Van Baalen, C., and J.E. Marler. 1966. Occurrence of hydrogen peroxide in sea water. *Nature*, 211(5052), 951.

Weller, R., and O. Schrems. 1993. H_2O_2 in the marine troposphere and seawater of the Atlantic Ocean (48°N–63°S). *Geophysical Research Letters*, 20(2), 125–128.

Zika, R.G., J.W. Moffett, R.G. Petasne, W.J. Cooper, and E.S. Saltzman. 1985. Spatial and temporal variations of hydrogen peroxide in Gulf of Mexico waters. *Geochimica et Cosmochimica Acta*, 49(5), 1173–1184.

Zika, R.G., E.S. Saltzman, and W.J. Cooper. 1985. Hydrogen peroxide concentrations in the Peru upwelling area. *Marine Chemistry*, 17(3), 265–275.

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.

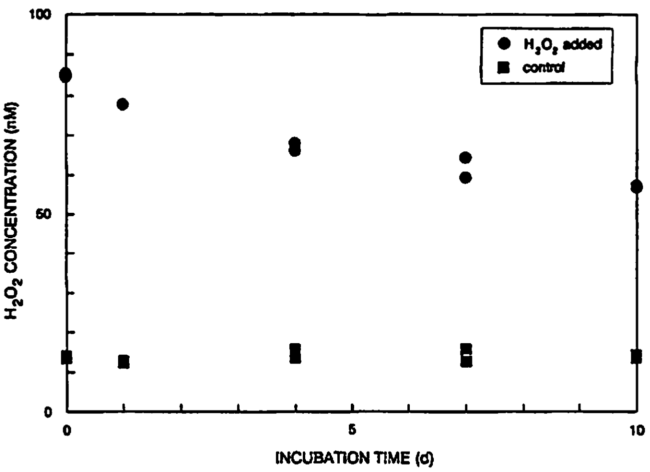
Freshly collected snow samples had consistently elevated concentrations of H_2O_2 relative to surface sea water (table); the regional average concentration was 349 (±192) nanomoles per liter. These results initially suggest that the atmosphere, through wet deposition, is a local source of H_2O_2 to surface 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 depths of 100–1,652 meters (m) beneath the antarctic polar plateau at Byrd (79°59'S 120°01'W) and South Pole stations, had H_2O_2 concentrations ranging from 100–500 nmol per kilogram (Neftel, Jacob, and Klockow 1984). The reasons for the differences between these two data sets are not apparent.

Two separate potential biological sources of H_2O_2 in antarctic coastal waters were also evaluated during the R/V *Nathaniel B. Palmer* 93-02 cruise. Dark incubations of H_2O_2-amended surface waters consistently consumed H_2O_2 (see below), so we concluded that *in situ* microbial (algae and bacteria) activities comprise a net sink. Nevertheless, two rather serendipitous observations provided evidence for potential biological production of H_2O_2 in Antarctica. During routine collections of krill (*Euphausia superba*) for physiological experiments by our colleague R. Ross, we observed elevated concentrations of H_2O_2 (up to 250 nM) in sea waters used for short-term (less than 1 hour) containment of dense populations of freshly captured animals and in darkened experimental tanks containing lower population densities (less than 100 adults per cubic meter). We suspect that the source of H_2O_2 in these samples is microbial but as yet have no experimental proof.

The second serendipitous observation was the discovery of elevated H_2O_2 levels (approximately 1–2 orders of magnitude above ambient surface water depending upon the location) in the R/V *Nathaniel B. Palmer*'s "uncontaminated seawater" system. With the assistance of Chief Engineer D. Munroe, we gained access to the aft centrifugal pump supply (positioned approximately 2 m inboard from the 3-inch diameter intake system in the hull of the ship) which supplies sea water to the main laboratories. The H_2O_2 concentration at the pump was a factor of 2–3 times (up to 20 nM) greater than the surface values collected by Niskin bottles, but was much lower than the H_2O_2 concentrations in the waters delivered at the laboratory. We conclude that there must be a strong and variable H_2O_2 source within the plumbing of this stainless steel (type 316)/carbon steel (ASTM-A53) sea-water delivery system, despite the fact that the flow rates are large enough for the water temperature at the downstream end to be within 1°C of the incoming sea water. At present, we hypothesize that the source of this H_2O_2 is microbial, rather than chemical.



Stability of H_2O_2 in dark incubations at *in situ* temperature. A surface-water sample with and without added H_2O_2 (85 nM) was collected at LTER station 100.140 and incubated in the dark at -0.5°C for 10 days. H_2O_2 concentrations were periodically determined.

We conducted several field experiments designed to investigate the nature and potential strength of the microbiological sink for H_2O_2. Changes in H_2O_2 concentrations were measured over time in sea water incubated in the dark at -0.5°C with and without exogenous H_2O_2 (figure). The H_2O_2 concentrations in unamended sea waters were relatively stable indicating low consumption rates (less than 0.2 nmol H_2O_2 per liter per day). If the sea water is supplemented with H_2O_2 to yield an initial concentration of 85 nM, however, the consumption rate increases to 5 nmol H_2O_2 per liter per day (figure). When the initial H_2O_2 concentration was increased to 1,000 nM, the consumption rate increased to approximately 40 nmol H_2O_2 per liter per day. These results indicate a large potential for dark H_2O_2 catalysis in antarctic surface waters despite a relatively low biomass of living microorganisms (0.5–1 µmol living carbon per liter). Nutrient-enriched sea-water cultures (1 gram peptone plus 100 milligrams yeast extract) of heterotrophic bacteria (approximately 5×10^6 cells per milliliter) consumed exogenous H_2O_2 (50 nM) at rates in excess of 50 nmol per liter per hour. The added H_2O_2 was relatively stable (loss rate less than 1 nmol per liter per hour) in sterile-filtered (0.2 µm) treatments.

From our initial investigations, we conclude that both biological and photochemical sources and microbiological sinks of H_2O_2 must be considered in studies of southern ocean H_2O_2 dynamics.

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References

Cooper, W.J., E.S. Saltzman, and R.G. Zika. 1987. The contribution of rainwater to variability in surface ocean hydrogen peroxide. *Journal of Geophysical Research*, 92(C3), 2970–2980.

Karl, D.M., and J. Resing. 1993. Palmer LTER: Hydrogen peroxide in the Palmer LTER region: IV. Photochemical interactions with dissolved organic matter. *Antarctic Journal of the U.S.*, 28(5).

Karl, D.M., J. Resing, G. Tien, R. Letelier, and D. Jones. 1993. Palmer LTER: Hydrogen peroxide in the Palmer LTER region: I. An introduction. *Antarctic Journal of the U.S.*, 28(5).

Neftel, A., P. Jacob, and D. Klockow. 1984. Measurements of hydrogen peroxide in polar ice samples. *Nature*, 311(5), 43–45.

Resing, J., G. Tien, R. Letelier, D.M. Karl, and D. Jones. 1993. Palmer LTER: Hydrogen peroxide in the Palmer LTER region: II. Water column distributions. *Antarctic Journal of the U.S.*, 28(5).

Thompson, A.M., and O.C. Zafiriou. 1983. Air-sea fluxes of transient atmospheric species. *Journal of Geophysical Research*, 88(C11), 6696–6708.

Zika, R., E. Saltzman, W.L. Chameides, and D.D. Davis. 1982. H_2O_2 levels in rainwater collected in South Florida and the Bahama Islands. *Journal of Geophysical Research*, 87(C7), 5015–5017.