

## A Study on Hydrogen Peroxide in the Atmosphere

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Received September 28, 1988

### ABSTRACT

Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) concentrations were measured at two sites. One was on Lushan Mountain in May, 1987. The other was in Beijing in August, 1987 and in December, 1986. The automated fluorometric method was used for the determination of  $\text{H}_2\text{O}_2$ . The concentrations of  $\text{H}_2\text{O}_2$  ranged from approximately 0.50 to 4.32 ppb on Lushan Mountain. The concentrations of  $\text{H}_2\text{O}_2$  ranged from approximately 0.05 to 1.49 ppb in August in Beijing, and it was only 0.01 ppb in December in Beijing.

### 1. INTRODUCTION

Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is an important product of photochemical reactions in the atmosphere.  $\text{H}_2\text{O}_2$  is directly related to the concentrations of HOx radical in homogeneous and heterogeneous processes in the stratosphere and troposphere (Crutzen and Fishman, 1977; Cox and Burrows, 1979). The oxidation by  $\text{H}_2\text{O}_2$  in atmospheric aqueous materials, such as rain, cloud and fog, is considered to be the principal pathway for the conversion of  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$  at the pH range of the acid rain (Penkett et al., 1979; Martin and Damschen, 1981) because of its high solubility in water (Henry's law constant is about  $10^5 \text{ M atm}^{-1}$ ). Thus, the determination of concentrations of  $\text{H}_2\text{O}_2$  in both real atmosphere and simulated system is of considerable interest.

Bufalini et al. (1972) reported  $\text{H}_2\text{O}_2$  concentrations of up to 40 ppb in Hoboken, N.J., and of up to 180 ppb in Riverside, C.A.—during a very severe smog episode when the oxidant concentration reached 0.65 ppm (Bufalini et al., 1972; Gay et al., 1972). They also reported that the maximum concentrations were measured at midday with strong solar radiation and on a day with moderate smog. On days when solar radiation was weak due to cloud no  $\text{H}_2\text{O}_2$  was detected.

In 1977, Kok et al. (1978) measured  $\text{H}_2\text{O}_2$  concentrations continuously in the California South Coast Air Basin by the chemiluminescent method. Typical mid-afternoon concentrations of  $\text{H}_2\text{O}_2$  ranged from approximately 10 to 30 ppb during moderate smog episodes (i.e.  $\text{O}_3$  150–200 ppb). The concentration was substantially lower than those obtained in the earlier work of Bufalini et al. The differences are probably caused by the measurement methods.

In the earlier study oxidant rather than ozone was measured as  $\text{H}_2\text{O}_2$  signal. When Lazrus et al.(1985) tested extensive interference of the gas-phase  $\text{H}_2\text{O}_2$  instrument they found that 130 ppbv of NO caused a 0.016 ppbv reduction in  $\text{H}_2\text{O}_2$  signal; 40 and 100 ppbv of  $\text{O}_3$  increased  $\text{H}_2\text{O}_2$  concentrations by 0.010 and 0.030 ppbv respectively; 0.5% and 5% losses in  $\text{H}_2\text{O}_2$  signal were caused by 10 and 100 ppbv of  $\text{SO}_2$ ; effects due to 15 ppbv of  $\text{NO}_2$  and light saturated hydrocarbons, 20 ppbv of HCHO, 10 ppbv of  $\text{HNO}_3$  and 92 ppbv of NO were not detectable ( $<0.010$  ppbv).

Kok et al.(1978) observed that  $\text{H}_2\text{O}_2$  concentrations in the mornings were likely in the range of 5–10 ppb with few cases when  $\text{H}_2\text{O}_2$  concentrations were between 25 and 35 ppb. These scientists thought that it would be very interesting to determine  $\text{H}_2\text{O}_2$  concentrations in the early morning prior to sunrise and obtain complete diurnal variation of  $\text{H}_2\text{O}_2$  concentration. Up to date no overnight data have been reported.

