Spatiotemporal variations and controlling factors of the surface $p\text{CO}_2$ in the northern South China Sea

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Abstract. The focal area of this study was the northern South China Sea (NSCS; 18.5°-22.5°N, 1.0°-8.0°E), located on the northwestern shelf of the SCS. The surface $p\text{CO}_2$ ($p\text{CO}_2\text{w}$), sea surface temperature (SST) and sea surface salinity (SSS) was measured by continuous measurement system during four field surveys to show their spatiotemporal variations in the NSCS. Low $p\text{CO}_2\text{w}$ in the southwestern region of PRE were observed in four seasons, particularly in spring and summer. The Pearl River diluted water (PRDW) discharged a large amount of nutrients into nearshore waters, which promoted phytoplankton propagation and $CO_2$ uptake in spring and summer. On the contrary, primary productivity was low in winter and late autumn, runoff input of dissolved inorganic carbon (DIC) played important role in increasing the $p\text{CO}_2$ in nearshore waters, so the PRDW controlled the spatiotemporal variations of $p\text{CO}_2\text{w}$ in the coastal and inner shelf. The $p\text{CO}_2\text{w}$ in the outer shelf and slope were relatively high in four seasons, and SST was the critical controlling factor of $p\text{CO}_2\text{w}$, sea-air $CO_2$ exchange also played role in the seasonal scales of $p\text{CO}_2\text{w}$, the impact of weather and climate events on the variations of $p\text{CO}_2$ and sea-air $CO_2$ flux in the short term also were remarkable. Generally, the NSCS acted as sink of atmospheric $CO_2$ in spring, late autumn and winter, particularly in latter two seasons, in contrast, it was weak $CO_2$ source in summer.

1. Introduction

The emissions of a large amount of $CO_2$ and other greenhouse gases into the atmosphere leaded global warming and ocean acidification since the onset of the industrial revolution. The oceanic sink has absorbed ~40% of the $CO_2$ due to human activities, which was emitted from the burning of fossil and industrial production [1]. Marginal seas, despite comprising only 7% - 8% of the global ocean, played critical role in global carbon cycle. First, marginal seas were important links of carbon exchange among sea, atmosphere and terrestrial ecosystem [2]. Second, marginal seas accounted for 15% - 30% of primary productivity and ~80% of organic matter burial in the global ocean [3]. Lastly, because ~60% of the world’s population lived near the 100km of coastlines [4], anthropogenic activities input abundant organic matter into coastal waters. Thus far, coastal waters have received increasing attention in studies of global carbon cycle [5-7]. However, the dynamic nature of coastal waters and the variations of $p\text{CO}_2\text{w}$ were complicated, and most marginal seas were absent of sufficient field investigations. Hence, the controlling factors of $p\text{CO}_2\text{w}$ and sea-air $CO_2$ flux should remain huge challenges in marginal seas.
The SCS covered an area of \(3.5 \times 10^6\) km\(^2\) and located in tropical and subtropical regions, was the third largest marginal sea in the world. It included central basins exceeding 5000 m in depth as well as wide northwestern and southern shelves. The northwestern shelf and slope regions were oligotrophic, had low productivity, and were net sources of atmospheric CO\(_2\), particularly in summer [8,9]. Carbon cycle in the SCS has been affected by other seas through water mass exchange. The deep water in the SCS and water at ~2000 m in the West Philippine Sea had similar characteristics [10]. The west area of Luzon Strait was affected by Kuroshio [11], the intrusion of the CO\(_2\)-enriched Kuroshio from North Pacific deep water might have influenced the carbon cycle in the SCS. The SCS was connected with the Sulu Sea via the 420 m deep Mindoro Strait and with the East China Sea (ECS) via the Taiwan Strait [12]. Moreover, the SCS was fed by the two major Pearl River and Mekong River runoff. Thus, the SCS encompassed various physical and biogeochemical domains, high resolution surveys should be warranted to explore controlling factors of \(p\text{CO}_2\) in the SCS.

