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HYDROGEN PEROXIDE CONCENTRATIONS IN THE PERU UPWELLING AREA

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ABSTRACT

Zika, R.G., Saltzman, E.S. and Cooper, W.J., 1985. Hydrogen peroxide concentrations in the Peru upwelling area. *Mar. Chem.*, 17: 265–275.

The concentration of hydrogen peroxide was measured in waters off the coast of Peru during June and July 1983. The study period coincided with the end of the 1982/83 El Niño and the onset of coastal upwelling. Depth profiles of hydrogen peroxide concentration exhibit surface maxima and decrease with depth to the base of the mixed layer. Surface peroxide concentrations ranged from 0.8 to 5×10^{-8} M. Below the mixed layer hydrogen peroxide was below the detection limit (5×10^{-9} M). Diel variations were observed, with surface peroxide levels increasing during the day and decreasing at night. The nearshore station exhibited lower hydrogen peroxide concentrations than offshore stations, a reversal of the trend found in other coastal regions. This is attributed to the lack of coastal vegetation and runoff, and to active coastal upwelling of deeper water with low hydrogen peroxide concentrations.

INTRODUCTION

Hydrogen peroxide in the surface ocean may have several sources. In sunlight the dissolved constituents in seawater can act as electron sources in the reduction of oxygen, resulting in the formation of the superoxide ion, O_2^- (Zika, 1981; Zafiriou, 1983). This species either reacts as a reducing agent with other constituents of seawater or undergoes disproportionation, producing H_2O_2 according to the reaction



(Zika, 1981). Biological production of hydrogen peroxide has also been suggested as a possible source, but little is known about it at present. Hydrogen peroxide is also produced photochemically in the atmosphere, both in gas phase and in aerosols. Peroxide production in gas phase is due to disproportionation of HO_2 and in aerosols to a number of aqueous phase reactions involving in situ photochemical production and scavenging of gas

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phase free radical precursors (Chameides and Davis, 1982; Saltzman et al., 1984). Atmospheric input of peroxide and free radical precursors to the sea surface may occur by both wet and dry deposition (Zika et al., 1982; Thompson and Zafiriou, 1983).

The occurrence of H_2O_2 in surface seawater, even at low concentrations, could have significant consequences for redox chemistry affecting trace metal speciation (Moffett and Zika, 1983), the composition of marine organic matter, and the marine biota. H_2O_2 is reactive with many species in seawater and can act as either an oxidant or reductant in different reactions. Van Baalen and Marler (1966) and Moffett and Zika (1983) have reported levels ranging from 1.5 to 19.7×10^{-8} MH_2O_2 in a few samples from coastal and open Gulf of Mexico waters. A more detailed study of H_2O_2 in the Gulf of Mexico has recently been reported (Zika et al., 1985). In this paper we present measurements of H_2O_2 in waters off the coast of Peru and qualitatively discuss the processes which may control its distribution.

STUDY AREA

This study was conducted aboard the R/V "Researcher" (NOAA R-103) off the southern coast of Peru from June 29 to July 15 1983 (Fig. 1). Depth profile data were collected at four stations: N-1 ($15^{\circ}02.5'S$, $75^{\circ}26.2'W$); N-2 ($15^{\circ}06.0'S$, $75^{\circ}30.0'W$); N-EX ($16^{\circ}32.5'S$, $77^{\circ}02.2'W$); Paracas (approximately $14^{\circ}07'S$, $76^{\circ}31'W$). In addition, surface and 5 m depth measurements were made along the two transects shown in Fig. 1. Under normal conditions the Peruvian coast is a site of active upwelling (Brink et al., 1981). However, in June 1982 the eastern equatorial Pacific ocean surface water temperature increased with a concomitant decrease in upwelling, a phenomenon known as El Niño (Rasmussen et al., 1983). The El Niño of 1982/1983 was particularly persistent, lasting through June/July 1983 at which time upwelling appeared to resume (Atwood et al., 1983).

The period of time during which this study took place was one of transition from El Niño to normal upwelling conditions. The increased nitrate levels and lower surface temperatures observed at stations N-1 and N-2 during early July, suggest that there was a rapid return to the nutrient-rich conditions observed during normal years (Atwood et al., 1983).

