Tellus (1991), *43B*, 280–290

Measurements of the partitioning of hydrogen peroxide in a stratiform cloud*

By KEVIN J. NOONE, JOHN A. OGREN, K. BIRGITTA NOONE and ANNELI HALLBERG, *Department of Meteorology, Stockholm University, S-106 91 Stockholm, Sweden,* and SANDRO FUZZI and JOHN A. LIND, *Istituto FISBAT, Consiglio Nazionale delle Ricerche, Via de'Castagnoli 1, 40126 Bologna, Italy*

(Manuscript received 14 May 1990; in final form 5 October 1990)

ABSTRACT

Simultaneous measurements of hydrogen peroxide in cloud droplets and in the air in which the droplets were suspended are presented. In addition, a description of the new technique used to make the measurements is also presented. The ratio of the measured cloudwater concentration to the equilibrium cloudwater concentration predicted using Henry's law and the measured gas-phase hydrogen peroxide was 0.64 (S.D = 0.32, $n = 74$). Analysis of both random and potential systematic errors indicate that while this ratio was statistically different from unity, the difference was not considered to be substantial. Henry's law appeared to have been valid for hydrogen peroxide in the ambient cloud we studied.

1. Introduction

Hydrogen peroxide (H_2O_2) has been postulated to be an important (if not the dominant) oxidant of SO_2 in aqueous solution (Penkett, et al., 1979; Hegg, 1989). Because of its role as an oxidant in the atmospheric liquid phase, it is necessary to know not only the concentrations of H_2O_2 in the atmosphere, but also the way it is partitioned between the gas and liquid phases. There have been a number of investigations into quantifying the amount of H_2O_2 in the atmosphere. These have been relatively recent, since reliable instrumentation for measuring atmospheric H_2O_2 concentrations has not been available for more than roughly a decade. Table 1 presents a summary of these investigations. This is intended to illustrate typical measured concentrations, and is not intended to be a comprehensive literature review. For the most part, these measurements have been made in a single phase; either in the liquid phase or in the gas phase. In many of these studies, H_2O_2 concentrations in the phase not measured were calculated assuming equilibrium conditions for H_2O_2 (i.e., that Henry's law was an accurate description of the partitioning between phases). In the last study included in the table (Barth, et al., 1989), simultaneous samples of both gas-phase H_2O_2 as well as liquid-phase concentrations in cloudwater were taken. In this case, the partitioning of H_2O_2 between the gas phase and the liquid-phase cloudwater could be calculated directly from the measurements. An interesting result of these measurements was that the H_2O_2 concentrations in the cloudwater were always below the Henry's law equilibrium value (for the purposes of brevity, this discrepancy will be referred to as a negative deviation from Henry's law). Another interesting observation was that the cloudwater concentrations became closer to the Henry's law predictions as the liquid water content of the cloud increased.

There are a number of potential explanations for negative deviations from Henry's law. If there is a sufficient concentration in the liquid phase of a compound that can be oxidized by H_2O_2 (such as SO_2) and if the reaction is sufficiently fast, then it is possible that peroxide concentrations in the cloudwater would be lower than expected from Henry's law. It has been observed (Heikes, et al., 1987) that gas-phase H_2O_2 concentrations just above cloud top were higher than inside the cloud.

---

* Contribution number 621.

Table 1. *Examples of hydrogen peroxide measurements*

Ref.	Gas phase (ppbv)	Cloudwater (μM)	Rainwater (μM)
Kok et al. (1978)	10–30		
Zika et al. (1982)			9–75
Daum et al. (1984)		<1–127	
Yoshizumi et al. (1984)			0.2–31
Calvert et al. (1985)	1–3		
Römer et al. (1985)		<1.2–45	0.5–62
Kelly et al. (1985)		<0.1–110	<0.1–63
Tanner et al. (1986)	<0.1–2		
Klockow & Jacob (1986)			0–65
Heikes et al. (1987)	0.2–4.1		
Van Valin et al. (1987)	<0.1–1		
Daum et al. (1987)		0.08–1	
Chandler et al. (1988)		0.2–2	
Olszyna et al. (1988)	0.02–2.6	<0.04–247	<0.04–39.8
Heikes et al. (1988)	<0.03–1.2		
Barth et al. (1989)	<0.2–0.9	0.3–112	
Radojevic et al. (1990)		0.3–80	

If out-of-cloud gas-phase concentrations of H_2O_2 are higher than in-cloud values, then entrainment of out-of-cloud air would (at least temporarily) cause a negative deviation from Henry's law. A third possibility is a rapid production of gas-phase H_2O_2 in cloud. For disequilibrium to exist, whatever the cause, the source or sink processes must be sufficiently fast that the droplets cannot adjust to the concentration changes caused by these processes. In the absence of such rapid source or sink mechanisms, one would expect that Henry's law would hold.

In this paper, we present simultaneous measurements of H_2O_2 in cloud droplets and in the air in which the droplets were suspended. The investigation had two goals; to determine whether the combination of the CVI (Counterflow Virtual Impactor: described later) and the fluorometric peroxide measurement techniques were capable of making rapid, in-situ measurements of peroxide in cloudwater, and to determine the partitioning of H_2O_2 between the gas and liquid phases in ambient clouds by direct measurements of both phases.

