Influence of the ITCZ on H_2O_2 in near surface waters in the equatorial Atlantic Ocean

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[1] H_2O_2 was measured in the upper water column (0–200 m) along a west-east transect through the Equatorial Atlantic as part of the German SOLAS (Surface Ocean Lower Atmosphere) cruise Meteor 55 (M55). Vertical profiles of H_2O_2 showed characteristic exponential decay consistent with light profiles and rainwater inputs. Integrated (0–100 m) water column H_2O_2 inventories ranged from 1.1–8.9 mmol m^{-2} with the highest values in the Amazon Plume. H_2O_2 inventories were also higher at the Equatorial Upwelling and after heavy rain showers in the region of the Inter Tropical Convergence Zone (ITCZ). Analysis of rain water samples collected during the cruise gave a volume weighted mean of 10.8 μmol L^{-1} (range 1.5–22.3 μmol L^{-1}). This work highlights the importance of rainwater as a major source for H_2O_2 in the surface waters under the ITCZ. INDEX TERMS: 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 3354 Meteorology and Atmospheric Dynamics: Precipitation (1854); 4852 Oceanography: Biological and Chemical: Photochemistry; 4504 Oceanography: Physical: Air/sea interactions (0312); 4835 Oceanography: Biological and Chemical: Inorganic marine chemistry. Citation: Croot, P. L., P. Streu, I. Peeken, K. Lochte, and A. R. Baker (2004), Influence of the ITCZ on H_2O_2 in near surface waters in the equatorial Atlantic Ocean, Geophys. Res. Lett., 31, L23S04, doi:10.1029/2004GL020154.

1. Introduction

[2] Hydrogen peroxide (H_2O_2) is the most stable intermediate in the four-electron reduction of O_2 to H_2O and may function as an oxidant or a reductant. H_2O_2 is principally produced in the water column by photochemical reactions involving dissolved organic matter (DOM) and O_2 [Cooper et al., 1988; Scully et al., 1996; Yocis et al., 2000; Yuan and Shiller, 2001]. Open ocean H_2O_2 concentrations show a distinct exponential profile with a maximum at the surface consistent with the photochemical flux. Concentrations can reach up to 300 nmol L^{-1} in Equatorial and Tropical regions with high DOM concentrations such as in the Amazon plume in the Atlantic [Yuan and Shiller, 2001]. In regions with low DOM and low sunlight, surface H_2O_2 levels are much lower with values in the Southern Ocean of 10–20 nmol L^{-1} [Sarthou et al., 1997]. Rainwater is a major potential source for H_2O_2 to surface seawater as it is preferentially removed from the atmosphere, relative to

other peroxides, during convective events. Due to its high solubility in water, scavenging of H_2O_2 in deep convection is around 55–70% [Cohan et al., 1999]. Mixing ratios of H_2O_2 in the marine troposphere show a strong latitude dependence with a maximum over the equator, suggesting that the air to surface flux at the equator should be high [Weller and Schrems, 1993].

[3] H_2O_2 can also be produced by biological processes in the ocean and dark production has been observed in the Sargasso Sea [Palenik and Morel, 1988] and in phytoplankton cultures [Palenik et al., 1987]. However studies to date have shown that the major production pathway in the water column is from photochemical production. In a few cases in the Southern Ocean, distinct H_2O_2 maximums at depth, corresponding to the chlorophyll maximum, suggest a significant biological source of H_2O_2 [Croot et al., 2004]. The 'dark decay life-time' of H_2O_2 can vary from hours to weeks in the ocean [Petasne and Zika, 1997], but typically may be around 4 days in the open ocean [Plane et al., 1987]. Filtration of seawater to remove the biota typically results in a dramatic reduction in the decay rate of H_2O_2 [Moffett and Zafiriou, 1990; Petasne and Zika, 1997], this rate is also influenced by the amount of colloidal material present [Yuan and Shiller, 2001]. Overall the decay rate of H_2O_2 is apparently controlled by several factors: H_2O_2 concentration, colloid concentration, bacteria/cyanobacteria numbers and temperature [Wong et al., 2003; Yuan and Shiller, 2001].

[4] In the present work we examined the vertical distribution and inventory of H_2O_2 in near surface seawater across the Equatorial Atlantic at 10°N as part of the German SOLAS programme. One of the aims of SOLAS is to understand the influence of atmospheric deposition on the biogeochemistry in the ocean; H_2O_2 is an important species in this regard because of its potential influence on trace metal redox cycling [Moffett and Zika, 1987; Croot et al., 2004] and on phytoplankton productivity [Willey et al., 1999].

