

**SPATIAL AND TEMPORAL PATTERNS OF
HYDROGEN PEROXIDE IN LAKE WATERS**

W.J. Cooper¹, D.R.S. Lean² and J.H. Carey³

NWRI Contribution No. 89-04

¹ Lakes Research Branch
National Water Research Institute
Canada Centre for Inland Waters
Burlington, Ontario, L7R 4A6
Canada

² Drinking Water Research
Center
Florida International
University
Miami, FL 33199, U.S.A.

Abstract

Depth profiles of H_2O_2 concentration were measured at three stations in Lake Erie, one in Lake Ontario and in Jacks Lake. Epilimnetic concentrations followed changes in solar radiation suggesting that the formation resulted from photochemical or perhaps photoautotrophic processes. Mid-day H_2O_2 concentrations of 100 - 200 nM were observed at all locations. Dark decay of H_2O_2 , determined at several depths at two locations, followed apparent first order kinetics with half-lives from 10-22 hours. H_2O_2 may be useful as a tracer for short term mixing processes and as a powerful oxidizing agent can influence metal speciation, degradation of some organic pollutants, as well as the survival and behavior of organisms.

Résumé

On a déterminé les profils de concentration de H_2O_2 à trois stations dans le lac Érié, une dans le lac Ontario et une dans le lac Jacks. La variation des concentrations épilimniques en fonction du rayonnement solaire indique que ce phénomène est le produit de processus photochimiques ou, peut-être, de la photo-synthèse. Des concentrations de H_2O_2 de 100 à 200 nM ont été relevées à midi à toutes les stations. La décomposition dans l'obscurité, observée à différentes profondeurs à deux endroits, a obéi à une réaction cinétique qui semble être du premier ordre avec des demi-vies biologiques de 10 à 22 heures. H_2O_2 pourrait servir de traceur dans les processus de brassage à court terme et, à titre d'oxydant énergétique, il peut avoir un effet sur la différenciation des espèces métalliques, la dégradation de certains polluants organiques, ainsi que la survie et le comportement des organismes.

Introduction

Hydrogen peroxide (H_2O_2) has been measured in oceans (Zika et al. 1985a; 1985b) and in fresh waters (Sineln'nikov 1971a; 1971b; Sineln'nikov and Demina 1974; Sineln'nikov and Liberman 1974; Draper and Crosby 1981a; 1981b; 1983a; 1983b; Cooper and Zika, 1983; Cooper et al. 1988; 1989; Klockow and Jacob 1986; Cooper and Lean submitted), but for lakes information on spatial and temporal patterns has never been obtained. Cooper and Lean (submitted) measured diel changes in lake surface H_2O_2 concentrations that were an order of magnitude greater than that previously observed in surface oceans. In the following investigation depth profiles of H_2O_2 concentration were obtained in Lake Erie, Lake Ontario and Jacks Lake and compared to light intensity, light penetration and temperature profiles.

When ultraviolet light is absorbed by humic substances, superoxide ($\text{O}_2^{\cdot-}$), a negatively charged radical and other reactive intermediates are formed (Larson et al. 1981; Baxter and Carey 1983; Draper and Crosby 1983a; 1983b; Cooper and Zika 1983; Petasne and Zika 1987; Zepp et al. 1987a). In situ formation of H_2O_2 results from a disproportionation of $\text{O}_2^{\cdot-}$. Algal H_2O_2 production has also been reported (Palenik et al. 1987; Zepp et al. 1987b) but the relative importance of this pathway is not known.

Because H_2O_2 is an oxidizing agent, it is not surprising that it has been shown to influence chemical (Draper and Crosby, 1984; Zepp and Baughman, 1978; Zika and Cooper, 1987, and references therein; Zepp et al., 1987b) and biological processes

in marine waters (Van Baalen, 1965; Morse et al. 1977). Studies of the oxidation of iron (McMahon, 1967; 1969; Collienne, 1983; Miles and Brezonik, 1981), manganese (Sunda et al., 1983), and chromium (van der Weijden and Reith, 1982), suggest that these metals may also play a role either in the formation or decomposition of $O_2^{\cdot -}$ and H_2O_2 . Moffett and Zika (1983; 1987a; 1987b) have discussed the formation of H_2O_2 in sea water resulting from the redox cycling of copper and iron. $O_2^{\cdot -}$ is known to react with organic chemicals (Bielski et al., 1985; Rotilio, 1986), may be important in the degradation of some organic pollutants (Cooper et al. 1989) and can have adverse effects on subcellular processes (Rotilio 1986). The relative stability of H_2O_2 and simple methods for its measurement enable it to be used to study $O_2^{\cdot -}$. Such information is a prerequisite for insight into metal speciation, the fate and transport of organic pollutants, as well as survival and behavior of organisms in freshwater.

