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## MEASUREMENTS AND ANALYSIS OF CONCENTRATIONS OF GASEOUS HYDROGEN PEROXIDE AND RELATED SPECIES IN THE RURAL CENTRAL PIEDMONT REGION OF NORTH CAROLINA

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**Abstract** Ambient concentrations of gas-phase total peroxides and hydrogen peroxide were measured during mid-July to mid-August 1991, and during June and early July, 1992 at a rural site, SONIA, in the rural Central Piedmont region of North Carolina as a part of the Southern Oxidants Study. Simultaneous measurements were also made of trace gases and meteorological parameters. The measurements of hydrogen peroxide were made in order to explore the behaviour of this photochemical oxidant in rural southeast U.S., and to study its correlation with ozone and meteorology.  $\text{H}_2\text{O}_2$  showed a pronounced diurnal variation with peak concentrations during the afternoon (1200–1600 EST). The maximum  $\text{H}_2\text{O}_2$  concentrations observed were  $\sim 2.2$  ppbv during the 1991 intensive, and  $\sim 1.6$  ppbv during 1992. The mean daytime  $\text{H}_2\text{O}_2$  concentrations observed were  $0.64 \pm 0.56$  ppbv during 1991, and  $0.52 \pm 0.36$  ppbv during 1992, which were found to be significantly higher (at the 95% confidence level) than the nighttime averages ( $\sim 0.15$  ppbv).  $\text{HO}_2$  radical concentration of  $\sim 14$  ppbv was determined from calculated  $\text{H}_2\text{O}_2$  production rates. On occasion high levels of nighttime  $\text{H}_2\text{O}_2$  was observed which was found to be associated with the breakdown in the stability of the nocturnal boundary layer. A 48 h back trajectory analysis performed on the air masses arriving at Site SONIA indicated that significant amounts of pollutants could be transported to this rural site from the surrounding urban areas and this could affect the  $\text{H}_2\text{O}_2$  levels at this site. An observational based statistical analysis was performed. The results of correlation matrices show that  $\text{H}_2\text{O}_2$  is most strongly correlated to ozone, temperature, solar radiation, and relative humidity. A multiple linear regression was carried out by regressing  $\text{H}_2\text{O}_2$  on all the measured physicochemical variables. The  $R^2$  was found to be 0.81 for the 1991 data and 0.71 for 1992. A simple linear regression between  $\text{H}_2\text{O}_2$  and ozone gave  $R^2$  of 0.60 and 0.39 for 1991 and 1992, respectively, when data from the entire period of measurement was included.

*Key word index:* Hydrogen peroxide, ozone, photochemistry, rural.

### INTRODUCTION

Hydrogen peroxide is considered to be an important oxidant for its role in the free radical balance of the atmosphere (Finlayson-Pitts and Pitts, 1986), and for the conversion of atmospheric  $\text{SO}_2$  in cloud water when the pH is 4.5 or lower (Penkett *et al.*, 1979; Martin and Damschen, 1981). In the eastern United States, the reported pH values for cloud and rainwater are generally below 4.5 (Lazrus *et al.*, 1983; Daum *et al.*, 1984; Kelly *et al.*, 1985; Aneja *et al.*, 1992; Li and Aneja, 1992; Kim and Aneja, 1992). Thus within this region, it is quite probable that the amount of atmospheric  $\text{H}_2\text{O}_2$  available largely controls the oxidation of  $\text{SO}_2$  during the summer months (NAPAP - SOS&T, 1991).

Atmospheric hydrogen peroxide and organic peroxides are believed to be products of photochemical processes in the atmosphere. The formation of these

secondary pollutants in air are generally thought to be due to recombination of peroxy radicals which have been produced by reactions during the photolysis of ozone and as oxidation products of hydrocarbons (Logan *et al.*, 1981; Calvert and Stockwell, 1983; Kleinman, 1986). However, recent studies (Becker *et al.*, 1990; Hewitt and Kok, 1991; Simonaitis *et al.*, 1991) have shown that  $\text{H}_2\text{O}_2$  can also be formed from the ozonolysis of alkenes in the presence of water vapour, via a reaction not involving  $\text{HO}_2$  radicals. The possibility of other sources of  $\text{H}_2\text{O}_2$  may also exist, i.e. Basevich *et al.* (1987) have reported of  $\text{H}_2\text{O}_2$  observations made during the incomplete combustion of natural gases.

Many measurements of atmospheric concentrations of hydrogen and organic peroxides have been made during the past decade. However, due to interference from ozone,  $\text{SO}_2$  and transition metals, data on ambient peroxide concentrations are not entirely reliable. (Heikes *et al.*, 1982; Zika and Saltzman, 1982). New monitoring techniques such as fluorescent,

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chemiluminescent and spectroscopic techniques have been developed (Lazrus *et al.*, 1986; Klockow and Jacob, 1986; Slemr *et al.*, 1986; Lee *et al.*, 1990). This has enabled aircraft measurements as well as measurements at ground level to be made (Olszyna *et al.*, 1988; Dollard *et al.*, 1989; Sakugawa and Kaplan, 1989; Boatman *et al.*, 1990; Daum *et al.*, 1990; Meaghar *et al.*, 1990; Van Valin *et al.*, 1990; Claiborn and Aneja, 1991; Gallagher *et al.*, 1991; Tremmel *et al.*, 1993) though reliable data are still hard to obtain (Lee *et al.*, 1993). Studies have revealed a high variability of  $\text{H}_2\text{O}_2$  mixing ratios with a pronounced dependence on the season, latitude, altitude, and water vapour content.