2. Methodology

2.1. Sampling

[5] Samples were collected during the German SOLAS cruise, Meteor 55 (M55 Curacao – Douala), from 13 October–16 Nov 2002 on board the German research vessel F.S. Meteor. The cruise track was predominantly along a west-east transect at 10–11°N, from 60°W to 10°W (shown in Figure 1). Analytical work was carried out in an over-pressurized class 100 clean air van on loan from the University of Bremen.

2.2. Sampling of Surface Waters

[6] Seawater samples were obtained either using Niskin bottles on a standard CTD rosette or from modified Teflon

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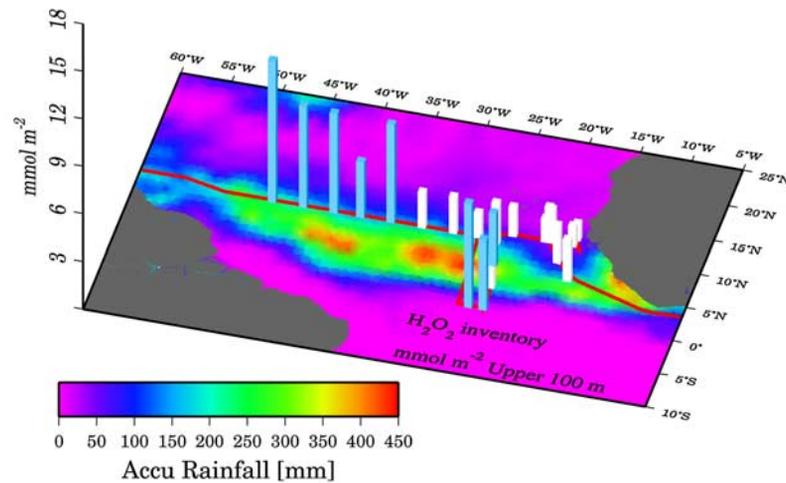
Figure 1. The Equatorial Atlantic, showing cruise track (red line) and the near surface (0–100 m) inventory of H_2O_2 (3D bar) at each station occupied during M55. Blue bars indicate stations where the inventory of $H_2O_2 > 3$ mmol m^{-2}, all other stations are shown as white bars. The colored contours show the integrated rainfall accumulation over the period of the cruise (Data from TRMM Product 3B42) indicating the position of the ITCZ at this time.

coated PVC General Oceanics (Miami, FL, USA) GoFlo (8 L) bottles. Samples were drawn into 100 mL low density polyethylene bottles which had been made impervious to light. Samples were analyzed within 1–2 hours of collection where possible and were not filtered. Stations for H_2O_2 sampling were occupied in the late afternoon immediately prior to sunset each day.

2.3. H₂O₂ and Light Measurements

[7] In the present work H_2O_2 was measured using a flow injection chemiluminescence (FIA-CL) reagent injection method [*Yuan and Shiller*, 1999]. In brief, the chemiluminescence of luminol is catalysed by the reaction of H_2O_2 present in the sample with Co^{2+} at alkaline pH. H_2O_2 standards were made by serial dilution from a primary stock solution (30% Fluka - Trace Select). The concentration of the primary standard was determined by direct spectrophotometry of the solution ($\varepsilon = 40.9$ mol L^{-1} cm^{-1} [*Hwang and Dasgupta*, 1985]). Secondary standards were analysed with a spectrophotometric method using Cu(II) and 2, 9-dimethyl-1, 10-phenanthroline [*Kosaka et al.*, 1998]. Seawater samples were measured directly by FIA-CL, while rainwaters were diluted, up to 1:100, with ultrapure water

(18 MΩ). Sample concentrations were corrected daily for the reagent blank [*Yuan and Shiller*, 1999] and for H_2O_2 in the ultrapure water (20–60 nmol L^{-1}). Vertically integrated (0–100 m) H_2O_2 inventories were estimated using the trapezoidal rule. Samples were analyzed using 5 replicates: typical precision was 2–3% through the concentration range 1–300 nM, the detection limit (3σ) was typically 0.6 nmol L^{-1}. Light profiles (PAR-Photosynthetically Available Radiation) were measured with a Li-Cor quantum radiometer.

