

# Measurements of atmospheric gas-phase and aqueous-phase hydrogen peroxide concentrations in winter on the east coast of the United States

By M. C. BARTH, D. A. HEGG, and P. V. HOBBS, *Department of Atmospheric Sciences AK-40, University of Washington, Seattle, WA 98195, USA*, and J. G. WALEGA, G. L. KOK, B. G. HEIKES and A. L. LAZRUS, *National Center for Atmospheric Research, Boulder, CO 80307-3000, USA*

(Manuscript received 13 January 1988; in final form 29 April 1988)

## ABSTRACT

Measurements of the concentrations of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) in the gas-phase and in cloud water were obtained in the vicinity of the Carolina Coast of the United States between late January and early March, 1986. The gas-phase concentrations were always less than 2.4 ppbv and generally less than 1 ppbv. Vertical profiles of  $\text{H}_2\text{O}_2$  in the clear air around clouds and storm systems were highly variable. The concentrations of  $\text{H}_2\text{O}_2$  in the cloud water ranged from the detection limit of 0.3  $\mu\text{M}$  to 112  $\mu\text{M}$ , with the higher values generally occurring in the vicinity of lightning activity. Hydrogen peroxide concentrations in cloud water were well below those calculated to be in Henry's law equilibrium with the gas-phase concentrations of  $\text{H}_2\text{O}_2$  in the cloudy air. This is attributed to the rapid depletion of aqueous-phase  $\text{H}_2\text{O}_2$  as it oxidizes S(IV).

## 1. Introduction

Several oxidants are important in the conversion of sulfur dioxide ( $\text{SO}_2$ ) to sulfuric acid ( $\text{H}_2\text{SO}_4$ ) in the atmosphere. In the gas phase, the hydroxyl radical (OH) is the dominant oxidant (Calvert et al., 1978). In the aqueous phase (i.e., cloud drops and raindrops), the oxidation of  $\text{SO}_2$  can occur through several pathways. If the pH of water is greater than 5 ozone ( $\text{O}_3$ ) is probably the major oxidant, but if the pH is less than 4.5 hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is most likely the dominant oxidant (Penkett et al., 1979). In the Eastern United States, the pH of water from precipitation and clouds is generally less than 4.5 (Ferek et al., 1983; MAP3S/RAINE, 1982; Weathers et al., 1986). Hence, provided the concentration of  $\text{H}_2\text{O}_2$  in the air is sufficiently high, it should be the dominant oxidant in the production of acidic precipitation in this region.

During the autumn of 1984, Heikes et al. (1987) used an automated fluorometric technique

to measure the concentrations of  $\text{H}_2\text{O}_2$  in the gas phase west of the Appalachian Mountains from upstate New York to the Gulf of Mexico. The  $\text{H}_2\text{O}_2$  concentrations, which ranged from the detection limit (0.2 ppbv) to 4.1 ppbv, generally increased with increasing altitude, reaching a maximum near cloud top. There was also a latitudinal variation, with higher concentrations of  $\text{H}_2\text{O}_2$  occurring to the south.

Van Valin et al. (1987) measured gas-phase concentrations of  $\text{H}_2\text{O}_2$  over the south-central United States during February 1987. The  $\text{H}_2\text{O}_2$  concentrations, which ranged from 0.1 ppbv to 1.0 ppbv, also increased from north to south. Although they measured only a small number of vertical profiles, the  $\text{H}_2\text{O}_2$  concentrations generally increased with altitude.

In this paper, we present airborne measurements of both gas-phase concentrations of  $\text{H}_2\text{O}_2$  and concentrations of  $\text{H}_2\text{O}_2$  in cloud water in the vicinity of the Atlantic Coast of the United States. The measurements were obtained aboard

the University of Washington's Convair C-131 research aircraft between late January and early March 1986 on 7 flights offshore of North and South Carolina and one flight off Wallops Island, Maryland. The aircraft flew in and around cumulus clouds on four of these flights, in and around rainbands on three flights, and in and around both cumulus clouds and a shallow rainband on one flight. On 6 of the flights, southwesterly flow from the continent prevailed, while on the other two flights the flow was from the north-northwest but still of continental origin.

## 2. Experimental

A fluorometric method was used to detect both gas phase and aqueous phase peroxide. The instrument used to detect gaseous peroxide is similar to that used by Heikes et al. (1987) and it has been described in detail by Lazrus et al. (1986). In this instrument, the airstream is split into two channels and peroxide is stripped from the air using a collection reagent that flows concurrently with the air through a coil. The stripping coil is close to 100% efficient and is not affected by temperature or pressure (Lazrus et al., 1986). The first channel receives a conditioning reagent and a fluorometric reagent (p-hydroxyphenyl-acetic acid-POPHA) to form a dimer that fluoresces, allowing soluble hydroperoxides to be detected. The second channel receives the conditioning and fluorometric reagents plus an enzyme catalase that destroys only  $\text{H}_2\text{O}_2$ ; this allows organic peroxide to be detected fluorometrically. Hydrogen peroxide is determined as the difference of the two channels. The detection limit of each channel is defined to be three times the standard deviation of the chemical blank. The detection limits for total peroxide and organic peroxide were 0.2 ppbv and 0.1 ppbv, respectively; the detection limit of  $\text{H}_2\text{O}_2$  was 0.2 ppbv. The instrument was calibrated prior to each flight using aqueous  $\text{H}_2\text{O}_2$  standards.

