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Diurnal and seasonal variations of carbonate system parameters on Luhuitou fringing reef, Sanya Bay, Hainan Island, South China Sea

Chenglong Zhang [a,b,c], Hui Huang [a,b,*], Cheng Ye [a,b,c], Liangmin Huang [a], Xiubao Li [a,b], Jiansheng Lian [a], Sheng Liu [a]

[a] Key Laboratory of Marine Bioresources Sustainable Utilization, South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou 510301, China
[b] National Experiment Station of Tropical Marine Biology, Sanya 572000, China
[c] Graduate University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

The 3-day diurnal dynamics of carbonate system and related parameters on Luhuitou fringing reef of Sanya Bay-adjacent to the South China Sea (SCS) were observed in December of 2009 (early winter), April (spring), July (summer) and November (late-autumn) of 2010. The Luhuitou fringing reef ecosystem was generally dominated by macro and planktonic algae throughout the year except by coralline algae in winter. The system parameters showed distinct diurnal trends in the four seasons. Averaged ranges of diurnal variation for dissolved oxygen and partial pressure of CO_2 (pCO_2) were higher in the autumn, 4.67 mg L^{-1} and 218.2 μatm, respectively than other seasons. Averaged ranges of diurnal variation for normalized total alkalinity (NTA) was higher in the winter (61.3 μmol kg^{-1}), and lower in the spring (16.0 μmol kg^{-1}). The diurnal variations are mainly controlled by biological activities, especially by the processes of photosynthesis and respiration in the reef ecosystem. In winter, however, calcification and dissolution contributed more to the diurnal variations, compared with the other three seasons. Total alkalinity was largely related to seasonal changes in river inflow rates. Dissolved oxygen, pH, total CO_2 and aragonite saturation also showed seasonal variations. These variations were mainly controlled by the seasonal changes of photosynthesis and respiration, which were mainly affected by changes in benthic community structure, temperature and river inflow rates. The oversaturated pCO_2 in the reef ecosystem with respect to the atmosphere in the winter and summer resulted in CO_2 discharge from the reef ecosystem to the SCS. The whole system served as net source of CO_2 to the atmosphere and the adjacent South China Sea on an annual time scale.

1. Introduction

Coral reefs around the world have been deteriorating since the industrial revolution as a result of globe change and anthropogenic activities (Bruno and Selig, 2007; Hughes et al., 2003). It is believed that global warming and ocean acidification will exert vital impacts on coral reefs in the near future (Hoegh-Guldberg et al., 2007). Many observations have demonstrated that a number of reef ecosystems have transferred from coral-dominated as net sources of CO_2 to algae-dominated as net sinks (Bensoussan and Gattuso, 2007; Gattuso et al., 1995, 1997; Kayanne et al., 1995). Moreover, most coastal zones and marginal seas have changed similarly (Borges, 2005; Cai et al., 2003; Mackenzie et al., 2004; Rivaro et al., 2010). However, subtropical and tropical estuaries mostly act as sources of CO_2 to the atmosphere, due to a combination of the processes of river inflows, biological metabolism, and sometimes upwelling (Borges, 2005; Borges and Frankignoulle, 2002; Fagan and Mackenzie, 2007).

Sanya Bay is a large tropical estuary, receiving freshwater from the Sanya River and Shaoqi River, as well as exchanging adequately with the South China Sea (SCS). At the mouth of the Sanya Bay, the Luhuitou fringing reef ecosystem has been significantly impacted by anthropogenic activities and global change, deteriorating continuously over recent decades (Zhao et al., 2010). It offers a model ecosystem which is suitable to study the effects that such deteriorated reef ecosystems are contributing to the dynamics of the dissolved oxygen (DO) and carbonate system, and to assess the contribution of these ecosystems to the global carbon cycle, under the influence of river inflows and tidal exchange.

Previous studies have discussed the processes that lead to impacts on the oxygen and carbon system dynamics in temperate and subtropical estuaries on diurnal and seasonal scales

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[*] Corresponding author at: Key Laboratory of Marine Bioresources Sustainable Utilization, South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou 510301, China.
E-mail address: huanghui@scsio.ac.cn (H. Huang).

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(Borges and Frankignoulle, 1999, 2002; Frankignoulle et al., 1998; Millero et al., 2001; Yates et al., 2007). However, fewer studies have been carried out on a deteriorated fringing reef in a tropical estuary. Furthermore, the effects that the deteriorated reef ecosystem and river inflows were contributing to the dynamics of the carbonate system and carbon budgets have not yet been well understood. Reef ecosystems along coasts and estuaries, which have high rates of primary production, make a great contribution to the global carbon cycle (Bates, 2002; Ianson et al., 2003; Kawahata et al., 1997). Currently, whether the estuaries and coasts act as carbon sinks or sources is still a matter of considerable disputes (Andersson and Mackenzie, 2004; Mackenzie et al., 2004). Thus, it is important to determine the roles that such reef ecosystems are playing in the global carbon cycle; in addition, high temporal resolution measurements of oxygen and carbonate system parameters should be carried out in such ecosystems when referring to the sinks and sources of the whole system.

Methods of pH-TA and pH-O_2 (continuous investigation of DO and carbonate system) have been used widely in measuring community metabolism of coral reef ecosystems in flowing seawater (Barnes, 1983; Smith and Key, 1975), which are also very useful for assessing the contribution of an ecosystem to the global carbon cycle (Gattuso et al., 1999).

The total concentration of dissolved inorganic carbon (TCO_2) in a seawater sample is defined in SOP 2 as below:

$$TCO_2 = [CO_2] + [HCO_3{}^-] + [CO_3{}^{2-}]$$

and the total alkalinity (TA) in seawater sample is rigorously defined by Dickson as below (Dickson, 1981):

$$\begin{aligned} TA = {} & [HCO_3{}^-] + 2[CO_3{}^{2-}] + [B(OH)_4{}^-] + [OH^-] + [HPO_4{}^{2-}] \\ & + 2[PO_4{}^{3-}] + [SiO(OH)_3-] + [NH_3] + [HS^-] + \ldots \\ & - [H^+]_F - [HSO_4{}^-] - [HF] - [H_3PO_4{}^-] - \ldots, \end{aligned}$$

where the ellipses stand for additional minor that they can be neglected.

