Hydrogen peroxide in tropical shelf Waters: The Northern South China Sea Shelf

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A B S T R A C T

The distribution of hydrogen peroxide was determined at 28 stations in four transects across the Northern South China Sea Shelf-sea (NoSoCS) in June 2010. The average concentration in the top 10 m ranged between 0.063 and 0.231 μM. Among the hydrographic regimes: the inner shelf outside of the influence of upwelling, the inner shelf under the influence of upwelling, the middle shelf, the outer shelf and the open South China Sea, the highest concentration was found in the day-time in the inner shelf outside of the influence of upwelling and the lowest concentration was found in the night-time in the inner shelf under the influence of upwelling. The average concentration at the day-time stations in each hydrographic regime was invariably higher than the corresponding concentration at the night-time stations. Across the shelf, the concentration was the highest in the inner shelf. The variations in the concentrations of hydrogen peroxide and total organic carbon (TOC) in the different hydrographic regimes followed a similar pattern. All these behaviors are consistent with the photochemical production of hydrogen peroxide, using dissolved organic matter as the chromophore, as a primary control on its occurrence in the surface waters. Moreover, at day-time stations at different locations in the NoSoCS and at a single location sampled through the day, the relationship between the concentration of hydrogen peroxide and the product of the concentration of TOC and the time-integrated irradiance at the time of sample collection fell on two distinct linear lines with different slopes and intercepts: one for mostly the inner and middle shelf waters and the other for mostly the water in the open northern SCS. These relationships suggest that the light history, the pre-existing concentration of hydrogen peroxide, and the concentration and the photochemical efficiency of the dissolved organic matter in the production of hydrogen peroxide play major roles in determining the temporal and spatial variations in the concentration of hydrogen peroxide in the surface waters in the day-time. In the subsurface, a notably large fraction, about one-third, of the profiles of hydrogen peroxide did not follow the typical distribution of a quasi-exponential decrease in concentration with depth. Almost all the profiles at the stations in the slope where the internal waves were most active were atypical. At these stations, the concentration of hydrogen peroxide was generally elevated down to about 100 m, well beyond the depths where solar irradiance was plentiful. Superimposed on these elevated concentrations was a persistent sub-surface maximum, with concentrations reaching about 0.5 μM, at 80 m. While the origin of these atypical distributions is not yet clear, dark biological production and the action of internal waves conceivably could have contributed to their occurrence.

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1. Introduction

Hydrogen peroxide is a reactive transient that is present rather ubiquitously in the surface oceans at concentrations of 10⁻¹ μM (Zika et al., 1985a, 1985b; Johnson et al., 1989; Moore et al., 1993; Miller and Kester, 1994; Sarthou et al., 1997; Avery et al., 2005; Yuan and Shiller, 2001, 2005; Steigenberger and Croot, 2008). It can act both as an oxidizing and a reducing agent (Zafiriou, 1983; Zafiriou et al., 1984; Moffett and Zafiriou, 1990) and can react with a fairly large suite of biologically important and redox-sensitive trace elements in the oceans such as iron (González-Davila et al., 2005; Millero and Sotolongo, 1989; Moffett and Zia, 1987; Santana-Casiano et al., 2006), copper (Millero et al., 1991; Sharma and Millero, 1989), chromium...
Hydrogen peroxide is formed primarily through indirect photochemical reactions in which dissolved organic matter acts as the chromophore. As these organic molecules capture the light energy, they become excited. Subsequently, the excited molecules react with oxygen to form superoxide which disproportionates to form hydrogen peroxide (Cooper and Zika, 1983; Cooper et al., 1994; Scully et al., 1996). The efficiency of the reaction depends on the composition of the organic matter, and, the intensity and the spectral composition of the incident light since ultraviolet light is more effective than visible light in inducing the formation of hydrogen peroxide (Scully et al., 1996; Wong and Wong, 2001; O’Sullivan et al., 2005). This photochemical production of hydrogen peroxide is rapid and can be readily detected in minutes to hours when samples of natural water are exposed to solar irradiation (Cooper and Zika, 1983; Cooper et al., 1988; Yocis et al., 2000; Avery et al., 2005; Yuan and Shiller, 2005; Clark et al., 2009). Traditionally, biological production (Palenik and Morel, 1988; Yuan and Shiller, 2004) and atmospheric deposition (Zika et al., 1992; Cooper et al., 1987; Hanson et al., 2001; Kieber et al., 2001) have been considered minor sources of hydrogen peroxide to the oceans. However, recent studies suggest that the biological production of hydrogen peroxide may be more widespread and its contribution to the total production of hydrogen peroxide in the aquatic environment may be more significant than previously thought (Kustka et al., 2005; Rose et al., 2005, 2008, 2010; Vermilyea et al., 2010; Dixon et al., 2013; Diaz et al., 2013; Shaked and Rose, 2013). On the other hand, the primary sink of hydrogen peroxide in the oceans is its biologically mediated decomposition (Moffett and Zafriou, 1990; Petasne and Zika, 1997). The efficiency in the decomposition is species-dependent. Thus, among the marine phytoplankton studied, Synechococcus sp. and Synechococcus costatum were found to be the most efficient and Pleurochrysis carterae and Dunaliella tertiolecta were the least efficient decomposers (Wong et al., 2003). Other minor sinks include chemical auto-decomposition (Szymszak and Waite, 1988; Cooper et al., 1994) and photochemical decomposition (Moffett and Zafriou, 1990). The life-times of hydrogen peroxide in seawater in the dark range between hours to days (Cooper et al., 1994; Petasne and Zika, 1997; Yuan and Shiller, 2001). Given its relatively short response times in its photochemical production and biological decomposition, the occurrence of hydrogen peroxide in the oceans represents primarily a kinetic balance between them. As a result of the separation of these two processes with depth, the concentration of hydrogen peroxide typically decreases quasi-exponentially with depth (Zika et al., 1985a, 1985b; Johnson et al., 1989). Yuan and Shiller (2004) recently reported that low concentrations, in 10^{-5} \mu M, of hydrogen peroxide may be found in deep water probably as a result of dark biological production.