Cloud water samples were collected aboard the aircraft with a slotted-rod collector similar to that described by Mohnen (1980), but enlarged to increase the amount of water collected (Hegg and Hobbs, 1981). Ice hydrometeor samples were collected with a polyethylene-coated aluminium impaction rod (Hegg and Hobbs, 1981). Immedi-

ately after collection, the pH of each sample was measured with a standard pH electrode and then the sample was stored at 4°C until chemical analysis could be carried out. Aqueous hydrogen peroxide plus soluble organic peroxide was measured by adding, immediately after sample collection, a reagent containing the conditioning reagent and the fluorometric reagent mentioned above to an aliquot of each cloudwater sample so that the peroxide would dimerize (Kok et al., 1987). The dimer was then detected with a fluorometer and the amount of total peroxide determined. The detection limit for aqueous  $\text{H}_2\text{O}_2$  was defined as 3 times the standard deviation of the chemical blanks, which was 0.3  $\mu\text{M}$ . While this technique in principle yields only an upper limit for aqueous  $\text{H}_2\text{O}_2$ , the low levels of organic peroxides in the gas phase in this study, coupled with previous studies that reveal generally low levels of organic peroxides in cloud water (Kelly et al., 1985), suggest that the aqueous peroxide measurements we obtained should be very close to the aqueous  $\text{H}_2\text{O}_2$  concentrations.

Cloud interstitial  $\text{SO}_2$  was measured using zinc oxide impregnated filters. The  $\text{SO}_2$  is oxidized to sulfate during extraction of the filter; the sulfate is extracted in distilled deionized water, to which  $\text{H}_2\text{O}_2$  is subsequently added, and measured with an ion chromatograph. The detection limit of this technique depends upon the volume of air pulled through the filter. For 1  $\text{m}^3$  of air, the detection limit of  $\text{SO}_2$  was generally about 0.5 ppbv. The liquid water content of the cloud was measured with a Johnson-Williams liquid water content meter, which has an uncertainty of  $\sim 0.05 \text{ g m}^{-3}$ . Ozone concentrations were measured with a Meloy Labs Model 8410A, which uses a chemiluminescence technique. A description of other instruments aboard the aircraft may be found in Hobbs (1986).

## 3. Results and discussion

### 3.1. Gaseous-phase measurements of hydrogen peroxide

To illustrate the raw data, we show in Fig. 1 measurements of the concentrations of gas-phase total peroxide (upper curve) and organic peroxide (lower curve) as a function of time for a flight on 19 February 1986. The  $\text{H}_2\text{O}_2$  concentration is

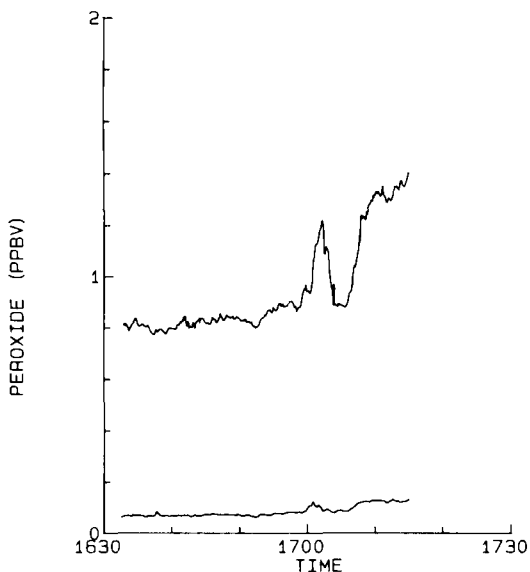


Fig. 1. Concentrations of total peroxide (upper curve) and organic peroxide (lower curve) measured at an altitude of 1.2 km on 19 February 1986 offshore of Wilmington, North Carolina.

taken as the difference between these two curves. All our measurements showed organic peroxide present at concentrations near the detection limit of 0.1 ppbv. Thus, for this data set, organic peroxide concentrations were insignificant compared to  $\text{H}_2\text{O}_2$  concentrations. Therefore, the measurements of total peroxide essentially reflect the concentrations of  $\text{H}_2\text{O}_2$ .

During each flight, the aircraft, which has an average cruise speed of  $80 \text{ m s}^{-1}$ , flew several legs at different constant altitudes in and around the cloud feature of interest. Vertical profiles of  $\text{H}_2\text{O}_2$  concentrations in clear air, averaged over 3 mb intervals, were generated for each of the eight flights. The concentrations for  $\text{H}_2\text{O}_2$  from all eight flights ranged from the detection limit (0.2 ppbv) to 2.4 ppbv.

The 14 February 1986 profile, which was measured in southwesterly flow in the afternoon near small cumulus clouds (cloud base  $\sim 935$  mb, cloud top  $\sim 865$  mb) located offshore of Myrtle Beach and Charleston, South Carolina, showed very low concentrations of  $\text{H}_2\text{O}_2$  (Fig. 2a).