In this paper we report the diurnal and seasonal variations of DO and the carbonate system on the rapidly deteriorating Luhuitou fringing reef, with emphasis on the seasonal variation of partial pressure of CO_2 (pCO_2) affected by freshwater input, photosynthesis/respiration and calcification/dissolution. We try to evaluate seasonal changes of the impacts exerted by the above factors. In a bid to shed light on the status of the reef ecosystem, we also compared historical data with the results we produced.

2. Study site

Sanya Bay, located to the southeast of Sanya city, Hainan Island in South China, is a large open tropical estuary with a long sandy beach in the northern and a short gravel beach in the eastern sector (Mao et al., 2006) (Fig. 1). Freshwater and sanitary sewage flows into the bay from the Sanya River and the Shaoqi River. The Sanya River is characterized by a length of 31 km, drainage area of 337 km^2, mean annual runoff of 5.86 $m^3\,s^{-1}$, while the Shaoqi River has a much smaller catchment area. Seawater salinity in the bay ranges from 29.9‰ to 34.2‰. Sanya city has a population of 0.504 million. Weather in the Sanya River area was usually wet over May–October, but dry over November–April. Typhoons usually impacted on the area in the wet season, bringing ~90% rainfall of the annual total (Huang et al., 2007). Located in the middle of the bay, West Maozhou, East Maozhou, and Shuangfan Stones are surrounded by narrow fringing reefs. Water depth in the bay averages at 15 m, of which 90% seabed is deeper than 5 m and covered by a mixture of terrigenous clast and calcareous chips of coral reef organisms (Feng et al., 1984). The tide in the bay is dominated by irregular diurnal type, while semi-diurnal type also prevails, where the tidal range averages at 0.79 m. Flood tides bring clean seawater flowing to the northern and northwestern areas of the bay, while ebb tides bring polluted seawater back to the South China Sea (Wang, 1996). According to monitoring by Ocean Observation Station in Yulin, Huang et al. determined that the annual mean Surface Seawater Temperature (SST) in the bay is 26.9 °C from December to February, during which annual minimum SST is 23.2 °C. Annual maximum SST is 29.5 °C during May–October (Huang et al., 2004).

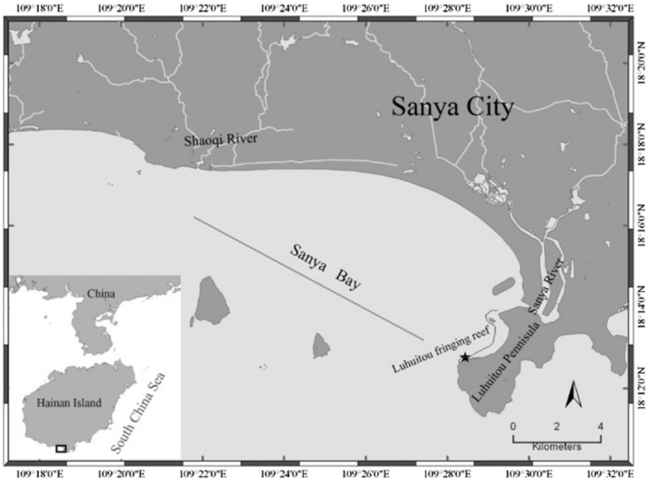

Fig. 1. The location of the study site on Luhuitou fringing reef in Sanya Bay, South China Sea. Continuous observations of DO and carbonate system parameters were conducted at the site during 27–30 December, 2009 (winter), 11–14 April, 2010 (spring), 28–31 July, 2010 (summer), and 19–22 November, 2010 (autumn). Solid star indicates the study site.

The Luhuitou fringing reef lies alongside the east bank of Sanya Bay (Fig. 1). With the affects of frequent water exchange and moderate waves, the reef is well-developed. It is characterized by a narrow sandy beach, a wide reef flat and a steep reef slope (Zhang, 2001). The 3500 m-long reef is 250 m wide (Huang et al., 2004), with the lowest limit of depth for live coral distribution ~6 m (Huanghui et al., unpublished). In 2006, live coral coverage of the whole reef was 12.16%, with *Porites* and *Acropora* as the dominant genera. Over 90% of the sand that covers the beach is biological material. The ratio of calcium carbonate in sandy or muddy sediments outside the reef slope is between 20%–80%. Seagrass, *Turbinaria ornate* and coralline algae are abundant nearby (Zhao et al., 2010). Our study site is situated at the end of the reef, which is flat with ~10% coverage of live coral, 60 m away from the sandy beach, and water ~3 m deep at high tide.

3. Methods

3.1. Sampling and analysis

Water temperature, salinity, DO, and carbonate system parameters including total alkalinity (TA) and pH were measured every 3 h on Luhuitou fringing reef flat for 3-day periods during four seasons: 27–30 December 2009 (winter), 11–14 April 2010 (spring), 28–31 July 2010 (summer), and 19–22 November 2010 (autumn). Seawater was continuously pumped, using a submersible pump (Hailea HX 6550) via a 60 mm-diameter hose, from the study site into a $100 \times 20 \times 20$ cm^3 flow-through glass tank on the beach. In-situ measurements of salinity, temperature and pH were carried out in the tank. The pump was attached to a 25 cm-high cement frame that was fixed on the reef surface. Salinity and

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temperature were measured by using an Orion 013010MD conductivity probe (±0.1 psu and ±0.1 °C). The conductivity probe was calibrated with standards acquired from YSI Company and then confirmed later by Certified Reference Materials (CRMs batch 101#) obtained from Dr. Andrew Dickson. pH was measured by using 8103BNUWP Ross semi-micro glass combination pH Electrode (±0.005) calibrated with seawater buffers as described in SOP 6a (Dickson et al., 2007). Thereafter, seawater samples for DO and TA analyses were diverted from the hose and collected into the two brown glass bottles with ground glass necks and stoppers, via a 10 mm-diameter flexible tube. The 125-ml bottle that had DO samples was kept in darkness for 24 h, after it had been treated with the Winkler reagents, sealed, and soaked in seawater. TA samples, stored in the 250-ml bottle, were treated with 100 μL of a saturated $HgCl_2$ solution, sealed, soaked in seawater, and then were transferred to an air-conditioned laboratory. Measurements were completed within 48 h. PAR was measured by Li-192 quantum sensor and Li-1400 Data Logger (LI-COR). Tidal data was calibrated with the results acquired in situ by a Hobo level set; and strong linear relationship existed between the two.

