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Coral reef ecosystems in the South China Sea as a source of atmospheric CO_2 in summer

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Field measurements of air-sea CO_2 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 CO_2 (pCO_2) showed regular diurnal cycles. Minimum values occurred in the evening and maximum values in the morning. Air pCO_2 in each of the three study areas showed small diurnal variations, while large diurnal variations were observed in seawater pCO_2. The diurnal variation amplitude of seawater pCO_2 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 CO_2 flux across the South China Sea (e.g. ~0.4 mmol CO_2 m^{-2} d^{-1} at Yongshu Reef, ~4.7 mmol CO_2 m^{-2} d^{-1} at Yongxing Island, and ~9.8 mmol CO_2 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 CO_2 to the atmosphere. Additional analyses indicated that diurnal variations of surface seawater pCO_2 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 pCO_2 variations in coral reef ecosystems.

coral reefs, pCO_2, carbon cycle, summer, South China Sea

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Both the 1997 Kyoto Protocol and 2009 United Nations Climate Change Conference (Copenhagen) recognized the potential role of CO_2 in contributing to global warming. Thus, a reduction in at least the anthropogenic component of CO_2 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 CO_2 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 CO_2 (~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,

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coral reefs contribute 7%–15% [6] of global $CaCO_3$ production. In recent years, several studies have examined the role of coral reefs and their contribution to atmospheric CO_2 by measuring seawater $p$$CO_2$ and atmospheric $p$$CO_2$ in coral reefs [6–11]. They indicate that although coral reefs are mostly net sources [7–16] of atmospheric CO_2, they may also act as sinks [6,17,18] for atmospheric CO_2. Suzuki et al. [6] suggested that the contribution of coral reefs to atmospheric CO_2 is largely dependent on their topographic and oceanographic settings. Reefs may act as a net source of CO_2 if they are dominated by corals, but may take up atmospheric CO_2 and act as a sink to the atmosphere if they are dominated by microalgae.

Coral reefs are widely distributed across the South China Sea (SCS), covering the areas from Zenmuansha (~4°N) in the south, to Leizhou Peninsula, Weizhou Island (~20°–21°N) and Hengchun Peninsula (~24°N) in the north. The SCS is dominated by fringing reefs, platform reefs (with sand cays) and atolls. The estimated total area of modern coral reefs in the SCS is about 8000 km^2 [19]. However, little information is available on the contribution of coral reefs in the SCS to global atmospheric CO_2. After a brief investigation at Yongxing Island, in the Xisha Islands, in the spring of 2006, Dai et al. [20] found that surface seawater $p$$CO_2$ shows significant regular diurnal variations, and that the studied area was a minor source of atmospheric CO_2. In order to fully understand the relationship between SCS coral reefs and atmospheric CO_2, we carried out detailed measurements of air-sea CO_2 exchange at Yongshu Reef (atoll), Nansha Islands, southern SCS; Yongxing Reef (platform reef with a sand cay), Xisha Islands, north-central SCS; and Luhuitou Fringing Reef at Sanya of Hainan Island, northern SCS. Thus, we were able to sample across the three major reef types of the SCS.

1 Geography and natural environment of the studied coral reefs

Yongshu Reef (9.52°–9.68°N, 112.88°–113.06°E, Figure 1) is located in the Nansha Islands. The reef is an open spindle-shaped atoll, about 25 km long in the NEE-SWW direction and 6 km wide in the NW-SE direction (with a total area ca. 110 km^2). Six basic biogeomorphologic units can be identified in the Yongshu Reef: the reef front slope, outer reef flat, reef ridge, inner reef flat, lagoon slope and lagoon [21]. Since Yongshu Reef is located >500 km away from the mainland, it is relatively undisturbed by human activities. An ecological survey carried out in 2006 at Yongshu Reef suggested that the living coral cover was ~60%. The lagoon of Yongshu Reef was selected for this investigation, because its coral atolls are among the most widespread reefs in the Nansha Islands, and its lagoons make up ~82% of the modern atoll systems in the broader Nansha area [19]. Instrumental data from the Yongshu Reef Observatory indicate 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 biogeomorphologic 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 CO_2 exchanges were carried out at Yongxing Island in July 2008, at Yongshu Reef in June 2009, and at Luhuitou Fringing Reef in

