

Correlation of Ozone and Meteorology with Hydrogen Peroxide in Urban and Rural Regions of North Carolina

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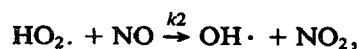
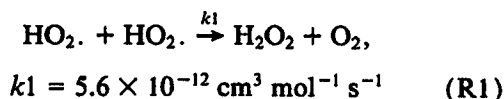
ABSTRACT

Gas-phase hydrogen peroxide (H_2O_2) and ozone (O_3) along with other trace gases and meteorology were monitored in two distinct regimes of high- and low- NO_x (urban and rural) areas in North Carolina during the summer of 1991 as part of the Southern Oxidants Study (SOS). Gas-phase hydrogen peroxide concentrations ranged from less than 0.05 to about 1.0 ppbv and from less than 0.05 to 2.0 ppbv at the urban and rural sites, respectively. A clear diurnal trend was observed at both locations, though at the urban site the H_2O_2 profile lagged the ozone profile by 2–3 h. At the rural site, high H_2O_2 concentrations were observed on certain nights. The various physical, chemical, and meteorological parameters affecting H_2O_2 concentrations were examined using observational-based statistical analysis. It was found that in the urban air, H_2O_2 concentrations increased with increasing temperature, solar radiation, and ozone concentrations but decreased with increasing NO_x , carbon monoxide, and relative humidity. In the rural air, hydrogen peroxide concentrations were also found to be affected in a similar way. The results of a multivariate statistical analysis indicates that the gas-phase H_2O_2 concentration observed at the sites is dependent on the atmospheric chemistry and the dynamical characteristics of the sites.

1. Introduction

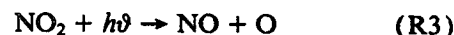
Both hydrogen peroxide (H_2O_2) and ozone (O_3) are important photochemical oxidants playing significant roles in acid formation and photochemistry of the troposphere (Penkett et al. 1979; Finlayson-Pitts and Pitts 1986; Aneja et al. 1994). Hydrogen peroxide is an important constituent of both clean and polluted air present mainly as a product of the photochemical mechanisms leading to the formation of ozone (Logan et al. 1981; Kleinman 1986). Though hydrogen peroxide plays an important role in the oxidizing capacity of the atmosphere, unlike ozone its formation, fate, and effects in the atmosphere are still not well understood (Sakugawa et al. 1990).

Atmospheric hydrogen peroxide is believed to be a product of hydroperoxyl (HO_2) radical recombination, which is produced by reactions during the photolysis of ozone and as an oxidation product of hydrocarbons. This reaction is most sensitive to NO concentration as NO competes for the HO_2 radicals by reacting with it (Kleinman 1986):



$$k_2 = 8.3 \times 10^{-12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}. \quad (R2)$$

Reaction (R1) proceeds only when the NO_x concentrations are considerably low as the presence of large concentrations of NO_x serves to suppress the formation of H_2O_2 (R2). At higher NO_x concentrations NO_2 produced in reaction (R2) is photolyzed and produces ozone [reactions (R3) and (R4)]:



At higher NO concentrations, the reaction of HO_2 with NO regenerates OH and depletes HO_2 (R2).

Photochemical models suggest that the production of H_2O_2 in the gas phase is a function of light intensity and the ambient concentrations of nonmethane hydrocarbons, aldehydes, carbon monoxide (CO), NO_x , and O_3 (Logan et al. 1981; Calvert and Stockwell 1983; Kleinman 1986). These parameters have also been evaluated in various field studies conducted over the continental United States and central Europe, and a correlation has been found between the presence of peroxides (hydrogen and organic), photo activity (seasonal variations, spatial and temporal variations), and photochemical smog (O_3 , NO_x) (Gunz and Hoffmann 1990, and references therein). Thus, the production rate of H_2O_2 is a complex function of the level of photochemical activity and air-mass age. Moreover, it is extremely soluble in water

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(Henry's law constant $H \approx 10^5 \text{ M atm}^{-1}$) and is easily removed by wet deposition and thus has a relatively short lifetime. Hence, the measured hydrogen peroxide concentration is a combination of rapid production and removal processes. Because hydrogen peroxide is formed from the combination of photochemically produced peroxy radicals when atmospheric levels of NO_x are low such that NO does not compete for consumption of HO_2 radicals, it is expected that hydrogen peroxide concentrations and trends will vary with changing NO_x conditions.

