

Spatial and diurnal dynamics of dissolved organic matter (DOM) fluorescence and H₂O₂ and the photochemical oxygen demand of surface water DOM across the subtropical Atlantic Ocean

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Abstract

Diurnal dynamics of dissolved organic matter (DOM) fluorescence and hydrogen peroxide (H₂O₂) concentrations were followed in the upper 100 m of the water column at five stations across the subtropical Atlantic Ocean in July and August 1996. The 10% levels of surface solar radiation for the ultraviolet (UV) B range (at 305- and 320-nm wavelengths) were at 16 and 23 m in depth and for the UVA range (at 340- and 380-nm wavelengths) were at 35 and 63 m in depth, respectively. The DOM fluorescence decreased over the course of the day, whereas H₂O₂ concentrations increased, especially in the diurnally stratified surface water layers extending to 10–50-m depth. In situ H₂O₂ net production varied between 5.5 nmol L⁻¹ h⁻¹ at 5-m depth and 1 nmol L⁻¹ h⁻¹ at 40-m depth, resulting in an H₂O₂ net production of ~38 μmol m⁻² d⁻¹ in the upper 50 m of the water column. Photochemical oxygen (O₂) demand of water collected at 10-m depth in the early morning and exposed to surface solar radiation varied between 0.9 and 2.8 μmol O₂ L⁻¹ d⁻¹ and was found to be consistently higher (by a 1.3–8.3-fold measure) than bacterial respiration (measured in 0.8 μm-filtered seawater in the dark). UVB radiation was responsible for 0–30% of the photochemical O₂ demand. A simple one-dimensional physical model was combined with a photochemical/biological model in order to describe the photochemical production of H₂O₂ at different depth layers over the course of the day and to determine the contribution of physical versus biological processes in terms of the loss of H₂O₂ from the surface layers in the late afternoon. The model reflects well the observed diurnal H₂O₂ dynamics. It further provides evidence that mainly biological breakdown determines the loss of H₂O₂ in the upper 50 m of the water column during the day; however, in the late afternoon, vertical mixing is important in transporting H₂O₂ from the uppermost 5-m layer to the 10–20-m layers.

Stratospheric ozone depletion has caused an increase in ground-level ultraviolet (UV) B radiation (280–320 nm), particularly in polar regions (Crutzen 1992) but also in temperate latitudes (Stolarski et al. 1992). In the subtropical zone, UVB radiation is stable, although it is much greater (≈10-fold) than that observed in Antarctica, even when the atmosphere over Antarctica is depleted in ozone (Holm-Hansen et al. 1993). UVB radiation accounts for only <1% of the total radiation intensity reaching the Earth's surface; nevertheless, it is a highly reactive component of sunlight. Direct exposure to UV radiation has been shown to be detrimental to aquatic organisms (Smith 1989; Cullen et al. 1992; Herndl et al. 1993). UV radiation, however, can also indirectly affect biological processes via photochemical alteration of dissolved organic matter (DOM), which might either stimulate (*see* review by Moran and Zepp 1997) or

inhibit microbial activity (Benner and Biddanda 1998; Tranvik and Kokalj 1998; Obernosterer et al. 1999).

The absorption of solar radiation (particularly in the UV range) by chromophoric DOM can lead to a variety of photochemical reactions. The organic chromophores can react either directly or indirectly as photosensitizers in reactions with other substrates (Zafiriou et al. 1984; Cooper and Lean 1989). Along with an overall loss in absorbance and fluorescence (Vodacek 1992; Morris and Hargreaves 1997), changes in the chemical and biological reactivity of the DOM have been reported (Zafiriou et al. 1984; Moran and Zepp 1997). Photochemical transformations of DOM have been shown to result in the formation of inorganic carbon (DIC) species, such as CO and CO₂ (Mopper et al. 1991; Miller and Zepp 1995; Graneli et al. 1996), a variety of low-molecular weight organic compounds—such as carbonyl compounds (Kieber et al. 1989; Bertilsson and Tranvik 1998) and amino acids (Amador et al. 1989), and inorganic nitrogen (Bushaw et al. 1996) and phosphorous (Francko and Heath 1982). However, only a small fraction of the photo-products formed from DOM has been identified thus far (Moran and Zepp 1997).

The interaction of UV radiation with DOM can also result in the formation of reactive oxygen species. Hydrogen peroxide (H₂O₂) is the least reactive of the reduced oxygen species and is formed in sunlight-initiated redox reactions involving DOM, O₂, and trace metals (Cooper and Zika 1983; Zika et al. 1985). Its stability, relative to other photochemically produced reduced-oxygen species, makes it a useful tracer for DOM photolysis. Photochemical formation

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is considered to be the major production mechanism of H_2O_2 in surface waters. However, biological (Palenik et al. 1987; Roncel et al. 1989) and chemical (Moffet and Zika 1983) formation of H_2O_2 as well as wet and dry deposition (Weller and Schrems 1993; Miller and Kester 1994) can also contribute to the H_2O_2 concentration in the upper water column. Several studies indicate that microbial processes play an important role in the decomposition of H_2O_2 (Cooper and Lean 1989); however, little is known with regard to the relative importance of chemical processes in the decomposition of H_2O_2 .

H_2O_2 has also been used as a sensitive tracer for diurnal stratification (Sikorski and Zika 1993; Scully and Vincent 1997). Diurnal thermoclines are known to occur in the upper ocean when solar heating causes a temperature increase in the surface layers (Imberger 1985; Price et al. 1986). Depending on the intensity of solar radiation, wind stress, and optical properties of the water column, this diurnal stratification can extend down to a 40-m depth (Price et al. 1986), thereby entrapping DOM and planktonic organisms in the sunlit surface layer over almost an entire diurnal cycle. The extension and the stability of the diurnal thermocline should therefore determine irradiation-related processes in this layer.

The objectives of this study were to evaluate the spatial and diurnal dynamics of DOM fluorescence and H_2O_2 concentrations in the upper 100 m of the water column across the subtropical Atlantic Ocean. These photoinduced processes were resolved, with special emphasis on the surface layers subjected to diurnal stratification. We also developed a simple model in order to describe the photochemical production of H_2O_2 and to evaluate the importance of biological versus physical processes for the dynamics of H_2O_2 in the top 50-m layers. Furthermore, the photochemical oxygen (O_2) demand was measured and related to bacterial respiration. To our knowledge, this is the first report on the photochemical O_2 demand of the surface layers of the oligotrophic subtropical ocean.

Materials and methods

Study sites—The study was carried out during a cruise in the subtropical Atlantic on the RV Hr.Ms. *Tydeman*. Five stations (Sta. I, 12°N, 48°W; Sta. II, 14°N, 40°W; Sta. III, 23°N, 38°W; Sta. IV, 34°N, 35°W; and Sta. V, 34°N, 23°W), each occupied for 4 d, were sampled during July and August 1996. Based on the comparatively low salinity (~36.05) of the top 50 m of the water column of Sta. I, we consider this station to be influenced by freshwater originating from the South American continent, whereas Sta. II–V (mean salinity, 36.93; range, 36.50–37.60) are considered truly oceanic. A pronounced deep chlorophyll maximum was detectable at all stations at 80–130-m depth.