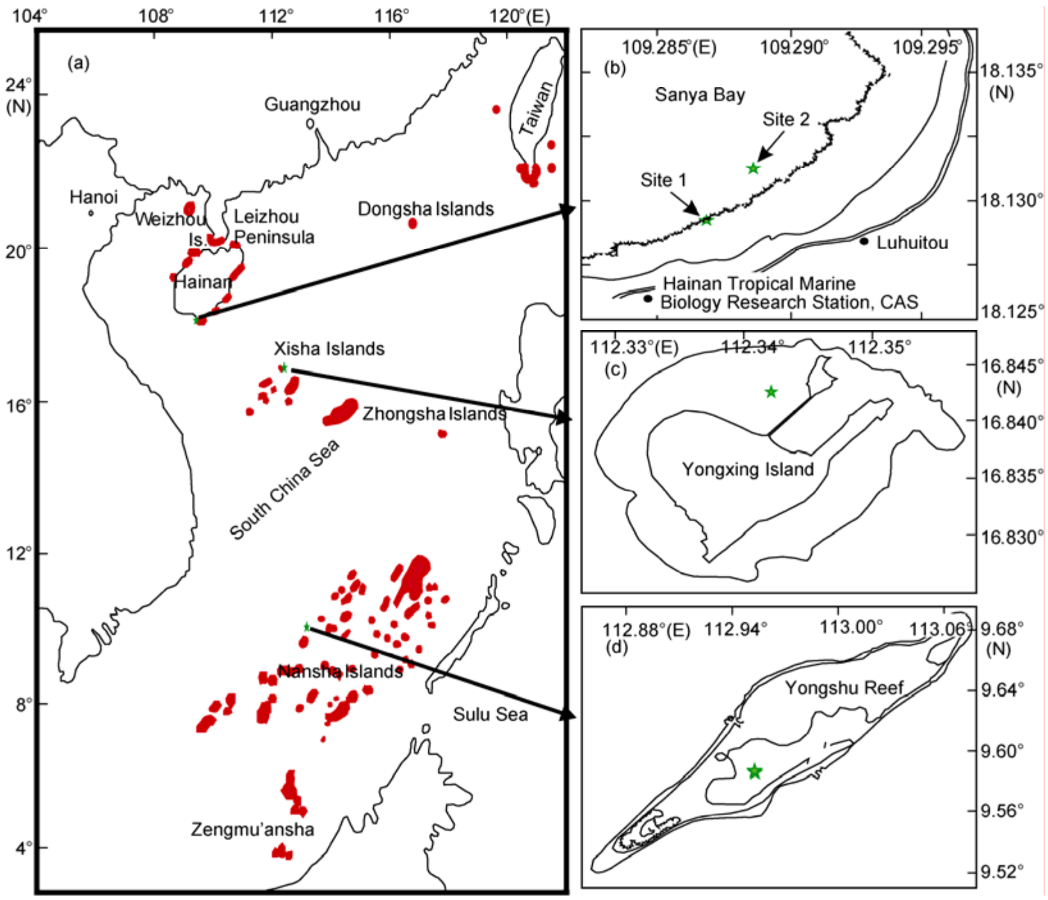

Figure 1 Location map of the investigated reefs in the SCS. Shaded areas represent the occurrence of coral reefs in the SCS [19]. ☆ symbols in (b), (c) and (d) indicate investigation sites. "Site 1" in (b) is located on a reef flat at Luhuitou Fringing Reef, and "Site 2" is located outside the reef.

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 Diskon and Millero [33].

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

$$F=ks(pCO_{2w}-pCO_{2a}), \tag{1}$$

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 (Sc). We used the Wanninkhof [34] function of wind speed (u) to calculate the value:

$$K = 0.31u^2(Sc/660)^{-1/2}, \qquad (2)$$

where Sc is the Schmidt number of CO_2 in seawater; 660 is the 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 pCO$_2$ variations in coral reef areas

