High-resolution distributions of O$_2$/Ar on the northern slope of the South China Sea and estimates of net community production

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Abstract. The dissolved oxygen-to-argon ratio (O$_2$/Ar) in the oceanic mixed layer has been widely used to estimate net community production (NCP), which is the difference between gross primary production and community respiration; it is a measure of the strength of the biological pump. In order to obtain the high-resolution distribution of NCP and improve our understanding of its regulating factors in the slope region of the northern South China Sea (SCS), we conducted continuous measurements of dissolved O$_2$, Ar, and CO$_2$ with membrane inlet mass spectrometry (MIMS) during two cruises in October 2014 and June 2015. An overall autotrophic condition was observed in the study region in both cruises with an average $\Delta$(O$_2$/Ar) of 1.1% ± 0.9% in October 2014 and 2.7% ± 2.8% in June 2015. NCP was on average 11.5 ± 8.7 mmol C m$^{-2}$ d$^{-1}$ in October 2014 and 11.6 ± 12.7 mmol C m$^{-2}$ d$^{-1}$ in June 2015. Correlations between dissolved inorganic nitrogen (DIN), $\Delta$(O$_2$/Ar), and NCP were observed in both cruises, indicating that NCP is subject to the nitrogen limitation in the study region. In June 2015, we observed a rapid response of the ecosystem to the episodic nutrient supply induced by eddies. Eddy-entrained shelf water intrusion, which supplied large amounts of terrigenous nitrogen to the study region, promoted NCP in the study region by potentially more than threefold. In addition, upwelling brought large uncertainties to the estimation of NCP in the core region of the cold eddy (cyclone) in June 2015. The deep euphotic depth in the SCS and the absence of correlation between NCP and the average photosynthetically available radiation (PAR) in the mixed layer in the autumn indicate that light availability may not be a significant limitation on NCP in the SCS. This study helps us to understand the carbon cycle in the highly dynamic shelf system.

1 Introduction

Oceanic carbon sequestration is partially regulated by the production and export process of biological organic carbon in the surface ocean. Net community production (NCP) corresponds to gross primary production (GPP) minus community respiration (CR) in the water (Lockwood et al., 2012) and is an important indicator of carbon export. At steady state, NCP is equivalent to the rate of organic carbon export and is a measure of the strength of the biological pump (Lockwood et al., 2012). NCP effectively couples the carbon cycle and oxygen (O$_2$) production through photosynthesis and respiration in the euphotic layer; thus, many previous studies have measured the mass balance of O$_2$ to quantify NCP (e.g., Emerson et al., 1991; Hendricks et al., 2004; Huang et al., 2012; Reuer et al., 2007). Argon (Ar), a biological inert gas, was commonly used to normalize the O$_2$ concentration in these studies. Based on the similar solubility properties of O$_2$ and Ar, the oxygen-to-argon ratio (O$_2$/Ar) can remove the influences of physical processes (i.e., temperature and pressure change, bubble injection) on the mass balance of O$_2$ (Craig and Hayward, 1987). Dissolved O$_2$/Ar has been developed as a proxy for NCP in a water mass (Kaiser et al.,...
2005). Biological production in the open oceans (i.e., Southern Ocean, Pacific, Arctic Ocean) has been inferred using the O$_2$/Ar ratio to estimate NCP in numerous research studies (e.g., Hamme et al., 2012; Lockwood et al., 2012; Ulfso et al., 2014; Shadwick et al., 2015; Stanley et al., 2010). During recent years, several high-resolution measurements of O$_2$/Ar and NCP in coastal waters have been reported (Tortell et al., 2012, 2014; Eveleth et al., 2017; Izett et al., 2018). Despite the coastal waters such as shelves and estuaries only accounting for 7% of the global ocean surface area, they are known to contribute 15%–30% of the total oceanic primary production (Bi et al., 2013; Cai et al., 2011) and play an important role in the marine carbon cycle and production. However, these regions still suffer from low-resolution measurements that cannot provide representative high-resolution NCP data.

The South China Sea (SCS) is one of the largest marginal seas in the world, with complex ecological characteristics. River runoff from the Pearl and Mekong River introduces large amounts of dissolved nutrients into the SCS (Ning et al., 2004). Due to the influence of seasonal monsoons, the surface circulation in the SCS changes from a basin-scale cyclonic gyre in winter to an anticyclonic gyre in summer (Hu et al., 2000). The surface water masses on the northern slope of the SCS can be categorized into three regimes: shelf water, offshore water (e.g., the intruded Kuroshio water), and the SCS water (Feng, 1999; Li et al., 2018). The shelf water is mixed with fresh water from rivers or coastal currents and thus usually has low salinity (S < 33) and low density (Uu and Brankart, 1997; Su and Yuan, 2005; Cheng et al., 2014). Both offshore water and SCS water originate from the northern Pacific. Thus, offshore water has similar hydrographic characteristics of high temperature and high salinity as the northern Pacific water. But the SCS water has changed a lot in its hydrographic property because of mixing processes, heat exchange, and precipitation during its long residence time of about 40 years in the SCS (Feng et al., 1999; Li et al., 2018; Su and Yuan, 2005). The distributions of phytoplankton and primary productivity in the SCS show great temporal and spatial variation (Ning et al., 2004). Low chlorophyll a (Chl a) and primary production are the significant characteristics of the SCS basin, which is considered an oligotrophic region, and macronutrients (i.e., nitrogen) are the main limitations on phytoplankton growth and productivity (Ning et al., 2004; Lee Chen, 2005; Han et al., 2013). Excessive runoff from the Pearl River can result in high N/P (nitrogen / phosphorus) ratios of > 100, shifting the nutritive state from nitrogen deficiency to phosphorus deficiency in the coastal region of the SCS (Lee Chen and Chen, 2006). Dissolved iron is also a potential limitation on primary production, especially in high-nutrient low-chlorophyll (HNLC) regions (Cassar et al., 2011). But on the northern slope of the SCS, the concentration of dissolved iron is high enough to support the growth of phytoplankton in the surface water (Zhang et al., 2019). The northern slope of the SCS is an important transition region between the coastal area and the SCS basin. In the summer, the shelf water intrusion is an important process changing the nutritive state in the northern slope region of the SCS (He et al., 2016; Lee Chen and Chen, 2006). But so far, the NCP enhancement caused by this process is still unknown.