The spatial and seasonal changes of the \(p\text{CO}_2\) in the PRE were reported [13,14], the spatiotemporal distributions of \(p\text{CO}_2\) and sea-air CO\(_2\) fluxes were studied in different seasons and domains in SCS [15], but the controlling mechanisms of the PRDW on affecting the distribution of \(p\text{CO}_2\) in nearshore waters should need further studies. The nearshore waters had high productivity and served as a strong CO\(_2\) sink because of the nutrient supply, and the productive estuarine plume might be extensive in flooding seasons [16]. However, primary productions promoted by runoff might be offset by heterotrophic activity enhanced by terrestrial organic carbon [17], and the runoff inorganic carbon input also directly elevated \(p\text{CO}_2\) in nearshore waters [18]. In addition, the weather and climate events significantly have affected the distribution of \(p\text{CO}_2\) and sea-air CO\(_2\) fluxes in the short term. In this study, spatiotemporal variations of \(p\text{CO}_2\) were investigated by using continuous and autonomous observation system and in-situ data from seasonal shipboard sampling, and the controlling dynamics of \(p\text{CO}_2\) in the NSCS were explored relative to the diluted waters, thermohaline characteristic, and weather and climate events, especially the controlling mechanisms of the PRDW was discussed.

## 2. Materials and methods

The focal area of this study was the NSCS, which was located on the northwestern shelf of the SCS (Figure 1). The SCS monsoon was an important part of the East Asian monsoon system. The northeast monsoon began to bring dry air to the SCS in August and reached its peak in December, at which time the maximum wind speed appeared around the Taiwan Strait and Luzon Strait [19]. The southwest monsoon brought moist air to the SCS in May, peaking in August. Typhoons were frequent from June to November in the SCS [20].

Four cruises were conducted in winter (February 20-28, 2011), spring (May 21-29, 2011), summer (August 21-25, 2011) and late autumn (November 23-December 31, 2013). Persistent strong cold air in the NSCS during November 2011 forced the termination of the November-December 2011 field survey. The autumn investigation was resumed in November 2013 and finished in December owing to the invasion of strong cold air again. The four cruises covered similar areas between 18.5°-22.5°N and 111.0°-118.0°E (Figure 1) including six transects: A, B, C, D, nearshore (NS), and offshore (OS). The underway continuous measurement system (GO8050) was used to measure \(p\text{CO}_2\), the average collected frequency of datasets was one group per two minutes. The device was calibrated by zero gas and the highest CO\(_2\) standard gas, the standard curve was drew by 4 standard gases at 0.00, 218.16, 346.40 and 584.75 ppm. These standard gases with < 0.03% uncertainty were made by the Chinese Academy of Meteorological Sciences. Seawater sample was continuously pumped from shaft in the fore deck and transported to the ship's laboratory at large flow and high speed to reduce heating. In order to avoid flue gas pollution and human disturbance, atmospheric air was sampling from front section and upper deck of ship.
Figure 1. Map of the NSCS and circulation patterns. (a) the six investigated transects include A, B, C, D, NS and OS. (b) NSCS circulation patterns [21], the solid line was winter, the dotted line was summer. 1. Kuroshio, 2. Loop Current, 3. SCS Branch of Kuroshio, 4. SCS Warm Current, 5. Guangdong Coastal Current.

The temperature in the equilibration system was measured by platinum resistance thermometer, there was small difference of less than 0.2 °C on temperature between the ship’s shaft in fore deck and the equilibrator. The $p_{\text{CO}_2}$ in the equilibrator was calibrated to in situ $p_{\text{CO}_2w}$ by using saturated water vapor pressure and the temperature effect coefficient of 4.23% °C$^{-1}$ [22]. SST and SSS was measured by CTD sensor (SBE21), SST and dissolved oxygen (DO) was measured by oxygen sensor (Aanderaa oxygen optode 3835), while SST, SSS and DO was also measured by multi-parameter water quality detector (YSI 6600 meter). All SST, SSS and DO data from different sensors were mutually corrected before or during the cruises, the results of different sensors were consistent. The error level between different SST sensors was less than 0.1 °C and the error between DO sensors was less than 1 μmol/L.