2. Experimental description

The experiment took place in the summer of 1989 at a field laboratory operated by the Department of Meteorology of Stockholm University. The laboratory is located near the summit of Mt. Åreskutan (63°26′N, 13°06′E, alt. 1250 m). The site is essentially uninfluenced by local contamination, and is considered to be representative of air transported over central Scandinavia (Ogren and Rodhe, 1986). The most prevalent cloud type at the site is stratocumulus.

2.1. *Sampling inlet: liquid phase*

Two sampling inlets were used to differentiate between cloud droplets and interstitial air. Cloud droplets were sampled using a counterflow virtual impactor (CVI; Ogren, et al., 1985, Noone, et al., 1988). The CVI inertially separates cloud droplets larger than a certain size (called the 50% cut radius, R_{50}) from smaller aerosol particles and interstitial gases. Once sampled, the cloud droplets are evaporated inside the sampling probe. After evaporation, any non-volatile material previously in the cloud droplets is left behind as a residual aerosol particle, and any volatile species (i.e., water, hydrogen peroxide) are driven into the gas phase. The water vapor concentration inside the CVI system is measured using a double-beam Lyman-α-hygrometer (Zuber and Witt, 1987). This corresponds to the liquid water content (LWC: g m^{-3}) of the droplets in the cloud larger than the cut size of the CVI. The number concentration of the residual aerosol particles (N: cm^{-3})

corresponding to the number of cloud droplets larger than the CVI's cut size is measured using a condensation nucleus counter (TSI Model 3760). It is assumed that a single droplet results in a sngle residual aerosol particle after evaporation. The concentration of H_2O_2 in the cloud droplets (H_2O_2 (cw)) was measured in the gas phase in the CVI, since any H_2O_2 dissolved in the cloud droplets will be driven into the gas phase when the droplets are evaporated inside the CVI. Two CVI probes were used during the experiment. One CVI inlet was dedicated to measurement of cloudwater H_2O_2. The interior plumbing of this CVI used the same type of teflon tubing as the gas-phase inlet to minimize potential losses of H_2O_2 in the sampling lines. The second CVI was used to measure the microphysical characteristics of the cloud. Both inlets operated at a R_{50} of 2 μm; that is, they sampled cloud droplets 2 μm radius and larger. The two CVI inlets, as well as the drop-free inlet were mounted side-by-side on the roof of the laboratory building.

2.2. *Sampling inlet: gas phase*

H_2O_2 concentrations in the gas phase were made using an inlet designed to be free of liquid droplets. This inlet consisted of 2 concentric tubes; the interior tube was $\frac{1}{4}''$ teflon, and served as the sampling tube for the peroxide instrument. The outer tube was $\frac{1}{2}''$ PVC. Droplet-laden air was pulled through the $\frac{1}{2}''$ tube at a flow rate of 47 lpm. The tube went into a 90° bend, through which the $\frac{1}{4}''$ teflon tube was introduced. Droplets larger than approximately 6 μm radius should have impacted in this bend. The air then passed through the annular space between the two tubes with a velocity of 98 m s^{-1}. Since the inlet to the interior teflon sampling tube was oriented opposite to this air flow, any droplets entering this tube would have to have made a 180° change in direction. This means that only droplets with radii less than approximately 1–2 μm could have entered the sampling tube. As a result of impaction of cloud droplets in the inlet, the interior tube walls of the inlet were coated with a layer of water. This layer of water flowed down the walls of the outer tube and was ejected out of the blower. Because of the high (98 m s^{-1}) velocity in the inlet, it is highly unlikely that any of this water could have been entrained into the interior sampling tube. Mechanically produced droplets from this water layer would have been too large to enter the sampling tube. Since the sampling tube was teflon, any entrained liquid should have formed drops in the tube. No such drops were observed during the experiment. It is possible that there could have been evaporation from the water layer. This could potentially release H_2O_2 from the cloudwater into the gas phase. If this were to occur, it would cause a systematic overestimation of the gas-phase concentration. The residence time for air in the inlet up to the entrance to the sampling tube was less than 20 ms. This short residence time, combined with the fact that the air entering the inlet was saturated with respect to water, lead us to believe that evaporation effects, if present, would have been small.

The CVI and gas inlets were compared in cloud-free air prior to the sampling period. This entailed pulling roughly 2 lpm of air through both inlets and measuring the total peroxide concentration in both sample streams. It should be noted that for this comparison, the CVI was not operating as a virtual impactor; rather we were simply pulling sample air through the CVI plumbing to determine whether there were any discrepancies between the inlets. From these tests, it appeared that the CVI inlet showed approximately 10% higher H_2O_2 concentrations relative to the gas inlet. This discrepancy will be the sum of errors due to any differences in the H_2O_2 sampling efficiency of the two inlets, as well as errors in flow measurements between the two systems. No correction for this difference is made to the data presented here. We could not specifically test whether any losses of H_2O_2 occurred when the droplets were evaporated in the CVI. The radius of mean mass of the sampled droplets was between 7 and 15 μm (discussed below). The evaporation time for droplets of this size under conditions found in the CVI is calculated to be approximately 500 ms (Ferron and Soderholm, 1990). Given the low levels of SO_2 at the site and the rapid evaporation time of the droplets, we anticipate that losses of H_2O_2 in the evaporation step itself would have been insignificant.

