

Short-term dynamics of nutrients influenced by upwelling in a small oligotrophic coastal ecosystem, Gan Bay, in the northwest Philippines

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Received 2 July 2008; received in revised form 10 October 2008; accepted 27 October 2008

Abstract

We present a time-series analysis of nutrient and $p\text{CO}_2$ (partial pressure of CO_2) levels in an oligotrophic coastal ecosystem (Gan Bay), which was likely to be influenced by upwelled subsurface water. Gan Bay is off Currimaio Harbor, in the northwest Philippines and is located at the boundary of the South China Sea (SCS). This 42-h time-series observation was conducted in December 2006. In addition to continuous observations of dissolved oxygen (DO) and $p\text{CO}_2$, discrete samples were collected at a depth of 5 m every 3 h for measurements of nutrients, including soluble reactive phosphorus (SRP) and inorganic nitrogen ($\text{NO}_3^- + \text{NO}_2^-$) in order to examine their dynamics and possible physical and biological controls. We observed remarkably large short-term variations in the surface water, spanning a 10-fold change for SRP (32–330 nM) and from $<0.3 \mu\text{M}$ to $4.3 \mu\text{M}$ for $\text{NO}_3^- + \text{NO}_2^-$. DO also varied substantially from a lower end of 171 to 205 $\mu\text{M O}_2$. Surface water $p\text{CO}_2$ changed from an equilibrium stage with the atmosphere ($\sim 386 \mu\text{atm}$) to a stage where it was a significant source for the atmospheric CO_2 (seawater $p\text{CO}_2 \sim 469 \mu\text{atm}$). We found that the variation of nutrients was driven neither by tidal mixing nor by biological activities, as was suggested by the variations in the total bacterial abundance and chlorophyll a. Instead, our inverse T – S relationship suggested a two end-member mixing process during the observation period. The N:P ratio throughout the observation period was ~ 13.2 , which is characteristic of SCS subsurface and deep waters. Moreover, $p\text{CO}_2$ was correlated inversely with the sea surface temperature. It is likely, therefore, that an upwelled subsurface cold water with high nutrients, low-temperature and high- $p\text{CO}_2$ existed. It should be noted that this upwelled cold water did not appear to impact the entire observation period (approximately 35 h of 42 h), which might suggest an extremely dynamic nature for this upwelled cold water mass.

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Keywords: Gan Bay; South China Sea; Nutrient dynamics; Upwelling

1. Introduction

Many physical and biogeochemical processes in the ocean exert dynamic changes at very short (such as diurnal) time scales. These include tidal cycling, radiation forcing [1] and temperature fluctuations in biological metabolism [2]. Knowledge of short-term variations of

physical, biological and chemical parameters is essential to our biogeochemical understanding of a specific system and this is particularly true in coastal sea systems [3], where tidal effects are usually prominent. Although our knowledge concerning the range of diurnal changes and their control is very limited, field studies of short-term variability are emerging. For example, Gago et al. [4] presented the effect of short-term variations (<1 week) of an upwelling event on CO_2 fugacity in a coastal upwelling ecosystem, the Ria de Vigo.

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In the tropical and/or subtropical portions of the world oceans, surface waters are generally nutrient depleted [5], and the regeneration of nutrients by heterotrophic grazers is not sufficient to maintain phytoplankton productivity [6]. Thus, additional pathways to supply nutrients into the euphotic zone are required. Growing evidence suggests that upward nutrient pumping may provide a significant fraction of the nutrients sustaining new production in the upper ocean [7]. In this context, it is arguable that the dynamic oceanographic processes occurring at the short time scale may be crucial in regulating upper ocean productivity. For example, Zhang et al. [8] noted an intensive diurnal cycle of surface water nutrients, and the biological consumption of which was balanced by supplies from depth through physical processes.

