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THE CONTRIBUTION OF RAINWATER TO VARIABILITY IN SURFACE OCEAN HYDROGEN PEROXIDE

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Abstract. Hydrogen peroxide concentrations have been determined in marine rain from the Gulf of Mexico (114-820 x 10^{-7} mol L^{-1}, $\bar{x}$ = 402 x 10^{-7} mol L^{-1}, s = 218 x 10^{-7} mol L^{-1}), the western Atlantic Ocean (84-206 x 10^{-7} mol L^{-1}, $\bar{x}$ = 127 x 10^{-7} mol L^{-1}, s = 45 x 10^{-7} mol L^{-1}), and one rain event off the Florida Keys ($\bar{x}$ = 284 x 10^{-7} mol L^{-1}, s = 38 x 10^{-7} mol L^{-1}). In several cases, simultaneous measurements of the concentration of H_2O_2 in the surface ocean were also determined. These measurements were made with the ship under way using a continuous flow sampling system with the intake at the bow. In shallow stratified layers, rain events can increase the existing hydrogen peroxide concentration by a factor greater than 10 and dramatically increase the mean H_2O_2 concentration of mixed depth layers of 50 m or more. Rain is a significant transient source of H_2O_2 in the surface ocean.

Introduction

In recent years, we have conducted a number of field, laboratory, and modelling studies directed toward understanding the distribution of H_2O_2 and its impact on redox processes in natural waters. In the surface ocean, the principal source of H_2O_2 is the photooxidation of dissolved organic matter. This process is thought to involve O_2^- as an intermediate, which subsequently disproportionates to H_2O_2 [Zika, 1981]. Spatial and diel variations in surface ocean H_2O_2 concentrations have been reported. These variations can be explained in terms of changes in solar radiation, dissolved organic carbon content, and surface ocean mixing processes [Zika et al., 1985a, b, and manuscript in preparation, 1986].

Atmospheric deposition of H_2O_2 or various precursors has also been proposed as a potential source of oceanic H_2O_2 [Thompson and Zafiriou, 1983]. Measurements of H_2O_2 levels in rainwater from marine or coastal air masses revealed concentrations of the order of 100 x 10^{-7} mol L^{-1} [Zika et al., 1982]; 2-3 orders of magnitude greater than those of surface seawater. Simple calculations suggest that episodic injections of rainfall would result in local transient increases of surface ocean H_2O_2 superimposed on the normal background H_2O_2 generated by "in situ" photochemical processes. The decay of this transient as a result of chemical reactions and mixing processes could provide an interesting field test of present concepts and numerical models of these processes. Because of the irregular spatial and temporal distribution of rainfall over the oceans and the short duration of shipboard field experiments, documentation of rainwater input of H_2O_2 to the ocean has proven elusive. On three recent cruises to the Gulf of Mexico, the western Atlantic, and off the Florida Keys, several rain events were encountered that allowed us to observe real time changes in surface ocean H_2O_2. In this report, we document these changes and briefly discuss their implications for spatial variability of H_2O_2 in the surface ocean.

Experimental

Sampling. Three types of samples were collected for H_2O_2 analysis in this study: rain water, surface ocean water at 1-2 m (continuously pumped), and discrete depth samples.

Rainwater samples were collected in hand-held vials that had been acid washed and rinsed with distilled water. Just prior to sampling, the vials were rinsed with low-residual organic water (Milli-Q^{R} water redistilled over permanganate). The samples were analyzed within 5 min of collection. The quantity of rainfall was not measured.

Two different flow-through seawater systems provided a continuous sample stream in the laboratory. The system aboard the R/V *Cape Florida* was constructed of polypropylene tubing and a peristaltic pump with silicon tubing. The influent tubing was attached to the bow of the ship approximately 1 m below the surface. Structurally, the tubing was cased in metal piping and extended approximately 12 cm from the end of the casing. The polypropylene tubing was enclosed in opaque hose to minimize any photochemically and thermally initiated reactions occurring in the flow-through system on deck, prior to sampling in the laboratory. The seawater flow in the system was approximately 1-2 L min^{-1} with a residence time of less than 30 s.

The systems aboard the R/V *Columbus Iselin* and R/V *Calanus* were through-the-hull all-Teflon^{R}. The intake on the R/V *Columbus Iselin* was approximately 2 m below the surface, while that of the R/V *Calanus* was 1 m below the surface. Both intakes were at the bow. A positive displacement pump with a Hypalon^{R} (DuPont, Inc.) chlorosulfonated polyethylene head was used. The flow rate was 3-5 L min^{-1} with a residence time of less than 10 s in the system, prior to sampling.

Discrete water samples were obtained in 5-L PVC Niskin samplers (General Oceanics, Miami, Florida). Samples were transfered to teflon-lined screw top glass 250-mL bottles. H_2O_2 was analyzed immediately after sampling.

Analysis. In this study, we used a recently developed continuous flow analyzer based on a

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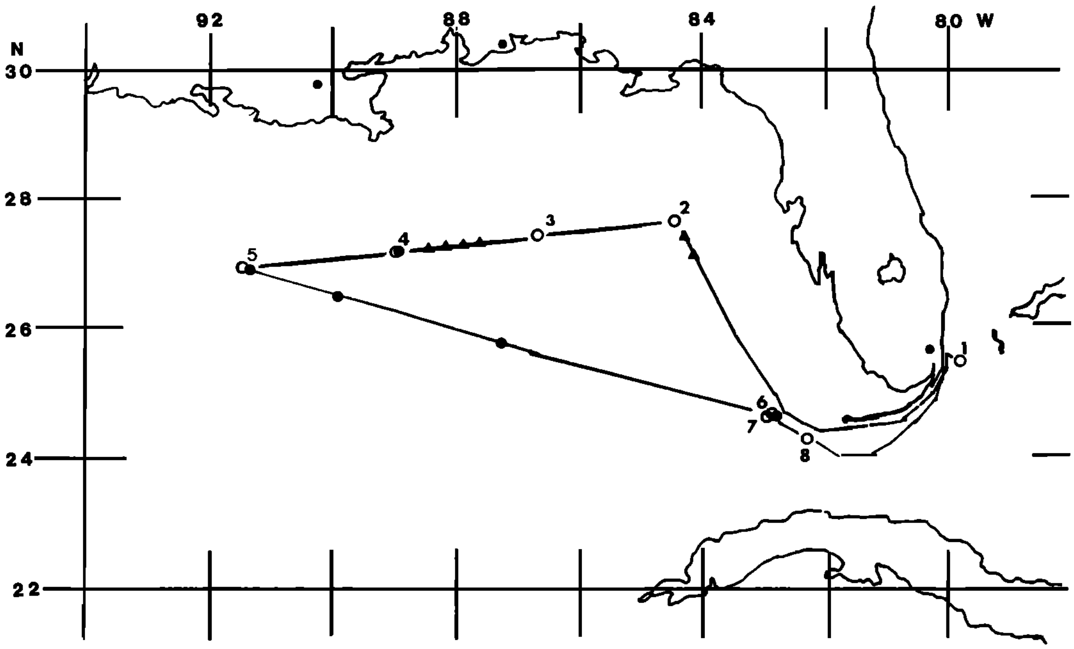

