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Photochemistry and organic complexation of iron

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Chapter 2

The influence of solar ultraviolet radiation on the photochemical production of H₂O₂ in the equatorial Atlantic Ocean

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Abstract

Hydrogen peroxide (H₂O₂) was measured in marine surface waters of the eastern Atlantic Ocean between 25°N and 25°S. H₂O₂ concentrations decreased from 80 nM in the north to 20 nM in the south, in agreement with earlier observations. A diel cycle of H₂O₂ production as function of sunlight in surface waters was followed twice whilst the ship steamed southward. Around 23°N a distinct diel cycle could be measured which correlated well with irradiance conditions.

The wavelength dependency of H₂O₂ formation was studied near the equator. For 16 hours water samples were incubated with wavelength bands of the solar spectrum, i.e. visible (VIS: 400-700 nm), VIS and ultraviolet A radiation (UVAR: 320-400 nm) and VIS, UVAR and ultraviolet B radiation (UVBR: 280-320 nm). A significant relationship was found between wavelength band and the production of H₂O₂. In addition, a clear positive relationship between intensity and production was found. UVAR was 6.5 times more efficient than VIS in producing 1 nM of H₂O₂, whereas UVBR was 228 times more efficient than VIS. When these data were weighted with respect to the energy of the solar spectrum at zenith hour, 28 % of the H₂O₂ was formed by VIS, 23% was formed by UVAR and 48 % was formed by UVBR. Considering the strong attenuation of UVBR in marine waters as compared with UVAR and VIS radiation, the role of UVAR deeper in the water column is recognized. Furthermore results of this research emphasize the importance of VIS radiation in the formation of H₂O₂.

1. Introduction

Hydrogen peroxide (H₂O₂) is an intermediate in the reduction of oxygen to water. It is a potential toxicant and it can affect the distribution and redox-chemistry of biologically active metals such as iron, copper and manganese. For example H₂O₂ is the dominant oxidation pathway of Fe(II) (Miller and Kester, 1994; Moffett and Zika, 1987).

H₂O₂ can be formed by photochemical reactions and (to a lesser extent) by biota (Hanson et al., 2001; Palenik and Morel, 1988; Palenik et al., 1987). It can be introduced to the marine environment by dry and wet deposition (Hanson et al., 2001; Kieber et al., 2001; Miller and Kester, 1994). The focus of the present study was on the photochemical origin of H₂O₂. Samples of natural surface and ground waters showed a rapid increase in H₂O₂ concentration after exposure to sunlight (Cooper and Zika, 1983). H₂O₂ is photochemically generated from organic constituents present in water. Humic materials are believed to be the primary agent producing the H₂O₂ (Cooper and Zika, 1983). Distinct diel variation of the H₂O₂ concentration was observed with highest concentrations in the late afternoon. The observations are consistent with patterns of H₂O₂ formation due to photo-oxidation of dissolved organic matter (Moore et al., 1993; Palenik and Morel, 1988; Zika et al., 1985). The H₂O₂ concentrations were not only related to light intensity, but also to wavelength (Plane et al., 1987). Plane et al. (1987) demonstrated that production occurs primarily between 300 and 400 nm. This wavelength dependence of H₂O₂ formation is related to the light absorbance of organic substances in the water (Cooper et al., 1988; Plane et al., 1987; Sikorski and Zika, 1993). The absorbance of organic substances is highest in the UVB region of the solar spectrum (280 - 320 nm), decreasing in the UVA region (320 - 400 nm) and lower at higher wavelengths (> 400 nm). The weighting function, relating wavelength band and H₂O₂ formation was assessed by Yocis et al. (2000).

Published data of H₂O₂ concentrations in the Atlantic Ocean are scarce (Miller and Kester, 1994; Obernosterer et al., 2001; Obernosterer, 2000; Weller and Schrems, 1993). Recently, diel cycles in H₂O₂ concentrations were reported by Yuan and Shiller (2001) in the western Central Atlantic Ocean. They observed a decrease of H₂O₂ concentrations with latitude from north to south.

In the present study we investigated factors affecting H₂O₂ formation in marine waters, such as solar irradiance and wavelength dependency. We measured surface H₂O₂ concentrations in the Eastern Atlantic, from 25° N to 25° S, encountering various water masses and irradiance conditions.