The formula for the sea-air CO$_2$ flux calculation was $F = k \times s \times \Delta p_{\text{CO}_2}$, $k$ (cm·h$^{-1}$) was the gas transfer velocity of CO$_2$ and calculated by $k = 0.31u^2 \left( \frac{Sc}{660} \right)^{-0.5}$ in the W92 formula [23]. It has been suggested that the parameterization of the W92 formula may overestimate the gas transfer velocity, as $k = 0.27u^2 \left( \frac{Sc}{660} \right)^{0.5}$ in the Sweeney equation [24]. However, for ease of comparison with most other studies, the $k$ value was calculated on the basis of the W92 formula, $s$ was the solubility of CO$_2$ in seawater [25], and $\Delta p_{\text{CO}_2} (p_{\text{CO}_2w} - p_{\text{CO}_2a})$ was the difference between $p_{\text{CO}_2w}$ and $p_{\text{CO}_2a}$. Wind speed was the major factor driving sea-air CO$_2$ flux, wind speed, barometric pressure and relative humidity was collected by shipborne meteorological station at height of 10 m above the sea level. Thus, the mean of wind speed during every cruise was used in this study to estimate the sea-air CO$_2$ flux. A negative value indicated that the sea was sink of atmospheric CO$_2$, a positive value represents that the sea was source of atmospheric CO$_2$.

3. Results and discussion

3.1. Spatiotemporal distributions of $p_{\text{CO}_2w}$, SST, and SSS

The spatiotemporal distributions of $p_{\text{CO}_2w}$, SST, and SSS in the NSCS for a composite year were shown in Figure 2. In order to better describe the distributions of $p_{\text{CO}_2w}$, SST, and SSS and research controlling mechanisms of $p_{\text{CO}_2w}$, the sea area influenced by PRDW was called the coastal area and inner shelf in this study where SSS was less than ~33, the other sea area was called the outer shelf and slope where SSS was more than ~33.

Low SST and high SSS in winter occurred in the entire observation zone (Figure 2a). The SST ranged from 14.85 °C to 24.59 °C, and the SSS was between 31.24 and 34.54 (Table 1). The low SST and high SSS can be attributed to the presence of cold air during the observation. The SST and SSS in the coastal area and inner shelf were both lower than other regions, averaging 15.99 °C and 32.09 (Table 1). The average of $p_{\text{CO}_2w}$ in the NSCS (except transect A) was $(340\pm19)\ \mu$atm (Figure 2c) in winter, and among the average of $p_{\text{CO}_2w}$ $(334\pm9)\ \mu$atm to $(367\pm11)\ \mu$atm [15], but the average of $p_{\text{CO}_2w}$ was $(381\pm3)\ \mu$atm in transect A and higher than other transects, $\Delta p_{\text{CO}_2w}$ between transect A and other transects reached $\sim41\mu$atm.
Figure 2. Spatiotemporal distributions of SST/℃, SSS and $p$CO$_2$w/$\mu$atm for (a)-(c) February 2011, (d)-(f) May 2011, (g)-(i) August 2011, and (j)-(l) November-December 2013 corresponding with winter, spring, summer and late autumn, respectively. The blue dotted line in Figure 2c, f, i, l was the rough SSS contour of 33.