Photochemical models suggest that  $\text{H}_2\text{O}_2$  should be present in both the polluted and clean air (Logan *et al.*, 1981; Calvert and Stockwell 1983; Kleinman, 1986) and the production of  $\text{H}_2\text{O}_2$  in the gas phase is a function of light intensity and the ambient concentrations of nonmethane hydrocarbons, aldehydes,  $\text{CO}$ ,  $\text{NO}_x$  and  $\text{O}_3$ . These have also been verified in various field studies conducted over the continental U.S. and Central Europe, and a correlation has been found between the presence of peroxides (hydrogen and organic), photoactivity (seasonal variations, spatial and temporal variations) and photochemical smog ( $\text{O}_3$ ,  $\text{NO}_x$ ) (Daum *et al.*, 1987; Heikes *et al.*, 1987; Kok *et al.*, 1990; Olszyna *et al.*, 1988; Sakugawa and Kaplan, 1989). Significant atmospheric levels of  $\text{H}_2\text{O}_2$  might thus be expected in the rural southeastern regions of the United States, where there is an abundance of warm temperatures, sunshine and natural hydrocarbon sources and low levels of atmospheric  $\text{NO}_x$  (Kim *et al.*, 1994). In this study the behaviour and trends in gaseous hydrogen peroxide concentrations is examined at a rural location (Southern Oxidant Study Site SONIA) in the southeast United States.

#### SITE DESCRIPTION AND METHODOLOGY

The measurement site is located in the central Piedmont region of North Carolina near the town of Candor (35.26° N, 79.84° W, ~170 m m.s.l.). The site is a Southern Oxidants Study - Southeastern Regional Oxidant Network, SOS-SERON enhanced chemistry site, Site SONIA. The site is collocated to a National Dry Deposition Network (NDDN) site and is classified as rural under the NDDN site classification scheme. At site SONIA, an intensive air quality field campaign was undertaken from 15 July to 13 August 1991, and from 6 June 1992 to 7 July 1992. Measurements of gas-phase hydrogen peroxide and total peroxides were made along with the measurements of other trace gases, PAN,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{SO}_2$ ,  $\text{CO}$ ,  $\text{HNO}_3$ , carbonyls and speciated NMHCs. Meteorological data and data on ozone concentrations from the adjacent NDDN site were used for the analysis. A map of the site and the surrounding region is given in Fig. 1.

The sampling site is in an open field (area ~1200 m<sup>2</sup>) which is surrounded by mixed deciduous and coniferous forest. The site is located on the eastern border of the Uwharrie National Forest. Four large urban areas of North Carolina are within a 100 mile radius of the sampling site. Three of the four sources of anthropogenic pollution, Raleigh-Durham, Greensboro, I-40 and I-85, are situated to the north and northeast of the site, while Charlotte is due west of the site. Thus the site may be impacted by polluted air masses when the prevailing winds are out of the west, north or northeast of the site and have crossed over these urban areas. Another possible source may also be from Columbia, South Carolina, located to the southwest of the site; however, it is outside the 100 mile radius.

Ambient, gas-phase hydrogen peroxide was measured, at 10 m above ground, using a continuous fluorometric analyzer based on the horseradish peroxidase method (Lazrus *et al.*, 1986). The level of detection of the instrument based upon the noise of the zero signal ( $3\sigma$ ) is estimated to be ~0.06 ppbv. The hydrogen peroxide analyzer was multi-point calibrated once daily against aqueous-phase standards which were also made up daily by serial dilutions of 3%  $\text{H}_2\text{O}_2$  solution. The hydrogen peroxide stock solution was checked weekly by titration against  $\text{KMnO}_4$  solutions, which in turn were titrated against a standard  $\text{Na}_2\text{C}_2\text{O}_4$  solution.

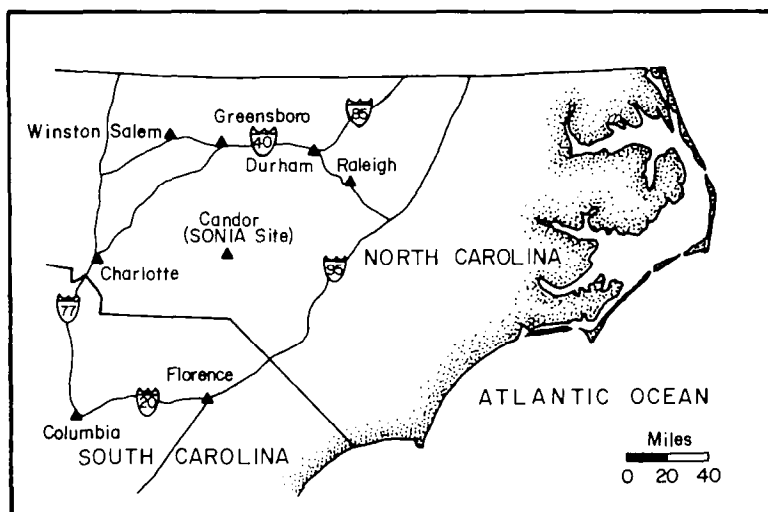


Fig. 1. Map of sampling site SONIA near Candor, North Carolina.

The uncertainty of these calibrations (at the 95% confidence interval) when all calibrations were considered was about  $\pm 10\%$  at the 1 ppbv level.

The dual-channel fluorometric analyzer measures total peroxides on one channel ( $S_p$ , following the nomenclature provided by Claiborn and Aneja, 1991), and by specific enzymatic destruction of H<sub>2</sub>O<sub>2</sub> by catalase, organic peroxides and some residual hydrogen peroxide on the second channel ( $S_c$ ). The hydrogen peroxide concentration is calculated from the residual fraction of hydrogen peroxide after reaction with catalase ( $x_0$ ) and the ratio of the pseudo-first-order reaction rate constant,  $k_i/k_0$  ( $K$ ) as follows

$$[\text{H}_2\text{O}_2] = \frac{x_0 S_p - S_c}{x_0 - x_0}$$

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  $k_0$  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 second channel, after the catalase enzyme is added, and is calculated as the ratio of H<sub>2</sub>O<sub>2</sub> detected after, to H<sub>2</sub>O<sub>2</sub> detected before, catalase addition. This fraction varied from batch to batch and ranged from 0.2 to 0.3. As recommended by Claiborn and Aneja (1991), a value of 1:14 was assumed for  $k_i$ . This value is applied with an uncertainty of  $\pm 15\%$  at  $x_0 = 0.2$  and  $S_c/S_p = 0.6$ . The gas-phase total and hydrogen peroxide data were recorded on a chart recorder and extracted manually as 12 min averages.