Furthermore, during the cruise two diel cycles were measured. Finally, water taken near the equator (2° N) was incubated on deck under different wavelength conditions during which H₂O₂ formation was followed.

2. Material and methods

Measurements were executed during a cruise from Bremerhaven (Germany) to Cape Town (South Africa) aboard RV Polarstern in October 2000 (Figure 1). Data on salinity, temperature, and the position of the ship were obtained from the “Polarstern” PODEV data

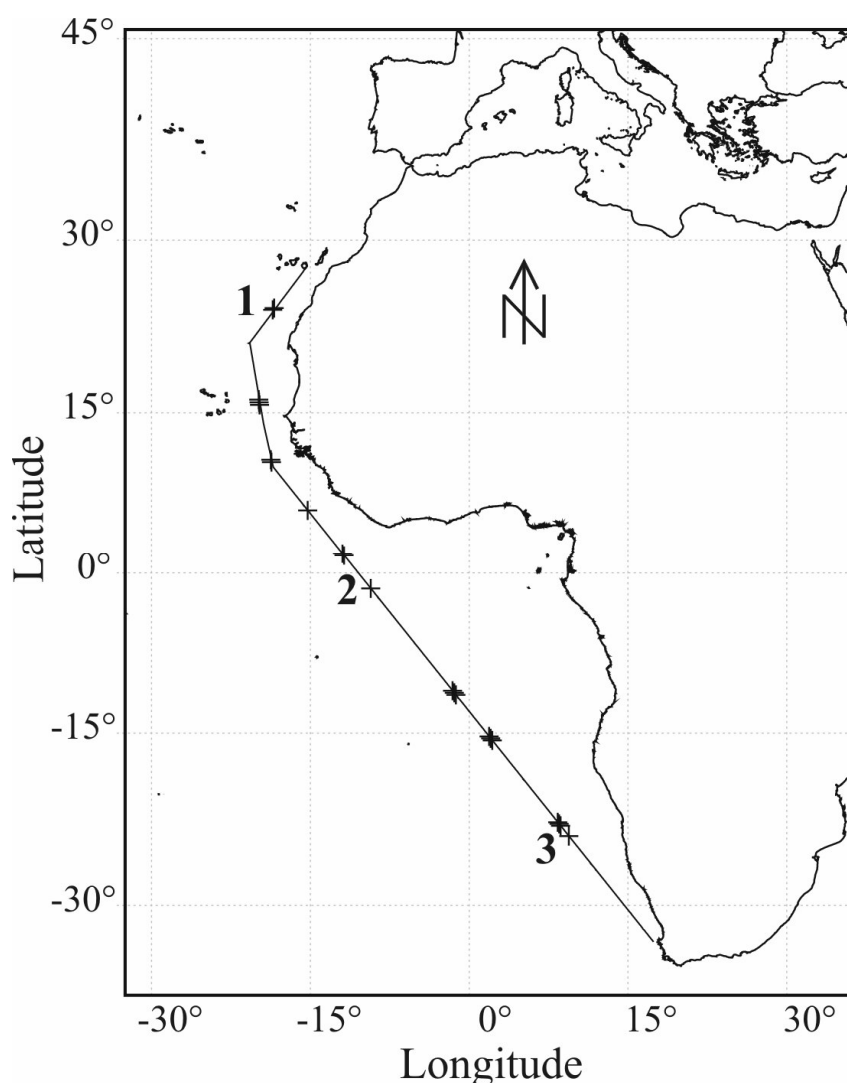


Figure 1. Cruise track of cruise ANT18/1 of the R.V. “Polarstern” from Bremerhaven (Germany) to Cape Town (South Africa). The positions of H_2O_2 measurements are indicated by crosses, the positions of the experiments by numbers.

acquisition system. Samples were taken underway by a FISH towed just under the sea surface, alongside the ship. The samples were filtered on-line through a $0.2 \mu m$ filter cartridge. Global radiation was measured by an artificially ventilated pyranometer (model CM11, Kipp & Zonen) mounted on the mast of the “Polarstern”. It was fixed horizontally with respect to the ship. Rolling and pitching will have had no significant influence on averaged values, but on individual measurements. The values given are 1-min averages (Figure 2 and 3). Light measurements used for the deck incubations were measured every hour using a high accuracy UV-Visible spectroradiometer (model OL 752, Optronic

