## Role of the Jiaozhou Bay as a source/sink of CO<sub>2</sub> over a seasonal cycle

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SUMMARY: The seasonal evolution of dissolved inorganic carbon (DIC) and CO<sub>2</sub> air-sea fluxes in the Jiaozhou Bay was investigated by means of a data set from four cruises covering a seasonal cycle during 2003 and 2004. The results revealed that DIC had no obvious seasonal variation, with an average concentration of 2035 µmol kg<sup>-1</sup>C in surface water. However, the sea surface partial pressure of CO<sub>2</sub> changed with the season. pCO<sub>2</sub> was 695 µatm in July and 317 µatm in February. Using the gas exchange coefficient calculated with Wanninkhof's model, it was concluded that the Jiaozhou Bay was a source of atmospheric CO<sub>2</sub> in spring, summer, and autumn, whereas it was a sink in winter. The Jiaozhou Bay released 2.60 × 10<sup>11</sup> mmol C to the atmosphere in spring,  $6.18 \times 10^{11}$  mmol C in summer, and  $3.01 \times 10^{11}$  mmol C in autumn, whereas it absorbed  $5.32 \times 10^{10}$  mmol C from the atmosphere in winter. A total of  $1.13 \times 10^{12}$  mmol C was released to the atmosphere over one year. The behaviour as a carbon source/sink obviously varied in the different regions of the Jiaozhou Bay. In February, the inner bay was a carbon sink, while the bay mouth and the outer bay were carbon sources. In June and July, the inner and outer bay were carbon sources, but the strength was different, increasing from the inner to the outer bay. In November, the inner bay was a carbon source, but the bay mouth was a carbon sink. The outer bay was a weaker CO<sub>2</sub> source. These changes are controlled by many factors, the most important being temperature and phytoplankton. Water temperature in particular was the main factor controlling the carbon dioxide system and the behaviour of the Jiaozhou Bay as a carbon sink. Phytoplankton is another controlling factor that may play an important role in behaviour as a carbon sink in regions where the source or sink nature is weaker.

Keywords: carbon source/sink, dissolved inorganic carbon (DIC), seasonal variation, control mechanism, Jiaozhou Bay.

RESUMEN: PAPEL DE LA BAHÍA DE JIAOZHOU COMO UNA FUENTE/DEPÓSITO DE CO<sub>2</sub> DURANTE UN CICLO ESTACIONAL. – La evolución estacional del carbono inorgánico disuelto (DIC) y el intercambio de flujos de CO<sub>2</sub> aire-mar en la bahía de Jiaozhou han sido investigados a partir de datos obtenidos en 4 campañas oceanográficas que cubren un ciclo estacional entre 2003 y 2004. Los resultados muestran que el DIC no presenta una clara variación estacional con una concentración promedio de 2035 µmol kg<sup>-1</sup> C en el agua de superficie. No obstante la presión parcial de CO<sub>2</sub> en el agua superficial cambiaba con la estación. La PCO<sub>2</sub> era de 695 µatm en Julio y 317 µatm en febrero. Utilizando el coeficiente de intercambio de gases calculado con el modelo de Wanninkhof concluíamos que la bahía de Jiaozhou era una fuente de CO<sub>2</sub> a la atmósfera en primavera, verano y otoño, mientras que era un depósito de CO<sub>2</sub> en invierno. La bahía proporcionaba 2.60 × 10<sup>11</sup> mmol C a la atmósfera en primavera, 6.18 × 10<sup>11</sup> mmol C en verano, y 3.01 × 10<sup>11</sup> mmol C in otoño, mientras absorbia 5.32 × 10<sup>10</sup> mmol C desde la atmósfera en invierno. Un total de 1.13 × 10<sup>12</sup> mmol C eran liberados a la atmósfera durante un año. El comportamiento como fuente/depósito de carbono, obviamente era diferente en las distintas regiones de la bahía de Jiaozhou. En Febrero, la parte interior de la bahía era un depósito para el carbono, mientras que la desembocadura y la parte exterior actuaba como fuente de carbono. En Junio y Julio, las partes interna y externa de la bahía eran fuentes de carbono, pero la intensidad era diferente, incrementando desde la parte interior a la exterior de la bahía. En Noviembre, la parte interior de la bahía era una fuente poco importante de CO<sub>2</sub>. Estos cambios están controlados por muchos factores, siendo los mas importantes la temperatura y el fitoplancton. Especialmente, la temperatura del agua era el factor principal en el control del dióxido de carbono en el sistema y del comportamiento de la bahía de Jiaozhou como fuente

Palabras clave: fuente/depósito de carbono, carbono inorgánico disuelto, variación estacional, mecanismo de control de la bahía de Jiaozhou.