The primary environmental conditions that affect the photochemical production and biological decomposition of hydrogen peroxide are: the concentration of dissolved organic matter, the solar irradiance and solar spectrum in its production, and, the level of biological activity in its decomposition. Relative to the oligotrophic ocean, the biological activities and the concentration of dissolved organic matter are both elevated in the shelf-seas. Moreover, total solar irradiance and the contribution of ultraviolet to the total irradiance tend to increase with decreasing latitude. These environmental characteristics intersect in the tropical shelf-seas which may provide a unique sub-environment for detecting how the interactions among these environmental conditions may affect the occurrence of hydrogen peroxide in the oceans. Past studies on the occurrence of hydrogen peroxide in the oceans tended to focus on the oligotrophic open oceans (Johnson et al., 1989; Miller and Kester, 1994; Sarthou et al., 1997; Yuan and Shiller, 2001, 2004, 2005; Avery et al., 2005) and inshore surface marine waters and freshwater (Cooper et al., 1989; Kieber and Helz, 1995). Systematic studies on the shelf-seas, and especially the tropical shelf-seas, are few. Here, we report the distribution of hydrogen peroxide in a sub-tropical shelf-sea, the Northern South China Sea Shelf-sea (NoSoCS).

2. Experimental

2.1. The study area

The Northern South China Sea Shelf-sea (NoSoCS) (Fig. 1) stretches southwestward from a ridge system, at about 23° N and 119° E, that delineates the southern end of the Taiwan Strait to the northeastern coasts of the Leizhou Peninsula and Hainan Island at about 20° N and 111° E, and, from the southeastern coast of China to the shelf-break at about the 120-m isobath. At the landward side, the highly urbanized Pearl River discharges into the middle section of the NoSoCS with an annual discharge of 330 km³ yr⁻¹, and it is the dominant source of freshwater to the NoSoCS. At the seaward side, a surface boundary current flows along the shelf edge and slope southwestward in the fall through the spring and northeastward in the summer in response to the forcing of the monsoonal wind (Gan et al., 2006). Furthermore, extensive activities of internal waves can be found along the entire outer-shelf and slope. These waves are formed at the Luzon Strait. As they propagate westward and reach the shallower waters at the outer shelf and slope of the NoSoCS, they undergo extensive refraction, transformation and dissipation (Lien et al., 2005; Li et al., 2008; Farmer et al., 2011; Guo et al., 2012). The largest of these waves, with amplitudes in excess of 150 m, are found around the Dongsha Atoll (Klymak et al., 2006; Farmer et al., 2011). Although the NoSoCS is connected to the Taiwan Strait to the north, free exchange is limited by a ridge which extends from Dongsha to the Taiwan Bank. The water depths along this ridge do not exceed about 40 m. The NoSoCS was connected to the Beibu Gulf to the southwest through the narrow Qiongzhou Strait which is situated between the Leizhou Peninsula and the Hainan Island. Coastal
upwelling, as a result of wind and/or topographic forcing, has been reported to occur in the NoSoCS in the summer off Shanwei to Shantou (Gan et al., 2009, 2010) and off the east coast of the Hainan Island (Lü et al., 2008). A more detailed description of the study area is given in other parts of this special issue (Pan et al., 2015; Wong et al., 2015-a, 2015-b).

2.2. Sampling

Fifty-four stations were occupied in four approximately equally spaced transects across the NoSoCS from the coast off Shantou (transect T1), Shanwei (transect T2), Macau (transect T3) and Maoming (transect T4) to the open northern South China Sea (SCS) in a direction that was approximately normal to the coast line aboard R/V Ocean Researcher I (OR-I) during cruise CR929 in the summer on June 2–15, 2010 (Fig. 1). At each station, the distributions of temperature, salinity, and fluourescence were recorded with a SeaBird model SBE 9/11 conductivity–temperature–depth (CTD) recorder and a Chelsea Aqua fluorometer. Discrete water samples were collected at 28 of the 54 stations, at approximately every other station, with GO-FLO bottles mounted onto a Rosette sampling assembly (General Oceanic). Of these 28 stations, 16 were occupied between 0800 and 2000 and these stations were designated as the day-time stations. The remaining 12 stations were occupied between 2000 and 0800 and they were designated as the night-time stations. Photosynthetically active radiation (PAR) was recorded with a Chelsea PAR sensor at 14 of the 16 day-time stations. Sub-samples were drawn from the discrete water samples, filtered immediately after sampling through 0.45 μm polyethersulfone filters (Millipore, Millex HP) and analyzed for the concentrations of hydrogen peroxide onboard ship. Sub-samples for the determination of total organic carbon (TOC) were drawn into and stored at −20 °C in pre-combusted brown borosilicate bottles immediately after sampling until they were analyzed in a shore-based laboratory. Sub-samples for the determination of chromophoric dissolved organic matter (CDOM) were filtered immediately after sampling through pre-combusted GF/F glass fiber filters (Whatman) and stored refrigerated at −5 °C until analyses. In addition, at a location northeast of the Dongsha Atoll, a station, Station A, was occupied over a 36-h period. CTD and fluorescence records were gathered once every two hours. Discrete water samples were collected simultaneously for the determination of hydrogen peroxide and TOC in the first 24 h at the station.

Solar irradiance was monitored continuously throughout the cruise onboard ship by using a Kipp and Zonen Model CMP22 broad band solar radiation measurement system.

2.3. Analytical method

Hydrogen peroxide was measured by the fluorometric method of Holm et al. (1987) as modified by Zhang and Wong (1999) and optimized by Wu (2012) by using a Turner Model 10-AU-005-CE filter fluorometer. This method is based on the bleaching effect of hydrogen peroxide on the fluorescence of scopoletin in the presence of horseradish peroxidase. In order to avoid any matrix effect, the concentration in each sample was quantified by internal addition individually. The precision and detection limit of the

Fig. 2. The vertical sections of potential temperature (θ), salinity (S) and chlorophyll-a across the shelf in transects (a) T1, (b) T2, (c) T3 and (d) T4. Locations of the stations are shown at the top of the figures.
method were ± 5% and 0.005 μM respectively. CDOM was determined by the method of Mitchell et al. (2002) and expressed as the absorption coefficient at 350 nm, α350 (Ferrari and Dowell, 1998), by measuring the absorbance of the sample from 280 to 800 nm with a Perkin Elmer Lambda 35 UV/VIS spectrophotometer. The precision of the measurement was about ± 0.02 m⁻¹. Total organic carbon (TOC) was determined by converting the organic carbon into carbon dioxide by high temperature combustion and then measuring the infrared absorption of the carbon dioxide formed (Knap et al., 1997; Hansell and Carlson, 1998) by using a Shimatsu Model TOC-V CPH total organic carbon analyzer. The precision of the measurement was about ± 2%. The concentration of chlorophyll-α was determined in particulate matter, which was collected on GF/F glass fiber filter, by high performance liquid chromatography (HPLC) (Wright et al., 1991) at a precision of ± 2% at a concentration of 4 μg L⁻¹. Supplemental data on the concentrations of chlorophyll-α were obtained from the fluorescence measurements by using the relationship between simultaneously measured fluorescence and the concentration of chlorophyll-α by HPLC.

