ATMOSPHERIC H_2O_2 FIELD MEASUREMENTS IN A TROPICAL ENVIRONMENT: BAHIA, BRAZIL

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Abstract—Concentrations of H_2O_2 in atmospheric gas and liquid phases were determined for the first time in the tropical Southern Hemisphere. Measurements were carried out in the Salvador area, Bahia, 13°S, 38° W) both at the seaside and 500 m away from it as well as at 270 km inland, in a rural area, during March–April 1988. Gaseous H_2O_2 was collected by cryogenic and rain by wet only sampling. Analyses were performed with the peroxyoxalate chemiluminescence method, employing a compact field apparatus. The measured gas phase concentrations ranged from 0.2 to 3.9 ppbv compared to 0.01–0.6 ppbv obtained from measurements with similar methodology in Dortmund (51°30′N, 7°30′E), F.R.G, during summer. The corresponding concentration ranges in rainwater are 0.9–6.8 ppmw (Bahia) and 0.1–2.2 ppmw (Dortmund, summertime). Gas/liquid H_2O_2 equilibrium during rain events is only attained at precipitation rates below 1 mm h^{-1}.

Key word index: Hydrogen peroxide, cryo sampling, tropical environment, gas/liquid distribution.

INTRODUCTION

The knowledge of atmospheric H_2O_2 levels in different parts of the globe is of great interest due to the following reasons.

First, gaseous H_2O_2 is involved with the gas phase radical chemistry, acting as a sink for HO_2 (Schwartz, 1984) and, by photolysis, as a source of OH (Chameides and Davis, 1982; McElroy, 1986). These radicals are the most important oxidizing species for the transformation of atmospheric pollutants (Hewitt and Harrison, 1985).

Second, as H_2O_2 is extremely soluble in water, the atmospheric liquid phase (such as cloud and fog droplets, rain and dew) is the most important sink for H_2O_2. In addition in acidic liquid phase, H_2O_2 is the major oxidizing agent for S(IV), transforming SO_3^{2-} into SO_4^{2-} (Hoffmann and Edwards, 1975; Penkett *et al.*, 1979; Möller, 1980; Martin and Damschen, 1981; Kunen *et al.*, 1983; McArdle and Hoffmann, 1983), and also for NO_2^- (Damschen and Martin, 1983; Lee and Lind, 1986).

Third, model calculations used for estimations and predictions of conversion rates of airborne matter call for cognizance of H_2O_2 levels in distinct environments and distribution between the different phases (Logan *et al.*, 1981; Thompson and Cicerone, 1982; Adewuyi *et al.*, 1984; Graedel and Goldberg, 1983).

A number of investigations have been carried out in the Northern Hemisphere (Farmer and Dawson, 1982; Römer *et al.*, 1985; Slemr *et al.*, 1986; Jacob *et al.*, 1986; Heikes *et al.*, 1987; Keuken *et al.*, 1988). Even natural background levels, traced back to 100,000 years, have been reported in deposited snow of the Arctic and Antarctic regions (Neftel *et al.*, 1984, 1986). From the predicted atmospheric behavior of H_2O_2 and the seasonal and diurnal variations of H_2O_2 concentrations found, both in liquid (Yoshizumi *et al.*, 1984) and in gas phase (Heikes *et al.*, 1987), it may be concluded that high solar irradiation and low anthropogenic emissions lead to high H_2O_2 concentrations. Therefore unpolluted tropical areas should be the greatest sources of atmospheric H_2O_2.

To the best of our knowledge no data for atmospheric H_2O_2 in the Southern Hemisphere are available. For this reason H_2O_2, in the gas (ambient air) as well as in the liquid (rain) phase, has been determined at three locations of the state of Bahia, Northeast Brazil, at different distances from the seaside and different levels of anthropogenic activities. Additionally distribution between liquid and gaseous phase during rain events has been studied.