Fig. 1. SOLARS III cruise track, R/V Cape Florida, September 10-22, 1986. Solid circles show location of rain squalls, and triangles show location of transects.

previously described batch method using the peroxidase enzyme mediated fluorescence decay of scopoletin to measure H_2O_2 [Andreae, 1955; Perschke and Broda, 1961; Zika et al., 1982; Zika and Saltzman, 1982]. Seawater was continuously sampled from the ship's flow system via a peristaltic pump. The peristaltic pump was also used to add, in sequential order, the reagents: 0.5 mol L^{-1}, pH 7 phosphate buffer, scopoletin, and horseradish peroxidase. The fluorescence was monitored with a LDC FluoroMonitor III, which provided a continuous signal of the surface concentration of hydrogen peroxide while the ship was under way.

Standard curves were made up in peroxide-free seawater using a volumetric dilution of a 10^{-2} mol L^{-1} H_2O_2 solution, which had been standardized by iodometric titration. Peroxide-free seawater was prepared by allowing samples to stand in the dark; for open-ocean surface water this requires several weeks. An alternative method has also been employed successfully, in which 0.1 mg of catalase is added to 20 L of freshly collected surface water and allowed to stand for 24 hours in the dark. Care must be taken to keep the water from light prior to use.

Direct comparison of field samples using the batch and continuous method agreed to within ±2%. Details of the continuous hydrogen peroxide analyzer will be published elsewhere.

Fluorescence of dissolved organic matter (DOM) was measured using a Turner Designs model 10 fluorometer. A CS 7-60 filter was used for excitation, and two filters, first a 2A followed by a 65A, were used for emission. Quinine sulfate dissolved in 0.1 N H_2SO_4 was used as the reference standard. A 1μg L^{-1} solution equals 1 QSU (quinine sulfate unit).

Salinity was measured continuously using a parallel flow-through system. The inlet depth was at 1-2 m. The signal was recorded at 10-min intervals on the ship's computer system.

On the R/V Cape Florida, continuous chlorophyll measurements were obtained using a Turner Designs model 10 fluorometer (excitation band centered at 430 nm and a broadband cut-off emission filter >650 nm), and the signal was recorded every 10 min on the ship's computer system. Chlorophyll was measured as a relative fluorescence during the Gulf of Mexico cruise. On the R/V Columbus Iselin, the all-Teflon system was used, and the chlorophyll signal was recorded both on the ship's computer system (every 10 min) and the IBM PC based data acquisition system used for H_2O_2 and DOM fluorescence. On the latter system, the chlorophyll signal was recorded every second and averaged every 10 s for display and permanent file. The chlorophyll signal was calibrated using a known concentration of fluorescein. To convert to chlorophyll, water samples with a known fluorescein fluorescence were collected and the chlorophyll *a* determined according to standard techniques [Strickland and Parsons, 1968]. It was found that 0.385 mg Chl m^{-3} was equal to 10 x 10^{-9} mol L^{-1} fluorescein.

Study Area

The first study was conducted aboard the R/V Cape Florida, in the Gulf of Mexico from September 10-22, 1985 (SOLARS III cruise). Figure 1 shows the cruise track with the approximate rain sampling locations indicated by solid circles. The locations of continuous measurements are indicated on the cruise track. The depth profile was obtained while at anchor off the Dry Tortugas, Loggerhead Key, latitude 24°38.0'N, longitude 82°52.9'W.

The second study was conducted aboard the R/V Columbus Iselin in the western Atlantic from February 22 to March 10, 1986 (SOLARS VI cruise). Figure 2 shows the cruise track with the approximate rain sampling locations indicated by

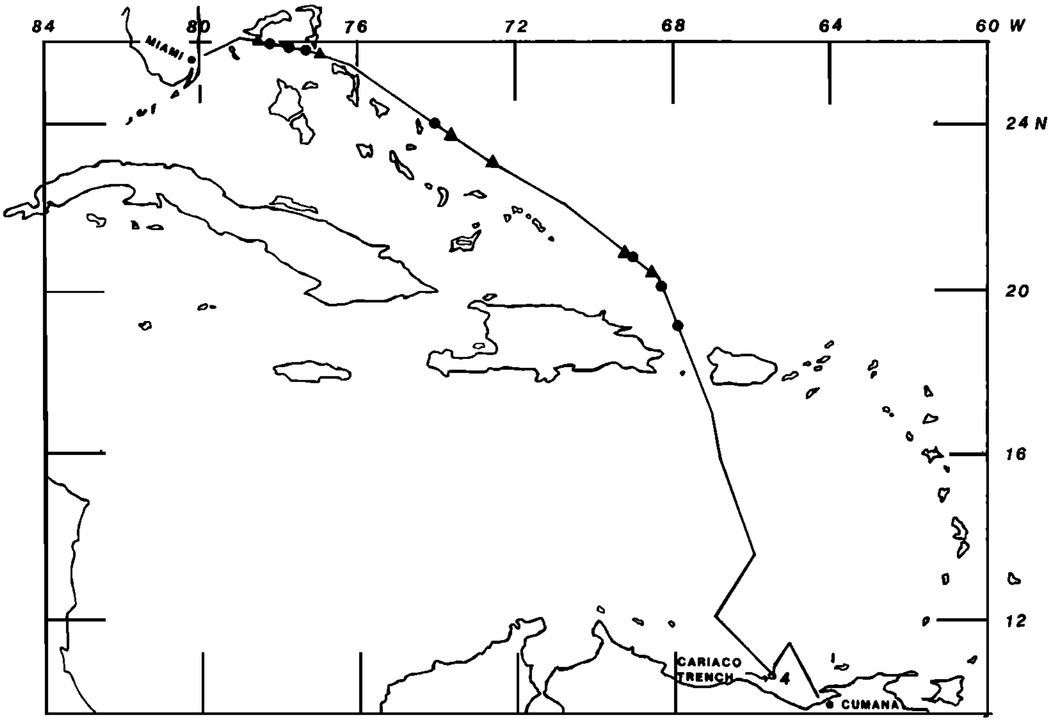

Fig. 2. SOLARS VI cruise track, R/V Columbus Iselin, February 22 to March 10, 1986. Solid circles show location of rain squalls, and triangles show location of transects.

solid circles. The locations of continuous measurements are also indicated on the cruise track.