### 3. Results and discussion

#### 3.1. The hydrography of and the hydrographic regimes in the NoSoCS

The distributions of temperature, salinity and chlorophyll-α in the four transects are shown in Fig. 2. Across the shelf from the coast to the northern SCS, the study area may be sub-divided into four hydrographic regimes: the inner shelf, middle shelf, outer shelf, and the open northern SCS. The open northern SCS may be further sub-divided into the continental slope and the deep SCS basin. In the inner shelf, in water depths of less than 40 m, the hydrography was significantly influenced by terrestrial input. The water column was vertically relatively well mixed and the water was frequently colder, fresher and the concentrations of chlorophyll-α were generally lower (Table 1). Nevertheless, a river plume associated with the Pearl River was not prominent during this cruise as sampling occurred prior to the arrival of the high flow in July (Wong et al., 2015-a, 2015-b) and waters with salinities below 33 were found only at one, the most landward, station in transect T4 off Maoming. On the other hand, in the outer shelf, in water depths of 90–120 m, the water was warmer, more saline and the concentrations of chlorophyll-α were lower. These hydrographic characteristics were similar to those in the adjoining continental slope, in water depths of 120 to 2000 m, and they indicated the dominating influence of mixing with the waters in the open northern SCS on the outer shelf. The deep SCS basin was located seaward of the slope in water depths exceeding 2000 m. The water in the middle shelf, in water depths of 40 to 90 m, was a mixture of the water in the inner and the outer shelf. With depth, as a first approximation, the NoSoCS was a two layer system: a warmer ( > 25 °C) and fresher ( < 34) mixed layer of about 40 m deep overlying a colder ( < 25 °C) and more saline ( > 34) bottom layer. This bottom layer on the shelf was actually a landward extension of the upper portion of the Tropical Water which formed the salinity maximum centering at around 150 m in the deep SCS basin (Wong et al., 2015-a, 2015-b).

Within the NoSoCS, summer coastal upwelling was indicated by the landward and upward tilting isotherms and isolahelines from about the middle shelf towards the coasts in transect T1 off Shantou. The undulations of the isotherms, isolahelines, and the isopleths of the sub-surface chlorophyll-maximum layer from about the middle shelf seaward to the adjoining continental slope in all four transects were indicative of the activities of internal waves along the entire shelf edge and continental slope. The undulations were most conspicuous along transect T2 at the vicinity of the Dongsha Atoll where the amplitude of the undulations reached around 50 m. A more detailed discussion of the climatology of the hydrography in the study area and the hydrography during this cruise are given in Pan et al. (2015) and Wong et al. (2015-a, 2015-b).

#### 3.2. Hydrogen peroxide in surface waters

Guided by the hydrographic characteristics, as a first approximation, the vertical distribution of hydrogen peroxide was treated as a two-layer system: a surface mixed layer where light was plentiful and photochemical production was prominent, and, a sub-surface layer where light was limited or virtually absent and decomposition dominated. Vertical mixing between these two layers was assumed to have only secondary effects on the distribution. This approximation seems reasonable as the production and decomposition of hydrogen peroxide occur in a time scale of hours to a few days (Petasne and Zika, 1997; Yuan and Shiller, 2001, 2005; Avery et al., 2005; Clark et al., 2009) while basin-wide vertical mixing is likely to occur in significantly longer time scales as the residence time of the mixed layer water in the adjacent northern SCS has been estimated to be in months to a year (Cai et al., 2004; Wong et al., 2007, 2015-a). Nevertheless, it is recognized that episodic vertical mixing by processes such as the actions of internal waves (Yang et al., 2004), eddies induced by cyclones (Lin et al., 2003) and upwelling (Gan et al., 2009, 2010) may occur at shorter time scales and the effect of vertical mixing has to be taken into account in a more refined modeling of the detailed vertical distributions of hydrogen peroxide (Sikorski and Zika, 1993a, b).

##### 3.2.1. Spatial variations

The average compositions of the water in the top 10 m of the water column at each station and in each hydrographic regime are listed in Table 1. (Since the average concentrations in the slope and the basin were similar to each other, they were combined and designated as the open northern SCS.) The range of concentrations of hydrogen peroxide, 0.063–0.231 μM, was well within those reported previously in other parts of the oceans (Zika et al., 1985a, 1985b; Johnson et al., 1989; Moore et al., 1993; Miller and Kester, 1994; Sarthou et al., 1997; Yuan and Shiller, 2001, 2005; Avery et al., 2005; Steigenberger and Croet, 2008). In each hydrographic regime, the average concentration in the day-time was invariably higher than that in the night-time, reflecting the dominating effect of photochemical production in the day-time and of biological decomposition in the night-time. The lowest average concentration, 0.07 μM, was found during the nighttime in transect T2 (Fig. 1) in the inner shelf off Shanwei where upwelling water, which is known to be low in hydrogen peroxide as found in the Peru upwelling region (Zika et al., 1985b), originated from the nearby Shantou (Gan et al., 2009, 2010) might have been brought to the surface. On the other hand, the highest concentration, 0.22 μM, was found during the day-time in the inner shelf away from the upwelling zone.