Despite the growing interest in atmospheric hydrogen peroxide, not many field investigations have been carried out until recently (Claiborn and Aneja 1991, and references therein). The data on atmospheric hydrogen peroxide is slowly growing with the development of improved techniques for the measurement of hydrogen peroxide in both the gas as well as aqueous phases (Lazrus et al. 1986; Klockow and Jacob 1986; Olszyna et al. 1988; Sakugawa and Kaplan 1989; Boatman et al. 1990; Daum et al. 1990; Lee et al. 1990; Gallagher et al. 1991; Tremmel et al. 1993). To understand the physicochemical processes affecting H_2O_2 formation and to study H_2O_2 behavior in high- and low- NO_x areas, gas-phase hydrogen peroxide was measured in conjunction with other physical, chemical, and meteorological parameters as part of the Southern Oxidants Study (SOS), which is a five-year project to characterize the urban and rural ozone problem in the southeastern United States and to elucidate the formation, fate, and effects of photochemical oxidants (including H_2O_2) in the south and develop strategies for their management.

In this paper, we report the results of continuous ground-level field measurements of H_2O_2 and O_3 and discuss the effect of O_3 and meteorology on H_2O_2 levels in urban and rural regions of North Carolina.

2. Methodology

a. Sampling sites

Hydrogen peroxide and total peroxides concentrations were measured in conjunction with other trace gases and meteorology at two different locations in North Carolina during the summers of 1991 and 1992. The urban site is located in downtown Raleigh, North Carolina (35.9°N , 78.7°W , 126.8 m MSL). The measurement period at this site was from 28 August to 19 September 1991.

The rural 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 MSL). The site is an SOS-Southeastern Regional Oxidant Network (SERON)-enhanced chemistry site, SONIA, and is collocated with a National Dry Deposition Network (NDDN) site. The sampling site is in an open field (area approximately 1200 m^2), which was previously used to grow soybeans (about 10 years ago), and is

surrounded by mixed deciduous and coniferous forest. At site SONIA, intensive measurements were conducted from 15 June to 13 August 1991. A map of the two sampling sites and the surrounding region is given in Fig. 1.

b. Atmospheric pollutants and meteorological data

The atmospheric trace gases used for the analysis are O_3 , NO , NO_2 , and SO_2 and were obtained using a differential optical absorption spectrometer during 1991 for both sites. The data on CO was provided by the North Carolina Department of Environmental Health and Natural Resources. The meteorological data from the Raleigh-Durham International Airport (which is representative of the overall meteorological conditions in the Raleigh area) were used for our analysis of the urban site. This data was obtained from the National Climatic Data Center, Asheville, North Carolina. Meteorological data and ozone concentrations from the adjacent NDDN site were used for the analysis of the rural site. Meteorological data included in the analysis are hourly averaged values of temperature, relative humidity, wind speed, wind direction, and solar radiation.

c. Measurement of gaseous hydrogen peroxide

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). This instrument has a level of detection for gaseous H_2O_2 of approximately 50 pptv. The dual channel fluorometric analyzer measures total peroxides on one channel, and by specific enzymatic destruction of hydrogen peroxide, organic peroxides only on the second channel. When using this method there can be substantial loss of H_2O_2 in the sampling line (Lee et al. 1991). To minimize line losses, new Teflon line was used, and the residence time of ambient air in the sampling manifold was reduced to

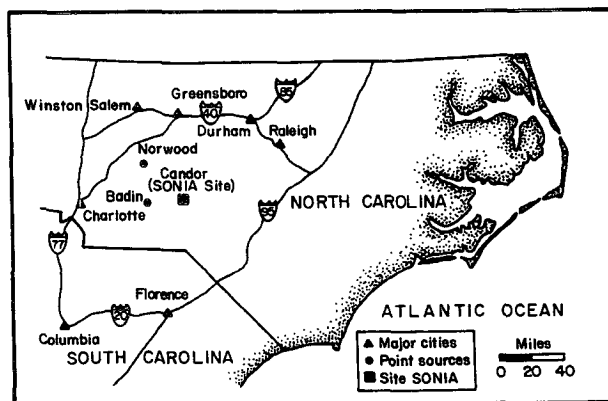


FIG. 1. Map of the urban and rural sampling sites and the surrounding cities and point sources.

TABLE 1. Summary of mean, maximum, minimum, and median values of ambient H₂O₂ gas-phase levels.

