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Hydrogen Peroxide in Deep Waters of the North Pacific Ocean

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[1] Hydrogen peroxide is a reactive oxygen intermediate that can play a role in a variety of redox cycles. In the ocean, it is generally considered to be dominantly photo-produced with negligible concentrations in deep waters. We have utilized a highly sensitive analytical method to investigate hydrogen peroxide in deep waters of the North Pacific Ocean. We present evidence that hydrogen peroxide exists in low nanomolar concentrations in these deep waters with an apparent minimum in the depth range of the oxygen minimum. A consideration of possible mechanisms and rates suggests both a short (~12 day) residence time as well as a biological origin for this deep hydrogen peroxide. Hydrogen peroxide is probably of minor importance to metal cycling in the deep ocean except in low oxygen environments. *INDEX TERMS:* 4851 Oceanography: Biological and Chemical: Oxidation/reduction reactions; 4808 Oceanography: Biological and Chemical: Chemical tracers; 4835 Oceanography: Biological and Chemical: Inorganic marine chemistry; 4825 Oceanography: Biological and Chemical: Geochemistry. **Citation:** Yuan, J., and A. M. Shiller (2004), Hydrogen peroxide in deep waters of the North Pacific Ocean, *Geophys. Res. Lett.*, *31,* L01310, doi:10.1029/2003GL018439.

1. Introduction

[2] Hydrogen peroxide is a reactive intermediate product of oxygen reduction. Photochemical processes play a dominant role in the formation of hydrogen peroxide in natural waters [*Cooper and Zika*, 1983] leading, for example, to concentrations of 10s of nM to over 100 nM in surface ocean waters [*Van Baalen and Marler*, 1966; *Zika et al.*, 1985a, 1985b; *Johnson et al.*, 1989; *Szymczak and Waite*, 1991; *Miller and Kester*, 1994; *Sarthou et al.*, 1997; *Price et al.*, 1998; *Yuan and Shiller*, 2001]. This photo-produced hydrogen peroxide appears to play a critical role in the surface ocean cycling of redox-active trace elements including Fe [*Millero and Sotolongo*, 1989], a trace limiting nutrient. Within the euphotic zone, hydrogen peroxide concentrations rapidly decrease with depth and reach the detection limit of most analytical techniques (~3 nM) near the base of the euphotic zone [*Johnson et al.*, 1989; *Miller and Kester*, 1994; *Price et al.*, 1998; *Sarthou et al.*, 1997; *Szymczak and Waite*, 1991; *Zika et al.*, 1985a, 1985b]. We report here the distribution of hydrogen peroxide in deep waters of the North Pacific Ocean, determined by utilizing a recently-developed, highly sensitive analytical method [*Yuan and Shiller*, 1999].

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2. Methods

[3] Hydrogen peroxide was determined during a cruise from Osaka, Japan to Hawaii during May/June 2002 (Figure 1). While the major focus of our work on the cruise was surface water chemistry, nonetheless we obtained deep profiles for hydrogen peroxide analysis at three locations (Figure 1). Hydrogen peroxide was determined by our previously reported modification of the Co-luminol method resulting in sub-nanomolar detection limits. The reproducibility of the method was found to be ±3% on a 0.6 nM sample; calibration uncertainty yields an uncertainty in absolute concentrations of <0.5 nM [*Yuan and Shiller*, 1999].