Irradiance measurements—Surface and underwater irradiance were measured at 305-, 320-, 340-, and 380-nm wavelengths and in the photosynthetic active radiation (PAR; 400–700-nm) range with a Biospherical PUV-500 radiometer using the correction factor for the 305-nm channel, as suggested by Kirk (1994). Surface irradiance measurements and irradiance-depth profiles were carried out over a 2–4-d

period per station, with more frequent measurements (every 2–4 h) over 1–2 d. Integrated daily surface irradiance was calculated from the surface irradiance recorded at the upper deck of the ship every 2–4 h. Additionally, at Sta. I and V, surface irradiance was recorded at 10-min intervals and was integrated over the time period between 0800 and 1900 h. Diffuse attenuation coefficients for downward irradiance (K_d) were determined from the slope of the linear regression of the log-transformed downwelling irradiance versus depth. For calculating K_d , irradiance measurements were taken from the upper 30 m of the water column only. Below this depth layer, no linear relationship was obtained between the log-transformed irradiance and depth, probably because of the increasing absorbance by plant pigments toward the deep chlorophyll maximum layers. The number of individual irradiance measurements used to determine K_d was >100 per profile, and correlation coefficients were always >0.97.

Temperature profiles—Measurements of temperature profiles were performed concurrently with the irradiance measurements with the PUV-500 radiometer, set at a recording interval of 1 s. The accuracy of the temperature sensor of this instrument is 0.03°C (Biospherical pers. comm.).

Depth profiles of hydrogen peroxide (H_2O_2) and DOM fluorescence—At each station, series of CTD hydrocasts (SeaBird) were performed over diel cycles down to 200 m depth at 2–4-h intervals. Water samples for the determination of H_2O_2 concentrations and DOM fluorescence were taken with 10-liter NOEX bottles mounted on the CTD frame. Additionally, at Sta. IV and V, surface water (top 50 cm) was sampled using an acid-rinsed polyvinyl chloride bucket. At each station, diel variations in H_2O_2 concentration and DOM fluorescence were followed in the upper-100-m water column over two consecutive days. In situ H_2O_2 net production rates were calculated from the increase in H_2O_2 concentration at a specific depth over daytime (from 0800 to 1500 h) using linear regression analysis. Only data sets with at least three H_2O_2 concentrations over this time period and exhibiting a $r^2 > 0.7$ were used for calculating in situ H_2O_2 net production rates.

Photochemical production of H_2O_2 in 0.2- μm -filtered seawater—At Sta. I, a 2-liter water sample was taken at 5-m depth shortly before dawn and immediately filtered through 0.2- μm polycarbonate filters (Nuclepore; 47-mm filter diameter, rinsed with Milli-Q water and surface seawater prior to filtration). The 0.2- μm filtrate was subsequently transferred to 120-ml quartz biological oxygen demand (BOD) bottles and exposed to surface solar radiation levels of between 1030 and 1600 h. Exposure to surface solar radiation was performed in triplicate, with one dark control wrapped in aluminum foil and incubated in a water bath connected to a running seawater system. All the solar irradiation-exposed BOD bottles and the dark control were subsampled (20 ml) after 1, 2.5, 4, and 7.5 h for the determination of H_2O_2 concentrations (described below). H_2O_2 concentrations in the dark treatments increased by 32 nM after 1.5 h and were stable thereafter; irradiation-exposed treatments were subsequently corrected for this increase in H_2O_2 concentra-

tion in the dark controls. H_2O_2 gross production rates were determined from the linear increase of H_2O_2 over time.

Photochemical oxygen demand of DOM and bacterial respiration—At Sta. II–V, water was collected at 10-m depth shortly before dawn and immediately filtered through either 0.8- or 0.2- μm polycarbonate filters (Nuclepore; 47-mm filter diameter) after rinsing the filters as described above. To determine the photochemical O_2 demand of the surface water DOM, the 0.2- μm filtrate was transferred to quartz BOD bottles (~ 120 ml) and exposed to surface solar radiation for 1–2 d. In order to determine the contribution of the UVB wavelength range on the photochemical O_2 demand, one set of samples was exposed to the full range of surface-level solar radiation and one set was wrapped in Mylar-D foil to shield off the UVB range. Dark controls were wrapped in aluminum foil. To compare the photochemical O_2 demand with bacterial respiration, 0.8- μm -filtered water was incubated in BOD bottles (~ 120 ml) in the dark. For both, photochemical and bacterial O_2 consumption, all the incubations (including the dark controls) were performed in triplicate in a water bath connected to a running seawater system to maintain in situ temperature conditions of the surface layers ($\sim 25^\circ\text{C}$). The initial dissolved O_2 concentration was measured also in triplicate. Photochemical O_2 demand was calculated from the difference in the dissolved O_2 concentration in the 0.2- μm filtrate between the irradiation-exposed and the dark treatments at the end of the 1–2-d incubation period. Bacterial respiration was calculated from the difference in the dissolved O_2 concentration in the 0.8- μm filtrate at the beginning and the end of the incubation period (1–2 d).

Hydrogen peroxide (H_2O_2) determination— H_2O_2 concentrations were measured using the enzyme-catalyzed dimerization of *p* hydroxyphenylacetic acid (POHPAA) into a fluorescent product (Miller and Kester 1988). All chemicals were obtained from Sigma Chemicals. The peroxidase stock solution was prepared in the laboratory and was kept frozen in 2-ml Eppendorf vials. The POHPAA stock solution (25 mM, prepared in Milli-Q water) was kept refrigerated during the 4 d of sampling per station. The POHPAA working solution was prepared daily in 0.25 M Tris buffer. Peroxidase (10,440 U L^{-1}) and POHPAA (255 μM) working solutions were mixed (1 : 1) resulting in a fluorogenic reagent that was subsequently added to the water samples. H_2O_2 standards were also freshly prepared daily by serially diluting the H_2O_2 stock solution (1 mM) with Milli-Q water.

All samples were immediately derivatized by adding the fluorogenic reagent (peroxidase and POHPAA) to a 5-ml sample. Samples were incubated in triplicate at in situ temperature ($\sim 25^\circ\text{C}$) in the dark for 30 min before the fluorescence was measured with a Jasco 820 spectrofluorometer. H_2O_2 concentrations in the samples were calculated using the daily established slope for standard additions (5–200 nM). Blanks were determined by adding the fluorogenic reagent to samples treated with catalase for 5 min (Miller and Kester 1988). The detection limit defined as three times the standard deviation of the blank was, on average, 4.0 ± 1.8 nM ($n = 10$) for the five stations.

Determination of dissolved oxygen—The concentration of dissolved O_2 was measured via the spectrophotometric determination of total iodine (Pai et al. 1993; Roland et al. 1999). Sample treatment principally followed the standard protocol for the determination of O_2 by Winkler titration (Parsons et al. 1984). The amount of iodine was measured spectrophotometrically at a wavelength of 456 nm using a Hitachi U-1000 spectrophotometer and a 1-cm flow-through cuvette. The sample was withdrawn from the BOD bottle with a sipper system; the end of the inlet tube was placed near the bottom of the BOD bottle in order to avoid possible loss of volatile iodine. The instrument was zeroed against Milli-Q water. Calibration was performed by standard additions of iodate to distilled water, resulting in an empirical coefficient of $0.54455 \text{ nM cm}^{-1}$ for the 456-nm wavelength (Kraay pers. comm.). A four-digit voltmeter (Metex M4650) was connected to the spectrophotometer in order to increase the sensitivity of the absorption readings. All incubations were done in triplicate; the analytical standard deviation was $<0.5\%$ ($n = 42$).