On the 17 February 1986, when the airflow was from the southwest,  $\text{H}_2\text{O}_2$  concentrations

measured near cumulus and stratocumulus clouds (cloud base  $\sim 905$  mb, cloud top  $\sim 800$  mb) in the afternoon offshore between Wilmington and Cape Hatteras, North Carolina, increased from 0.4 ppbv near the surface to 1.3 ppbv at 800 mb (Fig. 2b).

The 19 February 1986 profile (Fig. 2c), which was measured in southwesterly flow in the afternoon near small cumulus clouds (cloud base  $\sim 965$  mb) offshore of Wilmington, North Carolina, shows variable  $\text{H}_2\text{O}_2$  concentrations in the range 0.6–2.0 ppbv.

The 21 February 1986 profile, which was measured in the evening in southwesterly flow near stratocumulus clouds offshore of Wallops Island, Maryland, displays fairly low concentrations ( $\sim 0.6$  ppbv) of  $\text{H}_2\text{O}_2$  near 720 mb, but below cloud base ( $\sim 825$  mb) a hazy layer existed in which the  $\text{H}_2\text{O}_2$  concentrations reached 2.3–2.4 ppbv (Fig. 2d).

The 22 February 1986 profile (Fig. 2e), which was obtained at night in southwesterly flow, shows variable  $\text{H}_2\text{O}_2$  concentrations between 980 and 830 mb, which were measured near a shallow rainband (cloud top  $\sim 950$  mb) located offshore near Myrtle Beach, South Carolina, and Wilmington, North Carolina, and somewhat less variable concentrations from 800 to 700 mb, which were measured near cumulus and cumulonimbus clouds (cloud base  $\sim 765$  mb) offshore of Charleston, South Carolina.

The 24 February 1986 profile of  $\text{H}_2\text{O}_2$  concentrations, which was measured in the evening near a rainband (cloud base  $\sim 900$  mb, cloud top  $\sim 790$  mb) that was located southwest of Cape Hatteras, North Carolina, where light northerly winds prevailed, shows concentrations generally increasing with height from the detection limit of 0.2 to 1.2 ppbv (Fig. 2f).

On 1 March 1986, when measurements were made around midday near a rainband (cloud base  $\sim 903$  mb, cloud top  $\sim 700$  mb) offshore of Cape Hatteras in northerly flow,  $\text{H}_2\text{O}_2$  concentrations were below the detection limit of 0.2 ppbv (Fig. 2g).

The vertical profile of  $\text{H}_2\text{O}_2$  measured in the afternoon on the 6 March 1986 in the vicinity of a prefrontal rainband (cloud base  $\sim 875$  mb) located off Cape Hatteras, North Carolina, shows lower concentrations behind the rainband (B) than ahead of it (A) (Fig. 2h). This was no doubt