Following the general trend found in other coastal waters (Cauvet, 2002; Callahan et al., 2004), among the hydrographic regimes, the concentrations of TOC and CDOM were both the highest in the inner shelf and lower in the open SCS. The higher abundance of CDOM, which is indicative of the presence of chromophores, in the inner shelf would have enhanced the formation of hydrogen peroxide. Indeed, some of the highest concentrations of hydrogen peroxide, even exceeding 1 μM, have been found in surface inshore waters (Cooper and Zika, 1983; Clark et al., 2009). Across the NoSoCS, although the statistical
uncertainties were large, there were indications that the concentrations of hydrogen peroxide and TOC in the outer shelf were higher than those in the middle shelf and the open northern SCS. If these differences were real, they might have reflected the effect of the activities of internal waves which undergo transformation and dissipation in the outer shelf (Lien et al., 2005; Laurent, 2008; Farmer et al., 2011; Laurent et al., 2011). In the process, they may enhance the transfer of the nutrients in the sub-surface water to the mixed layer and elevate biological activity. Pan et al. (2012) reported that the temperature is lower, and, the nutrient concentrations and primary production are higher in these waters relative to those found in the deep basin at the Southeast Asian Time-series Study (SEATS) station. The higher biological productivity might have resulted in higher concentrations of TOC, which then in turn enhanced the photochemical production of hydrogen peroxide. Johnson et al. (1989) have reported that the concentration of hydrogen peroxide in the surface waters in the western Mediterranean Sea are positively correlated with the concentration of chlorophyll-a.

As a first approximation, this photochemical production of hydrogen peroxide may be treated as first order with respect to the time integrated irradiance, \(I_t\) (Wong and Wong, 2001) and the concentration of TOC, \([\text{TOC}]\) (Cooper and Zika, 1983; Cooper et al., 1988). Thus, it may be described by the rate law:

\[
d[H_2O_2]/dt=k[\text{TOC}]/I_t
\]

(1)

where \(t\) is the instantaneous light irradiance, and \(k\) is a rate constant which is related to the specific rate of absorption of photon by TOC and the quantum yield in the indirect reaction to produced hydrogen peroxide (Wong, 1989). In a given water type where the TOC stays the same qualitatively, then,

\[
[H_2O_2]=k[\text{TOC}]I_t+H_2O_2I_0
\]

(2)

where \([H_2O_2]_I\) is the concentration of pre-existing hydrogen peroxide at \(t=0\). For water types with similar \([H_2O_2]_I\) and qualitatively similar, but different concentrations of, TOC, \([H_2O_2]_I\) should be linearly related to \([\text{TOC}]I_t\). Indeed, there was a general trend of a direct relationship between the average concentration of hydrogen peroxide in the top 10 m at each day-time station, and, the product of \(I_t\) from the previous sunrise to the time of sample collection and the concentration of TOC (Fig. 3a). The data points lay along two approximately linear trends such that:

\[
[H_2O_2]_I(\mu M)=2.4(\pm 0.3) \times 10^{-7} ([\text{TOC}]I_t+0.07)(\pm 0.01), \ N=10; \quad r^2=0.89
\]

(3)
The relationship between the concentration of hydrogen peroxide, and, the product of the time-integrated irradiance ($I^*$) and (a) the concentration of TOC, and (b) CDOM in the top 10 m at individual stations in the different hydrographic regimes: ● – Inner shelf; ■ – Inner shelf upwelling area; △ – Middle shelf; ■ – Outer shelf; and ◆ – Open northern South China Sea.

\[
[H_2O_2] (\mu M) = 1.0 (\pm 0.5) \times 10^{-7} \left[ (\text{TOC}) \times + 0.18 (\pm 0.01) \right], \quad N=6; \quad r^2=0.54
\]

where $N$ is the number of data points and $r$ is the correlation coefficient. The data points from the inner and middle shelf fell mostly on relationship (3) while those from the outer shelf and open northern SCS fell mostly on relationship (4). These relationships suggest that the spatial and temporal variations in the concentrations of hydrogen peroxide in the day-time could be accounted for quite well by the light history of the water, and, the concentrations of TOC and pre-existing hydrogen peroxide in the water. The higher slope in the inner and middle shelf waters indicates that the quantum yield in the production of hydrogen peroxide might be higher in these waters and this is consistent with the reported pattern of decreasing yield from fresh and estuarine water to seawater (Avery et al., 2005). The difference in the intercepts suggests that the concentration of pre-existing hydrogen peroxide in the outer shelf and the open northern SCS was higher than that in the inner and middle shelf. This may reflect the higher biological activity and thus a more efficient biological decomposition of hydrogen peroxide in the coastal waters in the night-time so that the concentration might have reached a lower level at sunrise.

Likewise, there was also a general trend of a direct relationship between $[H_2O_2]$ and $[(\text{CDOM})\times]$, where (CDOM) is the absorption coefficient of CDOM at 350 nm. The data points clustered around two linear relationships (Fig. 3b):

\[
[H_2O_2] (\mu M) = 9.4 (\pm 4.2) \times 10^{-5} \left[ (\text{CDOM}) \times \right] + 0.07 (\pm 0.02), \quad N=6; \quad r^2=0.56
\]

\[
[H_2O_2] (\mu M) = 8.2 (\pm 4.2) \times 10^{-5} \left[ (\text{CDOM}) \times \right] + 0.17 (\pm 0.01), \quad N=10; \quad r^2=0.33
\]

Most of the data points from the inner and middle shelf fell on relationship (5) while most of those from the outer shelf and the open northern SCS fell on relationship (6). The correlation coefficients in these relationships were noticeably lower than those in relationships (3) and (4). This indicates that although CDOM may be linked more closely to the absorption of light by dissolved organic matter than TOC, it did not represent the subsequent production of hydrogen peroxide any better. The likelihood that CDOM from multiple sources, each with a different quantum yield in the photochemical formation of hydrogen peroxide, might have been present in varying proportions in different parts of the NoSoCS could have complicated the relationships and degraded the correlations. In fact, uniform relationships between CDOM or dissolved organic matter fluorescence and the photochemical production rate of hydrogen peroxide have not been found in previous studies (Moore et al., 1993; Scully et al., 1996; Herut et al., 1998; O’Sullivan et al., 2005; Steigenberger and Croot, 2008).

