

UC Irvine

UC Irvine Previously Published Works

Title

Spatial and temporal variations of hydrogen peroxide in Gulf of Mexico waters

Permalink

<https://escholarship.org/uc/item/2p68t116>

Journal

Geochimica et Cosmochimica Acta, 49(5)

ISSN

0016-7037

Authors

Zika, Rod G
Moffett, James W
Petasne, Robert G
[et al.](#)

Publication Date

1985-05-01

DOI

10.1016/0016-7037(85)90008-0

Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed

Spatial and temporal variations of hydrogen peroxide in Gulf of Mexico waters

ROD G. ZIKA, JAMES W. MOFFETT, ROBERT G. PETASNE, WILLIAM J. COOPER¹ and ERIC S. SALTZMAN

University of Miami, Rosenstiel School of Marine and Atmospheric Science,
4600 Rickenbacker Causeway, Miami, FL 33149

(Received November 9, 1984; accepted in revised form January 31, 1985)

Abstract—Hydrogen peroxide concentrations in the Gulf of Mexico were measured on two cruises in May and August, 1982, in a variety of locations ranging from oligotrophic oceanic stations to highly productive coastal sites. Measurements were made using a fluorescence decay technique. Depth profiles of H₂O₂ exhibit surface maxima of 1–2 × 10⁻⁷ mol L⁻¹ and decreasing concentrations with depth. Peroxide concentrations decreased only slightly or were invariant with depth in the mixed layer but decreased sharply to below the limit of detection (5 × 10⁻⁹ mol L⁻¹) in the region of the pycnocline at the base of the mixed layer. Surface concentrations were generally highest in coastal regions but did not vary by more than a factor of three among all stations studied. There was a marked diel variation in peroxide profiles, with the highest values occurring during the late afternoon, and the lowest values occurring at dawn. Diel variations were more pronounced in coastal surface waters than in oligotrophic waters. The observations are consistent with photochemical formation of H₂O₂ by photooxidation of dissolved organic matter. However, other formation pathways, such as biological formation or atmospheric deposition, cannot be ruled out at this point.

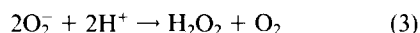
INTRODUCTION

HYDROGEN PEROXIDE is an important intermediate in aqueous redox processes involving oxygen. This is true for both biological and nonbiological processes; therefore, it is to be expected that hydrogen peroxide should be produced in substantial quantities in natural waters. In seawater, H₂O₂ may play an important role in redox reactions involving transition metals and organic compounds (ZIKA, 1981; ZAFIRIOU, 1983; MOFFETT and ZIKA, 1983). This reactive nature and the fact that H₂O₂ can be produced *in situ* by a number of different reaction pathways or introduced from the atmosphere, make its probable distributions dependent on many different characteristics of the environments (ZIKA, 1984). It is to be expected therefore that it will act as a highly non-conservative property of the seawater which exhibits considerable temporal and spatial variability.

Numerous specific reaction mechanisms are possible for the formation of H₂O₂ in seawater. Most of these mechanisms involve the single electron reduction of molecular oxygen to form the intermediate O₂⁻. The photooxidation of organic matter in seawater has been suggested to be the major *in situ* source of H₂O₂ in the ocean and evidence for the involvement of O₂⁻ as an intermediate in these reactions (ZIKA, 1980; COOPER and ZIKA, 1983; DRAPER and CROSBY 1983) leads to a general mechanism:



Subsequent disproportionation of O₂⁻ leads to H₂O₂ formation *via*



If this general photochemical mechanism is the source in seawater, then the concentration distributions should be controlled by a complex set of factors involving such things as light intensity, concentration of organic matter, and physical mixing processes. In addition, other potential sources like biological production and wet and dry deposition of atmospheric H₂O₂ (THOMPSON and ZAFIRIOU, 1983) may contribute to development of highly variable and dynamic surface ocean distribution of this important chemical species.

Little information on the concentration distribution of H₂O₂ in the ocean exists in the literature. The first report was by VAN BAALEN and MARLER (1966) who measured surface levels ranging from 1.5 to 19.7 × 10⁻⁸ mol L⁻¹ in the Gulf of Mexico. More recently, surface and depth profiles from marine coastal waters and the Florida Current (ZIKA, 1980), the central Gulf of Mexico (MOFFETT and ZIKA, 1983) and the Peru upwelling area have been reported (ZIKA *et al.*, in press). In view of the complex nature of the H₂O₂ system, considerably more measurements are necessary to understand its role in the marine environment.

In this study H₂O₂ was determined at a variety of locations in the Gulf of Mexico, from oceanic oligotrophic waters in the center of the Gulf to highly productive coastal waters off the western coast of Florida. Measurements were made aboard the R. V. "Researcher" (NOAA) on two cruises in May and August, 1982.

EXPERIMENTAL

Samples were collected in 5 liter PVC Niskin bottles (General Oceanics, Miami, Fl.) attached to a Neil Brown CTD rosette sampler suspended from the ship. Samples were immediately transferred to 250 ml Teflon lined screw

¹ Present Address: Drinking Water Research Center, Florida International University, Miami, FL 33199

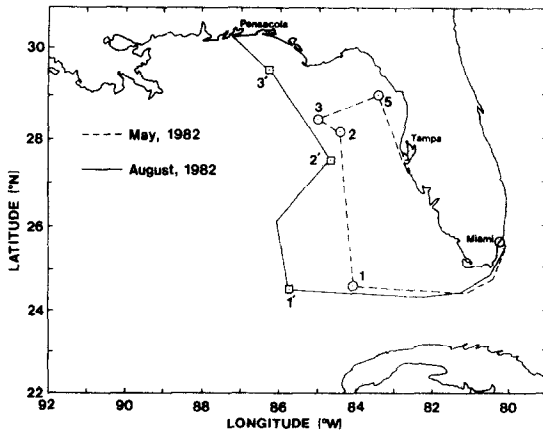


FIG. 1. Map of Gulf of Mexico showing station locations.

cap glass bottles. Analyses were begun immediately upon retrieval of each cast and all samples were analysed within two hours of collection. No significant formation or decay

of peroxide occurred during sampling or storage prior to analysis. Analyses were performed using a scopoletin horseradish peroxidase fluorescence decay procedure described elsewhere (ZIKA and SALTZMAN, 1982). The limit of detection of this procedure is approximately 5×10^{-9} mol L⁻¹. A Turner Designs Model 10 fluorometer was used for all fluorescence measurements, with excitation and emission wavelengths of 365 and 490 nm, respectively. The method is also sensitive to low molecular weight organic peroxides. These can be distinguished from H₂O₂ by examining the reaction kinetics of the scopoletin fluorescence decay or with the use of catalase (ZIKA *et al.*, unpublished). Application of these techniques during the cruises indicated that no detectable organic peroxides were present in the samples. Supporting hydrographic data was obtained for each cast. Salinity was determined in most instances using the CTD, but there were a few cases where salinities were determined using a shipboard Guildline Autosol 8400 Salinometer.