Previous studies about the organic carbon export in the SCS were mostly conducted on particulate organic carbon (POC) flux (e.g., Bi et al., 2013; Cai et al., 2015; Chen et al., 1998, 2008; Ma et al., 2008, 2011). Little research has been conducted on NCP in the SCS to date. Chou et al. (2006) estimated NCP in the northern SCS during the summertime to be 4.47 mmol C m$^{-2}$ d$^{-1}$ based on the time change rate of dissolved inorganic carbon (DIC) in the mixed layer at the South East Asia Time Series Station (SEATS) from 2002 to 2004. Wang et al. (2014) used GPP and CR data from a light–dark bottle incubation experiment to calculate NCP in the northern SCS and obtained a range from −179.0 to 377.6 mmol O$_2$ m$^{-2}$ d$^{-1}$ (−129.7 to 273.6 mmol C m$^{-2}$ d$^{-1}$). Huang et al. (2018) estimated monthly NCP from July 2014 to July 2015 based on in situ O$_2$ measurements on an Argo profiling float and reported the cumulative NCP to be 0.29 mol C m$^{-2}$ month$^{-1}$ (9.67 mmol C m$^{-2}$ d$^{-1}$) during the northeast monsoon period and 0.17 mol C m$^{-2}$ month$^{-1}$ (5.67 mmol C m$^{-2}$ d$^{-1}$) during the southwest monsoon period in the SCS basin. However, most of these studies in the SCS were constrained by methodological factors attributed to discrete sampling and cannot reveal rapid productivity responses to the highly dynamic environmental fluctuations of coastal systems. Discrete sampling suffers from low spatial resolution and cannot adequately resolve variabilities caused by small-scale physical or biological processes in the dynamic marine systems. In addition, each of the three methods for NCP estimates mentioned above has its limitation. DIC-based NCP estimates are not suitable for coastal regions because instead of biological metabolism, terrestrial runoff can be the strongest factor influencing DIC in a coastal system (Mathis et al., 2011). The unavoidable differences between in situ circumstances and on-deck incubation conditions can introduce uncertainties to NCP derived from light–dark bottle incubation (Grande et al., 1989). Though Argo profiling floats partly eliminate the limitations of discrete sampling, it is hard to control their movement in the study region. However, no high-resolution measurements of NCP have been reported for the SCS so far.

In this paper, we present high-resolution NCP estimates in the northern slope region of the SCS based on continuous shipboard dissolved O$_2$/Ar measurements. We discuss the regulating factors of NCP based on ancillary measurements of other hydrographic parameters. Our high-resolution measurements caught the rapid response of the ecosystem to the episodic nutrient supply induced by eddies and helped us to quantify the contribution of eddy-entrained shelf water intrusion to NCP in the summer cruise.
2 Methods

2.1 Continuous underway sampling and measurement

Continuous measurements of dissolved gases (O₂, Ar, and CO₂) were obtained using membrane inlet mass spectrometry (MIMS; HPR 40, Hiden Analytical, UK) (Tortell, 2005) onboard the RV Nanfeng during two cruises in the northern slope region of the SCS (Fig. 1a, b) from 13 to 23 October 2014 and from 13 to 29 June 2015. In addition, a cyclonic–anticyclonic eddy pair was observed in June 2015 (Fig. 1c) and resulted in dramatic influences on the study region.

We developed a continuous shipboard measurement system for dissolved gases following the method described by Guéguen and Tortell (2008). Surface seawater was collected continuously using the ship’s underway intake system (~5 m depth) and was divided into different lines for various underway scientific measurements. Seawater from the first line passed through a chamber at a flow rate of 2–3 L min⁻¹ to remove macroscopic bubbles and to avoid pressure bursts. A flow of ~220 mL min⁻¹ was continuously pumped from the chamber using a Masterflex peristaltic pump equipped with L/S® multichannel cartridge pump heads (Cole-Parmer). In order to minimize the O₂/Ar fluctuations due to temperature effects and water vapor pressure variations, the water samples flowed through a stainless-steel coil (~6 m) with 0.6 mm wall thickness immersed in a water bath (Shanghai Bilon Instrument Co. Ltd, China) to achieve a constant temperature (~2°C below the sea surface temperature), which avoided temperature-induced supersaturation and subsequent bubble formation. Then the water samples were introduced into a cuvette with a silicone membrane mounted on the inside. The analyte gases were monitored by a Faraday cup detector in the vacuum chamber after diffusion through the silicone membrane, and the signal intensities at the relevant mass-to-charge (m/z) ratios (32, 40, and 44 for O₂, Ar, and CO₂, respectively) were recorded by MASSoft. Based on the continuous measurement of 50 L of air-equilibrated seawater, the long-term signal stability (measured as the coefficient of variation) over 12 h was 1.57 %, 3.75 %, and 2.21 % for O₂, Ar, and CO₂, respectively. Seawater from the second line passed through a flow chamber, where an RBR Maestro (RBR, Canada) was installed to continuously record temperature, salinity, dissolved oxygen (DO), and Chl a. We did not obtain continuous DO data in October 2014 because the DO sensor of the RBR Maestro broke down. A third line was used to drain the excess seawater. Underway pipelines were flushed with fresh water or bleach every day to avoid possible in-line biofouling. The data from the underway transects were exported to spreadsheets and compiled into 5 min averages, and the comparisons of the gas data with other hydrographic variables were based on the UTC time recorded for each measurement.

The O₂/Ar ratio measurements were calibrated with air-equilibrated seawater samples at about 6–8 h intervals to monitor instrument drift and calculate Δ(O₂/Ar). These air-equilibrated seawater samples were prefiltered (0.22 µm) and bubbled with ambient air for at least 24 h to reach equilibrium at sea surface temperature (Guéguen and Tortell, 2008). For calibration, 800 mL of air-equilibrated seawater sample was transferred into glass bottles and immediately drawn into the cuvette, where the first 200 mL of the sample was used to flush the cuvette and pipelines. After a 3 min recirculation of the sample, the average signal intensity was obtained to calculate O₂/Ar. During the course of measurements, flow rate and the temperature of the water bath were both kept the same as in the underway measurements. The precision of MIMS-measured O₂/Ar was 0.22 % based on analyses of 20 duplicate samples in the laboratory test, which is comparable to previous studies and sufficient to detect biologically driven gas fluctuations in seawater (Tortell, 2005).