Ambient air was drawn from a height of 10 m through a 3 in ID glass sampling tower by an 1100 cfm pump in order to limit sample residence time ( $< 0.1$  s). A 16 port glass manifold was installed at the base of the glass sampling tower above the pump to permit sampling access. An  $\sim 3$  m length and 1/4 in OD Teflon tubing connected to one of the ports, served as the sampling line to the analyzer. The residence time of ambient air in the entire sampling manifold was  $< 0.25$  s, and the manifold was heated above the ambient temperature to prevent any moisture condensation.

#### METEOROLOGY AT THE SITE

During the measurement period at site SONIA, Candor, the afternoon temperatures were moderately warm ( $\sim 28$  C) and relatively cooler temperatures were observed during the night ( $\sim 22$  C). The average temperature was found to be higher during the 1991 intensive ( $24.16 \text{ C} \pm 3.24$ ) than during the 1992 intensive ( $22.42 \text{ C} \pm 3.87$ ). Relatively low wind speeds averaging about  $1.5 \text{ m s}^{-1}$  were observed during both

intensives. A strong inversion was observed during most nights and the relative humidity approached 95% on most days during the early morning hours before sunrise. Fog was also observed during most mornings and it lifted only after about 0800 EST. The occurrence of afternoon late afternoon thunder showers was also often observed. Forty-eight hour back trajectory analysis for air masses arriving at site SONIA show that during the 1991 summer intensive, the air masses were found to originate predominantly from the Tennessee, northern Alabama and northern Georgia areas during westerly to southwesterly flow; and from the Ohio River Valley during northerly to northwesterly flow. Easterly flow brought in clean air mass originating over the Atlantic Ocean. During the 1992 intensive, northerly, southerly and easterly flow was observed. During the intensives, the passage of low pressure troughs occurred about once a week. During these passages of the trough, prevailing winds gradually shifted from easterly to southerly as the trough approached the site and then backed to the northern direction and increased the wind speed intensity as the trough passed over the site. Of particular interest was the development of a persistent high pressure ridge during the 1991 intensive that remained over the area resulting in a stagnant air mass. Highest ozone as well as H<sub>2</sub>O<sub>2</sub> concentrations were observed during this period which is described in a later section.

#### RESULTS AND DISCUSSION

A statistical summary of the gas-phase hydrogen peroxide concentrations measured during the two summer intensives of 1991 and 1992 is given in Table 1. The results agree well with measured gas-phase H<sub>2</sub>O<sub>2</sub> concentrations at other rural sites. The mean gas-phase concentration of hydrogen peroxide measured during the daytime (1000–2000 EST) is found to be significantly higher than the nighttime concentration (Student's *t*-test at the 95% confidence level) for both years. The daytime mean as well as the mean for the entire period of measurement during 1991 is slightly higher than the observed means for 1992. But the corresponding median values are similar. The mean gas-phase concentration of hydrogen peroxide measured during the daytime of summer 1991

Table 1. Summary of ambient gas-phase levels at Candor for 1991 and 1992. Daytime period is from 1000–2000 EST

Period	N	Mean	SD	Median	Max	Min
1991	296	0.41	0.51	0.21	2.19	< LOD*
Days	156	0.64	0.56	0.42	2.19	< LOD
Nights	140	0.16	0.18	0.10	0.94	< LOD
1992	303	0.35	0.36	0.23	1.60	< LOD
Days	164	0.52	0.36	0.43	1.60	< LOD
Nights	139	0.15	0.22	0.10	1.05	< LOD

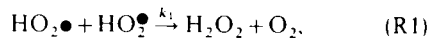
\* LOD = Level of detection ( $\sim 0.05$  ppbv).

( $0.64 \pm 0.56$  ppbv) is higher than that measured during the daytime of 1992 summer intensive ( $0.52 \pm 0.36$  ppbv) but mean  $O_3$  concentration during 1992 ( $44.1 \pm 16.2$  ppbv) was observed to be higher than that in 1991 ( $34.8 \pm 17.6$  ppbv).

The composite diurnal profiles of both  $H_2O_2$  and ozone is given in Fig. 2. The smooth rise during the morning to the afternoon is in accordance with expected photochemical production. It is also interesting to note that both share the same diurnal trend. This has been known for some time and is probably an indication of the closely related photochemical production and by depositional removal of both species. When the daily average hydrogen peroxide is plotted against the daily average ozone for the 1991 season, the  $R^2$  value turned out to be 0.79 indicating that in general the conditions favouring the formation of ozone favours the formation of  $H_2O_2$  too.

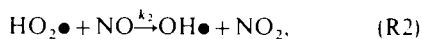
Another point of interest is that unlike the diurnal trend observed in the urban environments (Das and Aneja, 1993), where the  $H_2O_2$  maxima is observed

2–3 h after the peak in ozone concentration, in the rural environment peak concentrations for both  $H_2O_2$  and ozone are reached about the same time. This can be explained based on the  $HO_2$  chemistry in the high low  $NO_x$  areas.  $H_2O_2$  is mainly formed by the recombination of hydroperoxyl radicals



$$k_1 = 5.6 \times 10^{-12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

and this reaction is most sensitive to  $NO$  concentration as  $NO$  competes for the  $HO_2$  radicals by reacting with it (Kleinman, 1986).



$$k_2 = 8.3 \times 10^{-12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}.$$

Thus at higher  $NO_x$  concentrations, reaction R2 dominates. The recombination reaction of hydroperoxyl radicals, i.e. R1, begins to take place only when