All samples for DO were analyzed by Winkler titration with a precision of 0.05 mg L^{-1}, using an automated titration system consisted of a Metrohm 877 Titrino plus, a 20-mL Metrohm 806 Exchange unit and a Pt Titrode metal electrode. Sodium thiosulfate solution (0.05 mol L^{-1}), the titrant, was calibrated using potassium iodate solution. Samples for TA were filtered through 0.45-μm cellulose acetate membranes, which had been soaked in distilled water for 24 h, using a vacuum pump. Thereafter, the samples were measured in an air-conditioned laboratory with temperature being controlled at 26±0.5 °C, by using an automated titration system consisted of a Metrohm 877 Titrino plus, a 20-mL Metrohm 806 Exchange unit and an Ecotrode (a type of pH Electrode). The HCl titrant solution (0.1 mol L^{-1}, prepared as described in SOP3b) was calibrated by Tris solution in the first phase of the survey, and by CRMs (Batch 101#) from the laboratory of Dr. Andrew Dickson (Dickson et al., 2003) in the next three phases. Comparisons of the two methods of calibration showed a difference of ±3 μmol kg^{-1} ($N=6$). Measurements precision, determined from the repeated measurements ($N \geq 12$) of collected samples, averaged ±1.6 μmol kg^{-1} in the whole survey.

The other carbonate system parameters, including total carbon dioxide (TCO_2), pCO_2, calcite (Ω_{Cal}) and aragonite (Ω_{Ar}) saturation states, were calculated using the CO2SYS program (Lewis and Wallace, 1998) through in situ TA, pH, salinity, temperature data. The calculation used the CO_2 equilibrium constants K1 and K2 (Mehrbach et al., 1973) as refitted by Dickson and Millero (Dickson and Millero, 1987) and the Dickson constant for the HSO_4^- (Dickson, 1990).

The apparent oxygen utilization (AOU) is defined as the deviation of oxygen from a DO concentration in equilibrium with respect to the atmosphere, and was calculated by the solubility equation as follow (Benson and Krause, 1984):

$$\mathrm{AOU} = [O_2]_{\text{saturated in situ T and S}} - [O_2]_{\text{sample in situ T and S}}$$

3.2. Statistical

Pearson correlation analyses were conducted for the relationships between the system parameters. Seasonal differences in the system parameters were analyzed using one-way analysis of variance (ANOVA) followed by the Bonferroni post hoc test. The threshold value for statistical difference was taken as $p < 0.05$. Data analysis was performed using SPSS 11.0.

4. Results

4.1. Background data

Water levels changed between 64.0 cm and 212.5 cm throughout the survey periods at the study site, and the mean tide was largely equal in each season. Temperature variation was characterized by very similar and distinct diurnal trends in each season (Fig. 2a), climbing up to the highest between 12:00–15:00 and lowest at 6:00 am. Thus was mainly affected by photoperiod. For example, there is a strong correlation ($R=0.785$) between temperature and photosynthetically active radiation (PAR) in the autumn (not shown). Furthermore, temperature changed markedly in the different seasons, resulting in strong seasonality.

Salinity showed remarkably different levels in the four seasons, with higher levels in the spring and summer. In the winter, summer and autumn, it fluctuated in a wider average diurnal range, and stayed largely stably in a narrower average diurnal range in the spring (Fig. 2b; Table 1). In the November–April dry season, the northeast monsoon drove the dilute seawater from the northern coasts along China Mainland and Hainan Island flowing into the ecosystem. Then the southwest monsoon drove seawater on the surface of the western SCS flowing into the ecosystem in wet season (Shaw and Chao, 1994). Therefore, the lower salinity levels seen in the autumn and winter might be caused by the impacts from the northeast monsoon, but the sharp fluctuations were probably caused by freshwater inflows coming from the Sanya River. The significant positive correlations between the salinity and water level in the winter and spring confirmed the impacts from freshwater inflows (Table 2). The firm salinity (33.8±0.1) in the spring was probably because the monsoon brought less impacts, coupled with less freshwater coming from the Sanya River into the ecosystem in April (at the end of dry season), which was confirmed by the weak correlation between the salinity and water level (Table 2). The reason that the second highest level (widest range) of salinity fluctuated sharply in the summer might be the impacts caused by the southwest monsoon, as well as freshwater inflows coming from the Sanya River; thus was confirmed by the positive correlation between the salinity and water level in the summer (Table 2). In addition, the average diurnal change of salinity suggest influence of the amount of river inflows into the ecosystem in each season, with highest river inflows in the summer and autumn, and more inflows in the winter, compared with inflows in the spring (Table 1).

4.2. Diurnal and seasonal variations of TA and NTA

TA showed strong seasonality, similar to the seasonal trends of salinity (Fig. 2b and c). In order to examine the contributions of processes to the variations in TA, and removing the contributions from the changes in salinity, TA was normalized to a constant salinity of 35 as NTA (NTA=Total Alkalinity (TA)×35/S (salinity in situ)) (Millero et al., 1998), it increased sharply during the nighttime and decreased quickly during the daytime in the winter and autumn, while no diurnal trends were clearly detected in the spring and summer. Given nutrients in the bay used to be very low (Huang et al., 2003), the impacts that nutrients exerted on the change of NTA were negligible. The values of TA were obviously higher in the spring and summer, while the values of NTA were lower in these two seasons, which were due to the impact of high salinity seawater brought by the southwest monsoon. Furthermore, during the spring and summer, both TA and NTA fluctuated more smoothly, compared to the other two seasons.

