

RESEARCH ARTICLE

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Seasonal variations of seawater $p\text{CO}_2$ and sea-air CO_2 fluxes in a fringing coral reef, northern South China SeaHongqiang Yan¹, Kefu Yu^{1,2}, Qi Shi¹, Yehui Tan¹, Guohui Liu¹, Meixia Zhao¹, Shu Li¹, Tianran Chen¹, and Yinghui Wang²¹Key Laboratory of Marginal Sea Geology, South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou, China, ²Coral Reef Research Center of China, Guangxi University, Nanning, China

Key Points:

- Both sea surface partial pressures of CO_2 and sea-air CO_2 fluxes show significant seasonal variations
- Seasonal variations of the surface seawater $p\text{CO}_2$ were mainly affected by biological processes
- The studied fringing coral reef area acts as a weak source of atmospheric CO_2

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Abstract Evidence based on four field surveys conducted between July 2009 and April 2011 indicates that both sea surface partial pressures of CO_2 ($p\text{CO}_2$) and sea-air CO_2 fluxes at Luhuitou fringing reef in Sanya, Hainan Island, northern South China Sea (SCS) are subject to significant seasonal variations. The diurnal variation of seawater $p\text{CO}_2$ ranges from 264 to 579 μatm in summer, which is much larger than that in autumn (152–335 μatm), in winter (84–260 μatm), and in spring (114–228 μatm). The sea-air CO_2 flux in summer ($\sim 9.6 \text{ mmol } \text{CO}_2 \text{ m}^{-2} \text{ d}^{-1}$) is also larger than that in other seasons (i.e., $\sim 3 \text{ mmol } \text{CO}_2 \text{ m}^{-2} \text{ d}^{-1}$ in spring, $\sim 3.5 \text{ mmol } \text{CO}_2 \text{ m}^{-2} \text{ d}^{-1}$ in autumn, and $\sim 2.7 \text{ mmol } \text{CO}_2 \text{ m}^{-2} \text{ d}^{-1}$ in winter). The atmospheric $p\text{CO}_2$ in this reef shows small diurnal and seasonal variations. The integration of the time-series $p\text{CO}_2$ data shows that the reef area is a weak source of atmospheric CO_2 at $\sim 0.54 \text{ mol } \text{CO}_2 \text{ m}^{-2} \text{ yr}^{-1}$. Further analyses indicate that the seasonal variations of the surface seawater $p\text{CO}_2$ in Luhuitou fringing reef are mainly affected by seasonally-dependent biological metabolic processes (organic processes and inorganic processes), and that the organic processes play a more important role than the inorganic process. Seasonal sea surface temperature (SST) variations and hydrodynamic processes may also have some influence on seawater $p\text{CO}_2$ variation.

1. Introduction

Coral reefs play an important role in the global oceanic carbon cycle. For example, the ocean is thought to be able to absorb $2 \text{ Pg } \text{C yr}^{-1}$ [Sabine et al., 2000], of which coral reefs absorb $0.1 \text{ Pg } \text{C yr}^{-1}$; about 5% of the total [Kinsey and Hopley, 1991]. More previously, the “coral reef hypothesis” attributed the sudden increase in atmospheric CO_2 ($\sim 80 \mu\text{atm}$) during the retreat of the Wisconsin glaciers ca. 14 ka BP to variations in coral reef carbonate sedimentation rates [Berger, 1982]. Consequently, coral reefs have received considerable attention with regard to their contributions to atmospheric CO_2 [Gattuso et al., 1993; Kayanne et al., 1995; Frankignoulle et al., 1996; Gattuso et al., 1996a, 1996b, 1999; Bates et al., 2001; Bates, 2002; Fagan and Mackenzie, 2007; Yan et al., 2009, 2011; Massaro et al., 2012; Chen et al., 2013; Shaw and McNeil, 2014]. Photosynthesis, respiration and the precipitation and dissolution of CaCO_3 are the main processes through which coral reefs are involved in the carbon cycle. For example, photosynthetic fixation of CO_2 decreases the partial pressure of CO_2 ($p\text{CO}_2$), whilst the respiratory release of CO_2 increases $p\text{CO}_2$. The formation/dissolution of mineral CaCO_3 ($\text{Ca} + 2\text{HCO}_3^- \rightleftharpoons \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$) also increases/decreases seawater $p\text{CO}_2$ respectively, and influences the seawater CO_2 chemical equilibrium. As a result, the net contribution of coral reefs to the global carbon cycle is still a matter of debate [Yu and Zhao, 2009].

Field observation of atmospheric and seawater $p\text{CO}_2$ is the most widely used approach when investigating sea-air CO_2 exchange and CO_2 flux in coral reefs [Ware et al., 1991; Gattuso et al., 1996c; Gattuso et al., 1999; Kawahata et al., 2000a; Suzuki and Kawahata, 2004; Tan et al., 2004; Fagan and Mackenzie, 2007; Yan et al., 2011; Massaro et al., 2012; Drupp et al., 2013; Shaw and McNeil, 2014]. Many studies have suggested that the community structure of coral reefs may be the critical factor in determining whether they act as a source or sink of atmospheric CO_2 [Suzuki et al., 1995; Suzuki, 1998; Suzuki and Kawahata, 2004]; coral-dominated reef ecosystems are usually sources of atmospheric CO_2 [Ware et al., 1991; Gattuso et al., 1993; Frankignoulle et al., 1996; Gattuso et al., 1996c; Gattuso et al., 1999; Kawahata et al., 1999] while macroalgae-dominated reef systems are often sinks for atmospheric CO_2 [Kayanne et al., 1995; Yamamuro et al., 1995; Kraines et al., 1997]. Maintaining the balance between biological processes, such as calcification and organic carbon