Table 1 summarizes the mean SST, salinity, pH, TA, seawater pCO$_2$ and atmospheric pCO$_2$ at the study sites. Spatially, the seawater pCO$_2$ values show large differences between sites. The mean seawater pCO$_2$ at Yongshu Reef lagoon was the lowest amongst the three studied sites, and was slightly higher than the mean atmospheric pCO$_2$. The diurnal amplitude of seawater 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 pCO$_2$ amplitudes at different coral reef areas were relatively small, and the mean daily atmospheric pCO$_2$ values were similar among each of the coral reefs. Figure 2 shows that both atmospheric pCO$_2$ and seawater 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 pCO$_2$ reached its minimum (~67 μmol mol^{-1}) at 17∶00–19∶00 and its maximum (~899 μmol mol^{-1}) at 07∶00–09∶00. The diurnal seawater pCO$_2$ amplitudes were as high as 420–619 μmol mol^{-1}. At the reef flat of Luhuitou Fringing Reef, the seawater pCO$_2$ reached its minimum (~340 μmol mol^{-1}) at 16∶00–18∶00 and its maximum (~952 μmol mol^{-1}) at 06∶00–08∶00. The diurnal seawater pCO$_2$ amplitudes were 264–579 μmol mol^{-1} at Luhuitou reef flat and 386–492 μmol mol^{-1} just outside of the reef. At the Yongshu Reef lagoon, the diurnal cycle of seawater 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 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 pCO$_2$ and diurnal seawater pCO$_2$ amplitudes both showed a clear decrease from within the reef area to outside of the reef. Since the diurnal atmospheric pCO$_2$ amplitude was very small, its effect on air-sea CO$_2$ exchange at the studied coral reefs was minor. The large diurnal amplitudes and associated seawater pCO$_2$ variations indicate a significant exchange in air-sea CO$_2$.

3.2 Air-sea CO$_2$ flux

The air-sea CO$_2$ fluxes (Figure 2) within different reef areas were calculated using equation 1. At the Yongxing reef flat, air-sea CO$_2$ flux ranged from –19.9–30.5 mmol CO$_2$ m^{-2} d^{-1}. From 13∶00–23∶00, its seawater pCO$_2$ was generally lower than the atmospheric pCO$_2$, and the average air-sea CO$_2$ flux was –5.1 mmol CO$_2$ m^{-2} d^{-1}. Its seawater pCO$_2$ was larger than atmospheric pCO$_2$, and for the remaining part of the day, the mean air-sea CO$_2$ flux was 13.7 mmol CO$_2$ m^{-2} d^{-1}. At the reef flat in the Luhuitou Fringing Reef, the air-sea CO$_2$ flux varied from –1.6–26.5 mmol CO$_2$ m^{-2} d^{-1}. Apart from a few hours at night, the seawater pCO$_2$ was almost always larger than atmospheric pCO$_2$ at Luhuitou. At the Yongshu Reef lagoon, the air-sea CO$_2$ fluxes varied from –2.3–2.7 mmol CO$_2$ m^{-2} d^{-1}. From 20∶00–07∶00, seawater pCO$_2$ showed lower values with mean flux approaching 0; during the remaining portion of the day, the mean flux was ~0.8 mmol 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 pCO$_2$ data, the flux was ~4.7 mmol CO$_2$ m^{-2} d^{-1} at the Yongxing reef flat, ~0.4 mmol CO$_2$ m^{-2} d^{-1} at the Yongshu Reef lagoon, and ~9.8 mmol CO$_2$ m^{-2} d^{-1} at the Luhuitou Fringing Reef flat.

4 Discussion

4.1 Environmental controls of surface seawater pCO$_2$

In open ocean ecosystems, seawater pCO$_2$ is controlled by a

Table 1 Summary of mean SST, SSS, pH, TA, seawater pCO$_2$ and atmospheric pCO$_2$ at the observation sites

Reef site	Mean depth (m)$^{a)}$	SST (°C)	SSS (‰)	pH	TA (μmol kg^{-1})	Seawater pCO$_2$ (μmol mol^{-1})$^{b)}$	Atmospheric 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 pCO$_2$ was calculated from temperature, salinity, pH and TA.