On a third cruise off the Florida Keys (Lower Matacumbe), within 2 mi of shore, May 10-18, 1986 (SOLARS VII), one rain event occurred and several samples were obtained. The location of the samples is given in Table 1.

Results

Rain measurements. Table 1 summarizes the results of the analyses of rainwater H_2O_2 concentrations. In this study, a total of 36 rain samples were collected and analyzed immediately (within 5 min) to determine H_2O_2 concentration. In the Gulf of Mexico (n = 24), all of the rain events were squalls with active lightning and lasting approximately 30 min. The H_2O_2 concentration ranged from 114×10^{-7} to 820×10^{-7} mol L^{-1}, with an average of 402×10^{-7} mol L^{-1} ($s = 218 \times 10^{-7}$ mol L^{-1}). The data obtained from the western Atlantic (n = 9) ranged from 84×10^{-7} to 206×10^{-7} mol L^{-1}, with an average of 127×10^{-7} mol L^{-1} ($s = 45 \times 10^{-7}$ mol L^{-1}). The rain sample from near the Florida Keys (n = 3) resulted in an average of 284×10^{-7} mol L^{-1} ($s = 38 \times 10^{-7}$ mol L^{-1}).

The rain storm during which sample G was collected lasted nearly 4 hours and had lightning associated with it. Rain events H and I also had lightning associated with these shorter squalls, while events J, K, and L did not.

Continuous surface ocean measurements. Figure 3 shows the H_2O_2 and DOM fluorescence data record obtained while under way from station 3 (latitude 27°25.1'N; longitude 86°43.6'W) to station 4 (latitude 27°10.0'N; 89°01.7'W) from a depth of 1 m. The data record is 3.5 hours long and covers approximately 78 km. At 0600 (local EST) the ship was moving through heavy squalls. An almost immediate increase in the surface (1 m) H_2O_2 concentration was observed upon entering the squall. As the ship continued to steam, the hydrogen peroxide concentration reflected the recent rain activity in the area. The surface H_2O_2 concentration increased from approximately 0.85×10^{-7}, 0530 (local EST) to 1.85×10^{-7} mol L^{-1} at 0737 hours. The DOM fluorescence appeared to increase somewhat during the time the highest concentration of H_2O_2 was observed.

Figure 4 shows a second data record, obtained during the middle of the same day as Figure 3, with the ship under way from station 3 to station 4. The surface H_2O_2 concentration was initially 0.86×10^{-7} mol L^{-1} and increased to 2.03×10^{-7} mol L^{-1} in approximately 25 min. Once again, it was noted that the ship was steaming through rain squalls and through areas that had recently received rain, as indicated by the ship's radar. During the time in which the data for both Figures 3 and 4 were obtained, the wave height was from 0.5 to 1.5 m. It should be noted that the surface fluorescence increased during the time that the H_2O_2 concentration increased, while the salinity decreased slightly. No change in chlorophyll was observed.

Figure 5 shows another 2.0-hour record of surface H_2O_2, DOM fluorescence, salinity, and chlorphyll, obtained just prior to arriving at station 2. It is obvious that some event occurred that drastically increased the H_2O_2 concentration from an initial concentration of 0.76×10^{-7} to a maximum concentration of 1.92×10^{-7} mol L^{-1} in approximately 15 min. Rain was not noted during this time and the ocean was calm, with waves less than 10 cm. (The approximate location of this event was latitude

TABLE 1. Hydrogen Peroxide Concentration in Rainwater Collected in the Gulf of Mexico, Western Atlantic, and Florida Keys

Sample	Date	Location		Time,	H_2O_2,
		Latitude	Longitude	hours EST	$\times 10^{-7}$ mol L^{-1}
		Gulf of Mexico, $\bar{x}$ = 402 ± 218			
A	September 14, 1985	27°10.3N	89°01.7W	2025	168
				2030	114
				2035	168
					222
					230
B	September 15, 1985			0800-0900	396
					380
C	September 16, 1985	26°31.7N	89°52.3W	1930	386
					386
					394
D	September 17, 1985	25°46.3N	86°52.5W	1417	820
					820
E	September 18, 1985	24°38.0N	82°52.9W	1827	576
					576
F	September 19, 1985	24°38.0N	82°52.9W	0015-0030	513
				1015-1030	164
				1030-1040	164
				1040-1050	178
				1217	202
					202
				1805-1815	530
				1815-1825	560
					695
					668
				2020	550
		Western Atlantic, $\bar{x}$ = 127 ± 45			
G	February 23, 1986	25°59.2N	78°33.5W	2130	84
		25°56.3N	78°21.0W	2230-2250	102
		25°54.9N	78°13.4W	2255-2321	84
H	February 25, 1986	22°35.2N	71°20.4W	2210-2220	206
I	February 26, 1986	20°31.1N	68°44.1W	1025-1030	187
				1031-1034	154
				1035-1038	119
J	February 26, 1986	19°22.9N	68°04.4W	1800-1805	106
K	February 26, 1986	19°05.4N	67°54.7W	1940-1950	99
		Florida Keys, $\bar{x}$ = 284 ± 38			
L	May 14, 1986	25°13.5N	81°12.8W	1320	243
				1322	289
				1336	319

27°04.1'N; longitude 84°07.8'W.) The magnitude of this increase was greater than that observed over an entire day in similar oceanic environments with no rain [Zika et al., 1985a]. The DOM fluorescence appeared to increase slightly at the time the high H_2O_2 concentrations were observed. The salinity decreased slightly during this time, and no noticeable change was observed in the chlorophyll.