2.3. *H_2O_2 measurements*

H_2O_2 was measured using a fluorometric method utilizing a peroxidase enzyme (Lazrus, et al., 1986; Heikes, et al., 1987). The particular instrument used to make these measurements normally acquires two channels of data. One channel corresponds to total hydrogen peroxide plus some fraction of the organic peroxide present, and the other channel corresponds to the organic peroxide alone. Since only two channels were available (one for the CVI and one for the gas-phase peroxide) continuous monitoring of the organic peroxide concentration was impossible. Instead, organic peroxide was measured on 4 separate occasions over the course of the experiment. The average value for the organic peroxide molar ratio was 80 pptv ± 15%. This value was subtracted from the gas-phase total peroxide measurement to give a gas-phase H_2O_2 concentration. The CVI signal was also a total peroxide measurement, but the differences in solubilities between H_2O_2 and organic peroxides make it nearly certain that this signal corresponds to H_2O_2 alone. The baseline noise in both channels of the instrument was 2 to 3 pptv. The zero reproducibility over 10 zeroing cycles (an indication of instrumental drift) was approximately 5 pptv.

3. Results

The sampling period described here covers roughly three hours on 30 July, 1989. During this period, the wind at the site was from the WNW at 2–3 m s^{-1}. The ambient temperature was relatively steady at 4–6° C, and the pressure at the site was between 855 and 864 mb. The clouds were quite variable over the sampling period. One some occasions, the site was close to or above cloud top, while at other times, cloud base moved above the level of the station. Observations of cloud base height were made at 20-min intervals by the personnel operating a nearby aerial tramway. Cloud base varied from approximately 100 m below the station at the beginning of the sampling period, to approximately 150 m above the station after sampling was terminated. The clouds were also patchy, since during at least 2 of the 20-min periods during sampling, the valley terminus of the tramway (approximately 3 km south of the laboratory in the horizontal sense) was in sun, while at the same time, the laboratory was in cloud.

Fig. 1 presents a time series of two of the microphysical parameters measured in the cloud; the number of droplets 2 μm and larger (N_d, cm^{-3}), and the corresponding liquid water content (LWC, g m^{-3}). The shaded areas on the time series represent periods when calibrations or zeros of the instrumentation was performed. The liquid water content of the cloud varied from roughly

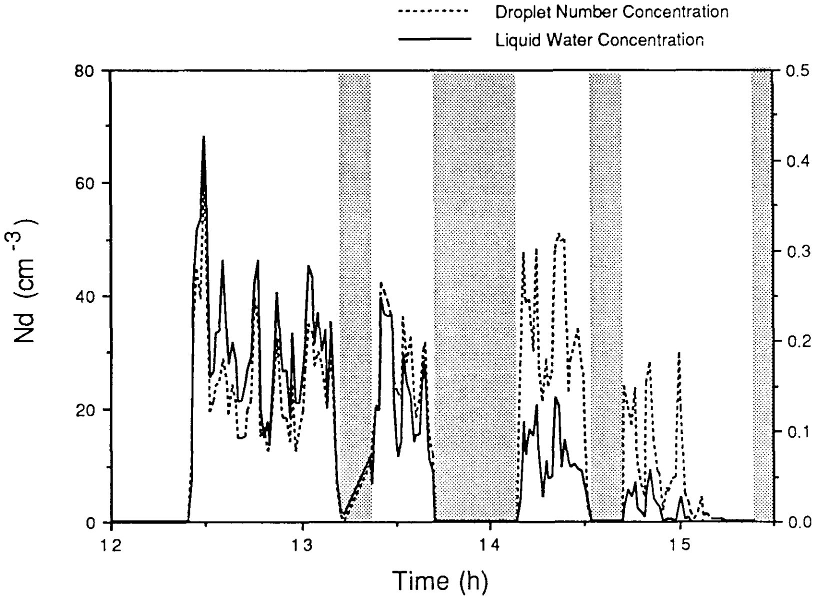

Fig. 1. Time series of droplet number (N_d) and liquid water content (LWC). The shaded areas represent periods when one of the instruments was being zeroed or calibrated.

0.2 g m^{-3} at the beginning of the period to some tens of mg/m^3 at the end of the period when the clouds were dissipating. The number of droplets in the cloud showed relatively less of a decrease over time than did LWC. The number of droplets varied from roughly 20–50/cm^3 over most of the sampling period. As a consequence, the radius of mean mass of the droplets in the cloud decreased from 15 μm at the beginning of the period to 7 μm towards the end. Droplet number concentrations and liquid water concentrations of these magnitudes are typical for arctic stratus clouds (Tsay and Jayaweera, 1984). Previous chemical measurements at the site (Ogren and Rodhe, 1986) have shown that it is often influenced by very clean arctic air masses. Given that the wind speed was between 2 and 3 m s^{-1}, the length scale of the peak-to-peak variations in N_d and LWC was roughly 1 km.

3.1. Peroxide measurements: time series

The time series of hydrogen peroxide measurements is presented in Fig. 2. The solid diamonds represent the liquid-phase concentrations expressed as a gas-phase equivalent mole fraction (pptv). The hollow squares represent the simultaneous gas-phase mole fraction measurements. The solid squares represent the total mole fraction, defined as the sum of the measured gas- and liquid-phase mole fractions. Gaps in the data series represent intervals when the instruments were off-line for calibration or zeroing. There is an apparent upward trend in these data; the total H_2O_2 concentration increased from approximately 100 pptv to approximately 150 pptv over the sampling period. Superimposed upon this trend was also a good deal of variation over shorter time scales. The reasons for this short-term variation are difficult to discern. Because of our fixed location on the mountain, we were exposed to clouds blown past the site. These clouds had varying cloud-base heights and varying cloud-top heights, making our location within the cloud uncertain. The variation in LWC and N_d over the sampling period indicate that entrainment processes were active. Without simultaneous measurements of H_2O_2 outside the clouds, it is impossible to determine what the possible consequences of entrainment are with regard to in-cloud H_2O_2.