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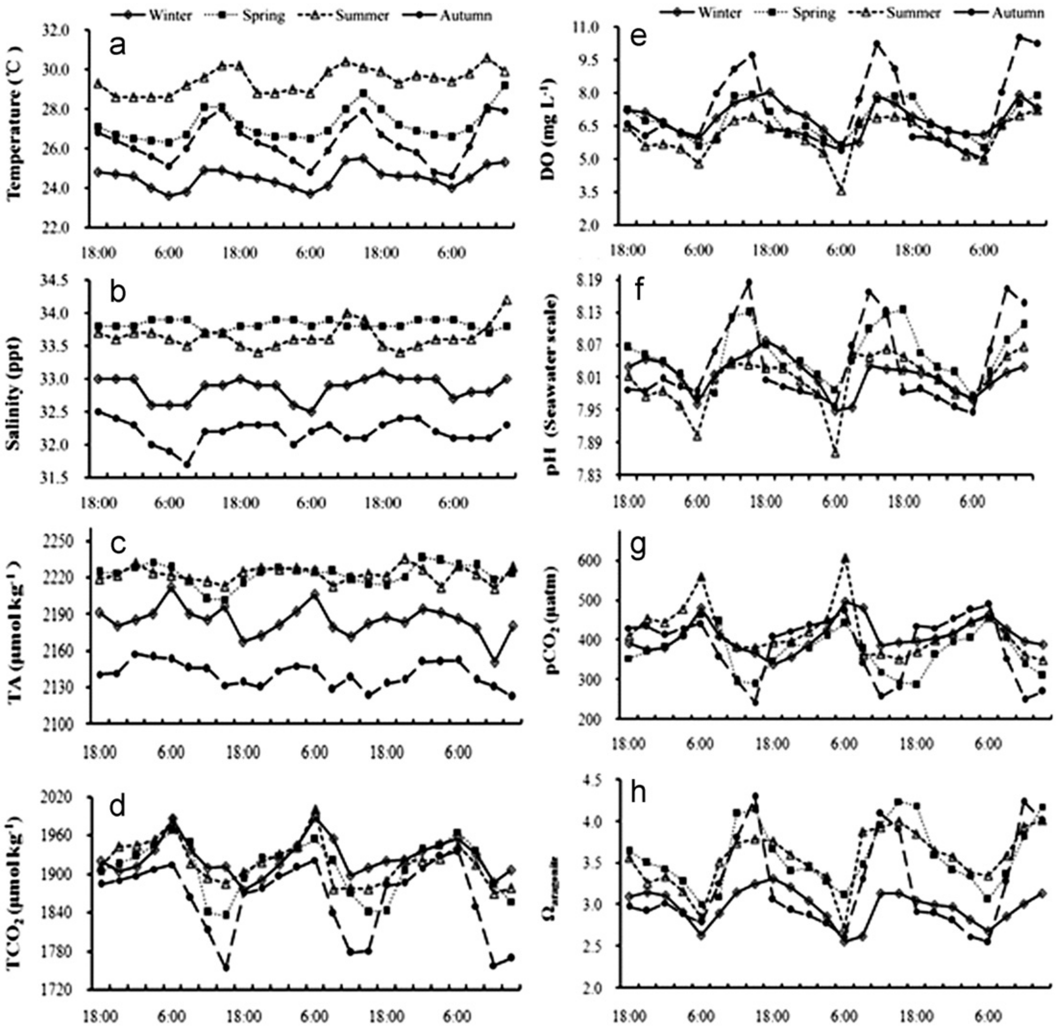

Fig. 2. Diurnal variations of the environment factors (including salinity and temperature), DO and carbonate system parameters (including TA, pH, TCO_2, pCO_2 and $\Omega_{Aragonite}$) during the four seasons for the Luhuitou reef system.

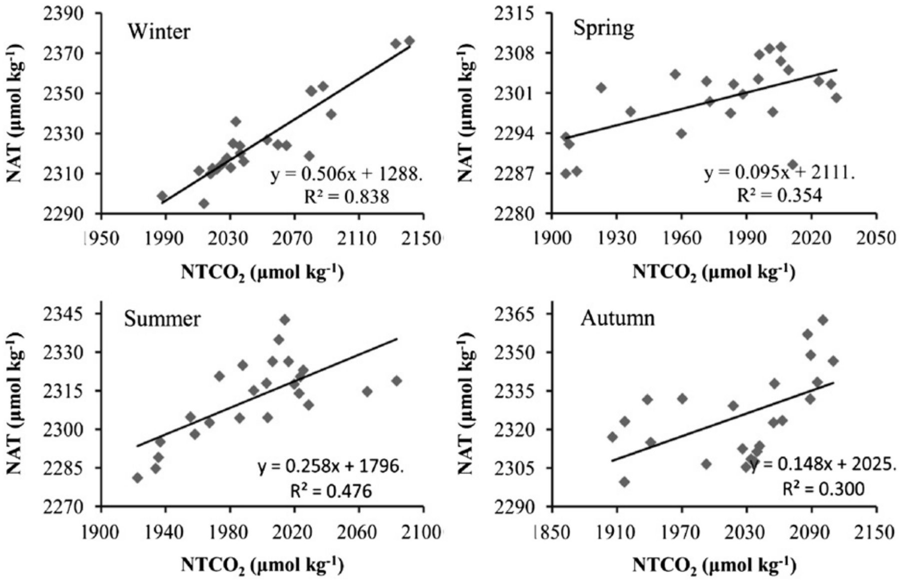

Fig. 3. Relations between NTA and $NTCO_2$ in the Luhuitou reef system during the four seasons.

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Table 1
Statistical summary of system parameters in the Luhuitou fringing reef ecosystem during the four seasons.

Variable	Season	Mean ± SD (N=24)	Averaged diurnal range (N=3)
Salt	Winter	32.9 ± 0.17	0.43
	Spring	33.8 ± 0.07	0.17
	Summer	33.6 ± 0.17	0.53
	Autumn	32.2 ± 0.18	0.47
AOU (mg L^{-1})	Winter	0.11 ± 0.77	2.17
	Spring	−0.22 ± 0.89	2.52
	Summer	0.25 ± 0.91	2.68
	Autumn	−0.46 ± 1.84	4.97
pH (Seawater scale)	Winter	8.016 ± 0.033	0.094
	Spring	8.051 ± 0.050	0.153
	Summer	8.007 ± 0.048	0.139
	Autumn	8.035 ± 0.077	0.214
NTA (μmol kg^{-1})	Winter	2326.9 ± 21.1	61.3
	Spring	2299.7 ± 6.5	16.0
	Summer	2312.1 ± 15.3	43.8
	Autumn	2327.1 ± 19.1	51.1
$NTCO_2$ (μmol kg^{-1})	Winter	2050.1 ± 38.2	115.4
	Spring	1975.8 ± 40.7	120.9
	Summer	1994.7 ± 40.9	119.8
	Autumn	2025.3 ± 62.9	179.6
pCO_2 (μatm)	Winter	408.1 ± 40.1	115.1
	Spring	372.5 ± 54.3	165.6
	Summer	420.1 ± 62.4	180.9
	Autumn	386.3 ± 79.3	218.2

In the spring and summer, the mean of TA collected at our study site was largely equal to the surface seawater TA (calculated from NTA and salinity obtained from the contours) in the SCS (Chen et al., 2006; Chou et al., 2007). But the study site value was lower than the surface seawater value in the other two seasons. Meanwhile, the mean of NTA in the Luhuitou fringing reef ecosystem, which was 2300 μmol kg^{-1} in the spring, was close to the surface seawater NTA (~2300 μmol kg^{-1}) of the western part of SCS, but in the winter, summer and autumn the study site value was significantly higher than the surface seawater value (Chen et al., 2006).

