambient hydrogen peroxide concentrations at Mt. Mitchell for 1988 monitoring season.

corresponded to an ozone episode, which has been discussed elsewhere [Aneja et al., 1991b].　This high-pressure system was characterized by low wind speed (less than 4 m/s) and east to southeasterly winds.　During this period, total peroxides levels increased, as did ozone concentrations.　Total peroxides were negatively correlated to solar radiation ($r = -0.45$), and peak concentrations in both ozone and total peroxides occurred during the night.　At night the wind speed was generally greater than 4 m/s between the hours of 0400 and 0700 eastern standard time (EST).　During this intensive the average peroxides concentration on a daily basis steadily increased, with increasing pressure ($r = 0.45$), temperature ($r = 0.15$), and dew point ($r = 0.48$).

During the first summer intensive there were a number of orographic cloud events that occurred during the early morning hours (Figure 4).　Nocturnal maxima were again observed in both the hydrogen peroxide and total peroxides concentrations.　However, when there was cloud activity, the maximum occurred before the cloud presence was detected, and the concentration decreased during the cloud.　Later during the intensive (J.D. 202) a cold front passed, bringing precipitation and some thunderstorm activity.　During this time the hydrogen peroxide, total peroxides, and ozone concentrations all decreased.　Toward the end of the intensive the hydrogen peroxide concentration was below the level of detection for the analyzer (0.1 ppbv).　Two excursions in the sulfur dioxide concentration were observed during this time.

The days preceding the second summer intensive were marked by considerable cloud activity; however, during the intensive itself, no cloud water samples were taken.　During the second summer intensive, nocturnal maxima in the hydrogen peroxide concentration were observed, and the hydrogen peroxide concentration seemed to be negatively correlated to solar radiation ($r = -0.24$) and dew point temperature ($r = -0.13$).　On average, concentrations of hydrogen peroxide and ozone were similar to those observed during the first summer intensive.

The fall intensive was marked by cloud activity, low solar radiation, and low temperatures, all of which would be expected to contribute to the low hydrogen peroxide levels observed during this time.　The hydrogen peroxide concentration decreased with temperature ($r = 0.64$) as a cold front passed.　The reversed diurnal variation observed in the earlier intensives (with a nocturnal maximum) was not observed during this period ($r = 0.15$ for correlation between solar radiation and hydrogen peroxide).　For a period during this intensive the atmosphere appeared to be
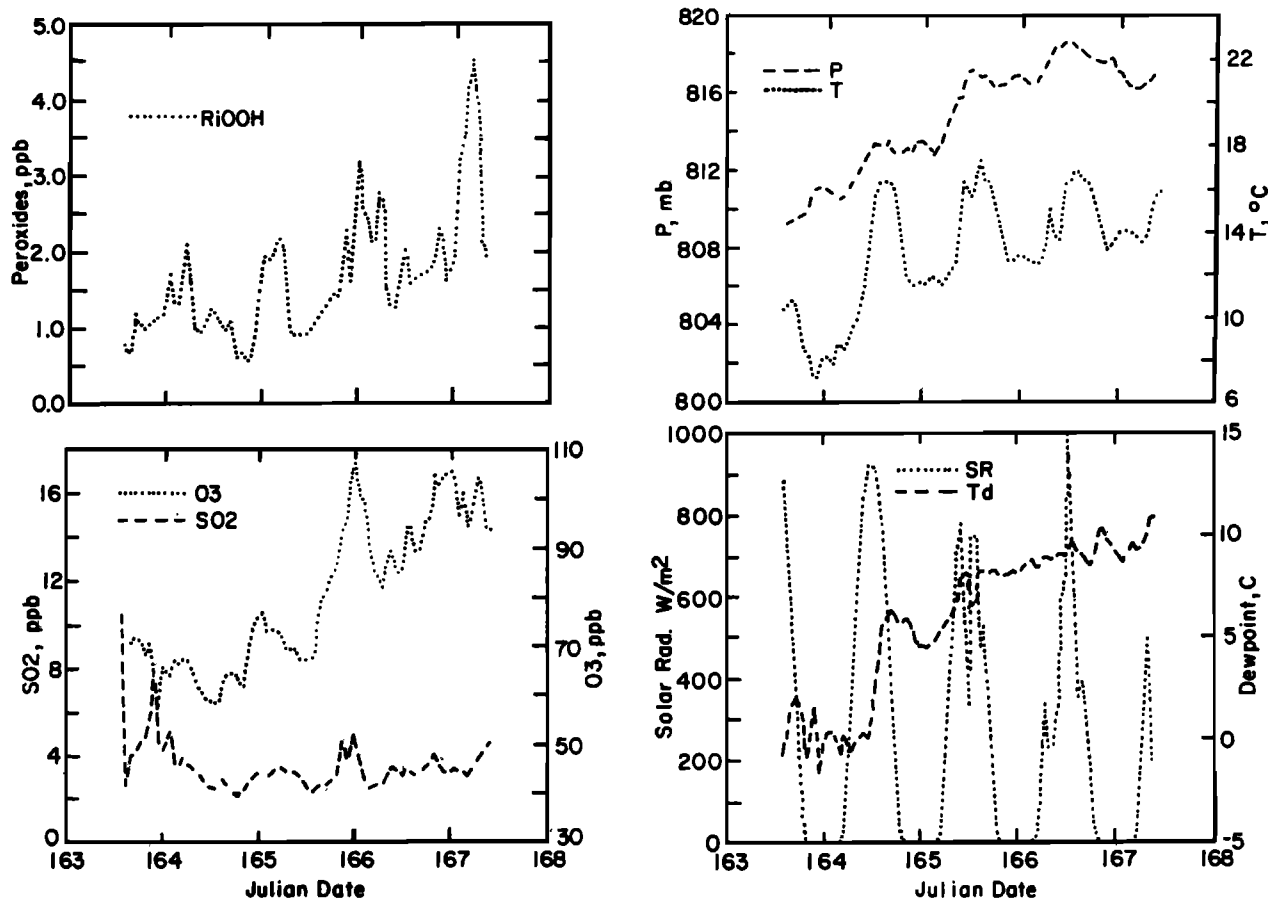
Fig. 3. Time plots for spring intensive, June 11 (J.D. 163) to June 16 (J.D. 168), 1988, monitoring season, for total peroxides, ozone, sulfur dioxide, pressure, temperature, solar radiation, and dew point temperature.

depleted in both gas-phase and cloud water hydrogen peroxide (early portion of J.D. 260); however, cloud water levels recovered in the second half of the day.

Cloudwater Hydrogen Peroxide

The cloud water data from site 1 for 1988 are summarized in Table 2. Site 1 was immersed in cloud during 30% of the time during the 1988 field season. Cloud water samples were collected for one third of the days during the season, representing 10% of the total time. Because of its higher elevation and orientation, site 1 (located on the top of the ridge) was exposed to more clouds than site 2, which is located down the mountainside. During the 1988 field season a much smaller number of cloudwater samples were obtained from site 2 than from site 1. The average cloud water hydrogen peroxide level at site 1 during the entire season of 1988 was 38.1±44.9 μM/L (Figure 7 and Table 2). The average value for the entire season at site 2 was 48.7±36.8 μM/L; however, this value was not found to be significantly higher than that for site 1. When we compared only those samples collected on days during which samples were collected at both sites, however, significant differences were found between the site 1 and site 2 cloud water hydrogen peroxide content. The site 1 cloud water hydrogen peroxide content was significantly greater (mean 65.5 μM/L) than that of site 2 cloud water (mean 41.2 μM/L) (95% confidence) during the month of June. In August, however, the site 1 cloud water hydrogen peroxide content was significantly less (mean 35.1 μM/L) than that at site 2 (mean 53.9 μM/L) (99%).

Table 2 also indicates the variation of cloud water hydrogen peroxide at site 1 with season. Levels for spring and early summer (May-June) 1988 (mean 54.7±57.1 μM/L) were not significantly higher than those of later summer (July-August) (mean 46.9±41.9 μM/L). However, the summer concentration was significantly higher than that of fall (99% confidence). Comparing month to month, there is a significant difference between July levels and August levels at site 1 and between August levels and September levels. There is not a significant difference between June and May or between June and July.