One particular period of interest with regard to out-of-cloud processes is the interval from 12:54 to 13:11. Just before this period, at 12:41, the visibility outside the laboratory was limited to less than 100 m. At 12:54, the disk of the sun became visible through the cloud. At 13:03, patches of blue sky began to become visible. At 13:07, the outlines of the surrounding clouds became visible; the

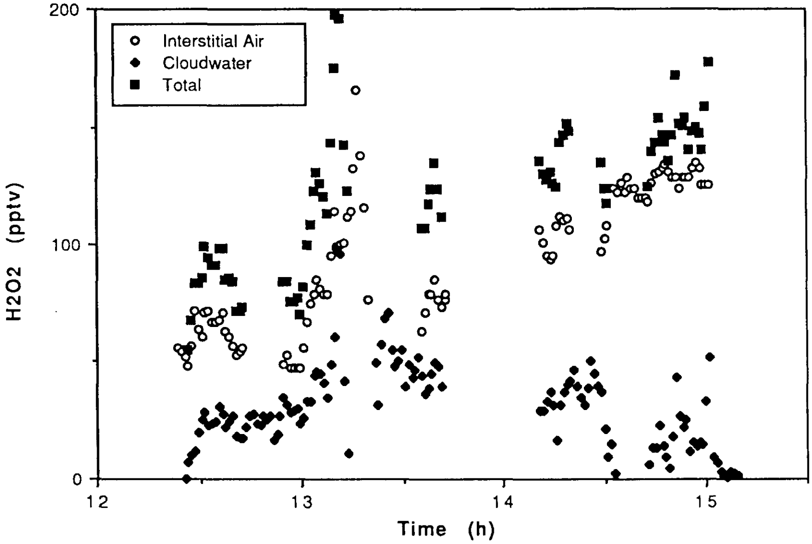

Fig. 2. Time series of H_2O_2 molar ratios. The solid diamonds represent the liquid-phase measurements, the hollow circles represent the gas-phase measurements, and the solid squares represent the sum of the gas and liquid molar ratios.

laboratory appeared to be close to cloud top. At 13:09, the valley below the laboratory became visible, and at 13:11, the cloud dissipated. Looking at the time series, there is a steady increase in both gas-phase and liquid-phase peroxide starting at around 13:00. At 13:00, the gas-phase concentration was 56 pptv, while the liquid-phase concentration was 41 pptv. At 13:07, when other clouds became visible and it appeared that the laboratory was near cloud top, the gas-phase concentration was 79 pptv and the liquid-phase concentration was 35 pptv. At 13:10, while the LWC and N_d values still reflected in-cloud values (0.125 g m^{-3} and 16.3 cm^{-3} respectively) the gas-phase concentration had increased to 99 pptv and the liquid-phase concentration was also 99 pptv. Over the period 13:00 to 13:10, then, the total peroxide concentration increased from 82 pptv to 198 pptv. This observation is consistent with previous observations (Heikes, et al., 1987) that gas-phase H_2O_2 concentrations at cloud top were often higher than in-cloud concentrations. In addition, both gas- and liquid-phase concentrations increased near cloud top, indicating that the droplets also reflected the increased H_2O_2 levels.

3.2. Peroxide measurements: partitioning

The partitioning of H_2O_2 between the gas and liquid phases can be examined by dividing the measured cloudwater hydrogen peroxide concentration ($H_2O_{2(cw)}$) by the cloudwater concentration predicted from the measured gas-phase hydrogen peroxide concentration and Henry's law ($H_2O_{2(eq)}$). If Henry's law holds, this ratio should be 1:

$$\frac{H_2O_{2(cw)}}{H_2O_{2(eq)}} = \frac{\text{meas}[H_2O_2]_{cw}}{\text{meas}[H_2O_2]_g^* \, HLRT} = 1. \qquad (1)$$

Here,

$\text{meas}[H_2O_2]_{cw}$ = measured aqueous-phase concentration,

$\text{meas}[H_2O_2]_g$ = measured gas-phase concentration,

H = Henry's law constant,

L = liquid water content,

R = gas constant,

T = temperature.

Ratios less than one indicate a deficiency of aqueous-phase H_2O_2. Ratios greater than one indicate a surplus of aqueous-phase H_2O_2.

Fig. 3a presents a time series of this partitioning ratio. The mean value over the sampling period was 0.64 (SD: 0.31, N: 74); that is, on the average, the aqueous-phase H_2O_2 concentration was approximately 36% below the equilibrium value. The ratio measurements are also presented as the leftmost of the box plots in Fig. 3b. The standard deviation of 0.31 indicates a fair amount of variation in this ratio, as is illustrated by the dotted lines in Fig. 3a. This mean value was calculated without the two circled points in Fig. 3a. These points represent values when the cloud was dissipating, and the associated N_d and LWC values are quite low.