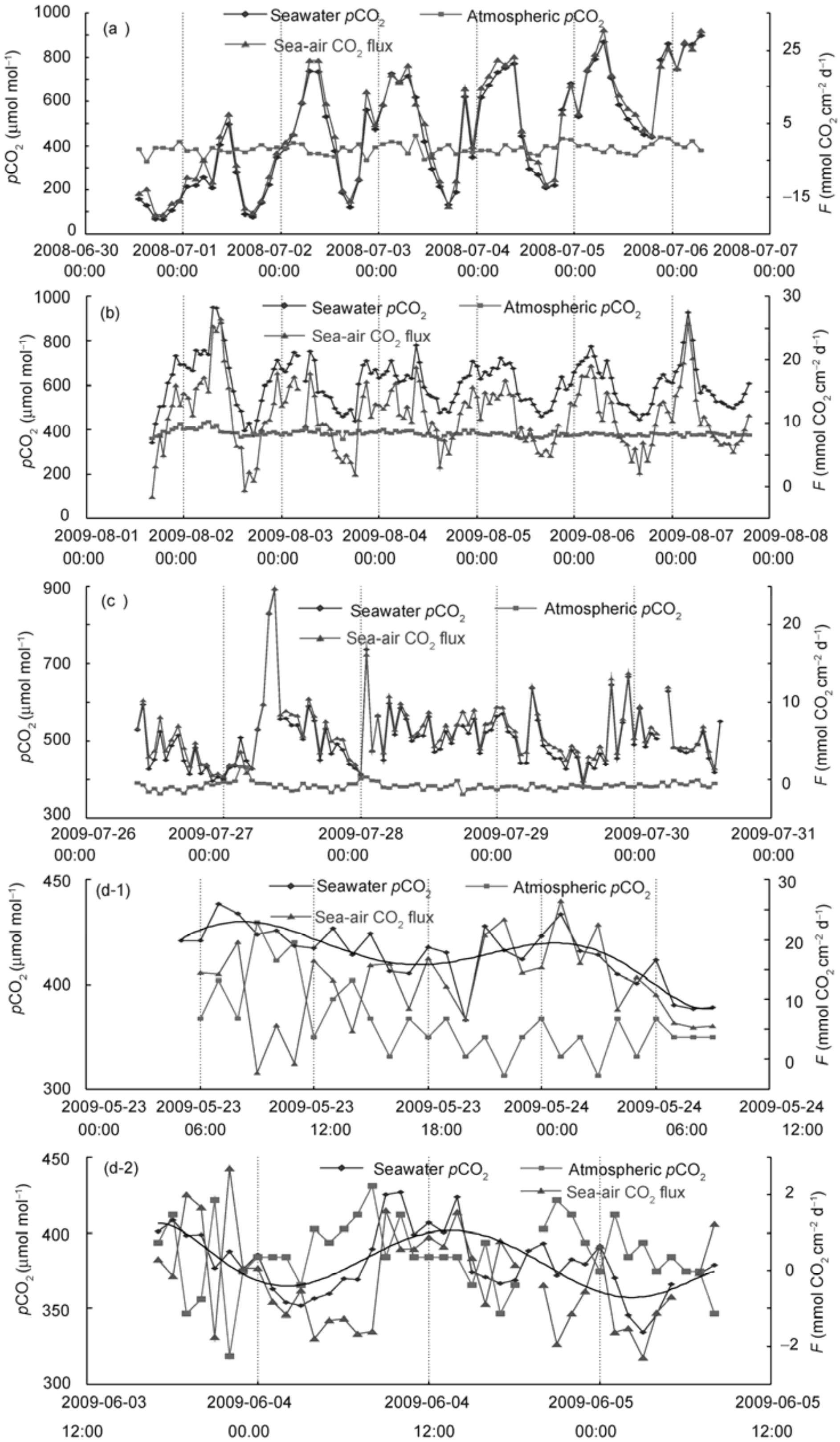

Figure 2 Diurnal variations of atmospheric pCO$_2$, seawater pCO$_2$ and air-sea CO$_2$ flux in the studied coral reef areas. (a) Reef flat at Yongxing Island; (b) reef flat at Luhuitou Fringing Reef; (c) outside of Luhuitou Fringing Reef; (d-1) and (d-2) Lagoon at Yongshu Reef. 2009-06-30 00∶00: midnight (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 pCO_2, the measured pCO_2 values were normalized to the mean SST during the observation period, using the following equation:

$$NpCO_2 = (in\ situ\ pCO_2) \times \exp\ [0.0423\ (T_{\mathrm{mean}}-T_{in\ situ})],$$

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 $NpCO_2$ values show that similar variations in measured pCO_2 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 pCO_2. To examine the contribution of SST on surface seawater pCO_2, we computed the offset between $NpCO_2$ and measured pCO_2 (Table 2), herein defined as δpCO_2 (δpCO_2=|measured pCO_2–$NpCO_2$|). The mean δpCO_2 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 pCO_2 variation amplitude during the observation period as ΔpCO_2, and then calculated the ratio (= $\delta pCO_2/\Delta pCO_2$) between δpCO_2 and ΔpCO_2 (Table 2). The results (Table 2) show that SST variation had a contribution of only 6.17% of the observed seawater pCO_2 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 pCO_2. The apparent minor variation in the contribution of SST to seawater pCO_2 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 pCO_2. For example, Table 1 demonstrates that the seawater pCO_2 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 pCO_2 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 pCO_2.