Table 1. Summary of SST, SSS and $p$CO$_2$w in the NSCS during the four cruises.

| Observation seasons | In the NSCS | In the coastal and inner shelf | In the outer shelf and slope |
|---------------------|-------------|--------------------------------|-------------------------------|
|                      | SST (°C)    | SSS     | $p$CO$_2$w (μatm) | SST (°C) | SSS     | $p$CO$_2$w (μatm) | SST (°C) | SSS     | $p$CO$_2$w (μatm) |
| Winter              | 14.85-24.59 | 31.24-34.54 | 263-387 | 14.85-17.68 | 31.24-32.98 | 263-363 | 14.86-24.59 | 33.02-34.54 | 286-387 |
|                     | 22.00±2.8   | 33.85±0.70 | 347±22  | 15.99±0.6  | 32.09±0.43 | 327±27  | 22.86±1.7   | 34.09±0.21 | 349±20 |
| Spring              | 25.30-29.35 | 25.16-33.98 | 198-413 | 25.30-28.81 | 25.16-32.89 | 198-379 | 25.65-29.35 | 33.03-33.98 | 320-413 |
|                     | 26.97±0.8   | 32.92±1.84 | 367±42  | 26.60±0.9  | 29.65±2.58 | 300±42  | 27.28±0.8   | 33.60±0.23 | 388±13 |
| Summer              | 29.50-32.12 | 28.66-33.83 | 188-435 | 29.50-32.12 | 28.66-33.00 | 188-417 | 28.92-31.48 | 33.07-33.83 | 343-435 |
|                     | 30.04±0.5   | 33.33±0.74 | 389±30  | 30.47±0.5  | 31.49±0.98 | 350±62  | 29.96±0.4   | 33.57±0.12 | 397±10 |
| Late autumn         | 17.03-25.10 | 30.66-34.23 | 292-397 | 18.83-21.21 | 30.66-33.00 | 292-366 | 17.03-25.10 | 33.02-34.23 | 310-397 |
|                     | 22.77±1.9   | 33.54±0.70 | 348±19  | 20.05±0.6  | 32.03±0.49 | 334±20  | 23.33±1.5   | 33.83±0.23 | 351±17 |

The SST in spring was between 25.30 °C and 28.80 °C, with an average of 26.97 °C (Table 1), and apparently higher than that in winter. The SSTs in transects NS, A, and B were lower than those in transects OS, C, and D (Figure 2d). This result was consistent with the changes of atmospheric temperature during the field investigation. The lowest SSS of 25.16 was observed in the southwestern region of the PRE (Table 1, Figure 2e), indicating the effect of Pearl River runoff on transect NS. The average of $p$CO$_2$w was (300±42) μatm and also low in the southwestern region of the PRE (Figure 2f), ranging from 198 μatm to 379 μatm (Table 1), and was obviously lower than the result off the Pearl River Estuary where the average of CO$_2$ was (361±10) μatm and ranged from 339 μatm to 378 μatm [15]. Interestingly, this result was consistent with the lowest SSS observed in the same region, which...
could demonstrate the obvious effect of Pearl River runoff on the distribution of pCO$_2$w. However, pCO$_2$w was not uniform with SSS in other transects, and the pCO$_2$w was higher in transect A and B than C, D and OS. Moreover, the distribution of pCO$_2$w was similar to that of SST, which indicated that SST was a probable controlling factor in the outer shelf regions. The low pCO$_2$w in the coastal area and inner shelf accompanied by a ΔpCO$_2$ value of approximately -85 μatm indicated a remarkable CO$_2$ sink.

The SST and SSS in summer was the highest in all the four seasons, varying from 29.50 °C to 32.12 °C and from 38.76 to 33.83, respectively (Table 1), but the ranges of SST and SSS were relatively small. The SSS was slightly lower in the southwestern region of the PRE than other transects, and the plume of PRDW was smaller in summer than that in spring (Figure 2e, 2h). The range of pCO$_2$w was from 188 μatm to 435 μatm and the average of pCO$_2$w was (389±30) μatm (Table 1). The low endpoint appeared in the transect NS, which was consistent with low SSS (Figure 2i). In contrast, the average pCO$_2$w in the outer shelf and slope was as high as (397±10) μatm (Table 1), the ΔpCO$_2$ was ~25 μatm, and was within the previous studies results which was between (383±11) μatm and (404±6) μatm [15].