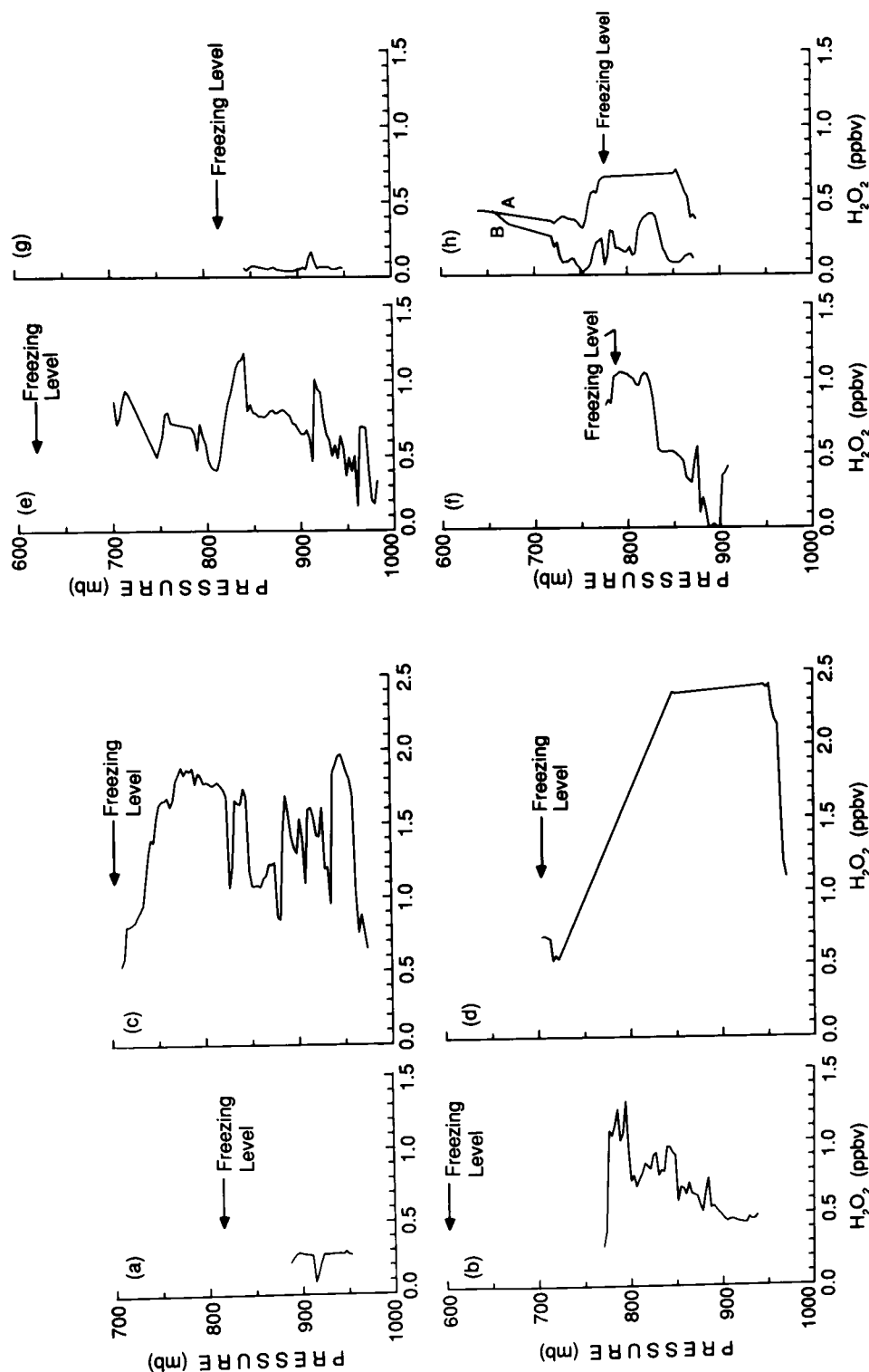


Fig. 2. Vertical profiles of  $\text{H}_2\text{O}_2$  measured in clear air. The  $\text{H}_2\text{O}_2$  concentrations are averaged in the vertical over intervals of 3 mb. (a) From 1400 to 1549 EST on 14 February 1986 offshore of Myrtle Beach and Charleston, South Carolina, near small cumulus clouds. (b) From 1309 to 1700 EST on 17 February 1986 offshore between Wilmington and Cape Hatteras, North Carolina, near cumulus and stratocumulus clouds. (c) From 1132 to 1505 EST on 19 February 1986 offshore of Wilmington, North Carolina, near small cumulus clouds. (d) From 1353 to 1630 EST on 21 February 1986 offshore of Wallops Island, Maryland, near stratocumulus clouds. (e) From 2315 to 0250 EST on 22 February 1986 offshore along the South Carolina Coast near cumulonimbus clouds and a low-altitude shallow rainband. (f) From 1810 to 2145 EST on 24 February 1986 southwest of Cape Hatteras, North Carolina, near a rainband. (g) From 1030 to 1700 GMT on 1 March 1986 offshore of Cape Hatteras, North Carolina, near a rainband. (h) From 1315 to 1710 GMT on 6 March 1986 offshore of Cape Hatteras, North Carolina, ahead of (A) and behind (B) a prefrontal rainband.

due to differences in the characteristics of the airmass. The air in front of the rainband was warm and moist and flowed from the southwest, while behind the rainband, the air was cool and dry and flowed from the west-southwest.

Concentrations of ozone measured during these flights ranged from 50 to 110 ppbv, with the highest values found on 21 February 1986 in a hazy region.

Fig. 3 shows a comparison of our measurements of gaseous  $\text{H}_2\text{O}_2$  in clear air obtained in winter off the East Coast of the United States with those measured west of the Appalachians in autumn by Heikes et al. (1987). Both curves are average concentrations of the median values from each flight measured over height intervals of 500 m. The results indicate that the average concentrations of gaseous  $\text{H}_2\text{O}_2$  may be less in winter than in autumn, although the two sets of measurements are generally within one standard deviation of each other. The lower  $\text{H}_2\text{O}_2$  concentrations in winter are probably due primarily to reduced photochemistry, although cloud effects could also play a role. Interestingly, the measurements of  $\text{H}_2\text{O}_2$  we obtained after sunset (Fig. 2d, e, f) do not reveal any systematic differences from those obtained in daylight (Fig. 2a, b, c, g, h). While this would be expected in clear air, because of the relatively long lifetime of  $\text{H}_2\text{O}_2$ , it is surprising for the cloudy conditions encountered in this study.

Finally, we note that our measurements show considerable spatial and temporal variations in  $\text{H}_2\text{O}_2$  concentrations, which make it difficult to quantify the effects of synoptic conditions on  $\text{H}_2\text{O}_2$  concentrations.