Methods

Lake water samples were collected in 6 L Niskin bottles on a Rosette sampler equipped with an electronic bathothermograph. Station locations are given along with related physical and chemical measurements on Table 1. Particulate organic carbon (POC) and particulate nitrogen analyses were conducted using a Hewlett Packard CHN elemental analyzer. Samples were collected by filtering 100-400 mL lake water through preignited ($525^{\circ}C$) Whatman GF/C filters which were then dried by vacuum desiccation.

Chlorophyll a (uncorrected for phaeopigments) was determined using the 90% acetone extraction method. Total phosphorus was measured after digestion with sulfurous acid. Particulate phosphorous was obtained by difference between results for unfiltered and filtered (0.45 μ m Sartorius 11103 cellulose nitrate) samples (Standard Methods Manual, Environment Canada 1979).

Photosynthetically active radiation (PAR), 400-700 nm, was measured using a Li-Cor 185 Quantum Sensor. A QSM2000 quanta spectrometer (Tectum Instruments, Sweden) was used to determine spectral composition of light with depth and the extinction coefficient for 400 nm.

H₂O₂ was analyzed using the scopoletin horse radish peroxidase fluorescent decay method (Kieber and Helz 1986; Holm et al. 1987; Cooper et al. 1988). In our experiments, the limit of detection was 5 nM. A Turner Designs Model 10 fluorometer equipped for excitation and emission wavelengths of 365 and 490 nm, respectively, was used. Replicate analyses on the same sample were within \pm 10% at concentrations of 50 nM.

H₂O₂ is a powerful oxidizing agent and can be lost as a result of either chemical or biological processes. Dark H₂O₂ decay was obtained by measuring the H₂O₂ concentration of samples stored in 300 mL BOD bottles at zero time and approximately every 4 hours for the next 16-20 h. The samples were incubated at the temperature of the depth sampled and not stirred except prior to analyses. The bottles had been previously acid washed, rinsed several times with boiling water and finally distilled water.

Apparent first order rate constants were calculated from the slope of $\ln H_2O_2$ concentration plotted as a function of time.

Results

Vertical gradients of H_2O_2

At the deepest part of the Eastern Basin of Lake Erie, station 23, H_2O_2 decreased from values near 100 nM at 0 - 10 m, to < 20 nM at the bottom of the 20 m deep epilimnion (Fig. 1A). A slight but measurable thermal gradient, less than $0.4^\circ C$, existed between 10 and 20 m. UV radiation does not penetrate lake water as well as the longer wavelengths and here the 1% PAR light level was at 13 m. Nevertheless measurable H_2O_2 was observed even to 30 m.

In contrast to the above example, the H_2O_2 concentration in Lake Ontario (10 Aug 1500 h) declined from subsurface maxima concentrations of 130 nM to undetectable at 15 m (Fig. 1B). Here the temperature change was about $1.5^\circ C$ down to 15 m. The depth of 1% PAR was 11.5 m.

In the Central Basin of Lake Erie, station 84, a decline in H_2O_2 concentration was observed across the epilimnion even though the thermal gradient was insignificant in the upper 16 m (Fig. 1C). The 1 % PAR depth was 16 m, so UV penetration to these depths would be unlikely.

In the eutrophic Western Basin of Lake Erie, the water column was isothermal at $24^\circ C$ and the 1 % PAR was only 3.7 m. The H_2O_2 concentration was fairly constant through the top 3 m but was still present at half the surface concentration at 5-8 m

(Fig. 1D).

In Jacks Lake, a metalimnetic chlorophyll *a* maxima (12 ug L^{-1}) occurred at the same depth as elevated H_2O_2 concentrations on 6 Aug (Fig. 2E). Epilimnetic chlorophyll *a* concentrations at this time were 0.9 ug L^{-1} but following rain and cloudy conditions on 7 Aug, chlorophyll *a* increased to 3.5 ug L^{-1} in the surface water, H_2O_2 concentrations were lower in the upper 4 m and no metalimnetic H_2O_2 was observed on 8 Aug. Such observations suggest that metalimnetic H_2O_2 production occurred but more rigorous experiments are required.

Diel patterns of H_2O_2 concentration.

Examples of changes observed during the day (Fig. 2) for the three basins of Lake Erie illustrate that H_2O_2 not only was distributed rapidly throughout the upper mixed zone but increased in the metalimnion and even the hypolimnion (Fig. 2A, 2B). Whether it was produced or somehow physically transported to these depths is not known. If in situ production of superoxide, and consequently H_2O_2 , depends on uv light, it would be impossible for the H_2O_2 to be produced at these depths. Despite the isothermal conditions at the western basin station (Fig. 2C), H_2O_2 increased most above 3 m but doubled at 5 and 8 m.