SAMPLING REGIONS

Data presented in this paper was collected during the two cruises in May and August, 1982. The approximate cruise tracks and sampling locations are shown in Fig. 1. Depth

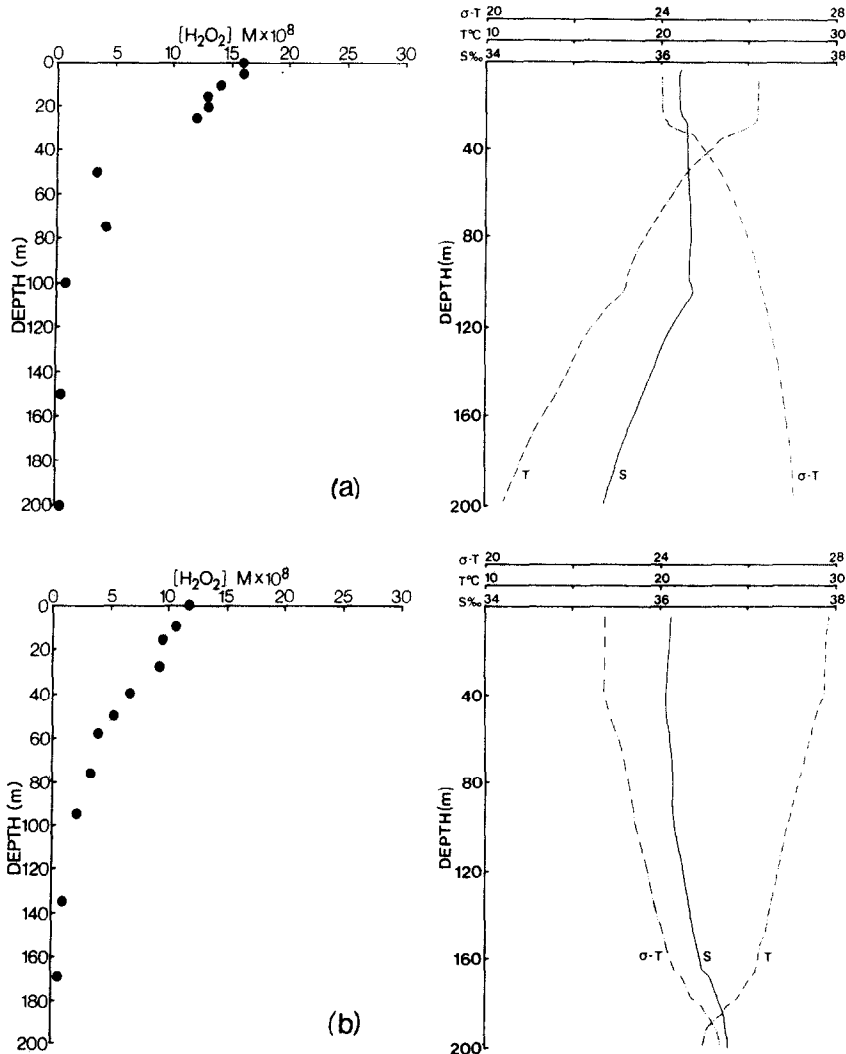


FIG. 2. Representative profiles from (a) station 1, 1900 h; (b) station 1', 1200 h.

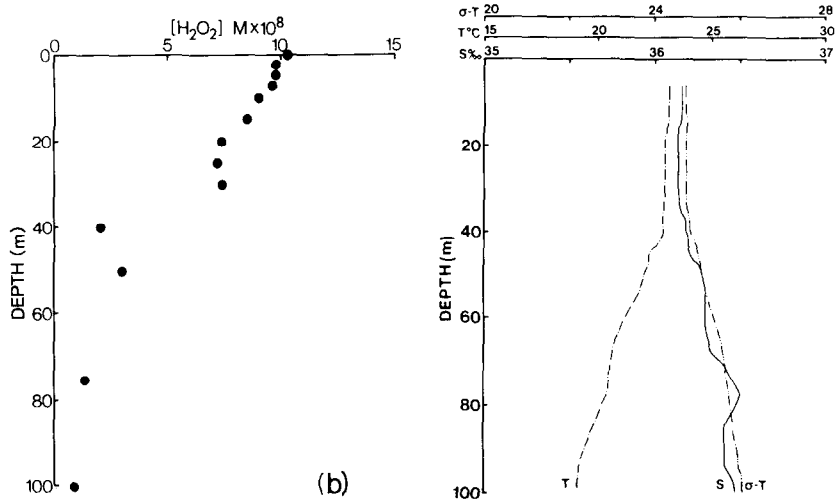
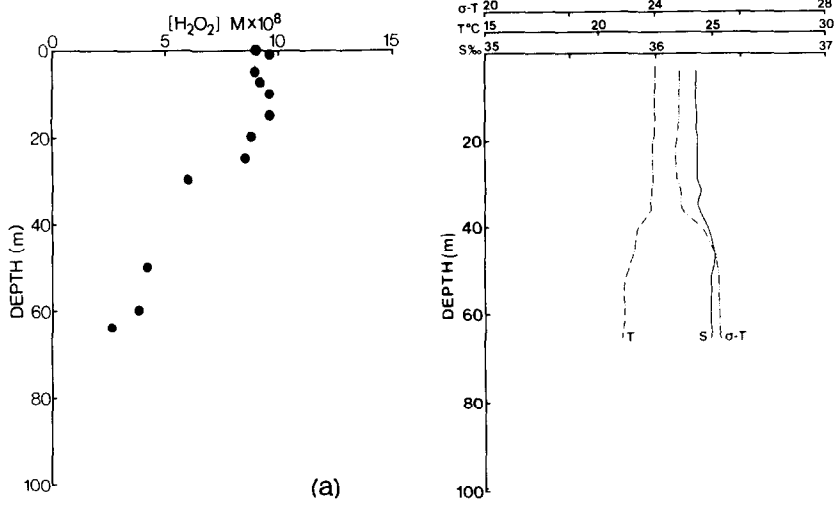


FIG. 3. Representative profiles from (a) station 2, 1430 h; (b) station 3, 1830 h.