Cloud water samples were analyzed according to whether the cloud event was "long" (8 hours or longer) or "short" (less than 8 hours) [Saxena et al., 1989]. This classification was intended to give an indication of the type of cloud; short cloud events are usually orographic in nature, while the long events generally tend to be frontal in origin. Based on this categorization, Table 3 summarizes the average hydrogen peroxide content, liquid water content (LWC) and pH for short and long events. The hydrogen peroxide content of orographic cloud water is significantly higher than that of frontal cloud water (95% confidence) (Figure 8).

DISCUSSION AND ANALYSIS

Comparison With Other Gaseous Hydrogen Peroxide Observations

We observed atmospheric gas-phase hydrogen peroxide concentrations at Mt. Mitchell that were comparable to values reported in the literature for other locations. The mean atmospheric hydrogen peroxide concentration at Mt. Mitchell during the summer of 1988 (0.76 ppbv, Table 1) was comparable
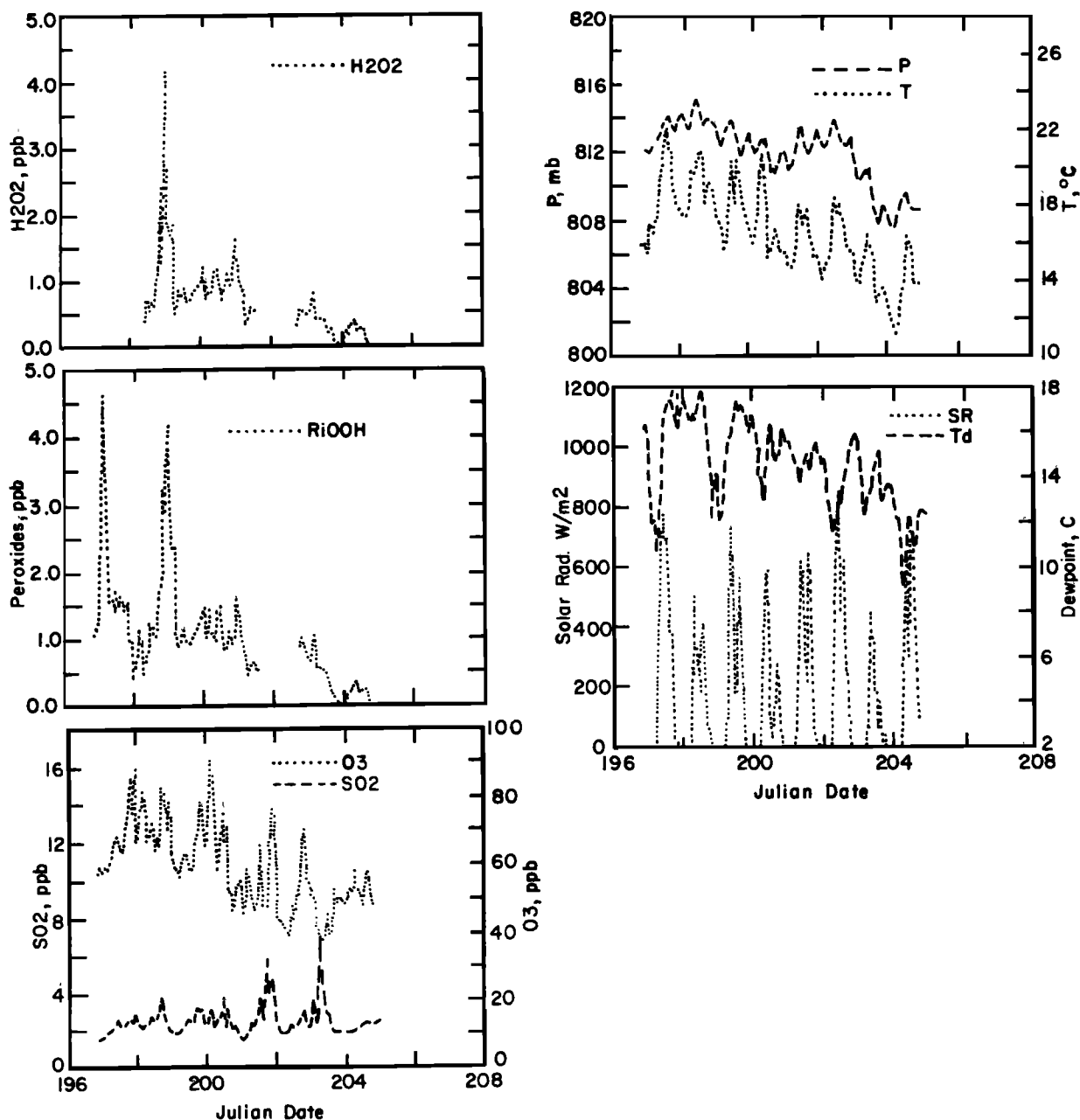
Fig. 4. Time plots for first summer intensive, July 14 (J.D. 196) to July 26 (J.D. 208), 1988 monitoring season, for hydrogen peroxide, total peroxides, ozone, sulfur dioxide, pressure, temperature, solar radiation, and dew point temperature.

to the average reported for the Whitetop Mountain, Virginia site (another southeastern United States high-elevation site), for which the mean was 0.8 ppbv in the summer of 1986 (*Olszyna et al.*, 1988). In the fall the levels of gaseous hydrogen peroxide at Mt. Mitchell (mean 0.20 ppbv) were also similar to those at Whitetop (mean 0.15 ppbv). The concentration of gas-phase hydrogen peroxide at Mt. Mitchell ranged from the level of detection (~0.1) to 4.2 ppbv. *Tanner et al.* [1986] reported atmospheric hydrogen peroxide ranging from 0.1 to 2 ppbv over rural areas in the eastern United States. Measurements made in the summer in southwestern Ontario, Canada, near the northern edge of Toronto were as high as 2.9 ppbv [*Slemr et al.*, 1986]. *Olszyna et al.* [1988] reported a maximum at Whitetop Mountain, Virginia, of 2.6 ppbv in the summer, and a maximum of 0.57 in the fall.

Higher values were reported by *Heikes et al.* [1987], who found levels aloft over 4 ppbv. Recently, high levels of hydrogen peroxide (up to 3.9 ppbv) have been reported for a tropical region at 13° south [*Jacob et al.*, 1990]. The highest tropospheric concentrations of which we are aware were reported by *Daum et al.* [1990], who found concentrations as high as 7 ppbv aloft over Ohio.

