

H₂O₂ accumulation from photochemical production and atmospheric wet deposition in Antarctic coastal and off-shore waters of Potter Cove, King George Island, South Shetland Islands

DORIS ABELE¹*, GUSTAVO A. FERREYRA² and IRENE SCHLOSS²

¹Alfred-Wegener Institut für Polar- und Meeresforschung, Columbusstrasse, D-27568 Bremerhaven, Germany, and Universität Bremen, FB2, Leobener Str/NW2, D-28359 Bremen, Germany

²Instituto Antartico Argentino, Depto Biología, Cerrito 1248, 1010 Buenos Aires, Argentina

*abele@awi-bremerhaven.de

Abstract: Temporal and spatial variations of the hydrogen peroxide accumulation were measured in off-shore waters and in intertidal rockpools near Jubany Station, King George Island, South Shetland Islands. As H₂O₂ photoformation is mainly driven by the short wavelength radiation in the UV-B and the UV-A range of the solar spectrum, the study was conducted between the beginning of October and the end of December 1995, the period of Antarctic spring ozone depletion. Wet deposition of H₂O₂ containing snow was identified as a major source of hydrogen peroxide in the surface waters of Potter Cove. As the concentrations of dissolved organic carbon (DOC) in Potter Cove surface waters were low ($121 \pm 59 \mu\text{mol C l}^{-1}$), when compared to the highly eutrophicated waters on the German Wadden coast ($6000\text{--}7000 \mu\text{mol C l}^{-1}$), direct UV-induced DOC photo-oxidation was of only limited significance in the Antarctic sampling site. Nonetheless, under experimental conditions, H₂O₂ photoformation in Potter Cove surface waters amounted to $90 \pm 40 \text{ nmol H}_2\text{O}_2 \text{ h}^{-1} \text{ l}^{-1}$ under a UV-transparent quartz plate. When high energy UV-B photons were cut-off by a WG320 filter formation continued at a rate of $66 \pm 29 \text{ nmol H}_2\text{O}_2 \text{ h}^{-1} \text{ l}^{-1}$ due to UV-A and visible light photons. Samples from freshly deposited snow contained between 10 000 and 13 600 nmol H₂O₂ l⁻¹, and a snowfall event in mid November resulted in a maximum concentration of 1450 nmol H₂O₂ l⁻¹ in the upper 10 cm layer of Potter Cove surface waters. Maximal H₂O₂ concentrations in intertidal rockpools were even higher and reached up to 2000 nmol H₂O₂ l⁻¹ after the snowfall event. During a grid survey on December 17 1995, H₂O₂ concentrations and salinity displayed a north to south gradient, with higher concentrations and PSU at the south coast of the cove. The reasons for this spatial inhomogeneity are as yet unknown, but may relate to a minor local input of photo-reactive organic matter from creeks entering the cove in the south-east, as well as to waste water discharge from the station, located on the south beach.

Received 11 June 1998, accepted 21 December 1998

Key words: atmospheric deposition, coastal environment, dissolved organic matter, hydrogen peroxide, King George Island

Introduction

Formation of hydrogen peroxide (H₂O₂) in temperate surface waters is primarily driven by UV-induced photochemical activation of dissolved organic carbon (DOC, Cooper & Zika 1983, Moffet & Zafiriou 1990, Karl *et al.* 1993), and daily changing accumulation patterns with maximum values around noon are observed in field studies (Herrmann 1996, Scully *et al.* 1996, Abele-Oeschger *et al.* 1997b). The net accumulation of H₂O₂ is largely determined by the rate of DOC photo-oxidation and biologically-mediated H₂O₂ breakdown (catalase, peroxidase) in water and surface sediments (Cooper & Zepp 1990, Cooper *et al.* 1994, Abele-Oeschger *et al.* 1997b). This rather simplistic view is challenged by the fact that atmospheric wet deposition of rainout and snow may carry high loads of H₂O₂, reaching micromolar

concentrations (Cooper *et al.* 1987, Gunz & Hoffmann 1990, Fujiwara *et al.* 1993, Kamiyama *et al.* 1996). However the actual contribution from these sources to surface water H₂O₂ concentrations is not easily quantified.

Hydrogen peroxide is a cytotoxic reactive oxygen species (ROS), which can elicit oxidative stress in marine organisms (Viarengo *et al.* 1998). As an uncharged molecule, H₂O₂ is of relative stability in seawater (Petasne & Zika 1997) and has the capacity of permeating cell membranes (Halliwell & Gutteridge 1985), thus entering living cells from outside. ROS induced damage is referred to as "indirect effect" of ionizing radiation in aqueous media and distinguished from the "direct effect" of radiation, where molecules are damaged directly by the absorbed light photons (Stark 1991). H₂O₂ elicits oxidative damage of membrane lipids (Thomas & Reed

1990, Stark 1991), proteins (Neuzil *et al.* 1993) and nucleic acids (Schulte-Frohlinde & Sonntag 1985) via liberation of highly reactive hydroxyl radicals inside the cells. Thereby it can interfere with membrane transport (Jones 1985, Hitschke *et al.* 1994, Mense *et al.* 1997) and generally disturb cellular homeostasis (Boraso & Williams 1994, Abele-Oeschger *et al.* 1997a, Abele *et al.* 1998).

The area of Potter Cove investigated receives considerable freshwater run-off during spring from the melting glaciers (Klöser *et al.* 1994), carrying an unknown load of DOC. Since the time of ice melting coincides with the Antarctic ozone minimum, increased UV-B radiation may enhance photo-oxidation of UV-absorbing DOC (Backlund 1992, Amon & Benner 1996, Miller & Moran 1997), increasing the bioavailability of the bulk of dissolved organic matter (DOC) and thereby fuelling microbial activities in surface waters (Moran & Zepp 1997). Concurrently, this could result in increased H_2O_2 concentrations in surface waters.

The objective of the present study was to describe the dynamics of H_2O_2 in surface waters of a permanently cold coastal ecosystem in Antarctica. The aim was to identify the primary sources for H_2O_2 , and ascertain if nearshore DOC water concentrations could sustain significant H_2O_2 -photoproduction during the ozone hole and ice melting period. The potential for other sources like atmospheric deposition or planktonic production (Palenik *et al.* 1987) to contribute significantly to bulk H_2O_2 accumulation was also considered.

Material and methods

Area of investigation

The investigation was carried out in Potter Cove, King George Island, South Shetlands (62°14'S, 58°40'W) during an Argentine-German spring expedition. Potter Cove is a small inlet opening into Maxwell Bay, one of the two large fjords of King George Island. The inner cove has a surface area of 3 km² and a maximum depth of 50 m. To the north-east the cove is bordered by a glacier, rising to 50 m height above sea level in a steep slope. Submerged glacier fronts and icefalls result in a patchy and intermittent release of fresh water and ice floes to the north side of the cove (Klöser *et al.* 1994). The southern coast is lined by a beach of coarse sand and gravel. This is also the location of the Argentine research station Jubany, where this study was carried out.