Interpretation of this ratio requires an estimate of the uncertainties in the measurements. The experimental uncertainty (95% confidence level) in the Henry's law constant used to calculate the predicted liquid-phase concentrations is ±8.3% (Link and Kok, 1986). In the temperature range that our observations were made, the partitioning of H_2O_2 is a strong function of temperature (roughly 10% change in partitioning per degree Celsius between 0°C and 5°C). The standard deviation of the difference between our temperature measurements and those taken by the Swedish Meteorological and Hydrological Institute at the site is 1°C, implying a approximately 10% random error in our calculated equilibrium liquid-phase H_2O_2 concentrations. The error in our LWC measurements for this experiment (estimated by comparisons of the Lyman-α instruments with an Assman hygrometer) is approximately 7%. As mentioned previously, we could not continuously monitor the gas-phase organic peroxide concentrations during these measurements. We subtracted a constant organic peroxide amount from the total gas-phase peroxide measurement to obtain gas-phase H_2O_2. The standard deviation in this organic peroxide value was ±15%. The standard deviation of 5 calibrations of total peroxide was 8%. In general, the concentration of a given substance measured in the CVI is enriched relative to ambient concentrations (Noone, 1987). In this experiment, this enrichment factor was 10. The relative standard deviation of this factor (SD/mean: measured during a different experiment) was 4%.

A Monte Carlo-type error analysis was carried

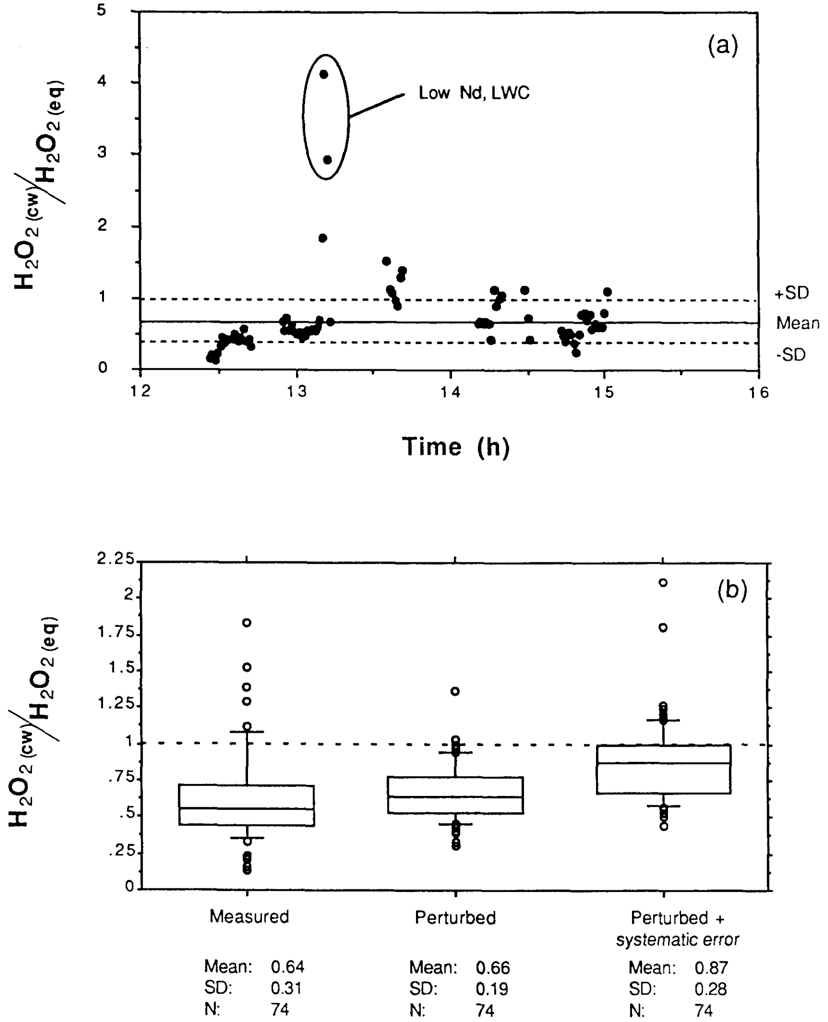

Fig. 3. (a) Time series of the deviation of partitioning from Henry's law equilibrium. The mean of the data (0.64) is shown with a solid horizontal line, and ± 1 standard deviation (0.31) by dotted horizontal lines. The two points inside the circle had low N_d and LWC values associated with them. (b) Box plots for the measured ratio values and the Monte Carlo error analysis. The horizontal lines represent the 10%, 25%, 50%, 75%, and 90% percentiles.

out for the ratio, where each of the terms having an associated measurement error in the equation was perturbed, and the ratio calculated for the perturbed cases. Here, the mean values of measured $[H_2O_2]_{cw}$, measured $[H_2O_2]_g$ (total), interstitial organic peroxide, liquid water content, temperature, and the Henry's law constant (evaluated at the perturbed temperature) were perturbed by random variable (Z-distribution) multiplying the estimated error in each term. This procedure was carried out for 74 cases. By doing this, we can obtain an estimate of how large of an effect the measurement errors may have in determining this ratio. The results are presented in Fig. 3b as the central box plot. The average ratio is 0.66 (SD: 0.19, N: 74). The 99% confidence interval for these perturbed values is 0.66 ± 0.058. As indicated in the box plot, including the estimated random measurement errors in the analysis still shows this ratio to be less than one. Because the gas-phase organic and hydrogen peroxide molar ratios are of the same order of magnitude for this data, any unknown variations in the gas-phase organic peroxide concentrations would be of special concern. Another Monte Carlo simulation was performed where the constant value of the organic peroxide was perturbed by twice its standard error. The mean value and 99% confidence interval for the partitioning ratio in this simulation was 0.71 ± 0.084.