Here we present a study of short-term variations in an oligotrophic coastal ecosystem (Gan Bay) to exemplify the nutrient dynamics within a very short-time scale (<2 days). In this study, we observed remarkably large-amplitude short-term variations of nutrients in the surface water, which appeared to be impacted by upwelled subsurface waters. A multi-parameter approach was used to assess the hydrological and biogeochemical processes in controlling nutrient variability.

2. Materials and methods

2.1. Study area and sampling

The SCS is the largest oligotrophic marginal sea in the tropics and subtropics. Climatic variations in the atmosphere and in the upper ocean of the SCS are primarily controlled by the East Asian Monsoon.

Gan Bay (Fig. 1), also known as Ga-ang Bay or Currimao Harbor, penetrates on the western coast of northern Luzon Island, which is located on the boundary between

the Provinces of Ilocos Sur and Ilocos Norte, in the Philippines. Gan Bay has a similar topography to the Ria de Vigo (NW Iberian peninsula, Spain) [9], but without any river input. Thus far, there is no information concerning the biogeochemistry of this bay in the available literature.

Our major observation station (Z86, Fig. 1b) is located at 120° 28'E and 18°N, ~4 km away from the coastline. The water depth at this site is about 37 m and the tide has a regular diurnal cycle with a tidal height varying from 0.5 to -0.3 m (Fig. 2).

At station Z86, a time-series of 15 hydrocasts were conducted at approximately 3-h intervals between 18:00 on December 18 and 12:00 on December 20, 2006 (GMT + 8), covering two diurnal tidal periods. Samples for soluble reactive phosphorous (SRP), nitrate + nitrite ($\text{NO}_3^- + \text{NO}_2^-$, referred to as N + N hereafter), dissolved oxygen (DO) and pH were collected with a 5 L Niskin bottle at 5 m depth. Together with the discrete samples, surface water (at a depth of ~5 m) was pumped aboard for continuous measurements of partial pressure of CO_2 ($p\text{CO}_2$), DO, pH, temperature and salinity using an underway pumping system. At the end of the time-series sampling, we conducted additional hydrochemical casts at station Z86 and two adjacent stations (Z87 and Z88, see Fig. 1b) to set a reference for the hydrochemical conditions of the region.

2.2. Analytical methods

SRP concentrations were measured using two independent methods. For SRP >500 nM, the detection was based on the standard molybdenum blue procedure [10]. The uncertainty of the measurements was $\pm 2\%$. For samples with low SRP concentrations (<500 nM), measurements were taken with a home-made ship-board C18 enrichment-flow injection analysis system [11,12]. The analytical

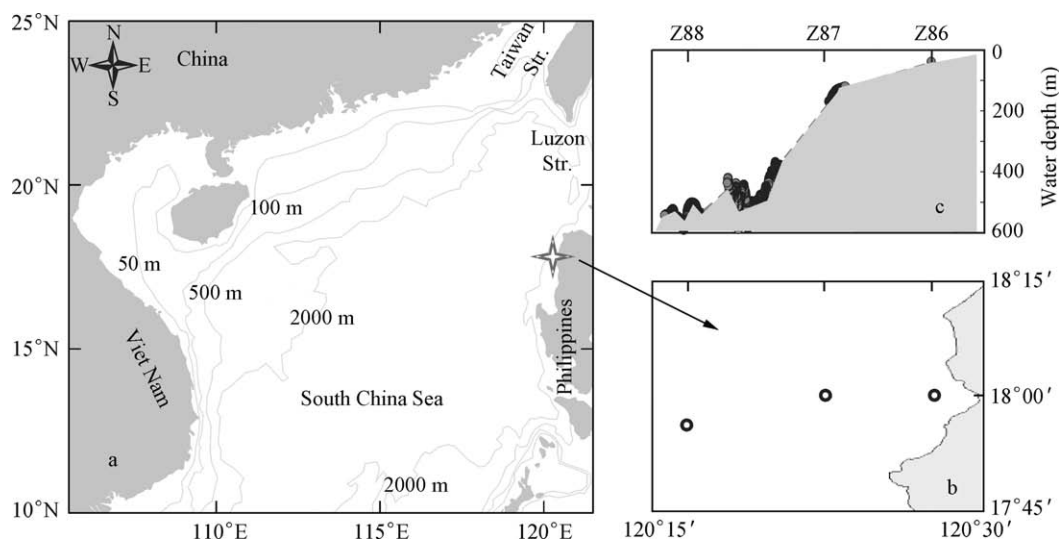


Fig. 1. Map of the study area. (a) the South China Sea; (b) the Gan Bay showing the sampling stations, where Z86 is the time-series station; (c) the water depth along the offshore track.