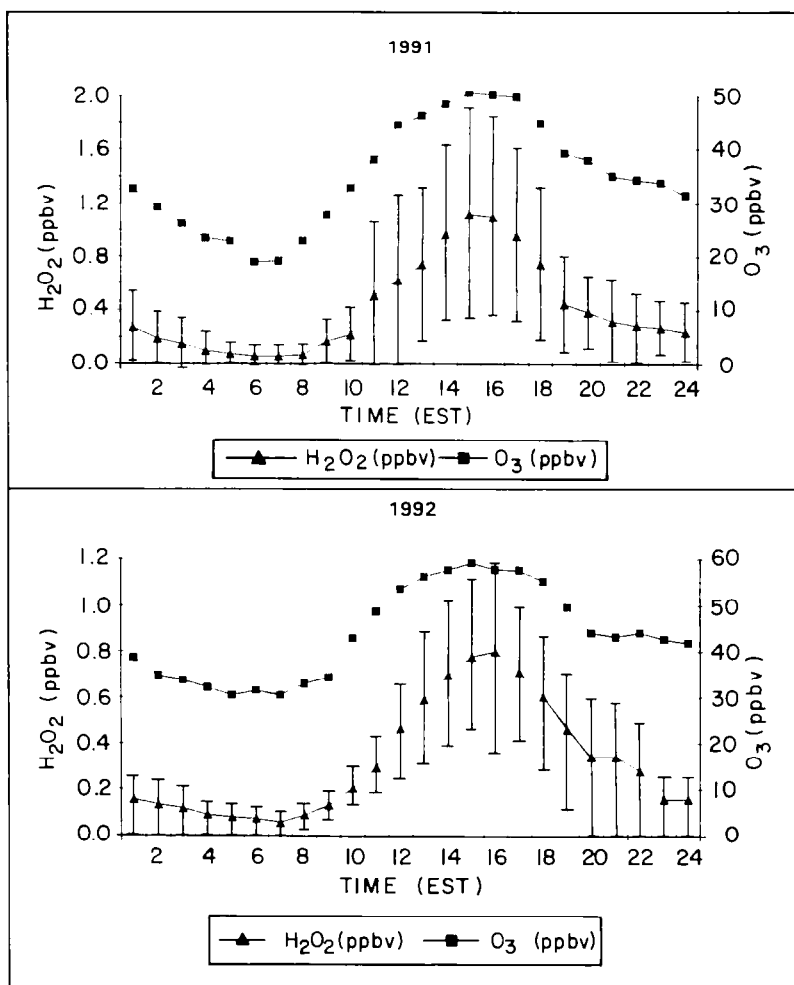


Fig. 2. Composite diurnal profiles of  $H_2O_2$  and ozone. The square triangles are the average values and the bars denote one standard deviation.

the NO<sub>x</sub> concentrations are low and hence a time lag between the formation of H<sub>2</sub>O<sub>2</sub> and ozone is observed in urban areas. Reaction R1 becomes important only under low NO<sub>x</sub> concentrations. The average NO concentration during the day was found to be 0.24 ± 0.13 ppbv at SONIA site indicating a low NO<sub>x</sub> regime and hence the maxima in both ozone and H<sub>2</sub>O<sub>2</sub> were observed at the same time.

Though the maxima and minima are collocated in time, there is a considerable amount of background ozone surviving the night whereas H<sub>2</sub>O<sub>2</sub> levels drop to below the detection limits (<0.05 ppbv). Also the fall in the H<sub>2</sub>O<sub>2</sub> concentrations is more rapid and takes place earlier when compared to ozone. Low H<sub>2</sub>O<sub>2</sub> levels during the nighttime have been observed in the past by many researchers and cannot be ac-

counted for by just surface losses due to dry deposition. One explanation put forward by Hastie *et al.* (1993), is that during the nighttime, aqueous aerosols, formed as a result of water condensing on atmospheric particles at the onset of nocturnal inversion, efficiently scavenge the highly soluble H<sub>2</sub>O<sub>2</sub>. We found a strong anticorrelation between H<sub>2</sub>O<sub>2</sub> concentrations and the relative humidity ( $r = -0.83$  and  $-0.77$  during 1991 and 1992 intensive, respectively) and the composite diurnal profile is given in Fig. 3. From an examination of Fig. 3, it is clear that H<sub>2</sub>O<sub>2</sub> begins to rise only after the relative humidity has fallen significantly low ~70–65% and the rapid fall is also coincident with increasing relative humidity. This apparent higher sensitivity of H<sub>2</sub>O<sub>2</sub> to relative humidity is explained by its higher water solubility. This