Sampling and experimental set-up

At the end of October 1995, a permanent sampling station (35 m water depth) was positioned in the cove about 200 m offshore by hacking a hole into the 1 m thick ice. The hole was thereafter kept open and marked with a buoy, to allow a return to this position after the ice retreat. Between 27 October and 15 December 1995, water temperature and salinity profiles were recorded daily at this station, using a CTD type ME

Ecosonde. After the sea ice melted, sampling was continued from an inflatable boat. Nineteen samplings of H_2O_2 were carried out between 1 November and 7 December 1995. All samplings were conducted with a Niskin sampler around noon and collecting 25 ml from 0, 5, 10, 20 and 30 m depth. Parallel samples for DOC analysis were collected in the surface layer only. Two additional high resolution profiles of H_2O_2 concentrations within the upper 1 m layer at 10 cm intervals were recorded on 10 November and 19 November 1995, using a specially designed syringe sampler (10 x 20 ml), which allowed simultaneous collection of the whole profile.

On 17 December 1995, a two-dimensional grid was sampled on three transects between the north side (glacier) and the south side (beach) of the inner cove. Each transect comprised four stations in N-S direction. At each station readings of temperature and salinity were done at 0 m and 5 m water depth and water samples were collected for subsequent analysis of the H_2O_2 concentrations at both water depths. At this time Potter Cove was ice-free and snowfall had not occurred.

Samples of about 500 ml of ice were collected from ice floes in Potter Cove. Each of these samples was melted at room temperature in the dark and analysed immediately after melting.

Water samples were obtained from a rocky shore about 1 km from the station by sampling individual rockpools during low tides. Parallel measurements of temperature and oxygen saturation were done with a WTW oxymeter. Water samples from the same rockpools were frozen to -20°C for analysis of DOC in Bremerhaven. These samplings were carried out at irregular intervals between 27 October and 20 December.

An incubation experiment was conducted on a sunny day with intermittent cloud cover (15 November) to study the effect of different UV-ranges and of PAR (photosynthetic active radiation) on photochemical hydrogen peroxide formation under *in situ* conditions. For these experiments three samples of 500 ml unamended seawater were exposed to natural radiation in glass jars (Ø: 15 cm) topped with 3 mm thick cut-off filters from Schott, Germany GG420 (only PAR), WG320 (PAR and UV-A) and a quartz plate which permits penetration of PAR, UV-A and UV-B. The incubated water volumes were bubbled with air and were thermostated with ice, so that the temperature remained below 7°C. The experiment started in the morning at 09h30 and 10 ml samples from each jar were taken at 30 min intervals to allow for triplicate determination of the H_2O_2 concentrations. Samples for DOC analysis were collected at the end of the experiments and stored frozen at -20°C. In parallel, H_2O_2 decomposition was measured in two 500 ml samples of the same water in the dark at 1.4°C.

Analyses

H_2O_2 analyses were carried out within 40 min of sampling in the Dallmann Laboratory at Jubany, using a Kontron SFM-25 fluorimeter which was connected to a y/t-chart recorder, and equipped with a 1 cm quartz cuvette. The assay was carried

out with scopoletin as fluorescence indicator in a peroxidase catalysed reaction according to Pamatmat (1990) as described in Abele-Oeschger *et al.* (1997b). Samples were centrifuged for 4 min at 6000 x g prior to analysis. The limit of detection is below 50 nmol l⁻¹ H₂O₂.

Water samples for DOC measurements were filtered through Whatman GF/F filters into sterilised 20 ml glass ampoules and stored at -20°C during shipment to Bremerhaven. DOC analysis was carried out with high temperature catalytic oxidation (HTCO) in a Shimadzu TOC 5000 Analyser with a platinumized-alumina catalyst.

Measurements of UV-B irradiation

Atmospheric UV-B radiation was measured at 305 ± 7 nm with a UV sensor which was equipped with a cosine diffuser for atmospheric measurements. The system was supplied by W. Wulfgen of the Deutsche Aerospace, Bremen, Germany and the sensor was calibrated with a 1000 Watt quartz-halogen lamp.

Statistics: We used parametric product-moment regression and non-parametric Spearman Rank analysis to test for correlation of parameters over the whole sampling period.

Results

Water column measurements

During fresh water run-off from the glaciers the surface water layer of Potter Cove (PC) displays lower salinity and consequently lower density with a pycnocline at about 5 m water depth (Klöser *et al.* 1994, Schloss *et al.* 1997). This stratification prevents rapid mixing of surface waters and thereby reduces vertical diffusion of H₂O₂ and instead enhances its accumulation above the pycnocline. Integrated over the entire investigation, the vertical profile of H₂O₂ concentrations was, therefore, inversely correlated with water column density. Figure 1 depicts higher mean concentrations of 247 ± 64 nmol l⁻¹ for the total of samplings in surface waters (0 m), while in a depth of 5 m the mean H₂O₂ concentration was only 141 ± 24 nmol l⁻¹ (n = 19).

Mean DOC concentrations of 121 ± 59 µmol C per l⁻¹, equalling 1.4 mg C l⁻¹, in the upper 5 m water column of PC are in the range expected for Antarctic waters. Thus, at King George Island, glacier run-off does not carry especially high DOC loads into the cove. Still, on days with slightly elevated DOC levels in the surface, peroxide concentrations, which normally ranged around 100 nmol l⁻¹, were also slightly higher (e.g. 09 November: DOC 293 µmol l⁻¹, H₂O₂ 300 nmol l⁻¹; 21 November: DOC 197 µmol l⁻¹, H₂O₂ 450 nmol l⁻¹). There was, however, no clear correlation between DOC and H₂O₂ over the entire time of our measurements, perhaps due to the small number of DOC data collected. Likewise, no correlation existed between hydrogen peroxide concentrations in 0 m and