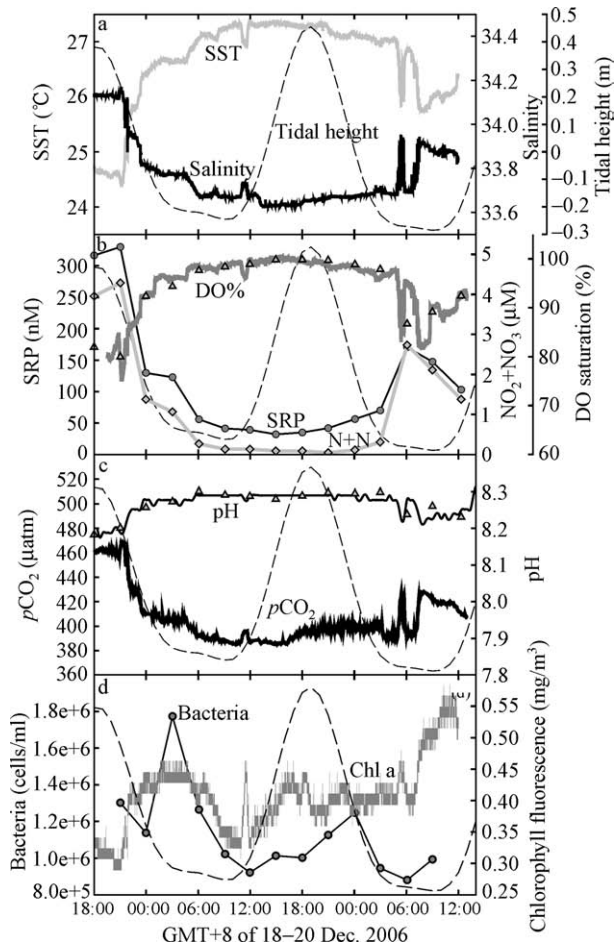


Fig. 2. Short-term variations of (a) SST, salinity and tidal height; (b) surface DO saturation, N + N and SRP; (c) $p\text{CO}_2$ and pH; (d) the total bacterial abundance (Jiao et al., unpublished data) and chlorophyll fluorescence values between December 18 and 20, 2006 at station Z86, Gan Bay, NW Philippines.

precision of this method was $\sim 3\%$. Samples were analyzed immediately after sampling or refrigerated at 4°C and analyzed within 3–6 h upon sampling.

N + N was measured by reducing NO_3^- to NO_2^- with a Cd column, and then determining NO_2^- using the standard pink azo dye method, and a flow injection analyzer [13]. The uncertainty of this method was about 1%.

A SEACAT thermosalinograph system (CTD, SBE21, Sea-Bird Co) was used to continuously determine sea surface temperature (SST) with a precision of $\pm 0.001^\circ\text{C}$, and salinity with a precision of ± 0.001 based on conductivity measurements. Chlorophyll *a* (Chl *a*) fluorescence was measured using a fluorometer (WETStar, WETLab Inc.) incorporated into the underway CTD. Another CTD system (SBE911+, Sea-Bird Co.) was used to obtain vertical profiles of temperature and salinity. Both CTD systems were calibrated just prior to the cruise. Depth profiles of Chl *a* concentrations were determined on acetone-extracted samples using the standard fluorometric spectrophotometer method [14].