Biological metabolism directly controls seawater pCO_2 variations. During the night, respiration and calcification by coral reef organisms releases CO_2, which increases seawater pCO_2. Conversely, during the daytime, the CO_2 that is fixed by photosynthesis is greater than that released from respiration and calcification, and therefore, seawater pCO_2 decreases. The observed diurnal cycles (i.e. surface seawater pCO_2 increasing at night and decreasing during the daytime) are significantly correlated with reef metabolic processes, suggesting that biological metabolism dominates seawater pCO_2 variations in coral reef waters [17,20,37].

Previous studies have indicated that seawater CO_2 chemical equilibrium determines the CO_2 absorption capacity of coral reefs [38]. Based on previous work [9], for each mole of $CaCO_3$ precipitated, seawater TA and DIC decrease by 2 eq and 1 mol. Thus, the slope (ΔTA/ΔDIC) 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 (ΔTA/ΔDIC) 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, (ΔTA/ΔDIC), 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 $CaCO_3$ production was more prominent at Luhuitou. Due to calcification causing CO_2 release, the Luhuitou Fringing Reef hypothetically should be a more significant source of atmospheric CO_2 than at Yongxing Island. Indeed, this is supported by the demonstrated air-sea CO_2 fluxes in section 3.2. Though Yongshu lagoon had the highest ratio, its air-sea CO_2 flux

Table 2 Contribution of SST to seawater pCO_2 variability

Reef site	δpCO_2 (μmol mol^{-1})			ΔpCO_2 (μmol mol^{-1})	$\delta pCO_2/\Delta pCO_2$ (%)		
	Minimum	Maximum	Mean		Minimum	Maximum	Mean
Luhuitou Fringing Reef	0.0	78.3	25.6	415	0.00	18.86	6.17
Yongxing Island	1.0	98.8	22.8	525	0.19	18.82	4.34
Yongshu Reef	0.0	8.8	1.6	60	0.00	14.71	2.66

was the lowest (~0.4 mmol $\text{CO}_2\,\text{m}^{-2}\,\text{d}^{-1}$), 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 $p\text{CO}_2$.

4.2 $p\text{CO}_2$ 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 $p\text{CO}_2$ between the inside and the outside of the studied coral reefs [40]. Following a previous study [39], we defined the difference in $p\text{CO}_2$ between the inside and outside coral reef area ($\delta p\text{CO}_2$) as

$$\delta p\text{CO}_2 = p\text{CO}_{2\text{L}} - p\text{CO}_{2\text{O}}, \quad (3)$$

where $p\text{CO}_{2\text{L}}$ and $p\text{CO}_{2\text{O}}$ are the partial pressure of carbon dioxide in the atoll lagoon water, and the oceanic water outside the coral reef, respectively. If the mean $p\text{CO}_2$ of lagoon water is higher than that of oceanic water (i.e. $\delta p\text{CO}_2 > 0$), the coral reef is likely to be a source of atmospheric CO_2. Conversely, if the mean $p\text{CO}_2$ of the lagoon water is lower than that of oceanic water (i.e. $\delta p\text{CO}_2 < 0$), the coral reef more likely acts as a sink of atmospheric CO_2. Considering that tidal mixing can influence seawater $p\text{CO}_2$ as far as 4 km from a coral reef [40], we used the averaged seawater $p\text{CO}_2$ data (370 $\mu\text{mol mol}^{-1}$) observed from 18 stations located up to 4 km away from Yongshu Reef to represent oceanic water $p\text{CO}_2$ of the region. We then calculated the seawater $p\text{CO}_2$ difference ($\delta p\text{CO}_2$) between the inner and outer Yongshu Reef as 25 $\mu\text{mol mol}^{-1}$. The results suggest that Yongshu Reef lagoon is a significant source of atmospheric CO_2. The observed seawater $p\text{CO}_2$ at stations located 4 km away from Yongxing Island and Luhuitou Fringing Reef were 379 and 381 $\mu\text{mol mol}^{-1}$, respectively. The calculated $\delta p\text{CO}_2$ for the reef flats at Yongxing Island and Luhuitou Fringing Reef were 77 and 229 $\mu\text{mol mol}^{-1}$, respectively. Even at Site 2 of the Luhuitou Fringing Reef, the seawater $p\text{CO}_2$ was 125 $\mu\text{mol mol}^{-1}$ higher than that of stations 4 km away. Collectively, the above calculations of $\delta p\text{CO}_2$ 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