[4] Because we are dealing with concentrations lower than previously reported, it is important to consider the possibility of artifacts. We note first, that each profile (Figure 2) was obtained from a combination of separate hydrocasts (<300 m, 300–1500 m, and >1500 m). The lack of discontinuities at cast boundaries argues against artifacts resulting from bottle contamination or the length of time between closing the bottle and sample analysis. Experiments on the rate of decay of deep ocean hydrogen peroxide (see below) also suggest that decay during sample recovery was negligible. Additionally, our previous work demonstrated that the concentrations of redox-active elements present in deep ocean water are unlikely to cause analytical interferences [*Yuan and Shiller*, 1999]. Most hydrogen peroxide methods are sensitive to organic hydroperoxides as well as hydrogen peroxide [*Miller and Kester*, 1994; *Zika et al.*, 1985a; *Lee et al.*, 2000]. We found that methyl hydroperoxide gave a response of only 11% that of hydrogen peroxide; much of that response is likely due to residual hydrogen peroxide introduced during the synthesis of methyl hydrogen peroxide. While we cannot rule out that some of the analytical signal we see results from organic peroxides, nonetheless, this seems unlikely given that previous studies found organic peroxide to be undetectable in surface seawater [*Zika et al.*, 1985a, 1985b].

3. Results and Discussion

[5] Hydrogen peroxide in the North Pacific Ocean shows near-surface profiles similar to those reported by us [*Yuan and Shiller*, 2001] and others [*Zika et al.*, 1985a, 1985b; *Johnson et al.*, 1989; *Szymczak and Waite*, 1991; *Miller and Kester*, 1994; *Sarthou et al.*, 1997; *Price et al.*, 1998] throughout the ocean (Figure 2, inset). Specifically, these profiles show concentrations >30 nM near the surface and rapidly decline in the upper 100 m. Below the euphotic zone, the three profiles (Figure 2) still show measurable hydrogen peroxide with concentrations up to 6 nM in deep waters. These three deep profiles show their lowest hydrogen peroxide concentrations in the depth range of the

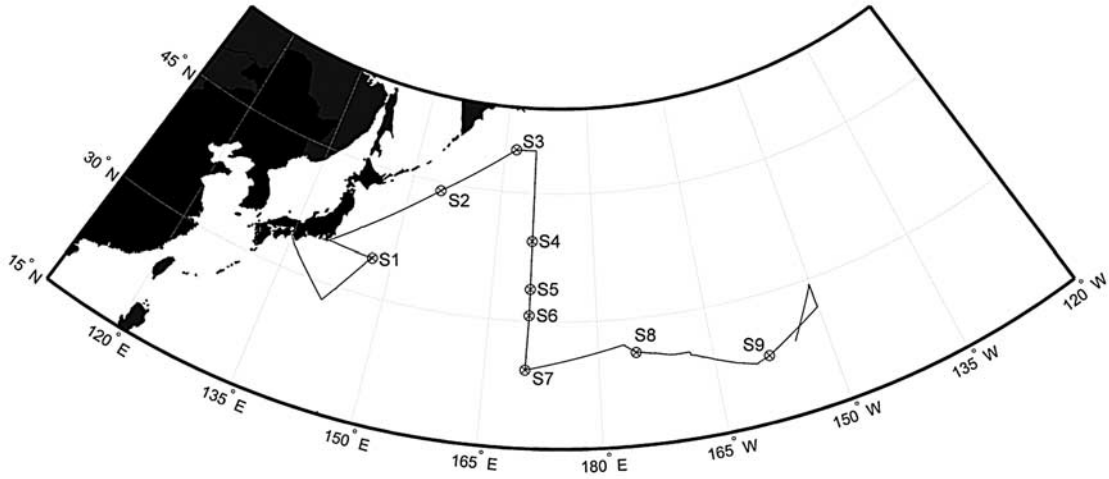

Figure 1. Cruise track map of the IOC 2002 to the North Pacific Ocean. Deep water profiles of hydrogen peroxide were obtained at stations S2, S7, and S9.

oxygen minimum. Hydrogen peroxide then tends to increase with depth. This behavior is most apparent in profiles S7 and S9 in the central gyre. In contrast, profile S2 in the northwest Pacific near the Kuril Trench shows lower deep water concentrations than the other profiles and also less variability.

[6] Understanding this deep water distribution and its significance requires some knowledge of the rates and mechanisms of production and decomposition of hydrogen peroxide at depth. Although it was not possible to perform *in situ* production or decay experiments during this cruise, previous work as well as a simple experiment we performed do constrain the rates and processes that are occurring.