The instrumental CO₂ ion current was calibrated at about 12–24 h intervals using equilibrated seawater standards as per Guéguen and Tortell (2008) during the survey in June 2015. Prefiltered seawater (0.22 µm) was gently bubbled with dry CO₂ standards (200, 400, and 800 ppm; provided by the Chinese National Institute of Metrology) at in situ temperature. After 2 d of equilibrium, these standards were analyzed by MIMS following the same procedure for measuring air-equilibrated seawater samples to obtain a calibration curve between CO₂ signal intensity and mole fraction. The reproducibility of these measurements was better than 5 % within 15 d. Then we used the empirical equations reported by Takahashi et al. (2009) to convert the CO₂ mole fraction derived from the calibration curve to the in situ partial pressure of CO₂ (pCO₂).

Chlorophyll a (Chl a) data from the RBR sensor were linearly calibrated against extracted Chl a measurements of discrete seawater samples taken from the same seawater outlet as for MIMS measurements. Samples were filtered through polycarbonate filters (0.22 µm). The filter membranes were then packed with pre-sterilized aluminum foil and stored in a freezer (~20°C) until extraction by acetone and analysis using a fluorimetric method (F-4500, HITACHI, Japan) described by Parsons et al. (1984). The mean residual of this calibration was 0.00 ± 0.07 µg L⁻¹.

2.2 Estimation of NCP based on O₂/Ar measurements

NCP in the mixed layer was estimated by the O₂/Ar mass balance from continuous measurements. Due to similar physical properties of O₂ and Ar, Δ(O₂/Ar) is used as a proxy for biological O₂ supersaturation and is defined as (Craig and Hayward, 1987)

\[
\Delta(O_2/Ar) = \frac{([O_2]/[Ar])_{eq} - 1}{([O_2]/[Ar])_{eq} - 1},
\]
where \( [O_2]/[Ar] \) is the measured dissolved \( O_2/Ar \) ratio of the mixed layer and \( ([O_2]/[Ar])_{eq} \) is the measured dissolved \( O_2/Ar \) ratio of the air-equilibrated seawater samples. \( \Delta(O_2/Ar) \) is the percent deviation of the measured \( O_2/Ar \) ratio from equilibrium. Assuming a steady state and negligible physical supply, NCP is the air–sea biological \( O_2 \) flux and can be estimated as (Reuer et al., 2007)

\[
NCP (\text{mmol C m}^{-2} \text{d}^{-1}) \approx k_{O_2} \cdot [O_2]_{sat} \cdot \Delta(O_2/Ar) 
\]

\[
\cdot r_{C:O_2} \cdot \rho ,
\]

where \( k_{O_2} \) is the weighted gas transfer velocity of \( O_2 \) (m d\(^{-1}\)); \( [O_2]_{sat} \) denotes the saturation concentration of dissolved \( O_2 \) (µmol kg\(^{-1}\)) in the mixed layer, which is calculated based on temperature and salinity (Weiss, 1970); \( r_{C:O_2} \) is the photosynthetic quotient of \( C \) and \( O_2 \) and was reported as 1:1.38 in the SCS (Jiang et al., 2011); and \( \rho \) is seawater density in units of kilograms per cubic meter (kg m\(^{-3}\)) (Millero and Poisson, 1981). We estimated \( k_{O_2} \) using the European Centre for Medium-Range Weather Forecasts (ECMWF) wind-speed reanalysis data product with a 0.25° × 0.25° grid (https://www.ecmwf.int, last access: 18 April 2020), the parameterization by Wanninkhof (1992), and the gas exchange weighting algorithm by Teeter et al. (2018). Teeter et al. (2018) pointed out that the modern \( O_2/Ar \) method does not strongly rely on the steady-state assumption. When this assumption is violated, our estimate does not represent the actual daily NCP but rather an estimate of NCP weighted over the residence time of \( O_2 \) in the mixed layer and along the path of the water parcel during that period. Thus, the residence time of \( O_2 \) in the mixed layer is an important implication of the weighted timescale of NCP before the measurement of \( O_2/Ar \). The residence time of \( O_2 \) (\( \tau, \text{d} \)) in the mixed layer is estimated as the ratio of mixed layer depth (MLD, m) to the gas transfer velocity of \( O_2 \left( k_{O_2}, \text{m d}^{-1}\right) \) (Jonsson et al., 2013).

### 2.3 Ancillary measurements and calculations

Surface water samples for the nutrient analysis were collected from Niskin bottles mounted on the conductivity–temperature–depth (CTD) instrument, where the samples were filtered through acid-cleaned acetate cellulose filters (pore size: 0.4 µm). The filtrates were poisoned by HgCl\(_2\) and stored in the dark at 4 °C. In the laboratory, the nutrients were
photometrically determined by an auto-analyzer (QuAAtro, SEAL Analytical, Germany) with a precision better than 3%. MLD was defined by the $\Delta \sigma = 0.125 \text{kg m}^{-3}$ criterion (Monterey and Levitus, 1997). The subsurface chlorophyll maximum layer (SCML) was observed using the fluorescence sensor mounted on the CTD. The SCML usually occurs at the bottom of the euphotic layer (Hanson et al., 2007; Teira et al., 2005). Because no PAR (photosynthetically available radiation) profile data were obtained in two cruises, we decided to regard the depth of the SCML as the euphotic depth ($Z_{eu}$). Both MLD and $Z_{eu}$ were calculated at each station where the vertical CTD casts were made. The MLDs for underway data between CTD stations were calculated using linear interpolation based on the distance between the underway points and nearest CTD stations. We matched the underway data to each CTD location using a combination of the latitude–longitude threshold (latitude–longitude of CTD station $\pm 0.05^\circ$) and time threshold (end and start of stationary time $\pm 1$ h), then took the averages of these underway data for further analysis with discrete nutrient concentrations.