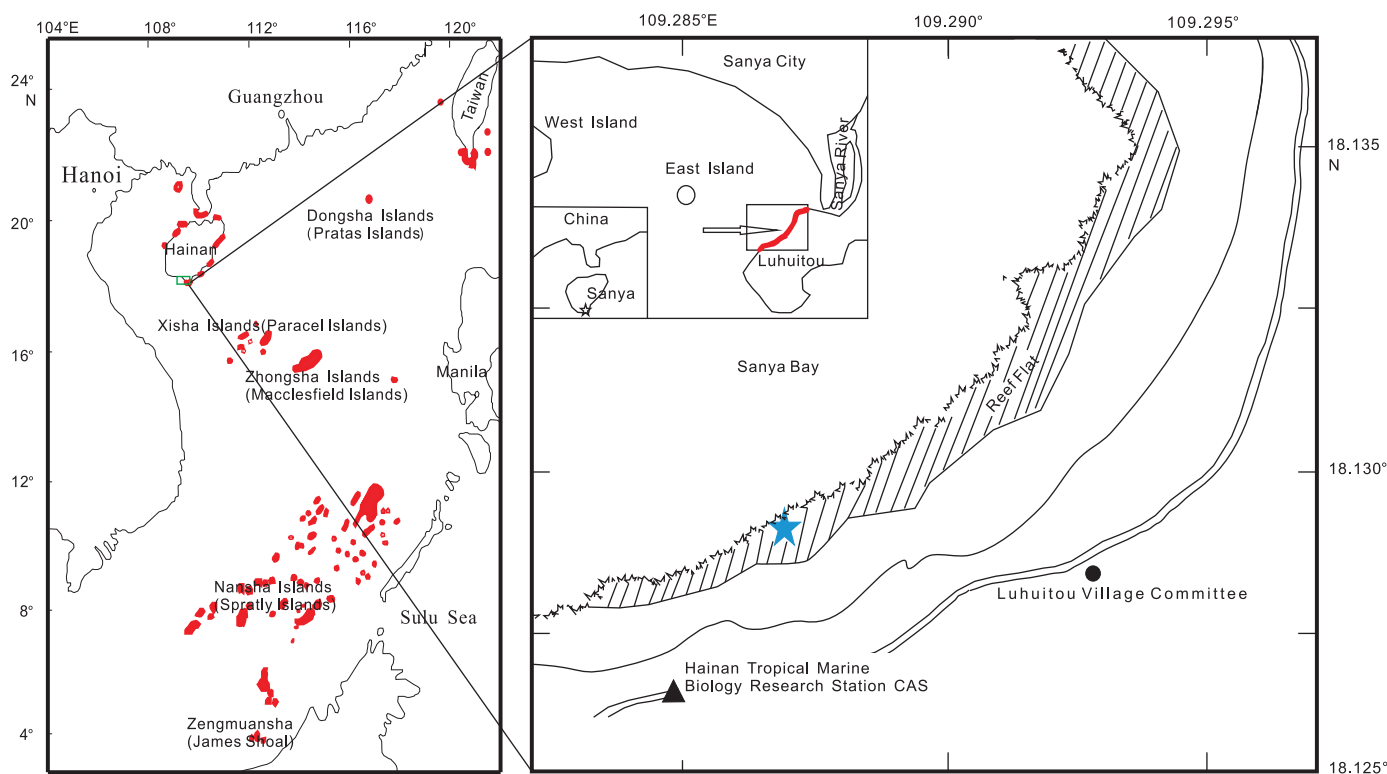


Figure 1. Location map of the coral reef at Hainan, northern SCS. Red areas represent the occurrence of coral reefs in the SCS. The five-pointed star indicates the field site. The triangle indicates the meteorological station of the Hainan Tropical Marine Biology Research Station in Sanya, Hainan.

production, is therefore critical for carbon cycling on reefs, as demonstrated by the fact that many coral-dominated reefs are shifting to become macroalgae-dominated systems due to environmental change (i.e., sea level, carbonate mineral saturation state, SST, visible and ultraviolet light, currents, sedimentation, salinity, nutrients, and other anthropogenic stresses) [Smith and Buddemeier, 1992]. Older studies have often been restricted to observations of seawater CO_2 over only a few days [Gattuso et al., 1993; Kayanne et al., 1995; Gattuso et al., 1996a, 1996b, 1996c; Dai et al., 2009; Yan et al., 2011; Gray et al., 2012], but more recently there has been, as a result of long-term observations, greater insight gained into the seasonal and interannual variability of CO_2 and sea-air CO_2 flux in coral reefs. Some results suggest that seasonal variations of environmental factors (i.e., SST, irradiance, and hydrodynamic processes) and biological metabolisms may be the main driving forces behind the changes in seawater $p\text{CO}_2$ and sea-air CO_2 flux. Bates [2002] studied the seasonal variation of the Bermuda coral reefs and showed that the reef acted as a source of atmospheric CO_2 over an annual cycle. The seasonal variation of sea-air CO_2 flux was attributed to biological and mixing processes between coral reefs and offshore water. Based on a full year's monitoring of seawater CO_2 in Ishigaki Island, Japan, Kayanne et al. [2005] suggested that community metabolism was the main driver on the reef flat. Shaw and McNeil's [2014] study investigated the seasonal variability of sea-air CO_2 flux in waters offshore to Lady Elliot Island, Southern Great Barrier Reef, and suggested that $p\text{CO}_2$ variability was driven primarily by seasonal temperature variations. Drupp et al. [2013] compared CO_2 chemistry in different tropical reef environments, and found that both biological processes and physical forces (temperature, residence time) controlled short-term (hourly-weekly) CO_2 variability, whilst temperature variations were the main cause of long-term seasonal variability. Using the data of CRIMP- CO_2 in the island of Oahu, Hawaii, Massaro et al. [2012] produced similar results. More observations on the seasonal variability of CO_2 and sea-air CO_2 flux in coral reefs are necessary to evaluate the contribution of coral reefs toward atmospheric CO_2 , and to clarify the factors controlling surface-water $p\text{CO}_2$ near coral reefs.

Coral reefs are widely distributed across the South China Sea (SCS), covering areas from Zenmuansha ($\sim 4^\circ \text{N}$) in the south, to Hengchun Peninsula ($\sim 24^\circ \text{N}$) in the north (Figure 1). The total area of modern coral reefs in the SCS is estimated to be $\sim 8000 \text{ km}^2$ [Yu and Zhao, 2009; Yu, 2012]. However, little

information is available on the seasonal or annual sea-air CO₂ exchange for coral reefs in the SCS. Previous studies of sea-air CO₂ exchange in coral reefs of the SCS were restricted to short time-series observations in summer, when the sea conditions are better for fieldwork [Dai *et al.*, 2009; Yan *et al.*, 2011]. Both studies [Dai *et al.*, 2009; Yan *et al.*, 2011] suggest that the SCS coral reefs are a source of atmospheric CO₂. In this study, the seasonal variations of seawater pCO₂ and sea-air CO₂ flux on Luhuitou fringing reef in the northern SCS were investigated to identify whether the coral reef systems in the northern SCS are a source or sink of CO₂ and to reveal its controlling mechanisms.