Values obtained from a more detailed examination of diel changes in concentration of H_2O_2 were integrated over the water column and expressed in areal units (Fig. 3). As PAR increased after sunrise, so did H_2O_2 but the latter peaked after the midday PAR maximum. At sunrise an amount of H_2O_2 equal to about half the daily maximum exists. This quantity is the result of not only

what was produced the day before but also the rate of overnight decay.

The depth for H_2O_2 production remains unknown and surface concentrations alone fail to provide the total production as H_2O_2 mixes downward in the upper mixed zone. Decay processes also reduce the observed concentration such that the observed accumulation represents the net rate not the formation rate. The areal accumulation rate for the Central Basin (Fig. 3, lower panel) was $4.8 \text{ mg m}^{-2} \text{ h}^{-1}$ calculated from 0650 to 1500. Using profiles provided on Fig. 3, areal rates of accumulation for the Eastern and Western Basins were 6.8 and $3.8 \text{ mg m}^{-2} \text{ h}^{-1}$ respectively.

Decay of H_2O_2 .

To distinguish decay losses of H_2O_2 from diffusive (mixing) losses, water samples were incubated in the dark in 300 mL BOD bottles. Analyses for H_2O_2 were conducted approximately every 4 h. Examples from the Central Basin of Lake Erie are shown on Figure 4 with all data summarized on Table 2. When samples were filtered through 0.45 μm membrane filters, H_2O_2 concentrations did not change over a seven hour period. Freshly collected sediment added to a water sample from 5 m to give concentrations of 8.6, 17.2 and 43 mg dry wt L^{-1} did not alter the rate of H_2O_2 loss. This indicates that sediment associated reduction was not a likely cause for the H_2O_2 decay and supports the hypothesis that bacteria and/or algae are the likely agents for the decline in H_2O_2 concentration.

Light Quality.

The spectral composition of the light (Fig. 5) changed with depth in the water column. At all three basins in Lake Erie (and Lake Ontario, data not shown), the blue (400 nm) and the red (700 nm) was absorbed to a greater extent than the green in the 560-580 nm range. Further investigations should include measurements in the near UV 300 - 400 nm range.

Discussion

Since areal production of H_2O_2 increased with light intensity, photochemical or photoautotrophic processes are responsible. Furthermore, the yield of H_2O_2 by photochemical production decreases with increasing wavelength (Cooper et al. 1988). If H_2O_2 formation is restricted to the depth of near UV penetration, then H_2O_2 provides a tracer to monitor physical transport of water masses. Alternatively, if other means of H_2O_2 production exist, such observations provide clues for further experimental investigations.

Photoautotrophic H_2O_2 production may be significant deep in the water column. Zepp et al. (1987b) found production of H_2O_2 in algal cultures ($40 - 800 \text{ nM L}^{-1} \text{ h}^{-1}$) that was related to light intensity and algal abundance but different algal cultures formed H_2O_2 with different efficiencies. Palenik et al. (1987) reported that a marine alga, Hymenomonas carterae, produced H_2O_2 under low light conditions.

In the Central Basin of Lake Erie sediments are mixed with surface waters during periods of high winds (Charlton and Lean 1988). Preliminary experiments were conducted to determine if concentrations of H_2O_2 could be altered by the presence of

surficial sediments. No effect was detected.

The decay of H_2O_2 , observed in this study, is an apparent first order process that is effectively stopped when samples are filtered through 0.45 μm filters. Decay is therefore associated with suspended particulate materials presumably phytoplankton and bacteria. Decay of H_2O_2 has been observed in cultures of fresh water green algae and cyanobacteria (Zepp et al. 1987b).

Patterns of superoxide and hydrogen peroxide production must be better understood for they certainly play a central role in the chemical transformations of not only metals and naturally occurring organic materials, but also of man made pollutants. Clearly, additional studies are required before a detailed understanding of the impact of H_2O_2 and related processes on lake ecosystems will evolve.

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Table 1. Location, physical and chemical features of the study sites. Epilimnetic concentrations of particulate material and dissolved nutrients (concentration units $\mu\text{g L}^{-1}$) at study sites.