Concentrations of hydrogen peroxide in cloud water at Mt. Mitchell have also been found to be comparable to or higher than most cloud water levels reported elsewhere. In the summer, maximum levels at Mt. Mitchell were as high as 219 μM/L, and maximum fall levels were much smaller (55 μM/L). *Olszyna et al.*[1988] reported the only higher values, with a maximum of 247 μM/L observed in the summer. The concentrations found at
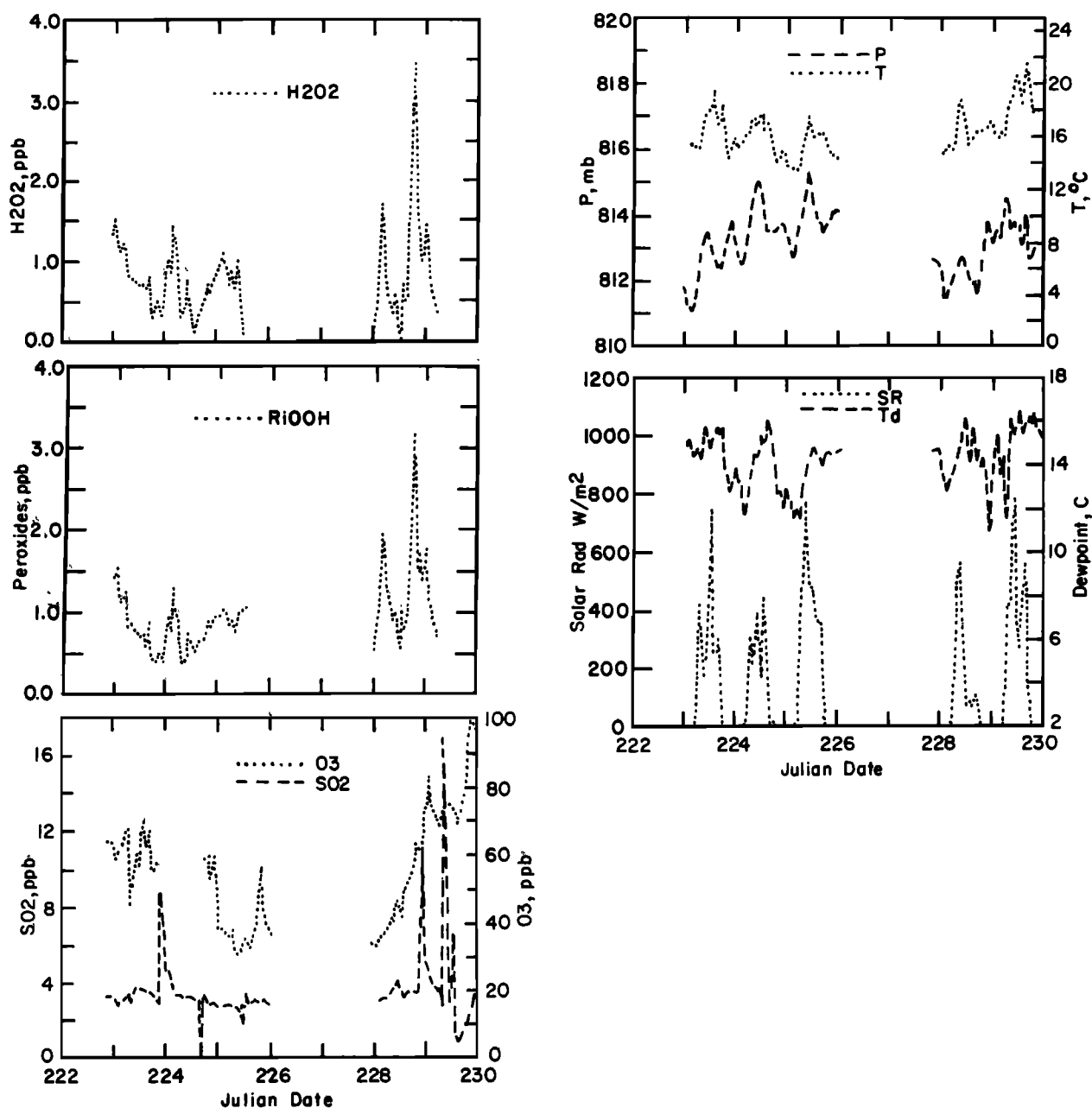
Fig. 5. Time plots for second summer intensive, August 9 (J.D. 222) to August 17 (J.D. 230), 1988, monitoring season, for hydrogen peroxide, total peroxides, ozone, sulfur dioxide, pressure, temperature, solar radiation, and dew point temperature.

Mt. Mitchell appear to be consistent with the range reported in the literature.

Factors Affecting Atmospheric Hydroperoxide Levels

Meteorological and chemical parameters. A good review summarizing the current understanding of the factors affecting atmospheric peroxide concentrations is given by *Sakugawa et al.* [1990]. There are no known emissions sources of hydrogen peroxide, and atmospheric concentrations are thought to result from the combination of perhydroxyl radicals (Table 4, reactions (7)-(10)) which were formed photolytically. From these reactions, meteorological parameters such as solar radiation, temperature, and water vapor content are expected to affect the atmospheric concentration of hydrogen peroxide.

Solar radiation is suspected of playing an important role in the seasonal [*Olszyna et al.*, 1988; *Boatman et al.*, 1989; *Sakugawa and Kaplan*, 1989], diurnal [*Olszyna et al.*, 1988; *Sakugawa and Kaplan*, 1989], and latitudinal variations [*Heikes et al.*, 1987; *Van Valin et al.*, 1987] in hydrogen peroxide concentrations reported in the literature. In contrast to the expected diurnal variation with maximum concentrations in the afternoon, at Mt. Mitchell the gaseous hydrogen peroxide concentration was found to be weakly, inversely correlated to solar radiation ($r = -0.19$), due to a nocturnal maximum that was commonly observed during the spring (in total peroxides) and summer intensives. A daytime minimum has been observed at high elevation on Mauna Loa (B.G. Heikes, personal communication, 1991) and a nocturnal maximum has been observed at Whitetop Mountain (J.F.
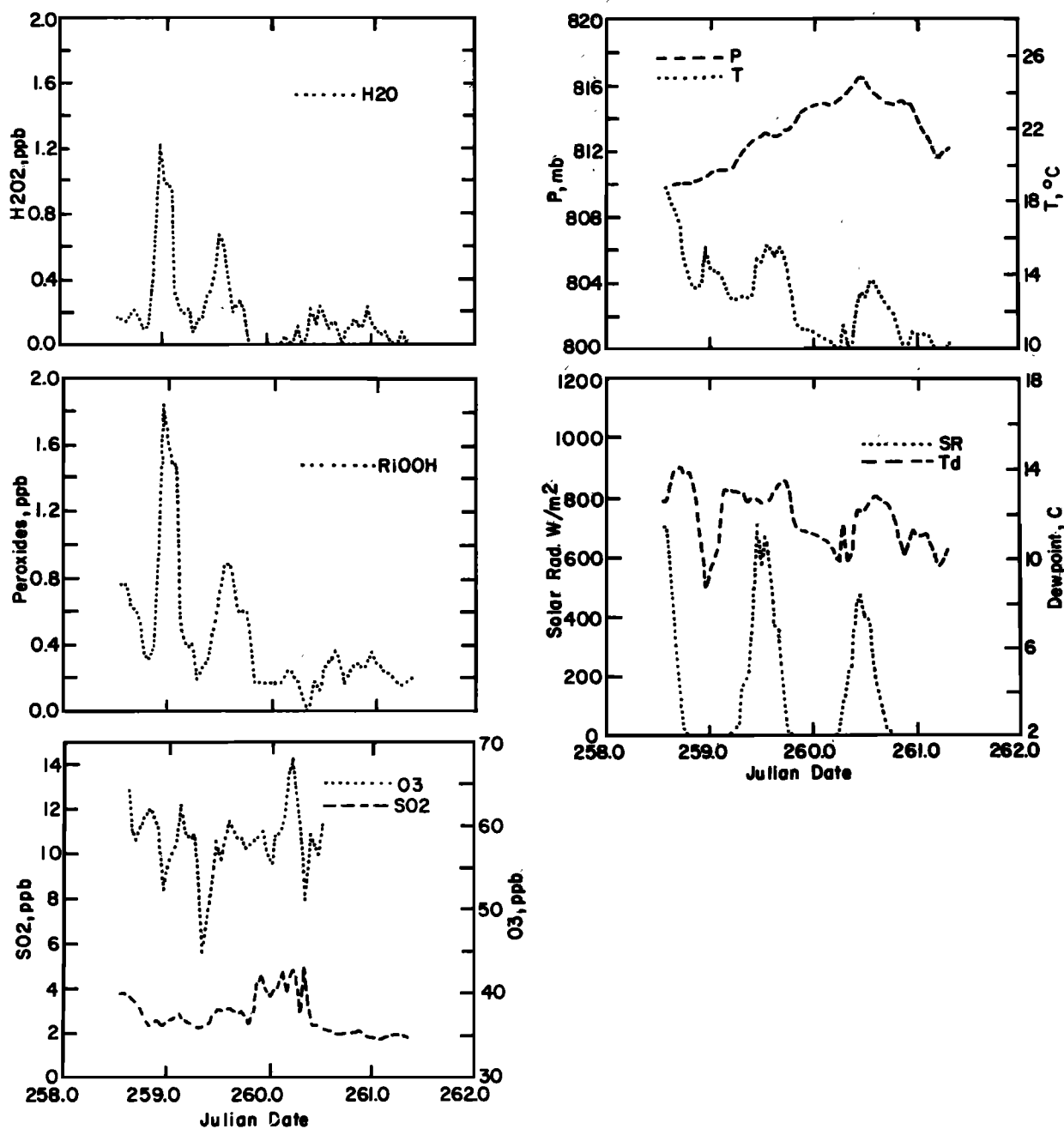
Fig. 6. Time plots for fall intensive, September 14 (J.D. 258) to September 18 (J.D. 262), 1988, monitoring season, for hydrogen peroxide, total peroxides, ozone, sulfur dioxide, pressure, temperature, and solar radiation.

Meagher, personal communication, 1990). Data showing the diurnal maxima in hydrogen peroxide were presented in the results section. This diurnal pattern was also observed in cloud water and is also discussed in more detail shortly.

Modeling studies [*Dodge*, 1989] indicate that hydrogen peroxide concentration will increase with increasing temperature. Consistent with these studies, the gaseous hydrogen peroxide concentration at Mt. Mitchell was found to be correlated to temperature ($r = 0.41$). Cloud water hydrogen peroxide content was also weakly positively correlated to temperature ($r = 0.29$).