EXPERIMENTAL

Sequential gas samples with approximately 1 h time resolution and fractioned rain samples with 3–7 min resolution for showers and around 1 h for light rain were collected during March–April 1988 in the state of Bahia at the following sites: Salvador ($\sim$ 1.8 million inhabitants), at the Campus of the Federal University of Bahia (13°0.5′S, 38° 31′ W, 500 m from seaside, 100 m above sea level); Itaparica Island, at Ponta da Cruz (13°4′ S, 38°42′ W) at the seaside, and 270 km inland, in Mucugé (13°S, 41° W), at the Paraguaçu River bank.

Gaseous samples were taken by a cryogenic technique (Jacob *et al.*, 1986) at 1.0–1.5 m above ground using a flow rate of only 470 ℓ h^{-1} to assure −45°C at all times in the cooler, since sampled air temperatures varied around 30°C.

During the sampling period r.h. and temperature were always registered in order to make possible the calculation of the absolute water vapor content of the air under study. Under these operational conditions and local r.h. most of the time above 80%, collection of ambient water vapor reached a rate of about 10 ml h^{-1}, thus allowing even greater time resolution than indicated. By the method employed H_2O_2 concentrations can be directly related to the water vapor content of air without taking into account collection efficiency (Jacob et al., 1986). Rainwater was collected with a borosilicate glass funnel (26 cm diameter) in polypropylene vessels. Precipitation rate was determined by weighing the total water amount sampled within a certain time period.

Hydrogen peroxide determinations in the condensate were carried out immediately in the field by a chemiluminescence technique using bis-(2,4,6-trichlorophenyl)oxalate (TCPO) as a reagent, perylene as a sensitizer, and acetone as a solvent. The method described elsewhere (Klockow and Jacob, 1986) was used with the following modifications for higher reproducibility: TCPO and perylene concentrations were 1/3 that of the original methodology. The borate buffer concentration could be lowered from 0.1 to 0.08 M since the pH values of the collected rain were high and varied around 6. A compact 5 kg field version of the original chemiluminescence equipment was employed (Jacob, 1987). It consists of a photomultiplier (Hamamatsu, R 268) and a multiplier socket (Dr Seitner, M 1030 FK-E) with high voltage power supply, amplifier, electronic damping and zero shifting. The photocurrent, proportional to the light intensity emitted from the flow cell, was registered by a 12 V recorder (Siber Kikei, SS 100 f). The flow cell is part of a flow injection system built up with a peristaltic pump (Ismatec, mini S-280), low pressure injection valve (Rheodyne, no. 5020), and 500 μl sample loop.

The expected limit of detection of the TCPO analytical method is 0.3 ppbv H_2O_2 and the limit of determination of the overall methodology (sampling included) varies between 0.2 and 6 pptv H_2O_2, depending on the water vapor content of ambient air (Jacob et al., 1986). As H_2O_2 concentrations in Bahia are high, acetone purification was not pursued to its complete possibilities, resulting in higher blanks and therefore higher detection limits. In this study the detection limit for rain water was 1.6 ppbw of H_2O_2 and the range of determination limit for gaseous H_2O_2 18–29 pptv.

In a few cases the water collected in the cryogenic trap was not only analyzed for its H_2O_2 content but also for aerosol particle constituents such as Cl^-, NO_3^-, SO_4^{2-} and Na^+. The results indicated that some particulate matter, especially sea spray components, was deposited at the ice layer covering the walls of the collection tube. This is, however, only a small fraction of total suspended particulate matter (Jacob et al., 1986) and is not assumed to cause significant interference in H_2O_2 determination.

A co-condensation of SO_2 along with H_2O_2 and water vapor could reduce the amount of H_2O_2 present in solution after melting of the ice in the collection tube. Such an interference, however, is not of major importance for the present study, since SO_2 concentrations in Salvador are below 1 ppbv, and only about 0.1% of SO_2 pumped through the cryo trap is collected in the ice phase (Jacob, 1988).