EXPERIMENTAL TECHNIQUES

Water samples were collected using 5-l PVC Niskin samplers or 8-l Teflon-lined Go-Flo bottles (General Oceanics, Miami, FL), which were tested for H_2O_2 loss or artifacts. After collection, the samples were immediately transferred to 250-ml teflon-lined screw cap glass bottles. The analyses were begun immediately upon retrieval of each cast. No significant decay of peroxide occurred during the period of analysis. Most samples were analyzed in duplicate. Hydrogen peroxide analyses were done using a modified

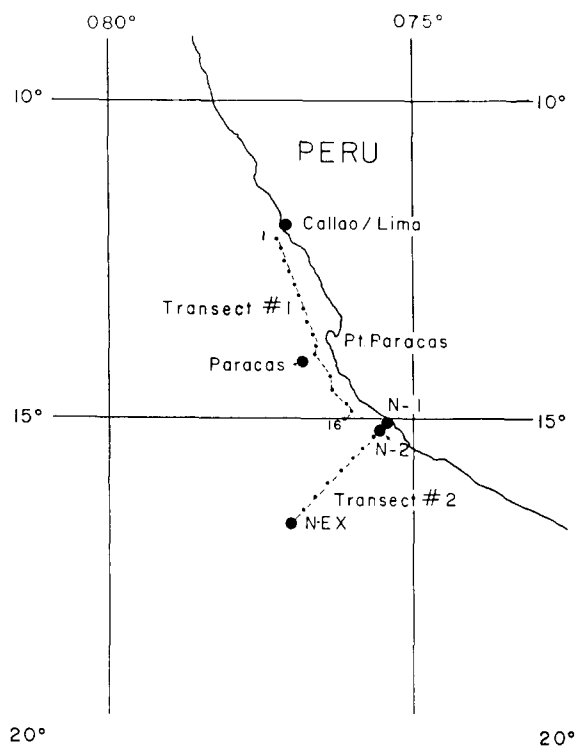


Fig. 1. Study area and hydrogen peroxide sampling locations from the NOAA R/V "Researcher" cruise off the southern coast of Peru, during June and July 1983.

scopoletin-horse radish peroxidase fluorescence decay technique (Perschke and Broda, 1961; Zika and Saltzman, 1982). A Turner Designs Model 10 fluorometer was used for all fluorescence measurements with excitation and emission wavelengths of 365 and 490 nm, respectively. While this technique does respond to some low molecular weight organic peroxides, as well as H_2O_2 , the kinetics of the fluorescence decay are different for organic peroxides and no evidence was found to suggest their presence during this study (Zika et al., unpublished data).

RESULTS

In this section we present depth profiles of hydrogen peroxide concentrations at four stations. Data are also reported from two transects. The profiles are shown in Figs. 2–5 and the transects in Figs. 6 and 7.

Depth profiles

Station N-EX is located 23 miles from shore in approximately 3000 m of water (Fig. 1). At this station, three hydrogen peroxide depth profiles