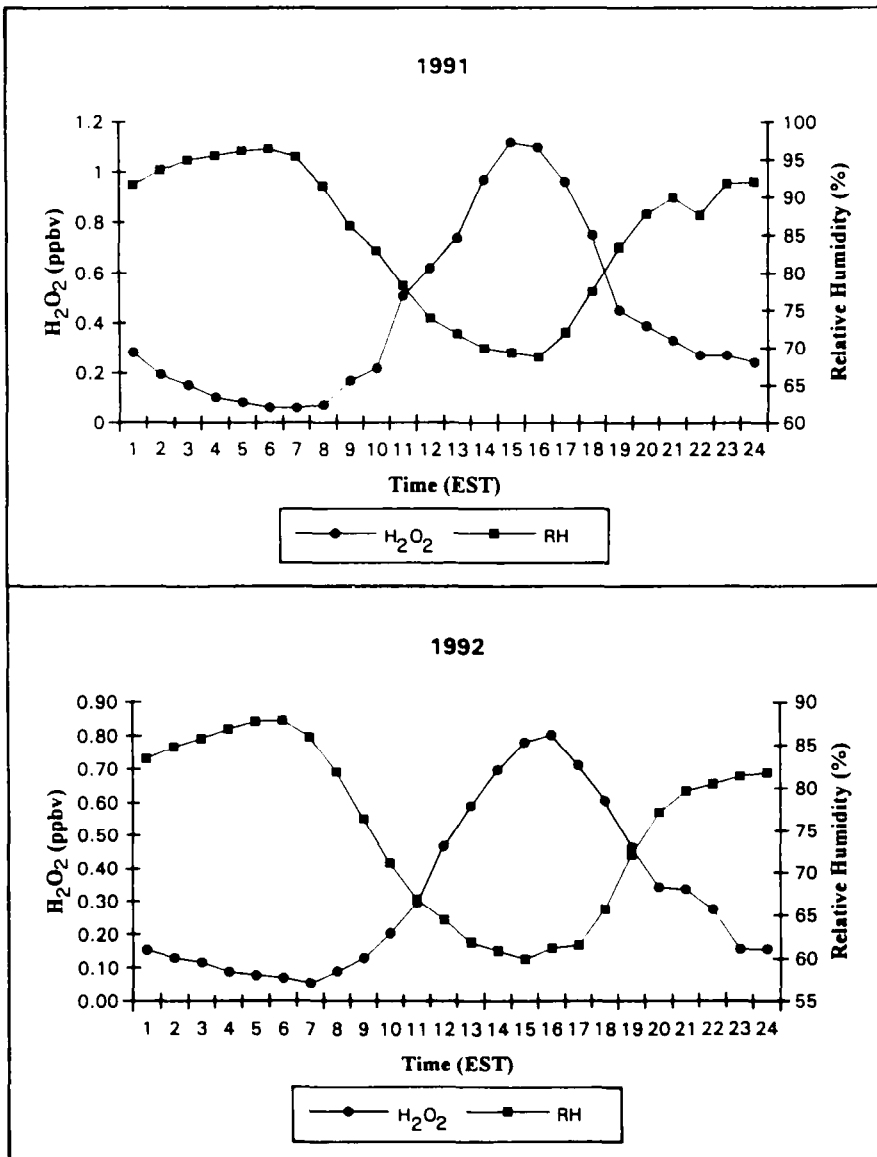


Fig. 3. Composite diurnal variation of H<sub>2</sub>O<sub>2</sub> concentrations and relative humidity.

points to the fact that after sunset, due to the radiative cooling of the Earth's surface, the increased relative humidity effectively scavenges the gas-phase  $\text{H}_2\text{O}_2$  trapped in the shallow nocturnal boundary layer. Thus the concentration of gaseous  $\text{H}_2\text{O}_2$  trapped within the inversion is lost by dry as well as wet deposition and the concentration of  $\text{H}_2\text{O}_2$  measured at the ground level falls without replenishment from above.

Occasionally, however, a secondary nighttime peak in  $\text{H}_2\text{O}_2$  accompanied by a secondary peak in ozone was observed. One such episode that occurred during the midnight between 5 and 6 August 1991 is examined here (Fig. 4). A secondary peak was observed which occurred just after midnight of the 5th. This nighttime peak could be the result of (1) nighttime production of  $\text{H}_2\text{O}_2$  or (2) breakdown in stability of the nocturnal boundary layer.

The possibility of nighttime production of peroxy radicals in highly polluted air has been suggested (Cantrell *et al.*, 1986; Carter, 1990). But even in remote forested and rural areas affected by urban emissions, nighttime sources of peroxy radicals (Platt *et al.*, 1990) and peroxides (Becker *et al.*, 1990; Simonaitis *et al.*, 1991) have been discussed recently. This involves reaction of ozone with naturally occurring alkenes and terpenes to yield  $\text{H}_2\text{O}_2$  via a route that does not involve photolytic production of  $\text{HO}_2$  radicals. Skov *et al.* (1992) on the basis of experimental evidence have shown that isoprene can react rapidly with nighttime  $\text{NO}_3$  radical to yield a number of oxidation products, the main product being an alkoxy radical which may further react with oxygen to form an unsaturated carbonyl nitrate compound and  $\text{HO}_2$ . The  $\text{HO}_2$  radical can then undergo self-reaction to form  $\text{H}_2\text{O}_2$ . Preliminary results of speciated hydrocarbon measurements at Candor (1992 SOS-SERON database) show isoprene to be one of the major constituents of

total nonmethane hydrocarbons. Thus this could be a possible source of nighttime  $\text{H}_2\text{O}_2$  concentration.

From an examination of the  $\text{H}_2\text{O}_2$  profile together with meteorology (Fig. 5), an unstable nocturnal boundary layer appears to be the most probable cause for the observed secondary peak for  $\text{H}_2\text{O}_2$  and ozone. From about 1700–2200 h EST there is a rapid decline in the  $\text{H}_2\text{O}_2$  concentration accompanied by falling temperatures and reduction in wind speed, is a typical scenario observed during the evening periods at this rural site. Thus during this period, peroxide concentration declines due to deposition at the surface and lack of replenishment from above. This continued until  $\sim 2200$  h when sudden increase in the wind speed induced downward mixing of more peroxides from aloft, i.e. free troposphere, causing the concentration of  $\text{H}_2\text{O}_2$  to rise. There is also evidence of a small increase in temperature during this time. It is also interesting to note that ozone concentration was restored to values typical of the previous day but  $\text{H}_2\text{O}_2$  concentrations failed to reach the values observed the previous day. This is probably because the rise in temperature was very small, not enough to bring down the relative humidity and the gaseous  $\text{H}_2\text{O}_2$  being mixed down was still being scavenged by the aqueous aerosols present in the air.