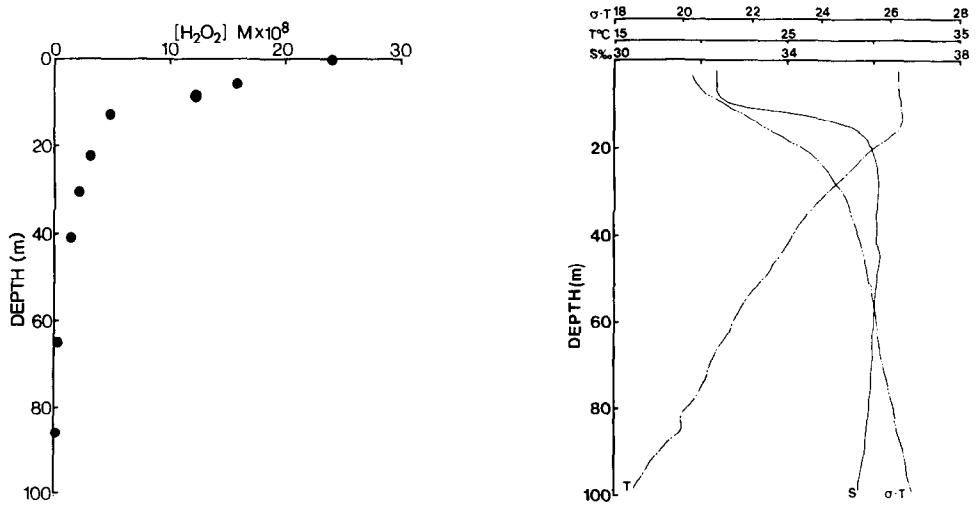


FIG. 4. Representative profile from station 2', 1800 h.

profiles were compiled from 35 rosette casts in May, 1982 and 25 casts in August, 1982. Sampling stations are listed below.

May, 1982:

1. Oceanic, oligotrophic water; depth 1500 m; 24°33'N, 84°05'W

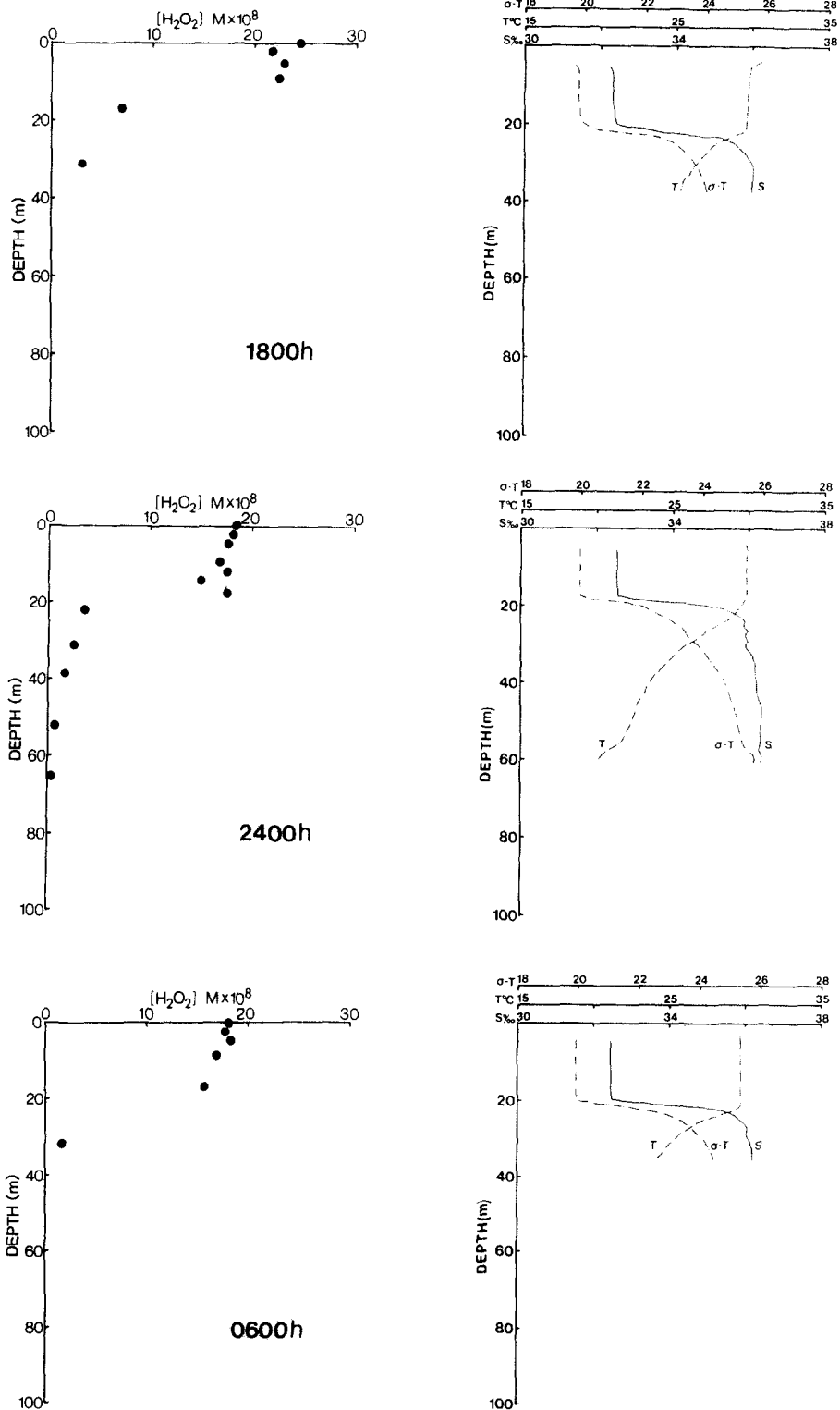


FIG. 5. 24 hour sequence of profiles from station 3'.

- 2. Intermediate shelf water; depth 66 m; 28°14'N, 84°34'W
- 3. Intermediate shelf water; depth 267 m; 27°55'N, 84°59'W

5. Coastal water; depth 14 m; 29°01'N, 83°27'W (approximately 10 miles from the mouth of the Suwannee River)

August, 1982:

- 1'. Oceanic, oligotrophic water; depth 3300 m; 24°32'N, 85°46'W
- 2'. Intermediate shelf water; depth 180 m; 27°50'N, 84°40'W
- 3'. Coastal water; depth 37 m; 29°50'N, 86°17'W (approximately 40 miles off Cape San Blas, Fla.)

RESULTS

Representative depth profiles of H₂O₂ for all stations are shown in Figs. 2-6, with accompanying hydrographic data. Profiles from the highly oligotrophic water at stations 1 and 1' were characterised by surface maxima of 1.0 to 1.5 × 10⁻⁷ mol L⁻¹. At these two stations the hydrographic data indicate that the mixed layer extended down to 30 m to 40 m.

Peroxide concentrations were fairly uniform or decreased only slightly with depth in the mixed layer region. Below the mixed layer there was a rapid decrease with depth. Below 150 meters hydrogen peroxide concentrations were below the limit of detection of 5 × 10⁻⁹ mol L⁻¹. Representative profiles from station 1 and station 1' are shown in Fig. 2.

Representative profiles from station 2 and station 3 are shown in Fig. 3. The H₂O₂ distribution was similar to that at the oceanic stations 1 and 1', with surface peroxide concentrations of 1 × 10⁻⁷ mol L⁻¹.