Dissolved organic carbon (DOC) analysis—Samples for DOC were filtered through presoaked and rinsed (with distilled water) 0.2- μm polycarbonate filters (Nuclepore) using combusted (450°C for 4 h) glass filtration sets. Duplicate 8-ml subsamples from the 0.2- μm filtrate were subsequently acidified with three drops of concentrated phosphoric acid (45% w/v) and sealed in combusted 10-ml ampoules. Samples were stored at 4°C for later analysis. DOC was measured by injecting 50 μl of sample into a Shimadzu TOC-5000A (Benner and Strom 1993). The DOC content was determined after sparging the samples with CO_2 -free air. Standards were prepared with potassium hydrogen biphthalate (Kanto Chemical Co). The blank was, on average, $15.2 \pm 7.7 \mu\text{M C}$ (range 5–32 $\mu\text{M C}$), and the average analytical precision of the instrument was $<4\%$.

DOM fluorescence measurements—The fluorescence of the DOM was measured on raw seawater immediately after collection from the NEOX bottles at an excitation wavelength of 350 nm and an emission wavelength of 450 nm using a 1-cm quartz cuvette. The fluorometer (Jasco 820) was standardized with a quinine sulfate solution (1 QSU = 1 ppb quinine sulfate in 0.05 M H_2SO_4).

Statistical analysis—A one-way analysis of variance (ANOVA) with a multiple post hoc (Tukey) test was used to check for differences among the five stations. The Wilcoxon test was used to check for treatment effects (full solar radiation versus exclusion of UVB) on variables. Statistics were performed with SYSTAT 5.2 (Wilkinson 1990).

Description of the model—A one-dimensional physical model based on the Princeton Ocean Model (Blumberg and Mellor 1987) was combined with a simple photochemical/biological model (see for details the Web Appendix at http://www.aslo.org/lo/pdf/vol_46/issue_3/0632a1.pdf) in order to describe the diurnal changes in H_2O_2 concentrations and to evaluate the importance of physical versus biological processes on the dynamics of H_2O_2 at different depth layers of

Table 1. Diel-integrated irradiance above the sea surface and at 5-m depth for the UVB (at 305- and 320-nm wavelengths) and the UVA (at 340- and 380-nm wavelengths) regions (in $\text{kJ m}^{-2} \text{nm}^{-1} \text{d}^{-1}$) and for photosynthetic active radiation (PAR) (400–700 nm, in $\text{E m}^{-2} \text{d}^{-1}$) at Sta. I–V. All the measurements were performed on nearly cloudless days.

Sta.	UVB		UVA		PAR
	($\text{kJ m}^{-2} \text{nm}^{-1} \text{d}^{-1}$)	($\text{kJ m}^{-2} \text{nm}^{-1} \text{d}^{-1}$)	($\text{kJ m}^{-2} \text{nm}^{-1} \text{d}^{-1}$)	($\text{kJ m}^{-2} \text{nm}^{-1} \text{d}^{-1}$)	($\text{E m}^{-2} \text{d}^{-1}$)
Surface	305 nm	320 nm	340 nm	380 nm	
I	1.7	7.6	14.0	19.3	52
II	1.6	7.0	12.7	17.4	46
III	1.4	7.0	13.2	18.5	51
IV	1.0	5.9	11.8	16.7	46
V	0.9	5.5	11.0	15.6	45
5-m Depth					
I	0.3	2.9	7.4	13.0	24
II	0.8	5.1	10.1	16.9	34
III	0.7	4.5	10.2	16.9	31
IV	0.4	4.0	9.1	16.6	26
V	0.3	3.2	6.5	12.1	24

the upper–50-m water column. For the model we assume that the processes regulating diurnal H_2O_2 dynamics are the same at all five stations. The physical model describes the diel hydrodynamics, including the development of a diurnal thermocline as forced by air temperature, humidity, cloud cover, wind speed, and irradiance. These parameters were measured during the cruise on board the ship. The photochemical production of H_2O_2 in the upper–50-m water column is modeled using measured surface solar irradiance, the Kd, and the DOC concentration (Cooper et al. 1994). In our model, diurnal H_2O_2 dynamics in different depth layers are determined by the photochemical production of H_2O_2 , its decomposition by bacterioplankton (Cooper and Lean 1992; Cooper et al. 1994), and vertical mixing (included in the physical model). The biological decomposition of H_2O_2 is regulated enzymatically (Moffet and Zafriou 1990), and in the model it is dependent on the concentration of H_2O_2 and the enzymes. The enzyme production is related to both the bacterioplankton activity and the increase in H_2O_2 concentration over time. Modeled bacterioplankton activity is, on the one hand, related to primary production, which is estimated from measured PAR intensities. On the other hand, high levels of UV radiation inhibit bacterioplankton activity in the present model (Herndl et al. 1993); this inhibitory

period is followed by a rapid recovery due to decreasing irradiation intensities in the late afternoon and a decline in the ratio of UVB to UVA radiation (Kaiser and Herndl 1997).

Results

Surface solar radiation and irradiance-depth profiles—Surface solar radiation during cloudless days integrated over the photoperiod ranged between 0.9 and 1.7 $\text{kJ m}^{-2} \text{nm}^{-1} \text{d}^{-1}$ (for 305 nm), between 5.5 and 7.6 $\text{kJ m}^{-2} \text{nm}^{-1} \text{d}^{-1}$ (for 320 nm), between 11 and 14 $\text{kJ m}^{-2} \text{nm}^{-1} \text{d}^{-1}$ (for 340 nm), and between 15.6 and 19.3 $\text{kJ m}^{-2} \text{nm}^{-1} \text{d}^{-1}$ (for 380 nm) at the five stations (Table 1). PAR varied between 45 and 52 $\text{E m}^{-2} \text{d}^{-1}$.

At the five stations, mean attenuation coefficients (Kd) varied in the UVB region between 0.126 and 0.156 m^{-1} (for 305 nm) and between 0.088 and 0.105 m^{-1} (for 320 nm) (Table 2). Thus, the 10% surface radiation levels for the 305- and 320-nm wavelengths were at 16 ± 1.5 and 23 ± 1.8 m in depth, respectively (Table 2). Mean Kd for the UVA wavelength range varied between 0.056 and 0.069 m^{-1} (for 340 nm) and between 0.031 and 0.041 m^{-1} (for 380 nm), resulting in mean 10% surface radiation levels at 35 ± 3.4 and 63 ± 7.5 m in depth, respectively (Table 2). The Kd for PAR were similar to those for 380 nm (Table 2). Among the five stations, Sta. III exhibited the lowest Kd for all wavelengths; however, only $\text{Kd}_{305 \text{ nm}}$ was found to be significantly lower at Sta. III than at Sta. I, IV, and V (ANOVA, $P = 0.014$). The highest Kd for 305 and 320 nm were generally detected in the morning and decreased at all stations (by about 7%) until 1300 h. From 1300–1700 h, a further decrease in the $\text{Kd}_{305 \text{ nm}}$ was detectable at two out of four stations, whereas at the other two stations, the $\text{Kd}_{305 \text{ nm}}$ was higher at 1700 h than at 1300 h. The $\text{Kd}_{320 \text{ nm}}$ increased at all stations in the late afternoon (Table 3).

