Coral reef ecosystems in the South China Sea as a source of atmospheric CO2 in summer

YAN HongQiang1,2, YU KeFu1,2*, SHI Qi1,2, TAN YeHui1,2, ZHANG HuiLing1,2, ZHAO MeiXia1,2, LI Shu1,2, CHEN TianRan1,2, HUANG LingYing1,2 & WANG PinXian3

1 CAS Key Laboratory of Marginal Sea Geology, Guangzhou 510301, China; 2 South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou 510301, China; 3 State Key Laboratory of Marine Geology, Tongji University, Shanghai 200092, China

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Field measurements of air-sea CO2 exchange in three coral reef areas of the South China Sea (i.e. the Yongshu Reef atoll of the Nansha Islands, southern South China Sea (SCS); Yongxing Island of Xisha Islands, north-central SCS; and Luhuitou Fringing Reef in Sanya of Hainan Island, northern SCS) during the summers of 2008 and 2009 revealed that both air and surface seawater partial pressures of CO2 (pCO2) showed regular diurnal cycles. Minimum values occurred in the evening and maximum values in the morning. Air pCO2 in each of the three study areas showed small diurnal variations, while large diurnal variations were observed in seawater pCO2. The diurnal variation amplitude of seawater pCO2 was ~70 μmol mol–1 at the Yongshu Reef lagoon, 420–619 μmol mol–1 on the Yongxing Island reef flat, and 264–579 μmol mol–1 on the reef flat of the Luhuitou Fringing Reef, and 324–492 μmol mol–1 in an adjacent area just outside of this fringing reef. With respect to spatial relations, there were large differences in air-sea CO2 flux across the South China Sea (e.g. ~0.4 mmol CO2 m–2 d–1 at Yongshu Reef, ~4.7 mmol CO2 m–2 d–1 at Yongxing Island, and ~9.8 mmol CO2 m–2 d–1 at Luhuitou Fringing Reef). However, these positive values suggest that coral reef ecosystems of the SCS may be a net source of CO2 to the atmosphere. Additional analyses indicated that diurnal variations of surface seawater pCO2 in the shallow water reef flat are controlled mainly by biological metabolic processes, while those of deeper water lagoons and outer reef areas are regulated by both biological metabolism and hydrodynamic factors. Unlike the open ocean, inorganic metabolism plays a significant role in influencing seawater pCO2 variations in coral reef ecosystems.

coral reefs, pCO2, carbon cycle, summer, South China Sea

Both the 1997 Kyoto Protocol and 2009 United Nations Climate Change Conference (Copenhagen) recognized the potential role of CO2 in contributing to global warming. Thus, a reduction in at least the anthropogenic component of CO2 emissions may assist in reducing the degree of possible future warming. However, a more comprehensive understanding of natural processes of absorption and emission of atmospheric CO2 is critical to identify its role in contributing to global warming. Widely-distributed coral reefs in tropical oceans have long played an important role in the global carbon cycle [1]. For example, the sudden increase in atmospheric CO2 (~80 μmol mol–1) during retreat of the Wisconsinan glaciers (ca.14 ka) has been hypothesized to have been the result of variations of coral reef carbonate sedimentation rates [2–4]. The contribution of coral reefs to the carbon cycle is driven mainly by organic carbon metabolism (photosynthetic fixation and respiration/degradation) and inorganic carbon metabolism (precipitation and dissolution of calcium carbonate); inorganic carbon metabolism also may play a significant role [5–8]. Importantly,
catalyze that mean annual sea surface temperature is 28.6°C. The surface salinity in this area ranges from 33.0 to 33.5, with monthly variability of 1.0. From June to September, the area is under the influence of southwest monsoons, and has an average wind speed of 6.5 m s⁻¹. From November to April, the area is affected by northeast monsoons, with an average wind speed of 8.0 m s⁻¹ [22].