[7] Production of this deep hydrogen peroxide is not likely to be photochemical. Not only does light not penetrate deeply enough in the ocean, but also measured rates of hydrogen peroxide decay [*Petasne and Zika*, 1997; *Yuan and Shiller*, 2001] in the surface ocean are too high to permit transport of photo-produced surface ocean hydrogen peroxide to depth. Indeed, as we show below, the deep water hydrogen peroxide residence time appears to be short enough that it must be produced *in situ* rather than being transported from elsewhere (e.g., surface waters, sediment boundary, hydrothermal vents).

[8] An alternative source of deep water hydrogen peroxide production is through the oxidation of reduced metal ions by oxygen to form superoxide [*Petasne and Zika*, 1987]. This mechanism, of course, requires a source of reduced metals ions. Measurements of metal redox speciation in deep waters are generally lacking, thus precluding a rigorous test of this hypothesis. But, one could surmise that reduced metals ions would be more common in the oxygen minimum zone and especially at station S2 which is in a productive region and close to the continental margin [*Honda et al.*, 2002]. However, we observe our *lowest* deep hydrogen peroxide concentrations at S2 as well as in the oxygen minimum of the other two stations. Likewise, in previous work we found subnanomolar concentrations of hydrogen peroxide in the 200–600 m depth range near the Amazon Shelf [*Yuan and Shiller*, 2001], another highly productive region with low oxygen shelf waters. We therefore conclude that oxidation of reduced metal ions is an unlikely mechanism for the formation of deep hydrogen peroxide.

[9] Several workers have noted dark biological production of hydrogen peroxide in near surface waters. For instance, *Palenik and Morel* [1988] observed dark production of hydrogen peroxide at 40–60 m in the Sargasso Sea and found that filtering seawater samples stopped the net rate of dark production, implying a biological origin. *Moffett and Zafiriou* [1990], using stable isotope methods, measured dark hydrogen peroxide production rates of 0.8–2.4 nM/hr in coastal surface waters. Both filtration and addition of an enzymatic inhibitor decreased the rate of dark production, again implying a biological origin. Additionally, *Palenik et al.* [1987] showed that at least one marine phytoplankter can produce extracellular hydrogen peroxide.

[10] A biological source for deep hydrogen peroxide thus seems reasonable, especially given our discounting of other potential sources. If deep ocean hydrogen peroxide results from biological processes, we would expect its rate of production to be ~100-fold lower in deep waters than in surface waters (i.e., ~0.01 nM/hr) just as the rate of biological activity decreases by approximately two orders of magnitude with depth in the ocean [e.g., *Packard et al.*, 1988; *Riley*, 1951]. With this production rate (~0.01 nM/hr), a mean deep ocean hydrogen peroxide concentration of 3 nM implies a deep hydrogen peroxide residence time on the order of 12 days.

[11] It is also important to consider the deep hydrogen peroxide decomposition rate and mechanism. In surface waters, evidence suggests that the decay of hydrogen peroxide is predominantly biological as mediated by the catalase and peroxidase enzyme systems [*Cooper and Zepp*, 1990; *Moffett and Zafiriou*, 1993]. Once again, with the substantial decrease in biological activity with depth in the water column, we would expect the biological rate of hydrogen peroxide decay likewise to decrease significantly with depth.