DOC and DOM fluorescence—Spatial aspects—DOC concentrations generally declined from the surface mixed layer to 150 m in depth. Mean DOC concentrations in surface waters ranged between 76.5 and 90.6 $\mu\text{M C}$; at 150 m in depth, DOC concentrations varied between 57.4 and 70.5 μM (Table 4). Fluorescence, expressed as DOC-normalized quinine sulfate units, was two to six times lower at the 50-m depth than at the 150-m depth (Table 4). At Sta. II and III, DOM fluorescence at the 50-m depth was significantly lower than at Sta. I, IV, and V (ANOVA, $P < 0.001$).

Table 2. Mean attenuation coefficients (Kd m^{-1}) of the UVB (at 305- and 320-nm wavelengths) and UVA (at 340- and 380-nm wavelengths) ranges and of photosynthetic active radiation (PAR) (400–700 nm) at Sta. I–V. Kd were calculated from measurements performed around noon on consecutive days; n = number of depth profiles from which Kd were calculated ($\pm\text{SD}$).

Sta.	n	$\text{Kd}_{305 \text{ nm}}$	$\text{Kd}_{320 \text{ nm}}$	$\text{Kd}_{340 \text{ nm}}$	$\text{Kd}_{380 \text{ nm}}$	Kd_{PAR}
I	3	1.155 (0.006)	0.105 (0.004)	0.068 (0.005)	0.041 (0.003)	0.038 (0.002)
II	4	0.140 (0.011)	0.104 (0.009)	0.069 (0.007)	0.041 (0.012)	0.038 (0.014)
III	2	0.126 (0.004)	0.088 (0.004)	0.056 (0.004)	0.031 (0.001)	0.034 (0.001)
IV	4	0.151 (0.008)	0.103 (0.008)	0.069 (0.007)	0.035 (0.009)	0.041 (0.005)
V	3	0.156 (0.006)	0.105 (0.003)	0.069 (0.006)	0.036 (0.004)	0.050 (0.001)

Table 3. Diurnal variation of the attenuation coefficients (K_d m^{-1}) at 305- and 320-nm wavelengths at Sta. I–V. At Sta. IV and V, K_d are mean values of measurements taken on two consecutive days; SD was always <5%; nd, not determined.

	Time of day	Sta.				
		I	II	III	IV	V
$K_{d_{305\text{ nm}}}$	0900	0.171	0.143	0.133	0.150	0.174
	1300	0.162	0.135	0.123	0.146	0.155
	1530	nd	nd	nd	0.138	0.150
	1700	0.128	nd	0.138	0.110	0.166
	$K_{d_{320\text{ nm}}}$	0.116	0.103	0.095	0.107	0.109
$K_{d_{320\text{ nm}}}$	1300	0.110	0.102	0.085	0.100	0.103
	1530	nd	nd	nd	0.106	0.108
	1700	0.112	0.112	0.099	0.106	0.105

Stratification and dynamics of DOM fluorescence and H_2O_2 —Diurnal aspects—Temperature, DOM fluorescence, and H_2O_2 concentrations were followed in the upper 100 m of the water column over diurnal cycles (Fig. 1). To determine whether the same water mass has been sampled throughout the day, we compared the measured and modeled salinity depth profiles at the corresponding sampling times. Pronounced differences between the measured salinity and the salinity derived from the one-dimensional physical model (>0.06 psu) were detectable at Sta. I (from 0 to 50 m in depth) and IV (>20 m in depth) between ~ 1100 h and 1500 h. This could indicate the temporary presence of a different water mass as a result of lateral transport. Thus, the observed changes in DOM fluorescence and H_2O_2 concentration at Sta. I and IV are most likely influenced by changing hydrographic conditions.

Temperature profiles indicate a pronounced diurnal stratification in the upper 10 to 50 m of the water column at all stations (Fig. 1). At Sta. IV and V, a shallow permanent thermocline was detectable at around 30 m in depth, and a diurnal stratification reached to ≈ 15 m in depth (Fig. 1). The diurnal increase in surface water (0–50-m layer) temperature varied between 0.35 and 1.5°C, with the highest temperatures reached in the early afternoon. This warming

of the uppermost water layers during the day at all stations was followed by mixing events in the late afternoon (as a result of surface cooling). This trend was particularly pronounced at Sta. II and III, as reflected by the temperature profiles taken at 1700 h (Fig. 1).

DOM fluorescence (given in DOC-normalized QSU) decreased during the day at all stations. At Sta. II, III, and V, variations in the DOM fluorescence were restricted to the diurnally stratified layers (Fig. 1). The pronounced decrease in DOM fluorescence throughout the upper 50 m of the water column at Sta. I and at Sta. IV at >20 m in depth probably results from changes in the hydrographic conditions, as indicated above.

Although DOM fluorescence decreased during the course of the day, H_2O_2 concentrations increased in the uppermost water layers from the morning to the early afternoon (1230–1500 h, Fig. 1). Generally, all H_2O_2 concentration profiles revealed a surface maximum (75–220 nM) and a decline with depth. A sharp decline in H_2O_2 concentrations was always detectable at the shallow thermocline (30–50 m in depth). At 100 to 150 m in depth, H_2O_2 concentrations ranged between 5 and 10 nM (data not shown). Similar to the DOM fluorescence, diurnal dynamics of H_2O_2 at Sta. II, III, and V were most pronounced in the upper-20-m water layers, whereas at Sta. I and IV, diurnal variations were detectable down to 50 m in depth (Fig. 1).

We consistently detected a linear increase in H_2O_2 concentrations in the individual depth layers (down to 50 m in depth) between 0800 and 1500 h, with highest diurnal in situ net production rates of H_2O_2 obtained close to the surface (Table 5). At Sta. II–V, H_2O_2 net production rates ranged from 5.5 $nmol\ L^{-1}\ h^{-1}$ at 5 m to 1 $nmol\ L^{-1}\ h^{-1}$ at 40 m depth (Table 5). At Sta. IV and V, water from the top-50-cm layer was also sampled. In this top-50-cm layer, H_2O_2 concentrations did not increase linearly during the course of the day but rather exhibited a sharp peak between 1230 and 1500 h, resulting in in situ net production rate of 42 and 30 $nmol\ L^{-1}\ h^{-1}$ at Sta. IV and V, respectively.

Modeling H_2O_2 dynamics—Modeled H_2O_2 dynamics principally followed the same diurnal pattern as the measured

Table 4. Concentration of dissolved organic carbon (DOC, in μm) and DOM fluorescence normalized to the DOC concentration (in quinine sulfate units [QSU], $\mu m\ DOC^{-1}$) at 50-m and 150-m depths at Sta. I–V. The mean (\pm SD) is given for samples taken at different times of the day.