It has been shown that there was some interference in the chemiluminescent method (Heikes, 1984; Heikes et al.,1982). It is difficult to measure the  $\text{H}_2\text{O}_2$  concentrations by this method accurately. The automated fluorometric method developed by Lazrus et al.(1986) is more advanced. The automated fluorometric method is employed in our study.

The purpose of this investigation was to measure the  $\text{H}_2\text{O}_2$  concentration in 24-hrs on clear and cloudy days, to find the diurnal variation of  $\text{H}_2\text{O}_2$  concentration. In addition, the relationship between concentrations of  $\text{O}_3$  and  $\text{H}_2\text{O}_2$  was investigated.

## II. EXPERIMENT

Field experiments were carried out at two sites, on Lushan Mountain in May 1987, and in Beijing in August 1987 and in December 1986. May is the rainy season on Lushan Mountain. Every day seems rainy and foggy. Overnight measurement of  $\text{H}_2\text{O}_2$  was difficult. Most of the data of  $\text{H}_2\text{O}_2$  were obtained in daytime. However, the  $\text{H}_2\text{O}_2$  concentration in Beijing were measured day and night every day.

The automated fluorometric method for measuring gas-phase  $\text{H}_2\text{O}_2$  was used. This method is based on the selective catalysis of  $\text{H}_2\text{O}_2$  and p-hydroxy-phenyl-acetic acid (POPHA) with horseradish peroxidase to form fluorescent dimer of POPHA (6,6'-dihydroxy-3,3'-biphenyl diacetic acid). The dimeric product fluoresces with a peak excitation wavelength of 320 nm and a peak emission wavelength of 400 nm. The fluorescence intensity of the dimer is directly proportional to the peroxide concentration.

Peroxidase also catalyzes the reaction of organic hydroperoxides to form the fluorescent dimer. To discriminate  $\text{H}_2\text{O}_2$  from organic hydroperoxides, a novel dual-channel chemical flow system with a dual-cell fluorometer has been used. In the first channel the total hydroperoxide was determined, and the organic hydroperoxide in the second channel was measured by adding the enzyme catalase to selectively destroy hydrogen peroxide before the peroxidase-catalyzed reaction occurs. The concentration of  $\text{H}_2\text{O}_2$  is then determined by the difference between fluorescence signals obtained without and with added catalase. The method can measure the  $\text{H}_2\text{O}_2$  automatically and continuously.

Details of the method can be found in Lazrus et al.(1986).

## III. RESULTS AND DISCUSSION

The variations of the concentration of  $\text{H}_2\text{O}_2$  with time are shown in Figs. 1,2 for Lushan Mountain and in Figs. 3,4 for Beijing.

It was found that the concentrations of  $\text{H}_2\text{O}_2$  on Lushan Mountain are higher than

those in Beijing. The maximum concentration on Lushan Mountain was 4.32 ppb, while the minimum was 0.50 ppb. The maximum and minimum concentrations in Beijing were 1.49 and 0.05 ppb respectively. The difference might be due to many causes that are related to the production of  $\text{H}_2\text{O}_2$ . The major gaseous sources of  $\text{H}_2\text{O}_2$  in the troposphere are reactions of  $\text{HO}_2$  and hydrated  $\text{HO}_2$  radicals (R1-R3) (McElroy, 1986).

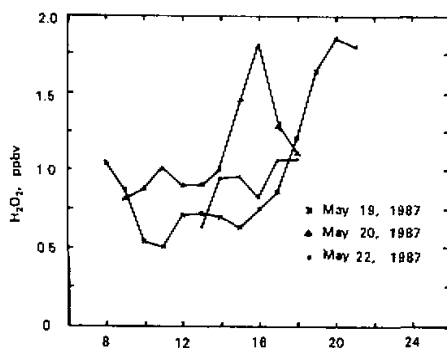
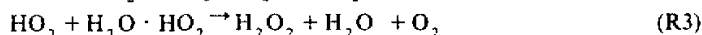
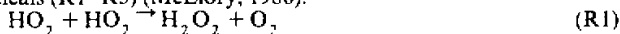


Fig.1. Ambient  $\text{H}_2\text{O}_2$  concentrations measured on Lushan Mountain.