$p\text{CO}_2$ was determined using a system that combined a Li-Cor[®] non-dispersive infrared (NDIR) spectrometer (Li-7000) with a continuous flow equilibrator, as detailed in Zhai et al. [15,16]. For calibration, a series of CO_2 gas standards with $x\text{CO}_2$ values of 200×10^{-6} , 386×10^{-6} and 468×10^{-6} (provided by the National Research Center for Certificated Reference Materials of China) were applied. The overall uncertainty of the contents of these standards was $< 1\%$. pH (NIST-scale) determination was as detailed in Zhai et al. [16].

Surface DO was continuously measured using a DO probe (WTW[®] CelloX 325). The DO probe had a resolution of 0.1% of saturated DO. The continuous DO data were calibrated against discrete DO data, which were collected on board using the classic Winkler titration method. The latter had an uncertainty of $1 \mu\text{mol O}_2 \text{ L}^{-1}$.

3. Results

3.1. Short-term variations of surface hydrochemistry

The variations of hydrographic and biogeochemical parameters between 18:00 on December 18, 2006 and 12:00 on December 20, 2006 are presented in Fig. 2a–d. High tides generally occurred at $\sim 18:00$ and low tides existed at $\sim 09:00$, with values ranging from 0.51 to 0.29 m, which showed a regular diurnal tide cycle. During this short-term period, there was a slight fluctuation in near-surface salinity (~ 0.54), which ranged from 34.17 to 33.63, suggesting that there was no major influence of any fresh water input. SST increased from 24.38 to 27.36°C with an amplitude in the fluctuation of 3°C (Fig. 2a). At the same time, SRP and N + N showed a distinct synchronous variation with the seawater $p\text{CO}_2$ and salinity, and a mirroring variation with DO%, pH and SST (Fig. 2). However, there were no apparent correlations between nutrients and tidal cycles.

It is known that the oligotrophic ocean is characterized by generally low (down to nanomolar) levels of nutrients in the surface water. Remarkably, we observed large short-term variations in the surface water, spanning a 10-fold change in SRP (32–330 nM) and N + N (from $< 0.3 \mu\text{M}$ to $4.3 \mu\text{M}$) (Fig. 2b). DO also varied substantially from 171 to $205 \mu\text{M O}_2$. Surface water $p\text{CO}_2$ changed from an equilibrium stage with the atmosphere ($\sim 386 \mu\text{atm}$) to a stage as a significant CO_2 degassing event ($\sim 469 \mu\text{atm}$) to the atmospheric CO_2 . pH ranged from 8.2 to 8.3 (Fig. 2c). The surface Chl *a* variation revealed a typical biological diel variation for oligotrophic waters, which was low during the day and high at night with the highest value at midnight and the lowest value at noon (Fig. 2d). The total bacterial abundance also showed similar biological diel variation (Fig. 2d – data from Jiao et al., unpublished). The time when the extreme values of a suite of chemical and hydrographic parameters appeared was consistent; thus, high values of salinity, nutrients (SRP, N + N) and $p\text{CO}_2$ occurred at 21:00 on December 18, whereas low

values existed at 15:00–21:00 on December 19; and SST, DO and pH followed the inverse pattern.

The amplitudes of fluctuation were 298 nM for SRP and 4.3 μM for N + N, respectively, and these changes in SRP and N + N were significantly larger than the analytical uncertainties and should therefore reflect real changes in nutrient dynamics. In contrast to the fluctuation from 1 μM to below 100 nM in an oligotrophic anticyclonic eddy in the northeast Atlantic [8] and from ~ 8 to 0.5 μM in the analog Ria de Vigo [17], our result described above was in the middle. The fluctuation of $p\text{CO}_2$ determined in this study (386–469 μatm) was slightly lower than that in 285–616 μatm in the Ria de Vigo [4].