Period	N	Mean	SD	Median	Max	Min
Candor						
1991	296	0.41	0.51	0.42	2.19	<LOD*
Days	156	0.64	0.56	0.46	2.19	<LOD
Nights	140	0.16	0.18	0.10	0.94	<LOD
Raleigh						
1991	188	0.21	0.22	0.15	0.97	<LOD
Days	86	0.39	0.24	0.35	0.97	<LOD
Nights	92	0.10	0.11	0.07	0.48	<LOD

* LOD—level of detection, 50 pptv.

less than 0.25 s. Ambient air was drawn from a height of 10 m through a 3-in. i.d. glass sampling tower by an 1100 ft³ min⁻¹ blower in order to limit sample residence time. A 16-port glass manifold was installed at the base of the glass sampling tower, above the blower, to permit sampling access. About 3-m length and 0.25-in. o.d. Teflon tubing, connected to one of the ports, served as the sampling line to the analyzer. The manifold was heated above the ambient temperature to prevent any moisture condensation. Gas-phase total and organic peroxide were recorded on a chart recorder and extracted manually as 12-min averages. These data were then consolidated into hourly averages. The analyzer was calibrated once daily, and the baseline checks were performed twice daily. Hydrogen peroxide solutions were standardized by titration with potassium permanganate, while sodium oxalate standard was used to standardize potassium permanganate solution. Calibration curves were obtained by serial dilution of the working standard.

3. Results and discussion

a. Gas-phase hydrogen peroxide concentration at the two locations

A statistical summary of the gas-phase H₂O₂ concentrations measured at the two locations is given in Table 1. The mean H₂O₂ concentration is significantly higher at the rural site than at the urban site (Student's t-test at the 95% confidence level) with concentrations at the rural site (0.40 ppbv) nearly twice those observed at the urban site (0.20 ppbv). The difference in the mean daytime and nighttime H₂O₂ levels was also found to be statistically significant at both locations. This difference can be attributed to the NO_x availability in these two different regions. The self-combination reaction (R1) to produce H₂O₂ is highly sensitive to NO concentration as stated earlier. Stockwell (1986) showed that H₂O₂ production is extremely sensitive to the rate of the reaction of NO₂ with hydroxyl radical (OH·) because this reaction removes both NO_x and

OH radicals from the pool of photochemical reactants. The average NO₂ concentration at the downtown site in Raleigh was found to be 11.43 ± 9 ppbv, whereas the average NO₂ concentration at site SONIA was 1.23 ± 0.66 ppbv during the 1991 intensive, indicating that site SONIA is located in a low-NO_x area.

b. Diurnal variations of H₂O₂ and O₃ concentrations at the two sites

The composite diurnal profiles of both H₂O₂ and O₃ are given in Fig. 2. A clear diurnal trend was observed at both sites with H₂O₂ concentrations often falling below the instrument's detection limits during the early morning hours. The maxima in both H₂O₂ and O₃ is reached in the late afternoon at approximately 1400–1600 EST, and the minima at 0600–0700 EST. The diurnal effect at both sites is probably due mainly to depositional removal of both species under the nocturnal boundary layer and the absence of photochemical production at night. However, unlike O₃, H₂O₂ concentrations fall to detection limits during the early morning hours at both sites. This behavior has been explained by Hastie et al. (1993) and others to be due to the removal of the highly soluble gas-phase H₂O₂ by aqueous aerosols formed in the nocturnal boundary layer (NBL) due to the radiative cooling of the earth's

