



Diel cycles of hydrogen peroxide in marine bathing waters in Southern California, USA: *In situ* surf zone measurements

Catherine D. Clark*, Warren J. De Bruyn, Charlotte M. Hirsch, Paige Aiona

Department of Chemistry, Schmid College of Sciences, Chapman University, One University Drive, Orange, CA 92866, United States

ARTICLE INFO

Keywords:

Peroxide
CDOM
Surf zone
Southern California
Diel

ABSTRACT

Hydrogen peroxide is photochemically produced in natural waters. It has been implicated in the oxidative-induced mortality of fecal indicator bacteria (FIB), a microbial water quality measure. To assess levels and cycling of peroxide in beach waters monitored for FIB, diel studies were carried out in surf zone waters in July 2009 at Crystal Cove State Beach, Southern California, USA. Maximum concentrations of 160–200 nM were obtained within 1 h of solar noon. Levels dropped at night to 20–40 nM, consistent with photochemical production from sunlight. Day-time production and night-time dark loss rates averaged $16 \pm 3 \text{ nM h}^{-1}$ and $12 \pm 4 \text{ nM h}^{-1}$ respectively. Apparent quantum yields averaged 0.07 ± 0.02 . Production was largely dominated by sunlight, with some dependence on chromophoric dissolved organic matter (CDOM) levels in waters with high absorption coefficients. Peroxide levels measured here are sufficient to cause oxidative-stress-induced mortality of bacteria, affect FIB diel cycling and impact microbial water quality in marine bathing waters.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

Hydrogen peroxide (H_2O_2) is a key intermediate in aquatic redox processes in chemical and biological systems, acting as a strong oxidizing agent that reacts with trace metals and pollutants (Cooper et al., 1989). It is a common transient in natural waters, with surface maxima on the order of 10 to 300 nM in a variety of marine environments (see review Clark et al., 2008a and references therein). H_2O_2 has been implicated in the oxidative-induced mortality of bacteria in natural waters (Xenopoulos and Bird, 1997; Angel et al., 1999; Weinbauer and Suttle, 1999; Fisher et al., 2008). Popular public bathing beaches in the USA are required to participate in microbial water quality monitoring programs based on fecal indicator bacteria concentrations (FIB; US EPA, 2000) which have been linked to adverse health outcomes in epidemiological studies (Jiang et al., 2001). H_2O_2 has been shown to reduce FIB concentrations in sewage fields (Chamberlain and Mitchell, 1978) and waste treatment ponds (Davies-Colley et al., 1999). A mesocosm study using unfiltered water sampled from Huntington State Beach, Southern California showed an anti-correlated relationship between FIB and H_2O_2 diel cycles (Boehm et al., 2002), suggesting a possible cause and effect. However, while diel cycling in H_2O_2 in aquatic environments has been previously observed in both fresh and marine waters (see references in Clark et al., 2008a), there have been very few direct *in situ* observations of H_2O_2 in the surf

zone where FIB are measured. It is not clear that surf zone sources and sinks of H_2O_2 are the same as open ocean sources and sinks.

The primary source of H_2O_2 in seawater is photochemical reactions that occur when chromophoric dissolved organic matter (CDOM) absorbs UV radiation; mechanistic details are discussed in a recent laboratory study of H_2O_2 production by Clark et al. (2009). CDOM is a highly complex colored material that contains humic substances (Miller, 1994), usually produced from plant degradation in fresh waters (McKnight and Aiken, 1998) and from degraded phytoplankton in the ocean (Hessen and Tranvik, 1998). Higher H_2O_2 concentrations and production rates are generally observed in waters with higher levels of CDOM as measured by absorbance (Cooper et al., 1988; O'Sullivan et al., 2005) and fluorescence (Fujiwara et al., 1993; Moore et al., 1993; Herut et al., 1998; Scully et al., 1996; Obernosterer et al., 2001). Additional sources of H_2O_2 to seawater are atmospheric input via dry and wet atmospheric deposition and precipitation (Kieber et al., 2001; Croot et al., 2004; Avery et al., 2005; Steigenberger and Croot, 2008), and biological production by small microorganisms (Moffett and Zafiriou, 1990; Avery et al., 2005). These sources are generally considered insignificant compared to *in situ* abiotic photochemical production in ocean water (Clark et al., 2008a). However, it is not clear that these sources are small in a dynamic and turbulent surf zone environment. It is also not clear that CDOM is the primary source of H_2O_2 in coastal waters. In a recent study, no correlation between H_2O_2 and absorbance was observed in coastal waters with low fresh water riverine inputs (Clark et al., 2010). This was attributed to possible additional non-CDOM