The SST was between 17.03 °C and 25.10 °C, the SSS ranged from 30.66 to 34.23 in late autumn, low SST and high SSS existed in NSCS and was similar to the results in winter (Figure 2j, 2k), SST and SSS was both lower in the transect NS affected by PRDW than other transects (Figure 2j, 2k). The pCO$_2$w sharply dropped down under the influence of cold air, the average of pCO$_2$w was (348±19) μatm with ranging from 292 μatm to 397 μatm (Table 1), that was similar to that in winter in the coastal area and extended to the entire shelf (Figure 2i). The pCO$_2$w in late autumn was lower than previous studies with the average of (358±4) μatm to (377±18) μatm [15].

3.2. Effect of diluted waters on pCO$_2$w in the coastal and inner shelf

The PRDW was the largest runoff in the NSCS, with an annual discharge of about 3.3×10$^{11}$ m$^3$. The PRDW flowed to the southwest after exiting the PRE under effect of Coriolis force [26]. Only in summer, the surface of PRDW might shift to flow toward the northeast away from the coast under the influence of the southwest monsoon. The SSS in the four seasons 2006 and 2007 decreased gradually from northeast to southwest in PRE [27], and the bottom of PRDW expanded westward for the whole year [28]. The lowest SSS was in the southwestern region off the PRE (Figure 2), and the outer boundary of PRDW was SSS of ~33 [29].

Since the temperature effect was usually the first-order controlling factor on pCO$_2$w, temperature-normalized pCO$_2$w (pCO$_{2ws}$) was used to explore the effect of SSS and biological productivity on pCO$_2$w. In this study, pCO$_{2ws}$ and SSS showed strong correlation when SSS was less than ~33 (Figure 3a), the correlations in spring and summer were positive (Figure 3a) and the linear correlation coefficients R$^2$ were > 0.75, that indicated that lower SSS (more PRDW) related to lower pCO$_2$w. And we found relationships between pCO$_2$w and DO were negative in spring and summer, the linear correlation coefficients R$^2$ were 0.77 and 0.58, respectively, so lower SSS coupled with lower pCO$_{2ws}$ and higher DO (Figure 3b). In fact, The PRDW input a large amount of nutrients into nearshore waters, biological productivity could be enhanced in the plume, photosynthesis produced O$_2$ and removed CO$_2$. The diluted waters of Changjiang River was also the main factor of pCO$_{2ws}$, and leaded to the decrease of pCO$_2$w and the increase of O$_2$ in summer, the variations of pCO$_2$w and DO generally mirrored in the Changjiang River plume [31]. And intensive primary productivity in spring owing to Changjiang diluted waters also induced the sharp drawdown of pCO$_2$w in the southern Yellow Sea [32]. The good negative correlations between pCO$_2$w and chlorophyll-a in spring were also found in the North Sea, and the pCO$_2$w was modulated by continental inputs and photosynthetic activity [33]. Generally, diluted waters carried nutrients into coastal sea, and promoted phytoplankton propagation in favorable season and conditions, phytoplankton absorbed CO$_2$ and released O$_2$, finally primary productivity induced low pCO$_{2ws}$ and high O$_2$.