The intermediate shelf station, 2', and the coastal station, 3', were more productive waters and were characterised by low salinity surface values (32.5 ppt) due to input from a freshwater source, presumably the Mississippi River. This gives rise to a sharp pycnocline at 16 m. Surface concentrations of peroxide were higher than in the oligotrophic stations by approximately a factor of two, ranging from 1.7 to 2.4 × 10⁻⁷ mol L⁻¹ at station 2' and from 1.7 to 2.8 × 10⁻⁷ mol L⁻¹ at station 3'. A representative

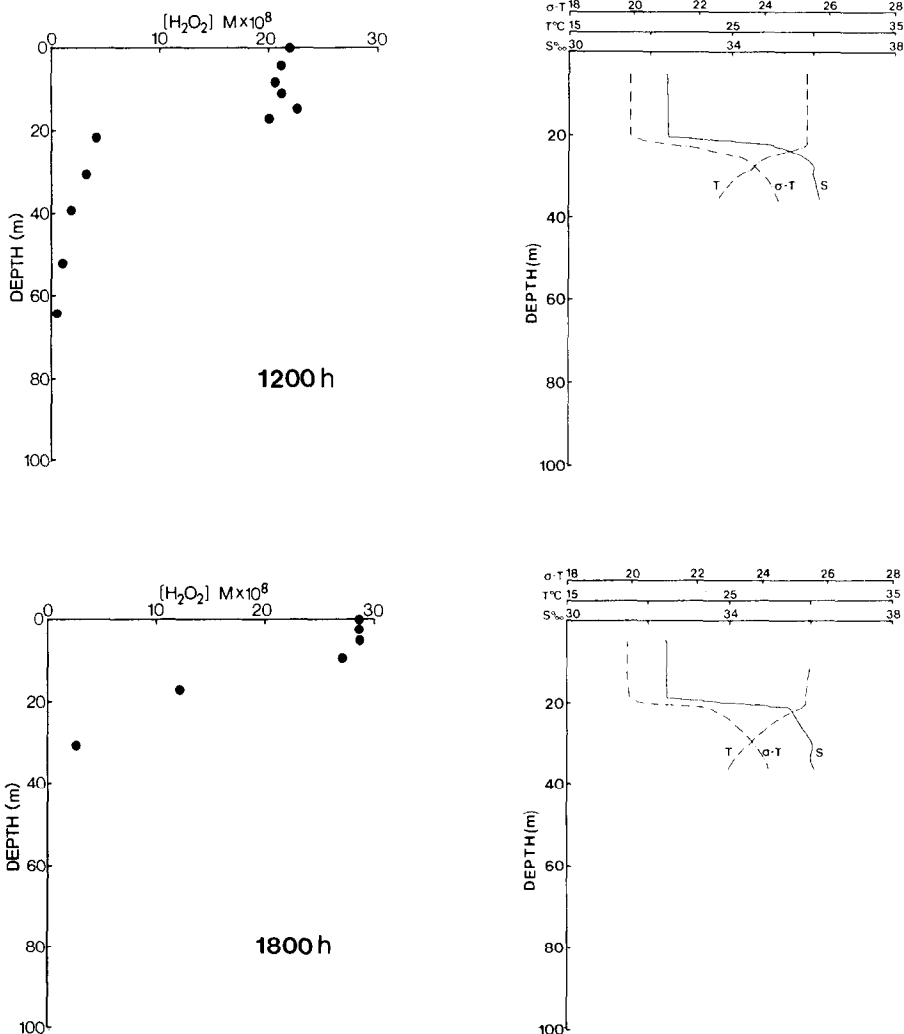


FIG. 5. (Continued)

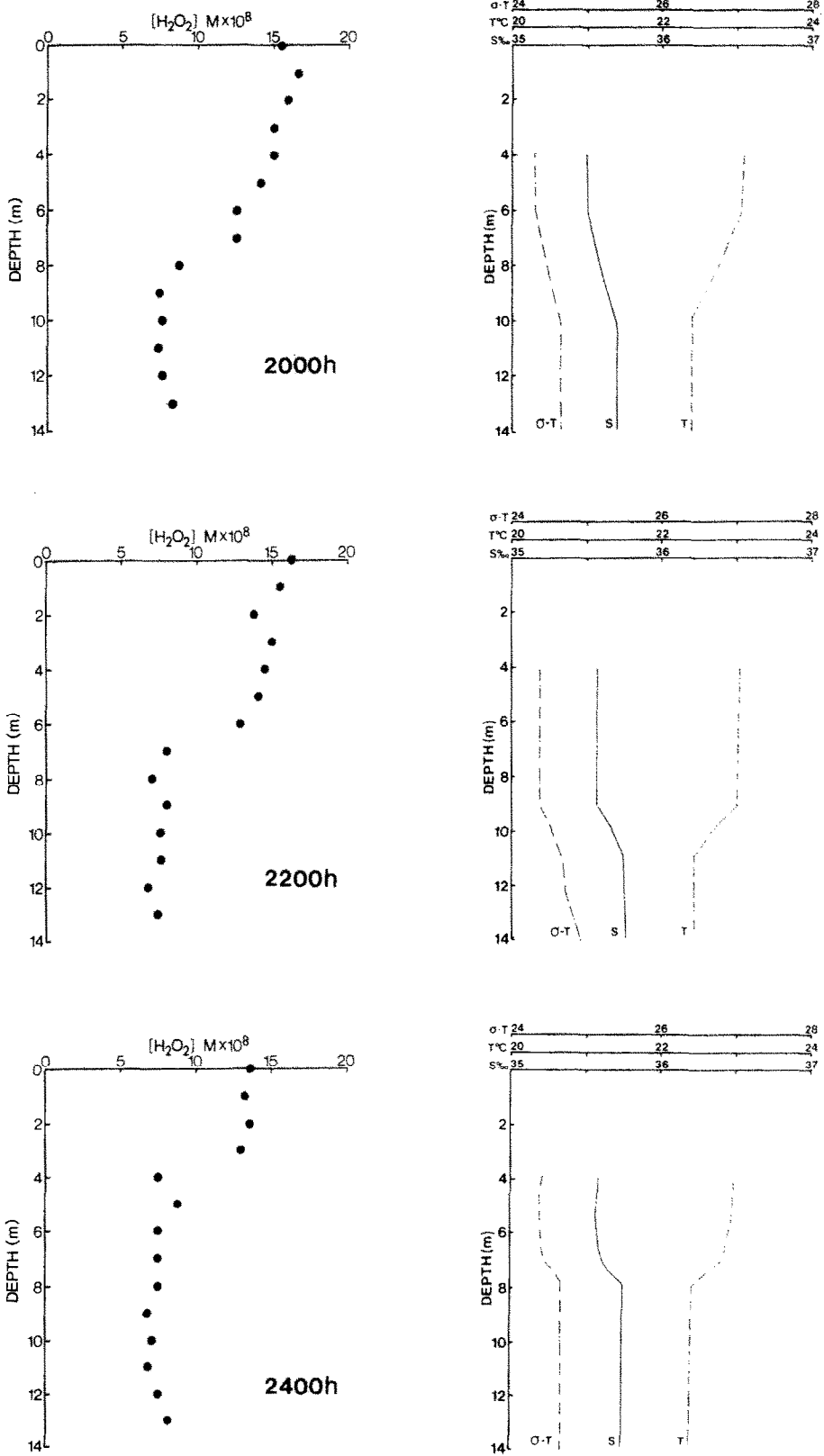


FIG. 6. 24 hour sequence of profiles from station 5.