Figure 6 is a comparison of two continuous nighttime data records, each of which is approximately 5 hours in duration (102 km). The data record at the left was collected during a rain storm (sample G, Table 1), and for comparison, the data on the right were collected on the following evening with no rain. The data gaps in the H_2O_2 record indicate where the rain samples were analyzed. The surface ocean H_2O_2 data for the evening with no rain was somewhat variable with a mean of between 0.5 and 0.6 x 10^{-7} mol L^{-1}. On the other hand, the H_2O_2 data for the evening with rain shows an initial surface ocean concentration of approximately 0.5 x 10^{-7} mol L^{-1}, increasing to as much as 1.3 x 10^{-7} mol L^{-1}. After the rain had ceased, the levels in the surface water decreased to 0.3 - 0.4 x 10^{-7} mol L^{-1}.

A comparison of the DOM fluorescence between the two samples indicates that some variability did occur but no noticeable increase was observed

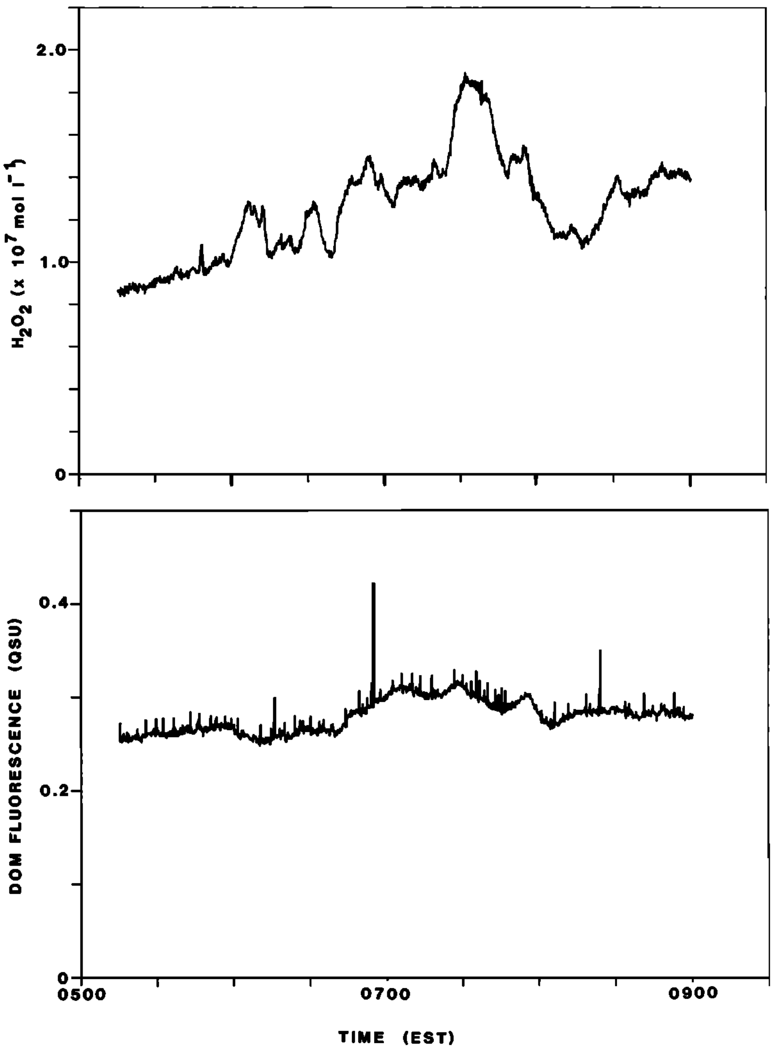

Fig. 3. Surface ocean measurements of H_2O_2 and DOM fluorescence, midway between station 3 and 4, SOLARS III.

during the rain. This is somewhat different than we observed in the earlier data, from the Gulf of Mexico. The continuous chlorophyll data records for each night showed several patches but were in general comparable with no relationship to either H_2O_2 or DOM fluoresence.

Figure 7 is a 3-hour data record (61 km) sampled during the middle of the day. During this time, the ship was moving through a rain squall that ended at 1040 hours (EST) (event I, Table 1). The H_2O_2 data record shows the initially high surface values of approximately 1.40 x 10^{-7} mol L^{-1}, associated with the rain, decreasing to 0.6 x 10^{-7} mol L^{-1}. This decrease was followed by a slight increase as the day progressed, to 0.65 - 0.70 x 10^{-7} mol L^{-1}. The DOM fluorescence and chlorophyll data records did not show any difference between the time it was raining and when there was no rain.

Water column study. While anchored in the Dry Tortugas, Loggerhead Key (latitude 24°38.0'N; longitude 82°52.9'W), several rain events occurred. The water depth was approximately 10 to 11 m. Several water profiles of salinity and temperature suggested a homogeneous water column. Samples of the water column were obtained using a rosette with five 5-L Niskin bottles (Figure 8). The samples showed no variation in H_2O_2 concentration with depth, as expected in a well-mixed system.

To examine the impact of rain on the water column H_2O_2 concentration, we obtained samples at five depths during a light rain (Figure 8). During the rain the H_2O_2 concentration increased, with the increase at the surface significantly greater than that at depths greater than 4 m.

Discussion

Hydrogen peroxide concentrations in marine rain. The H_2O_2 concentration in rainwater is a complex function of gas and liquid phase photochemistry, the dynamics of transport across the gas-liquid interface, and the macroscopic dynamics of transport within the cloud. The current state of knowledge of cloud chemistry, including H_2O_2, has been the subject of a number of recent reviews [e.g., Chameides, 1984; Calvert et al., 1986; Jacob, 1986]. In this discussion we will only briefly mention those characteris-