2. Geography and Natural Environment of the Studied Coral Reef

Luhuitou fringing reef (18.13°N, 109.29°E) is located on the southeast coast of Sanya, Hainan Island (Figure 1), in the northern SCS, and is a typical fringing coral reef. This reef is ~3 km long and has two typical biogeomorphologic units: a reef flat and a reef slope. The average width of its reef flat is ~250 m, with the widest point reaching 450 m. The present living coral cover is ~5% at the reef flat and ~12% on the reef slope. From 1962 to 2009, the mean coral cover decreased dramatically from 80–90% to ~12%, although a relatively high biodiversity was maintained [Zhao *et al.*, 2012, 2014]. Luhuitou fringing reef experiences a dry winter from November to April, dominated by east and northeast monsoons. From May to October, the area experiences a wet season under the influence of south and southwest monsoons. Sea currents inside Sanya Bay are weaker than the dominating tidal currents. The tides at Luhuitou fringing reef range from irregular diurnal-mixed tides to diurnal tides. The mean tidal level is ~1.02 m, and the mean tidal range is ~0.79 m, with the maximum reaching ~1.89 m [Yan *et al.*, 2011]. Yu *et al.* [2010] reported the climatic statistics for the region, including the follows: the mean annual air temperature is ~25.8°C (varying from 24.7°C to 27.0°C); the mean annual sea surface temperature (SST) is 27°C; the lowest monthly average SST is 23.8°C (varying from 20.5–24.7°C) and the highest as 29.8°C (varying from 28.7–30.9°C); the maximum sea surface salinity (SSS) reaches a high of approximately 33.8 in April and a low of 32.1 in October, with an annual mean SSS of 33.1; the mean annual precipitation is 1337 mm, with 90% of rain falling during the wet season (from May to October); the annual mean total sunshine duration is 2478 h (ranging from 1751 to 2873 h); the average wind speed is 2.4 m/s (ranging from 1.3 to 3.5 m/s).

3. Methods

Time-series of 7–10 day period measurements of sea-air CO₂ exchanges were carried out at Luhuitou fringing reef in July–August 2009, November 2010, February 2011, and April 2011, representing summer, autumn, winter, and spring respectively. Atmospheric pCO₂ was monitored every hour using a hand-held CO₂ meter (GM70) made by the Vaisala Company, Finland. The hand-held CO₂ meter was calibrated using standard CO₂ gas (National Research Center for Certified Reference Materials, China) with an uncertainty of <2%. The SST, SSS and dissolved oxygen (DO) were measured using a Yellow Spring Instrument meter (YSI6920V2). The pH and total alkalinity (TA) measurements were collected with the same frequency as those of atmospheric CO₂ at water depths of ~0.5 m (or ~0.2 m at the reef flat during low tide). These samples were collected in 500 mL polyvinyl chloride (PVC) bottles and preserved with a 100 μL HgCl₂ solution. The pH values were determined using a WTW's pH meter (Model pH 3210) with a precision of 0.005 pH units. The pH meter was calibrated on an NBS scale against buffers of pH 4.00, 7.00 and 10.00 before every measurement. Following collection, 25 ml of sample was taken from each bottle, and immediately prefiltered with a 0.45 μm film; these samples were then titrated using the classical Gran electro-titration method in the field to calculate the TA. The TA measurement was established with a certified reference material from the National Research Center for Certified Reference Materials, China. Seawater pCO₂ and dissolved inorganic carbon (DIC) were calculated from measured values of pH, TA, temperature, and salinity using the CO₂ sys program [Lewis and Wallace, 1998] with carbonic acid dissociation constants of Mehrbach *et al.* [1973] as refitted by Dickson and Millero [1987].

The sea-air exchange flux of CO₂ was determined from the following equation:

$$F = ks(p\text{CO}_{2w} - p\text{CO}_{2a}) \quad (1)$$

where k is the gas transfer velocity of CO₂, s is the solubility of CO₂ in seawater (calculated as a function of temperature and salinity) [Weiss, 1974], and $p\text{CO}_{2w}$ and $p\text{CO}_{2a}$ are the partial pressures of CO₂ in seawater

Table 1. Mean SST, SSS, Tide, DO, Seawater $p\text{CO}_2$ and Atmospheric $p\text{CO}_2$ in Luhuitou Fringing Reef

Observation Time	SST (°C)	SSS	Tide (cm)	DO (mg L ⁻¹)	Seawater $p\text{CO}_2$ (μatm)	Atmospheric $p\text{CO}_2$ (μatm)
8/1/2009–8/7/2009 (summer)	26.45 ± 0.95	33.45 ± 0.30	78 ± 38	6.05 ± 1.05	610 ± 112	383 ± 13
11/24/2010–12/3/2010 (autumn)	25.33 ± 0.33	33.01 ± 0.22	109 ± 36	6.85 ± 0.39	414 ± 62	389 ± 14
2/19/2011–3/1/2011 (winter)	23.18 ± 0.30	33.86 ± 0.06	86 ± 34	6.85 ± 0.41	428 ± 48	391 ± 14
4/13/2011–4/24/2011 (spring)	25.03 ± 0.58	34.07 ± 0.38	84 ± 36	6.96 ± 0.60	511 ± 49	393 ± 13

and air, respectively. Positive F values indicates a flux of CO_2 from the seawater to the atmosphere and a negative F indicates a flux of CO_2 from air to seawater. The gas transfer velocity (k) is commonly parameterized with wind speed (u) and Schmidt number (Sc). We used the Wanninkhof function [Wanninkhof, 1992] of wind speed (u) to calculate the value:

$$k = 0.31 u^2 (Sc/660)^{-1/2} \tag{2}$$

where u is wind speed at 10 m above mean sea level, and Sc is the Schmidt number of CO_2 in seawater. Sc was calculated using the equations of Wanninkhof [1992], and 660 is the Sc value in seawater (salinity = 35) at 20°C; 0.31 is a proportionality factor for short-term winds (0–12 m s⁻¹). The mean wind speeds were obtained from the meteorological station of the Hainan Tropical Marine Biology Research Station in Sanya (Figure 1).