### 3.2. Aqueous-phase measurements of hydrogen peroxide

Table 1 lists the hydrogen peroxide concentrations measured in cloudwater  $[(\text{H}_2\text{O}_2)_\text{c}]$ . The concentrations range from the detection limit (0.3  $\mu\text{M}$ ) to 112  $\mu\text{M}$ . Six cloudwater samples were obtained in the presence of nearby lightning activity; high concentrations of  $\text{H}_2\text{O}_2$  were measured in the cloudwater in four of these six samples. We speculate that the generally high values of  $\text{H}_2\text{O}_2$  measured in the presence of

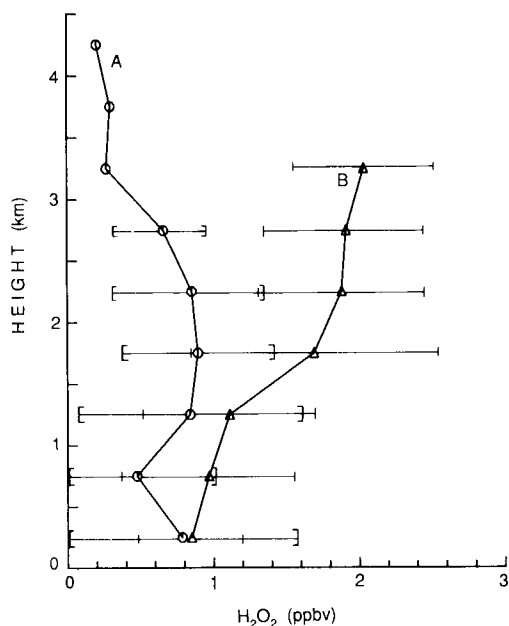


Fig. 3. Average vertical profiles of  $\text{H}_2\text{O}_2$  in clear air. Curve A is from the measurements presented in this paper, which were obtained between 15 January–15 March 1986 off the Carolina Coast. Curve B is from measurements obtained by Heikes et al. (1987) from October–November 1984 west of the Appalachian Mountains. Error bars are shown as horizontal lines.

lightning are due to photochemical reactions producing free radicals (such as OH), which presumably dissolved into cloud droplets and then reacted to produce  $\text{H}_2\text{O}_2$ . Kok (1980) also found elevated  $\text{H}_2\text{O}_2$  concentrations measured from rainwater samples obtained during electrical activity.

### 4. Comparison of hydrogen peroxide concentrations in cloud water and in the interstitial cloudy air

We now assess the extent to which the  $\text{H}_2\text{O}_2$  in the cloud water was in Henry's law equilibrium with the  $\text{H}_2\text{O}_2$  in the interstitial cloudy air.

Following Seinfeld (1986), we define the fraction (R) of the total  $\text{H}_2\text{O}_2$  in a cloud that is in aqueous solution as:

$$R \equiv \frac{\text{concentration of } \text{H}_2\text{O}_2 \text{ in cloud water}}{\text{concentration of } \text{H}_2\text{O}_2 \text{ in cloud water} + \text{concentration of } \text{H}_2\text{O}_2 \text{ in interstitial air}}, \quad (1)$$

Table 1. *Data Set. See text for definitions of symbols*

Date (1986)	Type of cloud	(H <sub>2</sub> O <sub>2</sub> ) <sub>L</sub> ( $\mu$ M)	(H <sub>2</sub> O <sub>2</sub> ) <sub>IG</sub> (ppbv)	(SO <sub>2</sub> ) <sub>IG</sub> (ppbv)	(SO <sub>2</sub> ) <sub>IG</sub> (H <sub>2</sub> O <sub>2</sub> ) <sub>IG</sub>	pH of cloudwater	Liquid water content (g m <sup>-3</sup> )	Air temperature (K)	Pressure* (atm)
18 January	rainband	0.3	—	—	—	—	—	270	0.68
19 January†	rainband	8.3	—	0.7	—	4.8	—	267	0.60
26 January	cumulus	5.5	—	—	—	3.4	—	276	0.88
26 January	cumulus	7.0	—	—	—	4.9	—	266	0.62
14 February	small cumulus	16.0	—	—	—	3.7	0.1	277	0.85
15 February	rainband	7.3	—	—	—	5.6	—	271	0.72
17 February	stratocumulus	26.0	0.6	0.7	1.2	3.7	0.1	282	0.86
17 February	stratocumulus	22.0	0.5	0.7	1.4	4.0	0.3	279	0.78
17 February	stratocumulus	10.0	0.3	—	—	4.3	0.6	278	0.77
21 February	stratocumulus	22.0	0.6	2.2	3.7	3.6	0.2	274	0.71
22 February†	cumulonimbus	112.0	0.9	—	—	4.4	0.1	275	0.71
22 February†	cumulonimbus	12.0	0.3	≤ 0.4	≤ 1.3	4.5	0.8	277	0.74
24 February	rainband	DL‡	—	—	—	3.5	0.1	274	0.85
24 February	rainband	DL	—	—	—	4.1	0.3	269	0.78
26 February	rainband	DL	—	—	—	4.8	—	267	0.72
26 February	rainband	DL	—	—	—	4.3	—	267	0.72
27 February	rainband	DL	—	—	—	3.8	0.1	271	0.91
1 March	rainband (ice sample)	6.1	0.5	—	—	5.1	< 0.1	266	0.71
1 March	rainband	DL	0.4	2.7	6.8	4.2	< 0.1	276	0.87
1 March	rainband	DL	0.5	2.7	5.4	3.9	0.1	274	0.84
6 March	rainband	4.9	—	—	—	4.4	0.1	269	0.71
6 March	rainband (ice sample)	5.1	0.3	—	—	5.6	< 0.1	263	0.63
6 March	rainband	8.0	≤ 0.2	0.9	≥ 4.5	4.1	0.1	274	0.80
6 March	rainband	7.0	≤ 0.2	—	—	3.9	0.3	272	0.77
13 March†	cumulus	90.0	—	—	—	4.4	0.1	289	0.91
13 March†	cumulus	65.0	—	—	—	4.8	0.2	286	0.84
13 March†	cumulus	47.0	—	—	—	5.2	0.1	279	0.73

\* 1 atm = 101325 Pa.