Yongxing Island (16.84°N, 112.34°E, Figure 1) is the largest island of the Xisha Islands, and is located in the north-central SCS. Five geomorphological zones are recognized around Yongxing Island: reef front slope, reef flat, sandy beach, sand bank, sand sheet and low-lying dried lagoon with beach-rock development on the northwest beach [23]. The reef flat is, on average, 400 to 800 m wide (but extending to as wide as 1500 m), and is the major geomorphological zone of Yongxing Island. A survey carried out in 2002 suggested that the coral cover ranged from 42.1% to 93.4% [24]. The Xisha area occurs within a tropical monsoon climate regime. The mean annual air temperature is 26.4°C, with the lowest monthly temperature of 23.8°C in January and the highest monthly temperature of 29.4°C in June and July. From October to March, the area is affected by northeast monsoons with an average wind speed of 6–9 m s⁻¹ [22]. From May to August, the area is under the influence of SE-SW monsoons with an average wind speed of 5–6 m s⁻¹ [25].

Luhuitou Fringing Reef (18.13°N, 109.29°E) is located at the southeast coast of Sanya, Hainan Island (Figure 1), northern SCS, and is a typical fringing reef. This reef is ~3 km long and has two typical biogeomorphic units, reef flat and 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 1960–2006, living coral cover in this fringing reef decreased from ~85% to ~12%, but it still preserves relatively high biodiversity [26]. Luhuitou Fringing Reef experiences a tropical monsoon climatic system, dominated by northeast to east winds. From October to April, the area is affected by east and northeast monsoons. From May to September, the area is under the influence of south and southeast monsoons. 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. The mean annual sea surface temperature (SST) is 27°C, and the lowest monthly SST is 23.8°C (varying from 20.5–24.7°C). The highest monthly SST is 29.8°C (varying from 28.7–30.9°C) [27].

## 2 Methods

Time-series measurements of air-sea CO₂ exchanges were carried out at Yongxing Island in July 2008, at Yongshu Reef in June 2009, and at Luhuitou Fringing Reef in
July–August 2009. Thus, all observations took place during summer. At Luhuitou Fringing Reef, measurements were taken from two locations: one inside (Site 1, Figure 1(b)) and one outside (Site 2, Figure 1(b)) the reef. Water depths at Site 1 and Site 2 were ~1.1 m and ~9 m, respectively. The measurements were carried out hourly over six consecutive days at both sampling sites. At Yongxing Island, the observation site was located on the northern reef flat (Figure 1(c)). Measurements were taken every two hours over six consecutive days. At Yongshu Reef, the observation site was at a lagoon (Figure 1(d)), with hourly measurements made on two separate occasions: during a single day, then later on two consecutive days. Additionally, we also measured the air and sea $pCO_2$ in the non-coral reef areas around the perimeter of the Nansha Islands (Figure 1(a)) during the South China Sea Institute of Oceanology (SCSIO) Nansha cruise in June 2009.

Atmospheric $pCO_2$ was monitored continuously using a hand-held $CO_2$ meter (GM70) made by the Vaisala Company, Finland. Sea surface temperature and sea surface salinity (SSS) were measured using a Yellow Spring Instrument meter (YSI6920V2), except at the reef flat of Yongxing Island, where SST and SSS were measured using an Ultrameter Model 4P (Myron L Company, USA). Water samples for pH and total alkalinity (TA) measurements were collected 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 then the samples were saturated with a 100 µL HgCl$_2$ solution. The pH values were determined using a pH meter with a precision of 0.01 pH units. The pH meter was calibrated against buffers of pH 6.86 and 9.18 before every measurement. Following collection, the samples (25 mL) were immediately pre-filtered with a 0.45 µm film and were then titrated in the field with 0.0006 mol/L HCl to calculate the TA. Seawater $pCO_2$ was calculated [12,19,28–31] using temperature, salinity, pH, TA, and constants from Mehrbach et al. [32] as refitted by Diskin and Millero [33].

The air-sea exchange flux of $CO_2$ was determined from the following equation:

$$F=ks(pCO_{2w}−pCO_{2a}),$$

where $k$ is the gas transfer velocity, $s$ is the solubility of $CO_2$ (calculated as a function of temperature and salinity), and $pCO_{2w}$ and $pCO_{2a}$ are the partial pressures of $CO_2$ in seawater and air, respectively. Positive $F$ values indicated a flux of $CO_2$ from the seawater to the atmosphere and a negative $F$ indicated a flux of $CO_2$ from air to seawater. $k$ is
commonly parameterized with wind speed \((u)\) and Schmidt number \((\text{Sc})\). We used the Wanninkhof [34] function of wind speed \((u)\) to calculate the value:

\[
K = 0.31u^{2}(\text{Sc}/660)^{-1/2},
\]

where \(\text{Sc}\) is the Schmidt number of \(\text{CO}_2\) in seawater; 660 is the \(\text{Sc}\) value in seawater \((S = 35)\) 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 NOAA [http://www.cdc.noaa.gov/data/].