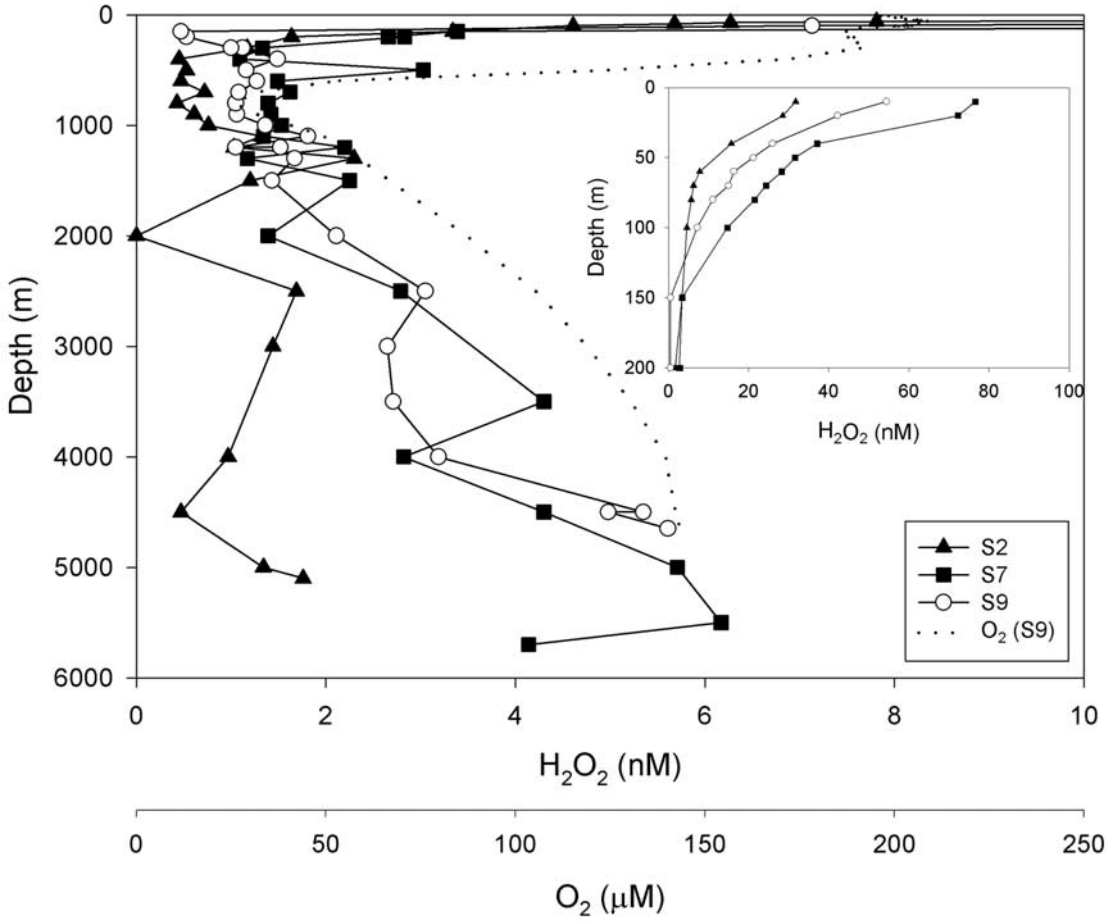

Figure 2. Vertical profiles of hydrogen peroxide at the North Pacific Ocean. The main graph shows deepwater profiles at stations S2 (44°N, 155°E), S7 (24.25°N, 170.33°E), and S9 (22.75°N, 158°W). The main graph also shows a vertical profile of dissolved oxygen at station S9. The insert shows shallow water profiles at these same stations.

[12] In previous work in surface waters of the Atlantic [*Yuan and Shiller*, 2001] as well as in surface waters of this North Pacific cruise, we found pseudo first-order rate constants for hydrogen peroxide removal ranging from $5-22 \times 10^{-3}$ hr^{-1}. We also determined pseudo first-order removal rate constants for water from 1500 m depth at S8 and 5000 m depth at S7. These experiments involved first exposing the water samples to sunlight in order to generate ~50 nM hydrogen peroxide and then following the decay while the samples were kept in the dark at ~21°C. In both experiments the rate constants were $3 \pm 0.7 \times 10^{-3}$ hr^{-1}. Interestingly, samples collected at 20 m depth showed removal rate constants of $8 \pm 1 \times 10^{-3}$ hr^{-1} at both locations.