If production of perhydroxyl radical proceeds predominantly through the photolysis of ozone, as one would expect in a relatively remote location such as Mt. Mitchell, then the radical production rate depends both on the ozone concentration (reaction

(2)) and on the water vapor concentration (reaction (3)). According to reaction (8) (Table 4), production of hydrogen peroxide from perhydroxyl radicals may also be enhanced in the presence of water vapor [*Calvert and Stockwell*, 1983]. Atmospheric hydrogen peroxide levels are therefore expected to be correlated to dew point temperature, and such a correlation has been observed in the field [*Daum et al.*, 1990]. At Mt. Mitchell, H_2O_2 was found to be very weakly correlated to dew point temperature ($r = 0.18$). There are a couple of factors acting at Mt. Mitchell that may influence the relationship between hydrogen peroxide concentration and dew point temperature. In addition to the process suggested by reaction (6) (which predicts a positive correlation) there is a diurnal variation in the dew point, which appears to correlate inversely with hydrogen peroxide.

TABLE 2. Summary of Values for Ambient, Cloudwater Hydrogen Peroxide Levels at Mt. Mitchell Sites

Period	N	Mean, μM/L	s.d.	Median	Minimum	Maximum
1988						
MM-1	252	38.1	44.9	20.5	0.2	219.1
May	57	46.5	53.8	25.2	0.2	191.2
June	39	65.5	60.6	56.9	0.6	203.7
Spring	96	54.2	57.1	31.0	0.2	203.7
July	36	54.5	49.8	38.7	3.2	219.1
Aug.	23	35.1	20.9	32.1	6.6	77.5
Late summer	59	46.9	41.9	36.6	3.2	219.1
Summer days	62	39.7	45.0			
Nights	93	59.3	54.8			
Sept.	97	16.8	14.7	9.9	1.9	54.6
Fall days	44	16.5	13.4			
Nights	53	17.1	15.8			
MM-2	32	48.7	36.8	41.0	0.2	122.9
June	13	41.2	36.5	27.4	0.2	97.0
Aug.	19	53.9	37.1	61.0	3.1	123.1
1987						
MM-1	42	44.0			0.5	196.0
Summer (Aug.)	17	106.8	59.6	95.0	10.0	196.0
Late fall (Oct.)	25	1.3	2.0	0.5	0.5	9.6

Site (MM-1) elevation is ~2006 m msl; site (MM-2) elevation is ~1760 m msl. Cloudwater   concentrations are in micro moles per liter, and values are for 1-hour averaged data.

The gas-phase hydrogen peroxide concentration is also inversely correlated to relative humidity ($r = -0.40$), a factor that is important in determining the exposure of the forest to air pollutants. It has been estimated that 60% of pollutant deposition to the forest canopy at Mt. Mitchell occurs through cloud deposition, compared to 10-15% for dry deposition (Lin and Saxena, 1991]. At relative humidity approaching 97%, Mt. Mitchell is generally immersed in cloud, so that the inverse relationship between relative humidity and hydrogen peroxide is expected due to cloud scavenging and wet deposition. Gaseous
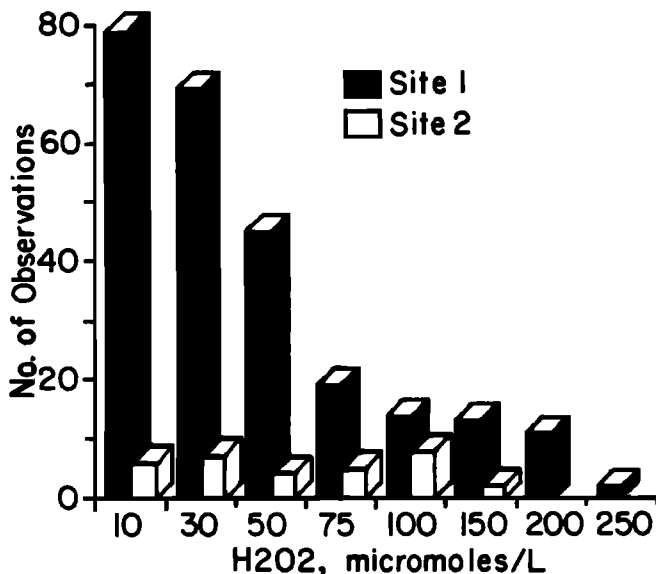

Fig. 7. Frequency distribution of cloudwater hydrogen peroxide content at Mt. Mitchell, 1988, showing difference between site 1 and site 2 samples. Bulk cloudwater samples were collected hourly.

hydrogen peroxide is very water soluble, so that for typical conditions of temperature and liquid water content observed at Mt. Mitchell a large fraction of the gas-phase hydrogen peroxide can be incorporated into cloud water. For example, at 15°C and liquid water content of 0.3 g/m³ (reasonable summer conditions at Mt. Mitchell [Aneja et al., 1991 a,b]) the atmospheric hydrogen peroxide concentration may be reduced to half its precloud level. Some simultaneous gas-phase and cloud water hydrogen peroxide measurements taken demonstrate the scavenging of gas-phase hydrogen peroxide by cloud water. For example, in Figure 9, at midnight on J.D. 201, the cloud appearance coincided with the reduction of the atmospheric concentration from approximately 1.2 ± 0.3 ppbv to 0.9 ± 0.1 ppbv, or to 75% of the precloud level. After the cloud disappeared, the gas-phase hydrogen peroxide concentration continued to decrease. However, this may have been due to the meteorological phenomena which apparently cause the nocturnal maximum at Mt. Mitchell. At any rate, the actual amount of reduction due to cloud presence alone is difficult to determine from this single event. However, we can make rough estimates. During this cloud event the temperature was approximately 15°C, and the cloud liquid water content ranged from 0.15 to 0.3 g/m³, so that the after-cloud concentration might be predicted to be between 50% and 65% of the precloud concentration.

Primary pollutant and other trace gas concentrations are expected to affect the ambient levels of hydrogen peroxide as well; modeling studies suggest that the major source of perhydroxyl radicals in polluted atmospheres is from the photolysis of formaldehyde, shown in reaction (1) [Calvert and Stockwell, 1983]. In clean atmospheres (presumably such as Mt. Mitchell) the major source of perhydroxyl radical is thought to be from the photolysis of ozone to form hydroxyl radical, followed by reaction with carbon monoxide (reactions (2)-(4)) [Kleinman, 1986]. Another source of radicals that would be important in forested regions may be from the reaction of ozone with biogenic

TABLE 3. Bulk, Hourly, Cloud Water Hydrogen Peroxide Content, Liquid Water Content, pH, and Cloudwater Ionic Content as a Function of Event Duration for Mt. Mitchell Site 1, Growing Season of 1988

Parameter	N	Mean	s.d.	Range	Median
Long					
H_2O_2, $\mu M/L$	152	33.7	45.0	0.5 - 203.7	18.3
LWC, g/m^3	174	0.374	0.295	0.00 - 2.975	0.325
pH	172	0.374		2.62 - 5.41	
SO_4^{2-}, $\mu eq/L$	172	3.41	225.2	0.4 - 1709.1	97.7
NO_3^-	172	177.0	256.2	0.3 - 2117.7	72.2
NH_4^+	172	147.0	248.4	1.8 - 2038.8	69.8
H^+	172	133.3	449.6	3.9 - 2398.8	242.7
Short		390.5			
H_2O_2	100	44.8	44.2	0.2 - 219.1	28.8
LWC, g/m^3	128	0.209	0.175	0.0 - 0.793	0.163
pH	150	3.17		2.24 - 4.39	
SO_4^{2-}	113	341.8	354.6	7.2 - 645.6	199.8
NO_3^-	113	281.2	340.3	7.5 - 2178.0	152.8
NH_4^+	113	265.5	304.4	5.0 - 1645.8	156.2
H^+	150	813.9	736.7	40.7 - 5754.4	562.5