4. Results

4.1. Diurnal Cycles and Seasonal Variations of Seawater $p\text{CO}_2$

The seasonal variations in seawater $p\text{CO}_2$ and atmospheric $p\text{CO}_2$ as well as SST, salinity, pH, mean tide, and DO are shown in Table 1. During the observed period, the SST range in summer was ~23.96–29.22°C, as compared to ~22.64–24.17°C in winter; the mean summer SST (26.45 ± 0.95°C) was approximately 3°C higher than that in winter (23.18 ± 0.30°C) due to changes in solar radiation. Seasonal variation in salinity was very small, with low salinity values of 33.45 ± 0.30 observed in summer and 33.01 ± 0.22 in autumn, and high salinity of 34.07 ± 0.38 recorded in winter.

The seawater $p\text{CO}_2$ values did show some large differences between different seasons. During the observed period, the mean seawater $p\text{CO}_2$ in autumn (~414 ± 62 μatm) was the lowest among the four seasons, and was slightly higher than the mean atmospheric $p\text{CO}_2$ during that same season. The mean seawater $p\text{CO}_2$ in summer (~610 ± 112 μatm) was the highest, and was higher than autumn by more than 200 μatm. The mean atmospheric $p\text{CO}_2$ values of the different seasons were similar, and were all lower than their corresponding mean seawater $p\text{CO}_2$ values. This data suggests that the CO_2 in Luhuitou fringing reef seawater is at a stage of relative supersaturation in comparison to atmospheric CO_2 . The CO_2 supersaturation value ($\Delta p\text{CO}_2 = \text{seawater } p\text{CO}_2 - \text{atmospheric } p\text{CO}_2$) was highest at ~227 μatm in summer, and was lowest in autumn at just ~25 μatm.

Figure 2 shows the clear diurnal cycles displayed by both atmospheric $p\text{CO}_2$ and seawater $p\text{CO}_2$, with a decreasing trend during daytime and an increasing trend at night. In summer, seawater $p\text{CO}_2$ reached its minimum (~360 μatm) at 16:00–18:00 and its maximum (~952 μatm) at 5:00–7:00, with diurnal fluctuations as high as 264–579 μatm. In autumn, seawater $p\text{CO}_2$ reached its minimum (~233 μatm) at 13:00–15:00 and its maximum (~623 μatm) at 4:00–6:00, with fluctuations between 152 and 335 μatm. In winter, the seawater $p\text{CO}_2$ reached its minimum (~329 μatm) at 17:00–19:00 and its maximum (~623 μatm) at 6:00–8:00, with diurnal fluctuations of 84–260 μatm. In spring, the seawater $p\text{CO}_2$ reached its minimum (~377 μatm) at 15:00–17:00 and its maximum (~679 μatm) at 5:00–7:00, with diurnal fluctuations of 144–288 μatm. The amplitude of diurnal seawater $p\text{CO}_2$ fluctuations was observed to be highest in summer, whilst the results for autumn, winter, and spring were all similar and relatively low. Incidentally, the number of daylight hours is also highest in summer. Because biological processes such as photosynthesis and coral calcification are directly related to the duration of sunshine, we suggest that biological processes may play an important role in diurnal and seasonal seawater $p\text{CO}_2$ variation. DO varied inversely with seawater $p\text{CO}_2$ and

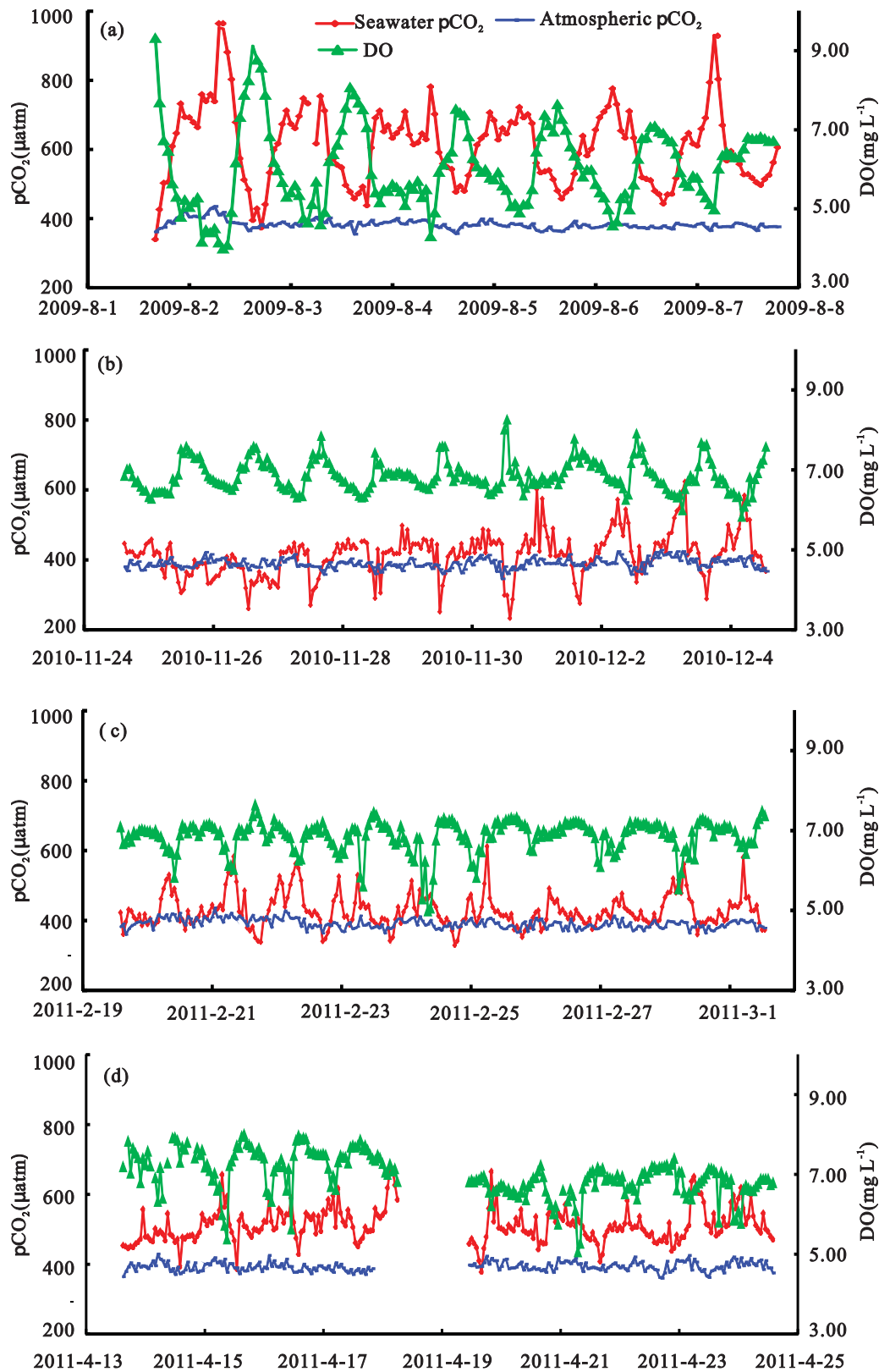


Figure 2. Diurnal variations in different seasons, including (a) August 2009 for summer; (b) November 2010 for autumn; (c) February 2011 for winter; and (d) April 2011 for spring.