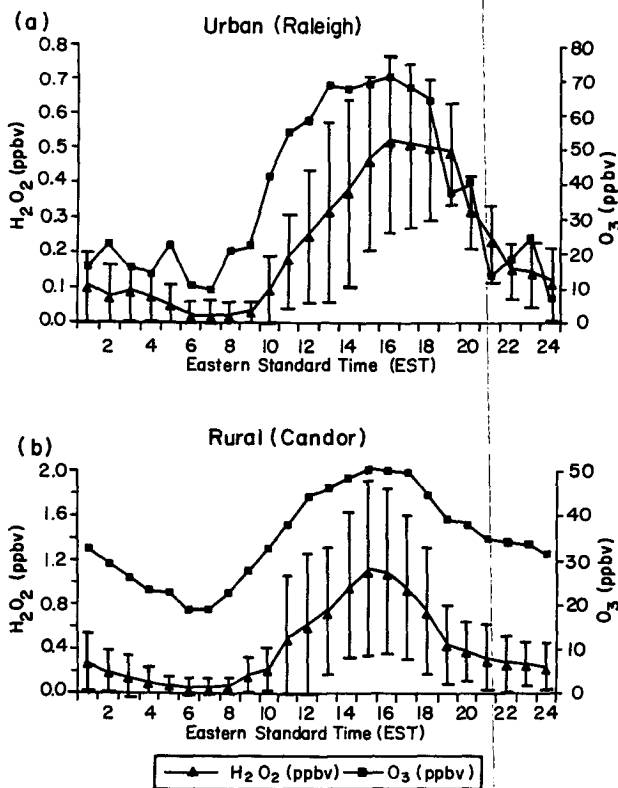


FIG. 2. Composite diurnal profiles of H₂O₂ and ozone during the 1991 intensives at the (a) rural site and (b) urban site.

TABLE 2a. Daily maximum H₂O₂ and O₃ levels and the associated weather on selected days during the measurement period at site SONIA, Candor, North Carolina.

Date	Max H ₂ O ₂ (ppbv)	Max O ₃ (ppbv)	Max T (°C)	Weather
25 Jul	1.98	69.25	30.9	Site under the influence of a weak surface trough under 500-mb ridging.
26 Jul	2.16	58.25	31.9	Hot and humid ahead of slow-moving broken frontal zone.
27 Jul	1.67	50.00	28.6	Weak cold front passed over the site, widespread clouds and thunderstorms, 25.66 mm of precipitation at the site from 1800 EST onward until midnight. H ₂ O ₂ concentration showed a sudden drop from 1.15 ppbv to 0.43 ppbv within the hour.
28 Jul	0.53	34.00	24.8	Stationary front across South Carolina and Georgia, northeast winds at the site due to high over eastern Canada; cloud, scattered showers.
29 Jul	0.51	38.25	26.2	Weak low pressure system moved eastward along stationary front, passing over site, cloud, showers, T-storms.
30 Jul	—	25.25	22.9	Stationary front over site: clouds, showers, T-storms. 28.8 mm of precipitation.
31 Jul	0.86	48.25	28.2	Site under influence of stationary front breaking up over coast as well as a weak cold front moving in from the west with associated 500-mb trough. T-storms, showers, cloudy.
1 Aug	0.29	32.00	24.2	Cold front becomes stationary over site, widespread clouds and precipitation.
2 Aug	0.33	36.25	26.4	Site under the influence of a persistent low pressure trough across the Carolinas and Georgia; 12.43 mm precipitation.
3 Aug	1.36	78.00	31.7	Site continues under the influence of low pressure trough. Mixture of clouds/sun, scattered showers in the area.
4 Aug	2.19	76.50	32.9	Hot and humid with weak SW winds, clear sky conditions, highest temperature recorded (32.9°C) of the experiment period.
5 Aug	1.28	67.50	30.0	Cold front passes over site and into South Carolina, partly cloudy skies, no precipitation, NE winds.
6 Aug	1.67	69.75	31.3	Site under influence of high pressure over eastern Canada, continued NE winds, partly cloudy, no precipitation.

surface after sunset. Thus, gas-phase H₂O₂ is deposited to the surface along with dew. A negative correlation has been found between H₂O₂ concentration and dew-point temperature at both sites ($r = -0.80$ and -0.83 at the urban and rural sites, respectively, during the 1991 intensives).

An examination of the diurnal profiles of H₂O₂ and O₃ further shows that at the rural site maxima in H₂O₂ and O₃ are collocated in time, whereas in the urban region, the peak in H₂O₂ lags the O₃ peak by about 2–3 h. This is probably due to the difference in NO_x levels in the two regions. At higher NO_x levels, NO preferentially reacts with HO₂ radicals removing it from the pool of reaction. The recombination reaction of hydroperoxyl radicals begin to take place only when the NO_x levels have fallen significantly low to allow the self combination of HO₂ radicals (Das and Aneja 1994a).