### 3 Results

#### 3.1 Diurnal cycles of atmospheric and seawater \(\text{pCO}_2\) variations in coral reef areas

Table 1 summarizes the mean SST, salinity, pH, TA, seawater \(\text{pCO}_2\) and atmospheric \(\text{pCO}_2\) at the study sites. Spatially, the seawater \(\text{pCO}_2\) values show large differences between sites. The mean seawater \(\text{pCO}_2\) at Yongshu Reef lagoon was the lowest amongst the three studied sites, and was slightly higher than the mean atmospheric \(\text{pCO}_2\). The diurnal amplitude of seawater \(\text{pCO}_2\) observed at Yongshu Reef lagoon also was much lower than that of the reef flats at Yongxing Island and Luhuitou Fringing Reef. The diurnal atmospheric \(\text{pCO}_2\) amplitudes at different coral reef areas were relatively small, and the mean daily atmospheric \(\text{pCO}_2\) values were similar among each of the coral reefs. Figure 2 shows that both atmospheric \(\text{pCO}_2\) and seawater \(\text{pCO}_2\) displayed clear diurnal cycles, with a decreasing trend during the daytime and an increasing trend at night. At the Yongxing Island reef flat, seawater \(\text{pCO}_2\) reached its minimum \((-76 \mu\text{mol mol}^{-1}\)) at 17:00–19:00 and its maximum \((-90 \mu\text{mol mol}^{-1}\)) at 07:00–09:00. The diurnal seawater \(\text{pCO}_2\) amplitudes were as high as 420–619 \(\mu\text{mol mol}^{-1}\). At the reef flat of Luhuitou Fringing Reef, the seawater \(\text{pCO}_2\) reached its minimum \((-340 \mu\text{mol mol}^{-1}\)) at 16:00–18:00 and its maximum \((-652 \mu\text{mol mol}^{-1}\)) at 06:00–08:00. The diurnal seawater \(\text{pCO}_2\) amplitudes were 264–579 \(\mu\text{mol mol}^{-1}\) at Luhuitou reef flat and 386–492 \(\mu\text{mol mol}^{-1}\) just outside of the reef. At the Yongshu Reef lagoon, the diurnal cycle of seawater \(\text{pCO}_2\) variations did not appear to be as significant in comparison to the other sampled reefs, but the overall trend (i.e. decreasing during the daytime and increasing overnight) was still observed. The values reached a minimum at 22:00–24:00, and reached a maximum at 10:00–12:00. In comparison with that of Yongxing Island and Luhuitou Fringing Reef, seawater \(\text{pCO}_2\) peaks at Yongshu lagoon lagged by about 3–4 h, which is possibly related to its low living coral cover and relatively deep water (\(-20\) m). As a result, mean seawater \(\text{pCO}_2\) and diurnal seawater \(\text{pCO}_2\) amplitudes both showed a clear decrease from within the reef area to outside of the reef. Since the diurnal atmospheric \(\text{pCO}_2\) amplitude was very small, its effect on air-sea \(\text{CO}_2\) exchange at the studied coral reefs was minor. The large diurnal amplitudes and associated seawater \(\text{pCO}_2\) variations indicate a significant exchange in air-sea \(\text{CO}_2\).