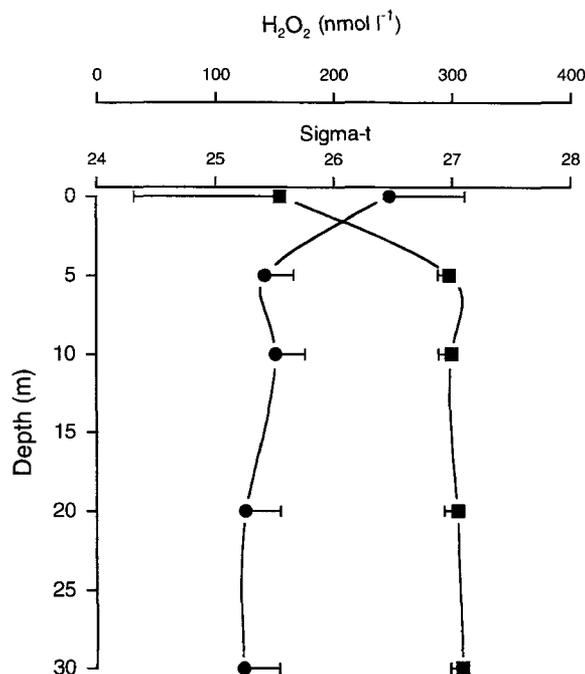


Fig. 1. Vertical density (■) and hydrogen peroxide (●) profile in the water column of Potter Cove. Data represent means of daily measurements between 1 November and 13 December 1995.

daily UV-B surface radiation (Fig. 2, correlation coefficient $r = -0.40$, $P > 0.05$). Although there was considerable UV-B radiation of 4–8 W m⁻² day⁻¹, comparable to a May situation in Germany, the amount of photodegradable DOC in Potter Cove was obviously too low to allow for significant photochemical H₂O₂ production in open waters, where surface

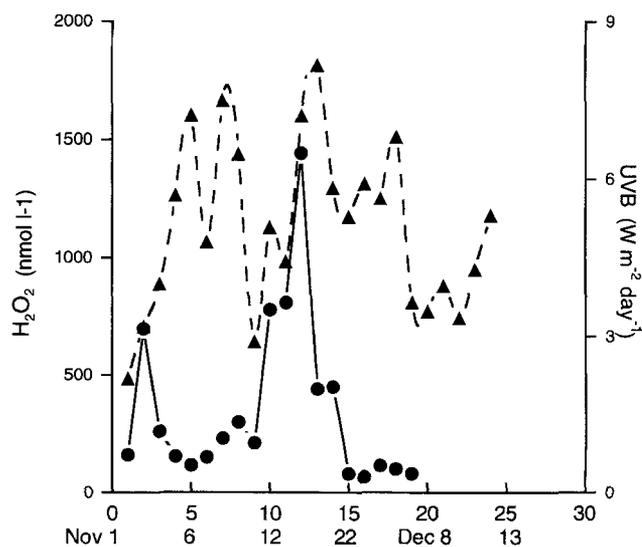


Fig. 2. Hydrogen peroxide surface concentrations in Potter Cove (nmol l⁻¹, ●) between 1 November and 13 December 1995 in relation to integrated daily UV-B surface irradiation (between 295 and 320 nm ▲).

concentrations are moreover rapidly reduced by mixing.

By contrast, the time series of H_2O_2 and salinity in surface waters displayed a significant inverse correlation (Fig. 3; $r = -0.94$, $P < 0.01$). In mid November, melting of the ice in the inner cove and a heavy snowfall amounting to 14 mm wet deposition between 19 November and 23 November caused a clear drop of surface salinity from 33 to below 20 PSU. Concurrently, H_2O_2 concentrations increased from around 200 to a maximum of 1450 nmol l^{-1} in the upper 10 cm layer of surface waters (Fig. 3). H_2O_2 concentrations measured in freshly fallen snow amounted to between 10 000 and 13 600 nmol l^{-1} ($n = 5$).

High resolution measurements of H_2O_2 in the upper 1 m surface layer before and during the snowfall event supported our finding that atmospheric wet deposition was responsible for the observed H_2O_2 maximum around 19 November (Fig. 4). Whereas the measurement from 10 November depicts a homogenous vertical distribution of peroxide with values around 100 nmol l^{-1} , on 19 November H_2O_2 concentrations in the upper 30 cm layer were significantly higher, maximal concentrations in the surface reaching as high as 800 nmol l^{-1} . Moreover, the latter profile documents downward mixing of H_2O_2 from the surface into the water column.

H_2O_2 concentrations in ice samples

Samples from brown ice, colonised with dense populations of diatoms of the species *Nitzschia cylindrus*, *N. curta* and *N. kerguelensis* had a concentration of $570 \pm 50 \text{ nmol l}^{-1} H_2O_2$ ($n = 6$), whereas white ice without diatoms had slightly higher values of $970 \pm 130 \text{ nmol l}^{-1} H_2O_2$ ($n = 6$). It seems that

colonization by ice algae leads to a decrease rather than to an enrichment of H_2O_2 in seawater.

Grid-survey of salinity and H_2O_2 concentrations in Potter Cove surface waters

Figure 5 depicts the topography of Potter Cove with N-S sampling transects (a), as well as salinity readings (b) and H_2O_2 concentrations (c) in surface waters (0 m) along these transects on 17 December 1995. Both parameters were less variable in surface waters (0 m) on the southern beach of Potter Cove and displayed greater inhomogeneity on the glacier front. Due to freshwater run-off from the glacier, mean salinity was lower along the northern coast line and increased on the transects towards the southern side. Only station 1 of transect 1 had a higher salinity, reflecting saltwater inflow from Maxwell Bay.

A clear trend of higher mean H_2O_2 concentrations was observed towards the beach side (south) of Potter Cove, while, on all transects, lower H_2O_2 concentrations were recorded along the glacier front (Fig. 5, $r^2 = 0.997$). H_2O_2 concentrations followed no obvious trend in 5 m water depth beneath the surface mixing layer (data not shown).

H_2O_2 concentrations in intertidal pools

Mean temperature and percentage oxygen saturation in intertidal rockpools followed no clear trend throughout the two months measuring period (data not shown). Temperature varied between 0° and 8°C depending on the warming effect of sunshine. Oxygen saturation ranged between 80 and 140%

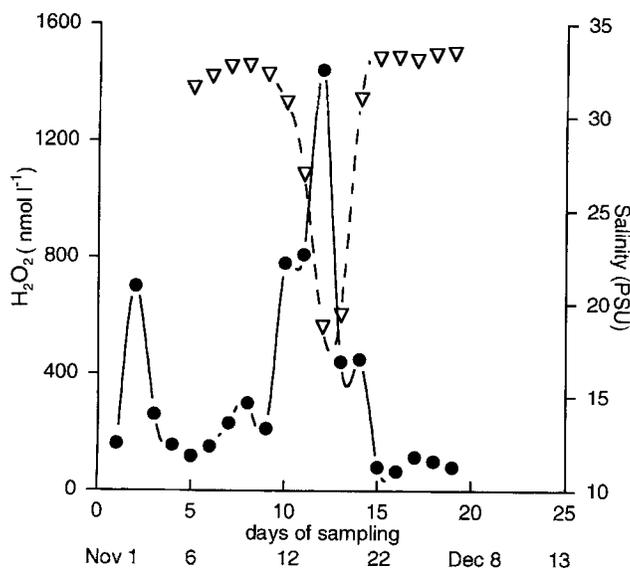


Fig. 3. Hydrogen peroxide surface concentrations in Potter Cove (nmol l^{-1} , ●) between 1 November and 13 December 1995 in relation to changes of salinity (▽) in surface waters during a snowfall event in mid November.