Another observation of interest is that considerable background ozone survives the night at the rural site (~25 ppbv), whereas at the urban site, nighttime ozone levels fall to as low as 10 ppbv. This again is probably due to the difference in NO_x concentrations at the two sites. Unlike at the rural site, there is considerable NO_x concentrations at the urban site even during the nighttime when photochemical production of O₃ has ceased. When the nocturnal boundary layer is well established, this NO_x then helps to titrate the existing O₃, and the concentration of ozone measured close to the ground falls without replenishment from the residual layer aloft. Hence, nighttime ozone levels

at the urban site are lower than at the rural site. The lower ozone levels at night and higher average daytime concentrations at the urban site, when compared to the rural site, result in a higher difference between the mean daily maximum and minimum ozone concentrations observed at the urban site (~55 ppbv) than that at the rural site (~30 ppbv). This implies a more intense photochemical production of ozone during the day and stronger destruction at night at the urban site.

c. Correlation of O₃ and meteorology with H₂O₂

The relationship between O₃, meteorology, and H₂O₂ was examined by applying statistical methods. The hourly averaged data used for the analysis were windowed for periods of photochemical activity. From the results of a correlation matrix showing the cross correlations between the various physicochemical variables used in our study, the more significant relationships for H₂O₂ appeared to be between H₂O₂ and O₃, temperature, relative humidity, and solar radiation.

To explore the effect of meteorology on the monitored H₂O₂ and O₃ concentrations, the data were analyzed with the meteorological situation prevailing at the sites on some of the days during the measurement period (Tables 2a,b). The daily maximum H₂O₂ and O₃ levels monitored during these days along with the daily maximum temperature are included in the table.

From Tables 2a,b, it is clearly seen that meteorology plays an important role in determining H₂O₂ levels at both the rural and urban sites. Particularly at the rural

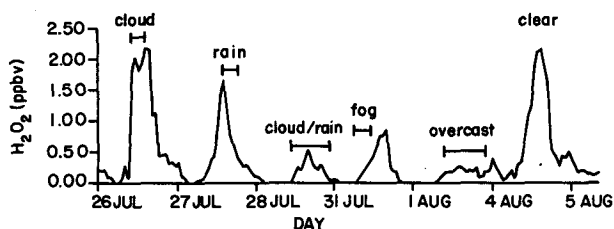
TABLE 2b. Daily maximum H₂O₂ and O₃ levels and the associated weather on selected days during the measurement period at Raleigh, NC.

Date	Max H ₂ O ₂ (ppbv)	Max O ₃ (ppbv)	Max T (°C)	Weather
8 Sep	0.64	69.00	29.4	Site under the influence of a weak high pressure in the Pennsylvania–Virginia areas, midday clear sky conditions over the site, weak NE winds.
9 Sep	0.97	73.43	28.9	High pressure located over North Carolina.
10 Sep	0.63	70.30	28.9	Persistent high pressure over North Carolina, clear skies.
11 Sep	0.34	78.31	31.7	Site under influence of prefrontal trough, partly cloudy skies.
12 Sep	0.44	72.85	31.1	A weak cold front passed over site during previous night, weak NE winds, partly cloudy skies.
13 Sep	0.43	75.39	30.0	Stationary front over the Carolinas in an east–west direction.
14 Sep	0.48	81.17	35.0	Weak high pressure located over Georgia–South Carolina–North Carolina areas, clear skies, hot and humid, highest temperature of the measurement period.

site, the H₂O₂ levels measured bear a direct relationship to the prevailing meteorological condition at the site. It is also interesting to note that high H₂O₂ levels are always accompanied by high O₃ at the rural site, but at the urban site, H₂O₂ levels failed to show such a relationship. In fact, a slight negative relationship is observed that is explained in terms of regression analysis later in this section.

Diurnal variation of H₂O₂ during days with cloud, rain, or haze (or fog) formation at the rural site is given in Fig. 3. It is clearly seen that a wet spell brings the H₂O₂ concentration down immediately. Cloud, haze, or fog formation also affects the H₂O₂ gas-phase concentration. From the data presented in Fig. 3, it is apparent that low photochemical activity due to high cloud cover or very moist air results in a decrease in the concentration of gaseous H₂O₂ in the air. This has been attributed to the reduction in the solar flux by clouds (Thompson and Cicerone 1982), and also cloud droplets can effectively scavenge H₂O₂ due to the high solubility of H₂O₂.

Meteorology was also found to play an important role in high nighttime levels of H₂O₂. At the rural site, there was occasionally a secondary nighttime peak in H₂O₂ accompanied by an O₃ peak (Figs. 4a,b). An examination of H₂O₂ levels, together with meteorology, shows increasing wind speed and also a slight increase in temperature, indicating the presence of a weak NBL. We hypothesize that downward mixing of undepleted air from aloft under such conditions can result in high nighttime concentrations (Das and Aneja 1994b). It

FIG. 3. H₂O₂ concentrations during cloud, rain, and fog conditions.

is also interesting to note that surface ozone concentrations were restored to the concentrations observed during the day, but the H₂O₂ level was lower than the daytime level.