### 3.2.2. Diurnal variations at Station A

The variations in the concentration of hydrogen peroxide with time at 2 m and 10 m at Station A north of the Dongsha Atoll (Fig. 1) over a 24 h time period starting from 1800 h are shown in Fig. 4a. Similar to what has been widely observed in other parts of the oceans (Zika et al., 1985a, 1985b; Cooper and Lean, 1989; Miller and Kester, 1994; Yuan and Shiller, 2001; Avery et al., 2005; Steigenberger and Croot, 2008), the concentrations followed a distinct diurnal cycle at both depths, reaching a minimum just before sunrise and a maximum in the afternoon. At 2 m, an abrupt increase in concentration was observed at 1200 during a rain event which lasted till 1600. Subsequently, the concentration decreased with time and, by 1800, it reached a level that was back in line with the increasing trend prior to 12 noon. The abrupt increase in concentration was accompanied by a prominent decrease in salinity from 33.70 to 33.64. In comparison, in the absence of any precipitation, the salinity only reached a low of 33.65 about 12 h earlier as a result of the action of the internal waves alone (Fig. 4a). A similar, though less dramatic, increase in the concentration of hydrogen peroxide was also found at 10 m although the arrival of the peak concentration was delayed to 1400. These trends were consistent with a local episodic input of hydrogen peroxide by precipitation, whose concentration in hydrogen peroxide can easily be one to two orders of magnitude higher than those in the surface ocean (Zika et al., 1982; Cooper et al., 1987; Willey et al., 1996; Yuan and Shiller, 2000), followed by mixing with surrounding surface and sub-surface water with lower concentrations of hydrogen peroxide. Similar elevations in the concentration of hydrogen peroxide in surface seawater as a result of precipitation events have been reported previously (Cooper et al., 1987; Miller and Kester, 1994; Hanson et al., 2001; Kieber et al., 2001).

For a given type of marine phytoplankton and at a constant biomass, laboratory studies (Wong et al., 2003) have shown that the rate of the dark decomposition of hydrogen peroxide may be represented by

\[
-d[H_2O_2]/dt = (k') M[H_2O_2]
\]

Thus,

\[
\ln[H_2O_2] = -(k') M t + \ln[H_2O_2]_0
\]

where $k'$ is the specific rate constant in L $\mu$g-Chl-a$^{-1}$ h$^{-1}$, $M$ is the biomass in $\mu$g-Chl-a L$^{-1}$, $t$ is time in hours, and $[H_2O_2]$ and $[H_2O_2]_0$ are the concentrations of hydrogen peroxide in $\mu$M at time $t$ and...
The pre-existing concentration at \( t = 0 \). By assuming that the types and the biomass of the organisms had not changed substantially during the sampling period at Station A so that \( M \) was approximately constant, this model may then be applied to the night-time variations in the concentration of hydrogen peroxide between 2000 and 0400. At both 2 m and 10 m, an approximately linear relationship between \( \ln [\text{H}_2\text{O}_2] \) and time was found (Fig. 4b). At 2 m

\[
\ln [\text{H}_2\text{O}_2] (M) = -0.028 (\pm 0.007) t - 1.91 (\pm 0.04), \quad N = 5; \quad r^2 = 0.84 \quad (9)
\]

At 10 m,

\[
\ln [\text{H}_2\text{O}_2] (M) = -0.022 (\pm 0.005) t - 1.99 (\pm 0.02), \quad N = 5; \quad r^2 = 0.86 \quad (10)
\]

Data from the two depths yielded similar relationships within their statistical uncertainties. They were consistent with the biologically mediated decomposition of hydrogen peroxide as a major control of its concentration in the night-time. The slopes, in unit of \( h^{-1} \), were similar to those found in coastal waters in dark illumination experiments (Moore et al., 1993; Petasne and Zika, 1997; Yuan and Shiller, 2001, 2005). The corresponding half-lives of hydrogen peroxide were 25 and 32 h at 2 and 10 m. Since the average concentrations of chlorophyll-\( a \) at 2 m and 10 m were 0.10 ± 0.02 and 0.09 ± 0.02 \( \mu g L^{-1} \), the specific rate constants would be 0.28 and 0.26 L.\( \mu g \text{-Chl} a^{-1} h^{-1} \) respectively. These values were within, albeit at the high end of, the range reported in laboratory experiments using cultures of individual species of marine phytoplankton (Petasne and Zika, 1997; Wong et al., 2003). Thus, the temporal and spatial variations in the concentrations of hydrogen peroxide in the night-time are likely controlled primarily by its pre-existing concentration at sun-set and its biologically mediated decomposition.

The change in the concentration of hydrogen peroxide in the day-time was examined by using Eq. (2). Assuming that [TOC] and [\( \text{H}_2\text{O}_2 \)] stayed approximately constant over the sampling period at Station A, and, at a given depth, the time integrated irradiance was an approximately constant fraction of the surface value, \( I_s \), during the day-time, Eq. (2) is reduced to:

\[
[\text{H}_2\text{O}_2] = k \Phi[I_s] + [\text{H}_2\text{O}_2]_0
\]

where \( k/\Phi = k' [\text{TOC}] \). Indeed, at both 2 m and 10 m, excluding the samples that might have been affected by atmospheric precipitation, \([\text{H}_2\text{O}_2]_0\), in \( \mu M \), was linearly related to \( I_s \), in W-h m\(^{-2}\) (Fig. 4c).

At 2 m, at 0600–1000 and at 1800

\[
[\text{H}_2\text{O}_2] = 2.0 (\pm 0.5) \times 10^{-5} I_s + 0.139 (\pm 0.005), \quad N = 4; \quad r^2 = 0.90 \quad (11)
\]

At 10 m, at 0600–1200 noon and at 1800,

\[
[\text{H}_2\text{O}_2] = 2.6 (\pm 0.7) \times 10^{-5} I_s + 0.129 (\pm 0.008), \quad N = 5; \quad r^2 = 0.82 \quad (12)
\]

These relationships were indistinguishable from each other within their statistical uncertainties. The slopes, in unit of \( \mu M \) m\(^2\) (W-h\(^{-1}\)), represent the rate constant in the photochemical production of hydrogen peroxide and they are within the range of values found in the irradiation of seawater samples (Moore et al., 1993; Yocis et al., 2000). Since the average concentrations of TOC at 2 and 10 m over the same time-period were 80 ± 6 and 75 ± 6 \( \mu M \), the corresponding values of \( k \) were 2.6 \( \times 10^{-7} \) and 3.5 \( \times 10^{-7} \) m\(^2\) (W-h\(^{-1}\)). These rate constants were similar to those estimated previously in Eqs. (3) and (4) in the surface 10 m of the NoSoCS as a whole. If the concentrations at 1200–1600 above the linear relationships are assumed to have originated from the precipitation event, then, the event would have led to up to a doubling of the ambient concentration. Such a significant episodic elevation in concentration could have an impact on the reactions between hydrogen peroxide and other trace species.