On the contrary, pCO$_{2ws}$ and SSS showed a negative relationship in winter and late autumn (Figure 3a), the linear correlation coefficients R$^2$ were 0.71 and 0.48, respectively, that indicated that lower
SSS (more PRDW) related to higher $pCO_2w$, the PRDW could have contributed DIC into coastal area and inner shelf, and the variation of SSS was slight and the DO content was stable in late autumn and winter (Figure 3a). Because autumn and winter was dry seasons in South China, the Pearl River runoff relative decreased in dry seasons than wet seasons, but DIC in the freshwater end-members were $>2700 \mu\text{mol} \cdot \text{kg}^{-1}$ in autumn and winter, and higher at $\sim1000 \mu\text{mol} \cdot \text{kg}^{-1}$ in spring and summer [34]. So runoff DIC input had significant impact on increasing CO$_2$ concentration in the plume, and directly elevated $pCO_2w$ owing to terrestrial sources [35]. The DO was nearly steady (Figure 3b) and primary productivity was low in late autumn and winter. Low primary productivity didn’t uptake abundant carbon and draw down $pCO_2w$, which the runoff delivered into nearshore waters, so $pCO_2w$ was high when SSS was low in late autumn and winter. The primary productivity in winter was only 1/10 of that in summer in ECS due to low temperature and light intensity, the Changjiang diluted water enhanced the $pCO_2w$ in plume [36]. The Liaonian nearshore waters of the Northern Yellow Sea in autumn was a source under influencing of runoff input [37].

Figure 3. Relationships between $pCO_2w$ and SSS (a), and between $pCO_2w$ and DO (b) when the SSS was less than $\sim33$.

3.3. Controlling factors of $pCO_2w$ in the outer shelf and slope

SST was the lowest in late autumn and winter, middle in spring and highest in summer when the SSS was more than $\sim33$, and the relationships between $pCO_2w$ and SST were strongly positive in the four seasons (Figure 4a), the all linear correlation coefficients $R^2$ were $>0.50$ and the highest value of $R^2$ was 0.93 in February 2011, SST was the major controlling factor in the variations of $pCO_2w$ in the outer shelf and slope [9,16]. However, $pCO_2w$ in late autumn was higher than that in spring when the SST was around 25°C, which was mainly because vertical mixing induced by monsoon forced deep water with high $pCO_2w$ to intrude into surface water and enhanced $pCO_2w$ in late autumn [38]. In addition, $pCO_2w$ in spring was higher than that in summer when the SST was around 28°C, the offshore waters absorbed CO$_2$ from atmosphere in late autumn and winter, and had a lot of accumulations on CO$_2$ because the carbonate system had buffering effect. CO$_2$ efflux just began when SST rose in spring, then accumulative effect on $pCO_2w$ decreased gradually with CO$_2$ release during three month period, so $pCO_2w$ in summer was lower than in spring at the same SST, the sea-air CO$_2$ fluxes was also a main factor of modulating $pCO_2w$ at seasonal time scales [39].

Figure 4. Relationships between $pCO_2w$ and SST excluding transect A and the southern region of transect B in winter. (a) Relationship between $pCO_2w$ and SST when SSS was more than $\sim33$. (b) Relationship between $pCO_2w$ and SST when the SSS was less than $\sim33$. 
Clear differences were noted in late autumn and winter when the SSS was less than ~33 (Figure 4b). The relationship between $pCO_2w$ and SST was negative, although it was weak. The low-temperature diluted waters input abundant inorganic carbon into nearshore waters in late autumn and winter, but the biological productivity was not active, that resulted in relatively high $pCO_2w$ and low SST. The relationship between $pCO_2w$ and SST in spring and summer was not clear.

3.4. Impact of weather and climate events on $pCO_2w$

Cold air was encountered during the winter and late autumn observation. The average of $pCO_2w$ and sea-air CO2 flux in transect A was $(381\pm3)\,\mu\text{atm}$ and $-1.30\,\text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ in winter, which was $(340\pm19)\,\mu\text{atm}$ and $-8.20\,\text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ in other transects, the $pCO_2w$ and sea-air CO2 flux in transect A after the occurrence of cold air was obviously higher than that in other transects (Figure 2c), and the wind speed during the transect A was $(11.8\pm2.0)\,\text{m}\cdot\text{s}^{-1}$, and bigger than $(8.20\pm2.2)\,\text{m}\cdot\text{s}^{-1}$ during the other transects observation. The cold air forced deep water with high $pCO_2w$ to intrude into surface waters, and the vertical mixing in the transect A abated the decrease of $pCO_2w$ through the cooling of the surface water.