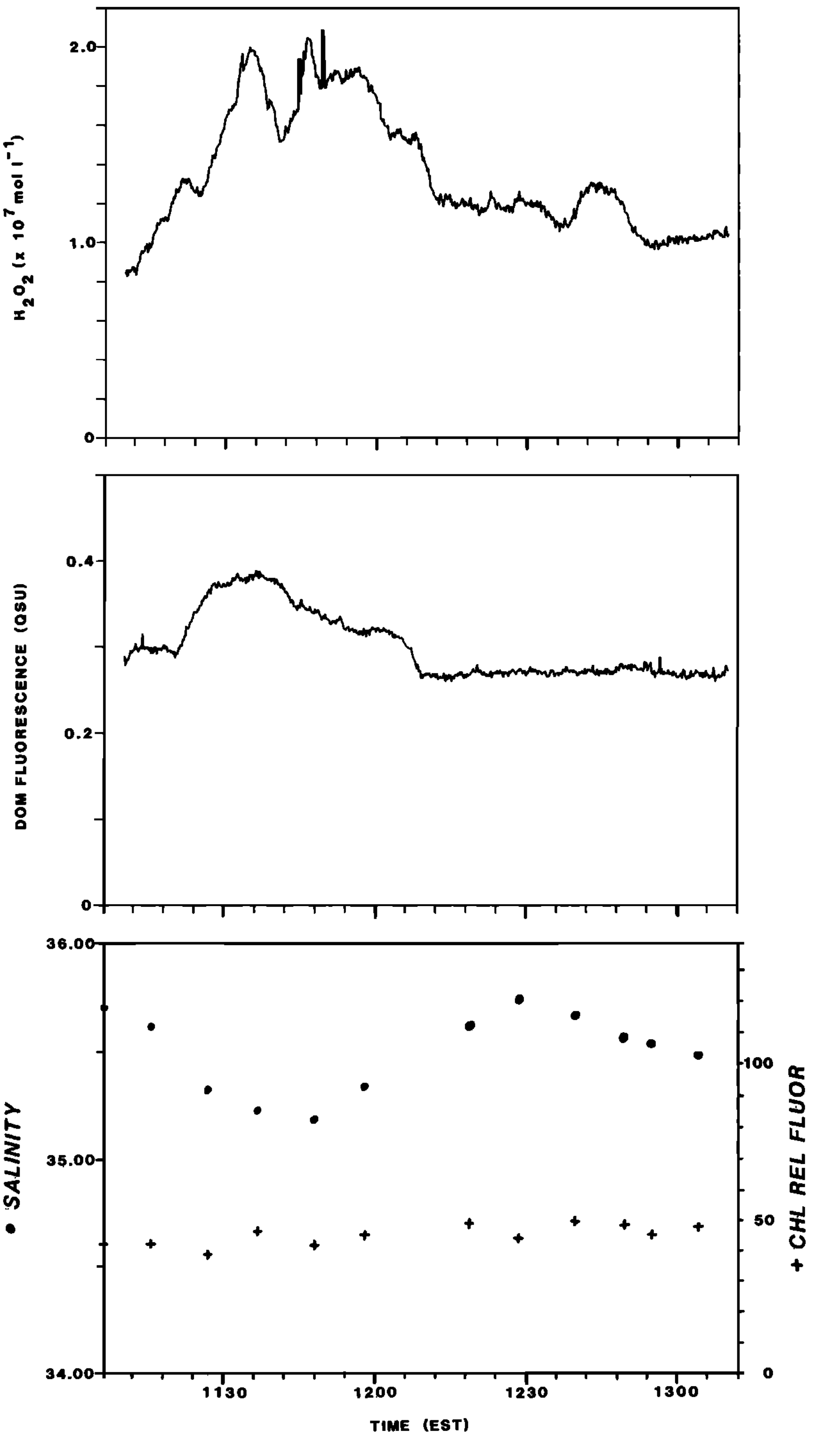

Fig. 4. Surface ocean measurements of H_2O_2, DOM fluorescence, chlorophyll, and salinity, nearing station 4, SOLARS III.

tics of marine air that may affect H_2O_2 concentrations and that may differ from those of continental air masses, particularly in polluted areas.

The principal pathway for the formation of tropospheric H_2O_2 is the disproportionation of HO_2 radicals in either gas or liquid phase; hence the production of H_2O_2 is increased by factors leading to the formation of HO_2 and decreased by reactions that consume HO_2. One of the major reactions consuming HO_2 is with NO:

$$NO + HO_2 \longrightarrow OH + NO_2$$

The low levels of NO characteristic of marine air result in less effective recycling of HO_2 to OH and, as a result, increased peroxide production relative to continental air. The situation may be further complicated in polluted air by the presence of variable concentrations of organic