The daily satellite chlorophyll data were obtained from the EU Copernicus Marine Service Information website (https://resources.marine.copernicus.eu, last access: 1 November 2020). The product we used was provided by the ACRI-ST company (Sophia Antipolis, France), with a space–time interpolation (“cloud free”). The M_Map package for MATLAB was applied to output satellite chlorophyll images (Pawlowicz, 2020). Daily and 8 d PAR data collected by the MODIS Aqua sensor were obtained from NASA’s ocean color website (https://oceancolor.gsfc.nasa.gov/l3, last access: 3 November 2020). The spatial resolution of both satellite products is 4 km, and we match the satellite PAR to CTD locations by choosing the closest PAR data point to the CTD location. A light attenuation coefficient ($K_d$, $\text{m}^{-1}$) was used to estimate the average PAR in the mixed layer (Kirk, 1994; Jerlov, 1976):

$$K_d = \frac{4.605}{Z_{eu}}.$$  \hspace{1cm} (3)

### 3 Results and discussion

#### 3.1 Distributions of hydrographic parameters and gases

The distributions of temperature, salinity, Chl $a$, and $\Delta(O_2/Ar)$ during the autumn cruise (October 2014) are shown in Fig. 2. Sea surface temperature (SST) ranged from 26.96 to 28.53 °C with an average of 27.82 ± 0.33 °C. Sea surface salinity (SSS) ranged from 33.28 to 34.11, with low values occurring in the southeast of the region. Chl $a$ concentration ranged from 0.01 to 0.71 µg L$^{-1}$, and was on average 0.18 ± 0.13 µg L$^{-1}$, which is comparable to the 11-year mean value ($\sim 0.2$ mg m$^{-3}$) in the same region in October reported by Liu et al. (2014). $\Delta(O_2/Ar)$ values were in the range of $-2.9\%$–$4.9\%$ (average $1.1\% \pm 0.9\%$) and slightly oversaturated in most areas (Fig. 2d). Please note that all averages we have published in this paper are reported in the format of mean ± standard deviation.

In June 2015, SST ranged from 29.28 to 32.24 °C and was on average 30.88 ± 0.59 °C (Fig. 3a). SSS ranged from 30.81 to 34.16. Transect 3 was significantly characterized by low salinity (Fig. 3b). He et al. (2016) reported that this phenomenon was influenced by the eddy-entrained Pearl River plume (shelf water) injected into the SCS. Chl $a$ varied in a range of 0.09–0.58 µg L$^{-1}$ in the study region. Under the influence of this eddy-entrained shelf water, Chl $a$ values higher than 0.30 µg L$^{-1}$ were observed along Transect 3 (Fig. 3c). In contrast, Chl $a$ was in the range of 0.09–0.18 µg L$^{-1}$ along Transects 1 and 2. It was obvious that DO was much higher on the east side than the west side in the study region (Fig. 3d). $\Delta(O_2/Ar)$ varied from $-3.9\%$ to 13.6 %. Most of the $\Delta(O_2/Ar)$ values were positive in the study region (average $2.7\% \pm 2.8\%$), whereas the negative values were concentrated along Transect 4 (Fig. 3f). $\Delta(O_2/Ar)$ along Transect 3 was on average $7.2\% \pm 2.6\%$, significantly higher than that of other transects (Fig. 3f). $\rho CO_2$ exhibited a high degree of spatial and temporal variability, and the high values mostly occurred on the west side of the study region (Fig. 3e). Resulting from the considerably low $\rho CO_2$ in Transect 3, the average $\rho CO_2$ (323 ± 93 µatm) in the study region was lower than values reported previously, i.e., 350–370 µatm by Zhai et al. (2009) and 340–350 µatm by Rehder and Sues (2001). Due to the influence of the shelf wa-

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Figure 3. Surface distributions of (a) temperature, (b) salinity, (c) chlorophyll $a$ (Chl $a$), (d) dissolved oxygen (DO), (e) $p$CO$_2$, and (f) $\Delta$O$_2$/Ar in June 2015.

Table 1. Basic information at all CTD stations in October 2014.

<table>
<thead>
<tr>
<th>Station</th>
<th>Date of observation$^a$</th>
<th>MLD$^b$ (m)</th>
<th>$Z_{eu}$$^b$ (m)</th>
<th>$k^c$ (m d$^{-1}$)</th>
<th>$\tau^d$ (d)</th>
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<tr>
<td>O-01</td>
<td>13 Oct 2014</td>
<td>58</td>
<td>82</td>
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<td>102</td>
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</tbody>
</table>

$^a$ All dates are in the format of day month year. $^b$ Euphotic depth, defined based on subsurface chlorophyll maximum layer. $^c$ Gas transfer velocity of O$_2$. $^d$ Residence time of O$_2$ in the mixed layer, estimated as per $MLD/k$. 

The average pCO$_2$ in Transect 3 was 222 ± 33 µatm, with a range of 144–321 µatm. In the summer, shelf water mixed with the Pearl River plume is the most important factor influencing pCO$_2$ in the coastal and shelf region of the northern SCS, which can result in pCO$_2$ values as low as 150 µatm (Li et al., 2020). Here we apply an average atmospheric pCO$_2$ of 382 µatm observed in July 2015 in the northern SCS (Li et al., 2020) to calculate the pCO$_2$ difference ($\Delta$pCO$_2$) between the surface water and the atmosphere. $\Delta$pCO$_2$ ranged from −238 to −61 µatm along Transect 3, indicative of a strong CO$_2$ sink. 

3.2 Mixed layer depth, euphotic depth, and residence time of O$_2$ in the mixed layer

The MLD, euphotic depth ($Z_{eu}$), and residence time of O$_2$ ($\tau$) in the mixed layer at CTD stations during two cruises are shown in Tables 1 and 2. In autumn 2014, MLD ranged from 27 to 81 m, with an average of 55 ± 15 m (Table 1). The average $Z_{eu}$ was 74 ± 12 m, approximately 20 m deeper than the MLD (Table 1). The residence time of O$_2$ in the mixed layer ranged from 3 to 13 d (Table 1), comparable to a range of 1–2 weeks reported by previous studies (Izett et al., 2018; Manning et al., 2017). The average residence time of O$_2$ was 9 ± 3 d, indicating that our estimate generally quantified NCP over 9 d prior to the underway observation of O$_2$/Ar during this cruise.