| | Ontario | Erie | | Jacks | |
|-------------------------------------|-----------|-----------|-----------|-----------|--------------|
| | | East | Central | West | Lake |
| Station No. | 212 | 23 | 84 | 357 | Williams Bay |
| Lat | 43°23'44" | 42°29'59" | 41°56'01" | 41°43'20" | 44°41'20" |
| Long | 79°24'52" | 79°54'06" | 81°39'49" | 81°39'40" | 78°02'54" |
| Date | 10 Aug | 11 Aug | 12 Aug | 13 Aug | 6 & 8 Aug |
| Depth (m) | 100 | 65 | 23 | 10 | 21 |
| PAR ext coef (m^{-1}) | 0.38 | 0.27 | 0.28 | 1.21 | 0.48 |
| 400 nm ext coef (m^{-1}) | 0.53 | 0.38 | 0.42 | 2.30 | 0.52 |
| Chlor <i>a</i> | 2.5 | 0.8 | 0.8 | 25 | 3.5 |
| POC | 609 | 320 | 445 | 1480 | 560 |
| C:Chl | 244 | 400 | 556 | 59 | 160 |
| Part. P | 6.6 | 3.7 | 3.0 | 26 | 2.1 |
| Total P | 13.0 | 8.1 | 8.0 | 37 | 6.1 |
| SRP | 1.2 | 0.8 | 0.2 | .0 | <0.2 |
| NH ₄ | 14 | 12 | 9 | 26 | 5 |
| NO ₃ | 150 | 130 | 120 | 25 | 12 |

Table 2. Apparent first order decay rate constants (h^{-1}) for H_2O_2 from stations in Lake Ontario and the Central Basin of Lake Erie. Also provided are the initial concentrations (H_2O_2), half lives, and the chlorophyll a concentration.

| Depth | (H_2O_2) | k | $t_{1/2}$ | Chlor <u>a</u> |
|----------------------------|----------------------------|-----------------|-----------|--------------------|
| m | nM | h^{-1} | h | ug L^{-1} |
| Lake Ontario (Station 212) | | | | |
| 0 | 112 | 0.047 | 14.7 | 2.7 |
| 1 | 114 | 0.046 | 15.1 | 2.8 |
| 3 | 130 | 0.047 | 14.7 | 2.5 |
| 5 | 116 | 0.040 | 17.3 | 2.2 |
| 10 | 44 | 0.032 | 21.6 | 2.9 |
| Lake Erie (Station 84) | | | | |
| 0 | 177 | 0.072 | 9.6 | 0.4 |
| 1 | 125 | 0.052 | 13.3 | 0.9 |
| 5 | 137 | 0.062 | 11.1 | 0.7 |
| 10 | 108 | 0.065 | 10.2 | 0.5 |
| 13 | 106 | 0.060 | 11.6 | 0.5 |
| 15 | 72 | 0.043 | 16.3 | 0.5 |
| 16.4 | 52 | 0.034 | 20.2 | 0.4 |

Figure Headings

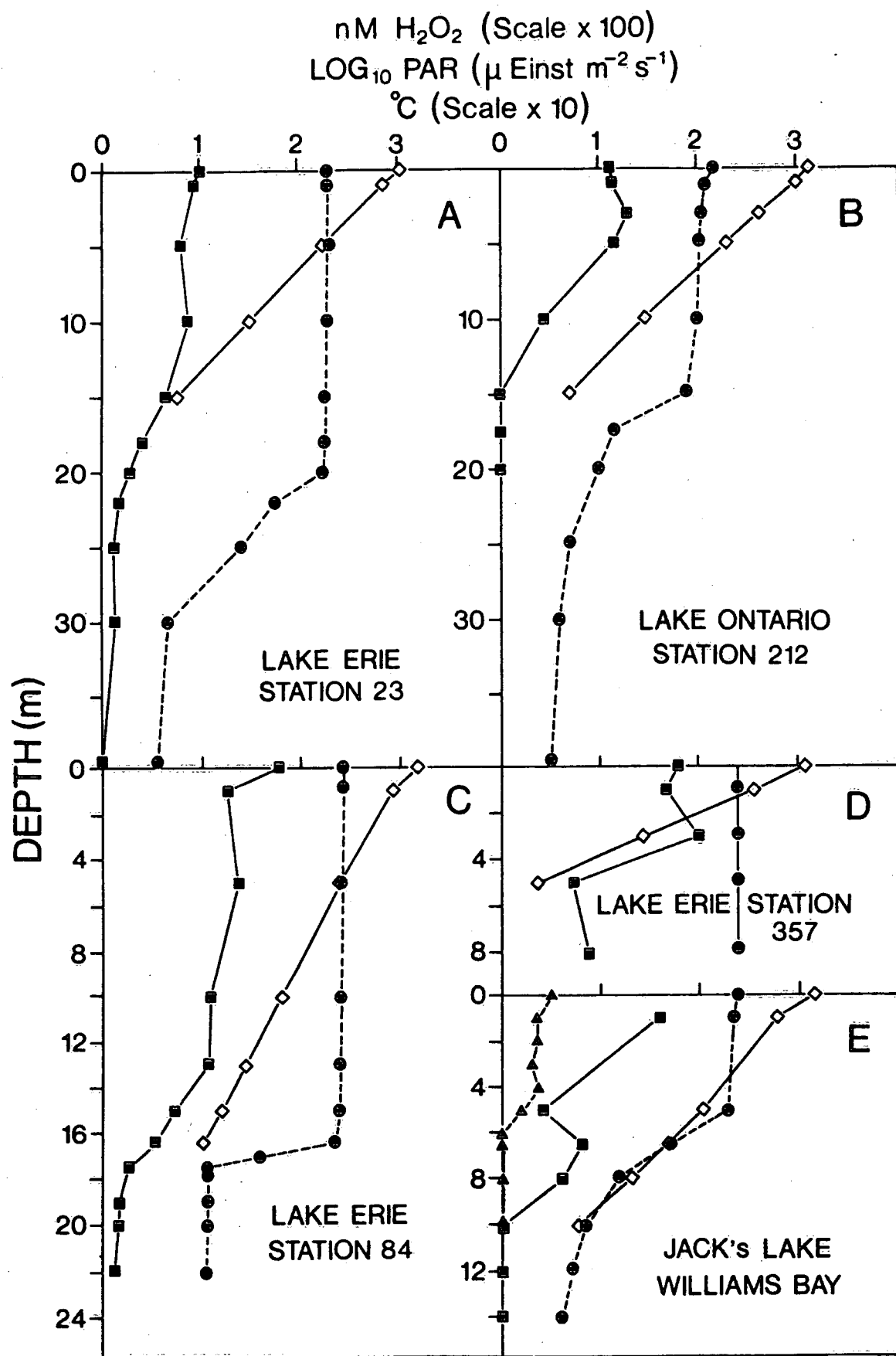
Figure 1. Depth profiles for H_2O_2 scale $\times 100 = \text{nM}$, (■); \log_{10} photosynthetically active radiation (PAR) (◇); and temperature (scale $\times 10 = ^\circ\text{C}$) in degrees centigrade (●) for (A) Lake Erie, Station 23 in the Eastern Basin on 11 Aug 87; (B) Lake Ontario, Station 212 on 10 Aug 87; (C) Lake Erie, Station 84 in the Central Basin on 12 Aug 87; (D) Lake Erie, Station 357 in the Western Basin on 13 Aug 87; (E) Jacks Lake, Ontario, collected on 6 Aug 87 (■) and 8 Aug 87 (▲). The depth of the water column at the 5 stations was 65, 100, 23, 10 and 21 m respectively.