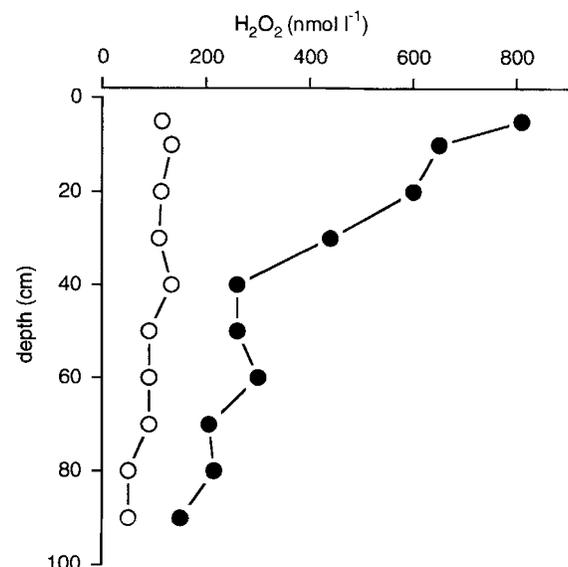


Fig. 4. Vertical distribution of the H_2O_2 concentration in the upper 1 m surface water of Potter Cove before (○ 10 November) and during (● 19 November) the snowfall event.

and was generally higher in pools colonized by macroalgae. Between 27 October and 6 November a mean H_2O_2 concentration of $220 \pm 40 \text{ nmol l}^{-1}$ was recorded ($n = 9$). As observed for off-shore surface waters, elevated concentrations of hydrogen peroxide were measured following the heavy snowfall in mid November. On 20 November, maximal H_2O_2 concentrations in two pools ranged around 2000 nmol l^{-1} with off-shore surface concentrations as high as 1450 nmol l^{-1} .

Photochemical H_2O_2 production under cut-off filters

Starting at a concentration of 130 nmol l^{-1} , mean H_2O_2 net production was considerably higher under WG320 ($66 \pm 29 \text{ nmol l}^{-1} \text{ h}^{-1}$) and under the quartz plate ($90 \pm 40 \text{ nmol l}^{-1} \text{ h}^{-1}$) compared to GG420 ($20 \pm 15 \text{ nmol l}^{-1} \text{ h}^{-1}$). Under the quartz plate as well as under WG320 maximal H_2O_2 concentrations were reached within four hours (at 13h10), culminating in a steady state. H_2O_2 production under all filters was best modelled by a second order polynomial function. The best fit was obtained for the quartz-topped sample ($y = -2.3968x^2 + 53786x + 130$, $r^2 = 0.8457$) and yielded end concentrations around 480 nmol l^{-1} . Correlation with the second order fit under WG320 was less good ($r^2 = 0.7089$), while there was next to no increase observable under GG420 ($r^2 = 0.2261$) which permits only PAR light to pass. Hydrogen peroxide concentrations under WG320 correlated with UV surface radiation (Fig. 6) (Spearman-Rank analysis, $r = 0.53$, $P = 0.05$, $n = 14$), but no correlation was found for the quartz sample ($r = 0.32$, $P = 0.252$, $n = 14$).

Dark decomposition of hydrogen peroxide was not observed. In natural seawater ($130 \text{ nmol l}^{-1} \text{ H}_2\text{O}_2$) no changes were observed during three hours. In seawater spiked with H_2O_2 ($1360 \text{ nmol l}^{-1} \text{ H}_2\text{O}_2$), concentrations diminished at an extremely slow rate of $10 \text{ nmol l}^{-1} \text{ h}^{-1}$.

Hydrogen peroxide production rates ($\text{nmol l}^{-1} \text{ h}^{-1}$) were far higher under the quartz plate than under WG320 in the beginning of the experiment (Fig. 7) and decreased linearly with time ($r^2 = 0.93$). By contrast, hourly UV-B surface radiation (305 nm) increased throughout the day. Peaks in UV-B surface radiation reflect cloudless periods around noon and in the afternoon. DOC concentrations in the incubation water varied between 135 and $166 \mu\text{mol C l}^{-1}$ at the end of the experiment.

Discussion

H_2O_2 photoproduction via UV-excitation of DOC appears to be of minor significance in the Potter Cove ecosystem, even during the spring ozone minimum. This can be concluded from the generally low H_2O_2 concentrations in off-shore and intertidal waters, in combination with low DOC concentrations in water and the lack of correlation between H_2O_2 surface concentrations and daily integrated surface radiation throughout the time series of our measurements. Surface H_2O_2 concentrations between 100 and 200 nmol l^{-1} have previously

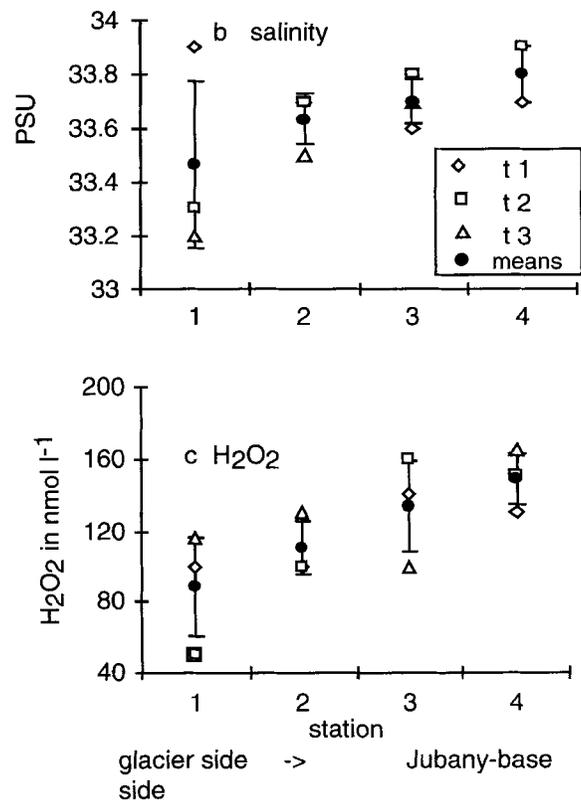
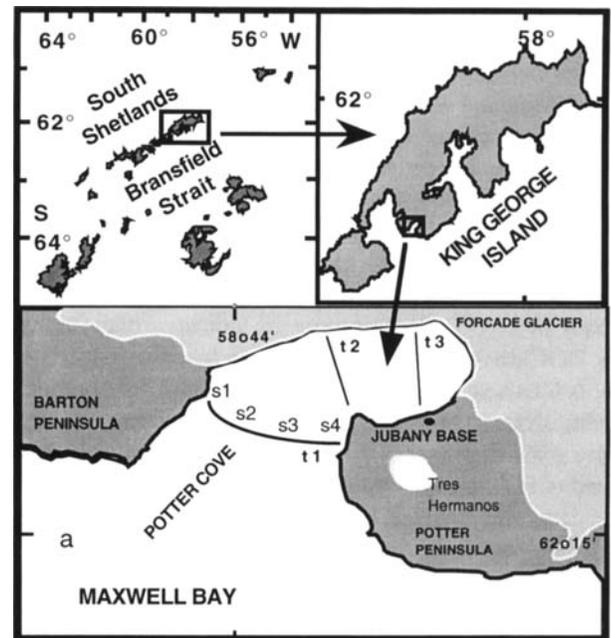