Table 2. Summary of Seawater $p\text{CO}_2$, Atmospheric $p\text{CO}_2$, and Air-Sea Fluxes in Luhuitou Fringing Reef

Observation Time	Seawater $p\text{CO}_2$ (μatm)	Atmospheric $p\text{CO}_2$ (μatm)	Mean wind speed (m s^{-1})	Flux of CO_2 (F , $\text{mmol CO}_2 \text{ m}^{-2} \text{ d}^{-1}$)
8/1/2009–8/7/2009	610	383	4.2	9.6
11/24/2010–12/3/2010	414	389	7.7	3.5
2/19/2011–3/1/2011	428	391	5.6	2.7
4/13/2011–4/24/2011	511	393	4.4	5.3

corresponded closely with related metabolic processes. In coral reef ecosystems, the balance of biological processes such as calcium carbonate (CaCO_3) formation and organic carbon production can ultimately determine whether a coral reef system is a source or sink of CO_2 [Suzuki and Kawahata, 2004].

4.2. Sea-Air CO_2 Flux

Table 2 summarizes the sea-air CO_2 flux on Luhuitou fringing reef for each season. During summer, the sea-air CO_2 flux in the reef was highest at $\sim 9.6 \text{ mmol CO}_2 \text{ m}^{-2} \text{ d}^{-1}$, while the mean $\Delta p\text{CO}_2$ was the highest attained in any season at $\sim 227 \mu\text{atm}$. During the observed spring period, the second highest mean, a $\Delta p\text{CO}_2$ value = $118 \mu\text{atm}$ was recorded and the sea-air CO_2 flux was $\sim 5.3 \text{ mmol CO}_2 \text{ m}^{-2} \text{ d}^{-1}$. The sea-air CO_2 exchanges were nearly in equilibrium in winter and autumn. Furthermore, the mean $\Delta p\text{CO}_2$ value in autumn was only $\sim 25 \mu\text{atm}$, which was slightly lower than the winter value of $\sim 37 \mu\text{atm}$. Because the mean wind speed in autumn is higher than winter, the sea-air CO_2 flux in autumn is slightly higher than winter, with the two values registering at $3.5 \text{ mmol CO}_2 \text{ m}^{-2} \text{ d}^{-1}$ and $2.7 \text{ mmol CO}_2 \text{ m}^{-2} \text{ d}^{-1}$, respectively. Based on the sea-air fluxes observed in the different seasons, we calculated the annual mean sea-air CO_2 flux at Luhuitou fringing reef to be $\sim 0.54 \text{ mol CO}_2 \text{ m}^{-2} \text{ yr}^{-1}$.

5. Discussion

5.1. Seasonal Variations of Sea Surface $p\text{CO}_2$ and Its Drivers

Global ocean surface-water $p\text{CO}_2$ variability is mostly driven by temperature change, biological metabolism and the mixing of water masses [Takahashi et al., 2002]. Temperature variation changes the thermodynamic equilibrium of the carbonate system, and makes the seawater $p\text{CO}_2$ double with a 16°C increase ($\partial \ln p\text{CO}_2 / \partial T = 0.0423^\circ\text{C}^{-1}$) [Takahashi et al., 1993]. Biological metabolism processes include photosynthesis/respiration and the precipitation/dissolution of CaCO_3 , which affects seawater $p\text{CO}_2$ by changing the balance of the carbonate system. The physical mixing processes among different water masses can also change seawater $p\text{CO}_2$. With different community compositions or environments, the dominating factors driving seawater $p\text{CO}_2$ variation in coral reefs are different. Pearson correlation analyses between in situ seawater $p\text{CO}_2$ and environmental parameters were calculated using SPSS 19.0. The results (Table 3) showed a good correlation between in situ seawater $p\text{CO}_2$ and DO, meaning that biological metabolism processes may be the primary factor controlling seawater $p\text{CO}_2$ variation. Compared to DO, SST and tide variations showed weaker correlations with those of seawater $p\text{CO}_2$. This suggests that SST and tide may be less influential on seawater $p\text{CO}_2$ variation.

To better understand the main factors which influence seasonal $p\text{CO}_2$ change, we use a simple decomposition according to McNeil et al. [2007]. The change in $p\text{CO}_2$ among different seasons ($\Delta p\text{CO}_2$) can be written as:

$$\Delta p\text{CO}_2 = \frac{\partial p\text{CO}_2}{\partial \text{SST}} \Delta \text{SST} + \frac{\partial p\text{CO}_2}{\partial \text{Sal}} \Delta \text{Sal} + \frac{\partial p\text{CO}_2}{\partial \text{ALK}} \Delta \text{ALK} + \frac{\partial p\text{CO}_2}{\partial \text{DIC}} \Delta \text{DIC} \quad (3)$$

Table 3. The Pearson Correlation Coefficients Between In Situ Seawater $p\text{CO}_2$ and Salinity, SST, Tide, and DO

Variable	Season	Salinity	SST	Tide	DO
Seawater $p\text{CO}_2$	Summer	0.02	-0.16	0.28 ^b	-0.91 ^b
	Autumn	-0.14 ^a	-0.35 ^b	0.03	-0.65 ^b
	Winter	-0.25 ^b	-0.23 ^b	-0.39 ^b	-0.47 ^b
	Spring	-0.02	0.15 ^a	-0.23 ^b	-0.34 ^b

^a $p < 0.05$.

^b $p < 0.01$.

Each component in this equation was calculated by one parameter observed and the other three parameters constant, so as to determine the relative contributions of each factor on seasonal $p\text{CO}_2$ variability.