[13] If we assume that hydrogen peroxide removal is biological, then we would expect deep removal rate constants to be roughly two orders of magnitude lower than surface ocean removal rate constants. This is because these pseudo first-order rate constants must incorporate the biological (i.e., enzymatic) concentration within them. That is, as biological activity decreases ~100-fold with depth, so too must the rate constant, if the removal process is biological. It is true that our deep removal rate constants are two orders of magnitude lower than our highest surface water rate constant; however, most of our surface and near surface rate constants are less than 10-fold greater than the deep rate constants. In other words, the apparent decrease in hydrogen peroxide decay rate with depth is not as rapid as the probable decrease in biological activity.

[14] The results of our deep rate constant experiments should be considered cautiously since we do not know the effect of the change in pressure in bringing the sample from depth to the surface. Additionally, since deep ocean temperature is significantly colder than our incubation temperature (2°C versus 21°C) the actual *in situ* decomposition rates are likely to be lower than what was measured in our experiments. Nonetheless, we note that our measured rate constant multiplied by a mean deep ocean hydrogen peroxide concentration of 3 nM yields a removal rate of 0.009 nM/hr which is similar to the magnitude of its production rate roughly estimated above. The comparison of rates at room temperature thus suggests that a mechanism in addition to biological decay may be required to explain the decay of hydrogen peroxide in deep ocean waters.

[15] In surface ocean waters, hydrogen peroxide appears to be involved in the cycling of certain redox-active trace metals such as Fe, Cu, and Cr [*Millero and Sotolongo*, 1989; *Moffet and Zika*, 1987; *Pettine and Millero*, 1990]. Could the oxidation of reduced metals in deep waters be

influenced by the hydrogen peroxide concentrations we report here and could this metal oxidation be an important sink for deep hydrogen peroxide? We again note that our lowest deep hydrogen peroxide concentrations are found at station S2 as well as in the oxygen minimum of the other two stations. It is certainly suggestive that these are the regions in which one would expect a greater source of reduced metals.

[16] *Pettine and Millero* [1990] reported on the kinetics of Cr(III) oxidation by hydrogen peroxide. Cr(III) is one redox species for which some deep water data have been reported. Using a Cr(III) concentration of 0.5 nM [*Jeandel and Minster*, 1987], our deep water hydrogen peroxide implies a Cr(III) oxidation rate (and hence a similar hydrogen peroxide consumption rate) of only 2×10^{-5} nM/hr. This is far lower than the hydrogen peroxide consumption rate estimated here. Additionally, the half-life for Cr(III) oxidation would be ~730 days, similar in magnitude to the timescale for Cr(III) oxidation by dissolved oxygen in well-oxygenated waters [*Schroeder and Lee*, 1975].

[17] For Fe(II), we can estimate a hydrogen peroxide based oxidation rate from the work of *Moffett and Zika* [1987]. Unfortunately, deep ocean Fe(II) concentrations are uncertain. Nonetheless, an Fe(II) concentration of ~0.01 nM would lead to an Fe(II) oxidation rate (and hydrogen peroxide decay rate) of ~0.002 nM/hr, similar to our estimated consumption rate. At these low deep water hydrogen peroxide concentrations, however, oxidation of Fe(II) probably occurs at a faster rate by oxygen than by hydrogen peroxide except in the oxygen minimum zone. We base this conclusion on a concentration adjustment of the pseudo first-order rate constants presented by *Moffett and Zika* [1987; Table III].

[18] At this point our most basic conclusion is that deep ocean hydrogen peroxide exists in low nanomolar concentrations and appears to increase with depth below the oxygen minimum. It is most likely biologically produced. In contrast to surface waters, where hydrogen peroxide is dominantly consumed by biological (i.e., enzymatic) processes but nonetheless appears to be important for metal cycling, in the deep ocean it is possible that chemical processes (e.g., Fe(II) oxidation) play an important role in hydrogen peroxide consumption and yet are of minor importance to metal oxidation compared with oxygen. Subsurface ocean regions where hydrogen peroxide may be important for metal cycling would be low oxygen regions such as the oxygen minimum zone. This scenario is obviously crude, though we believe logically constrained and contains an outline for future investigation.

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