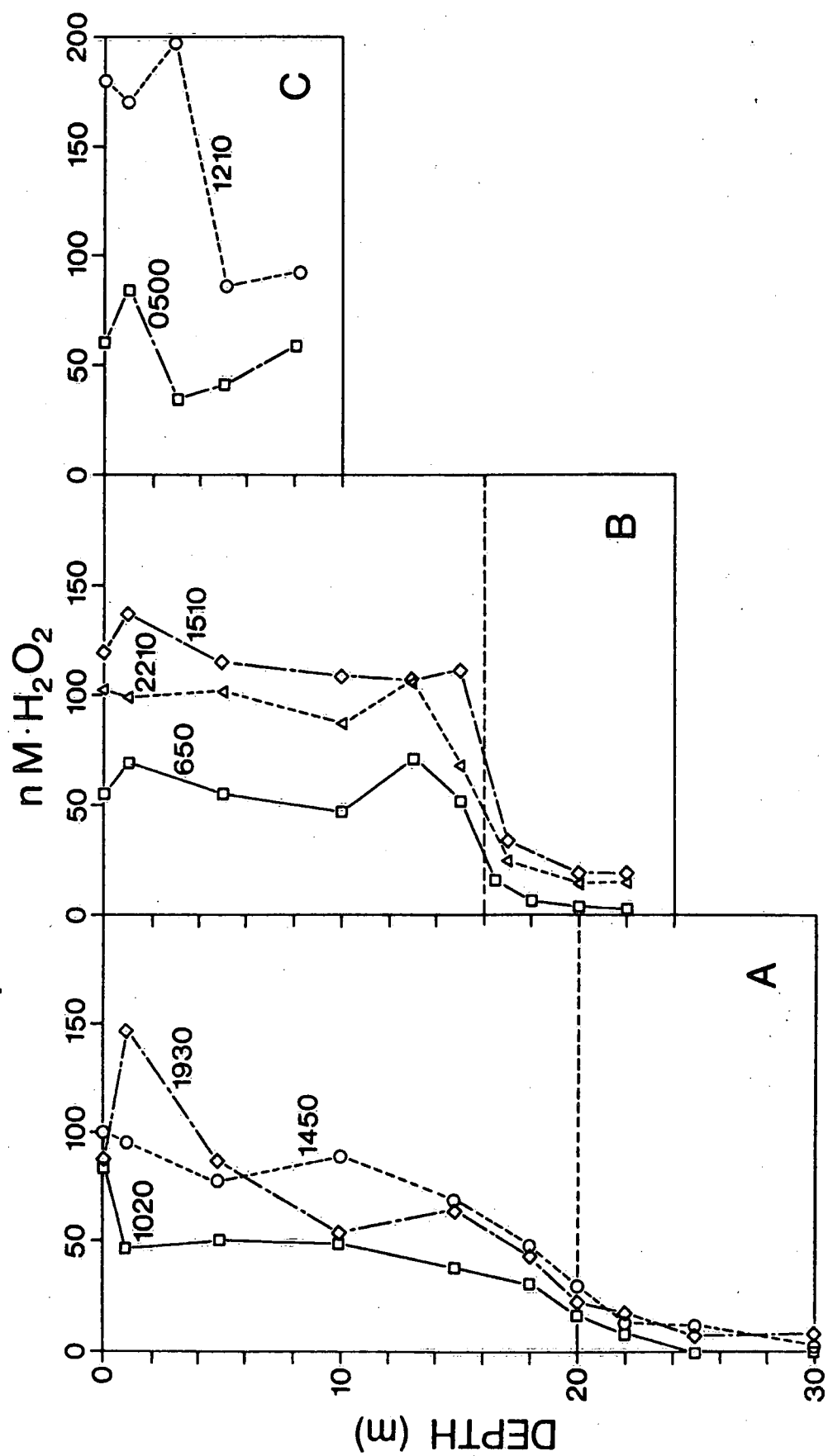
Figure 2. Examples of H_2O_2 profiles throughout the day in Lake Erie (A) station 23, (B) station 84 and (C) station 357 on Aug 11, 12 and 13 respectively. The bottom of the epilimnion is shown with a dashed line.