LWC, liquid water content

hydrocarbons such as isoprene and the terpenes [*Becker, et al.*, 1990]. Therefore in relatively clean atmospheres (i.e., low NO_x levels), hydrogen peroxide is expected to be correlated to ozone. This relationship was observed at Whitetop Mountain, Virginia [*Olszyna et al.*, 1988], a rural and somewhat remote location. A positive correlation was also noted at Mt. Mitchell between gas-phase hydrogen peroxide and ozone ($r = 0.28$) for the entire sampling season of 1988. Additionally, cloud water hydrogen peroxide content was also directly correlated with ozone ($r = 0.48$). Hydrogen peroxide was strongly correlated to total peroxides ($r = 0.94$), as might be expected, since both are formed
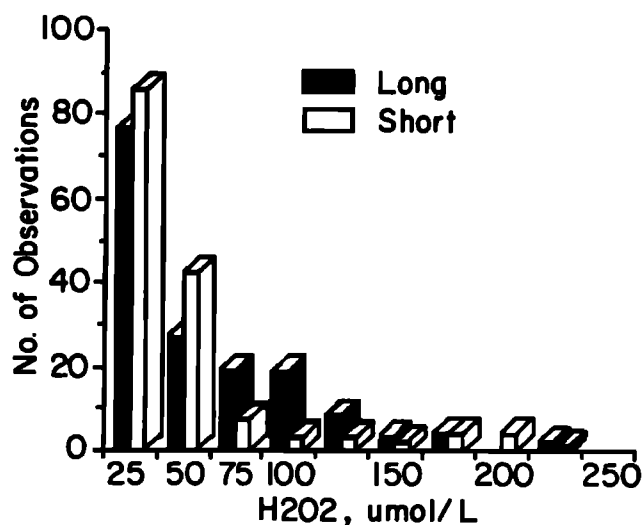

Fig. 8. Frequency distribution of hourly cloudwater hydrogen peroxide content at Mt. Mitchell, 1988, comparing "long" events (lasting 8 hours or longer) and "short" ones (less than 8 hours). This classification was intended to given an indication of the difference between frontal ("long") and orographic cloudwater ("short").

through related atmospheric processes involving perhydroxyl radicals (reactions (7)-(10)), and since hydrogen peroxide is the major component of total peroxides.

Role of long-range transport. If long-range transport plays a role in bringing either hydrogen peroxide or its precursors to Mt. Mitchell, then a relationship between back trajectory and hydrogen peroxide concentration should become apparent. The local wind direction reading as measured at the top of the meteorological tower at Mt. Mitchell site 1 is greatly influenced by the local topography. However, with the exception of northerly winds the local wind direction was found to correlate well to the back trajectory [*Saxena and Yeh*, 1988]. For this reason the influence of wind direction on the gas phase (Table 5) and cloud water (Table 6) hydrogen peroxide concentrations was examined. There were relatively few observations of winds out of the northeast sector; for the gaseous hydrogen peroxide measurements made, only 18 of 273 observations corresponded to this sector. Comparisons between the average hydrogen peroxide levels from the four different sectors showed that the average hydrogen peroxide level was significantly greater (at 95% confidence level) when the winds were out of the northeast or southwest (continental air parcels). The hydrogen peroxide levels were significantly lower when the winds were out of the southeast, from where, presumably, air parcels are marine in origin. Unlike the relationship between gas-phase hydrogen peroxide and wind direction there was not a statistically significant difference between hydrogen peroxide cloud water levels as a function of wind direction, except that the few samples taken when the wind was out of the northeast sector were found to be statistically lower in hydrogen peroxide content than those taken when the wind was out of the southwest. This is interesting, since the northeast sector was the source of the highest ambient levels of hydrogen peroxide. This apparent conflict in results could be due to the relatively low number of samples from this sector.

TABLE 4. Gas-Phase Reactions Affecting Atmospheric Hydrogen Peroxide Concentration

|	Reaction	Number
Perhydroxl radical formation	$HCHO + hv \xrightarrow{O_2} 2HO_2 \cdot + CO$	(1)
	$O_3 + hv \rightarrow O(^1D) + O_2$	(2)
	$O(^1D) + H_2O \rightarrow 2OH \cdot$	(3)
	$OH \cdot + CO \xrightarrow{O_2} HO_2 \cdot + CO_2$	(4)
	$NO_3 \cdot + HCHO \rightarrow HNO_3 + HO_2 \cdot + CO$	(5)
Hydroperoxide Formation	$HO_2 \cdot + HO_2 \cdot \rightarrow H_2O_2 + O_2$	(6)
	$H_2O \cdot HO_2 \cdot + HO_2 \cdot \rightarrow H_2O_2 + H_2O + O_2$	(7)
	$O_3 + terpenes \rightarrow H_2O_2 + carbonyls$	(8)
	$HO_2 \cdot + RO_2 \cdot \rightarrow ROOH + O_2$	(9)
Competing reactions	$HO_2 \cdot + NO \rightarrow OH \cdot + NO_2$	(10)
	$NO_2 OH \cdot \rightarrow HNO_3$	(11)
Ozone Formation	$NO_2 + hv \rightarrow O(^3P) + NO$	(12)
	$O(^3P) + O_2 \rightarrow O_3$	(13)
Hydrogen peroxide destruction	$H_2O_2 + OH \cdot \rightarrow H_2O + HO_2 \cdot$	(14)
	$H_2O_2 + hv \rightarrow 2OH \cdot$	(15)
Gas-phase SO_2 oxidation	$SO_2 + OH \cdot \rightarrow HOSO_2$	(16)
	$HOSO_2 + H_2O \rightarrow H_2SO_4$	(17)
	$SO_3 + H_2O \rightarrow H_2SO_4$	(18)
Aqueous-phase reactions	$HO_{2 \ aq} + O_2^- \rightarrow H_2O_2 + O_2 + OH^-$	(19)
	$H_2O_{2aq} + OH \cdot \rightarrow H_2O + HO_2 \cdot$	(20)
	$H_2O_{2aq} + hv \rightarrow 2OH \cdot$	(21)
	$HSO_3^- + H_2O_{2aq} + H^+ \rightarrow SO_4^{2-} + 2H^+ + H_2O$	(22)
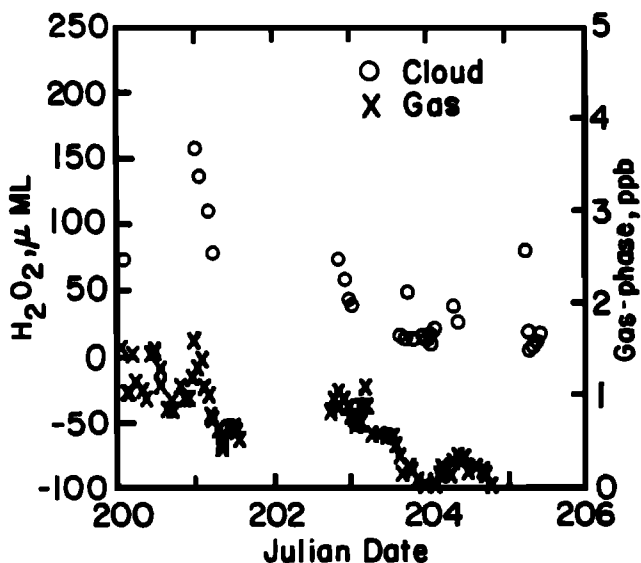
Fig. 9. Time plots for first summer intensive, showing both cloudwater and gas-phase hydrogen peroxide concentrations. The effects of cloud presence on gas-phase hydrogen peroxide concentration are particularly evident for J.D. 201; cloudwater samples corresponded to 15 °C and liquid water content varying from 0.15 to 0.3 g/m^3. Calculated fraction accounting for removal by cloud scavenging was 0.5-0.64 (see text).

Relative roles of various processes. In order to investigate the relative importance of the various processes that affect the concentration of gaseous hydrogen peroxide at Mt. Mitchell the steady state expression for hydrogen peroxide concentrations based on a simplified radical balance as given by *Daum et al.* [1990] is examined:

$$[H_2O_2] = \frac{\frac{j_1 k_2}{k'_2} [O_3] [H_2O] - \frac{1}{2} E_{NO_x}}{k_8 [OH \cdot] + k_9 + k_{10} [SO_2]_{(eq)}} \quad (2)$$

where E_{NO_x} is the rate of NO_x emission, k_2, k'_2, k_8, and k_{10} are reaction rate constants j_i is a photolysis rate constant, and k_9, is for deposition processes. The rate constant, k_{10}, takes into account the Henry's law constant for hydrogen peroxide and the presence of aqueous water.