Depth (m)	Sta.				
	I ($n = 3$)	II ($n = 4$)	III ($n = 5$)	IV ($n = 5$)	V ($n = 5$)
	DOC (μm)				
50	76.5 (2.7)	90.6 (6.9)	80.5 (6.8)	78.2 (5.7)	81.4 (12.4)
150	57.4 (4.4)	70.5 (8.7)	64.2 (7.0)	65.8 (6.2)	68.6 (15.8)
Depth (m)	Sta.				
	I ($n = 4$)	II ($n = 7$)	III ($n = 9$)	IV ($n = 8$)	V ($n = 8$)
	QSU ($\mu m\ DOC$)				
50	0.0057 (0.0013)	0.0025 (0.0003)	0.0022 (0.0002)	0.0060 (0.0010)	0.0051 (0.0004)
150	0.0157 (0.0013)	0.0147 (0.0008)	0.0081 (0.0016)	0.0104 (0.0008)	0.0128 (0.0004)

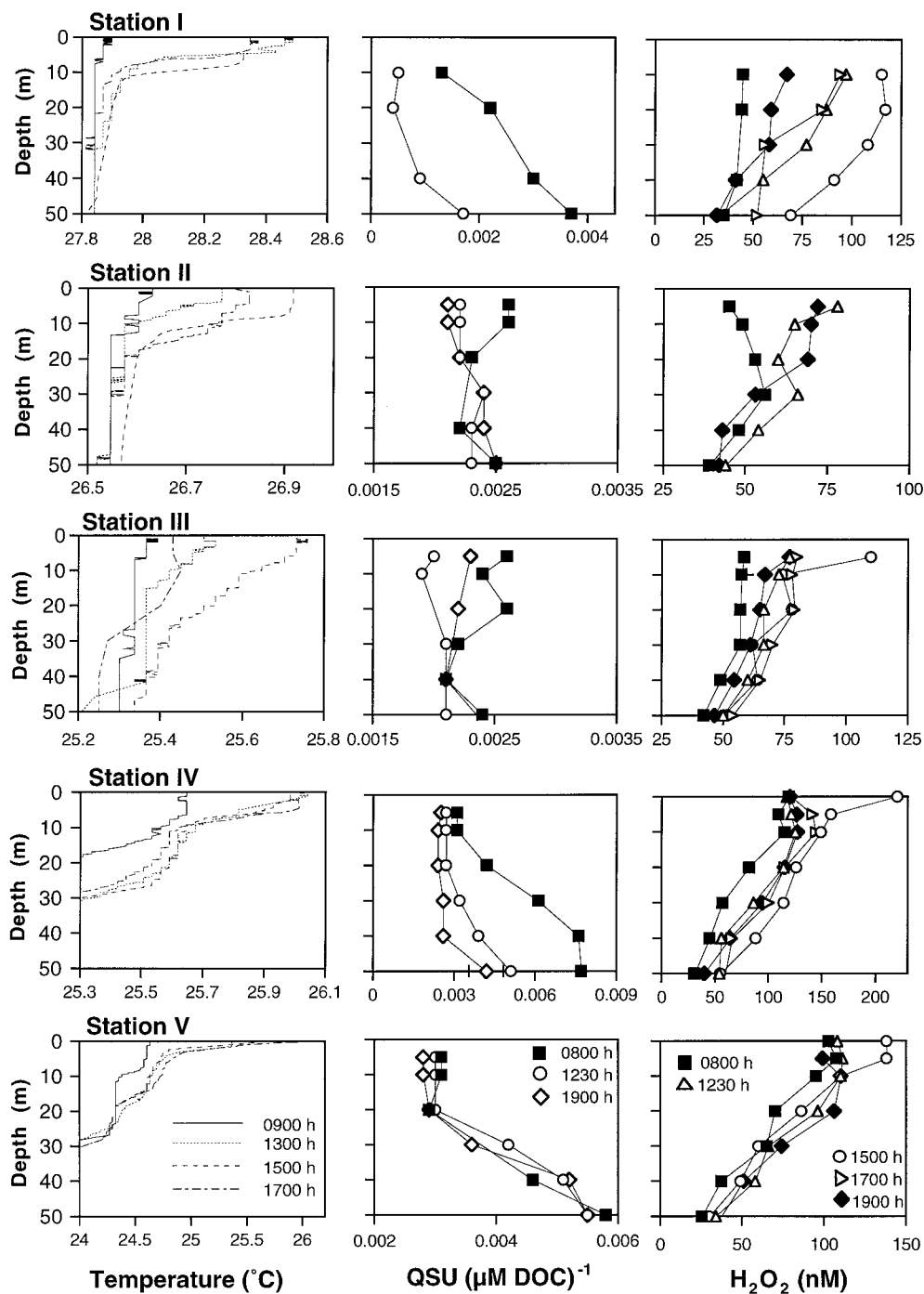


Fig. 1. Diurnal variations in temperature (in °C), DOM fluorescence (in DOC-normalized QSU), and hydrogen peroxide (H₂O₂, in nM) in the upper-50-m water column at Sta. I-V; QSU = quinine sulfate units.

H₂O₂ concentrations (Fig. 2). The photochemical production of H₂O₂ derived from the model led to an increase in H₂O₂ concentrations, particularly in the upper 20 m of the water column, during the course of the day. Modeled H₂O₂ net production was highest close to the surface around noon, when irradiation intensities are highest and biological decomposition of H₂O₂ is probably low due to the generally reduced bacterial activity caused by UV radiation (Herndl et

al. 1993). Furthermore, the development of a diurnal thermocline prevents mixing of H₂O₂ to deeper water layers. In the late afternoon, the model-derived bacterial activity increased because of a decrease in irradiation intensity. This increased bacterial activity and the concomitant vertical mixing of H₂O₂ because the breakup of the diurnal stratification resulted in a decrease in H₂O₂ concentrations in the surface layers (Fig. 2). Differences between the observed and the

Table 5. In situ and modeled (in parentheses) net production rates of H_2O_2 in different depth layers ($\text{nmol L}^{-1} \text{h}^{-1}$), which ranged from 5 to 50 m in depth, and daily H_2O_2 net production rate ($\mu\text{mol m}^{-2} \text{d}^{-1}$) integrated over the upper 50 m of the water column at Sta. I–V. Daily integrated H_2O_2 net production was calculated assuming the same net production rates at 0.1 m as at 5 m in depth and assuming a total exposure period to solar radiation of 7 h; a 7-h period was chosen because of the linear increase in H_2O_2 over this time period. No in situ H_2O_2 net production rates are given for Sta. I and for Sta. IV at >20 m in depth because of the apparently different water masses; nd, not determined.

Depth (m)	Sta.				
	I	II	III	IV	V
H ₂ O ₂ net production rates ($\text{nmol L}^{-1} \text{h}^{-1}$)					
5	nd (8.6)	5.5 (7.4)	5.2 (7.5)	4.8 (4.4)	3.6 (3.2)
10	nd (6.3)	3.6 (6.2)	2.1 (6.1)	4.1 (2.3)	1.8 (1.5)
20	nd (2.2)	1.3 (1.9)	2.5 (3.3)	nd (2.1)	nd (2.1)
30	nd (0.9)	1.7 (0.0)	1.3 (1.2)	nd (0.5)	0.0 (0.7)
40	nd (0.5)	1.0 (0.0)	1.5 (0.9)	nd (0.3)	0.0 (0.5)
50	nd (0.4)	0.0 (1.0)	0.0 (0.6)	nd (0.3)	0.0 (0.0)
Integrated H ₂ O ₂ net production rates ($\mu\text{mol m}^{-2} \text{d}^{-1}$)					
0.1–50	nd (52)	38 (44)	38 (56)	nd (28)	nd (26)

modeled H_2O_2 concentrations were highest for Sta. I and for Sta. IV at >20 m in depth, where different water masses were encountered during the course of the observations, as revealed by salinity profiles.

Photochemical H₂O₂ production and O₂ demand—At Sta. I, 0.2- μm -filtered water from the 5-m depth was exposed to surface solar radiation, and the increase in H_2O_2 concentration followed over time. A linear increase in H_2O_2 concentration was observed over the incubation period (1030–1600

h, $r^2 = 0.984$), resulting in a H_2O_2 gross production rate of $39.8 \pm 12.5 \text{ nmol L}^{-1} \text{h}^{-1}$ ($n = 3$, data not shown).