### 3.3. Sub-surface distributions of hydrogen peroxide

#### 3.3.1. Stations with typical vertical profiles

Typically, both the concentration of hydrogen peroxide (Zika et al., 1985a, 1985b; Johnson et al., 1989; Yuan and Shiller, 2001; Avery et al., 2005) and solar irradiance (Kirk, 1994) are known to decrease quasi-exponentially with depth and eventually reach close to undetectable or undetectable levels. Indeed, during this study, the distribution of PAR, the dominant fraction of the solar irradiance that may induce the photochemical production of hydrogen peroxide beyond several meters deep when ultraviolet light has been removed, could be represented well at all stations by the relationship:

\[
\text{PAR} (\text{W m}^{-2}) = a Z + b'
\]

where \( Z \) is depth in m, \( a' \) is the depth–decay constant of PAR, and \( b' \) is the natural log of the PAR at the sea surface. The correlation coefficients, \( r^2 \), clustered between 0.930 and 0.997 (Table 2). On the other hand, the distributions of hydrogen peroxide at only 12 out of the 16 day-time stations and 7 out of the 12 night-time
hydrogen peroxide increased towards the coast, from day-time photochemical production, additional processes, such as dark physical mixing process so that these chemical and biological stations might be represented well by the corresponding relationship:

\[
\ln[\text{H}_2\text{O}_2] = aZ + b
\]

where \(a\) is the depth–decay constant of hydrogen peroxide and \(b\) is the natural log of the concentration of hydrogen peroxide at the sea surface (Table 2). The correlation coefficients, \(r^2\), ranged between 0.75 and 1.00, and were mostly above 0.85. These relatively small fractions of the profiles that followed the typical pattern in parallel with the distribution of irradiance indicate that while the availability of light might have been a major control on the vertical distribution of the concentration of hydrogen peroxide, it was not the only controlling mechanism even in the daytime. In the night-time, the dominant process, the biological decomposition of hydrogen peroxide whose depth-dependence was related to that of bio-mass and would be different from that of irradiance in the daytime, could have modified the shape of the day-time profile so that, relative to the day-time stations, a larger fraction of the night-time stations behaved atypically. At the daytime stations, both the depth–decay constants of PAR and those of hydrogen peroxide increased towards the coast, from \(-0.062\) and \(-0.015\) m\(^{-1}\) in the open northern SCS to \(-0.112\) and \(-0.020\) m\(^{-1}\) in the inner shelf respectively. These were indicative of the expected increase in turbidity towards the coast and the effect of the associated light-availability on the concentration of hydrogen peroxide.

The depth at which the concentration of hydrogen peroxide and PAR have dropped to one half of their respective surface values, \(Z_{1/2}\), are given by

\[
Z_{1/2} = -\ln(2)/a
\]

The values of \(Z_{1/2}\) ranged between 24 and 78 m but mostly were less than 50 m (Table 2). Thus, the concentration of hydrogen peroxide could vary significantly even within the mixed layer which was about 40 m thick. This suggests that the time-scales of the chemical and biological processes that affected the concentration of hydrogen peroxide were at least comparable to that of the physical mixing process so that these chemical and biological processes may be the primary determining factor of the vertical distribution of hydrogen peroxide as assumed in the previous discussion in approximating the NoSoCS as a two-layer system. The values of \(Z_{1/2}\) could only be estimated at the day-time stations, and they varied between 5 and 11 m. The average values of \(Z_{1/2}\) at the different hydrographic regimes were four to six times the corresponding \(Z_{1/2}\) (Table 2). This indicates that significant concentrations of hydrogen peroxide were present in waters where light was virtually absent. Thus, in addition to photochemical production, additional processes, such as dark