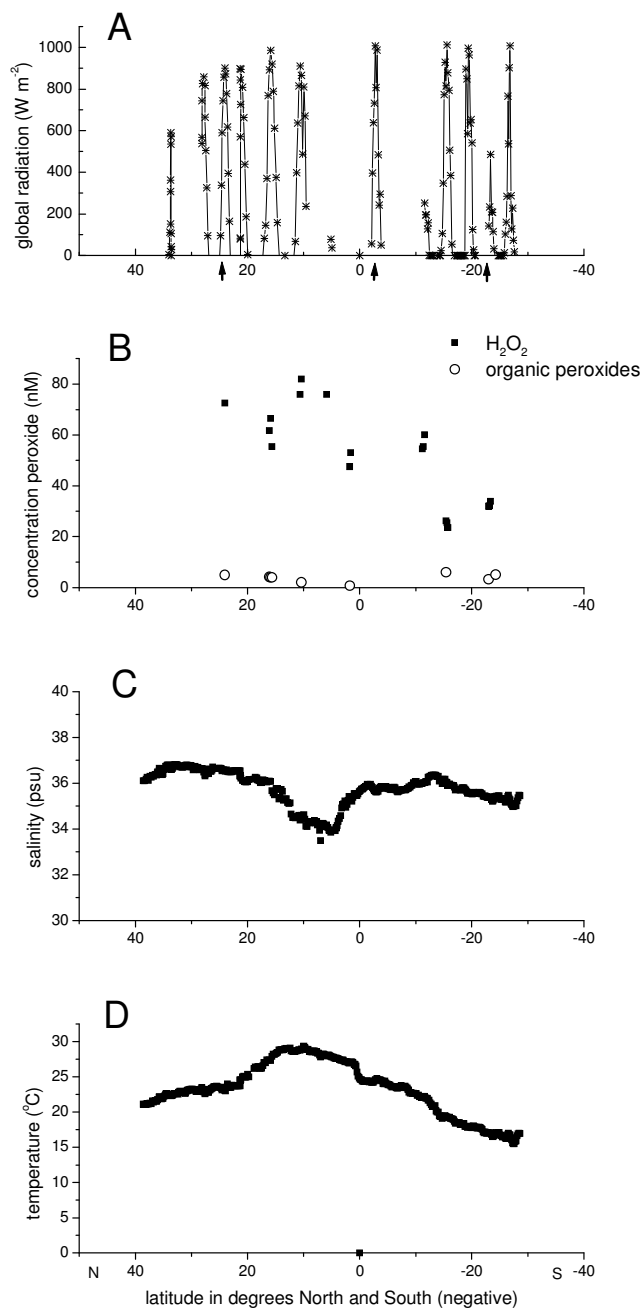


Figure 2. (A) Global solar radiation in W m^{-2} ; (B) H_2O_2 (■) and organic peroxide (○) concentrations (all in nM) in sea surface waters; (C) salinity in psu; (D) temperature in $^{\circ}\text{C}$ against latitude. In (A) the three days on which experiments were executed (9, 15 and 20 October 2000) are indicated by arrows. Where no data are shown, no measurements were made.

Laboratories). The OL 752 system consisted of an Optics Head (OL 752-O-PMT) and an OL 752-C Controller. One measurement of the solar spectrum, 280-750 nm, took ~ 28 minutes.

VIS is defined as light between 400 and 700 nm, UVA between 320 and 400 nm, and UVB between 280 and 320 nm. Diel cycles of H₂O₂ formation were followed on 9 October near 23°N 18°W (1 in Figure 1) and on 20 October near 23°S 8.5°E (3 in Figure 1). Unfortunately, on 20 October the sky was cloudy, resulting in a global radiation at noon that was half of the global radiation at noon on 9 October.