The average MLD in June 2015 was just 18 ± 6 m (Table 2). A significantly shallow MLD occurred at two stations (J-10, J-11) located in Transect 3 (Table 2, Fig. S1f in the Supplement). The low-salinity shelf water intrusion is the main cause of this shallow MLD of 8 m. The average $Z_{eu}$ was 58 ± 18 m, approximately 40 m deeper than the MLD (Table 2). The residence time of O$_2$ in the mixed layer ranged from 2 to 12 d (Table 2), indicating a fast gas exchange at some stations. In addition, we also observed relatively obvious subsurface O$_2$ maxima in Transects 1 and 2 in summer 2015. But this phenomenon did not exist in autumn 2014.

In both cruises, $Z_{eu}$ was observed to be obviously deeper than the MLD. This result partly suggests that light availability may not be a limitation on NCP in the northern slope of the SCS. Especially in the summer, $Z_{eu}$ extended to 2–7 times the MLD (Table 2), ensuring sufficient illumination in the mixed layer. But in the autumn when the thickness of the mixed layer accounts for about 74% of the euphotic layer, the average light intensity in the mixed layer might be
influenced by exponential light attenuation along the depth profile.

3.3 NCP in autumn and summer

In October 2014, NCP in the northern slope of the SCS ranged from −29.2 to 42.7 mmol C m$^{-2}$ d$^{-1}$ (average 11.5 ± 8.7 mmol C m$^{-2}$ d$^{-1}$), and most of the region was net autotrophic (Fig. 4a). The estimated NCP based on the O$_2$/Ar values measured in this cruise is about 34 % of the net primary production rates of 34.3 mmol C m$^{-2}$ d$^{-1}$ measured by $^{14}$C bottle incubation (Xiaoxia Sun, personal communication, 2017), which was in agreement with previous research (Quay et al., 2010). The average NCP in the study region was 11.6 ± 12.7 mmol C m$^{-2}$ d$^{-1}$ with a range of −27.6–61.4 mmol C m$^{-2}$ d$^{-1}$ in June 2015. A high NCP level was observed along Transect 3 (Fig. 4b). Eddy-entrained shelf water brought a large amount of terrigenous nutrients from the shelf to the slope region along Transect 3 (He et al., 2016). The average nitrate (NO$_3^-$) and nitrite (NO$_2^-$) concentrations in the surface water of Transect 3 were 2.31 ± 0.70 and 0.04 ± 0.01 µmol L$^{-1}$, respectively (Fig. S1a, b); both values were much higher than those found in the other three transects, for which NO$_3^-$ was in a range of <0.03–0.69 µmol L$^{-1}$ and NO$_2^-$ was mostly below the detection limit. Li et al. (2018) reported that all of Transect 3 and part of Transect 4 were dominated by shelf water at the surface, and we estimated NCP over these regions where salinity is lower than 33 as 23.8 ± 10.7 mmol C m$^{-2}$ d$^{-1}$ on average. We also observed a warm eddy (anticyclone) covering most stations in Transects 1 and 2 (Fig. 1b, c) during our survey in June 2015 (Chen et al., 2016). Anticyclonic eddies can cause downwelling, deepening of the thermocline, and blocking of the supply of nutrients from the deeper water (Ning et al., 2008; Shi et al., 2014). Consequently, a warm eddy is expected to result in an oligotrophic condition in the surface water associated with low Chl a concentrations and low production (Ning et al., 2004). As a result, in the summer of 2015, the observed NO$_3^-$, NO$_2^-$, and PO$_4^{3-}$ (phosphate) concentrations were almost below the detection limit in Transects 1 and 2 (Fig. S1a, b, d). NCP in Transect 1 and 2 was at a very low level (average 2.8 ± 2.7 mmol C m$^{-2}$ d$^{-1}$). Because of the significantly high values of NCP over the regions with shelf water intrusion, our NCP result in the summer of 2015 is on average higher than the previous values of 4.47 mmol C m$^{-2}$ d$^{-1}$ and 0.17 mol C m$^{-2}$ month$^{-1}$ (5.67 mmol C m$^{-2}$ d$^{-1}$) based on the DIC budget and Argo O$_2$, respectively, in the SCS (Chou et al., 2006; Huang et al., 2018). However, NCP estimates based on both methods mentioned above suffer from poor temporal and spatial coverage and do not allow for revealing rapid changes in shelf systems. In contrast, continuous measurements of O$_2$/Ar allow us to capture rapid variations in NCP along Transect 3 and resolve short-term productivity responses to environmental fluctuations.

3.4 Distribution of various parameters along representative transects

We chose Transect 5 (Fig. 1a) observed in October 2014 and Transect 4 (Fig. 1b) observed in June 2015 to show the distribution of various parameters.

The distribution of Chl a, Δ(O$_2$/Ar), and NCP showed a similar trend along Transect 5 in October 2014 (Fig. 5). There was a trough of temperature, showing a maximum drawdown of ~0.6°C compared to the average temperature in the study region (Figure 5a). But the temperature fluctuations shown here are too small to reflect a significant upwelling that can easily cause ~2°C of temperature drawdown in the upper layer (Jing et al., 2009; Manning et al., 2017; Ning et al., 2004). A spike of Chl a occurred between 115.6 and 115.7°C and was coincident with the peaks of Δ(O$_2$/Ar) and NCP (Fig. 5b, c). The highest surface concentration of ammonium (NH$_4^+$) of 0.35 µmol L$^{-1}$
was also observed between 115.6 and 115.7°E in this transect and was predominantly higher than the concentrations (0.07–0.17 μmol L\(^{-1}\)) in the other regions during this cruise (Fig. 5c, S2b). Because no significant obduction processes (i.e., upwelling, entrainment, and diapycnal mixing) were reported in this region, the most likely source of this abundant NH\(_4\)+ was in situ regeneration such as the excretion of zooplankton and the bacterial decomposition of organic matter (La Roche, 1983; Clark et al., 2008). Theoretically, NH\(_4\)+, an important nitrogen source of phytoplankton growth, can be quickly utilized by phytoplankton and contributes to primary production (Dugdale and Goering, 1967; Tamminen, 1982). However, we only got nutrient data at two CTD stations in this transect; thus, the result we obtained here just indicated that high NCP occurred at the station with a relatively high NH\(_4\)+ concentration, but this is not strong evidence that NH\(_4\)+ was the main factor influencing NCP in this transect.