This type of error analysis, however, does not take possible systematic errors into account. A recent analysis of the technique used here to measure H_2O_2 (Heikes, personal communication) indicates that when the organic/total peroxide ratio is 0.5, the gas-phase H_2O_2 concentration may be overestimated by 25%. Since our average organic/total peroxide ratio was 0.47, we repeated the Monte Carlo analysis using a 25% lower measured $[H_2O_2]_g$ value. These results are presented as the rightmost of the box plots in Fig. 3b. Here, the mean value is 0.87 (SD: 0.278, N: 74). The 99% confidence interval around these values is 0.87 ± 0.086. As seen in the figure, the upper quartile of the ratio is now 1. This indicates that if the type of systematic error described by

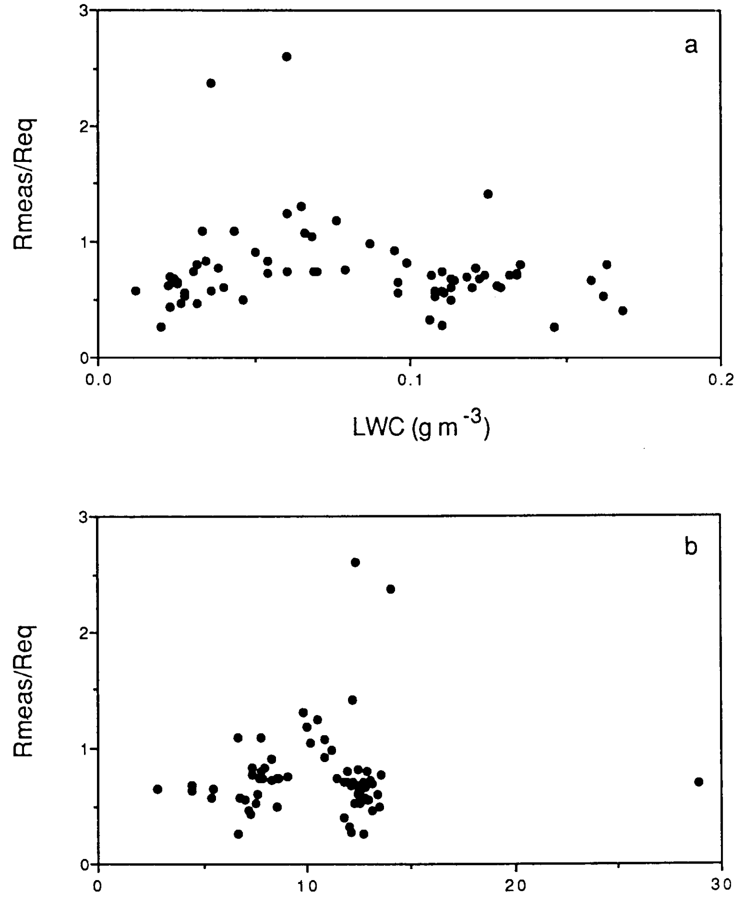

Fig. 4. Deviation from Henry's law versus (a) LWC and (b) droplet radius of mean mass. There does not appear to be any dependence of the deviaton on either of these two microphysical parameters.

Heikes occurred for our measurements, it would bring the partitioning closer to that predicted by Henry's law.

Barth, et al. (1989) define a ratio R to be the ratio of liquid-phase H_2O_2 to total H_2O_2:

$$R = \frac{[H_2O_2]_{\text{liquid}}}{[H_2O_2]_{\text{gas + liquid}}}. \tag{2}$$

Here, the square brackets indicate molar ratios (units: pptv) and not concentrations. Following their analysis, we define R_{meas} as:

$$R_{\text{meas}} = \frac{\text{measured}[H_2O_2]_{\text{CW}}}{\text{measured}[H_2O_2]_{\text{CW}} + \text{measured}[H_2O_2]_{\text{IA}}}, \tag{3}$$

where the subscripts CW and IA denote cloudwater and interstitial air. R_{meas} is the ratio of the measured liquid-phase H_2O_2 molar ratio to the measured total H_2O_2 molar ratio. We define one more parameter R_{eq} as:

$$R_{\text{eq}} = \frac{\text{predicted}[H_2O_2]_{\text{CW}}}{\text{predicted}[H_2O_2]_{\text{CW}} + \text{measured}[H_2O_2]_{\text{IA}}}. \tag{4}$$

Here the term "predicted $[H_2O_2]_{\text{CW}}$" is the liquid-phase H_2O_2 molar ratio that would be expected if the cloud droplets were in Henry's law equilibrium with the measured gas-phase H_2O_2. R_{meas} is then the measured liquid-phase H_2O_2 fraction, and R_{eq} is the equilibrium liquid-phase H_2O_2 fraction. If we take the ratio $R_{\text{meas}}/R_{\text{eq}}$, we obtain a measure of partitioning similar to the one described above. For comparison, our average partitioning ratio of 0.64 corresponds to a $R_{\text{meas}}/R_{\text{eq}}$ ratio of 0.7.