4.3. *Dynamics of DO, pH, AOU, TCO_2, $NTCO_2$, PCO_2 and Ω_{Ar} in line with the temperature trends*

DO and pH moved in line with the diurnal trends of temperature, falling to the lowest values at 6:00 am and rising to the highest between 12:00–15:00 when the temperature reached the peak of a day. pH, however, increased sharply in the mornings during the spring and autumn, and decreased steeply in the evenings during the summer. Similarly, DO climbed up quickly in the mornings during the autumn, but moderately in the mornings during the spring, and decreased to a slightly lower level in the evenings during the summer, compared with other seasons (Fig. 2e and f). Derived from DO, AOU showed completely opposite trends from DO.

Table 2
Standardized regression coefficients for each variable and significance between system parameters.

Variable	Season	Salt	Level	DO	AOU	pH	TA	NTA	TCO_2	$NTCO_2$	pCO_2	$\Omega_{Ar.}$
Temperature	Winter	0.703**	0.441*	0.791**	−0.815**	0.624**	−0.579**	−0.769**	−0.766**	−0.810**	−0.644**	0.738**
	Spring	−0.621**	−0.151***	0.885**	−0.903**	0.869**	−0.624**	−0.427*	−0.902**	−0.903**	−0.853**	0.923**
	Summer	0.406*	0.627**	0.697**	−0.727**	0.723**	−0.469*	−0.540**	−0.835**	−0.828**	−0.698**	0.813**
	Autumn	0.179***	0.272***	0.842**	−0.861**	0.849**	−0.719**	−0.537**	−0.908**	−0.934**	−0.856**	0.899**
Salt	Winter		0.696**	0.478*	−0.505*	0.565**	−0.379***	−0.815**	−0.629**	−0.784**	−0.582**	0.652**
	Spring		−0.098***	−0.726**	0.725**	−0.700**	0.727**	0.303***	0.729**	0.681**	0.701**	−0.683**
	Summer		0.641**	0.404*	−0.415*	0.319***	−0.176***	−0.899**	−0.408*	−0.617**	−0.300***	0.389***
	Autumn		0.656**	−0.180***	0.157***	−0.174***	−0.251***	−0.830**	0.051***	−0.133***	0.164***	−0.113***
Level	Winter			0.512*	−0.532**	0.695**	−0.247***	−0.556**	−0.613**	−0.684**	−0.689**	0.708**
	Spring			−0.058***	0.061***	−0.124***	0.204***	0.354***	0.169***	0.191***	0.092***	−0.151***
	Summer			0.467*	−0.490*	0.449*	−0.469*	−0.734**	−0.574**	−0.665**	−0.434*	0.516*
	Autumn			−0.143***	0.122***	−0.132***	−0.172***	−0.548**	0.034***	−0.087***	0.114***	−0.072***
AOU	Winter					−0.856**	0.632**	0.688**	0.902**	0.862**	0.861**	−0.889**
	Spring					−0.976**	0.689**	0.445*	0.972**	0.968**	0.973**	−0.981**
	Summer					−0.946**	0.343***	0.492*	0.951**	0.930**	0.942**	−0.946**
	Autumn					−0.988**	0.611**	0.245***	0.976**	0.940**	0.989**	−0.985**
pH	Winter						−0.497*	−0.638**	−0.916**	−0.890**	−0.998**	0.984**
	Spring						−0.700**	−0.477*	−0.986**	−0.985**	−0.998**	0.992**
	Summer						−0.227***	−0.361***	−0.967**	−0.918**	−0.997**	0.988**
	Autumn						−0.603**	−0.229***	−0.983**	−0.944**	−0.988**	0.995**
NTA	Winter								0.858**	0.916**	0.674**	−0.680**
	Spring								0.585**	0.597**	0.459*	−0.470*
	Summer								0.527**	0.693**	0.347***	−0.433**
	Autumn								0.383***	0.532**	0.249***	−0.279***
$NTCO_2$	Winter										0.909**	−0.917**
	Spring										0.977**	−0.988**
	Summer										0.906**	−0.949**
	Autumn										0.947**	−0.961**

* $p < 0.05$.
** $p < 0.01$.
*** $p > 0.05$.

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TCO_2 showed distinct diurnal trends during the four survey periods (Fig. 2d), increasing during the nighttime and decreasing during the daytime. Similarly, TCO_2 was normalized to a constant salinity of 35 as $NTCO_2$ ($NTCO_2 = TCO_2 \times 35/S$ (salinity in situ), which showed similar diurnal trends with TCO_2, and fluctuated more dramatically in the autumn and spring, but more steadily at a higher level in the winter. The mean of $NTCO_2$ was lowest in spring, and stood lower in summer, compared with autumn and winter. And it was obviously higher at our study site than the value in the surface seawater of SCS during the four seasons (Table 1) (Chen et al., 2006; Chou et al., 2007).

pCO_2 and Ω_{Ar} fluctuated with opposite diurnal trends during the four survey periods, with the mean values of pCO_2 always being lower (higher) in the daytime (nighttime), and the values for Ω_{Ar} being higher (lower) in daytime (nighttime). In general, both values changed relatively moderately in the winter, with a diurnal range of 115.1 μatm for pCO_2 and 0.60 for Ω_{Ar}; more dramatic changes were found in the autumn with a diurnal range of 218.2 μatm and 1.55 respectively (Fig. 2g and h; Table 1). In the winter and summer, the mean values of pCO_2 at the study site were higher than the pCO_2 in the atmosphere (~390 μatm, Tans and Keeling, 2013). The values however were 383.1 μatm and 386.3 μatm respectively in the spring and autumn, close to the pCO_2 in the atmosphere. Moreover, the minimum mean pCO_2 in the daytime occurred in the autumn with a sharper fluctuation (327.4 ± 70.7 μatm), and the maximum mean pCO_2 in the nighttime occurred in the summer with a sharper fluctuation (473.8 ± 64.6 μatm) (Table 1), but the minimum mean Ω_{Ar} occurred in the winter.