* Corresponding author. Tel.: +1 714 628 7341; fax: +1 714 532 6048.
E-mail address: cclark@chapman.edu (C.D. Clark).

sources like beach sediments and senescent kelp (Clark et al., 2009) and is not consistent with previous studies in well-mixed oceanic and coastal waters dominated by riverine waters (see references in Clark et al., 2008a).

The primary seawater sink has been attributed to biological decomposition involving peroxidase and catalase enzymes and phytoplankton (Moffett and Zafriou, 1990; Obernosterer et al., 2001; Steigenberger and Croot, 2008). Other potential oceanic sinks include catalytic decomposition mediated by chemical reductants (Moffett and Zafriou, 1993), photochemical decomposition (Moffett and Zafriou, 1993) and physical mixing dynamics (Steigenberger and Croot, 2008). Surf zone sinks could be significantly larger than oceanic sinks due to differences in biological populations and mixing processes.

Diel cycles in H_2O_2 typically show high concentrations during the day when photochemical production is occurring, with maxima near solar noon, and low concentrations at night when loss processes dominate (Clark et al., 2008a). There have been two recent *in situ* diel studies of H_2O_2 levels in local waters. Boehm et al. (2009) measured H_2O_2 in near-shore Southern California coastal waters off Avalon Beach at Santa Catalina Island, and saw no statistically significant difference in concentrations between day and night. In contrast, we recently published a diel cycle in surf zone waters at a mainland coastal beach in Southern California (Clark et al., 2010), with a maxima in concentrations measured in mid-to-late afternoon with a 2 h lag after solar noon.

To elucidate these discrepancies and examine the potential impact of H_2O_2 on FIB levels in recreational marine bathing waters, we conducted multiple diel studies in the surf zone at a popular Southern California beach in July 2009, the height of the summer holiday use season. We report apparent quantum yields and compare our measured concentrations and production and loss rates in the surf zone to previous coastal and oceanic studies in the literature. We also compare our observed diel cycles to variations in sunlight, tides and absorbance to probe production mechanisms.

2. Methods

Water samples were collected in 500 mL amber glass bottles from knee deep water (~1 m depth) every hour during four 24–28 h diel experiments at Crystal Cove State Beach (33.574 N 117.840 W) in Orange County, Southern California in July 2009. Field study dates and local times were: (1) 10 am 7/1 to 2 pm 7/2; (2) 10 am 7/8 to 2 pm 7/9; (3) 10.30 am 7/15 to 2 pm 7/16; (4) 10 am 7/29 to 10 am 7/30/2009. Sunlight irradiance (in $mW\ cm^{-2}$) was measured *in situ* with a handheld UV light intensity radiometer/dosimeter with a built-in UV A + B photodiode sensor with a response range of 280–400 nm and a peak response at 370 nm (VersaProbe, UV Process Supply Inc.). The meter was used as a qualitative measure of solar irradiance trends over the course of a day and was not calibrated. For comparative purposes, a maximum of $4.7 \times 10^{-3}\ W\ cm^{-2}$ was measured by this meter during this study, equivalent to a solar insolation of around 1.1 kW-hr/ m^2 /day, about 4–5 times lower than the typical values of 4.77–5.5 kW-hr/ m^2 /day observed in major metropolitan areas adjacent to this study site at this time of year (US Solar Radiation Resources Maps, National Renewable Energy Laboratory, Renewable Resources Data Center; <http://www.nrel.gov/rredc>). A thick early morning fog layer, typical for this region at this time of year, delayed the onset of a solar radiation increase in some of the field studies for 2–3 h after sun-rise occurred around 6 am local time. Temperature was measured *in situ*. Tidal data was obtained from the United States Geological Service (USGS).