This equation considers sources due to formation from radicals and losses of radicals due to competing reactions with NO_x, as well as losses of hydrogen peroxide due to reactions with sulfur dioxide and deposition processes. Dry deposition is characterized by the deposition velocity, which can be calculated from the "Big Leaf" model [*Hicks et al.*, 1987]:

$$V_d = (R_a + R_b + R_c)^{-1} \quad (3)$$

TABLE 5. Relationships Between Ambient Gas-Phase Hydrogen Peroxide and Wind Direction at Mt. Mitchell Site 1 for Growing Seasons of 1988

Sector	N	Mean	s.d	Range*
NE (0-90)	18	0.92	0.84	LOD- 3.48
SE (90-180)	84	0.42	0.51	LOD - 2.53
SW(180-270)	111	0.74	0.54	LOD- 4.18
NW (270-360)	60	0.62	0.51	LOD- 1.85

Taken from 1-hour averaged data.
*LOD denotes level of dectection. Units are ppbv,

where both the aerodynamic and diffusive boundary layer resistances, R_a and R_b, are functions of the wind speed (u) and the standard deviation in the wind direction (σ_θ),

$$R_a \sim \frac{1}{u\sigma_\theta^2}$$

(4)

$$R_b \sim \frac{1}{u^*}\left(\frac{Sc}{Pr}\right)^p$$

(5)

and the friction velocity, u_*, can be approximated from the aerodynamic resistance [*Hicks, et al.*, 1987]:

$$R_a = u u_*^{-2}$$

(6)

For a highly soluble and reactive gas such as hydrogen peroxide the canopy resistance is expected to be much less than the aerodynamic and boundary layer resistances, so that

$$V_d \approx (R_a + R_b)^{-1}$$

(7)

It can be shown that the deposition velocity varies with the wind speed and standard deviation in wind direction as follows:

$$V_d \sim \frac{u\sigma_\theta^2}{1+\sigma_\theta}$$

(8)

In addition to the factors accounted for in the above equations, the hydrogen peroxide level will also depend on the background level of hydrogen peroxide or its precursors in the air parcel approaching Mt. Mitchell. A multiple linear regression analysis was conducted on the gas-phase hydrogen peroxide data set considering the available meteorological data for temperature, wind speed, wind direction (which is characteristic of the back trajectory), pressure, solar radiation, and relative humidity and

including the calculated parameters ($[O_3]$ $[H_2O]$) (indicating radical formation from ozone), $(1 + \sigma_\theta)(\mu\sigma_\theta^2)^{-1}$ (characteristic of dry deposition), and $(K_HSO_2)^{-1}$ (characteristic of the air parcel's potential for aqueous losses to reaction with sulfur dioxide), as suggested by the above expression. Because we rarely observed NO_x concentrations above the level of detection of the instrument, the following analysis does not include a term representing the effects of NO_x. Also, since we did not measure hydroxyl radical concentration, the term representing destruction of hydrogen peroxide by reaction with OH• is not included.

When the entire data set for total peroxides was considered, formation from ozone, wet deposition (suggested by a negative correlation to relative humidity), the nocturnal maximum (indicated by an inverse correlation to solar radiation), transport (indicated by the wind direction), and presence of high-pressure systems (indicated by correlation to pressure) emerged as the statistically significant processes we considered, accounting for 61% of the variation. The statistically significant processes accounting for 46% of the variation in the hydrogen peroxide concentration were formation from radicals, the diurnal variation, wet deposition, heterogeneous losses to SO_2, and high pressure.

Because of the apparently different mechanisms active during the spring and summer days and nights, several subsets of the complete data set were considered separately. The data were classified according to fall, spring/summer days (referred to as summer days) and summer nights. During the summer days, presence of high-pressure systems, formation from radicals, and transport were the significant processes, accounting for 47% of the variation in the hydrogen peroxide concentration. In contrast, during the summer nights, relative humidity (assumed to be indicative of wet deposition or losses to wet surfaces), temperature, reversed diurnal variation (nighttime maximum), and wind direction indicating the role of transport were the significant processes (49% of variation). We interpret these results to indicate that both on-site formation and transport processes

TABLE 6. Relationships between Aqueous-phase, Cloud Water Hydrogen Peroxide and Wind Direction at Mt. Mitchell Site 1 for Growing Seasons of 1988

Sector	N	Mean	s.d.	Range		
NE (0-90)	9	18.3	17.7	3.5	-	63.6
SE (90-180)	74	33.7	47.7	1.9	-	191.2
SW (180-270)	55	46	39.3	3.1	-	156.1
NW (270-360)	111	38.8	47.1	0.2	-	218.9

Taken from bulk, hourly cloud water samples.

(which could be of either peroxides or their precursors) provide sources of hydrogen peroxide at Mt. Mitchell during the day and that at night, in addition to the nocturnal maximum, deposition is increased due to condensation.

Spring: Gas-phase hydrogen peroxide was not collected in June, but total peroxides were significantly correlated only to ozone during the day ($r^2 = 0.53$) and were positively correlated to ozone and wind direction and negatively correlated to solar radiation (nocturnal maximum, total $r^2 = 0.70$) at night, with concentrations decreasing markedly in the very early hours of the morning as the Sun came up. As mentioned earlier, the June data set was influenced by a synoptic high-pressure system, which dominated the Mt. Mitchell area during the greater part of June during which atmospheric hydroperoxide was measured. As mentioned in the results section, the prevailing winds were from the east to southeast, and wind speeds were generally less than 4 m/s, with the exception of brief periods during the night. During this time, ozone concentrations increased through the course of the high-pressure system, providing increased sources of radicals for hydroperoxides formation. During the night the peroxides level reached a maximum, declining with the onset of sunrise.

Summer: During the summer, hydrogen peroxide correlated positively to ambient temperature, wind direction, ozone, and pressure during the day (total $r^2 = 0.47$). At night the hydrogen peroxide was also negatively correlated to dew point temperature and to solar radiation, and the effects of wind direction and of ozone were not significant ($r^2 = 0.51$). The peroxides concentration was apparently influenced by the back trajectory of the air parcel as well as by radical formation and less influenced by loss processes associated with deposition and reaction with sulfur dioxide. At night the dew point temperature became an important factor, indicating a change in air mass. The dew point temperature generally decreased at night and increased rapidly again in the morning, between the hours of 0500 and 1000 (e.g., Figure 10).

Fall: During the fall, wet deposition, aqueous phase reaction with sulfur dioxide and an inverse relationship to temperature accounted for 78% of the variation in the hydrogen peroxide concentration. From these results it appears that on-site formation of hydrogen peroxide played a much less significant role in determining the September levels observed at Mt. Mitchell.

Cloud Water Hydrogen Peroxide

Because of the large solubility of gas-phase hydrogen peroxide in water we would expect that scavenging by cloud water would reduce the atmospheric gas-phase hydrogen peroxide by the factor $1/(LWC*H*R*T + 1)$, where LWC is the liquid water content, R is the gas constant, and T is the ambient temperature, and the Henry's law constant for hydrogen peroxide is given by [Lind and Kok, 1986]:

$$H(T) = exp\left(\frac{A}{T} - B\right) \qquad (9)$$

where $H(T)$ has units of M L^{-1} atm^{-1}, T is in Kelvin, $A = 6621$, and $B = 11$.

The cloud water hydrogen peroxide concentration, then, can be calculated from the following equation:

$$[H_2O_2]_{aq} = \frac{H(T)*[H_2O_2]_g}{LWC*H(T)*R*T + 1} \qquad (10)$$

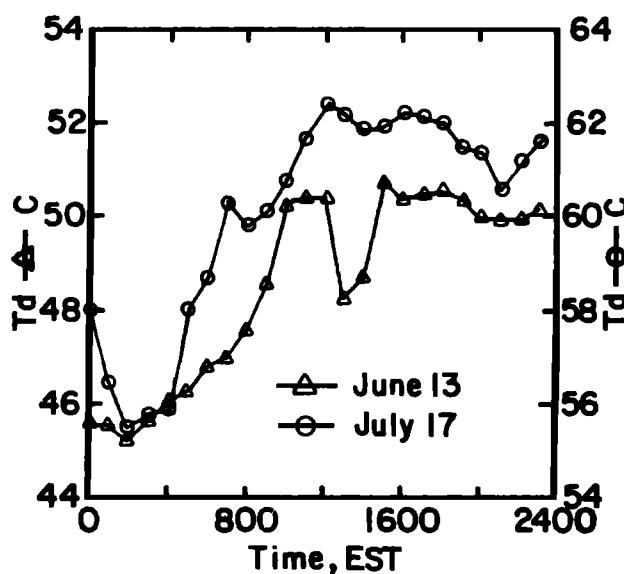From this equation it is evident that increasing liquid water