5. Discussion

This study aimed to figure out the diurnal and seasonal variations of the carbonate system on Luhuitou fringing reef, which are impacted by tides, river inflows, photosynthesis/respiration, calcification/dissolution and upwelling. In particular, we were more interested in finding how pCO_2 changed seasonally under the impacts of these factors and the status of the reef ecosystem. Like many other coastal reef ecosystems, Luhuitou fringing reef, which is being dramatically impacted by both global change and human activities, has been deteriorating. The coverage rate of live coral on the reef has declined from 80%–90% in 1960 to ~10% recently (Zhao et al., 2010). Meanwhile, large quantities of sanitary waste and agricultural wastewater discharged into the Sanya River, coupled with oxidation of organic material brought from the mangroves along the Sanya River, besides, upwelling, usually occurred over June–September in the northern of SCS (Jing et al., 2009), might impact the carbonate system greatly in the reef ecosystem The significant negative correlations between salinity and NTA, $NTCO_2$ (Table 2) indicated the extra NTA and $NTCO_2$ were brought by the freshwater, instead of the bottom seawater with higher salinity. That is probably because the southwest monsoon prevented the bottom seawater from flowing from the north to the southern survey ecosystem, with the upwelling at the adjacent northern coast having little impact on the ecosystem.

Furthermore, the high repeatability of diurnal variations of the system parameters indicated little cumulative effects of the parameters in the ecosystem during each season (Fig. 2), suggesting short residential times of the water, which was most likely due to the study site being at the mouth of the Sanya Bay. Reef waters in the site were thus continually renewed from offshore seawater of the SCS within a short time.

5.1. *Controls over diurnal variations of the system parameters: biological metabolisms and river inflows*

DO (AOU) and carbonate system parameters all showed distinct diurnal trends and strong correlations with temperature in the four seasons (Fig. 2c–h; Table 2), which was controlled by solar irradiance. This also suggested that the diurnal variations of the parameters were mainly controlled by biological activities in the Luhuitou fringing reef ecosystem. Furthermore, as indicated by the diurnal change of salinity, there were large quantities of river inputs during the summer, autumn and winter. During the winter and summer, correlations between the system parameters (excluding TA and NTA) and temperature were slightly weaker, but the correlations between the system parameters and water level were stronger (Table 2). These suggested water exchange, which brought river inflows, also substantially affected the diurnal variations of the parameters in the winter and summer. Though there were also sufficient river inflows inputted into the ecosystem in the autumn, correlations between the system parameters (excluding NTA) and water level were weaker than those in the winter and summer, which was likely due to the extra strong primary production, assimilating the extra DIC inflows in the autumn. During the autumn the values of chlorophyll and phytoplankton in Sanya Bay used to be highest (Zhou et al., 2009). Furthermore, the significant correlations between the NTA and water level (Table 2) seen in the autumn also indicated large quantities of river inflows into the survey ecosystem, but the NTA mostly should not be consumed by calcification. Daily variations of carbonate system and DO (AOU) usually fluctuate dramatically, and are commonly controlled by community metabolism in reef ecosystems dominated by coral or algae(Bates, 2002; Dai et al., 2009; Frankignoulle et al., 1996; Gattuso et al., 1997). Estuaries, however, are usually affected by the biological processes, as well as by river inputs, tide and upwelling (Borges and Frankignoulle, 1999, 2002; Millero et al., 2001).

Furthermore, during the spring, summer and autumn, correlations between DO (AOU) and pH, TCO_2 ($NTCO_2$), pCO_2, Ω_{Ar} ($p < 0.01$) were slightly stronger, while correlations between NTA and pH, TCO_2 ($NTCO_2$), pCO_2, Ω_{Ar} were slightly weaker compared with the winter (Table 2). These indicated photosynthesis/respiration was a dominant process in each season of the survey period, but calcification/dissolution plays a relatively more important role affecting the carbonate system in winter.

5.2. *Seasonal variations of biological metabolism and the related system parameters*

5.2.1. *Seasonal variations of photosynthesis and respiration*

Gross photosynthesis, indicated by the mean AOU during daytime in each survey period, was at lower level in the winter and summer (-0.35 ± 0.69 mg L^{-1}, -0.45 ± 0.35 mg L^{-1}), higher in the spring (-0.86 ± 0.75 mg L^{-1}) and sharply higher in the autumn (-1.84 ± 1.63 mg L^{-1}). Similarly, respiration, indicated by the mean AOU during nighttime in each survey period, was lower in the spring and winter (0.42 ± 0.44 mg L^{-1}, 0.57 ± 0.54 mg L^{-1}) and significantly higher in the summer and autumn (0.96 ± 0.71 mg L^{-1}, 0.93 ± 0.49 mg L^{-1}). Seasonal variations of photosynthesis and respiration in the reef ecosystem were mainly affected by the seasonal dynamics of the river inflows, temperature, and structure of benthic communities, as well as the phytoplankton community. River inflows were higher in the summer, autumn and winter, bringing lots of organic material discharged by urban activities, agriculture and the mangroves along the Sanya River. The higher river inflows and higher temperature should both have promoted respiration in the

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reef ecosystem. The higher respiration in the ecosystem during the summer and autumn was in accord with these seasonal changes in river inflows and temperature, compared to the lower respiration during the winter and spring. Temperature, however, was extremely high in the summer (the maximum temperature of 32 °C was detected near 1 m water level at noon), which probably not only promoted the respiration, but also synchronously inhibited gross photosynthesis (Barber and Behrens, 1985). These suggestions were confirmed by the higher respiration and lower gross photosynthesis during the summer. Benthic communities also showed great seasonal shifts. For example, it was observed that much macro-algae flourished in the reef ecosystem during the spring, and gradually perished in the summer (Huanghui et al., unpublished data), consistent with speculation that the gross photosynthesis in the summer was inhibited by high temperatures. Meanwhile, the concentration of chlorophyll-a was observed to change seasonally in the Sanya Bay, with an average of 2.3 and 2.1 μg L^{-1} in the winter and spring, 1.9 and 3.6 μg L^{-1} in the summer and autumn respectively (Zhou et al., 2009).