Barth, et al. (1989) observed that this ratio increased as LWC increased in their measurements of several different clouds. Fig. 4 shows $R_{\text{meas}}/R_{\text{eq}}$ plotted against two properties of the cloud we sampled; LWC and the cloud droplet radius of mean mass (MMR_d: units μm). This droplet radius is obtained by dividing the measured liquid water content by the measured number of droplets (Ogren, et al. 1989, Noone, et al. 1990). There does not appear to be any dependence of $R_{\text{meas}}/R_{\text{eq}}$ on either LWC or MMR_d in our data. This implies that transport of H_2O_2 from the gas phase into the droplets was sufficiently fast that modulations of the droplet size or the amount of water available were not limiting factors in establishing equilibrium conditions in the cloud. This can also be shown by analysis of the pertinent time constants for mass transfer and chemical reaction in the droplets (Schwartz and Freiburg, 1981). Taking 10 μm as a representative radius for the sampled cloud droplets, the characteristic times for gas-phase and aqueous-phase diffusion were 2.5×10^{-6} s and 0.01 s respectively. The characteristic time to establish equilibrium at the gas/liquid interface was 7 s. Gas-phase SO_2 measured by the Swedish Environmental Protection Agency approximately 400 m below the site using a DOAS (Differential Optical Absorption Spectroscopy) technique. The average value during the sampling period was 2 μg/m^3, close to the detection limit of the instrument. Using this value, assuming Henry's law equilibrium for SO_2, and assuming a pH of 4.6 for the droplets (Ogren and Rodhe, 1986) the characteristic time for the aqueous-phase reaction between SO_2 and H_2O_2 was calculated to be approximately 100–400 s. These calculations do not show any evidence for a rapid sink for H_2O_2 in the cloud droplets by reaction with S(IV).

4. Conclusions

In this paper, we have presented simultaneous measurements of gas-phase and liquid-phase H_2O_2 made at a mountain-top site in central Sweden during the summer of 1989. From these measurements we calculated the partitioning of H_2O_2 between the gas and liquid phases, and estimated the deviation of this partitioning from what would be expected if Henry's law accurately described the partitioning. Regarding this cloud event we can conclude the following.

(1) The combination of the CVI and the fluorometric peroxide measurement technique is suitable for making rapid, *in situ* measurements of the partitioning of hydrogen peroxide between the gas and liquid phases in clouds.

(2) The average measured partitioning ratio (measured cloudwater concentration divided by equilibrium concentration using Henry's law and the measured gas-phase concentration) was 0.64 (S.D. = 0.31). If a potential systematic error in the H_2O_2 measurement technique is included the ratio

becomes 0.87 (S.D. = 0.28). We cannot rule out the possibility that the combination of all of the other measurements involved could lead to a systematic error on the order of 13%. In our judgement, while the measured ratio is *statistically* different from zero, this difference is not a substantial one. Henry's law appeared to have been valid for the ambient cloud we studied.

(3) The partitioning of H_2O_2 in this cloud had no apparent dependence on the amount of liquid water in the cloud, nor on the average droplet size in the cloud.

These conclusions can only strictly apply to the clouds we observed. It would be of interest to have similar measurements under different conditions, such as clouds where LWC is greater or more variable, or clouds where the concentration of SO_2 is large. Continuous concurrent measurements of gas-phase organic peroxides would be desirable. It is difficult to characterize a cloud intercepted by a mountain in terms of its dynamic and microphysical properties. Making similar measurements from aircraft, when the cloud can be better characterized and the vertical profile of H_2O_2 can be determined, would also be desirable.

5. Acknowledgements

We are indebted to the staff of the aerial tramway (ÅKAB) for making cloud-base observations, and for their assistance during the campaign. Pedro Oyola of the Swedish Environmental Protection Agency supplied the DOAS data. C.-I. Nilson of the Swedish Hydrological and Meteorological Institute provided temperature data. The field laboratory was built through a donation from the Knut and Alice Wallenberg Foundation. Funding for the experiment was provided by the Swedish Environmental Protection Board as part of the EUROTRAC subproject Ground-based Cloud Experiments (GCE).

REFERENCES

Barth, M. C., Hegg, D. A., Hobbs, P. V., Walega, J. G., Kok, G. L., Heikes, B. C. and Lazrus, A. L. 1989. Measurements of atmospheric gas-phase and aqueous-phase hydrogen peroxide concentrations in winter on the east coast of the United States. *Tellus 41B*, 61–69.

Calvert, J. G., Lazrus, A., Kok, G. L., Heikes, B. G., Walega, J. G., Lind, J. and Cantrell, C. A. 1985. Chemical mechanisms of acid generation in the troposphere. *Nature 317*, 27–35.

Chandler, A. S., Choularton, T. W., Dollard, G. J., Gay, M. J., Hill, T. A., Jones, A., Jones, B. M. R., Morse, A. P., Penkett, S. A. and Tyler, B. J. 1988. A field study of the cloud chemistry and cloud microphysics at Great Dun Fell. *Atmos. Env. 22*, 683–694.

Daum, P. H., Kelly, T. J., Schwartz, S. E. and Newman, L. 1984. Measurements of the chemical composition of stratiform clouds. *Atmos. Env. 18*, 2671–2684.

Daum, P. H., Kelly, T. J., Strapp, J. W., Leaitch, W. R., Joe, P., Schemenauer, R. S., Isaac, G. A., Anlauf, K. G. and Weibe, H. A. 1987. Chemistry and physics of a winter stratus cloud layer: A case study. *J. Geophys. Res. 92*, 8426–8436.

Ferron, G. A. and Soderholm, S. C. 1990. Estimation of the times for evaporation of pure water droplets and for stabilization of salt solution particles. *J. Aerosol. Sci. 21*, 415–429.

Hegg, D. A. 1989. The relative importance of major aqueous sulfate formation reactions in the atmosphere. *Atmos. Res. 22*, 323–333.