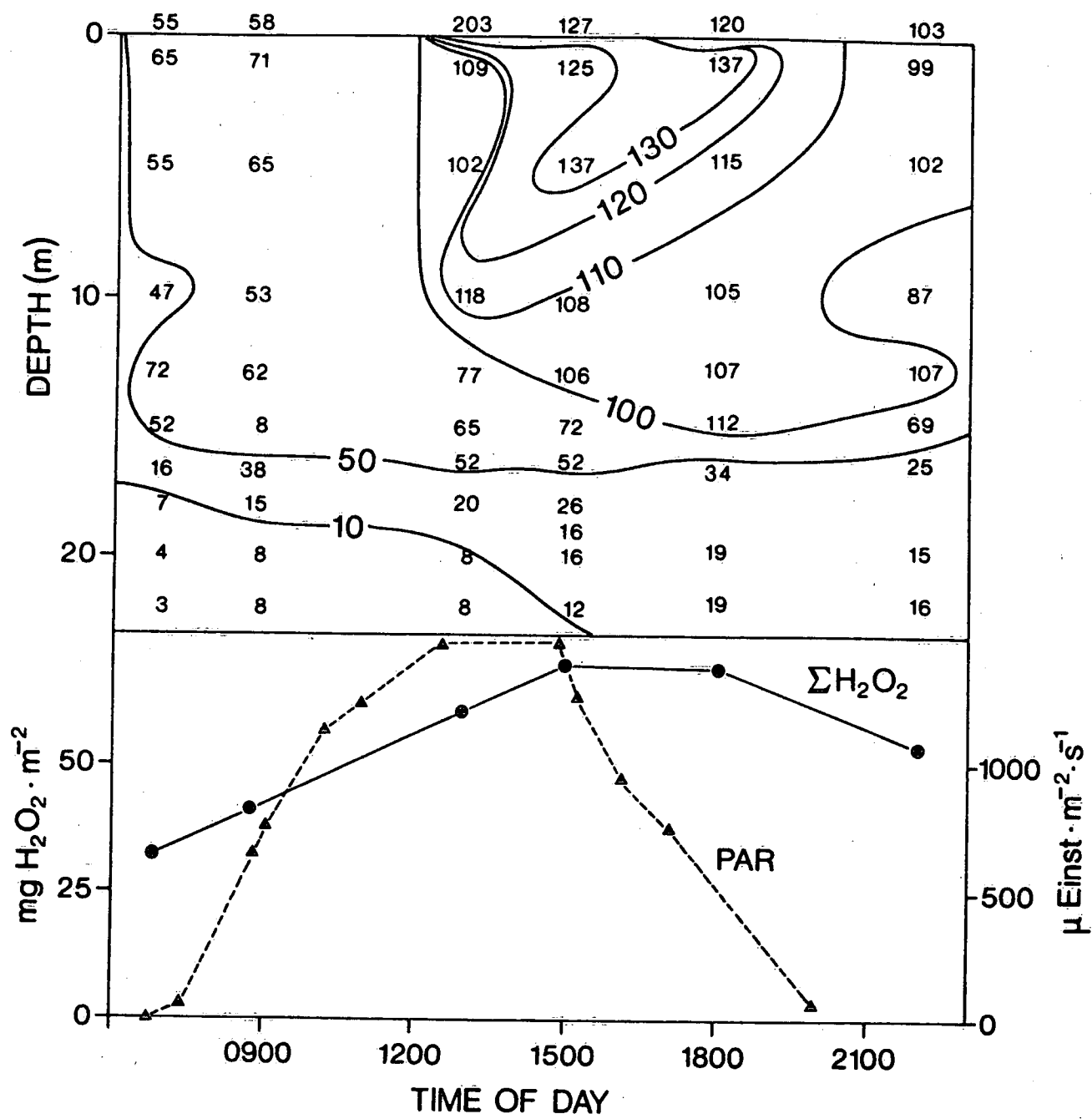
Figure 3. Top panel. Isopleths of H_2O_2 concentration (H_2O_2 in nM) throughout the water column at Lake Erie Station 84 on 12 Aug 87. The dashed line denotes the bottom of the epilimnion. Bottom panel. Integrated values for H_2O_2 from data in the upper panel. Also shown is incident PAR.