Ozone was regressed on H₂O₂ concentrations to understand the role of O₃ concentrations on H₂O₂ levels. Hourly averaged values of H₂O₂ and O₃ for the daytime period (1000–1800 EST) were used for all the statistical analysis. Only days with clear skies were chosen for the analysis. The results are presented in Table 3. It is

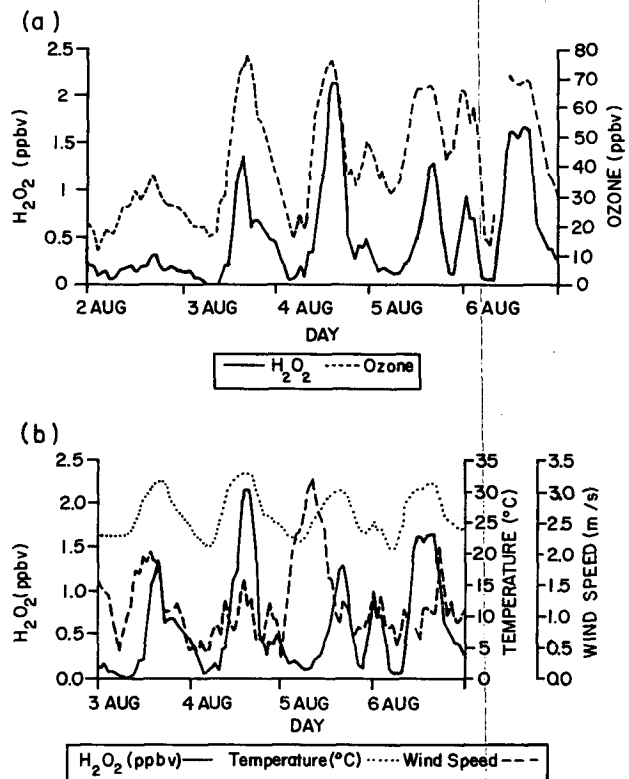
FIG. 4. (a) H₂O₂ and ozone concentrations at site SONIA during 2–6 August 1991. (b) H₂O₂, temperature, and wind speed at site SONIA during 2–6 August 1991.

TABLE 3. Simple regression analysis of O₃ and H₂O₂ for 1000–1800 EST and clear sky conditions.

	Regression	<i>n</i>	<i>R</i> ²
Candor			
Daytime hourly average	O ₃ = 32.86 + 19.10 H ₂ O ₂	107	0.57 ^a
Daily maximum	O ₃ = 39.28 + 20.61 H ₂ O ₂	13	0.69 ^a
Raleigh			
Daytime hourly average ^b	O ₃ = 54.20 + 18.65 H ₂ O ₂	65	0.16 ^c
Daily maximum	O ₃ = 79.09 + 10.38 H ₂ O ₂	8	0.16 ^c

^a Highly significant at *p* = 0.05.

^b Lag values of H₂O₂ were used.

^c Significant at *p* = 0.05.

seen that H₂O₂ correlates well with O₃ (*R*² = 0.57) at the rural site but not so at the urban site (*R*² = 0.09; not shown in table). The poor correlation at the urban site could be due to the fact that the H₂O₂ begins to peak with a lag of about 2 h of the O₃ peak. Hence, ozone was regressed on the H₂O₂ values with a lag of 2 h. A better fit was found in this case (*R*² = 0.16). From the slope of the linear least-squares fit, about 19 ppbv of O₃ is derived for 1 ppbv of H₂O₂ in both the rural and urban regions of North Carolina.

A further regression analysis of daily maximum H₂O₂ and O₃ concentrations reveals that in the rural region the formation of H₂O₂ is favored by increasing ozone, whereas in the urban region O₃ is formed at the expense of H₂O₂. This again is explained by the NO_x availability in the two regions [reactions (R1)–(R4)]. Hence, at higher NO_x concentrations (urban environment), O₃ is produced preferentially over H₂O₂ and a negative correlation is seen between maximum daily H₂O₂ and O₃, whereas in a rural environment a strong positive correlation is observed due to lower NO_x and the fact that in this environment O₃ is the major radical precursor source of H₂O₂. However, at the urban site, daily maximum H₂O₂ was found to be correlated to the total non-methane hydrocarbon concentration measured as a 3-h-integrated average (0500–0800 EST) (*R*² = 0.62).