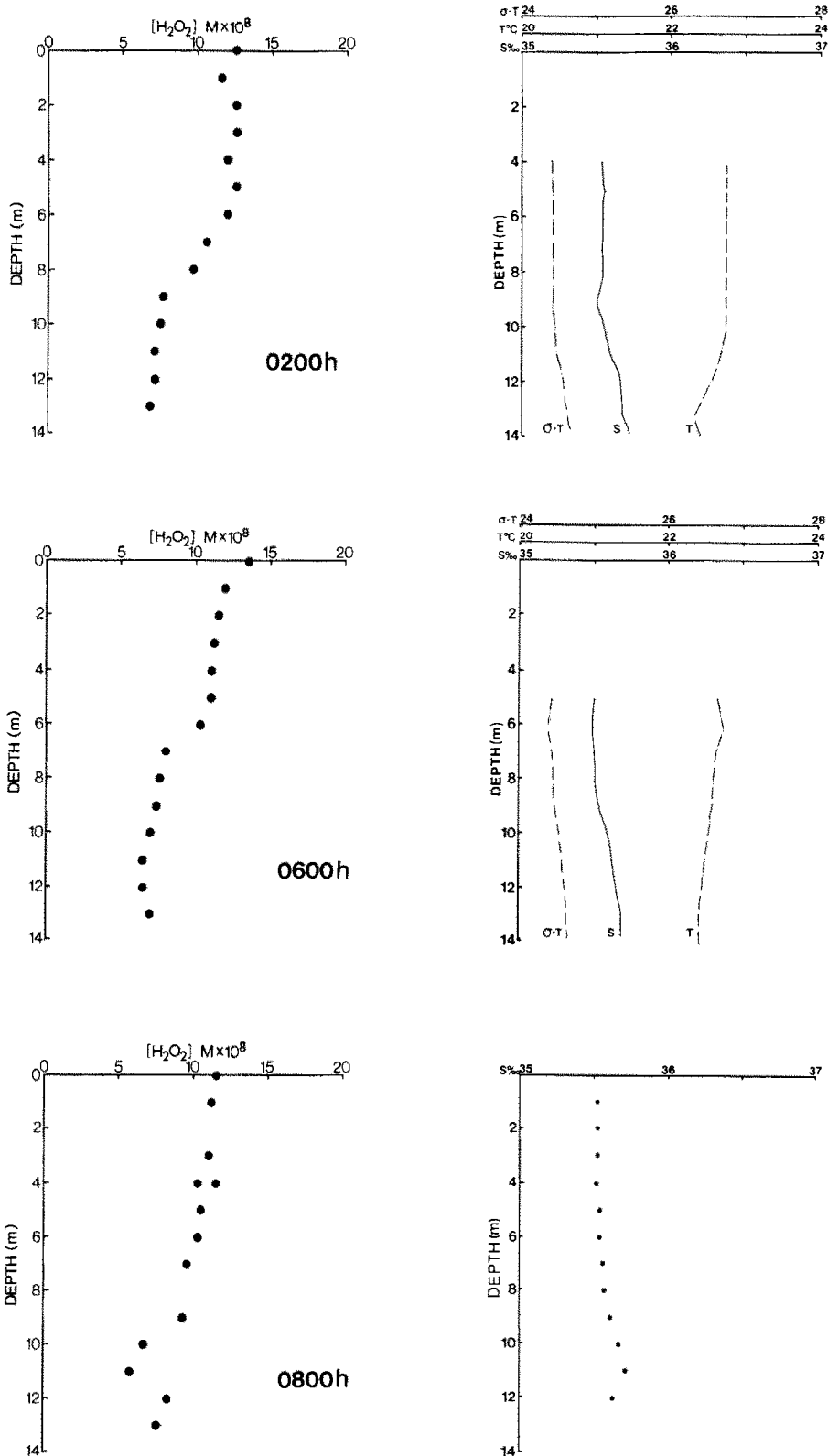


FIG. 6. (Continued)

profile from station 2' is shown in Fig. 4. Concentrations at station 2' in the upper 10 m were invariant with depth, but they decrease sharply with depth in

the region of pycnocline. No peroxide was detected below 80 m at station 2'. A 24 hour sequence of profiles at station 3' is shown in Fig. 5. Profile

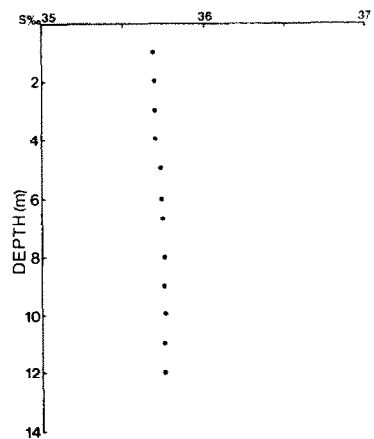
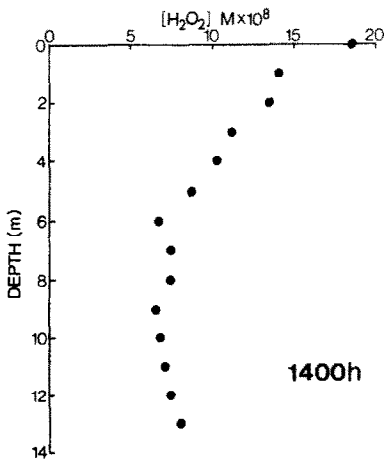
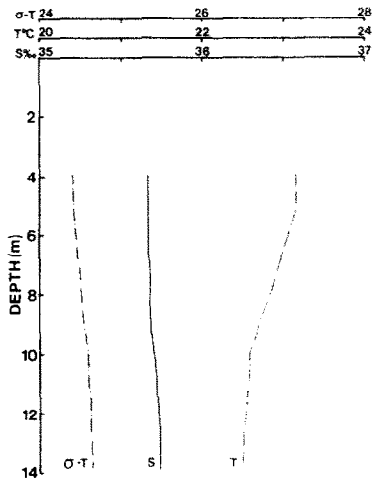
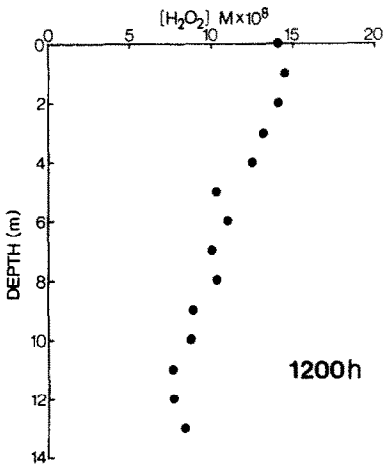
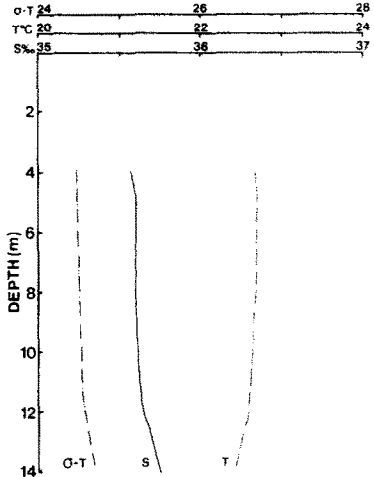
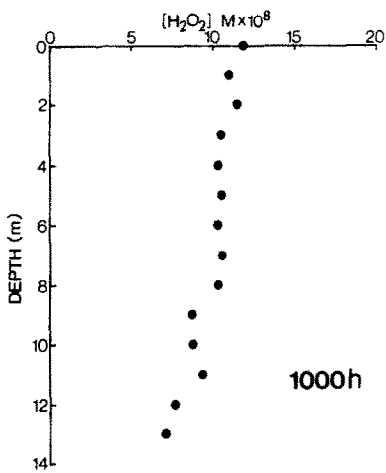