Figure 3 shows the effects of different properties on seasonal seawater $p\text{CO}_2$ variability. For the very small change in salinity (evaporation and precipitation of

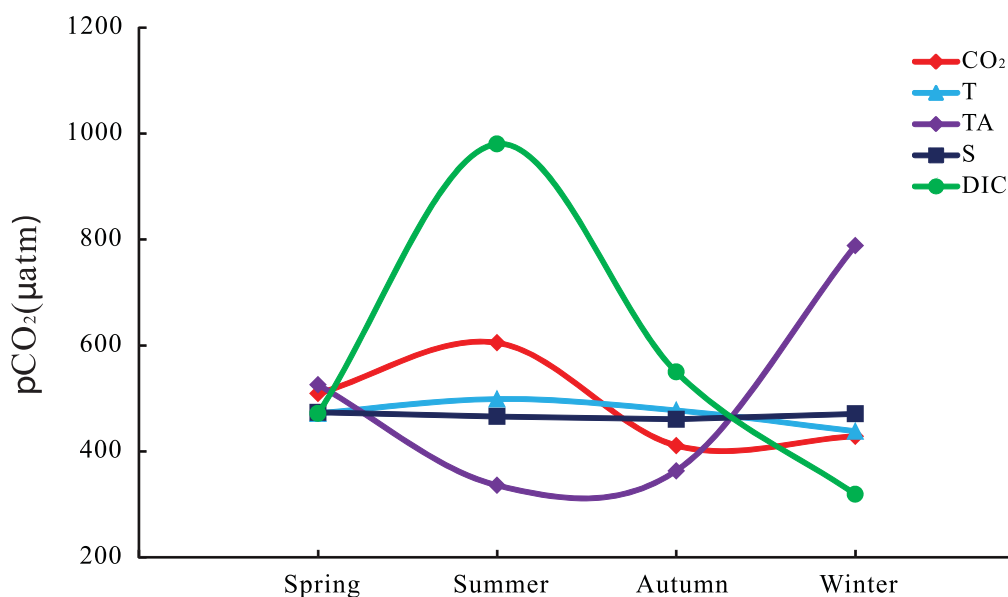


Figure 3. Different properties affect seasonal seawater $p\text{CO}_2$ variation. The contribution of each parameter was calculated using observed values whilst the other three parameters were kept constant

water) between different seasons, there was almost no change in seasonal $p\text{CO}_2$ variability. Seasonal variation of DIC and TA had significant effects on $p\text{CO}_2$ in opposite directions. Seasonal variations in temperature were quite small and had relatively little effect on $p\text{CO}_2$.

5.1.1. Influences of SST on Seawater $p\text{CO}_2$ Variations

In order to further evaluate the contribution of temperature change toward seasonal changes in $p\text{CO}_2$, we normalized observed $p\text{CO}_2$ to the average observed SST [Takahashi *et al.*, 1993],

$$Np\text{CO}_2 = (\textit{in situ } p\text{CO}_2) \times \exp [0.0423 (T_{\text{mean}} - T_{\text{in situ}})] \quad (4)$$

where T is the SST in degrees Celsius, and the subscripts “mean” and “*in situ*” indicate the averaged and the observed values, respectively. We used the annual mean temperature of 25°C as T_{mean} , and defined $Tp\text{CO}_2$ ($Tp\text{CO}_2 = \textit{in situ } p\text{CO}_2 - Np\text{CO}_2$) as the estimated contribution of temperature to the change in surface seawater $p\text{CO}_2$. The result revealed that the temperature effect ranged from $-19 \mu\text{atm}$ to $31 \mu\text{atm}$ (with an average of $1 \mu\text{atm}$ in spring, $-24 \mu\text{atm}$ to $95 \mu\text{atm}$ (with an average of $35 \mu\text{atm}$) in summer, $-7 \mu\text{atm}$ to $22 \mu\text{atm}$ (with an average of $5 \mu\text{atm}$) in autumn, and $-60 \mu\text{atm}$ to $-13 \mu\text{atm}$ (with an average of $-35 \mu\text{atm}$) in winter. The effect of temperature was greatest in summer, but considering that the $p\text{CO}_2$ daily amplitude range was 251–560 μatm , temperature could not have played an important role in the diurnal variation of $p\text{CO}_2$. In order to examine the contribution of SST toward seasonal seawater $p\text{CO}_2$ variability, we compared the seasonal average $Np\text{CO}_2$ with the seasonal average *in situ* $p\text{CO}_2$. During the surveys conducted in this study, SST in the reef had a seasonal variation of $\sim 3^\circ\text{C}$ between summer and winter. From summer to winter, the average *in situ* $p\text{CO}_2$ decreased about 182 μatm , while the mean seawater $Np\text{CO}_2$ only decreased about 111 μatm . This means that temperature affects up to $\sim 40\%$ of the seasonal $p\text{CO}_2$ change, which in turn suggests that temperature is an important factor controlling the observed $p\text{CO}_2$ seasonal variation.

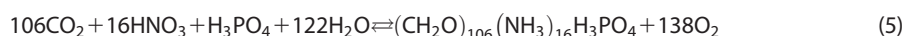
5.1.2. Influence of Hydrodynamic Processes on Seawater $p\text{CO}_2$ Variations

Hydrodynamic processes, such as tides, can affect the coral reef carbonate system by driving vertical mixing processes and horizontal seawater exchange between the reef area and the adjacent sea. At the Luhuitou fringing reef, vertical mixing processes did not contribute significantly to the observed seawater CO_2 changes due to shallow reef waters ($\sim 4\text{m}$), however the horizontal seawater exchange rate between the outer and inner reef, as well as water depth, could have affected the observed seawater $p\text{CO}_2$. Dai *et al.* [2009] proposed that the daily mass of seawater exchanged between the inner and outer sections of a given reef may be roughly estimated by determining the ratio between the average tidal range and the average water depth. Given that the average water depths were $\sim 4\text{ m}$ for the Luhuitou fringing reef, and the mean tide ranges were $\sim 0.85\text{ m}$, $\sim 0.77\text{ m}$, $\sim 1.08\text{ m}$, and $\sim 0.86\text{ m}$ in spring, summer, autumn, and