A sample of 50 L of filtered seawater was taken on 14 October, near 2° N, 12° W (2 in Figure 1). The salinity of the water was 35.6 ppt. The water was stored in the dark at ambient seawater temperature (24°C) during the afternoon. After sunset, the water was sub-sampled in 2-L home-made polymethylmetacrylate (PMMA) bottles, which have a high transmission in the UV region (Steeneken et al., 1995). To assure minimal shading the bottles were, immediately after filling, put in UV transparent PMMA incubators on the highest deck of the ship. The bottles were kept at a constant ambient temperature of 24 °C using running seawater from the ship's pumping system. Two PMMA bottles packed in light-tight black plastic functioned as dark controls. Two PMMA bottles received the full solar spectrum (UVB,UVA and VIS), two PMMA bottles were screened by glass, which served as a UVB cut-off filter, receiving only UVA and VIS, two PMMA bottles were screened by UV-opaque PMMA, only permeable for VIS and thus serving as a UVB and UVA cut-off filter. Total irradiance was varied by aluminum neutral density gauze, painted black, causing a 50% reduction in the full solar spectrum. 80% light reduction was obtained by wrapping two bottles in black plastic with tiny (1mm) holes. Light reduction of these materials was measured before use. Sampling during the deck incubation started at 5:00 h UTC in the morning of 15 October and continued until 23:00 h UTC. Each bottle was sampled at least every two hours, and all light conditions were sampled at least once every hour. The dark bottles were only sampled three times during the day.

H₂O₂ was measured as fluorescence (Waters fluorometer, type 470) after enzyme-catalyzed dimerisation of (*p*-hydroxyphenyl)acetic acid (POHPAA) (Miller and Kester, 1988; Miller and Kester, 1994). The POHPAA (Merck, purified by recrystallization) stock solution (25 mM in milliQ) was kept at 4°C. The peroxidase stock solution (horseradish, 10000 U/val, Merck; 3.6 mg in 100 ml 0.25 M TRIS, pH 8.8) was stored in 2 ml portions at -20°C. A fluorometric reagent of POHPAA and peroxidase was prepared daily in 0.25 M TRIS (pH 8.8). Concentrations and enzyme activities in the samples were 5.1.10⁻⁶ M POHPAA and 0.153 units/ml (U/ml) peroxidase.

The fluorometric reagent was immediately added to the sample to fix the hydrogen peroxide. The samples (in triplicate) were stored at 4°C and analysis was completed within 12 h. The fluorescence response is a combination of the signal of the hydrogen peroxide and the organic peroxides. To distinguish between these forms, 4 min before the addition of the

fluorometric reagent, catalase (65 U/ml) was added to the samples to remove the hydrogen peroxide. The resulting fluorescence signal represented the organic peroxides, whereas subtraction from the total signal resulted in the hydrogen peroxide concentrations. Corrections were made for the natural fluorescence of seawater (no reactants added to the seawater) and the fluorescence of catalase (only catalase added to the seawater).

The precision of the method was 3% (st dev after 15 analyses of the same sample). Its detection limit was smaller than 2 nM (three times the standard deviation of open ocean water blank). The H₂O₂ standard was checked by measuring the reaction with KI at 353 nm (Cotton and Dunford, 1973).

3. Results and discussion

3.1 Surface samples from the transect

The H₂O₂ concentrations in the surface samples decreased from 70-80 nM at 25°N to 20-30 nM at 25°S in samples taken at noon (Fig 2B). Obernosterer (2000) found surface values between 125 and 50 nM in the subtropical northern Atlantic Ocean in 1996. In 1992, Weller and Schrems (1993) measured concentrations from 150 nM at 30°N to 100 nM at 30°S over approximately the same cruise track as shown in Figure 1. A decrease from north to south was also observed by Yuan and Shiller (2001) in the central and southern Atlantic Ocean. They suggest that this latitude dependence is due to differences in precipitation. Rain is a well-known source of H₂O₂ in oceans (Hanson et al., 2001; Miller and Kester, 1988; Miller and Kester, 1994; Weller and Schrems, 1993; Yuan and Shiller, 2000).

Organic peroxides were measured irregularly; they varied between 1 and 6 nM (Figure 2B). To our knowledge no other data on organic peroxides in the Atlantic Ocean have been published, making comparison impossible.