3.2. Hydrochemistry at the time-series station and in nearby offshore coastal waters

Upon the completion of the time-series observation at station Z86, we conducted additional hydrochemical casts at station Z86 and at two adjacent stations (Z87 and Z88) in order to better characterize the region. The observed hydrography (Fig. 3a and b) revealed that surface water at the near shore station (Z86) was ca. 1.3 $^{\circ}\text{C}$ cooler

and 0.3 saltier than the surface water at the offshore stations (Z87 and Z88), which is clearly atypical in coastal regions, and apparently under the influence of upwelling (see further details in the discussion section). The surface water at the near shore station (Z86) contained 103 nM of SRP, 1.4 μM of N + N, and 192 μM of DO, while at station Z87, SRP and N + N concentrations were low, down to 31–38 nM or even undetectable in the upper 25 m of the water column. Similarly, SRP and N + N concentrations at station Z88 were down to 35–38 nM and undetectable in the upper 50 m of the water column. Surface DO at stations Z87 and Z88 was as high as up to 206 μM (Fig. 3c–e). A high Chl *a* value of $\sim 0.6 \text{ mg/m}^3$ was observed at the surface of station Z86, which was consistent with our continuous observation (Fig. 2d). As a comparison, surface Chl *a* declined to $\sim 0.1 \text{ mg/m}^3$ at adjacent stations Z87 and Z88, although the distance between these three stations is no more than 10 km. The maximum Chl *a* ($\sim 0.96 \text{ mg/m}^3$) occurred at a depth of $\sim 40 \text{ m}$ at station Z87 and relatively high integrated values (0.6–0.8 mg/m^3) were observed in the water column of station Z86. As for station Z88, the water column exhibited oligotrophic conditions typical of the SCS with a Chl *a* concentration of 0.1–0.3 mg/m^3 (Fig. 3f).

4. Discussion

Nutrients are typical nonconservative elements and hence the resulting patterns of their distribution in the seawater are reflective of both physical processes (i.e. tidal mixing, upward diffusion [8] and eddy pumping [7]) and biological processes (i.e. phytoplankton uptake [6] and bacterial degradation [18]). We observed a strong coupling between hydrographic and biogeochemical parameters and the time when the extreme values appeared was in general agreement among a suite of chemical and hydrographic parameters, which suggested that intrinsic progresses such as tidal mixing, biological activities and the water mass changes may have existed for driving the short-term nutrient dynamics.

4.1. Tidal mixing

Generally, in coastal areas such as Gan Bay, tidal currents may be one of the major physical forcings governing the nutrient dynamics. As has been shown, station Z86 has a regular diurnal tidal cycle; however, salinity did not show a diurnal pattern, i.e. without peaks at high tides or no low values at low tides (Fig. 2a).

If we selected the sampling periods at the same tidal height (Table 1), SRP concentrations changed from 330 nM to $\sim 32 \text{ nM}$, and N + N concentrations varied between 4.3 and $< 0.3 \mu\text{M}$ (i.e., below the detection limit). As further summarized in Table 1, SRP concentrations were 70, 171, 147 and 103 nM at the same tidal height at 03:00, 06:00, 09:00 and 12:00 on December 20, respectively. The amplitude in SRP fluctuation of 298 nM during the