RESULTS AND DISCUSSION

The H_2O_2 mixing ratios at the three sites in Bahia, Brazil, are presented in Table 1, along with those at Dortmund, F.R.G., obtained with the same methodology in summertime. Average levels of Bahia are 12–20 fold the ones of Dortmund. One reason for this difference is the increasing radiation intensity and higher humidity with lower latitude which leads to higher H_2O_2 formation rates. This has been shown from aircraft measurements by Heikes et al. (1987) and Van Valin et al. (1987). The latter, based on their results obtained between 40° and 28°N (91°30'W) at about 2000 msl, estimated a concentration gradient of 0.05 ppbv per degree latitude. Indeed, the difference in average atmospheric gaseous H_2O_2 level between the two site regions (Bahia, Brazil and F.R.G.) is compatible with this estimation. Another reason for lower H_2O_2 gas phase concentrations at Dortmund most probably are the higher NO_x mixing ratios, which suppress H_2O_2 formation, and higher SO_2 loads, which deplete H_2O_2 in the atmospheric liquid phase. Additionally, the ethanol used as vehicle fuel in Brazil results in aldehyde, especially acetaldehyde, emissions (Grosjean et al., 1990), and aldehydes establish an atmospheric route for H_2O_2 production (Seinfeld, 1986).

Whether differences in the concentrations of NO_x or SO_2 are responsible for the different H_2O_2 levels observed at the three sampling sites of Bahia, especially those at Salvador and at the site in the interior (background conditions), cannot be proved, since no data for these pollutants are available for all sites. Conclusions on the possible contribution of aldehyde emissions to H_2O_2 formation in the urban area cannot be drawn from the available results, since H_2O_2 levels are generally higher in the interior than in Salvador.

The averaged diurnal concentration variations of gas phase H_2O_2 at the four sites are illustrated in Fig. 1. Daytime maxima on clear days appear at about 14.00 h in Salvador and at the interior site, and at 18:00 to 19:00 h at Dortmund in summer. Similar summer diurnal variations have been reported by Heikes et al. (1987) from measurements at Whiteface Mountain, New York, with maxima around 18:00 h. Attention should be called for the fact, that in March daytime in Bahia starts at 5:30 h and ends at 18:00 h (local time), while during summer at Dortmund day-

Table 1. H_2O_2 mixing ratios at different locations of Bahia, Brazil and one site at Dortmund, F.R.G.

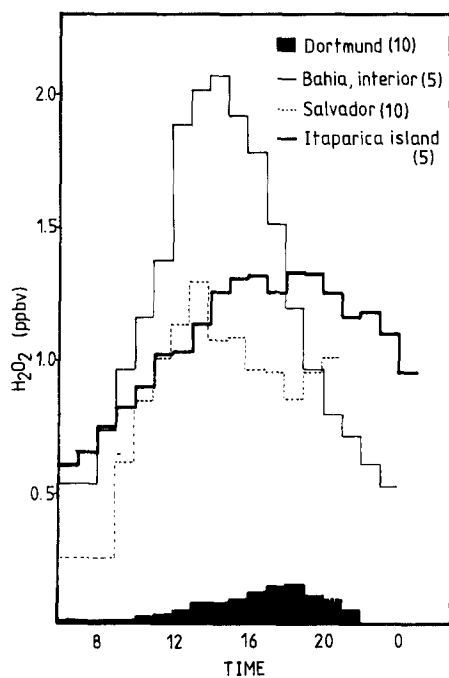| Site	Period (1988)	Number of measured diurnal variations	H_2O_2(ppbv) Maximum	Minimum	Daytime average
Salvador	3.3–17.3	10	2.3	0.20	0.90
Itaparica	29.3–4.4	5	2.4	0.23	1.10
Interior	19.3–25.3	5	3.9	0.42	1.50
Dortmund, F.R.G.	Summers 1985, 1986	10	0.54	0.01	0.07

Fig. 1. Averaged diurnal variation of H_2O_2 gas phase mixing ratio at different sites in Bahia, Brazil and one site at Dortmund, F.R.G. (number of measured diurnal variations in parentheses).

time is from about 5:00 h to 21:30 (local time). The unexpected late afternoon–early evening averaged maxima of Itaparica can only be explained by the repeated morning–early afternoon cloudiness during the study period.

