Palmer LTER: Hydrogen peroxide in the Palmer LTER region: II. Water column distribution

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Hydrogen peroxide (H_2O_2) is ubiquitous in surface waters of the world ocean (Van Baalen and Marler 1966; Zika et al. 1985; Zika, Saltzman, and Cooper 1985; Palenik and Morel 1988; Johnson et al. 1989). Typically, surface ocean concentrations range between 10 and 400 nanomolar (nM) decreasing with depth to undetectable levels (less than 1 nM) below the mixed layer. The two major suspected source terms for H_2O_2 are photochemical interactions with dissolved organic matter (DOM) and atmosphere-to-ocean transport (see Karl et al., *Antarctic Journal*, in this issue).

In general, the global "pristine" ocean data demonstrate a strong latitudinal dependence with maximum H_2O_2 concentrations of 100–200 nM in low latitudes (15°S to 15°N) decreasing to approximately 30 nM at 62°S (Weller and Schrems 1993). To our knowledge, these are the only data for oceanic samples collected south of 60°S. The data of Weller and Schrems (1993), however, are limited to only a few samples in the region of the Bransfield Strait. Aside from short-term diel variations, temporal H_2O_2 variations on seasonal time scales have been reported only for the Caribbean Sea (Moore, Farmer, and Zika 1993).

During the 1992–1993 field season, we had the unique opportunity to study the seasonal variability of H_2O_2 in the surface waters of the Palmer long-term ecological research (LTER) study region. In excess of 1,000 water samples were collected from 64°S to 68°S. Repeat hydrographic surveys were conducted on three separate cruises aboard the R/V *Polar Duke* (*PD*92-09, November 1992, and *PD*93-01, January and February 1993) and R/V *Nathaniel B. Palmer* (*NBP*93-02, March through May 1993). Water samples were collected using a bio-optical profiling system (BOPS; Smith, Booth, and Star 1984) or standard General Oceanics conductivity-depth-temperature- (CDT-) rosette sampling system. Upon recovery, replicate 30-milliliter (mL) subsamples were drawn into dark polyethylene bottles and immediately fixed for H_2O_2 analysis by addition of a mixture containing peroxidase, (para-hydroxyphenyl)-acetic acid (POHPAA) and Tris buffer, as described by Miller and Kester (1988). The measurement of H_2O_2 relies upon a H_2O_2-dependent, peroxidase-catalyzed dimerization of POHPAA. This dimer exhibits a strong fluorescence and was measured using a Perkin-Elmer spectrofluorometer model LS-5B or LS-30 (313 nanometer [nm] excitation, 400 nm emission). Standards were made fresh daily from 1 M stock solutions of reagent grade H_2O_2 which had been standardized using a molybdate-catalyzed iodate reaction (Patrick and Wagner 1949) and titration by NIST-traceable thiosulfate reference solutions. For measurement of organic peroxides, a separate 30-mL sample was spiked with catalase, incubated for 1 hour at 20°C to remove H_2O_2, then treated as described above. With the exception of a few samples, H_2O_2 dominated the total dissolved peroxide pools in the upper 100 m of the water column.