5.2.2. *Seasonal variations of calcification/dissolution*

The average diurnal range of NTA (ADR$_{NTA}$) was mainly affected by calcification/dissolution and river inputs. As the average diurnal range of salinity (ADR$_{sal}$) indicated the impact of river inputs during the four seasons, in order to eliminate the impact of river inputs, ADR$_{NTA}$ is normalized by ADR$_{sal}$ as ADR$_{NTA}$/ADR$_{sal}$, which suggests the intensity of the calcification/dissolution during each season. Therefore, the lower calcification/dissolution occurred during the spring and summer as the ADR$_{NTA}$/ADR$_{sal}$ was 95.8 and 82.1, a little increase showed in the autumn (ADR$_{NTA}$/ADR$_{sal}$=109.5), and the strongest calcification/dissolution occurred in the winter (ADR$_{NTA}$/ADR$_{sal}$=141.5). There are few reports about seasonal variation of calcification and dissolution rate of a reef ecosystem researched by means of field observations. Following full discussion, Bates assumed that the calcification rate of hard corals in Bermuda kept unchanged throughout the year that they surveyed (Bates, 2002). Other studies showed that calcification rates of reef ecosystem and colonies of coral increased with temperature or solar irradiance in temperate and subtropical zones (Carricart-Ganivet, 2007; Crossland, 1984; Dimond and Carrington, 2007; Langdon and Atkinson, 2005).

As for the calcification rate of the reef ecosystem at our study site, it turned out that the optimum season was winter and autumn, and the worse season was spring and summer. In other words, the optimum temperature for coral calcification in our region should be between 24 °C–27 °C (Table 1). Therefore, the coral in the Luhuitou reef ecosystem should experience thermal stress, as concluded by Hoegh-Guldberg et al. that the thresholds for thermal stress to coral communities is +2 °C from the optimum temperature (Hoegh-Guldberg et al., 2007). The coral bleaching observed during June–September, 2010 in the Luhuitou reef system (Huanghui et al., unpublished work) supported this view. It was reported that bulk carbonate sediments from a coral reef started dissolution when the aragonite saturation was 3.7, and the dissolution rate increased as the aragonite saturation falling (Yamamoto et al., 2011). And the thresholds for major changes to coral communities are indicated for aragonite saturation was 3.3 and pCO$_2$ was 480 ppm (Hoegh-Guldberg et al., 2007). Thus, the temperature stress, as well as the high pCO$_2$ and low aragonite saturation occurred during the nighttime, should obviously inhibit the calcification and promote the dissolution in the reef ecosystem in the summer. During the spring, it might be due to corals reducing energy supply for calcifying in the spring, when their reproduction used up large amount of the available energy (Kozlowski and Wiegert, 1986). This deduction is partly confirmed by the observation of Barnes and Crossland that the calcification rate of Acropora *acuminate* was markedly lower over September–October – the spawning season in Queensland – than the rate over June–November(Barnes and Crossland, 1980).

5.3. *The Luhuitou fringing reef ecosystem: source or sink of carbon?*

The mean pCO$_2$ in the ecosystem was supersaturated with respect to atmospheric levels in the summer and winter, but close to the atmospheric levels in the spring and autumn (Table 1). Furthermore, pCO$_2$ showed significant negative correlations with water level in the winter and summer (Table 2), indicating large CO$_2$ exports from the ecosystem to the SCS. The weaker pCO$_2$-water level correlations in the spring and autumn suggested lower CO$_2$ exchange between the ecosystem and the SCS. pCO$_2$ in the offshore seawater of the SCS was usually close to the level of the atmosphere (Dai et al., 2009), which also confirmed CO$_2$ output from the system to the SCS in the winter and summer. Therefore, impacted by river inflows, the Luhuitou fringing reef ecosystem is a source of CO$_2$ output to the SCS over the whole year. These should be mainly controlled by the photosynthesis and respiration, which were the dominant processes of metabolisms in the reef ecosystem. Accordingly, the data indicated that the mean DO was at undersaturation in the summer, led by net respiration, but during the winter, the mean pCO$_2$ indicated supersaturated with respect to the atmosphere, while the zero-mean AOU suggested that the photosynthesis and respiration were in balance in the ecosystem. This was probably due to the stronger calcification in the winter. During the spring and autumn, mean pCO$_2$ was close to the level of the atmosphere, while DO was supersaturated, caused by net primary production in the ecosystem. This indicated that the impacts of the net primary production on the system offset effects from the weaker calcification and river inflows.

5.4. *Seasonal change of the pattern of the community metabolisms in the Luhuitou fringing reef ecosystem*

When considering the seasonal variation pattern of community metabolism in reef ecosystems, ΔTA/ΔTCO$_2$ has been widely used to evaluate the proportions of calcification/dissolution and photosynthesis/respiration. The value of ΔTA/ΔTCO$_2$ could range from 0.0 to 2.0, depending on the ratios of the two processes. The higher value was seen when the calcification/dissolution was stronger, and lower value emerged when the photosynthesis/respiration was stronger (Fagan and Mackenzie, 2007; Gattuso et al., 1999; Suzuki et al., 1995; Yates et al., 2007). ΔNTA/ΔNTCO$_2$ was also used to evaluate the proportions while excluding the impact from salinity change (Bates, 2002). The survey on Luhuitou fringing reef showed the value of ΔNTA/ΔNTCO$_2$ was highest in the winter (0.51, R^2=0.84), which was close to the value of 0.54 observed by Yates and Halley (2006). Their study site was on the southern Molokai reef flat with 10% live coral cover where the calcification/dissolution was one of the dominant processes. Furthermore, the former result was consistent with stronger calcification/dissolution and weaker photosynthesis/respiration in winter. The value of ΔNTA/ΔNTCO$_2$ in the summer was at 0.26 (R^2=0.48), which was close to 0.23, the value observed by Yates et al. (2007) in Tampa Bay—a seagrass-dominant ecosystem. The results suggested the Luhuitou fringing reef ecosystem was mainly impacted by organic carbon metabolism in the summer. The values of ΔNTA/ΔNTCO$_2$ were extremely low (0.10, R^2=0.36) in the spring and 0.15 (R^2=0.30) in the autumn. The low values of ΔNTA/ΔNTCO$_2$, which had been seldom observed in reef ecosystems, were probably caused by weaker

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Table 3
Comparisons of $\Delta NTA/\Delta NTCO_2$ and diurnal range (DR) of NTA and PCO_2 in Molokai reef ecosystem, Bermuda reef ecosystem and Luhuitou fringing reef ecosystem during each season.