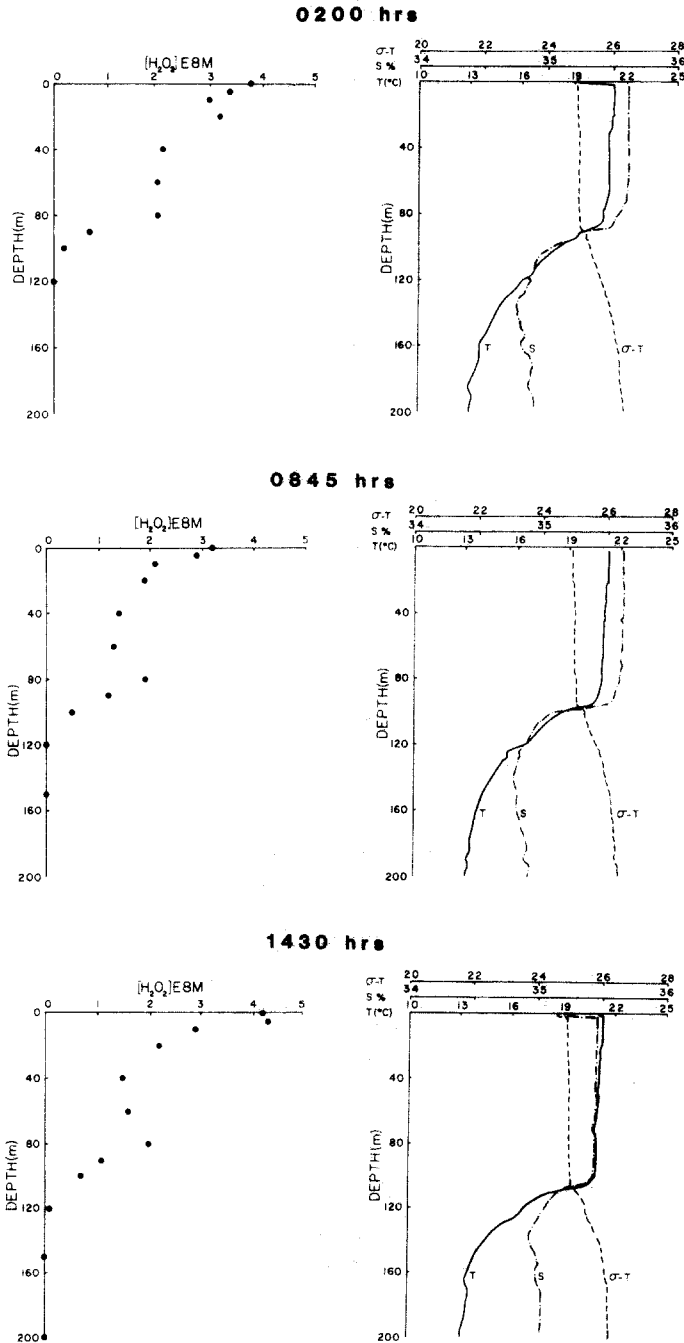
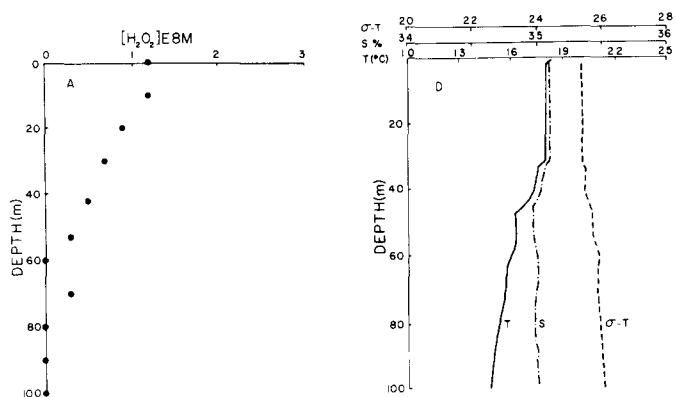
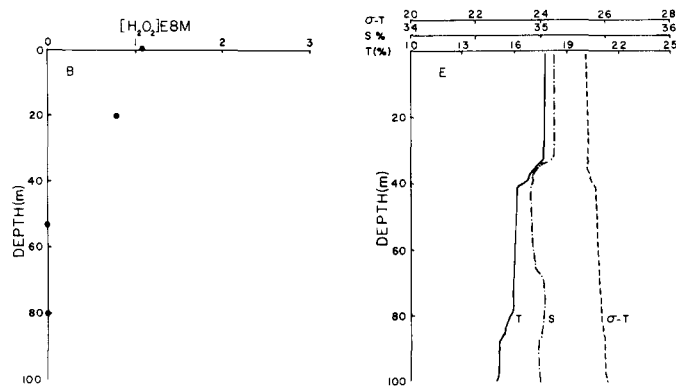


Fig. 2. Depth profiles of hydrogen peroxide, salinity, temperature, and sigma-T at station N-EX.

2350 hrs, July 3



0815 hrs, July 3



0230 hrs, July 10

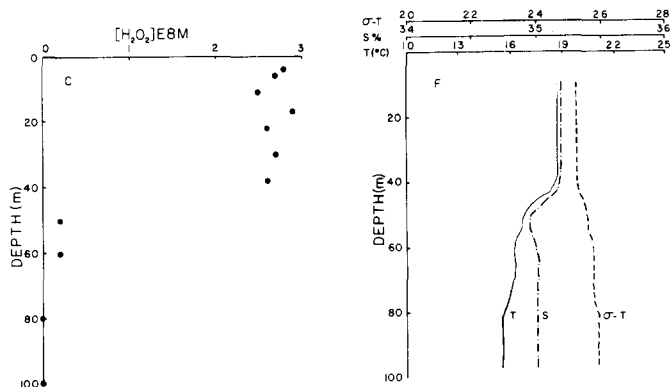


Fig. 3. Depth profiles of hydrogen peroxide, salinity, temperature, and sigma-T at station N-2.