SSTs in late autumn dropped sharply owing to the strong invasion of cold air prior to the investigation, and SSTs were close to those in winter (Table 1, Figure 4b). Intense cooling decreased the average of $pCO_2w$ to $(348\pm19)\,\mu\text{atm}$, and the $\Delta pCO_2$ was $\sim -40\,\mu\text{atm}$. The sea-air CO2 flux was $-8.49\,\text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$, the NSCS was a strong CO2 sink in late autumn. Moreover, the wind speed also increased by $10.1\,\text{m}\cdot\text{s}^{-1}$ at the arrival of the cold air (Table 2), because the sea-air CO2 flux was proportional to the square of wind speed, therefore, cold air not only influenced the distribution of $pCO_2w$, but also affected the sea-air CO2 fluxes. In addition, the tropical depression also contributed to the high $pCO_2w$ and CO2 effluxes in SCS by uplifting CO2-rich deeper water to the surface due to winds accompanied by it, and the CO2 effluxes during three typhoons were as high as 60% of the whole year in the ECS [40].

The El Niño also affected on the distributions of $pCO_2w$ by modulating global climate system. Rainfall in Guangdong province increased during May 2015 due to the influence of El Niño, a large amount of diluted water was discharged into nearshore waters, and the average of SSS in the coastal and inner shelf region decreased to $28.05 \pm 6.18$, which was lower than that in May 2011 ($29.65 \pm 2.58$), meanwhile the average of SST was $2.10 ^\circ\text{C}$ higher in May 2015 than May 2011. The abundant nutrients which brought by PRDW and the higher SST jointly promoted phytoplankton propagation in May 2015, which absorbed a mounts of CO2 from seawater and released O2 in the coastal and inner shelf region. The average of $pCO_2w$ in the coastal and inner shelf region was $(286 \pm 95)\,\mu\text{atm}$ in May 2015, which was lower than $(300 \pm 42)\,\mu\text{atm}$ in May 2011. SST was still the major controlling factor of the $pCO_2w$ in the outer shelf and slope region, SST rose by $1.96 ^\circ\text{C}$ during El Niño, the average of the $pCO_2w$ in offshore waters was $(421 \pm 9)\,\mu\text{atm}$ in May 2015 and $(386 \pm 13)\,\mu\text{atm}$ in May 2011, the difference was 35 $\mu$atm. The influences of El Niño made carbon sink increase in the coastal and inner shelf region and carbon source enhance in the outer shelf and slope region, the results of two processes offset mostly each other. The sea-air CO2 flux was $(-0.40 \pm 5.39)\,\text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ during El Niño, the difference was not significant comparing to $-0.67\,\text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ in May 2011 [41].

3.5. Sea-air CO2 flux estimation

The NSCS was CO2 source with the efflux of $1.40\,\text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ and released CO2 in summer. This result was consistent with $0\,\text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ to $1.9\,\text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ in the basin and $0.3\,\text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ to $5.5\,\text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ in the southern shelf of the SCS [42], but higher than previous estimations of $-1.49\,\text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ to $0.17\,\text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ in the NSCS [16]. However, the sea-air CO2 flux in summer was $-2.82\,\text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ in the coastal and inner shelf and nearshore water was a net sink, the sea-air CO2 flux was $2.00\,\text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ in the outer shelf and slope and offshore waters was a source.