In the Northern Hemisphere the H₂O₂ concentrations did show a clear positive relationship with the global radiation (Figure 3). A decrease in H₂O₂ concentrations, seen the night before, was followed by a sharp increase of more than 30 nM H₂O₂ with increasing radiation. Obernosterer et al. (2001) found diel variations of 42 nM in the northern subtropical Atlantic Ocean, whereas Yuan and Shiller (2001) found a variation of 25 nM in the central and southern Atlantic Ocean. A slight decrease in concentration in our data occurred after sunset on 9 October (Figure 3). Johnson et al. (1989) observed such a slow decrease of peroxide concentrations with time and with depth in the western Mediterranean Sea, where they used H₂O₂ as a tracer for vertical advection. Johnson et al. (1989) calculated a decay rate of 3.8 nM h⁻¹ during darkness. The decrease in the present data in Figure 3 for

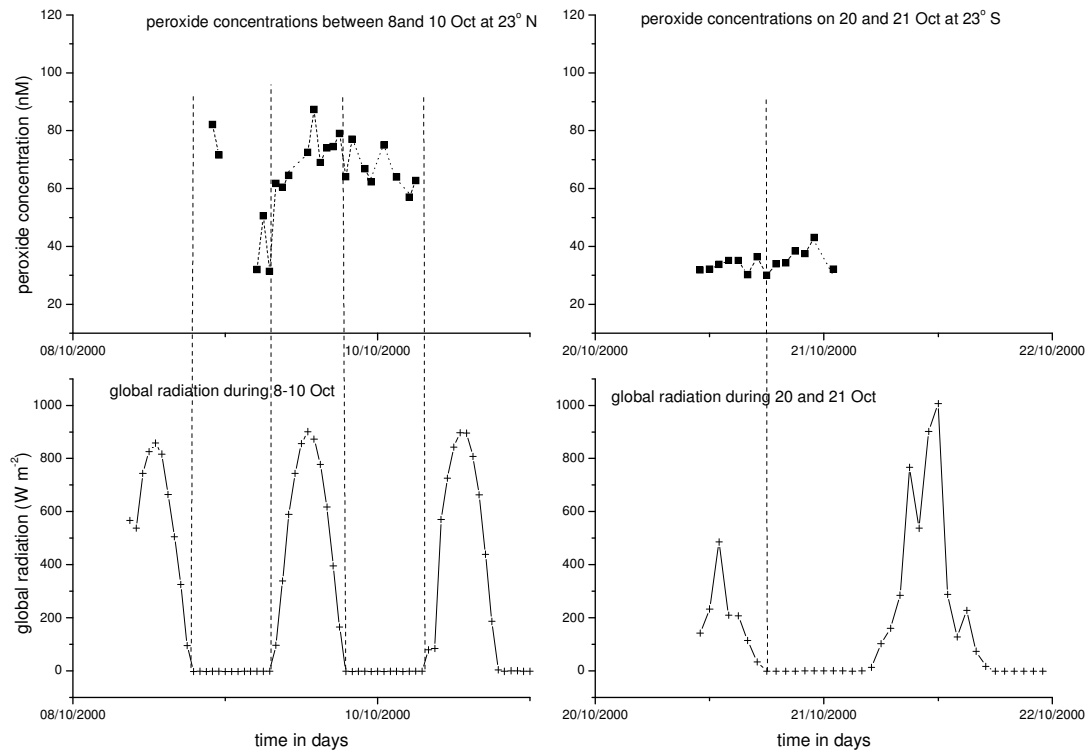


Figure 3. H_2O_2 concentrations (nM) and global solar radiation ($W m^{-2}$) of two diel cycles between 8 and 10 October 2000 at $23^\circ N$, and around 20 and 21 October 2000 at $23^\circ S$.

the Northern Hemisphere, measured from the slope through the middle of the data points, would give a rate of 1 nM h^{-1} . Johnson et al. (1989) did not observe a decline in concentration until after sunset as is also the case in our data. This is especially the case for seawater compared to a relatively rapid decrease observed in fresh water (Cooper and Lean, 1989).