A similar distribution pattern of Chl \(a\), NCP, and \(\Delta\)O\(_2\)/Ar was observed along Transect 4 in June 2015, whereas pCO\(_2\) showed the opposite trend for these three parameters (Fig. 6b, c). Low salinity (lower than 33) existed at both the southern and northern ends of this transect (Fig. 6a). The concentration of dissolved inorganic nitrogen (DIN, NO\(_3\)+ NO\(_2\)+ NH\(_4\)+) in the surface water was 0.81 and 0.27 μmol L\(^{-1}\) at the southern and northern end, respectively, which was higher than the concentrations at other stations for this transect (Fig. 6c). These results indicate that shelf water is imported at the northern and southern ends of this transect, along with higher levels of Chl \(a\) and NCP (Fig. 6c). A sharp drop in the temperature and an increase in salinity occurred from 19.7 to 19.8°N and from 21 to 20.7°N (Fig. 6a), manifesting an upwelling over this area together with dramatic spikes in pCO\(_2\) and an associated decrease in \(\Delta\)O\(_2\)/Ar (Nemcek et al., 2008) (Fig. 6b). Most regions of Transect 4 were dominated by upwelling and showed a negative sea level height anomaly (Chen et al., 2016; He et al., 2016). A localized cold eddy was considered the cause of this upwelling (Fig. 1c), resulting in a maximum temperature drawdown of \(\sim\)1.6°C in the mixed layer.

Vertical mixing is considered the largest source of error in O\(_2\)/Ar-based NCP estimates because upwelled subsurface water with different O\(_2\)/Ar signatures can produce either an overestimation or an underestimation of NCP in the mixed layer (Cassar et al., 2014; Izett et al., 2018). Previous research usually ignored the underestimated negative NCP caused by vertical mixing (Giesbrecht et al., 2012; Reuer et al., 2007; Stanley et al., 2010). Cassar et al. (2014) presented an N\(_2\)O-based correction method of O\(_2\)/Ar and NCP for vertical mixing. Although this method has been successfully adopted by Izett et al. (2018) in the sub-Arctic northeast Pacific, it is not suitable for our study region. This is because it is basically applicable in areas where the depths of the euphotic zone and mixed layer are similar, and this method is not suitable for oligotrophic regions (Cassar et al., 2014). The SCS is recognized as an oligotrophic region, and the depth of the euphotic zone can be 2–7 times that of the mixed layer in our study region in the summer. In addition, in the region (e.g., the SCS basin) of the subsurface oxygen maximum, the applicability of N\(_2\)O-based correction is limited (Izett et al., 2018). In Transect 4, the regions with negative NCP and the regions with salinity higher than 33.5 and temperature lower than 30°C are defined as influenced by upwelling. If we neglect these regions in Transect 4, the average NCP in June 2015 can rise slightly to 12.4 ± 0.17 mmol C m\(^{-2}\) d\(^{-1}\). If we also remove the influence of shelf water intrusion by neglecting the regions with salinity lower than 33, the average NCP can sharply decrease to 5.0 ± 6.2 mmol C m\(^{-2}\) d\(^{-1}\), which is similar to the results of 4.47 mmol C m\(^{-2}\) d\(^{-1}\) and 0.17 mol C m\(^{-2}\) month\(^{-1}\).
controlling and limiting phytoplankton biomass and primary production in the SCS (Ning et al., 2004; Lee Chen, 2005; Lee Chen and Chen, 2006; Han et al., 2013). After neglecting the two CTD stations (J-14, J-15) with negative NCP influenced by upwelling in June 2015, we performed a principal component analysis (PCA) to determine the dominant factors influencing NCP in both cruises. In October 2014, DIN (0.741), Δ(O$_2$/Ar) (0.858), and NCP (0.979) were significantly loaded on Factor 1, indicating a potential relationship among these three variables (Fig. 7a, Table S1b in the Supplement). The correlation coefficient between DIN and NCP was 0.706 ($p<0.01$; Table S1a), which was significantly higher than the coefficient between NCP and the other variables, except for Δ(O$_2$/Ar) and temperature; this indicated that DIN was an important factor influencing NCP in this cruise. Another two nutrients – dissolved silicate (DSi, SiO$_2$(aq)) and dissolved inorganic phosphorus (DIP, PO$_4^{3-}$) – had no correlations ($p>0.05$) with NCP (Table S1a). In June 2015, Factor 1 showed a strong loading by DIN (0.876), Chl a (0.950), DO (0.927), Δ(O$_2$/Ar) (0.902), and NCP (0.909), whereas salinity (−0.936) and pCO$_2$ (−0.908) were negatively loaded on Factor 1 (Fig. 7b, Table S2b). The injection of low-salinity shelf water appeared to have a strong effect on the study region because significant negative correlations were observed between salinity and DIN, Chl a, Δ(O$_2$/Ar), and NCP (Table S2a). DIN had strong correlations with NCP, Δ(O$_2$/Ar), and Chl a, with correlation coefficients of 0.747, 0.910, and 0.754, respectively (Table S2a), indicating that DIN was the dominant factor controlling the growth of phytoplankton and primary production in this cruise. DSi (0.582) and DIP (−0.601) were both moderately loaded on Factor 2 (Fig. 7b, Table S2b) and had no correlations with NCP ($p>0.05$, Table S2a). These results suggest the key role of nitrogen in regulating Δ(O$_2$/Ar), NCP, and phytoplankton biomass in the SCS. The supply of nitrogen may stimulate the growth of phytoplankton in the SCS, and nitrogen is an important participant in photosynthesis and a basic element that contributes to the increase in primary production (Dugdale and Goering, 1967; Lee Chen, 2005; Lee Chen and Chen, 2006; Han et al., 2013).