† Samples taken near lightning.

‡ DL = Detection limit (0.3  $\mu$ M).

where all the concentrations in (1) are expressed as moles per liter of air. If (H<sub>2</sub>O<sub>2</sub>)<sub>L</sub> is the concentration of H<sub>2</sub>O<sub>2</sub> in the cloud water in moles per liter of water, (H<sub>2</sub>O<sub>2</sub>)<sub>IG</sub> is the mixing ratio of the H<sub>2</sub>O<sub>2</sub> in the interstitial air, and LWC is the liquid water content of the cloud (in liters of water per liter of air), (1) may be written as

$$R_p = \frac{(H_2O_2)_L (LWC)}{p(H_2O_2)_{IG}/RT + (H_2O_2)_L (LWC)}, \quad (2)$$

where  $p$  and  $T$  are the total pressure and temperature of the air and  $R$  is the gas constant. We may use (2) together with the measurements listed in Table 1 to calculate values for  $R_p$ ; we will refer to those values as  $R_{\text{measured}}$ .

If the H<sub>2</sub>O<sub>2</sub> in the cloud water were in Henry's law equilibrium with the H<sub>2</sub>O<sub>2</sub> in the cloudy interstitial air:

$$(H_2O_2)_L = K_H (H_2O_2)_{IG}, \quad (3)$$

where  $K_H$  is the Henry's law coefficient for H<sub>2</sub>O<sub>2</sub> in water (we use values for  $K_H$  given by Lind and Kok, 1986). By combining (2) and (3) we can calculate a value for  $R_p$  for the equilibrium situation, which would be given by:

$$R_{\text{equilibrium}} = \frac{K_H (LWC)}{1/RT + K_H (LWC)} \quad (4)$$

Shown in Fig. 4 are the values of  $R_{\text{measured}}$  and  $R_{\text{equilibrium}}$  as a function of liquid water content. It

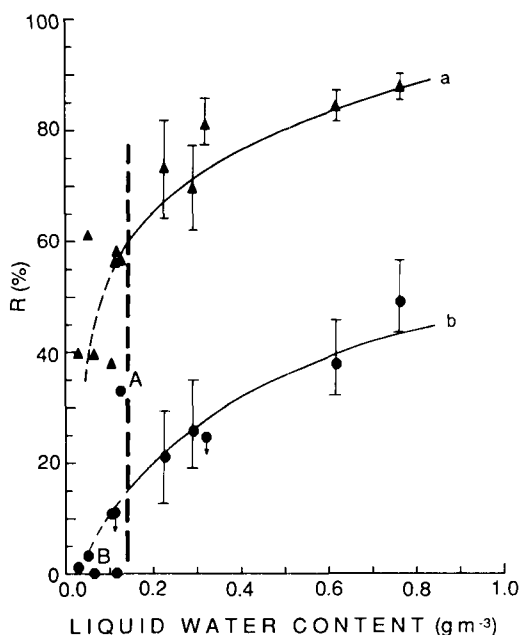


Fig. 4.  $R_{\text{equilibrium}}$  (curve a) and  $R_{\text{measured}}$  (curve b) versus liquid water content. The measurement indicated by point A was obtained near a thunderstorm and the measurement indicated by point B was for a melted ice sample. An arrow attached to a data point indicates that the concentration of  $\text{H}_2\text{O}_2$  in the aqueous phase was below the detection limit of  $0.3 \mu\text{M}$ . Error bars are shown by the vertical lines. Values plotted to the left of the vertical dashed line are highly uncertain due to low liquid water contents. The curves shown are rough fits to the data points.

can be seen that  $R_{\text{equilibrium}}$  is always greater than  $R_{\text{measured}}$ , indicating that the concentrations of  $\text{H}_2\text{O}_2$  in the cloudwater were always below the Henry's law equilibrium value. This is also seen in Fig. 5, where the ratio of  $R_{\text{measured}}$  to  $R_{\text{equilibrium}}$  is plotted against liquid water content. (Note that the point marked A in Figs. 4 and 5, which appears anomalous, was measured in the presence of lightning. As mentioned previously, this is a possible explanation for the anomalous character of point A. In any case, both point A and the other points at or below a liquid water content of  $\sim 0.1 \text{ g m}^{-3}$  are highly uncertain.) Fig. 5 shows that the  $\text{H}_2\text{O}_2$  in cloud water approaches (but does not reach) Henry's Law equilibrium as the liquid water content of the cloud increases.