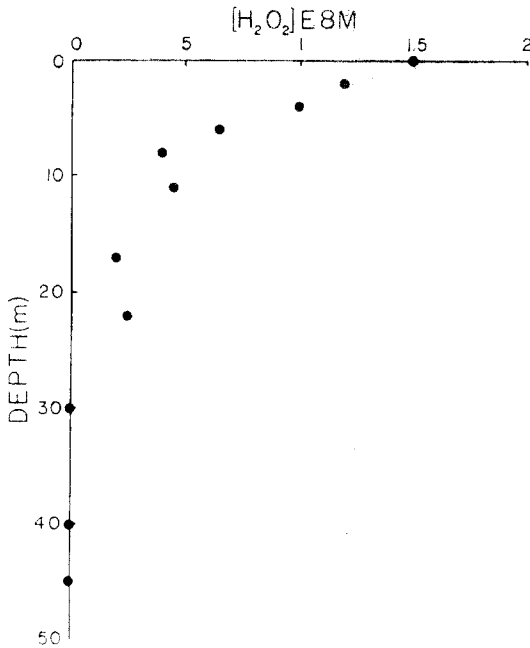


Fig. 4. Depth profiles of hydrogen peroxide, salinity, temperature, and sigma-T at station N-1.

were measured at 0200, 0845, and 1430 h local time (Fig. 2). Diel variations in the concentration of hydrogen peroxide were present, but relatively small. From 0200 to 0845 h the concentration of hydrogen peroxide decreased by roughly 30% in the upper 60 m. This was followed by an increase during daylight hours, observed almost entirely in the upper 20 m, with surface values increasing from 3.2×10^{-8} M at 0845 h to 4.3×10^{-8} M at 1430 h. The depth of the thermocline at this station was between 90 and 100 m with almost no stratification in either temperature or salinity between the surface and 75 m. In contrast, all three H_2O_2 depth profiles decrease sharply with depth from the surface to about 40 m. Between 40 and 80 m, the H_2O_2 profiles are more uniform with depth. Below this depth, peroxide levels rapidly decrease to below the detection limit (5×10^{-9} M).

Station N-2 is located approximately 6 miles from shore in 120 m of water (Fig. 1). This station was visited twice during the cruise. Three depth profiles were obtained, two at 0815 and 2350 h (3 July 1983) and the other at 0230 h (10 July 1983) (Fig. 3). For the two profiles on 3 July the hydrogen peroxide concentration decreased slightly (approximately 10%) from 2350 to 0815 h. The hydrogen peroxide depth profile showed the normal surface maximum with decreasing concentrations with depth. The temperature and salinity profiles show evidence of mixing down to 40–60 m with a stable layer between about 30 and 45 m. The deeper layer, below

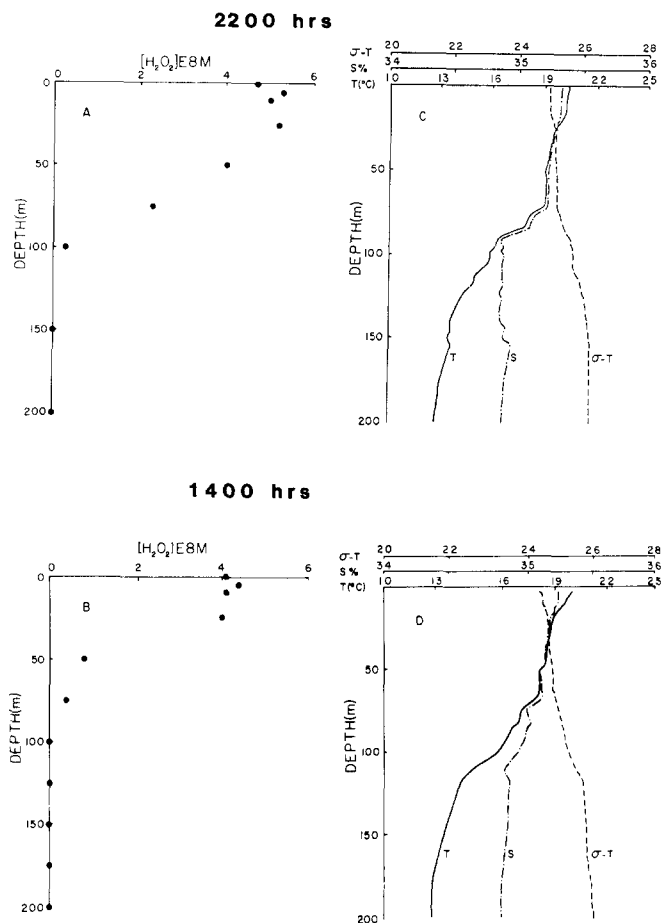


Fig. 5. Depth profiles of hydrogen peroxide, salinity, temperature, and sigma-T at station Paracas.