#### 3.2 Air-sea \(\text{CO}_2\) flux

The air-sea \(\text{CO}_2\) fluxes (Figure 2) within different reef areas were calculated using equation 1. At the Yongxing reef flat, air-sea \(\text{CO}_2\) flux ranged from \(-19.9–30.5\) mmol \(\text{CO}_2\) m\(^{-2}\) d\(^{-1}\). From 13:00–23:00, its seawater \(\text{pCO}_2\) was generally lower than the atmospheric \(\text{pCO}_2\), and the average air-sea \(\text{CO}_2\) flux was \(-5.1\) mmol \(\text{CO}_2\) m\(^{-2}\) d\(^{-1}\). Its seawater \(\text{pCO}_2\) was larger than atmospheric \(\text{pCO}_2\), and for the remaining part of the day, the mean air-sea \(\text{CO}_2\) flux was 13.7 mmol \(\text{CO}_2\) m\(^{-2}\) d\(^{-1}\). At the reef flat in the Luhuitou Fringing Reef, the air-sea \(\text{CO}_2\) flux varied from \(-1.6–26.5\) mmol \(\text{CO}_2\) m\(^{-2}\) d\(^{-1}\). Apart from a few hours at night, the seawater \(\text{pCO}_2\) was almost always larger than atmospheric \(\text{pCO}_2\) at Luhuitou. At the Yongshu Reef lagoon, the air-sea \(\text{CO}_2\) fluxes varied from \(-2.3–2.7\) mmol \(\text{CO}_2\) m\(^{-2}\) d\(^{-1}\). From 20:00–07:00, seawater \(\text{pCO}_2\) showed lower values with mean flux approaching 0; during the remaining portion of the day, the mean flux was \(-0.8\) mmol \(\text{CO}_2\) m\(^{-2}\) d\(^{-1}\). The above data indicate great variations of air-sea fluxes between different reefs within the SCS. In general, coral reefs appeared to behave as sinks at night and as sources during the day. By integrating all the time-series \(\text{pCO}_2\) data, the flux was \(-4.7\) mmol \(\text{CO}_2\) m\(^{-2}\) d\(^{-1}\) at the Yongxing reef flat, \(-0.4\) mmol \(\text{CO}_2\) m\(^{-2}\) d\(^{-1}\) at the Yongshu Reef lagoon, and \(-9.8\) mmol \(\text{CO}_2\) m\(^{-2}\) d\(^{-1}\) at the Luhuitou Fringing Reef flat.

### 4 Discussion

#### 4.1 Environmental controls of surface seawater \(\text{pCO}_2\)

In open ocean ecosystems, seawater \(\text{pCO}_2\) is controlled by a

| Reef site          | Mean depth (m) | SST (°C) | SSS (‰) | pH   | TA (μmol kg\(^{-1}\)) | Seawater \(\text{pCO}_2\) (μmol mol\(^{-1}\)) | Atmospheric \(\text{pCO}_2\) (μmol mol\(^{-1}\)) |
|-------------------|---------------|---------|---------|------|------------------------|------------------------------------------|---------------------------------------------|
| Yongxing Island   | 1.2           | 29.5±1.6| 32.6±0.4| 8.23±0.22 | 2421±142 | 456±249                    | 387±25                                          |
| Yongshu Reef      | -30           | 28.68±0.10| 33.07±0.19| 8.22±0.03 | 2240±56 | 395±25                     | 384±21                                          |
| Luhuitou Site 1   | 1.1           | 26.45±0.95| 33.45±0.30| 8.07±0.07 | 2497±71 | 610±112                    | 383±13                                          |
| Luhuitou Site 2   | 9             | 26.81±1.43| 33.27±0.40| 8.13±0.05 | 2375±80 | 506±81                     | 383±11                                          |

a) Mean depth corrected to relative mean sea level; b) seawater \(\text{pCO}_2\) was calculated from temperature, salinity, pH and TA.
Figure 2  Diurnal variations of atmospheric $p$CO$_2$, seawater $p$CO$_2$ and air-sea CO$_2$ flux in the studied coral reef areas. (a) Reef flat at Yongxing Island; (b) reef flat at Luhuitou Fringing Reef; (c) outside of Luhuitou Fringing Reef; (d-1) and (d-2) Lagoon at Yongshu Reef. 2009-06-30 00:00: midnight (00:00) of June 30, 2009.
variety of environmental conditions, including SST, hydrodynamics, and biological activities [20]. In order to eliminate SST effects on observed pCO₂, the measured pCO₂ values were normalized to the mean SST during the observation period, using the following equation:

\[ NpCO₂ = (\text{in situ } pCO₂) \times \exp [0.0423 \times (T_{\text{mean}} - T_{\text{in situ}})] \]