FIG. 6. (Continued)

characteristics were similar to station 2', with a sharp decrease associated with the pycnocline. There was a pronounced diel variation in surface peroxide con-

centrations, with a minimum of 1.8×10^{-7} mol L⁻¹ at 0600 and a maximum of 2.8×10^{-7} mol L⁻¹ at 1800 hrs (local time). Diel variation was less pro-

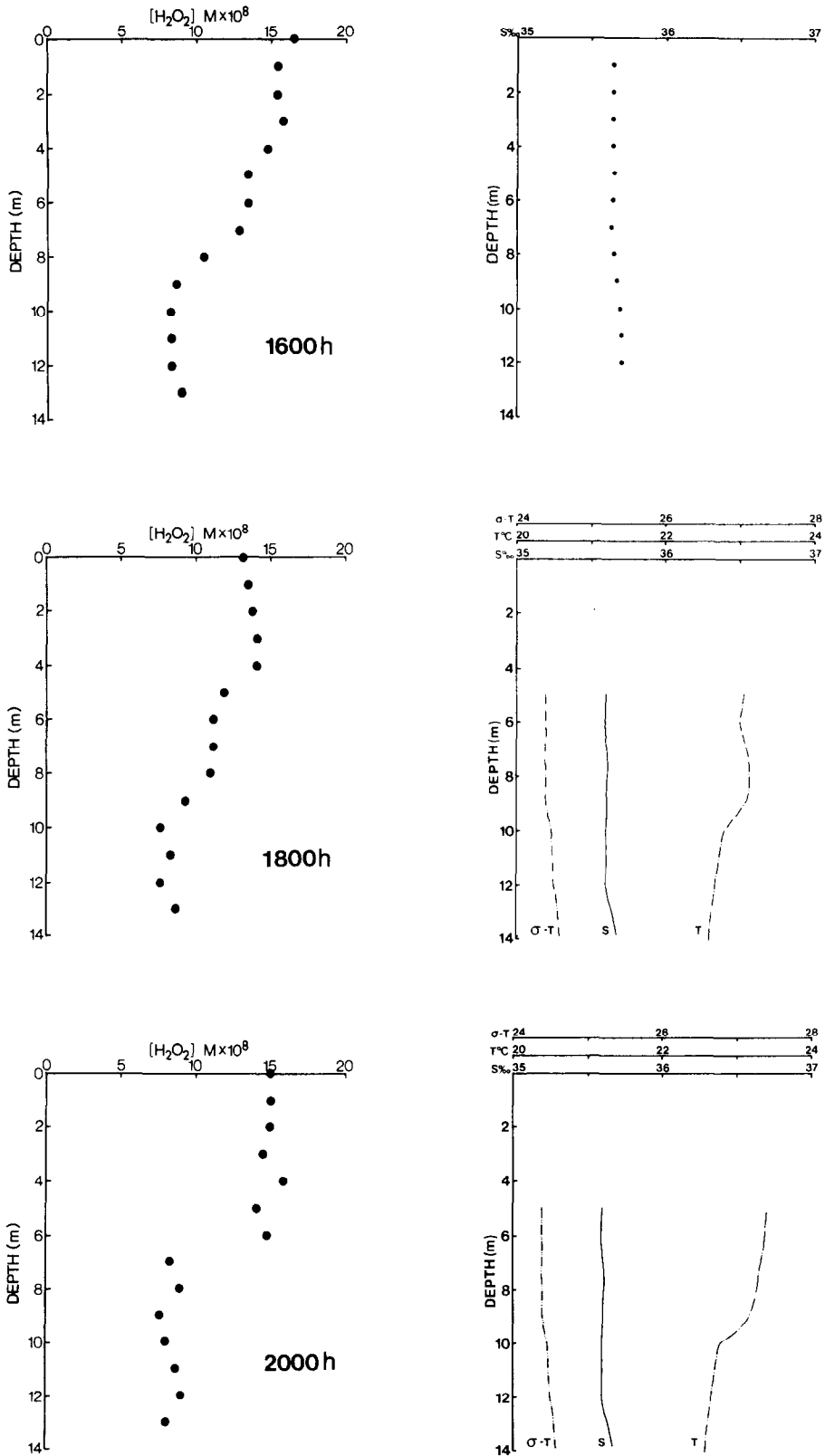


FIG. 6. (Continued)

nounced below the pycnocline. Hydrographic characteristics were invariant over the 24 hour time period.

Station 5 was located near the mouth of the Suwannee River, Florida. The water column displayed typically estuarine stratification. Salinity at the bottom

was 35.7 ppt and decreased to 32.5 ppt at the surface, indicating considerable freshwater input. Productivity and light attenuation at this station were the highest encountered in this study. A 24 hour sequence of profiles at this station is shown in Fig. 6. Surface peroxide levels ranged from 1.0 to 1.5×10^{-7} mol L^{-1} . At this shallow station (14 meters), peroxide was present at all depths. There was a slight increase in H_2O_2 near the bottom on some casts, but this was not consistently observed. Owing to the mode of sampling used, we were unable to sample nearer to the sediment water interface than 1 m. Hydrographic data indicates a slight pycnocline which ranged from 8–10 m at night to 4–6 m during the day. At 2000 hrs peroxide levels were elevated above the pycnocline and uniformly low below it. During the night there was a decrease in H_2O_2 levels, especially near the surface. At 0600–1000 hrs peroxide increased slightly from the bottom to the surface. By 1200 hrs there was an increase in H_2O_2 at 0–4 m but no increase below the shallow pycnocline which had formed by this time. At 1400 hrs the peroxide had continued to increase from 0–6 m, but below this depth peroxide values decreased. This was probably the result of the pycnocline preventing downward mixing. Because of the high light attenuation at this site, most of the sunlight was absorbed in the surface layer. Hence, peroxide decomposition exceeded production below the pycnocline. By 1600 hrs an intrusion of low salinity water at 8–10 m had disrupted the pycnocline and elevated peroxide levels extended to 9 m. At 2000 hrs the profile resembled that of the previous night. The importance of hydrographic and solar parameters on peroxide profile characteristics are demonstrated in the results obtained at Station 5.