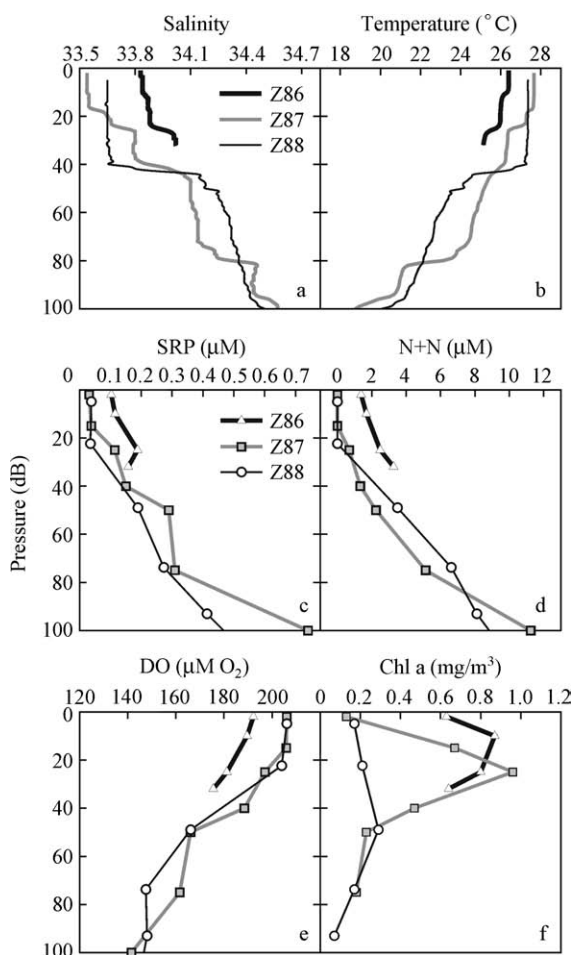


Fig. 3. Vertical profiles of (a) salinity, (b) potential temperature, (c) SRP, (d) N + N, (e) DO and (f) Chl *a* in the SCS at stations Z86, Z87 and Z88.

Table 1
Summary of the fluctuations in concentration of nutrients and tidal height at various tidal height segments.

Local time (GMT + 8)	Tidal height (m) error: ± 0.15	SRP (nM)	N + N (μM)
21:00 18th	0.25	330	4.3
16:00 19th	0.27	~ 32	< 0.3
22:00 19th	0.25	~ 42	< 0.3
6:00 19th	-0.22	56	< 0.3
9:00 19th	-0.25	41	< 0.3
12:00 19th	-0.17	39	< 0.3
3:00 20th	-0.23	70	0.3
6:00 20th	-0.27	171	2.7
9:00 20th	-0.29	147	2.1
12:00 20th	-0.22	103	1.4

observation period was just at the start-point and end-point of the monotonic decreasing of SRP. At the third point of the same tidal height, SRP slightly increased to 42 nM. We may thus contend that at the same tidal height, the tidal effect on SRP was not significant, i.e. the variation of SRP was not driven by the tidal mixing in this period. Moreover, results from Table 1 showed that during the end-point of the period of monotonic decrease of SRP (06:00, 09:00, 12:00 on Dec. 19), the fluctuation of SRP was 17 nM, in contrast to an extreme fluctuation of 298 nM. The N + N variation showed the same trend as SRP (Table 1). Therefore, tidal mixing may have had only minor influences on the nutrient dynamics in our case.

4.2. Biological activities

Biological activity is another important factor inducing the diurnal variation of nutrients through biological metabolism, i.e. decomposing organic matter and consuming inorganic nutrients. Wu et al. [5] found that surface samples from the SCS contained 5–25 nM of dissolved inorganic phosphorus and approximately 160 nM of dissolved organic phosphorus. On decomposition, organic molecules are liberated into the water as dissolved inorganic substances such as SRP, presumably by bacterial action [18,19]. During our short-term observation, the diel variation of the total bacterial abundance and Chl *a* did not match with the chemical parameters, i.e. SRP variation did not show a reverse pattern with the biological parameters (Fig. 2), which suggests that the variation of SRP was mainly driven by factors other than the biological activities. This leaves different water mass changes as a plausible explanation for the observed large SRP variations.

4.3. Influence of upwelled waters

December is a season with upwelling-favorable north-eastern winds to the west of the Luzon Island. The tight coupling between various parameters indeed showed the presence of an upwelling event, attributable to the

northeastern wind forcing and subsequent offshore Ekman transport.

The water column's physical properties reflected the presence of the upward injection from the subsurface. *T-S* (Fig. 4a) relationships between time-series results at stations Z86, Z87 and Z88 were good and probably resulted from a two end-member vertical mixing process of surface warm water with deeper and colder water. Note that at the beginning of the time-series observation, the surface water of short-term site exhibited a constant temperature (~ 24.4 °C) and salinity (~ 34.2) (Fig. 2) down to a depth of ~ 70 m (Fig. 3a and b).