The sea-air CO2 flux was $-0.58\,\text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ in spring and consistent with $-0.85\,\text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ in the NSCS [16], that indicated a weak CO2 sink. And the coastal and inner shelf was a moderate sink of $-3.07\,\text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$, but 0.10 $\text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ in the outer shelf and slope.
The sea-air CO$_2$ flux in the NSCS was -6.54 mmol·m$^{-2}$·d$^{-1}$ in winter and -8.49 mmol·m$^2$·d$^{-1}$ in late autumn, that demonstrated strong CO$_2$ uptake, which in the coastal and inner shelf was -9.67 mmol·m$^2$·d$^{-1}$ in winter and -11.64 mmol·m$^2$·d$^{-1}$ in late autumn, and respectively lower than -6.11 mmol·m$^2$·d$^{-1}$ and -8.05 mmol·m$^2$·d$^{-1}$ in the outer shelf and slope (Table 2). The sea-air CO$_2$ flux in winter was consistent with previous studies such as -4.16 mmol·m$^2$·d$^{-1}$ to -8.59 mmol·m$^2$·d$^{-1}$ in winter [16], but which in late autumn was slightly less than their results of -1.55 mmol·m$^2$·d$^{-1}$ to -6.29 mmol·m$^2$·d$^{-1}$.

Generally, the NSCS acted as net CO$_2$ sink in spring, late autumn and winter, particularly in latter two seasons, in contrast, it was weak CO$_2$ source in summer.

### Table 2. Summary of $p$CO$_2$a, wind speed, and sea-air CO$_2$ flux estimation.

| surveying seasons | $p$CO$_2$a (μatm) | Wind speed (m·s$^{-1}$) | Sea-air CO$_2$ flux (mmol·m$^{-2}$·d$^{-1}$) |
|-------------------|-------------------|----------------------|---------------------------------------------|
|                   |                   |                      | In the NSCS | In the coastal and inner shelf | In the outer shelf and slope |
| Winter            | 383-402 389±5     | 8.2 ± 2.5            | -6.54       | -9.67                         | -6.11                        |
| Spring            | 373-395 386±5     | 4.6 ± 2.3            | -0.58       | -3.07                         | 0.10                         |
| Summer            | 362-378 369±3     | 5.6 ± 2.4            | 1.40        | -2.82                         | 2.00                         |
| Late autumn       | 382-395 388±3     | 10.1 ± 2.4           | -8.49       | -11.64                        | -8.05                        |

4. Conclusions

Based on high resolution field surveys in the NSCS by underway continuous measurement system (GO8050) in four seasons, the average of $p$CO$_2$a was lower in late autumn and winter, and higher in summer, which in spring was between them. The NSCS absorbed a lot of atmospheric CO$_2$ in winter and late autumn, but released CO$_2$ into atmosphere in summer, both was in dynamic equilibrium in spring. The average of $p$CO$_2$a in the coastal and inner shelf was low and high in the outer shelf and slope in all seasons, the coastal and inner shelf was CO$_2$ sink in all seasons, the outer shelf and slope was only CO$_2$ source in summer.

The PRDW was critical controlling factor of $p$CO$_2$ws in the coastal and inner shelf. The PRDW promoted biological productivity in spring and summer, phytoplankton photosynthesis absorbed CO$_2$ and released O$_2$, $p$CO$_2$ws in the coastal and inner shelf sharply dropped down. However, runoff inorganic carbon input also directly elevated $p$CO$_2$w in winter and late autumn due to low biological productivity. SST was the major controlling factor of $p$CO$_2$a in the outer shelf and slope in all four seasons, sea-air CO$_2$ exchange also played role in the seasonal scales of $p$CO$_2$w, furthermore, the effects of weather and climate events on the variations of $p$CO$_2$w and sea-air CO$_2$ fluxes in the short term were remarkable.

We explored the controlling factors of $p$CO$_2$w in the NSCS by field data analysis and discussion, but the results of $p$CO$_2$w by underway continuous measurement were instantaneous. The controlling processes of $p$CO$_2$w needed to be explored by time-series measurement, including controlling mechanisms of key marine dynamic processes and weather and climate events on $p$CO$_2$w, it could quantitatively calculate various controlling processes to $p$CO$_2$w variation. And what was more, the SCS was one of the world’s major marginal sea systems, it was very important to have comprehensive understandings of carbon cycle in the SCS, especially migration and transformation of different forms of carbon.
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