The second diel cycle observation in the Southern Hemisphere gave a different result (Figure 3). A potential diel variation of 5-10 nM in H_2O_2 concentration disappeared in the noise of the measurements during the day and the following night. Since the global radiation was lower due to clouds, a lower production of H_2O_2 was expected. In order to check whether the difference in H_2O_2 production could be explained by the difference in the solar intensity a linear relationship between H_2O_2 production and the intensity of the global radiation of 9 and 20 October was calculated. The slope of the linear relation in the data of 9 October was 2.7 times higher than that of 20 October. Thus the lower magnitude in the diel cycle must have had an additional cause, most likely a lower concentration in organic matter in the Southern hemisphere sampling station (Scully et al., 1996). Both the northern and the southern experiments were performed in subtropical gyres, which presumably have relatively nutrient-

poor surface waters (Antoine et al., 1996; Field et al., 1998). The northern experiment was in warmer more saline waters ($S=36.5$, $T=23.1^{\circ}\text{C}$ versus $S=35.4$, $T=16.2^{\circ}\text{C}$, Fig 2). Both locations are relatively close to deserts, known to release dust into the adjacent ocean. Both positions are close to a zone of coastal upwelling (Krauss, 1996; Shannon and Nelson, 1996). However, the northern position is closer to the coast and it is thus more likely to receive organic-rich water from the coastal upwelling. Since the formation of H_2O_2 results principally from the excitation of humic substances (Cooper et al., 1988; Scully et al., 1996) differences in H_2O_2 can be expected from differences in water characteristics such as content of organic material. Moore et al. (1993) related peroxide production with organic matter fluorescence in the Eastern Caribbean. Fluorescence was measured continuously aboard the “Polarstern”, but values were very low and had the same order of magnitude for both regions. No rain fell during the cruise, giving no additional explanation for the relatively high diel cycle of H_2O_2 at the northern position or for the decrease of H_2O_2 concentrations from north to south in this part of the Atlantic Ocean.

3.2 Deck incubations

The results of the deck incubations showed a clear relationship between H_2O_2 concentration and the wavelength and cumulative dose of sunlight (Figure 4 and 5). More H_2O_2 was produced with decreasing wavelength (Figure 5A). Even when only VIS was allowed through the bottles, H_2O_2 concentrations increased during the day compared to the dark control bottles. The net H_2O_2 production rate at noon was 7 nM h^{-1} in the bottles with the full solar spectrum, 4 nM h^{-1} in the bottles without UVB and 2 nM h^{-1} in the bottles in which only VIS was allowed. In the dark control bottles 0.4 nM h^{-1} H_2O_2 formed. Taking into account that 88% of the energy of the solar spectrum consisted of VIS, 11% consisted of UVA, and less than 1 % of UVB, the relationship between wavelength and H_2O_2 was much stronger than the production rates show.

A net production rate under the full solar spectrum of 7 nM h^{-1} compares well with other studies. Yuan and Shiller (2001) found 8.3 nM h^{-1} at local noon in the central Atlantic Ocean. Obernosterer (2000) found a net production of 5.5 nM h^{-1} in the northern subtropical region of the Atlantic Ocean. Yocis et al. (2000) measured 4.5 nM h^{-1} in Antarctic waters and attributed this relatively low production to the high latitude, lower temperatures and lower UV irradiances in polar waters.

In order to calculate the wavelength dependency of the net H_2O_2 production, by UVA, the concentrations of H_2O_2 formed under the full solar spectrum were subtracted from those