Surface concentrations of SRP and N + N were enhanced at station Z86, as compared to the offshore stations (Z87 and Z88). SRP (~ 30 nM) and N + N (< 0.3 μM) concentrations were very low and constant in the upper layers at all stations, and began to increase at or slightly below the bottom of the mixed layer. The near-shore station (Z86) at which nutrients were measured had high surface SRP (~ 330 nM) and N + N (4.3 μM) concentrations, down to the 60–80 m depth (Fig. 3c and d).

The N:P ratio throughout the observation period was ~ 13.2 (Fig. 4b), which is characteristic of SCS subsurface and deep waters [20,21]. Moreover, in this case, there was also a negative and good correlation between *pCO*₂ and SST (Fig. 5). There should therefore exist an upwelled subsurface cold water with high nutrients, low-temperature and high-*pCO*₂ level that displaced warmer water with low nutrients.

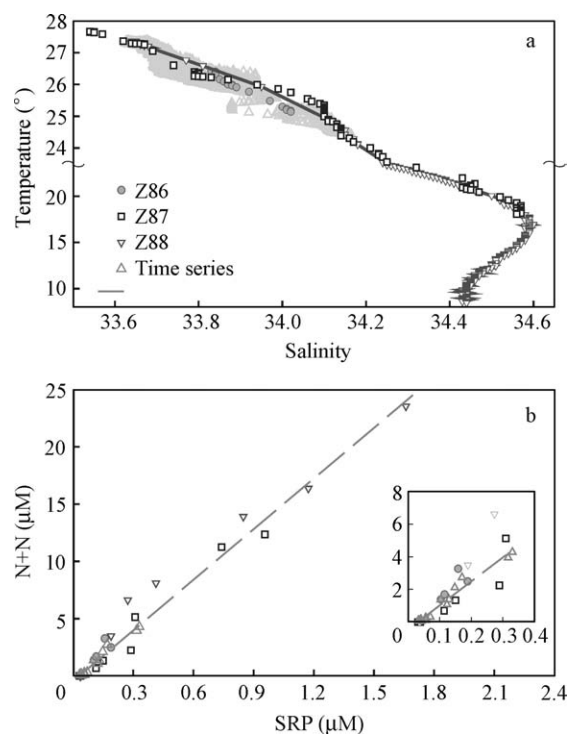


Fig. 4. Plots of (a) temperature versus salinity; (b) N + N versus SRP between December 18 and 20, 2006 at stations Z86, Z87 and Z88.

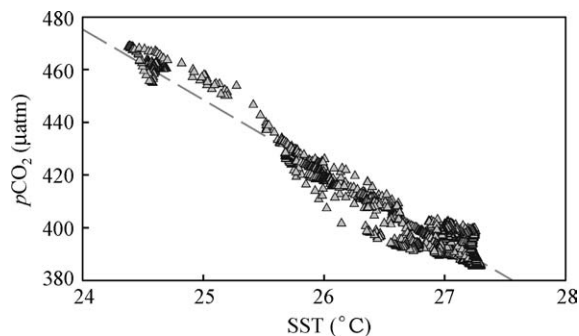


Fig. 5. The correlation between $p\text{CO}_2$ and SST between December 18 and 20, 2006 at station Z86.

As can be seen from Fig. 2, SRP and $p\text{CO}_2$ were high during low-temperature and high-salinity period and low during high-temperature and low-salinity period, which again lent support to the existence of the event influenced by the upwelled cold water mass with high nutrients and high $p\text{CO}_2$.

Taken together, in contrast to offshore stations Z87 and Z88, station Z86 was characterized by lower temperature and dissolved oxygen, but higher salinity and nutrients (Fig. 3), suggesting that this nearshore site (station Z86) was impacted by an upwelling event.