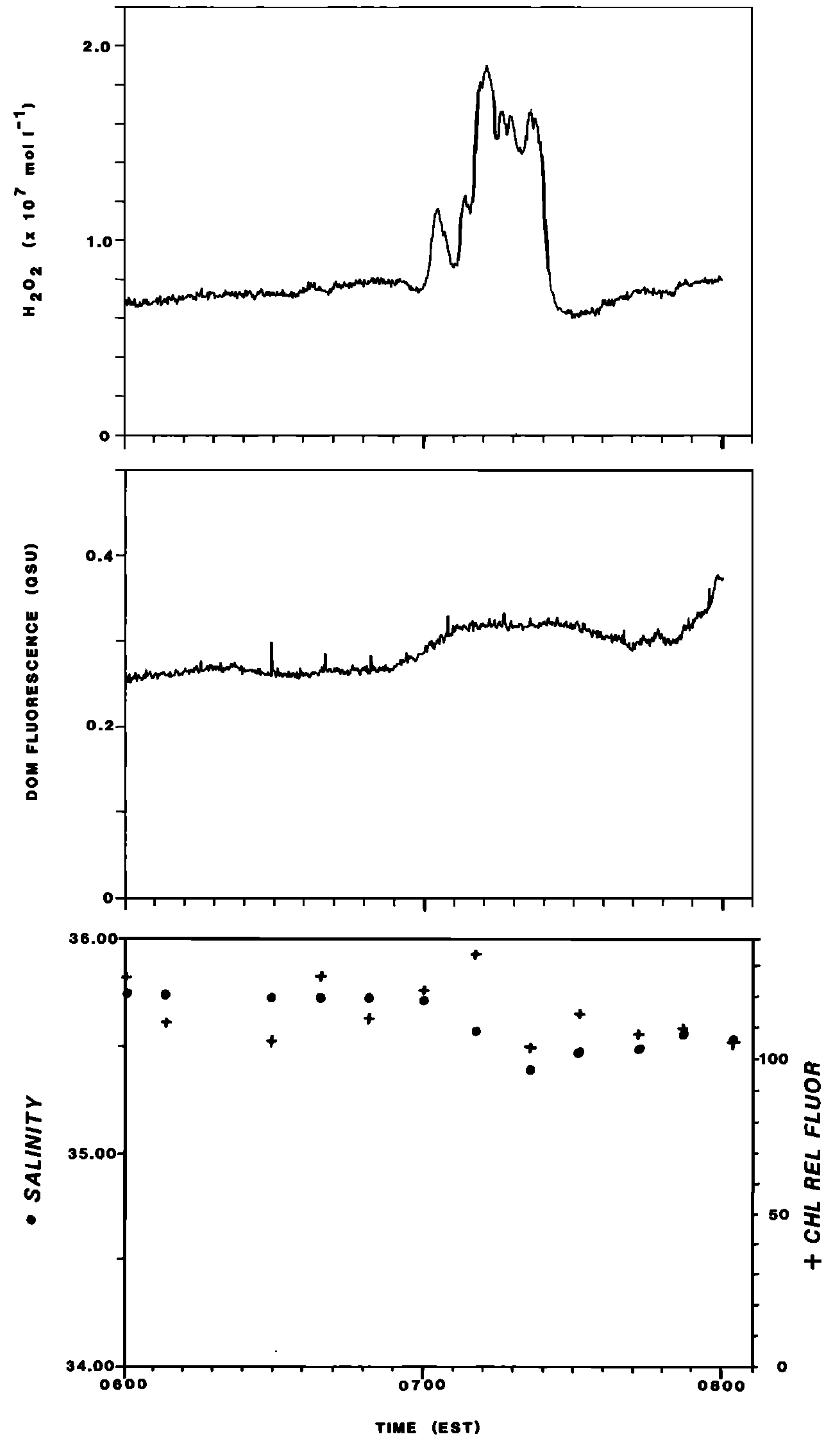

Fig. 5. Surface ocean measurements of H_2O_2, DOM fluorescence, chlorophyll, and salinity, just prior to arriving at station 2, seas were flat, SOLARS III.

compounds such as aldehydes and unsaturated hydrocarbons, which promote peroxide formation via production of gas phase peroxy radicals [Bufalini et al., 1972].

Another factor influencing the concentration of H_2O_2 in rain is the abundance of SO_2. Dissolved SO_2 reacts rapidly with H_2O_2 in droplets in the pH range of cloud and rainwater [Kunen et al., 1983; Martin, 1984]. In clean marine air, SO_2 concentrations are low and unlikely to modify the levels of H_2O_2 concentration in either cloud or rainwater. This is quite different from polluted air, where SO_2 concentrations may equal or exceed those of H_2O_2, resulting in rapid depletion of H_2O_2 within the cloud droplets [Jacob, 1986]. This effect may be offset to some extent in urban air by the presence of formaldehyde, which can stabilize

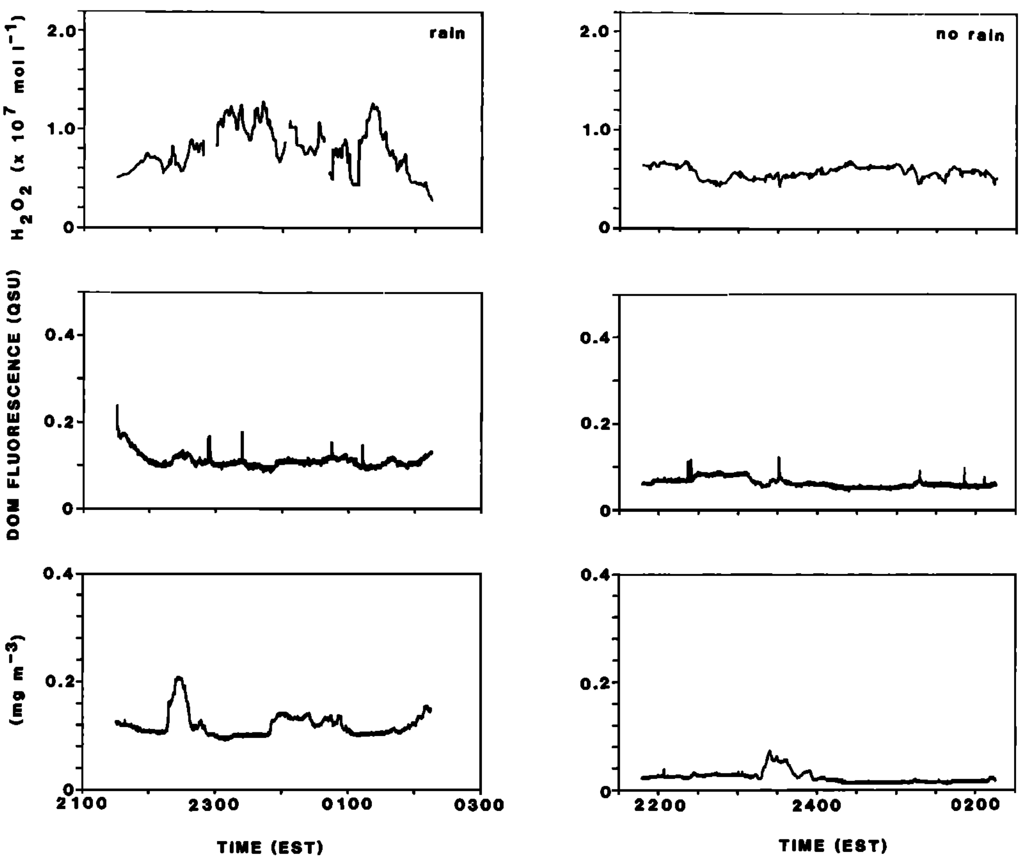

Fig. 6. Comparison between surface ocean H_2O_2, DOM fluorescence, and chlorophyll during a rain and with no rain, SOLARS VI. Rain occurred between longitude 78°50'W and 78°12'W. The location of the "no rain" was longitude 74°45'W and 73°00'W.

HSO_3^- as hydroxymethanesulfonic acid [Richards et al., 1983; Munger et al., 1986]. High concentrations of trace metals in urban air may also modify the peroxide levels in cloud and rainwater either through catalytic destruction of H_2O_2 or by photochemical production of peroxide precursors via photosensitization [Calvert et al., 1986].

In general, the factors controlling the concentration of H_2O_2 in rain appear to be somewhat more complex and variable in urban air than in marine air. Because of the spatial heterogeneity of the sources of many reactive species in continental air, we might expect a greater variability in H_2O_2 associated with continental rain as compared with marine rain. Except in special circumstances, we would expect the marine rain to exhibit generally high H_2O_2 levels as a consequence of the low NO and S(IV) levels.

The most important sources of variability of H_2O_2 in marine air are likely to be climatic, variations in temperature, insolation, and water vapor. The measurements to date for H_2O_2 in marine rain are limited to subtropical regions. We would expect to observe more dramatic and systematic variation as larger regions of the ocean are sampled.