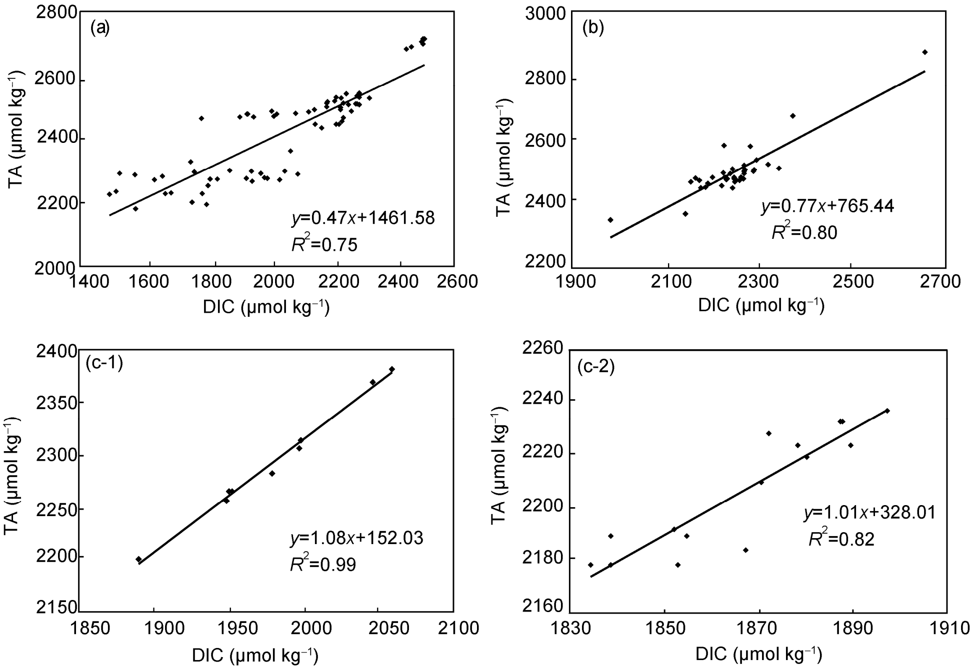

Figure 3 Plots of TA vs. DIC in the studied coral reefs. (a) Reef flat at Yongxing Island; (b) reef flat at Luhuitou Fringing Reef; (c-1) Yongshu Reef lagoon during 2009-05-23 to 2009-05-24; and (c-2) Yongshu Reef lagoon during 2009-06-03 to 2009-06-05.

identify coral reefs that act as a sink of atmospheric CO_2. Based on this principle and the calculated air-sea CO_2 flux values (Figure 2) for this study, Luhuitou Fringing Reef appears to be a strong source of atmospheric CO_2. Yongxing Island most likely acts as a sink for atmospheric CO_2 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 CO_2 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 CO_2 at night and release CO_2 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 CO_2 in summer. Due to seasonal variations within the physical and chemical environment, as well as the community metabolism in the coral reefs, air-sea CO_2 fluxes may differ between seasons. For example, an air-sea CO_2 flux value of ~1.48 mmol $CO_2\,m^{-2}\,d^{-1}$ was observed during spring at the reef flat at Yongxing Island, thus indicating that the reef is a minor source of atmospheric CO_2 [20]. Additional studies over different seasons are necessary to achieve a comprehensive evaluation of the actual contribution of atmospheric CO_2 by SCS coral reefs.

5 Conclusions

We observed time-series variations of air-sea CO_2 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 pCO_2 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 pCO_2 in each of the investigated areas showed a small-range of diurnal variations, whilst large-range diurnal variations were observed in seawater pCO_2 from all areas. The diurnal variation amplitude of seawater pCO_2 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 CO_2 flux from site to site (e.g. ~0.4 mmol $CO_2\,m^{-2}\,d^{-1}$ at Yongshu Reef; ~4.7 mmol $CO_2\,m^{-2}\,d^{-1}$ at Yongxing Island; and ~9.8 mmol $CO_2\,m^{-2}\,d^{-1}$ at Luhuitou Fringing Reef). In general, the positive values suggest that coral reef ecosystems of the SCS appear to be net sources of CO_2 to the atmosphere, at least during the observed summer season.

(4) Diurnal variations of surface seawater pCO_2 in the shallow water reef flat was mainly controlled by biological metabolism. However, diurnal variations of surface seawater pCO_2 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 pCO_2 variations.

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