where \( T \) is the SST in degrees Celsius, and the subscripts “mean” and “in situ” indicate the averaged and the observed values, respectively [20,35,36]. The calculated \( NpCO₂ \) values show that similar variations in measured pCO₂ occurred in all three study areas, suggesting that local SST variations over the observation period did not affect observed diurnal cycles or overall trends of seawater pCO₂. To examine the contribution of SST on surface seawater pCO₂, we computed the offset between \( NpCO₂ \) and measured pCO₂ (Table 2), herein defined as \( \Delta pCO₂ \) \( (\Delta pCO₂ = [\text{measured } pCO₂ - NpCO₂]) \). The mean \( \Delta pCO₂ \) values at the reef flats of Luhuitou Fringing Reef and Yongxing Island were greater than that at the Yongshu Reef lagoon. We defined the largest seawater pCO₂ variation amplitude during the observation period as \( \Delta pCO₂ \), and then calculated the ratio \( (\Delta pCO₂/\Delta pCO₂) \) between \( \Delta pCO₂ \) and \( \Delta pCO₂ \) (Table 2). The results (Table 2) show that SST variation had a contribution of only 6.17% of the observed seawater pCO₂ at the Luhuitou Fringing Reef, 4.34% at the Yongxing Island, and 2.66% at the Yongshu Reef. Thus, SST did not appear to be a major factor controlling diurnal variations of seawater pCO₂. The apparent minor variation in the contribution of SST to seawater pCO₂ across the three studied reefs is possibly the result of local SST amplitude differences.

Hydrodynamic processes, such as tides, can affect the coral reef carbonate system by driving seawater exchange between the reef area and the surrounding ocean. The seawater exchange rate between the outer and inner reef, as well as water depth, can impact the observed seawater pCO₂. For example, Table 1 demonstrates that the seawater pCO₂ value decreased between the shallow-water reef flat to the deep-water site just outside of the main reef at Luhuitou. Dai et al. [20] proposed that the daily seawater mass exchanged between the inner and outer sections of a given reef may be roughly estimated by determining the ratio of the average tidal range versus the average water depth. Given that the average water depths were ~10 m for the reef around Yongxing Island, ~4 m for the Luhuitou Fringe Reef, and ~25 m for the Yongshu Reef lagoon, and their average tidal ranges were ~1 m, ~0.8 m, and ~1.2 m, respectively, the estimated daily exchange amount of water mass between the inside and outside of the reefs were ~10%, ~20%, and ~4.8% of the total water mass in the reefs, respectively. This suggests that tide-dominated hydrodynamic processes are not the major factor controlling the observed pCO₂ diurnal variations in the studied reefs. This can be further supported by the fact that there does not appear to be a correlation between tidal height and seawater pCO₂.

Biological metabolism directly controls seawater pCO₂ variations. During the night, respiration and calcification by coral reef organisms releases CO₂, which increases seawater pCO₂. Conversely, during the daytime, the CO₂ that is fixed by photosynthesis is greater than that released from respiration and calcification, and therefore, seawater pCO₂ decreases. The observed diurnal cycles (i.e. surface seawater pCO₂ increasing at night and decreasing during the daytime) are significantly correlated with reef metabolic processes, suggesting that biological metabolism dominates seawater pCO₂ variations in coral reef waters [17,20,37].

Previous studies have indicated that seawater CO₂ chemical equilibrium determines the CO₂ absorption capacity of coral reefs [38]. Based on previous work [9], for each mole of CaCO₃ precipitated, seawater TA and DIC decrease by 2 eq and 1 mol. Thus, the slope \((\Delta TA/\Delta DIC)\) equals 2/1 if only calcification is considered. The slope will be nearly 0 if only photosynthesis is considered, as photosynthesis has no effect on TA. Assuming a given calcification: photosynthesis ratio of 1 unit inorganic to x units organic carbon, the slope \((\Delta TA/\Delta DIC)\) must equal 2/(1+x), and hence \(x = (2/slope)-1\). Figure 3 shows the linear regression lines of observed seawater TA and DIC of the coral reefs in this study. The calculated slope, \(T\), \((\Delta TA/\Delta DIC)\), was ~0.47 at the Yongxing reef flat, ~0.77 at the Luhuitou reef flat, and ~1.05 \((=1.08+1.01)/2\) at the Yongshu atoll lagoon. The ratio of inorganic to organic production was ~1:3.3 at Yongxing Island, ~1:1.6 at the Luhuitou reef flat, and ~1:0.9 at the Yongshu Reef lagoon. The ratio at the Luhuitou reef flat (~1:1.6) was larger than that at the Yongxing reef flat (~1:3.3), which suggests that CaCO₃ production was more prominent at Luhuitou. Due to calcification causing CO₂ release, the Luhuitou Fringing Reef hypothetically should be a more significant source of atmospheric CO₂ than at Yongxing Island. Indeed, this is supported by the demonstrated air-sea CO₂ fluxes in section 3.2. Though Yongshu lagoon had the highest ratio, its air-sea CO₂ flux