A period of high photochemical activity which occurred during the measurement period of 1991 (3–6 August) is examined here. During this period the skies were clear and the temperatures were higher ( $\sim 32^\circ\text{C}$ ) than the observed mean daytime temperature ( $\sim 27^\circ\text{C}$ ) for the measurement period. Both  $\text{H}_2\text{O}_2$  and ozone reached peak concentrations during this period. Ozone reached its peak concentration (78 ppbv) on 3 August and remained high the next day as well; whereas  $\text{H}_2\text{O}_2$  reached its peak concentration (2.2 ppbv) the next day, i.e. on 4 August (Fig. 5). Figure 6 shows 48 h back trajectories for air mass

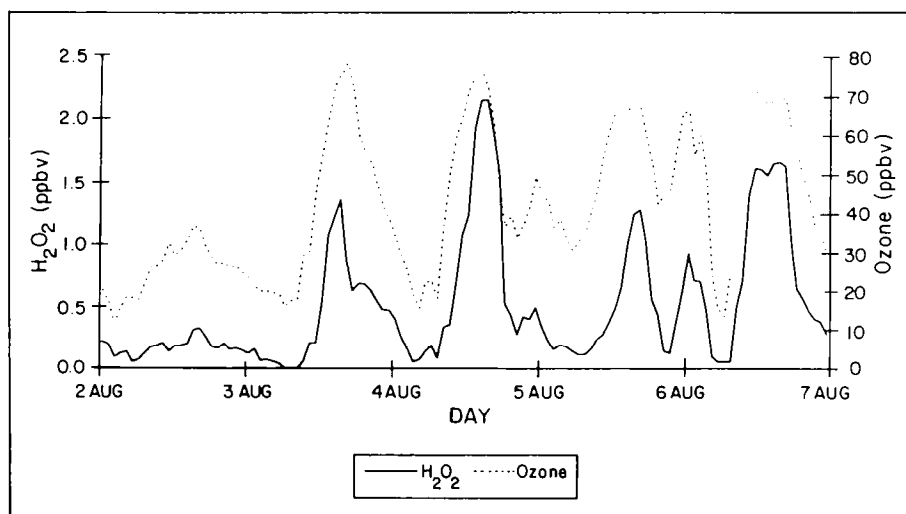


Fig. 4.  $\text{H}_2\text{O}_2$  and ozone concentrations from 2 to 6 August 1991 at Site SONIA.

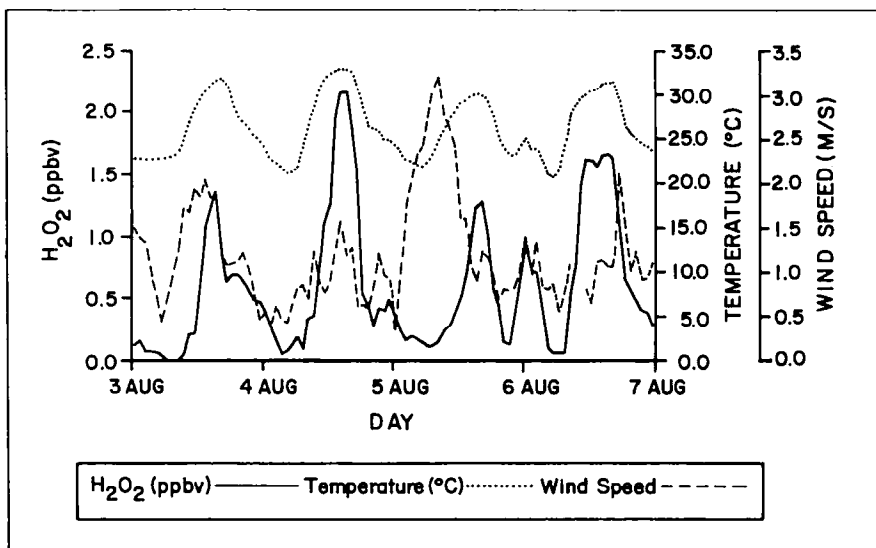


Fig. 5. H<sub>2</sub>O<sub>2</sub>, wind speeds and temperature from 3 to 6 August 1991 at Site SONIA.

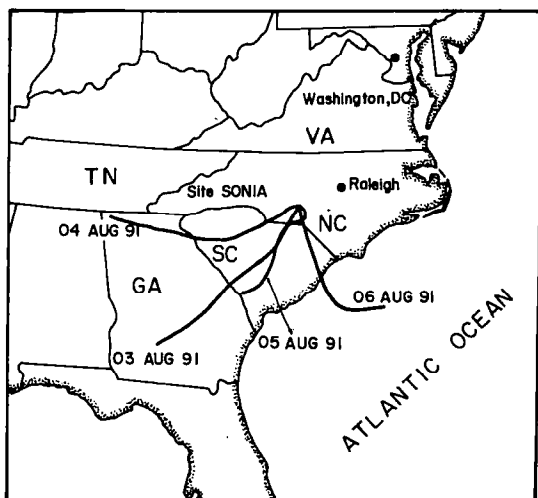


Fig. 6. 48 h back trajectory of air masses at Site SONIA in Candor, at 0700 EST from 3 to 6 August 1991.

arriving at the measurement site on 3–6 August at 0700 EST. The air arriving at the site on 3–5 August was continental in origin whereas the air arriving on the 6 August was marine in origin. It is speculated that as the air mass traveled to the site, it picked up pollutants over urban Columbia, SC, and this led to peak ozone production on 3 August; but H<sub>2</sub>O<sub>2</sub> did not peak on this day as the high levels of NO<sub>x</sub> from this urban air mass in the air would have inhibited the self-reaction of HO<sub>2</sub> radicals to form H<sub>2</sub>O<sub>2</sub>. The next day high ozone as well as peak H<sub>2</sub>O<sub>2</sub> concentrations were observed. The similarity in the peak shapes of both species leads to the conjecture that rather than the oxidants themselves being transported, it is more

likely that the precursors to the pollutants were transported and the clear skies, high temperatures and lots of sunshine led to peak production of these pollutants. On 5 August, the air mass arriving at the site was still continental in origin but lower levels of both H<sub>2</sub>O<sub>2</sub> as well as ozone concentrations were observed on this day. An examination of surface weather maps during this period showed the development of a high-pressure ridge which crossed site SONIA during the early hours of 5 August. This caused a sudden shift in the wind direction and high wind speeds and it was observed that this helped in the dispersal of the air mass containing the pollutants. Also a dense fog was observed to linger till about 0900 EST. Hence a drop in both ozone and H<sub>2</sub>O<sub>2</sub> concentrations were observed. However, on 6 August, the air mass originated over the Atlantic Ocean and yet considerable levels of both species were observed though the concentrations were lower than those observed on 4 August. A look at the meteorological conditions on this day suggests that it was a hot day with clear skies leading to enhanced biogenic precursor emissions (Kim *et al.*, 1994; Lamb *et al.*, 1987).