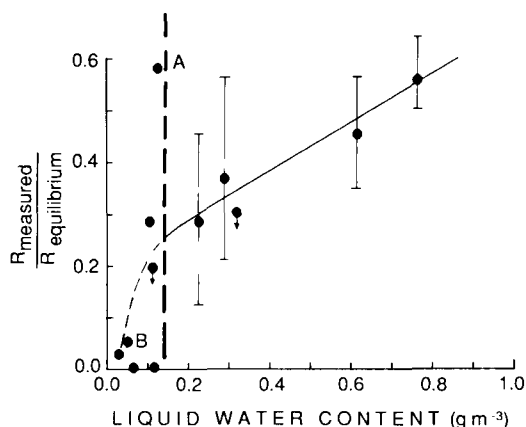


Fig. 5. As for Fig. 4 for  $R_{\text{measured}}/R_{\text{equilibrium}}$  versus liquid water content.

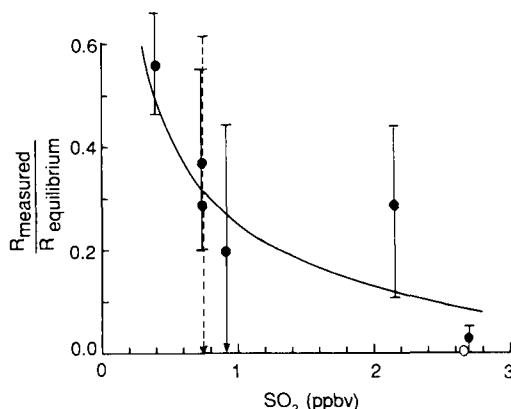


Fig. 6. As for Fig. 4 but for  $R_{\text{measured}}/R_{\text{equilibrium}}$  versus interstitial  $\text{SO}_2$ . All points for which  $\text{SO}_2$  values are available are plotted. The open hexagon is a highly uncertain point due to a low liquid water content.

The sub-equilibrium concentrations of aqueous  $\text{H}_2\text{O}_2$  suggest the presence of an aqueous sink that depletes the  $\text{H}_2\text{O}_2$  faster than it can be transported to and/or through the cloud droplets. As noted by Daum et al. (1984), one such sink is the reduction of  $\text{H}_2\text{O}_2$  by  $\text{S(IV)}$ . In this case, one would expect to see the ratio of  $R_{\text{measured}}$  to  $R_{\text{equilibrium}}$  vary inversely with interstitial  $\text{SO}_2$  concentrations. Such an inverse relationship is suggested by our data set (Fig. 6).

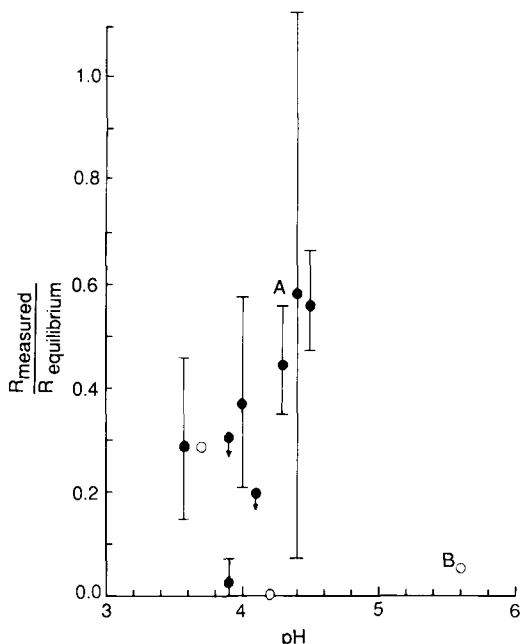


Fig. 7.  $R_{\text{measured}}/R_{\text{equilibrium}}$  versus the pH of the cloud water. Open symbols represent highly uncertain points due to low liquid water contents.

If the above explanation for the sub-equilibrium  $\text{H}_2\text{O}_2$  concentrations in cloud water is correct, then the aqueous  $\text{H}_2\text{O}_2$ -S(IV) reaction would have to be mass-transport limited. Application of the theory for mass transport of gases to and through droplets (cf. Schwartz and Freiberg, 1981) shows that the system is primarily limited by the transport of  $\text{H}_2\text{O}_2$  within the droplets.

A further inference follows from our hypothesis that the reduction of  $\text{H}_2\text{O}_2$  by S(IV) is responsible for the non-equilibrium concentrations of  $\text{H}_2\text{O}_2$  in cloud water. At low pH values,  $\text{H}_2\text{O}_2$  is readily depleted by reaction with S(IV). However, at high pH values, several other oxidants (e.g., ozone) compete to react with S(IV). Therefore, at high pH values more  $\text{H}_2\text{O}_2$  should be present in cloud water and thus the

$\text{H}_2\text{O}_2$  concentrations should more nearly approach the concentrations predicted by Henry's Law. Shown in Fig. 7 are values of  $R_{\text{measured}}/R_{\text{equilibrium}}$  versus pH for our data set. While the data are not inconsistent with our hypothesis, the measurement uncertainties preclude any definite conclusions on this point.

## 5. Summary and conclusions

In this paper we have described measurements of the  $\text{H}_2\text{O}_2$  concentrations in air and in cloud water on the east coast of the United States in winter. Gaseous organic peroxide concentrations were found to be insignificant compared to hydrogen peroxide concentrations. Gas phase  $\text{H}_2\text{O}_2$  concentrations measured in clear air ranged from the detection limit (0.2 ppbv) to 2.4 ppbv, and they varied greatly in space. Aqueous phase  $\text{H}_2\text{O}_2$  concentration ranged from the detection limit (0.3  $\mu\text{M}$ ) to 112  $\mu\text{M}$ .