### Table 2: Contribution of SST to seawater pCO₂ variability

| Reef site                  | \(\delta pCO₂ (\mu mol mol^{-1})\) | Mean | \(\Delta pCO₂ (\mu mol mol^{-1})\) | \(\delta pCO₂/\Delta pCO₂ (\%)\) |
|---------------------------|----------------------------------|------|-----------------------------------|---------------------------------|
| Luhuitou Fringing Reef    | 0.0                              | 25.6 | 415                               | 18.86                           |
| Yongxing Island           | 1.0                              | 22.8 | 525                               | 18.82                           |
| Yongshu Reef              | 0.0                              | 1.6  | 60                                | 14.71                           |

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was the lowest (−0.4 mmol CO$_2$ m$^{-2}$ d$^{-1}$), which may be a result of the buffering effect of its deeper waters. A ratio of 1:14 (inorganic to organic carbon production) was observed in the SCS basin area by Cao et al. [37] in 2005. This ratio is much lower than that in the coral reef areas of the SCS. This information suggests that the inorganic carbon metabolism in coral reefs of the SCS plays a significant role in coral reef carbon cycles. This may explain the observed large diurnal variations of seawater $p$CO$_2$.

### 4.2 $p$CO$_2$ difference between inner and outer coral reef areas

The net effect of air-sea CO$_2$ fluxes for a given reef can be masked if the oceanic water is already out of equilibrium with atmospheric CO$_2$ before entering the reef system [7,39,40]. Thus, the seawater exchange between an atoll lagoon and outer oceanic water can sometimes make it difficult to fully understand the coral reef carbon cycle system. In order to identify the net effect of reef systems on the air-sea CO$_2$ exchange, we first need to compare seawater $p$CO$_2$ between the inside and the outside of the studied coral reefs [40]. Following a previous study [39], we defined the difference in $p$CO$_2$ between the inside and outside coral reef area ($δpCO_2$) as

$$δpCO_2 = pCO_{2L} - pCO_{2O},$$

where $pCO_{2L}$ and $pCO_{2O}$ are the partial pressure of carbon dioxide in the atoll lagoon water, and the oceanic water outside the coral reef, respectively. If the mean $p$CO$_2$ of lagoon water is higher than that of oceanic water (i.e. $δpCO_2 > 0$), the coral reef is likely to be a source of atmospheric CO$_2$. Conversely, if the mean $p$CO$_2$ of the lagoon water is lower than that of oceanic water (i.e. $δpCO_2 < 0$), the coral reef more likely acts as a sink of atmospheric CO$_2$. Considering that tidal mixing can influence seawater $p$CO$_2$ as far as 4 km from a coral reef [40], we used the averaged seawater $p$CO$_2$ data (370 μmol mol$^{-1}$) observed from 18 stations located up to 4 km away from Yongshu Reef to represent oceanic water $p$CO$_2$ of the region. We then calculated the seawater $p$CO$_2$ difference ($δp$CO$_2$) between the inner and outer Yongshu Reef as 25 μmol mol$^{-1}$. The results suggest that Yongshu Reef lagoon is a significant source of atmospheric CO$_2$. The observed seawater $p$CO$_2$ at stations located 4 km away from Yongxing Island and Luhuitou Fringing Reef were 379 and 381 μmol mol$^{-1}$, respectively. The calculated $δp$CO$_2$ for the reef flats at Yongxing Island and Luhuitou Fringing Reef were 77 and 229 μmol mol$^{-1}$, respectively. Even at Site 2 of the Luhuitou Fringing Reef, the seawater $p$CO$_2$ was 125 μmol mol$^{-1}$ higher than that of stations 4 km away. Collectively, the above calculations of $δpCO_2$ suggest that the three studied coral reefs are a source of atmospheric CO$_2$.