Fig. 5. Data from a grid-survey of Potter Cove surface waters (0 m) on 17 December 1995. Potter Cove topography and **a.** three N-S transects, **b.** salinity readings, and **c.** H_2O_2 concentrations.

been reported from the Atlantic ocean south of 60°S (Weller & Schrems 1993) and seem comparably low to ours for a coastal environment.

Experimental exposure of Potter Cove surface waters to different ranges of the solar spectrum supports this view. Although the intensity of surface irradiance also increased during the early afternoon, steady state H_2O_2 concentrations were reached between 13h00 and 14h00 under the quartz plate and under the WG320 cut-off filter. As no biological decomposition was found under dark conditions, it seems that steady state H_2O_2 concentrations are indicative of the potential for DOC driven peroxide production being exhausted after about four hours exposure. Obviously, the concentrations of photoreactive chromophores in the water sample (500 ml) were exhausted (see Zika 1990). The linearly decreasing trend of H_2O_2 production rates under the quartz plate (Fig. 7) indicates that maximal DOC driven peroxide formation was independent of the variability of incident radiation in this particular sample. This means that throughout the entire duration of the experiment, photon energy per surface unit under the quartz plate exceeded the maximum yield of DOC driven H_2O_2 photoproduction. This was different under WG320, which keeps out photons in the UV-B range. (To be exact, the turning point of the cut-off characteristic of WG320 is at 320 nm, which means that at this wavelength 50% of all arriving photons are absorbed and that this proportion increases rapidly towards shorter wavelengths). Although they constitute only 1% of the total solar spectrum, depending on their wavelength, UV-B photons exhibit 1000 to 10 000-fold greater efficiency for H_2O_2 photoproduction, compared to a PAR photon at 550 nm (Abele-Oeschger *et al.* 1997b). Obviously, if these high-energy photons are removed, H_2O_2 formation proceeds at considerably lower rates and will not as quickly exhaust the DOC pool in a given water sample. This explains why the time course of the H_2O_2 concentrations

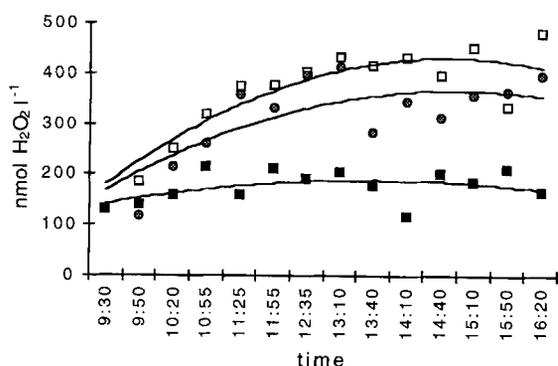


Fig. 6. Hydrogen peroxide concentrations (nmol l^{-1}) in water from Potter Cove, exposed to natural radiation under experimental conditions (15 November 1995). Three samples of 500 ml unamended seawater were exposed in glass jars (\varnothing : 15 cm) topped with 3 mm thick cut-off filters from Schott, Germany GG420 (■, only PAR); WG320 (●, PAR and UV-A) and a quartz plate (□, PAR, UV-A and UV-B).

correlates with incident radiation under WG320. The experiment clearly underlines the key role of UVR in DOC photooxidation during the ozone deficiency of the Antarctic spring season, as practically no H_2O_2 production occurred under GG420.

Nearshore areas in Antarctica can be highly productive (Clarke *et al.* 1988). In Potter Cove, local winds and water currents prevented an accumulation of phytoplankton biomass in spring during previous campaigns, while later on during the austral summer discharge of suspended particles from the melting glaciers and creeks restricted light penetration and thereby further inhibited phytoplankton growth (Schloss *et al.* 1997). This situation was not exceptional and phytoplankton production was also found to be low during the spring campaign 1995, when maximal chl *a* values were below $1 \mu\text{g l}^{-1}$ (Schloss 1997). Apparently, melt water discharge from the glaciers does not provide a significant source of allochthonous DOC. The ecological implications for the ecosystem in Potter Cove are that DOC photodegradation, which in other areas enhances DOC bioavailability and thereby fuels microbial biomass (Moran & Zepp 1997), could be another factor limiting water column heterotrophic and autotrophic production required. Further investigations of the microbial loop in the water column of Potter Cove are indicated, to elucidate, how a pelagic system of relatively low productivity can sustain a massive benthic production at the sea floor of the cove. First results indicate benthic diatoms to be a major food supply for many invertebrate filterfeeders (Klöser & Arntz 1994).