winter, respectively, the estimated daily exchange of water (ΔV_{water}) between the inside and outside of the reefs were respectively $\sim 21\%$, $\sim 19\%$, $\sim 27\%$, and $\sim 22\%$ of the total water mass in the reef. Obviously, the water exchange rates were similar between different seasons. The results in the SEATS time series site ($18^{\circ}15'N$, $115^{\circ}35'E$) in northern SCS show that the largest amplitudes of seasonal NDIC, NTA and $p\text{CO}_2$ are $\sim 25 \mu\text{mol kg}^{-1}$ (fluctuating between ~ 1972 and $1997 \mu\text{mol kg}^{-1}$), $\sim 30 \mu\text{mol kg}^{-1}$ (fluctuating between ~ 2190 and $2220 \mu\text{mol kg}^{-1}$), and $\sim 35 \mu\text{atm}$ (fluctuating between ~ 347 and $382 \mu\text{atm}$), respectively [Chou *et al.*, 2005]. This means that the carbonate properties (DIC, TA, and $p\text{CO}_2$) of open ocean water are differ significantly from the water of the reef flat (amplitudes of seasonal NDIC, NTA and $p\text{CO}_2$ variation being $\sim 248 \mu\text{mol kg}^{-1}$, $\sim 249 \mu\text{mol kg}^{-1}$, and $\sim 196 \mu\text{atm}$, respectively). In tropical oceans, sea-air $p\text{CO}_2$ exchange ($\Delta p\text{CO}_2$) was less than $30 \mu\text{atm}$ every month [Takahashi *et al.*, 1997], and was thus very small compared to the $\Delta p\text{CO}_2$ of coral reef ecosystems. Previous studies done on the northern SCS showed the similar results [Chou *et al.*, 2005; Zhai *et al.*, 2005]. We can use atmospheric $p\text{CO}_2$ as seawater $p\text{CO}_2$ in the surrounding oceans of Luhuitou fringing reef. With the similar ΔV_{water} , the effects of mixing caused by tide were also similar among different seasons. This suggests that tide-dominated hydrodynamic processes were not the major factor driving the observed $p\text{CO}_2$ seasonal variations in Luhuitou fringing reef.

5.1.3. Influence of Biological Activities on Seawater $p\text{CO}_2$ Variations

The net balance between calcification and organic carbon production in a coral reef ecosystem can determine whether it is a source or sink of atmospheric CO_2 [Bates, 2002]. Biological metabolism directly controls the daily variations in seawater $p\text{CO}_2$. During the night, respiration and calcification by coral reef organisms releases CO_2 , which increases seawater $p\text{CO}_2$. Conversely, during the daytime, the CO_2 that is fixed by photosynthesis is greater than that released because of respiration and calcification, and thus seawater $p\text{CO}_2$ decreases.



DO varied inversely with surface seawater $p\text{CO}_2$ and corresponded closely with related photosynthesis/respiration processes (Figure 2). Calcification/dissolution processes may produce or consume CO_2 , but not alter DO (equation (6)). Based on the observed data of surface seawater $p\text{CO}_2$, DO, the known proportions of major elements (e.g., the Redfield ratio ratios of C:N:P), and the air-sea exchange rates of CO_2 and O_2 , we evaluated the individual effects of the above two processes, i.e., photosynthesis/respiration and calcification/dissolution, on $p\text{CO}_2$ variations. Note that although calculations could be simplified by purely using the 106:16:1 C:N:P ratio, it would be inappropriate to do so in this case because the air-sea exchange rate of O_2 is much faster than that of CO_2 [Dai *et al.*, 2009].

Figure 3 shows that seawater $p\text{CO}_2$ seasonal variation is caused mainly by changes in DIC and TA, while DIC and TA vary mainly due to biological processes and mixing [Takahashi *et al.*, 2002]. Because the mixing processes (tide-dominated hydrodynamic processes) discussed before had little impact on seasonal $p\text{CO}_2$ variation, biological processes were left as the major controlling factor. As a result of this inference, we have made brief calculations to estimate the role of biological activities on seawater $p\text{CO}_2$ alteration following the method of Dai *et al.* [2009]. This was done by analysing the two metabolic processes using seawater carbonate parameters changes.

Previous studies have indicated that the seawater CO_2 chemical equilibrium determines the CO_2 absorption capacity of coral reefs [Ohde, 1995]. Based on previous work [Gattuso *et al.*, 1999], for each mole of CaCO_3 precipitated, seawater TA and DIC decrease by 2 mol and 1 mol respectively. Thus, the slope ($\Delta\text{TA}/\Delta\text{DIC}$) equals 2/1 when considering calcification only. The slope will be nearly 0 when considering photosynthesis exclusively, as photosynthesis has little effect on TA and can be ignored. Assuming a given calcification, a photosynthesis ratio of 1 unit inorganic to x units organic carbon, the slope ($\Delta\text{TA}/\Delta\text{DIC}$) must equal $2/(1+x)$, and hence $x = (2/\text{slope}) - 1$. Figure 4 shows the linear regression lines of observed seawater nTA and nDIC (with TA and DIC normalized to a salinity of 35 to reduce the effects of evaporation and precipitation of water) in seasons. The calculated slopes, T , ($\Delta\text{TA}/\Delta\text{DIC}$), were similar in all seasons. As a result, the ratio of inorganic to organic production was $\sim 1:1.2$ in spring, $\sim 1:1.5$ in summer, $\sim 1:2.3$ in autumn, and $\sim 1:1.5$ in winter. These results made clear that photosynthesis/respiration caused the major changes of $p\text{CO}_2$ between different seasons. These results also support those obtained in Yongxing and Yongshu Reef ($\sim 1:1.6$, $\sim 1:3.3$) [Yan *et al.*, 2011], which are much higher than the ratio of the SCS basin ($\sim 1:14$) [Cao *et al.*, 2009],