DISCUSSION

The peroxide profiles, from diverse marine environments have several common characteristics; all show a surface maxima in peroxide concentration, with the surface maxima from 1 to 2×10^{-7} mol L^{-1} , a general decline with depth, and a sharp decline beneath pycnoclines. There is a consistent pattern of diel variability, with mid to late afternoon maxima and a pre-dawn minimum. These observations are consistent with photochemical production of H_2O_2 in the photic zone dominating during the day and dark decay and downward mixing processes dominating at night. Surface peroxide concentrations are similar to those reported by VAN BAALEN and MARLER (1966), but comparison is difficult due to the paucity of data in the earlier work.

In open ocean waters, with low light attenuation, the photic zone extends deeper than in coastal areas. Therefore, photochemical generation of peroxide might be expected to occur at greater depth than at coastal stations. Detection of peroxide at greater depths at the oligotrophic stations supports this premise. The fact that ultraviolet radiation is rapidly

attenuated near the surface suggests that in order to maintain the observed H_2O_2 concentrations near the bottom of the mixed layer photochemically, the reactions must be occurring in the visible portion of the spectrum where the attenuation of solar flux is small. Hydrographic data at these stations indicate that the mixed layer depth varies in time, but typically extends to 40 m and consequently vertical mixing will also contribute to the high peroxide levels measured. Horizontal advective processes may also play a role in maintaining peroxide levels below the mixed layer depth if the depth of the mixed layer is horizontally inhomogeneous. There is evidence for this kind of process in the small scale structure frequently found in temperature and salinity profiles below the local mixed layer depth (CALDWELL, 1983). More profile measurements at individual stations are needed before the relative roles of transport and *in situ* production of H_2O_2 can be clearly separated.

In the coastal and shelf waters where light attenuation is greater owing to higher levels of DOM and particulate material, the H_2O_2 photochemical formation rate will decrease sharply with depth. Thus, peroxide levels decrease sharply with depth as observed. At stations 2' and 3' the presence of the sharp pycnocline at 16 m prevented mixing from the peroxide enriched surface waters and led to H_2O_2 depletion in the dimly irradiated water beneath. Consequently, surface peroxide at these stations was 2 to 2.5×10^{-7} mol L^{-1} , compared with 1 to 1.2×10^{-7} mol L^{-1} at the oceanic stations, owing to the shallow pycnocline and higher DOM. In coastal waters peroxide lifetimes are probably shorter due to higher concentrations of transition metals and organic compounds which are potentially important in peroxide degradation. Consequently, advective processes will not be as important in introducing peroxide into deep water, leading to the shallower profiles observed.

The diel variation results are summarised in Fig. 7 which shows diel variation at several depths at stations 1', 3 and 5. There is considerable scatter in the data, particularly in coastal surface casts, probably due to patchiness in the water being sampled over twenty four hours. Nevertheless, the data is suggestive of diel variability, with highest values in the mid afternoon and lowest between midnight and dawn. Diel trends are more pronounced in coastal waters than in oligotrophic waters. The trends are also more pronounced in surface waters than in deep waters. Deep waters, even in coastal areas show little evidence of diel variation. These results indicate the need for more field work to further elucidate this phenomenon.

The diel variation observations are consistent with photochemical formation. Diel variation is greatest in coastal surface waters where rates of H_2O_2 formation are highest. Rates of decay will also be higher in these waters (ZIKA, 1980), owing to higher concentrations of transition metals and organic compounds, as outlined above. In oceanic waters, concentrations of peroxide precursors and reactants which decay