It should be noted that this upwelled cold water did not seem to have impacted the entire observation period (approximately 35 h of 42 h), which might suggest the extremely dynamic nature of this upwelled cold water mass. In comparison to the paradigm of a coastal embayment under the influence of coastal upwelling – the renewal time in Ria de Vigo ~ 1 week [22], a shorter time scale (< 2 days) was found in our study region. This was possibly determined by the unstable wind field during our observation, which was under the influence of both the winter monsoon and a tropical storm that occurred during the observation period.

Nevertheless, this upwelled water did provide a source of nutrients from depth to the surface. Based on our observation on December 20, SST changed from ~ 27 to ~ 25.5 °C and salinity from ~ 33.65 to ~ 33.95 in ~ 3 h (Fig. 2). The latter numbers equaled a depth of ~ 45 m in Fig. 3a and b), which might suggest that the subsurface water of ~ 45 m was pumped to the surface (5 m) in a “pulse” of 3 h. The change in concentrations of nutrients (Fig. 2) also illustrated a similar scenario. Remarkably, such a pulse may be equivalent to a significant upwelling velocity of ~ 13 m h^{-1} . As a consequence, a net upward flux of 2.0 $\text{mmol P m}^{-2} \text{h}^{-1}$ and 30 $\text{mmol N m}^{-2} \text{h}^{-1}$ can be calculated in this pulse. Although we cannot give a similar estimation for another “pulse” beginning on December 18, it should be stronger than that of the December 20 upwelling pulse as can be seen from the larger amplitude of variations shown in Fig. 2. At the same time, since the upwelling did not impact the entire observation period (approximately 35 h of 42 h), we extrapolated the daily average nutrient supply as 8 $\text{mmol P m}^{-2} \text{d}^{-1}$ and

120 $\text{mmol N m}^{-2} \text{d}^{-1}$ and further converted this into a new production of ~ 10 $\text{g C m}^{-2} \text{d}^{-1}$ by assuming Redfield ratios of 106 and 6.6 (for the C:P and C:N ratios, respectively).

Jenkins and Goldman [23] reported new production determined from oxygen flux methods to be ~ 0.2 $\text{g C m}^{-2} \text{d}^{-1}$ in the Sargasso Sea. The current model estimate of upward flux was ~ 0.11 $\text{g C m}^{-2} \text{d}^{-1}$ in the Sargasso Sea [7]. A study in the oligotrophic ocean based on GEOSECS from Lewis et al. [24] showed that more nitrogen fluxes should be taken into account in order to support the rate of new production. A significant nutrient supply flux of up to 10- to 50-folds was observed in our case. Although the short duration of a pulse may lead to a possibility that much of the upwelled nutrients returned to deep waters before phytoplankton could utilize them, the overall high nutrient supply rates were still likely. Therefore, the high nutrient supply rates should be able to support a high level of phytoplankton biomass (Fig. 3f) and also potentially high productivity in the area under study.

5. Conclusions

The example from the Gan Bay time-series study demonstrates the striking relationship between the hydrological process and large-amplitude fluctuation of nutrients in the surface water. Nutrients (SRP and N + N) exhibited a 10-fold variability and seemed to show a dominant transport mode into the euphotic zone. The N:P ratio throughout the observation period was ~ 13.2 , which is characteristic of SCS subsurface and deep waters. Moreover, in this case, there was a negative and good correlation between $p\text{CO}_2$ and SST. There should therefore exist an upwelled subsurface cold water with high nutrients, which may provide a significant amount of nutrients. In this context, this case showed that, although the duration of nutrient supply was relatively short, it supported a relatively high phytoplankton population and potentially high primary production in this generally oligotrophic bay.

Acknowledgements

This study was supported by the National Natural Science Foundation of China (Grant No. 40521003). We thank Dr. Zhenwen Wan for providing the tidal height data. The crew of R/V Dongfanghong II provided much help during the sampling cruise. Dr. Nianzhi Jiao is thanked for the total bacterial abundance data. Jian Ma collected the low SRP data for the three vertical profiles and Yi Wang provided the discrete pH data. Prof. John Hodgkiss is thanked for his assistance with the English.

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