Fig. 10. Diurnal variation of dew point temperature at Mt. Mitchell, for two days, June 13 and July 17, 1988. Data taken from hourly averaged data; time is eastern standard time.

content (LWC) should decrease both the gas-phase and cloud water hydrogen peroxide concentrations. Furthermore, if heterogeneous decomposition follows cloud scavenging, the inverse relationship between LWC and H_2O_2 would become even more pronounced. Therefore even with varying precloud H_2O_2 concentrations, increased cloud liquid water content might be expected to result in lower cloud water concentration, and in fact, a slight, but statistically significant, inverse relationship between cloud water hydrogen peroxide and liquid water content was observed at Mt. Mitchell ($r = -0.24$). Negative correlations between liquid water content and concentrations of ionic species are observed, as well (for example, $r = -0.34$ for correlation coefficient between liquid water content and sulfate ion). In general, at Mt. Mitchell the relative amounts of the various ionic species remain fairly constant (for example, $r = 0.92$ for correlation coefficient between sulfate and hydrogen ion, and $r = 0.78$ for correlation between ammonium and hydrogen ion). However, the total ionic content varies considerably, at least in part due to changes in the cloud liquid water content [Aneja et al., 1990, 1991a]. In fact, it has been found that dilution apparently plays an important role in determining the cloud water content of ionic species at Mt. Mitchell [Aneja et al., 1990].

There is a weaker, but statistically significant, correlation between hydrogen peroxide and ionic species, such as hydrogen ion ($r = 0.43$), sulfate ion ($r = 0.46$), and ammonium ion ($r = 0.47$). Although both cloud water hydrogen peroxide and the ionic species concentrations respond to the cloud liquid water content, the mechanisms are entirely different. The liquid water content affects the hydrogen peroxide concentration through cloud scavenging, while dilution is probably the major mechanism accounting for the relationship between liquid water content and the ionic species concentrations. The existence of a correlation between the ionic species and hydrogen peroxide content is therefore not expected except to the extent that all these concentrations respond to the liquid water content. To further investigate the relationships between cloud water hydrogen peroxide, liquid water content, the various ionic species and meteorological parameters, a multiple linear regression analysis

was performed. However, it failed to confirm that the important factor was liquid water content but rather indicated that hydrogen peroxide is (in descending order of importance) positively related to ozone, temperature, ammonium ion content and negatively related to the sulfur dioxide content of the air (total $r^2 = 0.53$). Further work is desirable to determine the relationships, if any, between ionic species and cloud water hydrogen peroxide concentrations.

It is somewhat surprising that site 1 clouds contain a higher content of hydrogen peroxide than the site 2 clouds in June but not in August. Since the site 2 clouds tend to be thinner than the site 1 clouds, they have a lower liquid water content. However, there was only a slight negative correlation between liquid water content and hydrogen peroxide content ($r = -0.24$). This might explain why during August the site 2 clouds contain more hydrogen peroxide. On the other hand, since site 1 is at at higher elevation and is more exposed, it is possible that deposition losses are not as great at site 2. Alternatively, the orientation of these two sites with respect to the wind field may contribute to the differences between the two sites. At any rate, this apparent anomaly is probably due to a number of reasons, which also might include temperature differences, elevation of cloud base, or gradients in other pollutant gases such as ozone or sulfur dioxide, and warrants further study.

As indicated in Table 3, short events exhibit significantly higher concentrations of all ionic species than long events exhibit. Short events also have significantly lower liquid water content, and therefore in view of the above discussion dilution is, at least in part, responsible for the difference in concentrations of ionic species between long and short events (*Aneja et al.*, 1990). In fact, the ratio of concentration in the long-event cloud water to the concentration in the short-event cloud water was 0.52, 0.52, 0.50, and 0.58 for SO_4^{2-}, NO_3^-, NH_4^+, and H^+, respectively. The ratio of liquid water content for the short event to the long event was 1.8 (the inverse of which is 0.56). The hydrogen peroxide content of the short event is also significantly higher than that of the long event; the ratio of the concentration in long events compared to short events is 0.71, indicating that there seems to be a weak, inverse relationship between cloud liquid water content and hydrogen peroxide content ($r = -0.24$). This ratio, however, is significantly higher than the ratio for other cloud water species, again indicating that dilution is not important to the hydrogen peroxide concentration as it is to the concentrations of the major ionic species.

Seasonal Variation

Both gas-phase and cloud water hydrogen peroxide concentrations were measured during the entire 1988 field season; either gas-phase or cloud water hydrogen peroxide was measured on 57 days. Therefore although the data set collected is limited in that gas-phase data were collected periodically throughout the season as opposed to continuously, when both gas-phase and cloud water levels are considered, the data are consistent with the expected seasonal trend, with the higher levels observed in the early summer and lower levels in the spring, as observed by other investigators at other locations. For example, a strong seasonal dependency was also observed at Whitetop Mountain [*Olszyna et al.*, 1988], with highest levels in both the gas and liquid phases occurring during the summer and lowest values in the spring and fall. The total hydroperoxides were highest in June, which would be consistent with the maximum in solar radiation. However, during the spring (June) intensive a high-pressure system

accompanied by low wind speeds, warm temperatures, low relative humidity, and high ozone dominated the synoptic conditions [*Aneja et al.*, 1991b], and this high-pressure system is suspected of contributing as well to the high total hydroperoxide concentrations measured during this time.

There was generally a good correlation between organic peroxides measured by the fluorometric analyzer and the hydrogen peroxide content of the atmosphere ($r = 0.94$); therefore this suggests that early summertime levels of hydrogen peroxide may also be significantly higher than later summertime levels. Cloud water concentrations were high in June, July, and May as well. Therefore it would be interesting to monitor hydrogen peroxide levels earlier in the spring, in order to determine whether the maximum occurs in the spring or in the summer. *Aneja et al.* [1991b] reported that at Mt. Mitchell site 1, ozone levels were also significantly higher in the late spring than in the summer. A springtime maximum has been reported for other photochemical oxidants as well in the northern hemisphere troposphere [e.g. *Penkett and Brice*, 1986].

Reversed Diurnal Variation

Nighttime levels of gas-phase hydrogen peroxide (mean 0.95 ± 0.70 ppbv) measured during the summer of 1988 were significantly higher than daytime levels (mean 0.57 ± 0.28 ppbv) (Table 1 and Figure 11). A significant difference between nighttime and daytime levels was observed for the total peroxides as well during the summer (Figure 12). Average nighttime values of cloud water hydrogen peroxide (mean 59.3 ± 55 μM/L) were also significantly higher than average daytime values (mean 39.7 ± 45 μM/L) during the summer (Figure 13). The reversed diurnal trend in gaseous hydrogen peroxide was most detectable during July (Figure 4), when a maximum occurred around midnight. Secondary peaks occurred at night in August and September as well; however, the primary peaks were during the day. The total peroxides signal showed nocturnal maxima in June (between 0000 and 0400 hours) and July (between 2000 and 0400). Again, secondary peaks were observed during the night in both August and September. There was no significant difference in the fall between nighttime concentrations of cloud water
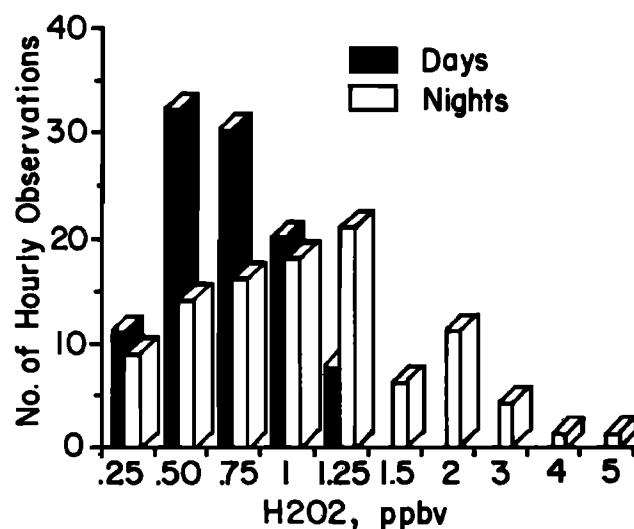

Fig. 11. Frequency distribution of daytime and nighttime ambient hydrogen peroxide concentrations at Mt. Mitchell, for 1988 monitoring season, illustrating the statistically significant difference between day and night values (nighttime concentrations were greater than daytime).
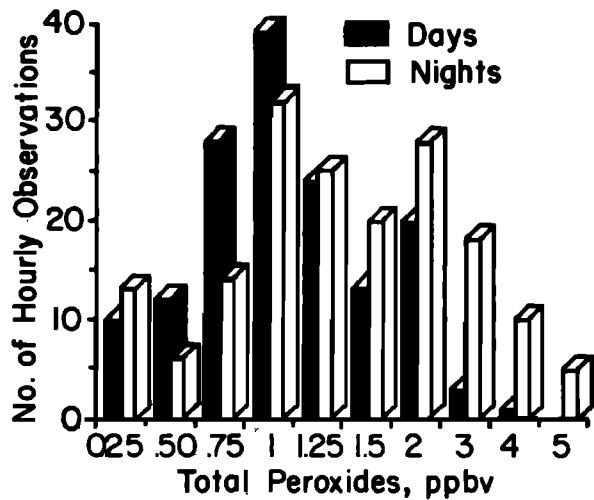
Fig. 12. Frequency distribution of daytime and nighttime gas-phase, total peroxides at Mt. Mitchell, for 1988 monitoring season.

hydrogen peroxide (mean 17.1 ± 16 µM/L) and daytime concentrations (mean 16.5 ± 13 µM/L).