Our measurements of the concentrations of  $\text{H}_2\text{O}_2$  in air are systematically lower than those measured over the Eastern United States in autumn by Heikes et al. (1987). We attribute this to lower photochemical production rates in winter and to possible cloud effects.

When lightning was present,  $\text{H}_2\text{O}_2$  concentrations in the cloud water was considerably elevated. This was probably due to the production of free radicals by lightning.

The  $\text{H}_2\text{O}_2$  concentrations in the cloud water were always less than those predicted by Henry's Law. We attribute this to the depletion of  $\text{H}_2\text{O}_2$  in cloud water due to it serving as an oxidant for S(IV).

## 6. Acknowledgments

This work was supported by the National Science Foundation under grant ATM-8419000. NCAR is supported by the National Science Foundation.

## REFERENCES

- Calvert, J. G., Su, F., Bottenheim, J. W. and Strausz, O. P. 1978. Mechanisms of the homogeneous oxidation of sulfur dioxide in the troposphere. *Atmos. Environ.* 12, 197-226.
- Daum, P. H., Kelly, R. J., Schwartz, S. E. and Newman, L. 1984. Measurements of the chemical composition of stratiform clouds. *Atmos. Environ.* 18, 2671-2684.

- Ferek, R. J., Lazrus, A. L., Haagenson, P. L. and Winchester, J. W. 1983. Strong and weak acidity of aerosols collected over the Northeastern United States. *Environ. Sci. Technol.* 17, 315–324.
- Hegg, D. A. and Hobbs, P. V. 1981. Cloud water chemistry and the production of sulfates in clouds. *Atmos. Environ.* 15, 1597–1604.
- Hobbs, P. V. 1986. Field studies of cloud chemistry and the relative importance of various mechanisms for the incorporation of sulfate and nitrate into cloud water. In *Chemistry of multiphase atmospheric systems* (ed. W. Jaeschke). *NATO ASI Series, Vol. G6*. Berlin: Springer-Verlag, 191–211.
- Heikes, B. G., Kok, G. L., Walega, J. G. and Lazrus, A. L. 1987.  $\text{H}_2\text{O}_2$ ,  $\text{O}_3$  and  $\text{SO}_2$  measurements in the lower troposphere over the eastern United States during fall. *J. Geophys. Res.* 92, 915–931.
- Kelly, T. J., Daum, P. H. and Schwartz, S. E. 1985. Measurements of peroxides in cloud water and rain. *J. Geophys. Res.* 90, 7861–7871.
- Kok, G. L. 1980. Measurements of hydrogen peroxide in rainwater. *Atmos. Environ.* 14, 653–656.
- Kok, G. L., Thompson, K., Lazrus, A. L. and McLaren, S. E. 1986. Derivatization technique for the determination of peroxides in precipitation. *Anal. Chem.* 58, 1192–1194.
- Lazrus, A. L., Kok, G. L., Lind, J. A., Gittin, S. N., Heikes, B. G. and Shetter, R. E. 1986. Automated fluorometric method for hydrogen peroxide in air. *Anal. Chem.* 58, 594–597.
- Lind, J. A. and Kok, G. L. 1986. Henry's law determination for aqueous solutions of hydrogen peroxide, methyl hydroperoxide, and peroxyacetic acid. *J. Geophys. Res.* 91, 7889–7896.
- MAP3S/RAINE. 1982. The MAP3S/RAINE precipitation chemistry network: Statistical overview for the period 1976/1980. *Atmos. Environ.* 16, 1603–1631.
- Mohnen, V. 1980. Cloud water collection from aircraft. *Atmos. Tech.* 12, 20–25.
- Penkett, S. A., Jones, B. M. R., Brice, K. A. and Eggleton, A. E. J. 1979. The importance of atmospheric ozone and hydrogen peroxide in oxidizing sulphur dioxide in cloud and rain water. *Atmos. Environ.* 13, 123–137.
- Schwartz, S. E. and Freiberg, J. E. 1981. Mass-transport limitation to the rate of reaction of gases in liquid droplets: Application to oxidation of  $\text{SO}_2$  in aqueous solutions. *Atmos. Environ.* 15, 1129–1144.
- Seinfeld, J. H. 1986. *Atmospheric Chemistry and Physics of Air Pollution*. New York: John Wiley and Sons, 235–236.
- Van Valin, C. C., Ray, J. D., Boatman, J. F. and Gunter, R. L. 1987. Hydrogen peroxide in air during winter over the south-central United States. *Geophys. Res. Letts.* 14, 1146–1149.
- Weathers, K. C., Likens, G. E., Bormann, F. H., Eaton, J. S., Bowden, W. B., Anderson, J. L., Cass, D. C., Galloway, J. N., Keene, W. C., Kimball, K. D., Hutch, P. and Smiley, D. 1986. A regional acidic cloud/fog water event in the Eastern United States. *Nature*. 319, 657–658.