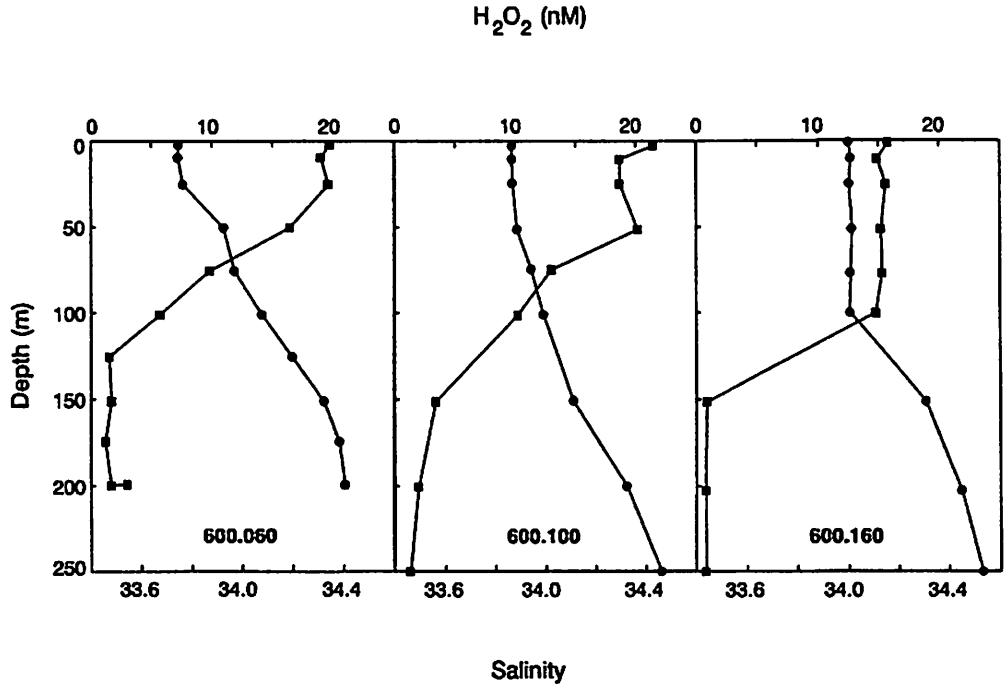

Figure 1. Depth profiles for H_2O_2 concentration (in nanomolar) and salinity (in practical salinity units) for LTER stations 600.060, 600.100 and 600.160 during November 1992.

Depth profiles of H_2O_2 were strongly correlated with water column salinity (that is, density), with greatest concentrations in the mixed layer (figure 1). The shapes of these

profiles are consistent with those from other regions of the world ocean, but the overall concentrations and water column inventories are significantly reduced (table). A surface-water (0–5 m) contour map of H_2O_2 concentrations in the Palmer LTER grid during the period from March through May 1993 failed to reveal any systematic latitudinal or onshore-to-offshore gradients in H_2O_2 over the approximately 1.8×10^5-square-kilometer study area (figure 2). During this same observation period, however, the total solar radiation varied considerably both with latitude and time. Thus, despite evidence for H_2O_2 photoproduction (Karl and Resing, *Antarctic Journal*, in this issue), the steady-state H_2O_2 concentrations during late austral autumn appear to be controlled by factors other than total solar radiation. Furthermore, the concentrations and water-column inventories measured in the LTER grid did not vary appreciably over the course of the austral summer season (cruise data collected in November 1992, January 1993, and March through May 1993).

Concentrations of H_2O_2 in representative marine environments

Location	Surface water H_2O_2 concentration[a]	Upper water column inventory[b]	Reference
LTER-600 transect (Nov 1992 to May 1993)	12–21	0.5–2.1	This study
Paradise Harbor (Nov 1992)	8.5–25	0.4–1.1	This study
Peru Upwelling	10–40	1.7–3.5	Zika, Saltzman, and Cooper 1985
Mediterranean Sea	100–140	5.1–7.0	Johnson et al. 1989
Gulf of Mexico	100–300	3–7.5	Zika et al. 1985
Caribbean Sea	50–100	2.6–2.7	Moore et al. 1993

[a]In nanomolar.
[b]0–100 m depth-integrated H_2O_2 concentrations. (In millimoles per square meter.)

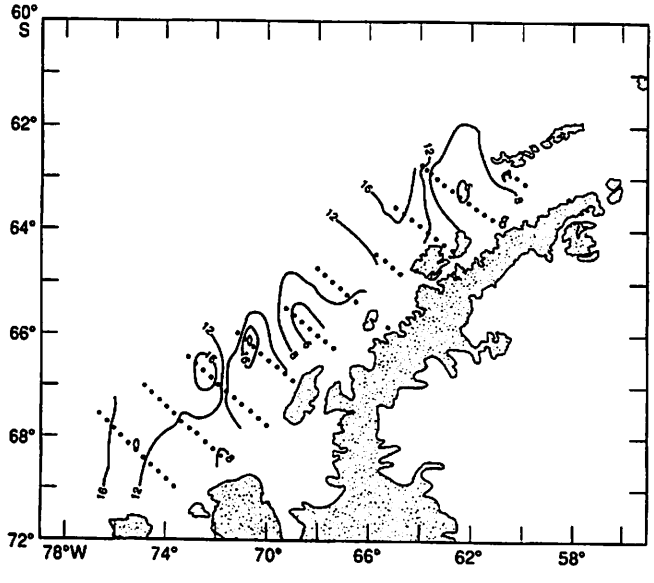

Figure 2. Surface (0–5 m) contour map of H_2O_2 concentrations (in nanomolar) for the LTER-grid for March through May 1993.