There is a less pronounced but still definite nocturnal maximum at Mt. Mitchell in ozone levels as well, evident particularly during the summer months at site 1. The average nighttime value for the ozone at Mt. Mitchell site 1 was found to be significantly greater than the daytime value at the 95% confidence level in 1988 and at the 90% confidence level in 1987 [Aneja et.al., 1991b]. Similar to the hydrogen peroxide diurnal behavior, nighttime levels of ozone were significantly higher than daytime levels during the summer but not during the fall. A statistically significant difference between night and daytime ozone levels was not reported at site 2. Reversed diurnal cycles in surface ozone concentrations at Whiteface Mountain have been observed [Samson, 1978].
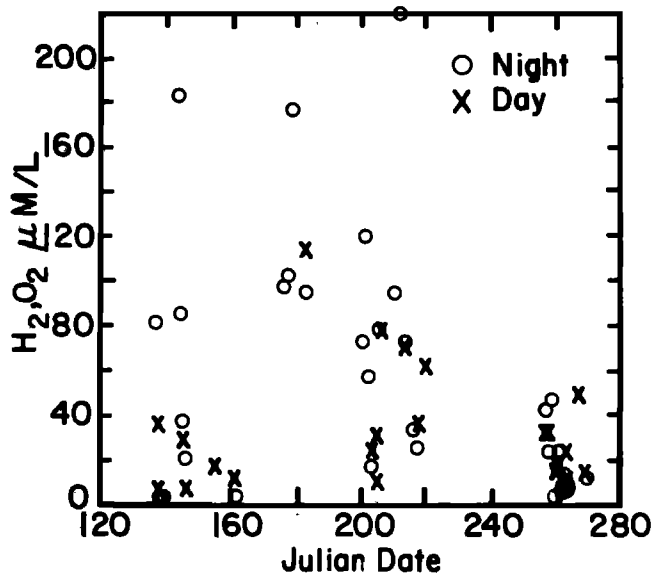

Figure 13. Daily averaged cloudwater hydrogen peroxide content for entire 1988 monitoring season at Mt. Mitchell, site 1. Daytime and nighttime averages are indicated. Most of the highest concentrations were observed at night.

The diurnal variation in hydrogen peroxide at Mt. Mitchell is different from the typical pattern reported for most other sites [Olszyna et al., 1988; Sakugawa and Kaplan, 1989]. [Olszyna et al. [1988] reported daytime values exceeding the nighttime values by 26%. In southern California [Sakugawa and Kaplan, 1989] a daytime maximum in hydrogen peroxide was generally noted in the early afternoon, corresponding to a minimum in the NO_x and a maximum in the O_3, approximately 1-3 hours 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 [B.G. Heikes, personal communication, 1991] and at Whitetop Mountain [J.F. Meagher, personal communication, 1990].

The nocturnal maxima in both ozone and hydrogen peroxide are thought to be predominantly due to meteorological, rather than chemical, phenomena. The deposition of hydrogen peroxide to vegetation surfaces is very high [Ennis et al, 1990] and contributes to the vertical gradient. The hydrogen peroxide concentration is known to increase with height in the planetary boundary layer [Heikes et al., 1987; Boatman et al., 1989]. The elevation of Mt. Gibbs is sufficiently high to place it above the boundary layer at night, after convective mixing has subsided and the mixed layer has collapsed. Therefore at night the lower troposphere is essentially decoupled from the sink provided by vegetation, so that the high nocturnal concentrations are representative of higher hydrogen peroxide levels present in the lower troposphere. The increase in dew point in the morning hours bears this out; generally, air aloft is drier than that at the surface (examples of this phenomenon are shown by Daum et al. [1990] and Heikes et al. [1987]) and as convective mixing brings up air from the surface layer, the dew point at the mountaintop should increase. The inverse relationship between nocturnal hydrogen peroxide and dew point temperature is consistent with this mechanism, which probably also accounts for the lack of a daytime maximum in ozone at some high-elevation sites [Aneja et al., 1991b]. Because of the higher deposition velocity of hydrogen peroxide compared to ozone the difference between daytime and nighttime values should be more pronounced in the hydrogen peroxide profile, which is what is observed at Mt. Mitchell.

It is interesting to note that the reversed diurnal pattern (nocturnal maximum) was not observed in the fall. Due to the frequent presence of clouds and the lower temperatures during the days during which hydrogen peroxide was sampled, this lack of a nocturnal maximum during September is probably related to the specific meteorological conditions during the observation period and is not a true indication of the seasonal behavior. Furthermore, the September data set is limited; therefore the diurnal behavior of hydrogen peroxide at Mt. Mitchell in the fall warrants further study.

SUMMARY AND CONCLUSIONS

Atmospheric gas-phase hydrogen peroxide concentrations at Mt. Mitchell (mean 0.63 ± 0.57 ppbv; range LOD to 4.2 ppbv) were comparable to, or higher than, those concentrations previously reported in the literature. Levels higher than those reported at this site have generally been found aloft. To our knowledge, cloud water concentrations at Whitetop Mountain, Virginia, were the only cloud water levels found to be higher than those at Mt. Mitchell. Considering the southern location of Mt. Mitchell, with its abundance of sunshine, relatively warm temperatures, low levels of NO_x and adequate levels of ozone, the high levels

reported at this site are consistent with our current understanding of the formation of atmospheric hydrogen peroxide.

Contrary to the typical diurnal variation observed at most monitoring sites, with midday maxima, gas-phase hydrogen peroxide at Mt. Mitchell exhibits a significant reversed diurnal variation in the summer but not necessarily in the fall. This nocturnal maximum is due to meteorological, rather than chemical, phenomena and may be related to the behavior of the mixed layer and its relationship to the elevation of the mountaintop.

At Mt. Mitchell, atmospheric hydrogen peroxide concentrations appear to be affected by radical formation from ozone, by the back trajectory of the air mass, by the presence of high-pressure systems, and by loss processes particularly related to deposition and reaction with sulfur dioxide. Additionally, meteorological phenomena leading to a nocturnal maximum during the summer also influence the hydrogen peroxide climatology at this site.

The hydrogen peroxide data collected at Mt. Mitchell during the 1988 field season are consistent with our expectation of a seasonal variation, with levels dropping in the late summer and fall, although admittedly this data set was limited in that the gas-phase data were not collected continuously and were only collected for one season. To definitively establish a seasonal variation in atmospheric hydrogen peroxide at Mt. Mitchell requires further investigation. Springtime levels also need further study, based on high cloud water levels observed in May and June. High levels of total hydroperoxide observed in June may be due to the presence of a synoptic high-pressure system that was over the region during the measuring period in June.

Cloud water hydrogen peroxide content was positively correlated to ozone and temperature, correlations which were also observed in the gas-phase data. There was also a positive correlation between cloud water hydrogen peroxide and ammonium ion content that was not expected. Both cloud water hydrogen peroxide and the ionic species concentrations can be affected by the liquid water content of the cloud; however, the mechanisms involved are very different. The observed negative correlation between cloud water hydrogen peroxide concentration and cloud liquid water content is consistent with scavenging and deposition of hydrogen peroxide by cloud droplets, whereas the relationship between ionic species and liquid water content is due at least in part to dilution effects.

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