Season	Study site	Pattern of ecosystem	Date	Temperature (°C)	Salinity (ppt)	DR of NTA (μmol kg^{-1})	DR of pCO_2 (μatm)	$\Delta NTA/\Delta NTCO_2$	Reference
Spring	Luhuitou	Tropical estuary (10%)	11–14/04/2010	27.2 ± 0.8	33.8 ± 0.1	16.0	169.5	0.10 (N=24, R^2=0.35)	This Study
Summer	Molokai reef	Patch reef (10%)	28–29/07/2001	27.3 ± 0.9	34.4	29.5	764	0.25 (N=6, R^2=0.81)	Yates and Halley (2006)
	Luhuitou	Tropical estuary (10%)	28–31/07/2010	29.5 ± 0.6	33.6 ± 0.2	43.8	185.2	0.26 (N=24, R^2=0.48)	This Study
Autumn	Luhuitou	Tropical estuary (10%)	19–22/11/2010	26.3 ± 1.0	32.2 ± 0.2	51.1	218.2	0.15 (N=24, R^2=0.30)	This Study
Winter	Bermuda reef	Reef (30%)	03/1998	~18.5	~35.0	12	30–50	~2 (unknown)	Bates (2002)
	Molokai reef	Patch reef (10%)	15–16/02/2000	25.9 ± 1.2	35.0	96	274	0.54 (N=7, R^2=0.81)	Yates and Halley (2006)
	Luhuitou	Tropical estuary (10%)	27–30/12/2009	24.5 ± 0.5	32.9 ± 0.2	61.3	115.1	0.51 (N=24, R^2=0.84)	This Study

calcification/dissolution in these two seasons (far weaker in the spring), and with extremely higher photosynthesis/respiration. These observations indicated that the Luhuitou fringing reef ecosystem was totally algae-dominated in the spring and autumn.

Thus, the Luhuitou fringing reef ecosystem appears to seasonally shift between coral-dominated (in the winter) and algae-dominated (in the spring and autumn), with an overall tendency leaning to an annual algae-dominated ecosystem. Furthermore, processes of organic and inorganic carbon production both showed obvious seasonality changes, more obviously for the former process. Similarly, observations showed that La Saline fringing reef ecosystem at Reunion-Island also changed seasonally, and the benthic algal community displayed obvious seasonal variation in abundance and structure (Naim, 1993). Furthermore, under impacts from eutrophication brought about by rapid development in coastal regions, algae, replacing coral, were dominant on the La Saline and Luhuitou fringing reef flats.

Studies at Molokai reef, Bermuda coral reef and Florida bay showed that $\Delta NTA/\Delta NTCO_2$ was very useful in revealing the status of the ecosystems (Bates, 2002; Millero et al., 2001; Yates et al., 2007; Yates and Halley, 2006). For example, the Bermuda coral reef system was shown to be a net source of CO_2 to the overlying water during the fall-winter, suggesting calcification exerted a stronger impact on the carbonate system compared with primary production (Bates, 2002). With the processes of organic and inorganic carbon production compensating each other over May–July, the effect of the source of CO_2 to the carbonate system in the ecosystem was minimal or even zero. The dynamics of the Bermuda coral reef system were mainly led by seasonal change in the processes of organic carbon production, given the process of calcification was assumed to be constant throughout the year (Bates, 2002). But on the Luhuitou fringing reef, the strongest organic carbon production emerged in the autumn, contrasting with what was seen in the summer on the Bermuda coral reef (Bates, 2002). The difference was probably due to their different locations, with Luhuitou fringing reef located in tropical zone, and Bermuda coral reef in subtropical zone. The high temperature in the summer on the Luhuitou fringing reef might prohibit primary production. The observations showed the process of calcification in the Luhuitou fringing reef ecosystem also changed seasonally, being weakest in the spring. The value of $\Delta NTA/\Delta NTCO_2$ was lowest in the spring, which was different from the Florida bay (Table 3). This is probably because the calcifying community, which dominated the Florida bay ecosystem, was mainly made up of numerous other benthic calcifying organisms instead of coral that might spawn during the spring. There are limited observations of seasonal variation of the process of inorganic carbon production in other reef ecosystems, as well as seasonal variation of the $\Delta NTA/\Delta NTCO_2$. Given that, the reasons for the lowest calcification rate being observed in the spring on the Luhuitou fringing reef remain unclear. More studies on the seasonal variation of the processes of inorganic carbon production are needed. Furthermore, the values of $\Delta NTA/\Delta NTCO_2$ surveyed in the four seasons in the Luhuitou fringing reef ecosystem (Table 3) were lower than the values in the Bermuda coral reef, Florida bay and Molokai reef ecosystems in the corresponding season (Bates, 2002; Yates et al., 2007; Yates and Halley, 2006). The lower values indicated that the process of calcification was weak in the Luhuitou fringing reef ecosystem, which implied there was a great risk that algae would dominate the Luhuitou fringing reef ecosystem.

6. Conclusions

1) DO (AOU) and carbonate system parameters showed distinct diurnal variations, which were controlled by biological activities, mainly by photosynthesis and respiration. In the winter and summer, river inputs also exert moderate impacts on these diurnal variations.
2) TA showed obvious seasonal variation affected by river inputs. Also, pH, DO (AOU), TCO_2 showed distinct seasonal variations, which were under the influence of seasonal dynamics of benthic biological community structure, river inputs and temperature.
3) Calcification/dissolution was seen as stronger in the winter, but weaker in the spring and summer compared with the autumn. The maximum primary production occurred in the autumn, while the maximum respiration occurred in the summer and autumn.
4) Generally, the reef ecosystem was algae-dominated in the spring and autumn, leading to the ecosystem itself acting as a carbon sink over the whole year. However, river inputs exerted influence on the whole system, resulting in it actually acting as a source of CO_2 to the SCS.

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