<table>
<thead>
<tr>
<th>Hydrographic regime</th>
<th>Station</th>
<th>(\ln[\text{H}_2\text{O}_2] = aZ + b)</th>
<th>(Z_{1/2}) (m)</th>
<th>(\ln\text{PAR} = a'Z + b')</th>
<th>(Z'_{1/2}) (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day-time stations</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I-U</td>
<td>10</td>
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<td>34</td>
<td>(-0.099 \pm 0.001)</td>
<td>35</td>
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<td>I-U</td>
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<td>34</td>
<td>(-0.132 \pm 0.003)</td>
<td>28</td>
</tr>
<tr>
<td>I</td>
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<td>34</td>
<td>(-0.107 \pm 0.003)</td>
<td>27</td>
</tr>
<tr>
<td>I</td>
<td>44</td>
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<td>42</td>
<td>(-0.111 \pm 0.003)</td>
<td>28</td>
</tr>
<tr>
<td>Average I</td>
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<td>(-0.020 \pm 0.003)</td>
<td>35</td>
<td>(-0.112 \pm 0.014)</td>
<td>6</td>
</tr>
<tr>
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<td>26</td>
<td>(-0.079 \pm 0.001)</td>
<td>38</td>
</tr>
<tr>
<td>M</td>
<td>8</td>
<td>(-0.015 \pm 0.005)</td>
<td>7</td>
<td>(-0.067 \pm 0.021)</td>
<td>60</td>
</tr>
<tr>
<td>M</td>
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<td>NR</td>
<td>41</td>
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<td>12</td>
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<tr>
<td>M</td>
<td>34</td>
<td>(-0.018 \pm 0.001)</td>
<td>39</td>
<td>(-0.067 \pm 0.001)</td>
<td>9</td>
</tr>
<tr>
<td>M</td>
<td>46</td>
<td>(-0.016 \pm 0.002)</td>
<td>44</td>
<td>(-0.057 \pm 0.001)</td>
<td>9</td>
</tr>
<tr>
<td>Average M</td>
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<td>(-0.019 \pm 0.005)</td>
<td>38</td>
<td>(-0.059 \pm 0.001)</td>
<td>9</td>
</tr>
<tr>
<td>O</td>
<td>30</td>
<td>(-0.013 \pm 0.002)</td>
<td>52</td>
<td>(-0.067 \pm 0.001)</td>
<td>9</td>
</tr>
<tr>
<td>P-S</td>
<td>21</td>
<td>NR</td>
<td>47</td>
<td>(-0.069 \pm 0.001)</td>
<td>10</td>
</tr>
<tr>
<td>P-S</td>
<td>23</td>
<td>NR</td>
<td>47</td>
<td>(-0.062 \pm 0.001)</td>
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</tr>
<tr>
<td>P-S</td>
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<td>NR</td>
<td>47</td>
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</tr>
<tr>
<td>P-B</td>
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<td>38</td>
<td>(-0.067 \pm 0.001)</td>
<td>10</td>
</tr>
<tr>
<td>P-B</td>
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<td>38</td>
<td>(-0.067 \pm 0.001)</td>
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</tr>
<tr>
<td>P-B</td>
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<td>53</td>
<td>(-0.067 \pm 0.001)</td>
<td>11</td>
</tr>
<tr>
<td>Average P</td>
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<td>47</td>
<td>(-0.062 \pm 0.005)</td>
<td>11</td>
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<tr>
<td>Night-time stations</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
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<td>9</td>
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<tr>
<td>I</td>
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<td>9</td>
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<tr>
<td>I</td>
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<td>NR</td>
<td>24</td>
<td>(-0.067 \pm 0.001)</td>
<td>9</td>
</tr>
<tr>
<td>I</td>
<td>38</td>
<td>NR</td>
<td>24</td>
<td>(-0.067 \pm 0.001)</td>
<td>9</td>
</tr>
<tr>
<td>I</td>
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<td>9</td>
</tr>
<tr>
<td>M</td>
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<td>(-0.067 \pm 0.001)</td>
<td>9</td>
</tr>
<tr>
<td>M</td>
<td>48</td>
<td>(-0.019 \pm 0.001)</td>
<td>36</td>
<td>(-0.067 \pm 0.001)</td>
<td>9</td>
</tr>
<tr>
<td>O</td>
<td>19</td>
<td>(-0.014 \pm 0.003)</td>
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<td>(-0.067 \pm 0.001)</td>
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<tr>
<td>O</td>
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<td>NR</td>
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<td>NR</td>
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<td>P-S</td>
<td>26</td>
<td>NR</td>
<td>42</td>
<td>(-0.067 \pm 0.001)</td>
<td>9</td>
</tr>
</tbody>
</table>

I = inner shelf; U = upwelling area; M = middle shelf; O = outer shelf; P = open northern SCS; S = continental slope; B = basin.

\(a\), \(b\) = slope and intercept in \(\ln[\text{H}_2\text{O}_2] = aZ + b\) where \([\text{H}_2\text{O}_2]\) is the concentration of hydrogen peroxide and \(Z\) is depth.

\(a'\), \(b'\) = slope and intercept in \(\ln\text{PAR} = a'Z + b'\); \(N\) = number of data points; \(r\) = correlation coefficient; \(ND\) = no data.

\(Z_{1/2}\), \(Z'_{1/2}\) = the depth at which the concentration of hydrogen peroxide and PAR have dropped to one half of their surface values.

\(NR\) = not logarithmically related. Uncertainties given represent one standard deviation.
These stations may be separated into two groups: six stations, 70 m deep. The inner shelf and one in the middle shelf, in waters of no more than water depths exceeding 100 m, and, three stations, with two in the outer shelf (night-time Station 50 (Δ)) and slope (day-time station 21 (●), 23 (●) and 52 (●)); night-time station 26 (○) and 28 (●)); (b) Stations in the inner shelf (night-time station 36 (●) and 38 (○)) and the middle shelf (day-time station 32 (●)). The dot-dash line denotes the profile in the basin at day-time station 25.

3.3.2. Stations with atypical vertical profiles

At nine out of the 28 stations, or about a third of the stations, the profiles of hydrogen peroxide did not follow the typical shape. These stations may be separated into two groups: six stations, with five in the continental slope and one in the outer shelf, in water depths exceeding 100 m, and, three stations, with two in the inner shelf and one in the middle shelf, in waters of no more than 70 m deep. The first group of stations was located in an area where the activities of the internal waves were especially prominent (Li et al., 2008; Farmer et al., 2011; Guo et al., 2012) and it included all but one of the stations situated in the continental slope. Their depth profiles in hydrogen peroxide are shown in Fig. 5a. These profiles were characterized by generally elevated concentrations down to about 100 m. The concentrations did not dip below 0.15 µM in the top 100 m at five of these six stations. In contrast, in the deep basin of the northern SCS, the concentration dropped below this value by about 40 m. Furthermore, sub-surface maxima were superimposed on these elevated concentrations. A particularly prominent and persistent one, centering at around 70–80 m at the vicinity of the chlorophyll maximum (Fig. 2), was present in all six profiles. The highest concentration found at this maximum reached around 0.5 µM, a concentration that exceeded the surface concentrations, at both the day-time and the night-time stations at Stations 23, 26 and 28. Profiles of similar shape and at these concentration levels have not been reported previously in the open oceans. Several lines of reasoning indicate that these features were not likely a sampling or analytical artifact. First, the elevated concentrations were found consistently at approximately the same depth within a defined hydrographic regime. Secondly, at three out of the six stations, the maximum was defined by more than one data point. Thirdly, while the concentrations above 100 m were elevated, below the maximum, the concentration dropped precipitously and reached the low concentrations found at similar depths in the deep basin of the SCS where the depth profile of hydrogen peroxide followed the typical distributional pattern.