DOC concentrations of between $150\text{--}400 \mu\text{mol C l}^{-1}$ in King George Island rockpools are also insufficient to sustain significant photochemical H_2O_2 formation in intertidal environments. These concentrations are lower by far, than in pools on temperate zone intertidal mudflats, in which extremely high DOC concentrations between 6000 and $7000 \mu\text{mol C l}^{-1}$ have been measured (Abele-Oeschger *et al.* 1997b). Consequently, at a comparable surface irradiance (8 Watt $\text{m}^{-2} \text{ nm}^{-1}$ at 305 nm in Germany and 6 Watt $\text{m}^{-2} \text{ nm}^{-1}$ at 305 nm in Jubany), photochemical H_2O_2 formation on intertidal

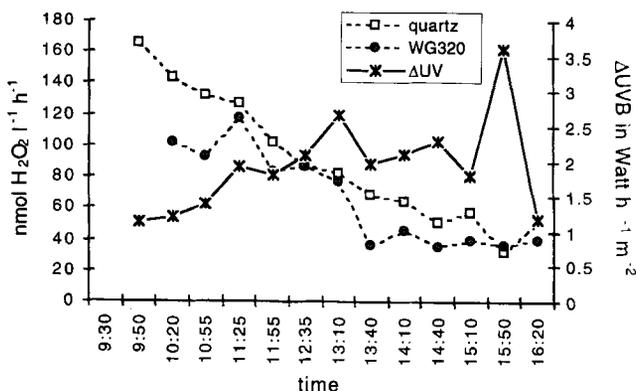


Fig. 7. Daily integrated UV radiation at 305 nm ($\text{W h}^{-1} \text{ m}^{-2}$) vs hydrogen peroxide production under WG320 and under the quartz plate. Data from 15 November 1995.

mudflats near Bremerhaven yielded a gross production of more than 300 nmol l⁻¹ h⁻¹ (Abele-Oeschger *et al.* 1997b), whereas at King George Island gross production in the morning amounted to only 110 nmol l⁻¹ h⁻¹, i.e. one third of the Bremerhaven values.

Elevated hydrogen peroxide accumulation of between 1000 and 2000 nmol l⁻¹ H₂O₂ in intertidal and off-shore surface waters of Potter Cove primarily relate to deposition of snow on the sea surface. Moreover, melting of peroxide containing ice floes may contribute to enrichment of off-shore waters with H₂O₂. Both ice melting and the snowfall reduce surface salinity and thereby contribute to the stratification in off-shore waters of Potter Cove (Schloss *et al.* 1997). Atmospheric hydrogen peroxide is concentrated in water vapour and snow (Kamiyama *et al.* 1996). Therefore, H₂O₂ concentrations in Antarctic snow deposits reflect the intensity of atmospheric UV-radiation, yielding higher concentrations in summer, especially during the ozone minimum period, while concentrations decrease during the Antarctic winter.

It has generally been found that atmospheric wet deposition can contain micromolar amounts of H₂O₂ (Cooper *et al.* 1987, Cooper & Lean 1989), especially in polar regions, where snow deposits accumulate on the ice plateaus without the chance of vertical mixing. Sigg & Neftel (1991) measured highest concentrations of 13 000 nmol l⁻¹ in Greenland ice-cores. Slightly lower concentrations of between 53 and 5020 nmol l⁻¹ were measured in snow samples from the surface of the Weddell Sea sea ice (Eicken *et al.* 1994). In spite of a rapid H₂O₂ decomposition in surface snow after deposition (Jacob & Klockow 1993), several authors could clearly distinguish strong seasonal cycles of H₂O₂ deposition in ice core profiles, which are, however, smoothed out during firnification (Sigg & Neftel 1988). These authors also propose to use H₂O₂ as a marker for ice core dating. A seasonal study of H₂O₂ concentrations in snow deposits at Queen Maud Land (Antarctica) is documented by Kamiyama *et al.* (1996), who found concentrations ranging between 6700 and 12 000 nmol l⁻¹ in October 1991, while during July/August 1992 maximal concentrations were 1700 nmol l⁻¹. Thus, the concentrations between 10 000 and 13 600 nmol l⁻¹ found in Potter Cove snow samples appear in the range of what can be expected during the ozone minimum of the Antarctic spring. The corresponding increase of surface water concentrations is indicative of the considerable importance of H₂O₂ atmosphere-to-ocean flux in Antarctic coastal ecosystems.

Another detailed study of hydrogen peroxide dynamics has been carried out by Karl *et al.* (1993) during the long-term Palmer ecological research study (LTER 1992-93). In this investigation, comparable salinity/H₂O₂ depth profiles have been recorded in off-shore waters, although maximum H₂O₂ concentrations were only around 20 nmol l⁻¹ (Resing *et al.* 1993) in the LTER region of Bransfield Strait during November 1992. According to these authors, steady-state H₂O₂ concentrations in surface waters in the Palmer LTER-region are controlled by other processes than DOC photo-oxidation.

Tien & Karl (1993) also published data on H₂O₂ concentrations in snow samples collected in the LTER region in March 1993. They came up with relatively low values between 55 and 600 nmol H₂O₂ l⁻¹ of melted snow and concluded that atmospheric wet deposition was only a weak source of H₂O₂ in surface waters around Palmer Station. Additionally, thawed samples from ice floes yielded no more than 5 nmol l⁻¹ H₂O₂, but these samples were thawed for between 10 and 15 hours, so that H₂O₂ decomposition during thawing time may have been significant. By contrast, our October/November 1995 data set from King George Island indicates that atmospheric wet deposition is indeed an important source for H₂O₂ in intertidal and off-shore surface waters in Potter Cove, during the period of the Antarctic ozone depletion.

Inverse H₂O₂/salinity depth profiles have been reported from the Palmer LTER-study, as well as from the Mexican Gulf (Zika *et al.* 1985) and the Mediterranean Sea (Johnson *et al.* 1989). These latter authors propose H₂O₂ to be a useful marker for vertical mixing. This also applies to the highly stratified waters of Potter Cove during the time of glacial melting (Fig. 1). Small scale recordings of diminishing H₂O₂ surface concentrations throughout the upper 1m surface layer (Fig. 4) show that this may even apply for high resolution studies of the stratification in the air-water boundary layer, especially when H₂O₂ surface deposition is high.

Likewise, horizontal zonations of H₂O₂ concentrations, like the north to south gradient we found in the grid survey of H₂O₂ surface concentrations, may reflect different water bodies or water qualities with respect to DOC concentrations. As melt water does obviously provide only a minor source of allochthonous DOC, it might well have been an input from two small creeks and presumably also the waste waters from Jubany, which could have led to a minor local enrichment of dissolved organic matter along the southern shore of Potter Cove. As waste waters are now being cleaned by a newly installed sewage plant, H₂O₂ concentrations could provide a useful indicator for any changes this may have initiated in the Potter Cove ecosystem.