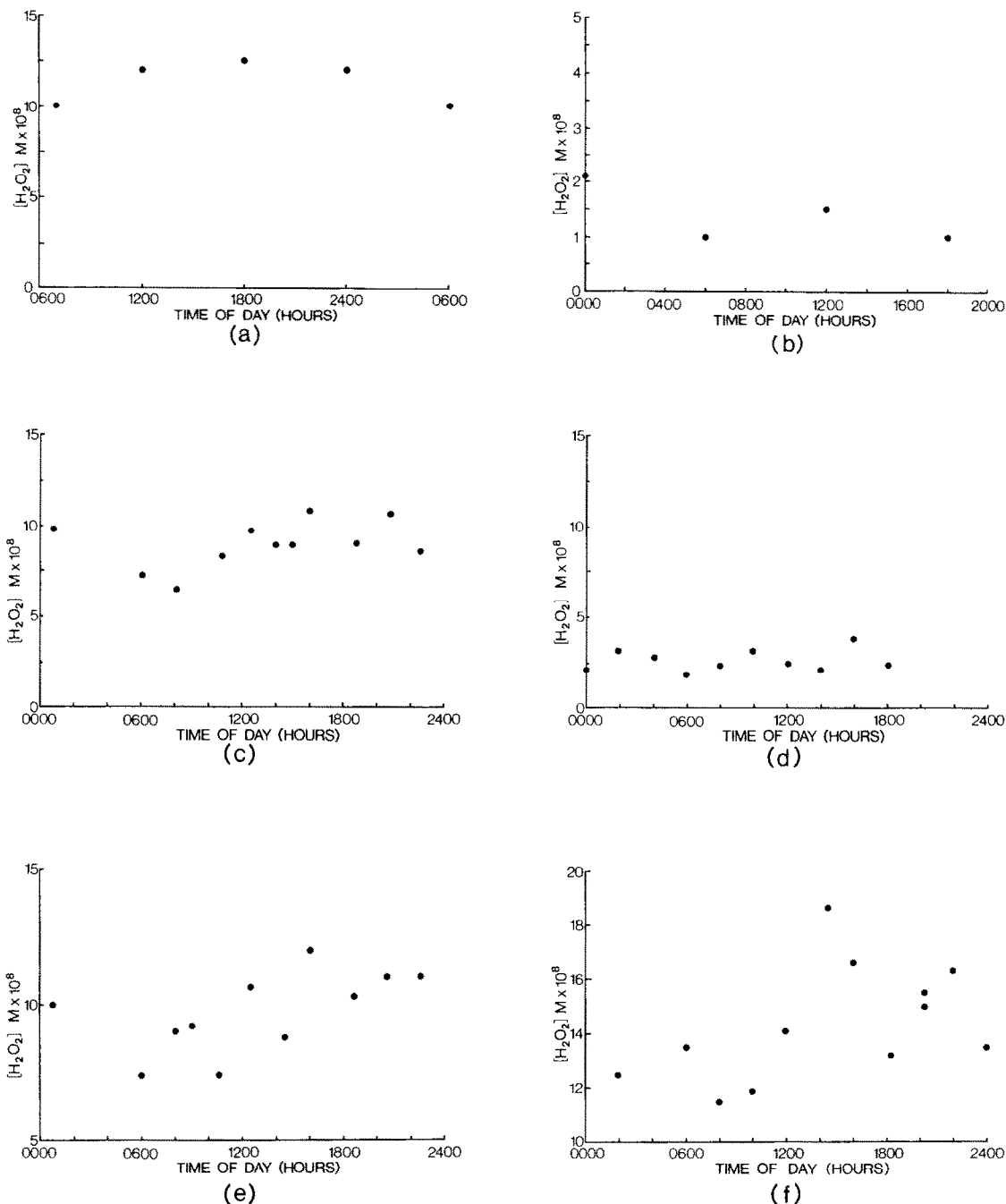


FIG. 7. Summary of diel variation observations. a) station 1', surface; b) station 1', depth 95 m; c) station 2, surface; d) station 2, depth 60 m; e) station 3, surface; f) station 5, surface.

H₂O₂ are lower, leading to lower rates of formation and decomposition and less pronounced diel variation. In deep water, peroxide is introduced primarily through advection rather than *in situ* production. Consequently, diel variation is slight at depth, even in coastal waters.

The data is explained by photochemical production of H₂O₂ in the photic zone. However, other plausible mechanisms should be considered. Biological production may also lead to H₂O₂ formation, concentrated in the photic zone, where biological activity is

highest. It would also be expected to lead to higher levels in highly productive coastal waters as we have observed. However, no correlation was observed with chlorophyll levels, a commonly used parameter of biological activity. A strictly biological origin would probably lead to a subsurface maximum as has been observed for other constituents of biological origin such as chlorophyll, oxygen and nitrite.

An atmospheric source of H₂O₂, either gas or aqueous phase deposition could also explain the surface maxima observed. Model estimates indicate

that dry deposition of gas phase peroxide is probably of little importance (THOMPSON and ZAFIRIOU, 1983), but that rain could have a significant impact on peroxide levels in the surface ocean. Peroxide levels as high as 10^{-5} to 10^{-4} mol L⁻¹ have been recorded in marine rain (ZIKA *et al.*, 1982). However, it rained lightly only once during this study and no effect on peroxide levels was observed.

If the source of peroxide is marine organic matter there must be a mechanism for replenishing it. Advection from deep water may be important or if the material is of more recent biological origin it may be generated *in situ*. In coastal waters terrigenous sources of DOM may lead to peroxide production. Peroxide production in irradiated groundwaters and surface waters has been observed (COOPER and ZIKA, 1983; DRAPER and CROSBY, 1983; SINEL'NIKOV and LIBERMAN, 1974; COOPER *et al.*, unpub.) so terrigenous DOM does contain peroxide producing compounds.

SUMMARY

Hydrogen peroxide has been detected in the Gulf of Mexico at levels exceeding 10^{-7} mol L⁻¹ in surface waters. Profiles indicate that it is generated in the photic zone, possibly by an abiotic photochemical process, and that it has a lifetime on the order of days. Peroxide distribution in the water column is influenced primarily by sunlight, hydrographic characteristics of the water column, and the concentration of minor constituents which are involved in peroxide production and decomposition.

Hydrogen peroxide has potential significance for marine redox processes. However, it is impossible to evaluate its significance at this time because kinetic data for potentially important reactions is not available.

Acknowledgements—This research was supported by the Office of Naval Research on grant NO0014-80-C-0042, by the National Science Foundation on grant OCE 78-25628 and by the National Oceanographic and Atmospheric Administration on grant NA82RAC00096. We wish to thank Dr. L. T. Gidel for his useful comments and NOAA/AOML-Miami for the opportunity to participate on these cruises

and for providing the hydrographic data. Technical assistance from the Captain and crew of the NOAA ship R/V Researcher was greatly appreciated.

Editorial handling: G. Thompson

REFERENCES

- CALDWELL D. R. (1983) Small scale physics of the ocean. *Rev. Geophys. Space Phys.* **21**(5), 1192–1205.
- COOPER W. and ZIKA R. G. (1983) Photochemical formation of hydrogen peroxide in surface and groundwaters exposed to sunlight. *Science* **220**, 711–712.
- DRAPER W. M. and CROSBY D. G. (1983) Photochemical generation of superoxide radical anion in water. *Agric. Food Chem.* **31**, 734–737.
- DRAPER W. M. and CROSBY D. G. (1983) The photochemical generation of hydrogen peroxide in natural waters. *Arch. Environ. Contam. Toxicol.* **12**, 121–126.
- MOFFETT J. W. and ZIKA R. G. (1983) Oxidation kinetics of copper(I) in seawater: implications for its existence in the marine environment. *Mar. Chem.* **13**, 235–251.
- SINEL'NIKOV V. E. and LIBERMAN A. S. (1974) Factors influencing the concentration of hydrogen peroxide and other oxidants in natural waters. *Trans. Inst. Biol. Vnutr. Vod. Akach. Nauk. (USSR)* **29**, 27–40.
- THOMPSON A. M. and ZAFIRIOU O. C. (1983) Air sea fluxes of transient atmospheric species. *J. Geophys. Res.* **88**, 6696–6708.
- VAN BAALLEN C. and MARLER J. E. (1966) Occurrence of hydrogen peroxide in seawater. *Nature* **211**, 951.
- ZAFIRIOU O. C. (1983) Natural water photochemistry. In *Chemical Oceanography*, vol. 8, (eds. J. P. RILEY and R. CHESTER), pp. 339–379. Academic Press.
- ZIKA R. G. (1981) Marine Organic Photochemistry. In *Marine Organic Chemistry* (eds. E. K. DUURSMA and R. DAWSON) pp. 299–326. Elsevier.
- ZIKA R. G. (1980) Photochemical generation and decay of hydrogen peroxide in seawater. *EOS* **61**, 1010.
- ZIKA R. G. (1984) Short-lived oxidants in natural waters. In *Proc. Conf. Gas-Liquid Chemistry of Natural Waters*, Brookhaven National Laboratory, NTIS Pub. No. BNL 51757 Paper No. 51, 10 pp.
- ZIKA R. G. and SALTZMAN E. S. (1982) Interaction of ozone and hydrogen peroxide in Water: Implication for Analysis of H₂O₂ in Air. *Geophys. Res. Lett.* **9**, 231–234.
- ZIKA R. G., SALTZMAN E., CHAMEIDES W. L., and DAVIS D. D. (1982) H₂O₂ levels in rainwater collected in South Florida and the Bahama Islands. *J. Geophys. Res.* **87**, 5015–5017.
- ZIKA R. G., SALTZMAN E. S. and COOPER W. J. (1984) Hydrogen peroxide concentrations in the Peru upwelling area. *Mar. Chem.* (in press).