Coupled with biochemical variations, physical processes also play important roles in the slope region of the SCS by transporting abundant nutrient-rich shelf water into the SCS and bringing deep water to the surface by enhancing water mixing (Chen and Tang, 2012; Ning et al., 2004; Pan et al., 2012). The surface waters in the slope region of the northern SCS are primarily composed of waters originating from SCS water, Kuroshio water, and shelf water (Li et al., 2018). In the summer, the shelf water exists where the potential density anomaly is lower than 20.5 kg m$^{-3}$ (Li et al., 2018). In the autumn, there is a weak offshore transport of the shelf water in the SCS, and the salinity of the water mixed with the shelf water is usually lower than 33 (Fan et al., 1988; Uu and Brankart, 1997; Su and Yuan, 2005). In October 2014, the observed surface salinity was in the range

3.5 Factors influencing NCP in the SCS

The SCS is an oligotrophic region with low biomass and primary production (Lee Chen, 2005; Ning et al., 2004). Previous research has shown that the nutrient content, especially nitrogen and phosphorus, is the most important factor

5.67 mmol C m$^{-2}$ d$^{-1}$) reported in previous research in the same season (Chou et al., 2006; Huang et al., 2018). Here we regard 5.0 ± 6.2 mmol C m$^{-2}$ d$^{-1}$ as the background value of NCP in the study region. Since an average NCP of 23.8 ± 10.7 mmol C m$^{-2}$ d$^{-1}$ was observed over regions with salinity lower than 33, we can conclude that the summer shelf water intrusion significantly promoted NCP by potentially more than threefold in June 2015.

Figure 6. Meridional variations in (a) temperature, salinity, (b) Δ(O$_2$/Ar), pCO$_2$, (c) Chl a, NCP, and the surface concentration of DIN along Transect 4 in June 2015. The plots of Δ(O$_2$/Ar), pCO$_2$, and NCP are 10-point Savitzky–Golay smoothed.

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of 33.28 to 34.11; thus, the surface waters were mainly derived from mixing of the Kuroshio water and the SCS water. In the summer of 2015, a cyclonic–anticyclonic eddy pair was observed in the study region (Fig. 1c). Low-salinity shelf water mixed with the intruding river plume from the Pearl River in the upper 50 m and was transported to the slope and basin along the intersection of the two eddies (Chen et al., 2016; He et al., 2016; Li et al., 2018). In both seasons, the surface waters in the study region were generally found to be nitrogen-deficient, with NO$_2^-$ at < 0.01–0.04 µmol L$^{-1}$ (Figs. S2a, S1b), NO$_3^-$ at < 0.03–2.82 µmol L$^{-1}$ (Fig. S1a), and NH$_4^+$ at 0.04–0.35 µmol L$^{-1}$ (Figs. S2b, S1c). The concentrations of NO$_2^-$ and NO$_3^-$ were below the detection limit at almost 80% of the sampling stations during both cruises. Due to the injection of shelf water with low salinity and abundant terrestrial nutrients, significantly high concentrations of DIN (Fig. 8a) that were intruded by shelf water and characterized by surface salinity lower than 33, we obtained an average surface DIN concentration of 1.82 ± 1.16 µmol L$^{-1}$ (0.27–3.01 µmol L$^{-1}$), which was significantly higher than the mean of 0.10 ± 0.03 µmol L$^{-1}$ (0.04–0.16 µmol L$^{-1}$) at other stations (independent sample t test, p < 0.01). After neglecting the two stations (J-14, J-15) influenced by upwelling, a strong correlation between NCP and DIN was observed in the cruise of June 2015 ($r = 0.747, p < 0.01$), with higher NCP (average 15.4 ± 4.5 mmol C m$^{-2}$ d$^{-1}$) occurring at the stations where shelf water intruded, consistent with the DIN concentration higher than 0.27 µmol L$^{-1}$ (Fig. 8b). At other stations without the influence of shelf water, the average NCP was just 2.3 ± 1.7 mmol C m$^{-2}$ d$^{-1}$. These results further suggest that the supply of DIN from shelf water can greatly stimulate the primary production at these stations, resulting in an NCP increase of nearly 7 times compared to other stations.

The correlations between NCP and sea surface temperature as well as between NCP and salinity also support the influence of physical forcing on NCP. In June 2015, we obtained a strong negative correlation between NCP and salinity.
NCP significantly increased in the water with salinity lower than 33 (Fig. 9d). Temperature had weak correlations with NCP (Fig. 9c), and the negative NCP values were concentrated in the water with temperatures below 30.5 °C and salinity values over 33.5 (Fig. 9c, d). This surface water was mostly observed along Transect 4 where vertical mixing caused by a cold eddy brought deep water to the surface. The undersaturated \( \Delta(O_2/Ar) \) entrained by deep water caused the negative NCP estimates at the surface, resulting in a considerable underestimation of NCP. Unlike in June 2015, all the correlations were very weak between NCP and temperature as well as between NCP and salinity in October 2014 (Fig. 9a, b). The Kuroshio water and the SCS water had similar hydrological characteristics, and their mixing in October 2014 may not have resulted in significant changes in the hydrological characteristics of the surface water.

The nutrient concentrations and hydrographic characteristics we observed just reflect the marine environment at the moment of sampling, partly contradicting our estimates that quantified NCP over a period prior to the observation. Especially for the regions with a significant influence of shelf water in June 2015, tracking the history of shelf water intrusion is important. We used daily satellite chlorophyll data to monitor the intrusion of shelf water and roughly set satellite chlorophyll to \( \geq 0.2 \mu g \text{ L}^{-1} \) as the criterion for shelf water. This figure was made based on the M_Map mapping package for MATLAB (Pawlowicz, 2020).

And Transect 4 where J-12 and J-13 were located on 13 June (Figs. 1b, 10). Until 25 June when we finished the observation of Transect 4, the entirety of Transect 3 (J-9 to 12) as well as J-13 and J-16 had been dominated by shelf water for more than 10 d (Figs. 1b, 10). We report these findings in Ta-
Table 4. Satellite PAR data and NCP at the selected stations in October 2014.