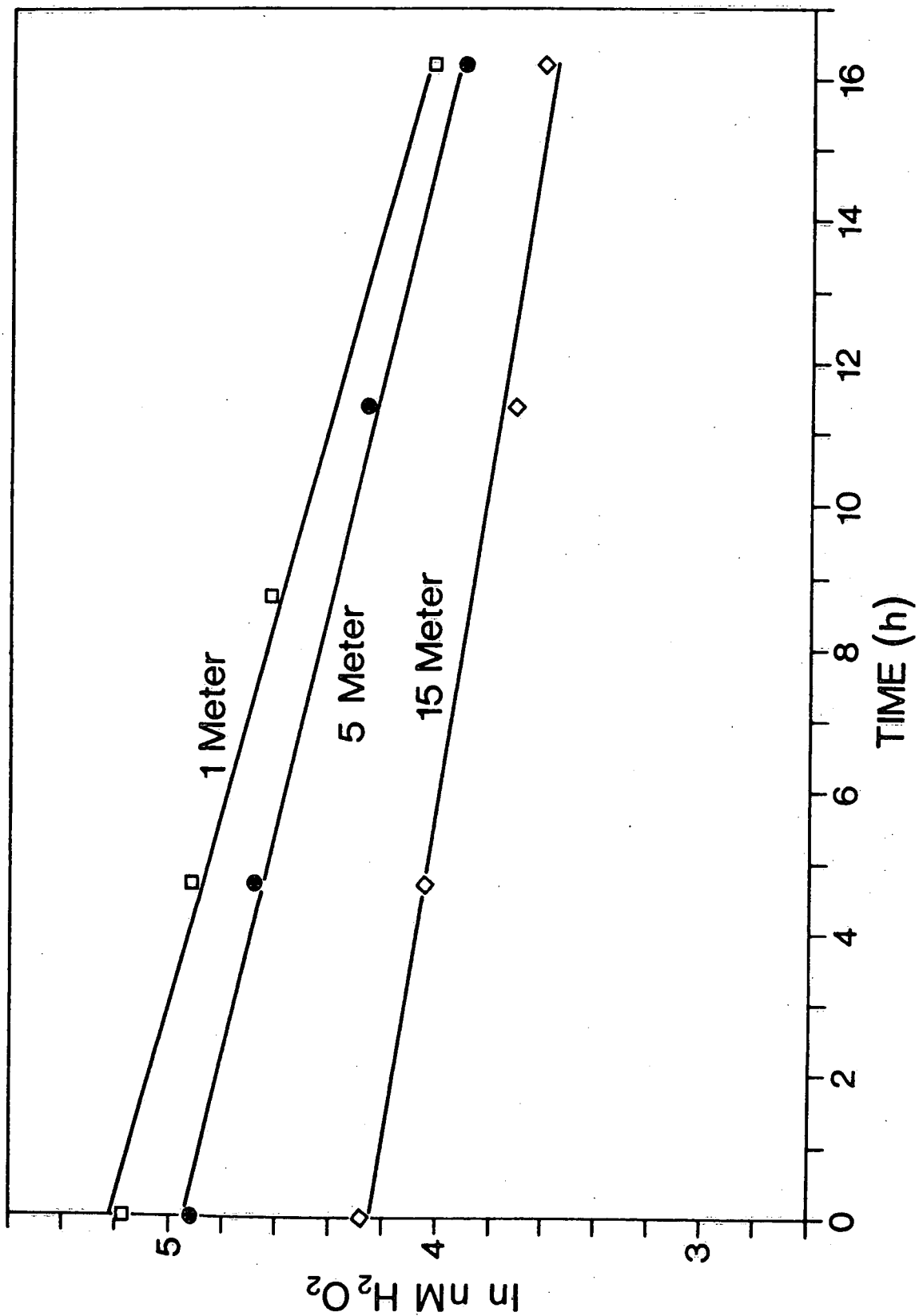
Figure 4. Graph of $\ln \text{H}_2\text{O}_2$ concentration in bottles as a function of time for Central Basin Lake Erie, Station 84, water from 1 (□), 5 (●) and 15 (◇) m.