A stepwise multiple linear regression analysis of H₂O₂ on the measured air quality variables was carried out to examine the effect of various physicochemical variables on H₂O₂ levels (Table 4). From an examination of the table, it is found that 1) O₃ accounts for 0.09 of *R*² for H₂O₂ in the urban area, whereas the *R*² value in the rural area is 0.57; 2) the *R*² is increased when the meteorological variables (solar radiation, temperature, and relative humidity) are added to O₃ at both locations (*R*² = 0.33 at the Raleigh site and *R*² = 0.76 at site SONIA); and 3) when all the measured physicochemical variables were used for the

analysis, *R*² was found to be 0.51 at the urban site and 0.87 for the rural region.

Another interesting point that can be noted from Table 4 is that at the rural site, H₂O₂ levels are most strongly correlated with temperature (*R*² = 0.73). Most of the variance in H₂O₂ levels can be explained by temperature alone. Ozone was also found to be highly correlated with temperature (*R*² = 0.82). There could be two possible reasons for this. First, photochemical activity is higher at higher temperatures. Second, this correlation is probably due to enhanced emission of isoprene at this rural site at higher temperatures and the more intense photochemical reactions resulting in the formation of free radicals including HO₂. Thus, the observed dependence of H₂O₂ and O₃ concentrations on temperature due to enhanced emissions of radical precursors leads to the generation of both H₂O₂ and O₃.

From the results it is seen that, for the rural site, O₃ and meteorology (which represent a general condition for photochemical processes) describe most of the variability in H₂O₂ levels and the *R*² is not much improved when other variables, mainly trace species concentration, were added. However, at the urban site, other trace species concentrations, mainly primary pollutants in addition to O₃ and meteorology, played an important role in explaining the variability in H₂O₂ levels. Also a larger percentage of variability in H₂O₂ levels is explained by the measured physicochemical variables at the rural site than at the urban site. This is probably due to the more complex photochemistry leading to the generation of H₂O₂ in an urban area than at a rural area.

Principal component analysis (PCA) was performed on the correlation matrix obtained from the cross cor-

TABLE 4. Multiple regression analysis of H₂O₂. Daytime (1000–1800 EST) hourly averages were used for the analysis.

Physicochemical variables	<i>R</i> ²	<i>n</i>	Significance (<i>p</i> < 0.05)
Raleigh			
O ₃	0.09	65	Highly significant
O ₃ , temperature, solar radiation, relative humidity	0.33	65	Highly significant
O ₃ , NO, NO ₂ , SO ₂ , CO, solar radiation, temperature, relative humidity, wind speed	0.51	65	Highly significant
Candor			
O ₃	0.57	107	Highly significant
Temperature	0.73	107	Highly significant
O ₃ , temperature, solar radiation, relative humidity	0.76	107	Highly significant
O ₃ , NO, NO ₂ , SO ₂ , solar radiation, temperature, relative humidity, wind speed	0.87	74	Highly significant

TABLE 5a. Regression analysis on principal components for the Candor dataset ($n = 77$).

Variable	PC1 photochemical processes	PC2 photolysis of NO ₂	PC3 atmospheric stability
H ₂ O ₂	0.84	-0.24	0.05
Ozone	0.88	0.04	0.05
NO ₂	-0.04	0.92	-0.05
SO ₂	-0.76	0.16	-0.02
T	0.84	-0.42	0.12
SR	0.59	-0.69	-0.08
RH	-0.87	0.39	-0.06
WS	0.08	-0.21	-0.74
WD	0.19	-0.25	0.78
Total variance	46%	12%	12%
R ² for H ₂ O ₂	0.69	0.01	0.02
Regression coefficients	0.22	0.03	0.06

relations between hourly averaged values of the measured air quality variables from the Raleigh and Candor datasets. In addition, PCA explained the variance in the two datasets, yielding a physical interpretation of the principal components isolated by this method. PCA has been used in air quality (Henry and Hidy 1979) to remove multicollinearity effects in regression analysis (as most of the air quality variables used as regressors are not independent) and make it more reliable by the application of PCA on the dataset (not including the dependent variable) that produces statistically independent linear combination of the original variables. A more detailed description of the application of PCA can be found in Cooley and Lohnes (1971), Anderson (1958), and Johnson and Wichern (1988). The results are presented in Tables 5a,b. Three principal components, which account for more than 70% in total variance in the original dataset, were extracted. Loadings (which are the correlation coefficients between the original variables and the factors/components) for variables are considered to be a member of a component if they are at least 0.5. For the rural site (Table 5a) the first component with high loadings on H₂O₂, O₃, temperature, solar radiation, and relative humidity