40 m, is cut off from the surface mixed layer and is probably older, which would explain why the peroxide in the deeper mixed layer is more uniformly mixed within that layer. A small, but analytically reproducible, increase in concentration was observed at 70 m (Fig. 3), but no additional profiles were made to confirm the existence of this deep layer of elevated peroxide concentrations.

The depth profile obtained on 10 July showed two distinct differences from the earlier profiles. The surface concentration of hydrogen peroxide was greater (2.8×10^{-8} M) and the concentration was nearly constant to 40 m, with a sharp decrease to 0.2×10^{-8} M at 50 m. This is consistent with the temperature and salinity profiles which show a well mixed layer to 40 m and a well-defined thermocline. The profiles measured one week earlier showed a shallower surface mixed layer (30 m) with a gradient in H₂O₂.

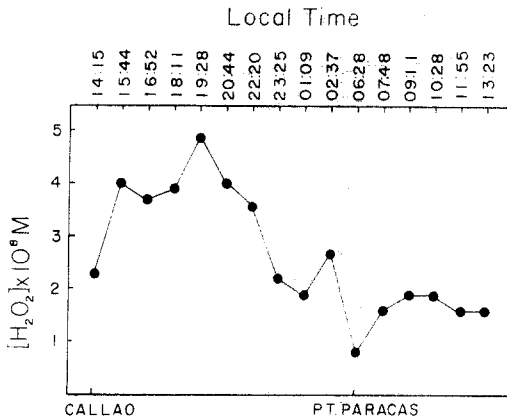


Fig. 6. Hydrogen peroxide concentrations at 5 m depth in transect samples collected from Callao to south of Point Paracas.

Station N-1 is located approximately 1 mile from shore in 50 m of water (Fig. 1). One depth profile was taken at this station at 0915 on 12 July (Fig. 4). The concentration of hydrogen peroxide at 5 m was 1.5×10^{-8} M. The depth profile shows a sharp decrease in concentration to 0.5×10^{-8} M at a depth of 10 m, followed by a slower decrease to below the detection limit at 30 m. The mixed layer appeared to be about 20 m deep. Unfortunately, a CTD was not recorded at this station, but low surface temperatures and upward sloping isotherms offshore indicate active upwelling of water from 50 to 80 m depth (Atwood et al., 1983). The low concentrations and shallow depth of depletion of H₂O₂ at this station were probably due to the short near-surface residence time and low residual peroxide concentration in this upwelled water.

Station Paracas was located off Point Paracas. Two depth profiles were

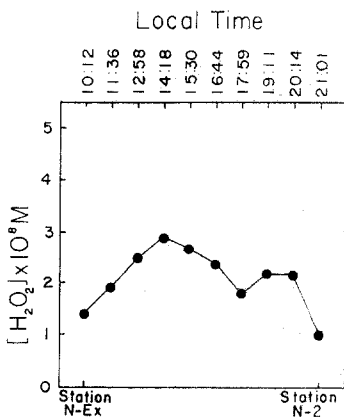


Fig. 7. Hydrogen peroxide concentrations at 5 m depth in transect samples collected from station N-EX to station N-2.

obtained, one at $14^{\circ}07.5'S$, $76^{\circ}32.2'W$ and the other at $14^{\circ}05.7'S$, $76^{\circ}30.1'W$ at 2200 and 1400 h, respectively (Fig. 5). The depth profile obtained at 2200 h showed an average of 5×10^{-8} M hydrogen peroxide at the four uppermost sample depths (less than 25 m), then a gradual decrease in concentration to the detection limit below 100 m. The temperature and salinity profiles show a shallow mixed layer, down to only 20 m, and a strong thermocline at 75 m. The break in the temperature profile at 20 m is consistent with the break in the H_2O_2 profile. The depth obtained at 1400 h showed an average of 4.1×10^{-8} M hydrogen peroxide at the four uppermost sample depths, then a sharp decrease to 0.9×10^{-8} M at 50 m followed by a gradual decrease to the detection limit at 100 m. The sharp break in the H_2O_2 profile is again consistent with a shallow surface mixed layer.