The results obtained to date suggest that H_2O_2 concentrations in the Palmer LTER region are lower than those observed in temperate and tropical marine habitats. Initial analyses of these data suggest that there is little variation in H_2O_2 concentrations of the course of the austral summer. Determination of the annual variability of H_2O_2 in this region with a winter cruise planned for August 1993 will be important to supplement our current understanding of H_2O_2 dynamics in this region. Finally, we hope to understand the distribution of H_2O_2 in this region, by carefully considering the competing source mechanisms such as atmospheric input photo- and microbial production vs. removal mechanisms such as mixing, diffusion, oxidation of organic matter, and microbial decay (Tien and Karl, *Antarctic Journal*, in this issue).

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Palmer LTER: Hydrogen peroxide in the Palmer LTER region: III. Local sources and sinks

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During the austral spring and autumn long-term ecological research (LTER) cruises aboard the R/V *Polar Duke* (*PD*92-09, November 1992) and R/V *Nathaniel B. Palmer* (*NBP*93-02, March through May 1993), we had an opportunity to investigate selected sources and sinks of hydrogen peroxide (H_2O_2) in a variety of antarctic coastal habitats. These measurements constituted one component of our comprehensive study of H_2O_2 dynamics (Karl et al.; Karl and Resing; Resing et al.; *Antarctic Journal*, in this issue). The potential source terms we evaluated were wet deposition (snow), glacial ice meltwater and land runoff, and *in situ* biological processes; photochemical processes are discussed in a companion paper (Karl and Resing, *Antarctic Journal*, in this issue). The primary H_2O_2 sink we investigated was bacterial enzymatic activity.

H_2O_2 wet deposition (snow) in the Palmer LTER study region during austral autumn 1993

Date	Location	Precipitation H_2O_2[a]	Sea water H_2O_2[a]
13 April 1993	64°45'S 64°05'W	432 552	13.6
24 April 1993	67°12.3'S 69°44.5'W	217	10.2
22 April 1993	64°45'S 64°05'W	275	10.1
24 April 1993	67°19.0'S 71°03.6'W	161	8.9
30 April 1993	67°51.3'S 76°00.2'W	55	14.9
7 May 1993	65°55.2'S 65°14.3'W	532 608	15.9
9 May 1993	Humble Island, Arthur Harbor	306	6.5

[a]In nanomoles per liter.

Freshly collected snow samples had consistently elevated concentrations of H_2O_2 relative to surface sea water (table); the regional average concentration was 349 (±192) nanomoles per liter. These results initially suggest that the atmosphere, through wet deposition, is a local source of H_2O_2 to surface waters. Based on previous studies, enrichment of H_2O_2 in marine precipitation was expected (Thompson and Zafiriou 1983), but the values for the LTER study region are lower, by 1–2 orders of magnitude, than rainwaters collected in either the Gulf of Mexico, South Florida, or the Bahama Islands (Zika et al. 1982; Cooper, Saltzman, and Zika 1987). From estimates of the upper water column [0–100 meters (m)] inventories of H_2O_2 [400–2100 micromole (μmol) per square meter]; Resing et al., *Antarctic Journal*, in this issue), the mean precipitation rate at Palmer Station [mean of 6.7 millimeters (mm) snow per day during the period November 1992 to January 1993 which is approximately equal to 670 milliliters per square meter per day according to the National Climate Center, Asheville, North Carolina], and our measured dark decay rates of more than 100 μmol per square meter per day (see below), we conclude that wet deposition of H_2O_2 is a weak source term for the LTER study region. Unfortunately, no measurements of H_2O_2 gas-phase deposition are available.

In addition to the concentrations of H_2O_2 in fresh precipitation, meltwater runoff also contains high levels of H_2O_2 [up to 450 nanomolar (nM)] especially near penguin rookeries. We presently attribute this to an "organic" enrichment and enhancement of H_2O_2 by photoproduction (Karl and Resing, *Antarctic Journal*, in this issue).

Several measurements of the H_2O_2 contents of glacial ice were also made. Floating freshwater ice samples (approximately 10 kilograms each) of unknown origin, were collected during sampling operations in Palmer Basin and Arthur Harbor. Each sample was first rinsed with warm (30°C) H_2O_2-free distilled water to clean the outer surface, then placed into a clean polyethylene bag and partially melted at room temperature (approximately 20°C). After 10–15 hours, the cold (0°C) meltwaters were collected and analyzed for H_2O_2. All samples were less than 5 nanomoles (nmol) per kilogram and were consistently lower than the ambient surface sea waters. In contrast to our results, glacial ice samples collected from