In Dortmund the appearance of clouds leads to a significant decrease in H_2O_2 gas phase levels (Jacob et al., 1987). This has been attributed to an uptake of gaseous H_2O_2 by cloud water droplets and subsequent reaction with S(IV) (Penkett et al., 1979), as modeled by Carmichael et al. (1986). This behavior should be less striking in Bahia, where a distinct excess of H_2O_2 over S(IV) exists, and gas liquid water equilibrium is not affected by other side reactions. The clouds arriving at the coast of Bahia are formed over the Atlantic Ocean and presumably are 'clean'. In fact the presence of clouds leads to lower gaseous H_2O_2 levels when compared to equivalent sunny clear time

periods. However, the arrival of individual, low, fast moving, raining cumulus clouds resulted in an increase in H_2O_2 mixing ratios prior to the sharp decrease at the onset of rainfall at the sampling site. As rain stopped and the cumulus clouds were moving away, a sharp increase in gaseous H_2O_2 concentration occurred. This phenomenon of 'before cumulus' and 'after cumulus' enlargement of H_2O_2 mixing ratio might be related to cloud droplet evaporation at cloud edges and subsequent release of dissolved H_2O_2.

Rainwater H_2O_2 concentrations in tropical Bahia are obviously higher than those in temperate zones, as can be seen in Table 2. However, due to strong variations in rainfall rate and pattern, a general comparison is difficult to be made. Figures 2 a and 2b show that lower precipitation rates lead to higher H_2O_2 concentrations in rain, with a linear correlation over a certain range. A correlation between gas phase and liquid phase H_2O_2 concentration was established at different precipitation rates (Fig. 3), based on simultaneous measurements of H_2O_2 concentrations in ambient air and in rain water. During low rate precipitation the correlation seems to obey Henry's Law, whereas during heavy showers no equilibrium could be observed.

From several such field investigations Henry's Law constants for different ambient temperatures were obtained and ranged between 1.3×10^5 at $20°C$ and 0.7×10^5 M atm^{-1} at $32°C$. These values are somewhat higher than those determined by other authors (Hwang and Dasgupta, 1986; Lazrus et al., 1986; Martin and Damschen, 1981; Yoshizumi et al., 1984) through laboratory experiments.

Results from three other events are shown in Fig. 4. Here the measured H_2O_2 concentration in rain is compared to a calculated equilibrium concentration in rain derived from measured gas phase mixing ratios and Henry's Law constant (Martin and Damschen, 1981). It can be seen that the differences between measured and calculated concentration decrease with decreasing rainfall rate $\bar{R}$.

Hydrogen peroxide concentrations in gas and liquid phases were measured simultaneously several times. Results obtained during a typical rain event have been plotted in Fig. 5 along with the precipitation rate. At the beginning and at the end of the event the precipitation rate was lower, favouring

Table 2. H_2O_2 concentrations in rainwater at different locations of Bahia, Brazil and one site at Dortmund, F.R.G.

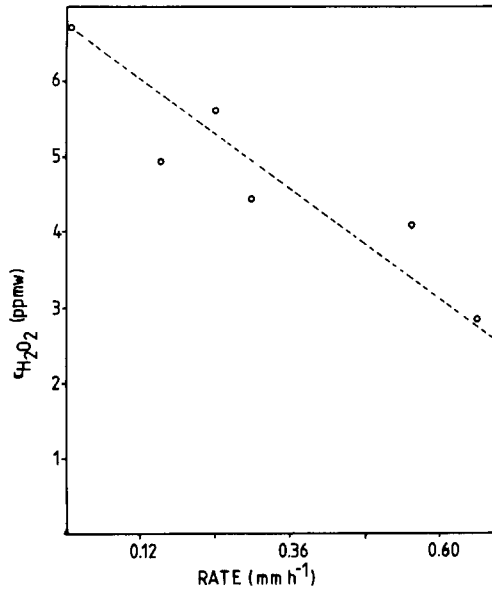| Site	Date	Time	H_2O_2 ppmw (μmol ℓ^{-1})		
			Minimum	Maximum	Average
Salvador	9.03.88	12.40–16.30	2.9 (85)	6.8 (200)	4.2 (124)
	11.03.88	12.20–14.30	0.64 (19)	3.9 (115)	1.0 (29)
Itaparica	29.03.88	12.47–13.30	0.95 (28)	1.7 (50)	1.3 (38)
Interior	23.03.88	13.50–13.58	0.82 (24)	1.1 (32)	0.95 (28)
	24.03.88	16.15–16.30	4.0 (118)	5.7 (168)	4.8 (141)
Dortmund	Summers 1985, 1986	Daytime	0.1 (2.9)	2.2 (65)	0.3 (8.8)