Conclusions

Although, during the Antarctic spring UV radiation over the Antarctic Peninsula can reach intensities comparable to a spring situation on the North German coast, H₂O₂ photoproduction in intertidal and off-shore waters of the Potter Cove ecosystem yields far lower levels. This relates to the lower concentrations of DOC in off-shore as well as in tidal pool waters which amount to only between 2 and 5% of the DOC loads measured in intertidal pools on mudflats off the north German Wadden Sea coast. Elevated H₂O₂ concentrations in offshore and intertidal surface waters of Potter Cove result from snow deposition, which can carry micromolar H₂O₂ concentrations during the Antarctic spring, when stratospheric UV radiation is high. At only slightly higher concentrations H₂O₂ affects marine organisms. We

have shown that this reactive oxygen species induces oxidative damage and reduces the metabolic rates of the Antarctic intertidal limpet *Nacella concinna* at concentrations of $4 \mu\text{mol l}^{-1}$ (Abele *et al.* 1998), which is only twice the maximum concentrations measured in tidal pools of Potter Cove. The problem may become crucial if the progressive destruction of the ozone layer continues. This will then result in a further increase of UV-B surface irradiance (Frederick & Snell 1988) and consequently lead to increasing atmospheric wet deposition of hydrogen peroxide in Antarctic environments. Moreover, given that photochemical H_2O_2 formation in surface waters is limited by the relatively low DOC water concentrations, changes may be expected in the vicinity of Antarctic stations with uncontrolled wastewater outflows. The significance of DOC photo-oxidation under elevated UV-irradiation for the heterotrophic production in DOC limited Antarctic coastal areas warrants further investigation.

Acknowledgements

The authors would like to thank the staff of Jubany Station and especially the diver Augusto Fernandez for technical support during the field campaign. Thanks go to Dipl. Ing. Wolfgang Wulfgen, Deutsche Aerospace, Bremen (Germany), for providing a very suitable UV-radiometer to measure the UV-B surface radiation in Jubany. We are indebted to Dr Jörg Lobbes (AWI) for support with the HTOCO analysis of DOC. We thank Professor R. Herrmann and an anonymous referee for their comments. This work was supported by the Alfred-Wegener Institute at Bremerhaven and the Argentinean Antarctic Institute at Buenos Aires and forms part of the research project ARG-AD-P 38 (DLR). This is Alfred-Wegener-Institute publication no 1536.

References

- ABELE-OESCHGER, D., SARTORIS, F.J. & PORTNER, H.O. 1997a. Effect of elevated hydrogen peroxide levels on aerobic metabolic rate, lactate formation, ATP homeostasis and intracellular pH in the sand shrimp *Crangon crangon*. *Comparative Biochemistry and Physiology*, **117C**, 123–129.
- ABELE-OESCHGER, D., TÜG, H. & RÖTTGERS, R. 1997b. Dynamics of UV-driven hydrogen peroxide formation on an intertidal sandflat. *Limnology and Oceanography*, **42**, 1406–1415.
- ABELE, D., BURLANDO, B., VIARENGO, A. & PÖRTNER, H.O. 1998. Exposure to elevated temperatures and hydrogen peroxide elicits oxidative stress and antioxidant response in the Antarctic intertidal limpet *Nacella concinna*. *Comparative Biochemistry and Physiology*, **120B**, 425–435.
- AMON, R.M.W. & BENNER, R. 1996. Photochemical and microbial consumption of dissolved organic carbon and dissolved oxygen in the Amazon River system. *Geochimica et Cosmochimica Acta*, **60**, 1783–1792.
- BACKLUND, P. 1992. Degradation of aquatic humic material by ultraviolet light. *Chemosphere*, **25**, 1869–1878.
- BORASO, A. & WILLIAMS, A. 1994. Modification of the gating of the cardiac sarcoplasmic reticulum Ca^{2+} -release channel by H_2O_2 and dithiothreitol. *American Physiological Society*, **H**, 1010–1016.
- CLARKE, A., HOLMES, L.J. & WHITE, M.G. 1988. The annual cycle of temperature chlorophyll and major nutrients at Signy Island, South Orkney Islands, 1969–82. *British Antarctic Survey Bulletin*, No. 80, 65–86.
- COOPER, W.J. & ZIKA, R.G. 1983. Photochemical formation of hydrogen peroxide in surface and ground waters exposed to sunlight. *Science*, **220**, 711–712.
- COOPER, W.J., SALTZMANN, E.S. & ZIKA, R.G. 1987. The contribution of rainwater to variability in surface ocean hydrogen peroxide. *Journal of Geophysical Research*, **29/C3**, 2970–2980.
- COOPER, W.J. & LEAN, D.R.S. 1989. Hydrogen peroxide concentration in a northern lake: photochemical formation and diurnal variability. *Environmental Science and Technology*, **23**, 1425–1428.
- COOPER, W.J. & ZEPP, R.G. 1990. Hydrogen peroxide decay in waters with suspended soils: evidence for biologically mediated processes. *Canadian Journal of Fishery and Aquatic Science*, **47**, 888–893.
- COOPER, W.J., SHAO, C., LEAN, D.R.S., GORDON, A.S. & SCULLY, F.E. 1994. Factors affecting the distribution of H_2O_2 in surface waters. In *Environmental chemistry of lakes and reservoirs. Series of the American Chemical Society*, **237**, 393–422.
- EIKEN H., LANGE M.A., HUBBERTEN, H.-W. & WADHAMS, P. 1994. Characteristics and distribution patterns of snow and meteoric ice in the Weddell Sea and their contribution to the mass balance of sea ice. *Annales Geophysicae*, **12**, 80–93.
- FREDERICK, J.E. & SNELL, H.E. 1988. Ultraviolet radiation levels during the Antarctic spring. *Science*, **241**, 438–440.
- FUJIWARA, K., USHIRODA, T., TAKEDA, K., KUMAMOTO, Y. & TSUBOTA, H. 1993. Diurnal and seasonal distribution of hydrogen peroxide in seawater of the Seto Inland Sea. *Geochemical Journal*, **27**, 103–115.
- GUNZ, W.J. & HOFFMANN, M.R. 1990. Atmospheric chemistry of peroxides: a review. *Atmospheric Environment*, **24**, 1601–1633.
- HALLIWELL, B. & GUTTERIDGE, J.M.C. 1985. *Free radicals in biology and medicine*. Oxford: Clarendon Press. 543 pp.
- HERRMANN, R. 1996. The daily changing pattern of hydrogen peroxide in New Zealand surface waters. *Environmental Toxicology and Chemistry*, **15**, 652–662.
- HITSCHKE, K., BÜHLER, R., APELL, H.-J. & STARK, G. 1994. Inactivation of the Na,K-ATPase by radiation-induced free radicals. Evidence for a radical-chain mechanism. *FEBS Letters*, **353**, 297–300.
- JACOB, P. & KLOCKOW, D. 1993. Measurements of hydrogen peroxide in Antarctic ambient air, snow and firn cores. *Fresenius Journal of Analytical Chemistry*, **346**, 429–434.
- JOHNSON, K.S., WILLASON, S.W., WIESENBERG, D.A., LOHRENZ, S.E. & ARNONE, R.A. 1989. Hydrogen peroxide in the western Mediterranean Sea: a tracer for vertical advection. *Deep-Sea Research*, **36**, 241–254.
- JONES, D.P. 1985. The role of oxygen concentration in oxidative stress: hypoxic and hyperoxic models. In SIES, H., ed. *Oxidative stress*. London: Academic Press & New York: Harcourt Brace Jovanovich, 152–195.
- KAMIYAMA, K., MOTOYAMA, H., FUJII, Y. & WATANABE, O. 1996. Distribution of hydrogen peroxide in surface snow over Antarctic ice sheet. *Atmospheric Environment*, **30**, 967–972.
- KARL, D.M., RESING, J., TIEN, G. & LETELIER, R. 1993. Palmer LTER: Hydrogen peroxide in the Palmer LTER region: I. An introduction. *Antarctic Journal of the United States*, **28**, 225–226.
- KLÖSER, H. & ARNTZ, W.E. 1994. RASCALS. Untersuchungen zur Struktur und Dynamik eines antarktischen Küstenökosystems. *Polarforschung*, **64**, 27–41.
- KLÖSER, H., FERREYRA, G., SCHLOSS, I., MERCURI, G., LATURNUS, F. & CURTOSI, A. 1994. Hydrography of Potter Cove, a small fjord-like inlet on King George Island (South Shetlands). *Estuarine and Coastal Shelf Sciences*, **38**, 523–537.
- MENSE, M., STARK, G. & APELL, H.-J. 1997. Effects of free radicals on partial reactions of the Na, K-ATPase. *Journal of Membrane Biology*, **156**, 63–71.