At the present time it is not known whether the emission of reactive species from the sea surface can influence H_2O_2 concentrations in marine air. If so, then there may be observable variation relating to the productivity on the underlying waters. As in urban air, the species of primary interest would be precursors of NO_x and unsaturated hydrocarbons and aldehydes.

Survey of hydrogen peroxide in rain. In comparing data on the concentration of H_2O_2 in rain, it is necessary to recognize that many of the early reports used the chemiluminescent luminol method. This method has since been shown to have interferences from SO_2 [Yoshizumi et al., 1984] and several heavy metals [Ibusuki, 1983]. However, several reports using alternate or modified methods have been recently published, and these data bases are briefly discussed here. A detailed statistical comparison of the data base is not meaningful because of the limited nature of the data.

Zika et al. [1982] reported H_2O_2 concentrations in rain collected in Miami, Florida, and the Bahamas. The H_2O_2 concentrations ranged from 115 to 750 x 10^{-7} mol L^{-1}, with a mean of 312 x 10^{-7} mol L^{-1}. They noted that their data reflected substantial input of oceanic air. Yoshizumi et al. [1984] reported data from rain collected near Tokyo, Japan. Over the entire year they observed monthly averages ranging from 3.15 to 134 x 10^{-7} mol L^{-1}, with a yearly average of 64 x 10^{-7} mol L^{-1}. Kelly et al. [1985] reported data from nonurban areas in the southeastern United States. Fifty percent of the samples (total samples n = 54) in that study had less than 50 x 10^{-7} mol L^{-1} H_2O_2, and another 20% fell between 50 and 100 x 10^{-7} mol L^{-1}.

In general, our data from the Gulf of Mexico

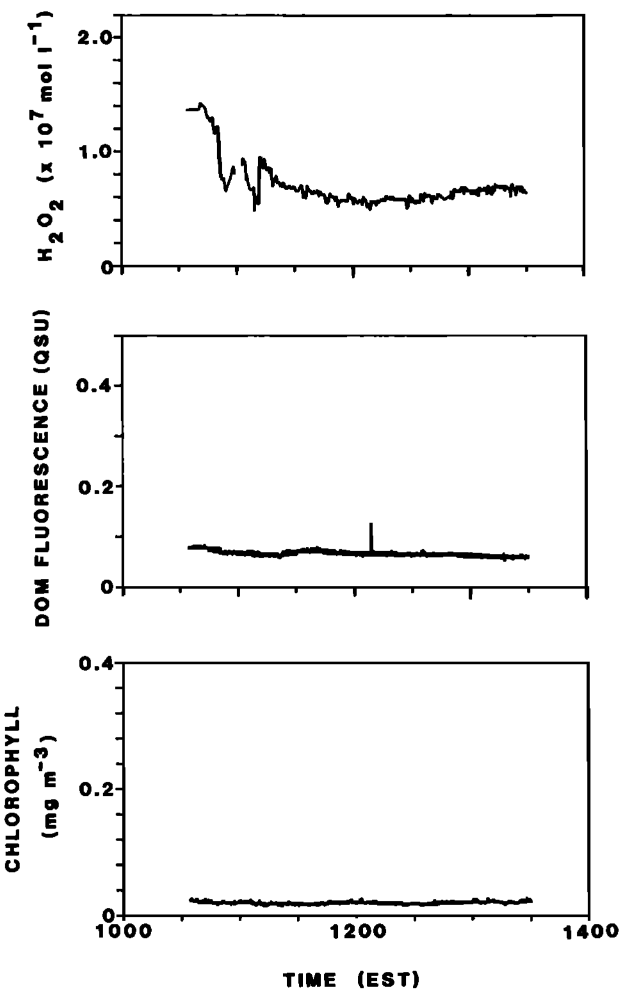

Fig. 7. Surface ocean measurements of H_2O_2, DOM fluorescence, and chlorophyll during midday, longitude 68°46'W, SOALRS VI.

are higher than those observed over land and similar to those reported by Zika et al. [1982]. The H_2O_2 concentrations observed in the western Atlantic and off the Florida Keys, although lower than those from the Gulf of Mexico, are also higher than those over land.

Diel variability of the H_2O_2 concentration in rain has been observed. Yoshizumi et al. [1984] observed a diel variation during a summer month, June, while no diel variability was observed in November. The low was observed in the early morning and late afternoon, ≈18 x 10^{-7} mol L^{-1}, and the high just after noon, ≈220 x 10^{-7} mol L^{-1}. From our limited data set there was no apparent relationship of H_2O_2 concentration to time of day. Additional sampling is required to determine the extent, if any, of diel variability in marine rain.

In this study, sequential samples were taken during rainstorms whenever possible. For the most part, no noticeable decrease in H_2O_2 concentration was observed. The one possible exception to this was the samples during rain event I (Table 1), which decreased from 187 to 119 x 10^{-7} mol L^{-1} in a very short time. A more extensive data base is necessary to determine the diel, seasonal, or spatial variability of H_2O_2 concentrations, as well as the effect of "washout" on H_2O_2 in oceanic rains.

The effect of marine rain on surface ocean hydrogen peroxide. We have presented measurements of marine rain H_2O_2 concentrations and have shown that the surface H_2O_2 concentrations can be dramatically affected by local rain events. The effect of rain in elevating surface concentrations of H_2O_2 will depend on the extent of rain events, the H_2O_2 concentration in rain, and mixing (R. G. Zika et al., manuscript in preparation, 1986). The effect of varying amounts of rainfall on the concentration of H_2O_2 in homogeneous mixed layers to different depths is shown in Figure 9. It is obvious that when conditions exist that support stable near-surface stratification (i.e., 0.1-2.0 m), the H_2O_2 concentration can attain levels that are 1-2 orders of magnitude higher than the mean concentration normally found at this time of year in the Gulf of Mexico. Heavy rains, such as those encountered in the tropics or in hurricanes, can substantially increase the mean water column H_2O_2 concentration locally to depths of 50 m and greater.