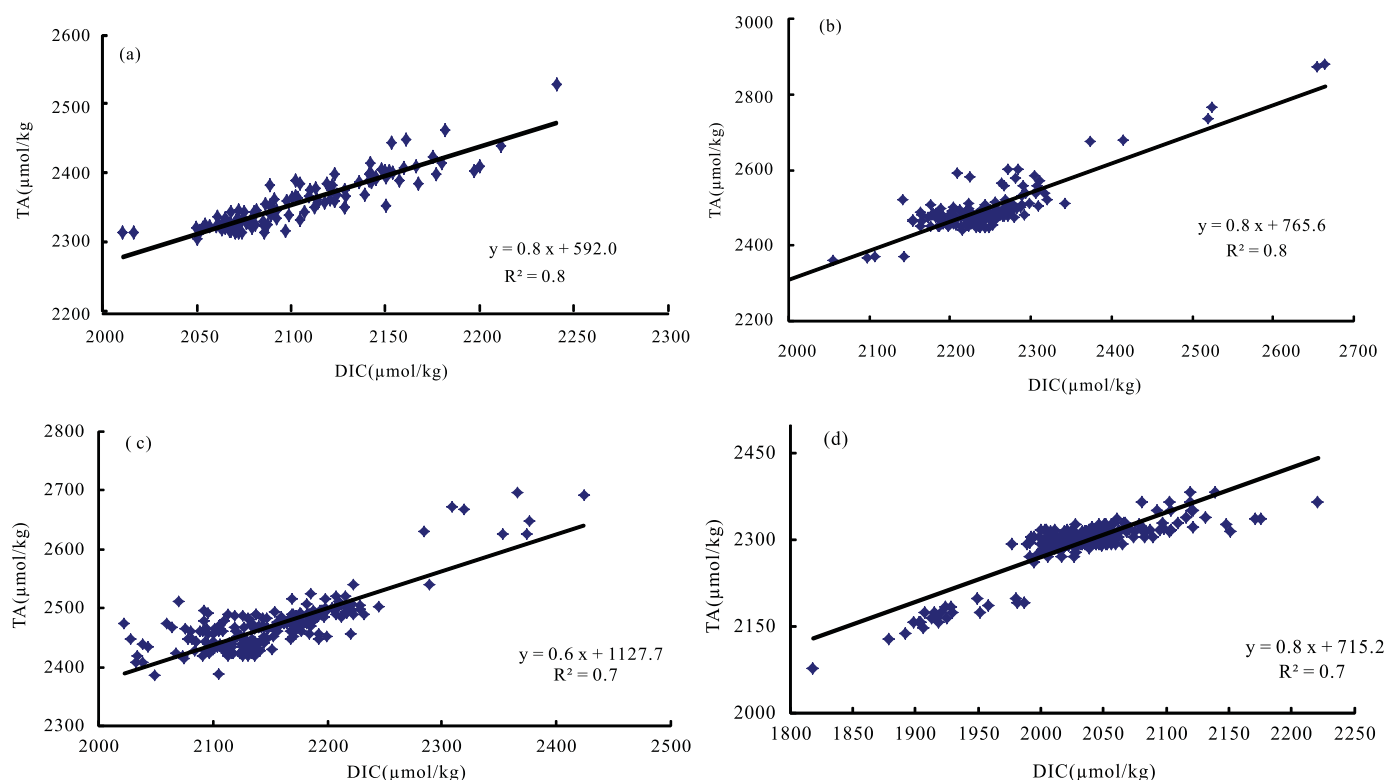


Figure 4. Seasonal plots of nTA versus nDIC in Luhuitou fringing reef, including (a) April 2011 for spring; (b) August 2009 for summer; (c) November 2010 for autumn; (d) February 2011 for winter.

suggesting CaCO_3 production is much more prominent in the coral reef system. The Luhuitou fringing reef flat may therefore function as other typical coral systems in terms of the metabolic processes. This suggested that coral reef metabolic processes (organic processes and inorganic processes) are dominant factors driving seawater $p\text{CO}_2$ change, and that organic processes play a more important role in this matter than inorganic processes.

5.2. Luhuitou Fringing Reef Acting as a Source of Atmospheric CO_2

This study used the equation of Wanninkhof [1992] so that the results could be compared with some similar studies. Sea-air CO_2 flux values may be used to differentiate coral reefs that act as either sinks or sources of atmospheric CO_2 [Ware et al., 1991; Gattuso et al., 1993; Kayanne et al., 1995; Frankignoulle et al., 1996; Gattuso et al., 1996c; Kawahata et al., 1997; Suzuki, 1998; Gattuso et al., 1999; Kawahata et al., 1999; Kawahata et al., 2000a; Kawahata et al., 2000b; Suzuki and Kawahata, 2004; Tan et al., 2004; Fagan and Mackenzie, 2007]. Positive values typically characterize coral reefs as a source of atmospheric CO_2 , while negative values may identify coral reefs that act as a sink of atmospheric CO_2 . Based on this principle and the calculated sea-air CO_2 flux values (Table 2) for this study, Luhuitou fringing reef is a source of atmospheric CO_2 . Previous studies on coral reef sea-air CO_2 exchanges of the SCS have shown similar results. Observed results, e.g., $\sim 0.4 \text{ mmol C m}^{-2} \text{ d}^{-1}$ at Yongshu reef and $\sim 4.7 \text{ mmol C m}^{-2} \text{ d}^{-1}$ at Yongxing reef of SCS by Yan et al. [2011], showed that these two reefs act as sources of atmospheric CO_2 in summer. The Yongxing reef acts as a weak source of atmospheric CO_2 at $\sim 1.48 \text{ mmol C m}^{-2} \text{ d}^{-1}$ in winter [Dai et al., 2009]. The sea-air CO_2 fluxes at both Yongxing Island and Luhuitou fringing reef showed a decreasing trend from summer to winter, and this trend corresponds closely with the variations of seasonal metabolic processes. Similar to diurnal variations of surface seawater $p\text{CO}_2$, seasonal variations of surface seawater $p\text{CO}_2$ were also mainly controlled by biological metabolism.

In summary, the Luhuitou fringing reef, as a whole, serves as a net source of atmospheric CO_2 on a yearly basis. In the largest tropical marginal sea, the SCS, this research was the first attempt to resolve seasonal variation in a coral reef region. Results show the largest sea-air CO_2 flux was about $9.6 \text{ mmol CO}_2 \text{ m}^{-2} \text{ d}^{-1}$

in summer and the smallest about $2.7 \text{ mmol CO}_2 \text{ m}^{-2} \text{ d}^{-1}$ in winter. Biological processes were suggested as the most important driver behind changes in seawater $p\text{CO}_2$, while temperature and hydrodynamic processes also had some effect. Based on all the observed data, we calculated the mean sea-air CO_2 flux for each of the four seasons as well as the mean annual CO_2 flux, and the results show that Luhuitou fringing reef acts as a source of atmospheric CO_2 at $\sim 0.54 \text{ mol CO}_2 \text{ m}^{-2} \text{ yr}^{-1}$.

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