### 4.3 Coral reefs of the SCS act as sources of atmospheric CO$_2$

Air-sea CO$_2$ flux values may be used to differentiate coral reefs that act as either sinks or sources of atmospheric CO$_2$ [6–18]. Positive values typically characterize coral reefs as a source of atmospheric CO$_2$, whilst negative values may

![Figure 3](https://example.com/figure3.png)

Figure 3 Plots of TA vs. DIC in the studied coral reefs. (a) Reef flat at Yongxing Island; (b) reef flat at Luhuitou Fringing Reef; (c-1) Yongshu Reef lagoon during 2009-05-23 to 2009-05-24; and (c-2) Yongshu Reef lagoon during 2009-06-03 to 2009-06-05.
identify coral reefs that act as a sink of atmospheric CO₂. Based on this principle and the calculated air-sea CO₂ flux values (Figure 2) for this study, Luhuitou Fringing Reef appears to be a strong source of atmospheric CO₂. Yongxing Island most likely acts as a sink for atmospheric CO₂ between 13:00 and 23:00, but as a source at all other times during the 24 h cycle. Yongshu Reef appears to be a source of atmospheric CO₂ from 07:00 to 20:00, but acts as a sink for the rest of the day. In general, coral reefs in the SCS appear to absorb atmospheric CO₂ at night and release CO₂ to the atmosphere during the daytime. The averaged data show that each of the three studied reefs in the SCS act as a source of atmospheric CO₂ in summer. Due to seasonal variations within the physical and chemical environment, as well as the community metabolism in the coral reefs, air-sea CO₂ fluxes may differ between seasons. For example, an air-sea CO₂ flux value of ~1.48 mmol CO₂ m⁻² d⁻¹ was observed during spring at the shallow water reef flat at Yongxing Island, thus indicating that the reef is a minor source of atmospheric CO₂ [20]. Additional studies over different seasons are necessary to achieve a comprehensive evaluation of the actual contribution of atmospheric CO₂ by SCS coral reefs.

5 Conclusions

We observed time-series variations of air-sea CO₂ exchange at Yongshu Reef (atoll) of Nansha Islands, southern SCS; Yongxing Island (platform reef), Xisha Islands, north-central SCS; and at Luhuitou Fringing Reef at Sanya of Hainan Island, northern SCS, during the summers of 2008 and 2009. We concluded that:

(1) Both air and surface seawater pCO₂ of the three studied coral reef areas showed significant diurnal cycling, with a decreasing phase during the daytime and an increasing phase during the night. This cyclic variation was particularly clear in areas that had high proportions of coral cover, such as the reef flats of Luhuitou Fringing Reef and Yongxing Island.

(2) Air pCO₂ in each of the investigated areas showed a small-range of diurnal variations, whilst large-range diurnal variations were observed in seawater pCO₂ from all areas. The diurnal variation amplitude of seawater pCO₂ was ~70 μmol mol⁻¹ at the Yongshu Reef lagoon; 420–619 μmol mol⁻¹ at the Yongxing Island reef flat; 264–579 μmol mol⁻¹ on the reef flat of Luhuitou Fringing Reef; and 324–492 μmol mol⁻¹ at an adjacent area just outside of this fringing reef.

(3) Within spatial scales, there were large differences in air-sea CO₂ flux from site to site (e.g. -0.4 mmol CO₂ m⁻² d⁻¹ at Yongshu Reef; ~4.7 mmol CO₂ m⁻² d⁻¹ at Yongxing Island; and ~9.8 mmol CO₂ m⁻² d⁻¹ at Luhuitou Fringing Reef). In general, the positive values suggest that coral reef ecosystems of the SCS appear to be net sources of CO₂ to the atmosphere, at least during the observed summer season.

(4) Diurnal variations of surface seawater pCO₂ in the shallow water reef flat was mainly controlled by biological metabolism. However, diurnal variations of surface seawater pCO₂ of the deeper water lagoons and outer reef area was controlled by both biological metabolism and hydrodynamic processes. In comparison with the open oceanic realm, inorganic metabolism plays a far more significant role in coral reef ecosystems by influencing seawater pCO₂ variations.

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