Fig. 2a. H_2O_2 concentrations in rainwater as a function of precipitation rate, Salvador/Bahia; low precipitation rates.

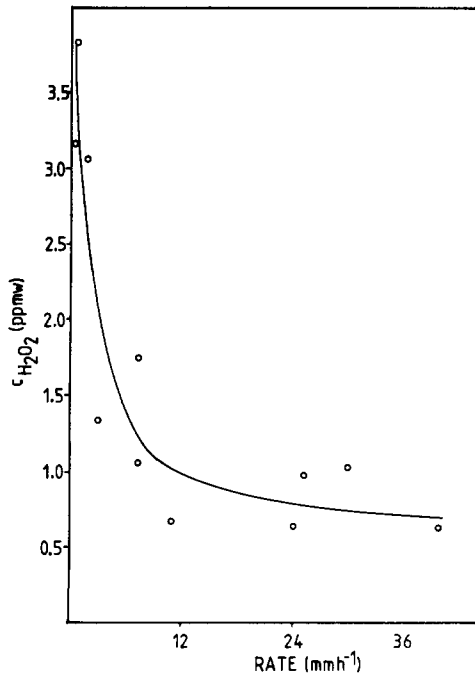Fig. 3. Correlation between atmospheric H_2O_2 gas and liquid phase concentrations.

Fig. 2b. H_2O_2 concentrations in rainwater as a function of precipitation rate, Salvador/Bahia; low to high precipitation rates.

scavenging of gaseous H_2O_2. At higher precipitation rates lower H_2O_2 concentrations were found in the liquid phase. During the rainy period no significant change was observed in the H_2O_2 gas phase concentration. This means that either a constant input of
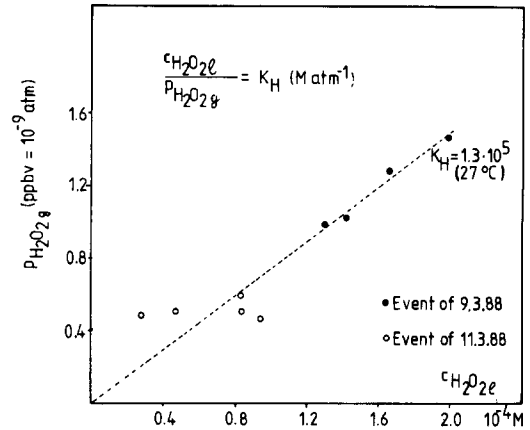
gaseous H_2O_2 from an unknown source existed or that an efficient mixing of air masses took place. This last possibility is most likely since the rain events investigated were always accompanied by winds of $\sim 5\ \mathrm{m\,s^{-1}}$.

CONCLUSIONS

Cryo sampling is a suitable technique for collection of gas phase H_2O_2 in humid tropical environments, offering sufficient time resolution. Intercalibration exercises are however desirable. The TCPO chemiluminescence field equipment is appropriate for *in situ* measurements offering much lower detection limits than necessary for not heavily polluted areas in the tropics.

Average gas phase H_2O_2 levels in Bahia are 12–20 times greater than those measured with the same methodology at Dortmund, F.R.G., in summertime. Concentration maxima on clear days in Bahia are found between 12:00 and 16:00 h, whereas in F.R.G., in summertime, they appear between 18:00 and 19:00 h. Gaseous H_2O_2 levels are lower in presence of clouds. However, the coming in of raining cumulus clouds increased temporarily the H_2O_2 mixing ratios. Rainfall generally lowered the H_2O_2 gas phase concentrations.