Photochemical O₂ demand of water sampled at the 10-m depth at Sta. II–V and exposed to the full range of surface solar radiation varied between 0.9 and 2.8 $\mu\text{mol O}_2 \text{ L}^{-1} \text{d}^{-1}$ (Fig. 3a). Shielding off the UVB radiation range decreased the photochemical oxygen demand by 0–30%. Overall, however, no significant influence of UVB on the photochemical O₂ demand was detectable (Wilcoxon, $P = 0.4$, $n = 6$). Normalizing the photochemical O₂ demand to the DOC con-

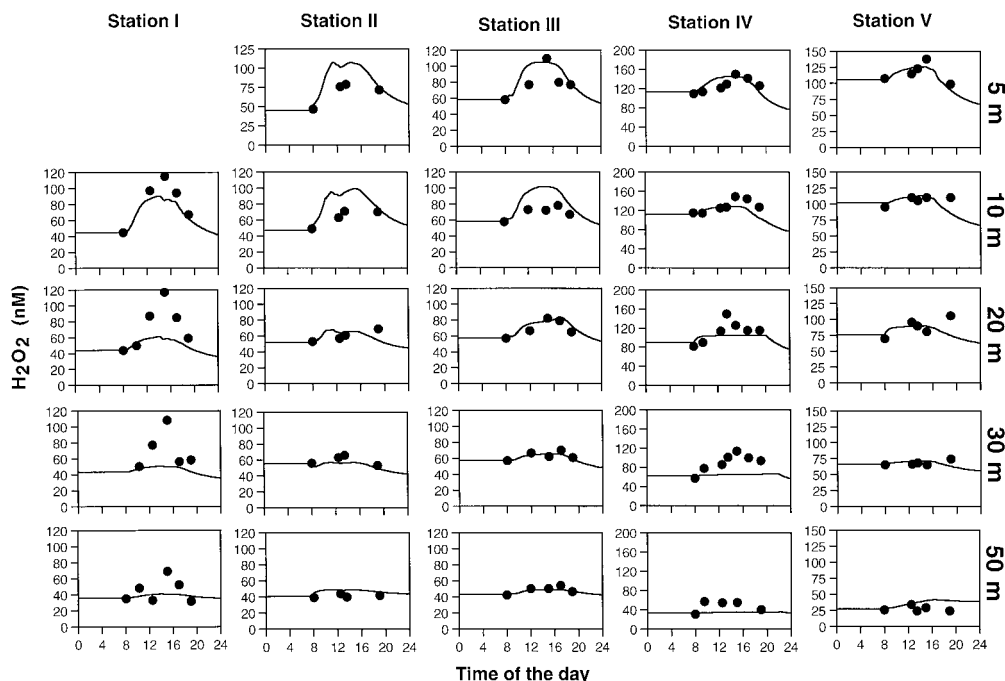


Fig. 2. Comparison of the observed (dots) and modeled (line) diurnal dynamics of H_2O_2 concentrations at different depth layers at Sta. I–V.

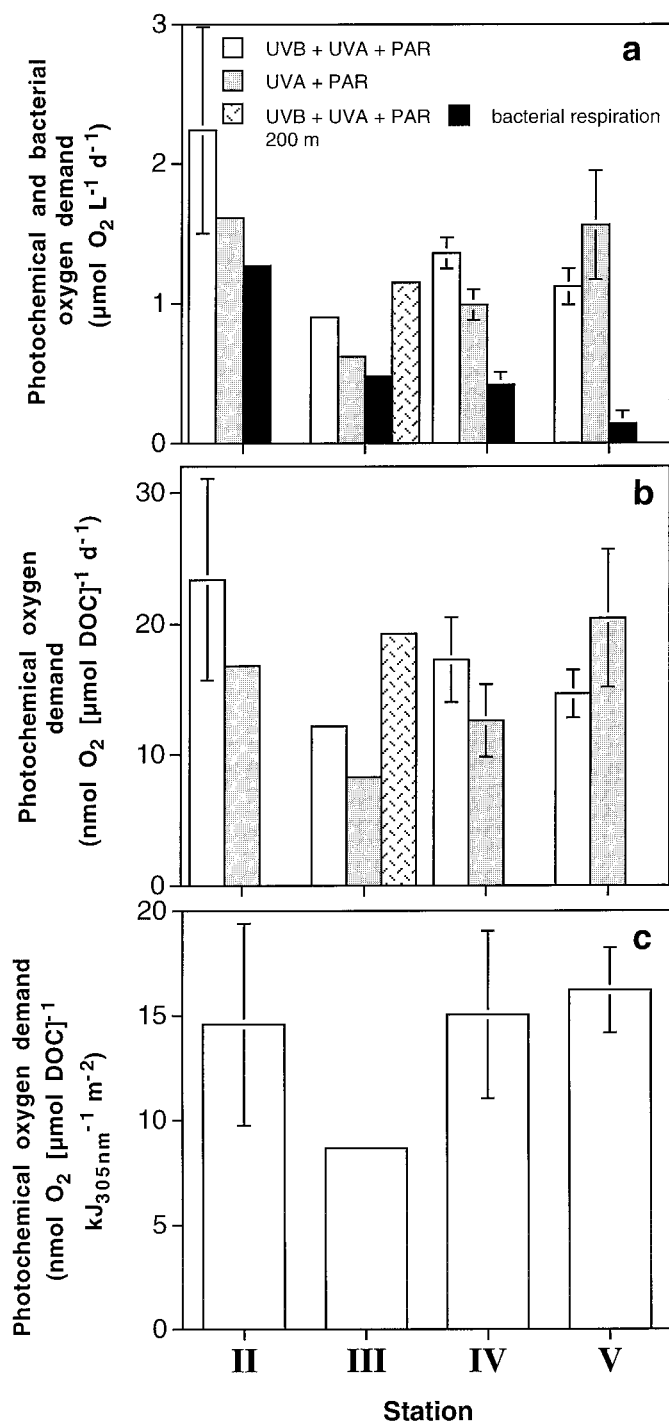


Fig. 3. Photochemical and bacterial oxygen demand (a) (in $\mu\text{mol O}_2 \text{ L}^{-1} \text{ d}^{-1}$), as (b) DOC-normalized photochemical oxygen demand (in $\text{nmol O}_2 \mu\text{mol DOC}^{-1} \text{ d}^{-1}$), and (c) normalized to UVB radiation at the 305-nm wavelength. The water was sampled at the 10-m depth at Sta. II–V. At Sta. III, water was also sampled at the 200-m depth. For the photochemical oxygen demand, quartz BOD bottles were either exposed to full surface solar radiation or wrapped in Mylar-D foil to shield off the UVB range. Bacterial respiration was measured in the dark. Bars (\pm SD) represent means of two individual experiments performed on consecutive days. UVB = ultraviolet B; UVA = ultraviolet A; PAR = photosynthetic active radiation.

centration revealed that between 12 and 29 $\text{nmol O}_2 \mu\text{mol DOC}^{-1} \text{ d}^{-1}$ was consumed under surface solar radiation (Fig. 3b). The photochemical O_2 demand of water collected at 200 m in depth (at Sta. III, Fig. 3a) and exposed to the full range of surface solar radiation was about 20% higher when compared with water originating from a 10-m depth. This difference is more pronounced (\sim 40% higher) if the O_2 demand is normalized to the DOC concentration (Fig. 3b). If the photochemical O_2 demand is normalized to the dose received at the 305-nm wavelength, only minor variations among Sta. II, IV, and V were detectable (Fig. 3c). Bacterial respiration consumed between 0.1 and 1.3 $\mu\text{mol O}_2 \text{ L}^{-1} \text{ d}^{-1}$, amounting to 12–76% of the photochemical O_2 demand under the full range of surface solar radiation (Fig. 3a). Mean bacterial abundance in the upper-70-m water layer of Sta. II–V was about $5 \times 10^5 \text{ cells ml}^{-1}$ (Kuipers et al. 2000).