Further, Zika et al. [1985a] have shown diel variations in H_2O_2 concentration in several areas of the Gulf of Mexico that result primarily from photochemical processes. In general, there is an increase in surface H_2O_2 concentration during the

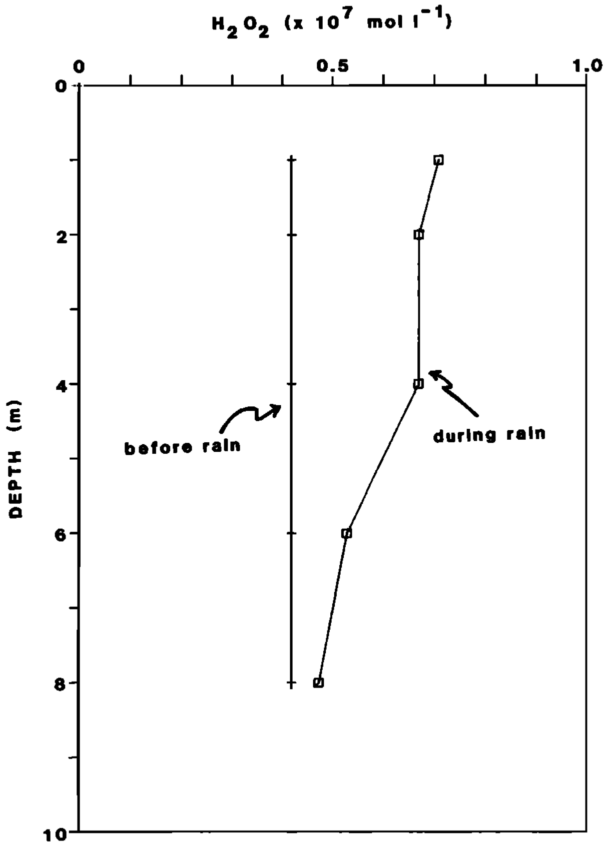

Fig. 8. Hydrogen peroxide concentration depth profile while at anchor in the Dry Tortugas (latitude 24°38.0'N, longitude 82°52.9'W). Crosses show H_2O_2 concentration before rain, and squares show H_2O_2 concentration during a light rain.

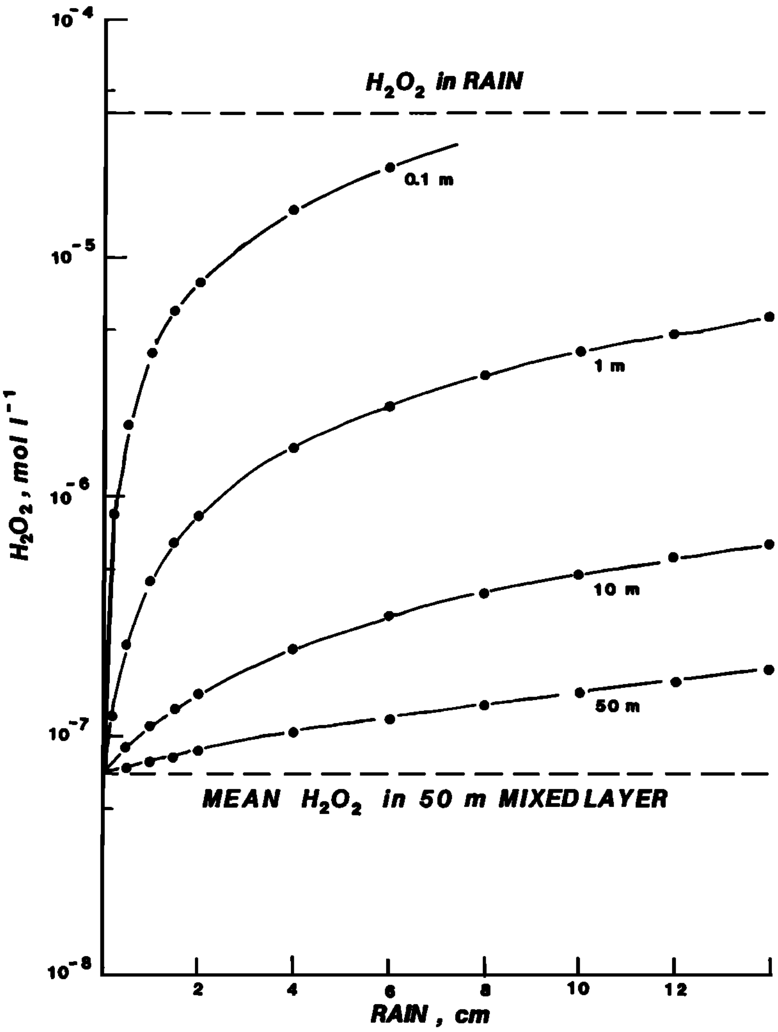

Fig. 9. Model calculations of the impact of rain on the concentration of H_2O_2 at different depths of a homogeneous mixed layer in the Gulf of Mexico.

day. At night the H_2O_2 concentration decreases as a result of a combination of chemically and biologically mediated processes, as well as convective mixing of the water column. The changes in H_2O_2 concentrations observed in this study were, in most cases, rapid and of a magnitude that far exceeded the normal diel variability in the open ocean. The increases and decreases observed during the day were superimposed on the variability caused by the photochemical processes leading to the formation of H_2O_2.

The persistence of a transient input, such as rain, on surface ocean H_2O_2 concentrations is possible, in the event of weak mixing. An example is shown in Figure 5, where a rapid increase in the H_2O_2 concentration most likely resulted from an earlier rain squall. In environments where rainfall is common, local patchiness is likely to be observed and may account for the significantly greater spatial variability than would otherwise have been present under clear conditions in the same environments [Zika et al., 1985a].

The increase in fluorescence in surface water, associated with the rain events in the Gulf of Mexico, is presently unexplained. It is possible that these increases are associated with terrestrial input of DOM in the surface ocean from major tributaries (i.e., Mississippi River) in the Gulf of Mexico. The coincidental occurrence of freshwater sources and rainwater input occurring several times during the cruise is unlikely. These increases may reflect rain input; however, this was not confirmed with the data obtained while in the western Atlantic. Further studies are in progress to investigate this phenomenon.

It has recently been reported that H_2O_2 may be formed in association with freshwater algae [Zepp et al., 1987], and the possibility of this in marine waters has been suggested Palenik and Morel, 1985]. From the data presented here, in areas of low productivity, there does not appear to be a relationship of chlorophyll *a* and H_2O_2 concentration. It is necessary to extend these studies to other environments to better define these relationships.

In summary, we have shown that rain may significantly increase the H_2O_2 in surface oceans. Variations of the magnitude we have shown could significantly affect the redox chemistry of the surface ocean [van der Weijen and Reith, 1982; Sunda et al., 1983; Moffett and Zika, 1983, 1987, and Reaction kinetics of hydrogen peroxide with copper and iron in seawater, submitted to Environmental Science and Technology, 1986].

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