2.4. Airmass Back Trajectories and Satellite Rainwater Estimates

[8] The air masses sampled were classified according to 5-day back trajectories calculated for arrival heights of 10, 500 and 1000 m above the ship's position (NOAA Air Resources Laboratory HYSPLIT model, FNL data set). Rainwater accumulation and rain rates over the study region were obtained from the Tropical Rainfall Measuring Mission (TRMM) product 3B42 (http://lake.nascom.nasa.gov/data/dataset/TRMM/index.html). This data is archived and distributed by the Goddard Distributed Active Archive Center. TRMM is an international project jointly sponsored
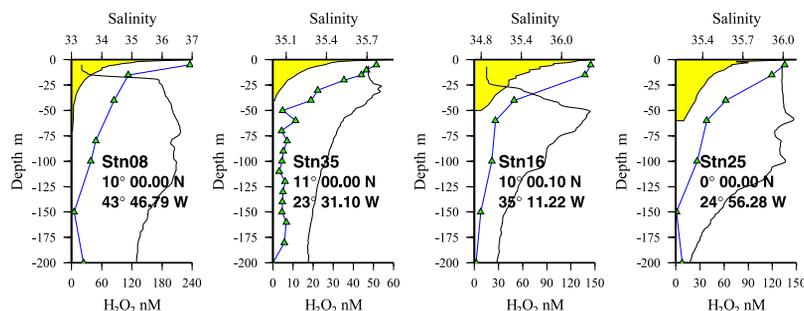

Figure 2. Selected vertical profiles of H_2O_2 (green triangles and blue line) and salinity (solid black line) from 4 stations occupied during M55 representative of the different conditions encountered: Amazon Plume (Stn 8), Open Ocean (Stn 35), Equatorial Upwelling (Stn 25) and under the ITCZ rain band (Stn 16). The light (PAR) profiles obtained at each station are also shown (solid yellow, 100% light is the full width of the x-axis).

Table 1. H$_2$O$_2$ Concentrations in Marine Rain Events During M55

Event	Date/Time (DD),[a] UTC	Date/Time Local	Latitude	Longitude	Volume, mL	5 Day Back Trajectory[b,c]	[H$_2$O$_2$], μmol l^{-1}
MR03	(293) 23:20	20:20	10.000	−43.253	170	N, NH	14.7 ± 0.5
MR06	(294) 19:20	16:20	9.999	−40.773	350	N, NH	10.7 ± 1.3
MR07	(295) 18:55	15:55	10.000	−38.164	410	surface NH, upper SH	13.7 ± 0.5
MR09	(301) 01:40	23:40	4.612	−26.304	340	SE, SH	1.5 ± 0.2
MR11	(305) 17:53	15:53	6.498	−24.250	260	SE, SH	22.8 ± 1.8
MR13	(313) 20:20	19:20	8.253	−18.351	170	SE, SH	8.1 ± 1.0
MR14	(314) 17:15	16:15	6.100	−15.900	970	SE, SH	10.0 ± 0.2

[a]DD denotes decimal day where Jan 1 = 01.
[b]First letter denotes direction from which the wind is coming from (i.e., N – Northerly).
[c]NH/SH denotes Northern/Southern Hemisphere air mass.

by the Japan National Space Development Agency (NASDA) and the U.S. National Aeronautics and Space Administration (NASA) Office of Earth Sciences.

2.5. Rainwater Collection at Sea

[9] During M55 clean marine rain was collected using poly-propylene funnels (28 cm diameter) and low density polyethylene bottles which had been cleaned for major ion sampling [*Losno et al.*, 1998]. These were mounted on a support on the pile deck above the bridge, as far as possible from any overhanging parts of the ship's superstructure. Funnels were only deployed during rain events to prevent contamination from dry deposition.

3. H$_2$O$_2$ in Surface Waters

[10] Mixed layer H$_2$O$_2$ values found during this study ranged from 31–236 nmol L^{-1} (Figure 2) with the highest values found in surface waters of the Amazon Plume (Stn 8, S < 35), crossing our transect at around 50°W. An earlier study [*Yuan and Shiller*, 2001] also found high concentrations in the Amazon Plume resulting from the high organic matter load in these low density surface waters. High near surface concentrations were also found along the equator in the Equatorial Upwelling, presumably from higher DOM levels associated with increased primary productivity, and under the rain band of the northern ITCZ (Stn 16, S < 35.7) [*Liu and Xie*, 2002]. Profiles of H$_2$O$_2$ were similar to profiles of PAR light attenuation at each station as expected for a photochemically produced compound (Figure 2). Diel variations in seawater H$_2$O$_2$ have also been observed [*Yuan and Shiller*, 2001], but investiga-

Figure 3. Integrated H$_2$O$_2$ concentrations for each station occupied during M55 plotted against the preceding 4 day accumulated precipitation from the TRMM satellite based estimate for each station location. Data used in preparing this figure can be found in the auxiliary material[1].

tion of this phenomena was not possible in the present study as we did not occupy the same station for more than a few hours.