Water samples were immediately vacuum filtered through 0.7 μm glass fiber filters (Whatman, Inc.). Hydrogen peroxide lev-

els were measured after filtering using an enzyme-mediated fluorescence peroxidase method (Zika and Saltzman, 1982). The reagents and method have been previously described in detail (Clark et al., 2009, 2010). Measurements were made in triplicate; average standard deviations for the four studies were 4.4 nM, 2.0 nM, 1.8 nM and 3.1 nM, respectively. Detection limits during the studies were estimated at 6 nM based on the minimum measurable change in fluorescence. Linear calibration curves were obtained periodically during each study; slopes averaged 0.131 ± 0.007 with an average r^2 of 0.982 ± 0.009 .

The remaining water samples were stored in the dark at 4 °C and transported back to the laboratory at Chapman University within 24 h of collection. Salinity and pH were measured in the laboratory with a conductivity meter (Model 162A, Thermo ORION) and an Acument Basic AB15 pH meter, respectively. Absorbance spectra from 200 to 700 nm were obtained with a UV/VIS spectrophotometer (Agilent Technologies, Model 8453, Wilmington, DE) in quartz cylindrical cells with a 10 cm path length. Absorbances at 300 nm were converted to absorption coefficients (a in m^{-1}) using the approach of Hu et al. (2002); 300 nm is a characteristic wavelength typically reported for CDOM (Miller, 1998).

3. Results and discussion

Clear diel cycles in H_2O_2 concentrations were obtained for all four field experiments for surf zone waters (Figs. 1–4). Overall, studies 1, 2 and 3 were very consistent with respect to overall trends, measured maximum and minimum concentrations and the relationship between sunlight intensity and peroxide. However, field study four showed different results; we attribute this to the fact that this study occurred immediately after a major storm which caused significant increases in the amount of plant wrack and surf zone turbulence.

In general, peroxide levels increased linearly from sun-rise (6 am) to a maximum within 1 h of solar noon. Maximum peroxide levels reached in the afternoon ranged from 168 nM in study 3 to 200 nM in study 2, with an average of 182 ± 14 nM. These numbers are comparable to the averages of 183 nM (range from 93 to 329 nM) recently measured 80 km off-shore from our study site at Avalon Beach, Santa Catalina Island (Boehm et al., 2009) and 122 nM (range from 49 to 175 nM) measured at Huntington State Beach, 15 km up coast from this study site (Clark et al., 2010). Net day-time peroxide production rates were estimated from a

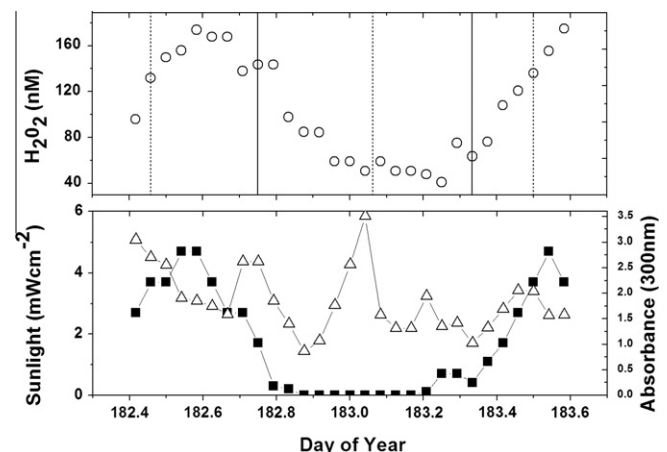


Fig. 1. H_2O_2 concentrations (\circ) (nM), measured uncorrected total solar irradiance (\blacksquare) ($mW\ cm^{-2}$), and absorption coefficient (\triangle) (m^{-1} at 300 nm) as a function of fractional day of the year for field study 1 (10 am 7/1 to 2 pm 7/2/2009). Dashed and solid lines represent the peaks of ebb and flood tides, respectively.

Download English Version:

<https://daneshyari.com/en/article/6361775>

Download Persian Version:

<https://daneshyari.com/article/6361775>

[Daneshyari.com](https://daneshyari.com)