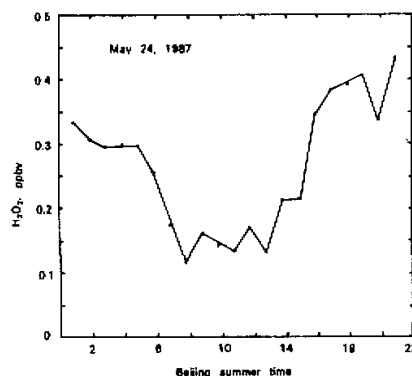


Fig.2 Diurnal concentration-time profile for  $\text{H}_2\text{O}_2$  on Lushan Mountain.

The reaction of hydroxyl radicals with carbon monoxide (R4) leads to the formation of  $\text{HO}_2$  via the recombination of H atoms with  $\text{O}_2$  (R5).



In the polluted atmosphere there is a strong competition for  $\text{HO}_2$  radicals by NO (R6).

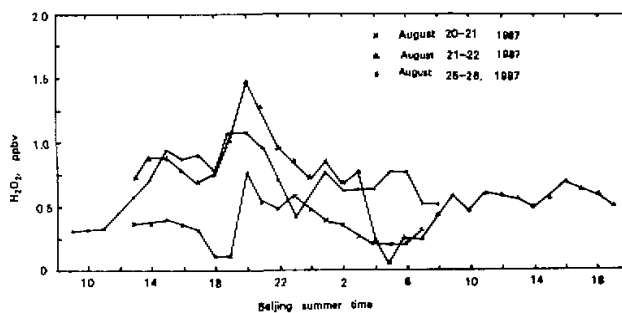
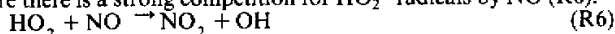


Fig.3. Diurnal concentration-time profiles for  $\text{H}_2\text{O}_2$  in Beijing.

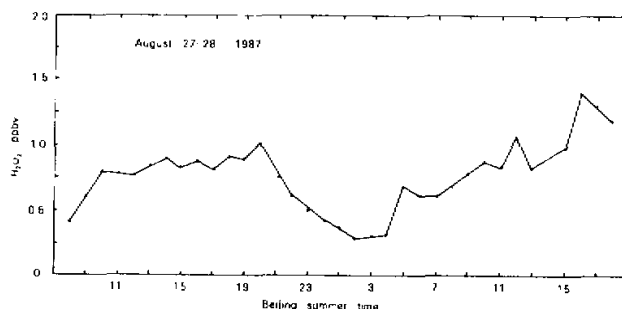


Fig.4. Diurnal concentration-time profile for H<sub>2</sub>O<sub>2</sub> in Beijing.

Therefore, the rate of H<sub>2</sub>O<sub>2</sub> generation is a complex function of NO, CO, hydrocarbons and aldehydes by which HO<sub>2</sub> is derived or destroyed.

Extensive investigations on the kinetics and mechanisms of R1 have been carried out (Paukert and Johnston, 1972; Hochanadel et al., 1972; DeMore, 1979; Cox and Burrows, 1979; Lii et al., 1981). The acceleration of H<sub>2</sub>O on the reaction was first reported by Hamilton and Lii (1977) who suggested that the reaction of a hydrogen-bonded complex with HO<sub>2</sub> (R3) was more efficient than that of two hydroperoxy radicals. An enhancement by a factor of about 3 in the rate constant of second order reaction (k) has been found for relative humidities approaching 100% (Calvert and Stockwell, 1983). Thus, the concentration of H<sub>2</sub>O<sub>2</sub> in the troposphere depends not only on the concentration and type of pollutants but also on the water content.