Figure 5. Spectral composition of incident light and light at 5 m for each of the study sites in Lake Erie. Measurements were made near solar noon with a cloudless sky. The quanta ($q\ m^{-2}\ nm^{-1}$) is obtained by multiplying the scale by the factor shown in brackets.









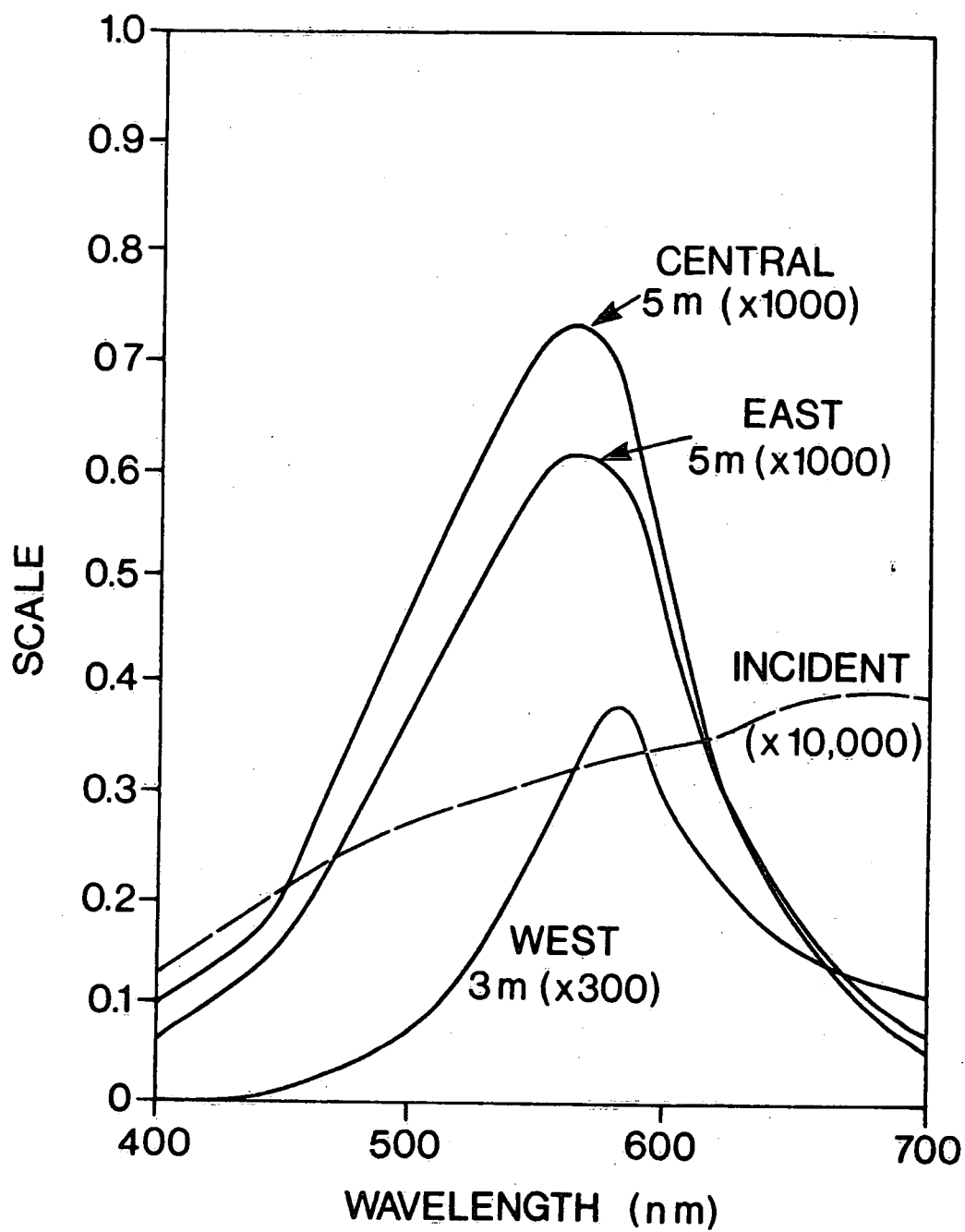


FIG 5 CORP ET AL