From the distribution of hydrogen peroxide and total peroxides for the measurement period, it is found that organic peroxides constitute ~10–20% of the total peroxide concentrations. H<sub>2</sub>O<sub>2</sub> was also found to be the major constituent of total peroxides at Raleigh during 1991. It is found that the concentrations of both hydrogen as well as organic peroxides are higher at the rural site than at the urban site in Raleigh. Higher H<sub>2</sub>O<sub>2</sub> concentrations observed at this rural site may be explained by the following two processes in a rural atmosphere. (1) Lower NO<sub>x</sub> and SO<sub>2</sub> concentration favor higher concentrations of the H<sub>2</sub>O<sub>2</sub> because these two species in air promote the removal or scavenging of H<sub>2</sub>O<sub>2</sub> from the ambient air

(Kleinman, 1986; Sakugawa and Kaplan, 1989) (2) Biogenic emissions of hydrocarbons from trees, may lead to H<sub>2</sub>O<sub>2</sub> production by reacting with O<sub>3</sub> and NO<sub>3</sub> radicals (Becker *et al.*, 1990; Platt *et al.*, 1990).

Significant amounts of naturally emitted hydrocarbons have been reported in rural and forested areas, isoprene being the dominant nonmethane hydrocarbon species in rural southeastern U.S. (Trainer *et al.*, 1987a, b; Rasmussen and Khalil, 1988; Montzka *et al.*, 1993). Production of HO<sub>2</sub> radicals via the photooxidation of isoprene by its reaction with OH radicals has been studied in detail by Atkinson *et al.* (1989) and Tuazon and Atkinson (1990). The production of HO<sub>2</sub> radicals may also occur via alkene oxidation initiated by ozone (Atkinson and Lloyd, 1984; Calvert and Madronich, 1987). Alkenes have been reported to constitute about 17% of the total hydrocarbons in rural atmospheres (Duce *et al.*, 1983). Not only are there abundant sources of HO<sub>2</sub> radicals present in the rural southeastern U.S. but also the NO<sub>x</sub> levels are low during the day time, allowing the self-combination reaction of peroxy radicals to proceed. The relatively higher concentrations of H<sub>2</sub>O<sub>2</sub> than organic peroxides can be explained by the laboratory studies by Madronich and Calvert (1990). They found that for low NO<sub>x</sub> conditions, production of peroxy radicals are suppressed and higher HO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> concentration is observed.

The peroxy radical (RO<sub>2</sub>) concentration can be estimated by assuming that peroxy radicals are the only oxidants besides ozone that convert NO to NO<sub>2</sub> in the reaction sequence describing the photostationary state of ozone formation (Kelly *et al.*, 1980; Parrish *et al.*, 1986; Trainer *et al.*, 1991). This assumption leads to the following relationship for RO<sub>2</sub>:

$$[\text{RO}_2] = \frac{J[\text{NO}_2]}{k_3[\text{NO}]} \frac{k_2[\text{O}_3]}{k_3} \quad (\text{R3})$$

The average RO<sub>2</sub> concentration has been calculated to be ~30 pptv using R3 at Site SONIA (Kim *et al.*, 1993). However, the estimation of HO<sub>2</sub> radical concentration is more difficult. But assuming that HO<sub>2</sub> accounts for about 30% of the peroxy radical concentrations (Trainer *et al.*, 1991), the average HO<sub>2</sub> radical concentration is then ~10 pptv. Trainer *et al.* (1991) have found that when the isoprene is the major constituent of total nonmethane hydrocarbons, then this is approximately true. The measurements of H<sub>2</sub>O<sub>2</sub> concentrations may also be utilized to obtain observational estimates of the free radical HO<sub>2</sub> precursor concentrations. The rate of formation of H<sub>2</sub>O<sub>2</sub> based on (R1) may be represented by

$$\frac{d[\text{H}_2\text{O}_2]}{dt} = k_1[\text{HO}_2]^2$$

where  $k_1$  is the apparent second order rate coefficient. The  $[\text{HO}_2]^2$  term may be evaluated from the observed rate of formation of H<sub>2</sub>O<sub>2</sub>. An average HO<sub>2</sub> concentrations of  $14.3 \pm 5.6$  pptv was obtained from

the H<sub>2</sub>O<sub>2</sub> production rates calculated on certain days assuming 50% relative humidity. This value is similar to the previously estimated HO<sub>2</sub> concentrations.