Great variations in H_2O_2 liquid phase concentrations were found during different rain events and could be correlated with rain fall rate. Gas/liquid equilibrium for H_2O_2 during rain events was only attained when the precipitation rate was below $1\ \mathrm{mm\,h^{-1}}$.

To complete the still tentative scenario, further H_2O_2 measurements in the tropics are needed, not only in other types of area, such as forests, plantations or heavily polluted areas, but also in other atmospheric phase systems such as fog, dew, clouds, sea spray etc.
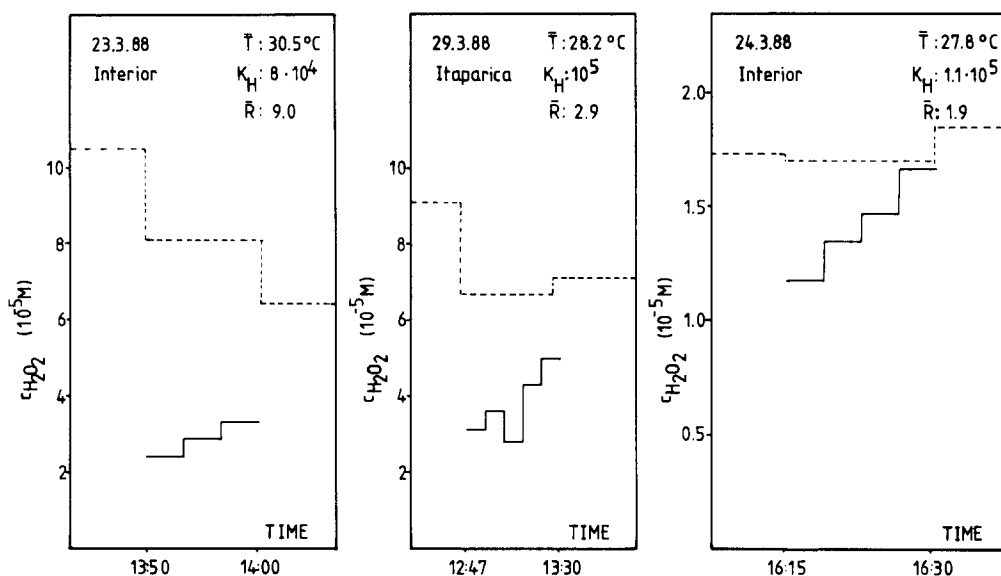
Fig. 4. Measured (———) and calculated (- - -) equilibrium H$_2$O$_2$ concentrations in rainwater during different events; T: average air temperature, K_H: Henry's Law constant (M atm^{-1}), $\bar{R}$: average precipitation rate (mm h^{-1}).
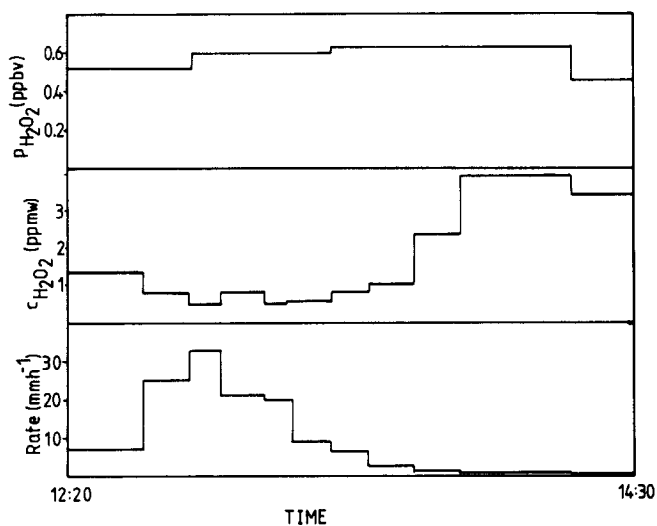

Fig. 5. Gas and liquid phase H$_2$O$_2$ concentrations and rainfall rate during a precipitation event on 11 March 1988, at Salvador/Bahia.

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