Heikes, B. G., Kok, G. L., Walega, J. G. and Lazrus, A. L. 1987. H_2O_2, O_3 and SO_2 measurements in the lower troposphere over the eastern United States during fall. *J. Geophys. Res. 92*, 915–931.

Heikes, B. G., Walega, J. G., Kok, G. L., Lind, J. A. and Lazrus, A. L. 1988. Measurements of H_2O_2 during WATOX-86. *Global Biogeochem. Cyc. 2*, 57–61.

Kelly, T. J., Daum, P. H. and Schwartz, S. E. 1985. Measurements of peroxides in cloudwater and rain. *J. Geophys. Res. 90*, 7861–7871.

Klockow, D. and Jakob, P. 1986. The peroxyoxalate chemiluminescence and its application to the determination of hydrogen peroxide in precipitation. In: *Chemistry of multiphase atmospheric systems* (ed. W. Jaeschke). NATO ASI Series, Vol. G6. Berlin: Springer-Verlag, 117–130.

Kok, G. L., Darnall, K. R., Winer, A. M., Pitts, J. N. and Gay, B. W. 1978. Ambient air measurements of hydrogen peroxide in the California South Coast air basin. *Environ. Sci. Technol. 12*, 1077–1080.

Lazrus, A. L., Kok, G. L., Lind, J. A., Gitlin, S. N., Heikes, B. G. and Shetter, R. E. 1986. Automated flourometric method for hydrogen peroxide in air. *Anal. Chem. 58*, 594–597.

Lind, J. A. and Kok, G. L. 1986. Henry's law determinations for aqueous solutions of hydrogen peroxide, methylhydroperoxide, and peroxyacetic acid. *J. Geophys. Res. 91*, 7889–7895.

Noone, K. J. 1987. Size-selective cloud drop sampling using a counterflow virtual impactor: Design, calibration, and field studies. PhD thesis, University of Washington, Seattle, WA, USA.

Noone, K. J., Ogren, J. A., Heintzenberg, J., Charlson, R. J. and Covert, D. S. 1988. Design and calibration of a counterflow virtual impactor for sampling of atmospheric fog and cloud droplets. *Aerosol. Sci. Tech. 8*, 235–244.

Noone, K. J., Ogren, J. A. and Heintzenberg, J. 1990. An examination of clouds at a mountain-top site in central Sweden: the distribution of solute within cloud droplets. *Atmos. Res. 25*, 3–15.

Ogren, J. A., Heintzenberg, J. and Charlson, R. J. 1985. In-situ sampling of clouds with a droplet to aerosol converter. *Geophys. Res. Lett. 12*, 121–124.

Ogren, J. A. and Rodhe, H. 1986. Measurements of the chemical composition of cloudwater at a clean site in central Scandinavia. *Tellus 38B*, 190–196.

Ogren, J. A., Heintzenberg, J., Zuber, A., Noone, K. J. and Charlson, R. J. 1989. Measurements of the size-dependence of solute concentrations in cloud droplets. *Tellus 41B*, 24–31.

Olszyna, K. J., Meagher, J. F. and Bailey, E. M. 1988. Gas-phase, cloud and rain-water measurements of hydrogen peroxide at a high-elevation site. *Atmos. Env. 22*, 1699–1706.

Penkett, S. A., Jones, B. M., Brice, K. A. and Eggleton, A. E. 1979. The importance of atmospheric ozone and hydrogen peroxide in oxidizing sulfur dioxide in cloud and rainwater. *Atmos. Env. 13*, 123–137.

Radojevic, M., Tyler, B. J., Wicks, A. J., Gay, M. J. and Choularton, T. W. 1990. Field studies of the SO_2/aqueous S(IV) equilibrium in clouds. *Atmos. Env. 24A*, 323–328.

Römer, F. G., Viljeer, J. W., van den Beld, L., Slangewal, H. J., Veldkamp, A. A. and Reijnders, H. F. R. 1985. The chemical composition of cloud and rainwater. Results of preliminary measurements from an aircraft. *Atmos. Env. 19*, 1847–1858.

Schwartz, S. E. and Freiburg, J. E. 1981. Mass-transport limitation to the rate of reaction of gases in liquid droplets: Application to oxidation of SO_2 in aqueous solutions. *Atmos. Env. 15*, 1129–1144.

Tanner, R. L., Markovits, G. Y., Ferreri, E. M. and Kelly, T. J. 1986. Sampling and determination of gas-phase hydrogen peroxide following removal of ozone by gas-phase reaction with nitric oxide. *Anal. Chem. 58*, 1857–1865.

Tsay, S.-C. and Jayaweera, K. 1984. Physical characteristics of arctic stratus clouds. *J. Climate App. Met. 23*, 584–596.

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. Lett. 14*, 1146–1149.

Yoshizumi, K., Aoki, K., Nouchi, I., Okita, T., Kobayashi, T., Kamakura, S. and Tajima, M. 1984. Measurements of the concentration in rainwater and of the Henry's law constant of hydrogen peroxide. *Atmos. Env. 18*, 395–401.

Zika, R., Saltzman, E., Chamides, W. L. and Davis, D. D. 1982. H_2O_2 levels in rainwater collected in south Florida and the Bahama Islands. *J. Geophys. Res. 87*, 5015–5017.

Zuber, A. and Witt, G. 1987. Optical hygrometer using differential absorption of hydrogen Lyman-α radiation. *Appl. Optics 26*, 3083–3089.