can be interpreted to indicate the "photochemical processes." The first component also has a strong negative loading from SO₂ and relative humidity. This again implies the uptake of H₂O₂ on the surfaces of wetted aerosol and its role in the atmospheric oxidation of SO₂ to H₂SO₄ and SO₄²⁻ aerosol. Components 2 and 3 can be similarly interpreted to be indicative of "photolysis of NO₂" and "atmospheric stability," respectively. These three components were used in regressors for the regression analysis on H₂O₂. The results indicate that photochemical activity strongly affects the concentration of gaseous H₂O₂ at this rural area. Similar analysis of the Raleigh dataset indicates that primary pollutant concentration, in addition to photochemical activity, significantly affects the gaseous H₂O₂ concentrations in an urban environment like Raleigh.

4. Conclusions

Hydrogen peroxide and ozone concentrations exhibited diurnal variation at both the urban as well as rural sites with maximum concentrations during the late afternoon and minimum concentrations during the early morning hours, displaying the photochemical

TABLE 5b. Regression analysis on principal components for the Raleigh dataset ($n = 65$).

Variable	PC1 photochemical processes	PC2 primary pollutants	PC3 emission and transport of SO ₂
H ₂ O ₂	0.62	-0.08	-0.07
Ozone	0.82	-0.38	-0.13
NO ₂	-0.27	-0.91	-0.18
SO ₂	0.06	0.07	0.98
CO	-0.23	-0.81	-0.27
T	0.81	-0.30	0.22
RH	-0.94	0.10	-0.21
WS	0.07	0.04	0.98
SR	0.86	-0.33	-0.10
Total variance	47%	20%	10%
R ² for H ₂ O ₂	0.26	0.04	0.02
Regression coefficients	0.15	0.03	0.02

generation of these species. At the rural site, the maxima in both H_2O_2 and O_3 concentrations were reached at the same time (1400–1600 EST). However, at the urban site, the H_2O_2 peak lagged the O_3 peak by about 2 h, indicating the role of NO_x chemistry in the photochemical generation of H_2O_2 .

The mean concentration of H_2O_2 was found to be approximately 0.2 ppbv at the urban site and 0.4 ppbv at the rural site. The mean daytime H_2O_2 concentration at Raleigh was about 0.36 ppbv, whereas at site SONIA this value was 0.64 ppbv during the 1991 intensive. This difference in the mean H_2O_2 concentrations at the two sites is found to be statistically significant at the 95% level of confidence and is attributed to the difference in the NO_x levels in the two regions. However, the ozone concentrations at the two sites during the 1991 intensives are similar. The difference in the mean daytime and nighttime H_2O_2 concentration is also found to be statistically significant. The nighttime H_2O_2 concentration was often found to be below the level of detection (~ 50 pptv) at both sites, and this is attributed to the deposition of H_2O_2 under the shallow nocturnal boundary layer and the absence of photochemical production at night.

Ozone and meteorology were found to play important roles in determining the H_2O_2 concentrations at both the urban as well as rural sites. Higher H_2O_2 concentrations were observed on hot, humid days at both sites. Frontal passages accompanied by thunderstorms immediately brought the H_2O_2 levels down. Hydrogen peroxide levels were also found to be highly correlated to ozone concentrations, solar radiation, temperature, and relative humidity, indicating the importance of photochemical processes in the generation of H_2O_2 . At the rural site, a secondary peak in H_2O_2 accompanied by an O_3 peak was observed in 10% of the experiments and is explained to be the result of an unstable NBL.

The results of multivariate statistical analysis again indicated that photochemistry played a significant role in determining the H_2O_2 levels at both sites. At the urban site, primary pollutant concentrations, in addition to photochemical processes, were found to be important factors in regulating H_2O_2 concentrations, whereas at the rural site, photochemical processes alone played a significant role.

Clearly, further studies, reliable measurement techniques, and longer periods of field observations on hydrogen and organic peroxides coupled with measurements of nonmethane hydrocarbons (NMHCs), other pollutants, and meteorology are needed in understanding the climatology of peroxides in the urban and rural regions. The effect of NO_x on the formation of gaseous H_2O_2 also needs to be further investigated. Finally, the distribution of individual NMHCs and their emissions and/or photochemical generation processes must be understood in order to estimate the extent of

NMHCs involved in the generation of gaseous hydrogen peroxide in the rural southeastern United States.

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