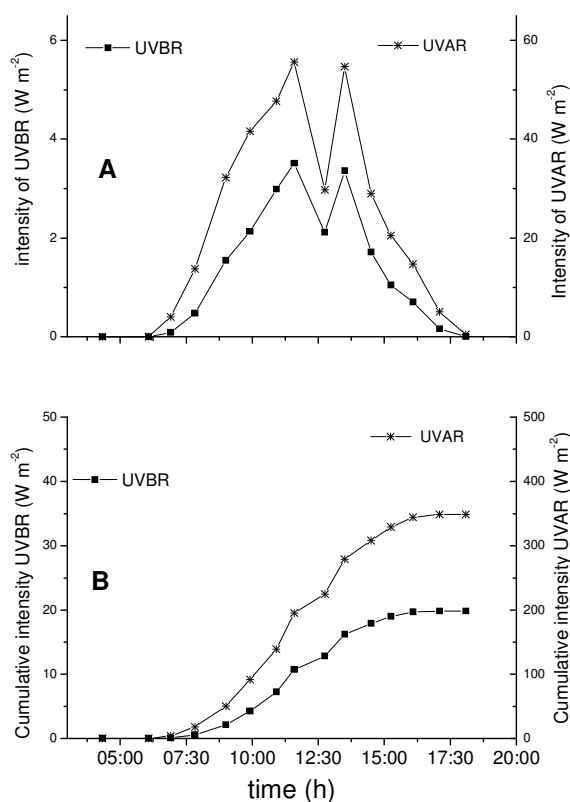


Figure 4. (A) UVA and UVB ($W m^{-2}$) of the solar spectrum of 15 October 2000 against time (UTC); (B) the cumulative energies for UVA and UVB against time (UTC).

formed under UVA and VIS. By subtracting concentrations formed under UVA and VIS from those under VIS we obtained the production caused by UVA.

The light intensities of the UVB, UVAR and the VIS portion of the solar spectrum were fitted into a model in order to explain the increases in H_2O_2 . It was assumed that the relation between H_2O_2 production and light intensity is linear Cooper et al. (1994). It was assumed that the increase in peroxide concentration C at time t_{x+1} was due to the energy of the incoming light E between t_x and t_{x+1} multiplied by a factor L , according to:

$$C_{x+1} = C_x + \frac{(E_x + E_{x+1})}{2} \cdot (t_x - t_{x+1}) \cdot L \quad (1)$$

L ($nM min^{-1} W^{-1} m^2$) was found by minimising the root mean square (RSQ) of the differences between measured and calculated concentrations. To account for the oxidation of peroxides, a