Based on the natural conditions and air pollution situation, it can be predicted that the concentrations of NO<sub>x</sub> on Lushan Mountain maybe are relatively lower, and the water content is relatively higher. Conversely, the concentrations of NO<sub>x</sub> in Beijing, maybe, are higher, and the water content is lower. Field measurements showed that: On Lushan Mountain the concentrations of NO<sub>x</sub> were  $1.85 \times 10^{-3}$  to  $5.93 \times 10^{-3}$  mg/m<sup>3</sup>, SO<sub>2</sub> concentrations were  $1.92 \times 10^{-4}$  to  $1.23 \times 10^{-3}$  mg/m<sup>3</sup>, and the relative humidity 90–100%, while in Beijing the concentrations of NO<sub>x</sub> were  $1.0 \times 10^{-2}$  to  $1.4 \times 10^{-1}$  mg/m<sup>3</sup>, SO<sub>2</sub> concentrations  $1.89 \times 10^{-3}$  to  $1.30 \times 10^{-1}$  mg/m<sup>3</sup>, relative humidity 40–90%. Therefore, it is reasonable that the difference of H<sub>2</sub>O<sub>2</sub> concentration between Beijing and Lushan Mountain was caused by the different situation of air pollution.

The maximum concentration of H<sub>2</sub>O<sub>2</sub> was not found at midday, but at about 20:00 in the evening, while the minimum was found at the early morning. The similar tendencies were observed by Kok et al.. This pattern of concentration variation might be caused by two reasons. First, H<sub>2</sub>O<sub>2</sub> can be photolyzed in the day. Second, the relatively rapid removal of HO<sub>2</sub> radicals by NO (R6) competes the rapid reaction (R1) and (R3) until all the NO is converted to NO<sub>2</sub> and other products. This takes place at later afternoon and during the nighttime because the reaction (R7) converts NO to NO<sub>2</sub> very effectively. At this time HO<sub>2</sub> is generated by Reactions (R 8–10).



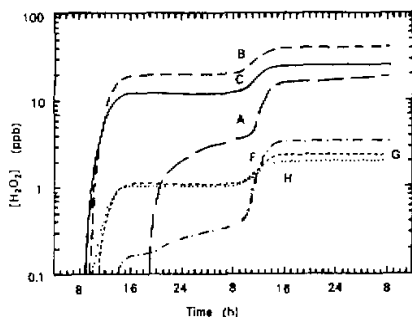


Fig.5. Theoretical time dependence of  $\text{H}_2\text{O}_2$  in the various two-day polluted air scenarios A-H.

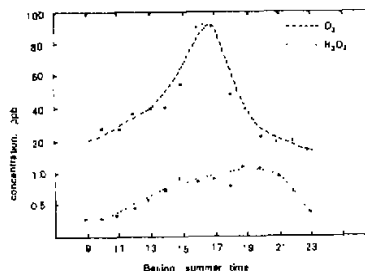


Fig.6. Ambient  $\text{O}_3$  and  $\text{H}_2\text{O}_2$  concentrations measured on Lushan Mountain.

Our results are similar to that of theoretical calculation by Calvert and Stockwell (1983). The calculated  $[\text{H}_2\text{O}_2]$  diurnal variations for various polluted air scenarios A-H (Table 1) are shown in Figure 5. Theoretically,  $\text{H}_2\text{O}_2$  generation is expected to occur even at nighttime in cases A and F. In all other cases, the  $\text{H}_2\text{O}_2$  generation at nighttime is unimportant. Thus, it is easy to explain the maximum  $\text{H}_2\text{O}_2$  occurred late in the day. The polluted air mass in Beijing is similar to A, while that on Lushan Mountain is similar to F.

Experimental result shows that  $\text{H}_2\text{O}_2$  concentrations are not proportional to  $\text{O}_3$  concentration. Generally, concentrations of  $\text{H}_2\text{O}_2$  declined more slowly than those of  $\text{O}_3$  after the  $\text{O}_3$  maximum. (see Fig. 6).

Measurements of  $\text{H}_2\text{O}_2$  were also carried out in Beijing in December 1986. The results show that  $\text{H}_2\text{O}_2$  concentrations are very low, about 0.01 ppb, without distinct diurnal variation. This is caused by the fact that both ultraviolet radiation and relative humidity are relatively low in winter. In addition, the combustion of coal in winter leads to an increase of  $\text{SO}_2$  that reacts with  $\text{H}_2\text{O}_2$ .