The processes that might have given rise to these atypical profiles are uncertain. Photochemical production was not a plausible explanation since the elevated concentrations and especially the persistent concentration maximum were found at depths where light had become virtually absent and PAR had dropped to a percent or less of the surface value. Furthermore, similar distributions were found at the day-time and the night-time stations (Fig. 5a). In fact, the highest concentration of hydrogen peroxide at the maximum was found at the night-time stations, Station 25 and 28. On the other hand, while the process is still not fully understood, there is increasing evidence indicating that many more species of marine organisms than previously thought, including multiple species of phytoplankton and microalgae (Palenik et al., 1987; Kustka et al., 2005; Rose et al., 2005; Marshall et al., 2005), symbionts in corals (Lesser, 1997; Smith et al., 2005; Suggett et al., 2008; Saragosti et al., 2010), and heterotrophic bacteria (Diaz et al., 2013), can produce hydrogen peroxide or its immediate precursor, superoxide, even in the dark. Field observations also reported dark, likely biological, production of hydrogen peroxide at rates that could even be comparable to the local photochemical production rate (Palenik and Morel, 1988; Vermilyea et al., 2010). If there is indeed a widespread occurrence of dark biological production of hydrogen peroxide as suggested in a recent report (Shaked and Rose, 2013), it can be a viable explanation for the elevated concentrations found in this group of atypical profiles.

The actions of internal waves along the outer shelf and slope of the NoSoCS might also have played a role in the occurrence of these atypical profiles. When the internal waves reach these shallower waters as packages of solitons with progressively smaller amplitudes, they undergo wave interference, refraction, transformation and even dissipation (Orr and Mignerey, 2003; Duda et al., 2004; Ramp et al., 2004; Yang et al., 2004; Farmer et al., 2011) and release their energy as turbulence (Lien et al., 2005; Laurent, 2008; Laurent et al., 2011). Since individual solitons can reach depths exceeding 150 m with a life time of a fraction of an hour in this area (Farmer et al., 2011), they may conceivably influence the distribution of hydrogen peroxide in the top 100 m in several ways. First, surface water, which is rich in hydrogen peroxide, may be injected into different depths in the sub-surface, even below the mixed layer and the euphotic zone. Secondly, the associated turbulence in the transformation and dissipation of the internal waves will tend to homogenize the upper water column.
and cause a general elevation in the concentration of hydrogen peroxide. Thirdly, the internal waves may bring sub-surface water with different concentrations of chlorophyll-*a* from various depths to the photic zone, where it may be exposed to sunlight and acquire different concentrations of hydrogen peroxide before it is returned to the sub-surface since Johnson et al. (1989) have reported that the efficiency in the photochemical production of hydrogen peroxide in seawater is directly related to the concentration of chlorophyll-*a*. Fourthly, in companion studies in the study area, Shiah and his co-workers (Lai et al., 2014; Kuo et al., 2015; Shiah, private communication) found elevated bacterial activities, as much as eight times those in the surrounding ambient waters, in the waters around the Dongsha Atoll where internal waves are active. The higher bacterial production could reach 100 m and they could be punctuated with sub-surface maxima. If superoxide, and thus hydrogen peroxide, is produced in bacterial activity (Diaz et al., 2013), these elevated bacterial activities at the outer shelf and slope of the NoSoCS would favor the dark production of hydrogen peroxide. Qualitatively then, the combined effects of these processes may account for the generally elevated concentrations and the presence of sub-surface maximum in hydrogen peroxide in these atypical profiles.

At Station A, which was located in the slope north of the Dongsha Atoll (Fig. 1), in a 36-h period, the temporal variations in temperature clearly indicated the effects of the internal tides (Fig. 6a). The isotherms undulated regularly with a period of about 12 h and an amplitude of about 50 m. The undulations were asymmetrical. The peaks were found at around 0000, 1100 and 2200 on June 9 while the troughs were located at about 0300, 1300 on June 9 and 0200 on June 10. At a sampling interval of two hours, the occurrence of the highly dynamic solitons, which should have appeared between the trough and the ensuing peak of the internal tides (Liu et al., 1998; Farmer et al., 2011), was not captured by the isotherms. The corresponding isopleths in hydrogen peroxide at the three shallow depths and the isopleths of hydrogen peroxide with concentrations exceeding 0.15 μM at the top 40 m between 1300 and 1800 on June 9 in the broad trough of the internal wave when solitons should have been active may be interpreted as the evidence for the combined effect of the accumulation of photochemically and biologically produced hydrogen peroxide and vertical mixing by the solitons. A similar pattern was not found in the night-time between 0300 and 0800 on June 9 when there was no photochemical production of hydrogen peroxide. However, the concentration of hydrogen peroxide was quite uniform down to 40 m and this might be an indication of the combined effect of biological production and the mixing by the solitons.

The atypical profiles of hydrogen peroxide at the three shallow stations are shown in Fig. 5b. The concentrations were high, exceeding 0.1 μM at all depths, and were rather uniformly distributed with depth. In these coastal waters, the concentrations of organic carbon (Pan et al., 2015) and chlorophyll-*a* (Fig. 2) and the bacterial production (Lai et al., 2014) were high so that both the photochemical and the biological production of hydrogen peroxide would be favored and they may have given rise to the elevated concentrations. These major sources and the major sink, namely, biological decomposition, of hydrogen peroxide could have varied with depth independently but efficient physical mixing, as indicated by the almost isothermal and isohaline water column, might have effectively masked their effects at these shallow depths and resulted in the approximately uniform distribution with depth.

4. Conclusions

In the surface waters in the NoSoCS, the temporal and spatial variations in the concentration of hydrogen peroxide were controlled in the day-time primarily by the pre-existing concentration, the light history, and, the concentration and the chemical nature of the organic matter, and, in the night-time by the pre-existing concentration and biological decomposition. Atmospheric precipitation probably had resulted in episodic but significant elevations in the concentration.

With depth, about a third of the profiles did not follow the typical pattern of a quasi-exponential decrease in concentration with depth. Almost all the stations in the slope where the activity of internal waves was extensive were atypical. In these waters, the concentration of hydrogen peroxide was generally elevated, with concentrations exceeding 0.15 μM to about 100 m, and a concentration maximum at 80 m was persistently found. Although the exact origin of these atypical distributions cannot yet be

![Fig. 6. The variations in (a) temperature over a 36 h period of time, and (b) the concentration of hydrogen peroxide over the first 24 h in the top 100 m at time-series station A.](image)