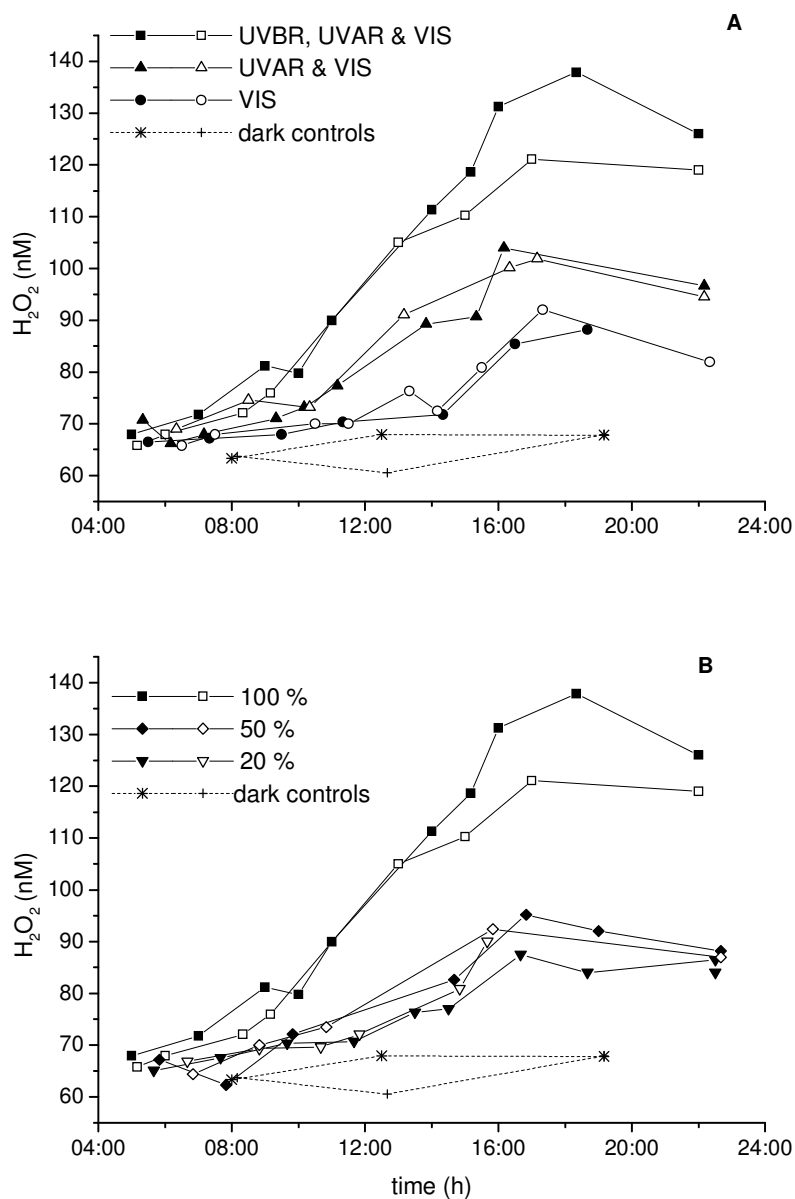


Figure 5. Peroxide concentrations (nM) in the incubated bottles against time (UTC). Two bottles per light condition were used, distinguished by filled and open symbols. (A) Peroxide production related to wavelength of the incoming light. (B) peroxide production related to light intensity. In both figures the data of the dark control bottles are presented. 100% light intensity in (B) is similar to the data of UVBR, UVA and VIS in (A).

Wavelength dependent H₂O₂ production

Table 1. The factor L indicating the relation between light intensity ($W\ m^{-2}$) and peroxide increase ($nM\ min^{-1}$). L was obtained by fitting the data in equation (1). The obtained root mean square of the differences between measured and calculated concentrations ($RSQ\ C_{x+1}-C_x$) are given.

Experimental conditions	Factor L * 10^{-3} ($nM\ min^{-1}\ W^{-1}m^2$)	RSQ(C_{x+1},C_x)
20% of full spectrum	0.112	0.76
50% of full spectrum	0.175	1.46
100% of full spectrum	0.347	1.77
VIS	0.121	1.2
UVA	0.785	1.29
UVB	27.5	2

loss function was included in the model, assuming $dC/dt = LE-KC$. However, this loss factor (K) did not improve the model and was left out.

A 50% light reduction indeed gives half of the peroxide production, a reduction to 20% of the original light causes the production to decrease to 30 % compared to full light conditions (Figure 5B, Table 1). This discrepancy between 20 and 30% is difficult to explain. The light reduction to 20% by the plastic was valid for the entire solar spectrum, independent of wavelength.

The importance of UVB for production of H₂O₂ is evident, confirming the results of Cooper et al. (1994). This radiation is 227 times more efficient for the production of H₂O₂ than VIS and 35 times more efficient than UVA (Table 1). The result of Yocis et al. (2000) showed a comparable ratio in the UVB-UVA region, demonstrating a factor 100 in the relationship between wavelength and peroxide production for the wavelengths at 290 and at 410 nm. However, some care must be taken in directly comparing the results from Yocis et al. (2000) and our results. We did not incorporate wavelength-related differences in absorption into our results.

The energy distribution of the solar spectrum at noon on 14 October near the equator consisted of 88% of VIS, 11.4 % of UVA and 0.65 % of UVR (280-700 nm: $391\ W\ m^{-2}$, 400-700 nm: $346\ W\ m^{-2}$, 320-400 nm: $43\ W\ m^{-2}$, 280-320 nm: $2.8\ W\ m^{-2}$). Considering the contribution of the energies in the solar spectrum and using the L factors from Table 1, we

obtained a H₂O₂ production rate at noon of which 28 % originated from the VIS region, 24 % from UVA and 48% from UVB.

UVA penetrates to greater depths than UVB, so the role of UVA may become increasingly important at greater water depths (Obernosterer, 2000; Scully et al., 1996; Yocis et al., 2000). The decrease with depth found paralleled decrease in UV penetration. However, the data from our study showed an important contribution of VIS to H₂O₂ formation as well. This was also concluded by Sikorski and Zika (1993). They constructed a model in which the optical properties of light in water play an important role. They found that the attenuation of light was very sensitive to the solar angle of incident light and that this effect has a large wavelength dependency. They concluded that due to these optical properties of the solar spectrum, the visible part of the irradiance penetrates much deeper into the water column compared to the UV part of the spectrum than was thought before. They therefore concluded that part of the solar spectrum above 400 nm caused a significant production of hydrogen peroxides, especially at larger depth and at smaller zenith angles.

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