The role of various physicochemical variables were examined in order to determine their relationship to the concentration of H<sub>2</sub>O<sub>2</sub> for the entire period of measurement during the summer intensives of both 1991 and 1992. Table 2 contains the correlation coefficient values ( $r$ 's) between H<sub>2</sub>O<sub>2</sub> and the various measured physicochemical variables obtained from correlation matrices for both the years. The data set contained just the daytime (1000–2000 EST) values to eliminate the influence of the nocturnal boundary layer on H<sub>2</sub>O<sub>2</sub> concentrations, since the formation of a shallow nocturnal inversion layer reduces gas-phase H<sub>2</sub>O<sub>2</sub> concentration. From an examination of the table several correlations are observed. It is found that during both intensives H<sub>2</sub>O<sub>2</sub> was most strongly correlated to ozone, solar radiation, temperature and relative humidity indicating that H<sub>2</sub>O<sub>2</sub> levels were strongly affected by photochemical activity. It was also found that among all the environmental parameters, H<sub>2</sub>O<sub>2</sub> was most strongly negatively correlated to relative humidity an explanation to which has already been provided. It was also found to have a strong correlation to solar radiation and temperature ( $r=0.50$  and  $0.48$  and  $r=0.64$  and  $0.60$ , respectively, for 1991 and 1992). This is consistent with modeling studies (Kleinman, 1986). High solar radiation and temperature levels result in intense photochemical reactions of chemical species resulting in the formation of free radicals including HO<sub>2</sub> and given the abundance of isoprene at this rural site (1992 SOS-SERON Database) higher temperatures would lead to increased emission of isoprene resulting in higher peroxy radical concentration. H<sub>2</sub>O<sub>2</sub> was found to be strongly correlated to ozone ( $r=0.78$  and  $0.63$ , respectively, for 1991 and 1992). This is probably an

Table 2. Correlation of H<sub>2</sub>O<sub>2</sub> with some of the measured air quality variables for 1991 and 1992 data. The  $r$ 's are the Pearson's correlation coefficient obtained from a cross-correlation matrix containing all the measured air quality variables

Variable	SOS-SERON Site SONIA	
	(1991) $r$	(1992) $r$
Ozone	0.78* (+)	0.63* (+)
NO <sub>y</sub>	0.04	0.07
HONO	0.31* (+)	—
HCHO	0.07	—
CO	—	0.03
SO <sub>2</sub>	0.39* (+)	0.22 (+)
Temperature (°)	0.64 (+)	0.60* (+)
Rel. humidity (%)	-0.77* (-)	0.75* (-)
Sol. rad. (W m <sup>-2</sup> )	0.50* (+)	0.48* (+)

\* Significant values.

The sign inside the parentheses indicates positive or negative correlations with H<sub>2</sub>O<sub>2</sub>.



Table 3. Regression analysis of hourly average, daytime and daily maximum ozone and H<sub>2</sub>O<sub>2</sub> for Candor data (1991 and 1992)

	Hourly average	Daytime	Daily maximum
	(1991)		
Regression equation	O <sub>3</sub> = 25.3 + 26.8H <sub>2</sub> O <sub>2</sub>	O <sub>3</sub> = 32.8 + 19.1H <sub>2</sub> O <sub>2</sub>	O <sub>3</sub> = 29.2 + 20.6H <sub>2</sub> O <sub>2</sub>
R <sup>2</sup>	0.60	0.57	0.69
n	293	107	13
	(1992)		
Regression equation	O <sub>3</sub> = 34.1 + 29.2H <sub>2</sub> O <sub>2</sub>	O <sub>3</sub> = 43.7 + 18.3H <sub>2</sub> O <sub>2</sub>	O <sub>3</sub> = 42.1 + 21.4H <sub>2</sub> O <sub>2</sub>
R <sup>2</sup>	0.39	0.35	0.48
n	301	120	8

indication of the photochemical production of these two species. No significant correlation between H<sub>2</sub>O<sub>2</sub> and other primary pollutant species like NO<sub>x</sub> and CO were found. However, during both measurement periods, a surprising positive correlation between H<sub>2</sub>O<sub>2</sub> and SO<sub>2</sub> was observed ( $r=0.39$  and  $r=0.22$  for 1991 and 1992, respectively). A positive correlation between ozone and SO<sub>2</sub> was also found ( $r=0.56$  and  $r=0.34$  for 1991 and 1992, respectively). This suggests the role of long-range transport of pollutants to this rural site as there are no significant sources of SO<sub>2</sub> at this rural site.

An analysis of day time (1000–2000 EST) H<sub>2</sub>O<sub>2</sub> and ozone hourly average concentrations and also of daily maximum data were made. The results are summarized in Table 3. The ratio of O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> obtained from the slope is examined. For the hourly average data a ratio of 26.8 ppbv ozone to 1 ppbv H<sub>2</sub>O<sub>2</sub> is derived for 1991 and a O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> ratio of 29.2 for 1992. This compares well with 26 ppbv ozone to 1 ppbv H<sub>2</sub>O<sub>2</sub> obtained by Dollard *et al.* (1989) in rural southern England. For summer daytime H<sub>2</sub>O<sub>2</sub> hourly average concentration they gave an O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> ratio of about 30. Comparisons of data of this type may be complicated by the contribution of the ozone background which can introduce a variable and sometimes substantial offset depending upon season and time of day (Dollard *et al.*, 1991). Finally, from the regression analysis of daily maximum H<sub>2</sub>O<sub>2</sub> as well as ozone it is found that the R<sup>2</sup> value is increased when compared to the hourly average and daytime data. This indicates that the formation of H<sub>2</sub>O<sub>2</sub> is favored by increasing ozone in this rural area and the conditions favoring the formation of ozone also favor the formation of H<sub>2</sub>O<sub>2</sub>.

The results of a multiple regression analysis of H<sub>2</sub>O<sub>2</sub> on all the measured physicochemical variables for both the 1991 and 1992 data shows a R<sup>2</sup> of 0.81 for the 1991 data and 0.71 for the 1992 data. Thus all the measured physicochemical variables are able to explain a large percentage of the variability observed in the H<sub>2</sub>O<sub>2</sub> concentrations. When H<sub>2</sub>O<sub>2</sub> was regressed on just ozone, solar radiation, and temperature the R<sup>2</sup> was found to be 0.74 for the 1991 data and 0.62 for the 1992 data. This indicates that photochemical activity

alone can explain most of the variability in the H<sub>2</sub>O<sub>2</sub> concentrations observed at this rural site and hence at this rural SOS site SONIA in Candor, NC the most important factor affecting the concentration of gaseous hydrogen peroxide can be attributed to photochemical processes.

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