[11] At all stations significant concentrations of H$_2$O$_2$ were found below the euphotic depth (1% PAR light level) showing evidence for H$_2$O$_2$ mixing down through the water column (Figure 2) away from the sources: sunlight and rainwater. This mixing of the upper waters can be controlled principally by the wind stress or it has also been shown that convective overturn, caused by nocturnal cooling, can transport significant amounts of hydrogen peroxide to depth [*Plane et al.*, 1987; *Sikorski and Zika*, 1993]. H$_2$O$_2$ transported to deeper waters will also have a reduced decay rate, as below the photic zone the major removal process, transformation by phytoplankton and bacteria, will be greatly reduced [*Wong et al.*, 2003]. For instance at station 35, we estimate H$_2$O$_2$ half-lifes of approximately 4 days in the surface waters, consistent with early studies [*Petasne and Zika*, 1997; *Yuan and Shiller*, 2001], increasing to ~10–30 days at 100 m (P. L. Croot et al., manuscript in preparation, 2004).

4. Water Column Inventories of H$_2$O$_2$

[12] Upper water column inventories of H$_2$O$_2$ across the equatorial Atlantic ranged from 1.1–8.9 mmol m^{-2} (Figure 1). Highest values were again found in waters influenced by the Amazon plume (50°W). High values (3.6–6.4 mmol m^{-2}) in the region from 45°–35°W corresponded with heavy rain encountered while crossing the edge of the ITCZ, as evidenced by lowered surface salinities indicating heavy precipitation, increased values were also found at the equator (4.4–6.5 mmol m^{-2}). Away from these three regions H$_2$O$_2$ inventories were relatively uniform (2.1 ± 0.6 mmol m^{-2}) and similar to data from the Caribbean Sea [*Moore et al.*, 1993] and other studies in the Tropical Atlantic [*Yuan and Shiller*, 2001].

5. H$_2$O$_2$ in Rainwater

[13] Rainwater H$_2$O$_2$ values (Table 1) ranged from 1.5–22.8 μmol L^{-1} with a volume weighted mean of 10.8 μmol L^{-1}. Our data is similar to that for marine rains collected over the South and Central Atlantic, 4–71 μmol/kg (average 26 μmol/kg) [*Yuan and Shiller*, 2000], the Western Atlantic, 8–21 μmol/kg (average 13 μmol/kg) [*Cooper et al.*, 1987]
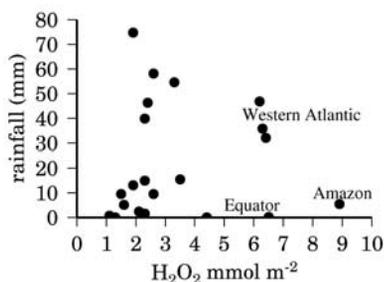
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[1]Auxiliary material is available at ftp://ftp.agu.org/apend/gl/2004GL020154.

and at BATS, 5–85 μmol/kg (average 9 μmol/kg winter and 37 μmol/kg summer) [*Kieber et al.*, 2003].

[14] Highest concentrations of H_2O_2 in rainwater are normally found in summer when solar fluxes are highest. Similarly on a diel cycle, highest rainwater H_2O_2 levels are found in the mid-late afternoon, with the lowest values in the late evening as found recently at BATS [*Kieber et al.*, 2003]. The concentration of H_2O_2 in rain is also a function of the amount of previous scavenging of H_2O_2 from the atmosphere [*Cohan et al.*, 1999] and this may account for the lower values found in the vicinity of the ITCZ in this study and during a rain squall in the Equatorial Pacific [*Hanson et al.*, 2001], where frequent rain events may lower atmospheric H_2O_2 levels.

6. H_2O_2, Rainwater and the ITCZ

[15] The ITCZ is the area where the tropical trade winds converge and is a natural barrier for inter-hemispheric atmospheric transport. The ITCZ is also a region of high precipitation and at the time of this study the maximum rainfall band of the ITCZ was located in the central part of the ITCZ band [*Yuan and Miller*, 2002] (see also Figure 1). Satellite estimates of the rainfall (TRMM product 3B42) in the vicinity of the stations in the region of 45°–35°W gave rainfall accumulations of ~60–90 mm for the preceding 4 days (half-life for decay in surface seawater) before our arrival (Figure 3). Budgeting for the increased H_2O_2 inventory at station 16, 3.8 mmol m^{-2}, requires a rainwater concentration of 42–63 μmol L^{-1}, well above our rainwater measurements, possibly suggesting that the rainfall accumulation time for H_2O_2 at this site may have been longer than 4 days, or that our rainwater sample was low due to earlier scavenging of much of the H_2O_2 from the atmosphere. Our work suggests that rainfall in the ITCZ may play a major role in supplying H_2O_2 to surface waters in the Equatorial regions with implications for phytoplankton physiology and biogeochemical redox processes, such as oxidation of Fe(II) derived from aerosols, in the upper ocean.

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