<table>
<thead>
<tr>
<th>Station</th>
<th>Date of observation</th>
<th>MLD (m)</th>
<th>$Z_{eu}$ (m)</th>
<th>Surface PAR$^a$ (mol m$^{-2}$ d$^{-1}$)</th>
<th>$K_d$ (m$^{-1}$)</th>
<th>ML PAR$^b$ (mol m$^{-2}$ d$^{-1}$)</th>
<th>NCP (mmol C m$^{-2}$ d$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-01</td>
<td>13 Oct 2014</td>
<td>58</td>
<td>82</td>
<td>42.0</td>
<td>5.6 × 10$^{-2}$</td>
<td>12.0</td>
<td>3.0</td>
</tr>
<tr>
<td>O-02</td>
<td>13 Oct 2014</td>
<td>64</td>
<td>74</td>
<td>42.0</td>
<td>6.2 × 10$^{-2}$</td>
<td>10.0</td>
<td>15.1</td>
</tr>
<tr>
<td>O-03</td>
<td>14 Oct 2014</td>
<td>56</td>
<td>84</td>
<td>41.1</td>
<td>5.5 × 10$^{-2}$</td>
<td>12.4</td>
<td>10.1</td>
</tr>
<tr>
<td>O-08</td>
<td>21 Oct 2014</td>
<td>49</td>
<td>72</td>
<td>38.7</td>
<td>6.4 × 10$^{-2}$</td>
<td>11.4</td>
<td>15.7</td>
</tr>
<tr>
<td>O-10</td>
<td>15 Oct 2014</td>
<td>68</td>
<td>81</td>
<td>40.0</td>
<td>5.7 × 10$^{-2}$</td>
<td>9.8</td>
<td>4.4</td>
</tr>
<tr>
<td>O-13</td>
<td>16 Oct 2014</td>
<td>48</td>
<td>52</td>
<td>39.2</td>
<td>8.9 × 10$^{-2}$</td>
<td>8.7</td>
<td>15.3</td>
</tr>
<tr>
<td>O-15</td>
<td>22 Oct 2014</td>
<td>49</td>
<td>68</td>
<td>38.6</td>
<td>6.8 × 10$^{-2}$</td>
<td>10.8</td>
<td>16.3</td>
</tr>
<tr>
<td>O-20</td>
<td>18 Oct 2014</td>
<td>35</td>
<td>61</td>
<td>39.2</td>
<td>7.5 × 10$^{-2}$</td>
<td>13.3</td>
<td>16.4</td>
</tr>
<tr>
<td>O-22</td>
<td>17 Oct 2014</td>
<td>76</td>
<td>102</td>
<td>42.2</td>
<td>4.5 × 10$^{-2}$</td>
<td>11.6</td>
<td>15.7</td>
</tr>
</tbody>
</table>

$^a$ Average surface PAR over the residence time of O$_2$ in the mixed layer.
$^b$ Average PAR in the mixed layer.

Table 3, along with the residence time ($\tau$) of O$_2$ in the mixed layer and the difference ($\Delta$d$_{day}$) between the date of observation and the start date of shelf water intrusion at the stations with surface salinity lower than 33. $\Delta$d$_{day}$ can represent the duration of the shelf water intrusion at each station before our observation. The residence time of O$_2$ in the mixed layer at most stations listed in Table 3 is shorter than or equivalent to $\Delta$d$_{day}$. This result suggests that our estimate has appropriately integrated the NCP during the period of shelf water intrusion, which can effectively reflect the influence of shelf water on the productive state of the northern slope of the SCS in the summer.

The amount of light may also play a role in the extent of primary production. The MLD is considered a driver of light availability in the mixed layer (Cassar et al., 2011; Hahm et al., 2014). The euphotic layer was on average 40 m thicker than the mixed layer in the study region during the summer cruise; thus, it is not very significant to discuss the light limitation in June 2015. We conducted an analysis of light availability based on daily satellite PAR data and NCP in October 2014. To minimize the influence of DIN concentrations, we selected nine stations with surface DIN concentration in the range of 0.10–0.17 µmol L$^{-1}$. The average surface PAR (mol m$^{-2}$ d$^{-1}$) at each station was integrated over the residence time of O$_2$ before our observation. Then an average PAR in the mixed layer was calculated based on $K_d$. At the selected stations, the surface PAR varies over a range of 38.6–42.2 mol m$^{-2}$ d$^{-1}$, while the average PAR in the mixed layer (ML PAR) ranged from 8.7 to 13.3 mol m$^{-2}$ d$^{-1}$ (Table 4). There is no significant correlation between the average PAR and NCP in the mixed layer (Table 4), partly suggesting that light intensity may not be a factor for NCP in the autumn. Light availability in the northern slope region of the SCS is enough to support the primary production of phytoplankton.

4 Conclusion

The distribution of $\Delta$(O$_2$/Ar) and NCP on the northern slope of the SCS was strongly affected by nutrient availability, especially nitrogen. The nitrogen limitation on NCP was found both in the autumn and summer. In June 2015, we observed strong biological responses to the supply of nitrogen induced by eddy-entrained shelf water intrusion. NCP in the region with the influence of shelf water was 23.8 ± 10.7 mmol C m$^{-2}$ d$^{-1}$ on average, with a maximum of 61.4 mmol C m$^{-2}$ d$^{-1}$. In addition, vertical mixing caused considerable underestimation of NCP in the transect influenced by a cold eddy. Removing the regions with the influence of shelf water intrusion and vertical mixing, the average NCP in other regions was 5.0 ± 6.2 mmol C m$^{-2}$ d$^{-1}$. This value agrees well with previously published NCP estimates for the study area. Our results also reveal the rapid response of the ecosystem to physical processes. Summer shelf water intrusion may significantly promote NCP by potentially more than threefold in the study region. This is the first report that quantifies the contribution of shelf water intrusion to NCP on the northern slope of the SCS in the summer. Because of the sufficient illumination in the tropical SCS, light availability may not be a significant limitation on NCP in both seasons. The high-resolution NCP estimates derived from continuous measurement of O$_2$/Ar presented in this paper are of significance for understanding the carbon cycle in the highly dynamic system of the SCS.

Data availability. All data presented in this paper are available on Zenodo (https://doi.org/10.5281/zenodo.4496886, Qin et al., 2021).

Supplement. The supplement related to this article is available online at: https://doi.org/10.5194/os-17-249-2021-supplement.
Author contributions. GZ and YH designed and set up the underway measurement system. WZ attended both cruises (in June 2015 and October 2014) in the South China Sea and was mainly responsible for operating the underway measurement system during the cruises. SL provided the nutrient data from both cruises. CQ attended the cruise in June 2015 and prepared the paper with contributions from all co-authors.

Competing interests. The authors declare that they have no conflict of interest.

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