- MOFFETT, J.W. & ZAFIRIOU, O.C. 1990. An investigation of hydrogen peroxide chemistry in surface waters of Vineyard Sound with $H_2^{18}O_2$ and $^{18}O_2$. *Limnology and Oceanography*, **35**, 1221–1229.
- MILLER, W.L. & MORAN, M.A. 1997. Interaction of photochemical and microbial processes in the degradation of refractory dissolved organic matter from a coastal marine environment. *Limnology and Oceanography*, **42**, 1317–1324.
- MORAN, M.A. & ZEPP, R.G. 1997. Role of photoreactions in the formation of biologically labile compounds from dissolved organic matter. *Limnology and Oceanography*, **42**, 1307–1316.
- NEUZIL, J., GEBICKI, J.M. & STOCKER, R. 1993. Radical-induced chain oxidation of proteins and its inhibition by chain-breaking antioxidants. *Biochemical Journal*, **293**, 601–606.
- PALENIK, B., ZAFIRIOU, O.C. & MOREL, F.M.M. 1987. Hydrogen peroxide production by a marine phytoplankter. *Limnology and Oceanography*, **32**, 1365–1369.
- PAMATMAT, M.M. 1990. Catalase activity: a variable affecting H_2O_2 distribution in Kiel Bight. *Meeresforschung*, **32**, 261–275.
- PETASNE, R.G. & ZIKA, R.G. 1997. Hydrogen peroxide lifetimes in south Florida coastal and offshore waters. *Marine Chemistry*, **56**, 215–225.
- RESING, J., TIEN, G., LETELIER, R. & KARL, D.M. 1993. Palmer LTER: hydrogen peroxide in the Palmer LTER region: II Water column distribution. *Antarctic Journal of the United States*, **28**, 227–228.
- SCHLOSS, I.R. 1997. *Escalas témporo-espaciales de variabilidad del fitoplancton costero antártico*. Ph.D thesis, University of Buenos Aires, 209 pp. [Unpublished]
- SCHLOSS, I.R., FERREYRA, G.A., CURTOSI, A., KLÖSER, H., MERCURI, G., SPOLSKY, B., VARELA, L. & PINOLA, E. 1997. Factors governing phytoplankton and particulate matter variation in Potter Cove, King George Island (Antarctica). In BATTAGLIA, B., VALENCIA, J. & WALTON, D.W.H., eds. *Antarctic communities: species, structure and survival*. Cambridge: Cambridge University Press, 135–141.
- SCHULTE-FROHLINDE, D. & SONNTAG, V.C. 1985. Radiolysis of DNA and Model Systems in the presence of oxygen. In SIES, H., ed. *Oxidative stress*. London: Academic Press & New York: Harcourt Brace Jovanovich Publishers, 152–195.
- SCULLY, N.M., MCQUEEN, D.J., LEAN, D.R.S. & COOPER, W.J. 1996. Hydrogen peroxide formation: the interaction of ultraviolet radiation and dissolved organic carbon in lake waters along a 43–75°N gradient. *Limnology and Oceanography*, **41**, 540–548.
- SIGG, A. & NEFTEL, A. 1988. Seasonal variations in hydrogen peroxide in polar ice cores. *Annals of Glaciology*, **10**, 157–162.
- SIGG, A. & NEFTEL, A. 1991. Evidence of a 50% increase in H_2O_2 over the past 200 years from a Greenland ice core. *Nature*, **351**, 557–559.
- STARK, G. 1991. The effect of ionizing radiation on lipid membranes. *Biophysica et Biophysica Acta*, **1071**, 103–122.
- THOMAS, C.E. & REED, D.J. 1990. Radical-induced inactivation of kidney Na^+, K^+ -ATPase: sensitivity to membrane lipid peroxidation and the protective effect of vitamin E. *Archives of Biochemistry and Biophysics*, **281**, 96–105.
- TIEN, G. & KARL, D.M. 1993. Hydrogen peroxide in the Palmer LTER region: III. Local sources and sinks. *Antarctic Journal of the United States*, **28**, 229–230.
- VIARENGO, A., ABELE-OESCHGER, D., BURLANDO, B. 1998. Effects of low temperature on prooxidants and antioxidant defence systems in marine organisms. In PÖRTNER, H.O. & PLAYLE, R., eds. *Cold ocean physiology*. Cambridge: Cambridge University Press, 213–235.
- WELLER, R. & SCHREMS, O. 1993. H_2O_2 in the marine troposphere and seawater of the Atlantic Ocean. *Geophysical Research Letters*, **20**, 125–128.
- ZIKA, R.G. 1990. Hydrogen peroxide as a relative indicator of the photochemical reactivity of natural waters. In BLOUGH, N.V. & ZEPP, R.G., eds. *Effects of solar ultraviolet radiation on biogeochemical dynamics in aquatic ecosystems*. Woods Hole: Woods Hole Oceanographic Institution Reports, 61–63.
- ZIKA, R.G., MOFFETT, J.W., PETASNE, R.G., COOPER, W.J. & SALTZMAN, E.S. 1985. Spatial and temporal variations of hydrogen peroxide in Gulf of Mexico waters. *Geochimica et Cosmochimica Acta*, **49**, 1173–1184.