Transects

A series of 5-m samples was analyzed along two transects (Fig. 1) to assess the spatial variability of hydrogen peroxide over a broad geographic area. The first transect extended from Callao to south of Point Paracas and consisted of 16 samples collected over a 24-h period. The results ranged from 0.8 to 4.9×10^{-8} M (Fig. 6). There is some suggestion of diel variations in the data, as the highest concentrations were obtained in the late afternoon and early evening and the lowest concentrations were found in the early morning. However, it should be noted that the track traversed a large geographic area, and variability in other factors may account for the observed trend.

The second transect, from N-EX to N-2, consisted of ten samples over a 12-h period. Concentrations ranged from 1.0 to 2.9×10^{-8} M (Fig. 7). In this case the highest concentrations were observed in the early afternoon and decreased steadily through the night. We do not feel that this reflects a real diel cycle, but rather a general decrease in peroxide concentrations with proximity to the coast, which was the site of active upwelling as evidenced by low water temperatures and enriched nutrient levels (Atwood et al., 1983).

DISCUSSION

In this study, all of the hydrogen peroxide depth profiles exhibit similar characteristics: a surface maximum, a general decrease with depth to the base of the mixed layer, and no detectable peroxide below the mixed layer. These features, along with the diel variations observed at station N-EX are consistent with the photochemical generation of hydrogen peroxide during daylight hours with downward mixing and dark decay processes dominating at night. Similar profiles and diel cycles have been found in the Atlantic ocean and the Gulf of Mexico (Zika, 1980; Zika et al., 1985).

Hydrogen peroxide concentrations in Peruvian coastal waters did not

exceed 5×10^{-8} M. These values are considerably lower than those measured in the Atlantic ocean and the Gulf of Mexico, where surface peroxide concentrations are frequently greater than 10^{-7} M, even in oligotrophic waters. In these areas a strong coastal effect was noted, with peroxide levels increasing nearshore, presumably due to the input of terrestrial humic material (Zika, 1981; Cooper and Zika, 1983). In Peru, this effect was notably absent; in fact, peroxide levels were lowest nearshore. This is probably the result of two factors: the lack of vegetation on and runoff from the arid Peruvian coastline; and dilution of nearshore surface waters by upwelled water devoid of peroxide. Offshore the generally low levels of peroxide may reflect, at least in part, the low light levels (heavy cloud cover was always present) and the lack of rainwater input of hydrogen peroxide. Marine rainwater has been shown to contain high concentrations of hydrogen peroxide (of the order of 10^{-5} M; Zika et al., 1982) and may constitute a major source to the surface ocean in some regions.

Another factor of potential importance to peroxide levels in Peruvian coastal waters is the nature of the marine organic matter present and its variability in upwelling regions. The highest surface concentrations of peroxide were measured off Point Paracas. It was at this station that the highest biomass and productivity were observed. This could indicate direct biological production or indirect production via the reduction of oxygen by sunlight-initiated reactions with extracellular materials (e.g., photosynthetic pigments or flavins). The lower peroxide concentrations found at the stations nearest to and farthest from the coast (N-1 and N-EX) may be related to the low biomass and level of biological productivity observed at these stations.

It is clear that a number of processes may affect the levels of H_2O_2 in the oceans. It is not possible from the data presented in this paper to assess their relative importance. A mechanistic understanding of hydrogen peroxide in the marine environment will require detailed field and experimental investigation into a variety of potentially important production and decay mechanisms which are at present poorly understood.

SUMMARY

(1) Hydrogen peroxide profiles measured off the coast of Peru exhibit surface maxima and decrease with depth to the base of the mixed layer. Maximum peroxide concentrations ranged from 0.8 to 5.2×10^{-8} M. Below the mixed layer peroxide levels were less than 5×10^{-9} M, the lower detection limit of the analysis.

(2) Diel variations were observed with surface peroxide levels increasing during the day and decreasing at night.

(3) Hydrogen peroxide concentrations off Peru do not exhibit the strong nearshore increase found in other areas. This is probably related to the lack of coastal vegetation and the presence of coastal upwelling.

(4) The data support the idea that hydrogen peroxide is formed via photochemical processes and is destroyed by dark decay reactions. The exact nature of these processes and their rates are as yet unknown.

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