Discussion

Integrated daily surface irradiance of the specific UV wavelengths continuously decreased (by up to a twofold measure for the 305-nm wavelength) from the southernmost Sta. I toward the stations at higher latitudes. This latitudinal trend was not as pronounced for the integrated surface irradiance in the PAR range (Table 1). However, underwater irradiance was similar at Sta. I, IV, and V and was substantially higher (by an up to 2.7-fold measure) at Sta. II and III (as demonstrated for the 5-m depth layer in Table 1). Only $\text{Kd}_{305 \text{ nm}}$ was found to be significantly lower at Sta. III compared to the other stations (Table 2). Similarly, DOM fluorescence of the upper-50-m water layer was lowest at Sta. II and III (Table 4).

The diurnal stratification was detectable at all stations for the uppermost 10–50-m depth layer (Fig. 1). Although models have been established to describe the development of diurnal thermoclines (Imberger 1985; Price et al. 1986), there are only a few reports on in situ measurements. Price et al. (1986) describe the development of a diurnal thermocline in the Pacific Ocean reaching to a 40-m depth, whereas in freshwater systems, diurnal stratification extends only down to \sim 5 m in depth (Imberger 1985; Scully and Vincent 1997). At Sta. I, IV, and V, diurnal thermoclines were relatively shallow (\sim 10 m in depth), whereas they reached 20 and 50 m in depth at Sta. II and III, respectively (Fig. 1).

Diurnal dynamics of H_2O_2 —A distinct diurnal pattern was found at all stations, with highest H_2O_2 concentrations during mid- to late afternoon and lowest concentrations in the morning. The diurnal range in H_2O_2 concentration in the top surface layer was, on average, 42 nM, a value that corresponds to previously reported values ranging from 25 to 40 nM at different oceanic sites (Zika et al. 1985; Palenik and Morel 1988; Miller and Kester 1994). In situ H_2O_2 net production rates varied between 1 and 5.5 $\text{nmol L}^{-1} \text{ h}^{-1}$ (for the 40- and 5-m layers, respectively) (Table 5) and are comparable to those reported by Miller and Kester (1994) from the Sargasso Sea (\sim 4 nM at 1- and 3-m depths). For comparison, the modeled H_2O_2 production rates are given in Table 5 as well. Integrating the in situ H_2O_2 net production rates obtained from the measured increase in H_2O_2 concentrations at

the individual depth layers down to a 50-m depth over the diurnal cycle, a H_2O_2 net production of $38 \mu\text{mol m}^{-2} \text{d}^{-1}$ for Sta. II and III is obtained (Table 5). Integrated H_2O_2 net production calculated from the modeled net production rates varies between 26 and $58 \mu\text{mol m}^{-2} \text{d}^{-1}$ for the five stations (Table 5).

In situ H_2O_2 net production rates at the 5-m depth, calculated from the increase in H_2O_2 concentration over the daytime period, were almost 10 times lower compared to the H_2O_2 production rates in 0.2- μm -filtered seawater exposed to surface solar radiation. This difference can be explained by the rapid attenuation, particularly that of the UVB wavelength range (Table 1). In addition, in situ decomposition of H_2O_2 and physical transport may contribute to the observed difference between the in situ net production and in the 0.2- μm -filtered seawater. The latter resembles gross H_2O_2 production, since the photodecomposition of H_2O_2 amounts to only $\sim 5\%$ of the H_2O_2 photoproduction rate (Moffett and Zafriou 1993). However, net production rates calculated from the increase in H_2O_2 in the top-50-cm water layer at Sta. IV and V between 1230 and 1500 h resulted in in situ H_2O_2 production rates of 42 and $30 \text{ nmol L}^{-1} \text{h}^{-1}$, respectively, and were thus similar to the H_2O_2 gross production rates ($39.8 \pm 12.5 \text{ nmol L}^{-1} \text{h}^{-1}$). The depth limit of diurnal variations in H_2O_2 concentration was variable, ranging between the 10% surface solar radiation level of the 340- and 380-nm wavelengths, corresponding to a depth of ~ 30 –60 m. Scully and Vincent (1997) defined the depth limit of H_2O_2 production in a subarctic lake at the 1% depth of the 380-nm wavelength, which would correspond to a depth of 112–150 m at the stations sampled in the subtropical Atlantic. At these depth layers, however, we did not observe diurnal patterns in H_2O_2 .

In order to determine whether the decrease in H_2O_2 concentration in surface waters in the late afternoon is caused by downward mixing or by biologically mediated decay, we can compare the depth-integrated (0–100-m) H_2O_2 concentrations at different times of the day at Sta. III. The depth-integrated H_2O_2 concentration was highest at 1500 h and did not exhibit a significant decrease until 1700 h. A 20% decrease in H_2O_2 concentration integrated over the 0–100-m depth was observed between 1700 and 1900 h. A subsurface maximum in H_2O_2 concentration was detectable at 1500 h, and this was followed by a rapid decrease until 1700 h in the upper-50-m water layer (Fig. 1). The constant depth-integrated H_2O_2 concentration between 1500 and 1700 h indicates that, at least over this time period, mixing events might account for the rapid decline in H_2O_2 in the top-10-m water layer.

This is consistent with the result obtained from our model. In order to define the relative contribution of biological versus physical processes for the modeled H_2O_2 concentrations, which were similar to in situ H_2O_2 concentrations at different depth layers during the course of the day (see Fig. 2, Table 5), we calculated the H_2O_2 loss ratio (R_L) as follows

$$R_L = \frac{L_{BD}}{L_{BD} + L_T}$$

where L_{BD} is the loss of H_2O_2 due to biological degradation

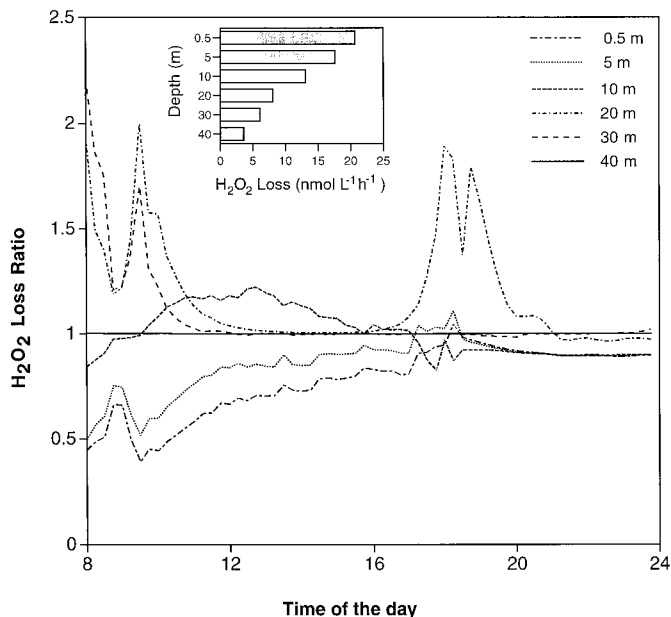


Fig. 4. Diurnal changes of the H_2O_2 loss ratio (R_L , see Discussion for details). A R_L of 0.5 indicates that biological degradation and physical transport are equally important, whereas at a R_L of 1, transport is negligible. A R_L of >1 indicates that transport processes are responsible for the import of H_2O_2 to the respective depth layer. The inset shows the loss of H_2O_2 derived from the model (in $\text{nmol L}^{-1} \text{h}^{-1}$), averaged over the time period between 0800 and 2400 h, resulting from both biological degradation and transport processes.