It is concluded from our experiments that although hydrogen peroxide is the product of photochemical reactions in the atmosphere, its concentration depends largely on the generation of  $\text{HO}_2$  and the water content in the air.

#### IV. CONCLUSIONS

1. The concentrations of  $\text{H}_2\text{O}_2$  on Lushan Mountain are higher than those in Beijing. This may be explained by the lower  $\text{NO}_x$  concentration and higher water content on Lushan Mountain.

2. The maximum concentration of  $\text{H}_2\text{O}_2$  occurred at about 20:00 in the evening, not at midday, while the minimum occurred at the early morning.

3. The field observations are similar to the theoretical simulation by Calvert and Stockwell.

4. The ratio of concentration of  $\text{H}_2\text{O}_2$  to that of  $\text{O}_3$  was not constant.  $\text{H}_2\text{O}_2$  concentrations declined more slowly than that of  $\text{O}_3$  after the  $\text{O}_3$  maximum.

Table 1. Initial Concentrations and Emission Rates for Pollutants Used in the Two-day Simulations of Tropospheric Chemistry

Reactant	Concentration (ppb)							
	A	B	C	D	E	F	G	H
NO <sub>2</sub>	25	2.5	0.25	25	25	2.5	0.25	0.025
NO	75	7.5	0.75	75	75	7.5	0.75	0.075
CO	2000	2000	2000	200	100	200	100	100
Alkene	100	100	100	10	1.0	10	1.0	0.10
Alkane	400	400	400	40	4.0	40	4.0	0.40
O <sub>3</sub>	30	30	30	30	30	30	30	30
CH <sub>2</sub> O	20	20	20	2.0	0.2	2.0	0.2	0.02
CH <sub>3</sub> CHO	10	10	10	1.0	0.1	1.0	0.1	0.01
Ketone	5	5	5	0.5	0.05	0.5	0.05	0.005
SO <sub>2</sub>	60	60	60	6	0.6	6	0.6	0.06
CH <sub>4</sub>	2500	2500	2500	1400	1400	1400	1400	1400
H <sub>2</sub> O (relative humidity) varied from 10% ( $3.12 \times 10^6$ ppb) to 100% ( $3.12 \times 10^7$ ppb)								
Rates of emission ( ppm min <sup>-1</sup> )								
NO <sub>2</sub>	$1.74 \times 10^{-5}$	$1.74 \times 10^{-6}$	$1.74 \times 10^{-7}$	$1.74 \times 10^{-3}$	$1.74 \times 10^{-3}$	$1.74 \times 10^{-6}$	$1.74 \times 10^{-7}$	$1.74 \times 10^{-8}$
NO	$5.21 \times 10^{-5}$	$5.21 \times 10^{-6}$	$5.21 \times 10^{-7}$	$5.21 \times 10^{-3}$	$5.21 \times 10^{-3}$	$5.21 \times 10^{-6}$	$5.21 \times 10^{-7}$	$5.21 \times 10^{-8}$
Alkene	$6.94 \times 10^{-6}$	$6.94 \times 10^{-6}$	$6.94 \times 10^{-6}$	$6.94 \times 10^{-7}$	$6.94 \times 10^{-8}$	$6.94 \times 10^{-7}$	$6.94 \times 10^{-8}$	$6.94 \times 10^{-9}$
Alkane	$2.78 \times 10^{-5}$	$2.78 \times 10^{-5}$	$2.78 \times 10^{-5}$	$2.78 \times 10^{-6}$	$2.78 \times 10^{-7}$	$2.78 \times 10^{-6}$	$2.78 \times 10^{-7}$	$2.78 \times 10^{-8}$

5. Hydrogen peroxide concentrations are very low and without significant diurnal variation in Beijing in winter.

6. The generation of  $\text{H}_2\text{O}_2$  depends largely on the  $\text{HO}_2$  concentration and the water content in the atmosphere.

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