and L_T is the net downward transport of H_2O_2 . The term L_T is negative if import of H_2O_2 to the respective depth layer takes place. The transport of H_2O_2 can be mediated by vertical mixing and diffusion. A R_L of 0.5 indicates that both processes (biological degradation and physical transport) are of similar importance, whereas at a R_L of 1, the net effect of transport on the H_2O_2 concentration is negligible (Fig. 4). A R_L of >1 indicates that transport processes are responsible for the import of H_2O_2 to the respective depth layer. As indicated in Fig. 4, the significance of physical transport in exporting H_2O_2 is restricted to the upper-5-m water layer during the day. In this depth layer, physical transport and biological degradation are of similar importance in the morning, and the contribution of biological degradation increases in the afternoon (as indicated by ratios of >0.5). In the 10–30-m depth layer, a R_L of >1 indicates the import of H_2O_2 as a result of transport processes. A pronounced diurnal pattern becomes obvious in the 20- and 30-m depth layer, where R_L are ~ 1 between 1200 and 1600 h. The R_L is >1 in both layers in the morning and in the 20-m depth layer in the late afternoon. Concomitantly, in the upper-5-m depth layer, the R_L is <1 (Fig. 4). This indicates that in the morning and in the late afternoon, transport processes are primarily responsible for the export of H_2O_2 from the 5-m depth layer and for the import of H_2O_2 to the 20–30-m depth layer, whereas around noon these transport processes are negligible. This is consistent with the observed establishment of a diurnal thermocline that entraps DOM photoproducts in these layers for several hours during the period of high solar radiation. According to the model, the R_L is ~ 1 at a 30-m depth from

1200 h onwards and at a 40-m depth during the entire course of the day, indicating that the diurnal photochemical production of H_2O_2 is matched by biological degradation (Fig. 4). In order to illustrate the quantitative importance of biological degradation of H_2O_2 versus transport processes at distinct depth layers, the modeled absolute loss of H_2O_2 resulting from both processes is shown in the inset in Fig. 4. Similar to H_2O_2 photoproduction, the H_2O_2 loss rates resulting from biological degradation and transport processes decrease with depth.

Photochemical O_2 demand—Photochemical O_2 demand of surface water DOM at the five stations varied between 0.9 and 2.8 $\mu\text{mol O}_2 \text{ L}^{-1} \text{ d}^{-1}$, or between 0.1 and 0.3 $\mu\text{mol O}_2 \text{ L}^{-1} \text{ h}^{-1}$, assuming a 12-h photoperiod. Similar values are reported by Laane et al. (1985) from an oligotrophic station in the coastal Caribbean Sea. Most studies on photochemical O_2 demand, however, were conducted in humic-rich freshwater systems (Lindell and Rai 1994; Amon and Benner 1996; Reitner et al. 1997), yielding up to ~40-fold higher photochemical O_2 consumption rates compared with those obtained during our study. However, DOC-normalized photochemical O_2 demand between the open Atlantic Ocean and the humic-rich freshwater systems differs only by a factor of about two to five, indicating substantial concentrations of photoreactive DOM in the surface waters of the subtropical Atlantic. DOC-normalized photochemical O_2 demand of water collected at a 200-m depth was about 1.4-fold higher compared to that of water from the 10-m depth, which indicates that there is a higher contribution of photochemically reactive DOM to the bulk DOM pool in waters below the euphotic zone (Kieber et al. 1989; Mopper et al. 1991). This was also obvious from the significantly higher DOM fluorescence at the 150-m depth compared with that obtained at the 50-m depth (Table 4). Assuming that the photochemical O_2 demand roughly equals the decrease in DOC concentration (Amon and Benner 1996), ~1–3 $\mu\text{mol DOC L}^{-1} \text{ d}^{-1}$ are photochemically transformed to DIC in surface waters. This accounts for ~1–4% of the total DOC (assuming a mean surface water DOC concentration of ~80 μM , Table 4). A similar percentage has been found for the northern Adriatic Sea (1.6–5.0 $\mu\text{mol O}_2 \text{ L}^{-1} \text{ d}^{-1}$; ~100 $\mu\text{M DOC}$) (Obernosterer and Herndl 2000). It has been demonstrated that the photochemical O_2 demand is directly correlated with the DOC concentration (Lindell and Rai 1994; Amon and Benner 1996). In our study, DOC concentrations in surface waters were similar (~80 μM) at all stations (Table 5) and therefore cannot explain the difference in photochemical O_2 demand. Relating the photochemical O_2 demand to the UVB dose received results in similar values for Sta. II, IV, and V, whereas at Sta. III, the DOC-normalized photochemical O_2 demand is lower. At Sta. III, both $K_{d_{305 \text{ nm}}}$ and DOM fluorescence have been found to be significantly lower compared to similar values for the other stations, indicating differences in the optical properties of the DOM at this station compared with the other stations.

Shielding off UVB radiation decreased the photochemical O_2 demand by 0–30% at Sta. II–IV; however, the overall contribution of UVB to the photochemical O_2 demand was not significant. The effect of UVB on the photochemical O_2

demand was most pronounced at Sta. II and III, where the intensity of surface UVB radiation was higher, as indicated by higher surface 305-nm:340-nm wavelength ratios at Sta. II and III (~0.12) compared to similar values for Sta. IV and V (~0.08). Previous studies have shown that the UVB, UVA, and PAR ranges are roughly equally in terms of their contribution to the photooxidation (measured as photochemical production of inorganic carbon and photochemical O_2 demand) of humic-rich DOM (Graneli et al. 1996; Reitner et al. 1997). Surface water bacterial respiration was lower than the photochemical O_2 demand at all stations, amounting to about 12–76% of the photochemical O_2 demand. In contrast to that, in the northern Adriatic Sea, bacterial O_2 demand was about equal to the photochemical O_2 demand of surface waters, and in the coastal North Sea, bacterial O_2 demand was, on average, about threefold higher compared to the rates of photochemical O_2 demand of surface waters (Obernosterer and Herndl 2000).

Our results demonstrate that H_2O_2 is a sensitive tracer for photochemically driven processes, as indicated by the similar diurnal dynamics of H_2O_2 and DOM fluorescence. As indicated in this study, the development of a diurnal thermocline is important in structuring the uppermost water column, ultimately leading to the exposure of DOM to high irradiation intensities over almost an entire daylight period. Similar diurnal dynamics (as shown here for H_2O_2) can also be assumed for other photoproducts, and a number of these photoproducts are potentially available to bacterioplankton. Bacterioplankton activity has been shown to recover quickly from UV stress (Kaiser and Herndl 1997; Arrieta et al. 2000). If we assume that the response of the bacterioplankton activity to newly formed photoproducts is as fast as indicated in our model, the diurnally stratified water layer can be considered to be highly dynamic with respect to photochemical and biological processes.

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