## INTRODUCTION

It has been shown that the ocean is a net sink for atmospheric carbon dioxide and can absorb 2 pg C every year (Sabine et al., 2000; Dyrssen, 2001; Miller et al., 2002; Takahashi et al., 2002). However, the role of shelf seas has not been fully understood yet. Some results indicate that shelf seas are a source of atmospheric carbon dioxide (Naqvi et al., 2005). However, other studies show that they can absorb about 0.2 to 1 pg C every year (Tsunogai et al., 1999; Liu et al., 2000; Frankignoulle and Borges, 2001; DeGrandpre et al., 2002; Chen, 2004; Thomas et al., 2004). It is currently uncertain whether shelf seas act as a net sink or source of atmospheric  $CO_2$ , because shelf seas are strongly affected by both natural and human activities. On the one hand, the gradient of partial pressure between air and seawater will be reversed with the continually increasing atmospheric CO<sub>2</sub>, so the source or sink nature may change. For example, the Weddell Sea was a relatively strong source of atmospheric CO<sub>2</sub> in pre-industrial times, but it turned into a  $CO_2$  sink in recent times because of the steadily rising atmospheric  $CO_2$  (Hoppema, 2004). On the other hand, the carbon budget of shelf seas and coastal areas has been altered dramatically by human activities. Anderson and Mackenzie (2004) modelled in detail the change of air-sea fluxes for the coastal ocean since pre-industrial times and suggested that the shallow-water ocean environment has served as a net CO<sub>2</sub> source throughout most of the past 300 years, but its role as a source has substantially decreased and the net flux is expected to be reversed at some point in time. Human activities are the main reason for this. Sabine and Machenzie (1991) estimated that the flux of nutrient from rivers to coastal seas has increased 2.5-fold due to human activities. In addition, particulate organic carbon, dissolved organic carbon and dissolved inorganic carbon have undergone an apparent increase too (Wollast and Mackenzie, 1989). Additional mass input has resulted in conflicting conclusions about whether shelf seas act as net sinks or sources of  $CO_2$ to the atmosphere (Walsh et al., 1981). For examples, the SW of the Caribbean Sea was a source of  $CO_2$  to the atmosphere throughout 2002, but the NE was a sink during winter and spring, and a source during summer and autumn (Olsen et al., 2004). Although some studies have estimated the air-sea  $CO_2$  flux of coastal seas (Borges, 2005), more data

are necessary to fully understand the coastal contribution to the marine carbon cycle.

The Jiaozhou Bay is a semi-enclosed bay situated in the western part of the Shandong Peninsula, China. The bay is surrounded by Qingdao city with an area of about 340 km<sup>2</sup> and an average water depth of about 7 m. The bay mouth is narrow, only about 2.5 km wide where the Bay is connected to the south Yellow Sea. There are more than 10 small rivers along the Jiaozhou Bay coast, the largest of which is the Dagu River with an annual average runoff of 21 m<sup>3</sup> s<sup>-1</sup>. Most of these rivers have become a repository for industrial and urban waste from Qingdao city. The water quality, biological species and abundance, and nutrient concentrations in the Jiaozhou Bay have been changing recently along with the rapid development of Qingdao city (Shen, 2001).

Research cruises covering a seasonal cycle were primarily designed to examine the carbon system variables and the mechanisms controlling the carbon exchange across the air-water interface during 2003 and 2004. In this paper, we describe the seasonal variation of DIC and the behaviour of the Jiaozhou Bay as a carbon source/sink. We also discuss the physical and biogeochemical mechanisms controlling the strength of the bay as a carbon source/sink.

## MATERIAL AND METHODS

### Sampling

In order to characterize the carbon system and its seasonal change in the Jiaozhou Bay, 22 stations were sampled on 20-21 June, 19-20 July and 19-21 November 2003, and on 21-23 February 2004 on board the kejiao II (Fig. 1). An ORION 420A+ pHmeter equipped with an ORION (8135BN) combined electrode was used to determine pH at 25°C onboard. The temperature was controlled using a refrigerated circulating water bath that regulates the temperature to  $\pm 0.1$  °C. The temperature was measured using a digital platinum resistance thermometer. The pH-meter was calibrated using a Tris (2-carboxyethyl) phosphine hydrochloride solution (pH 7.0) and a solution of Malic acid, MES and Tris (pH 10). The method has a shipboard precision of 0.002 pH units and an accuracy of 0.004 pH units. Salinity and temperature were measured with a Seabird CTD. Samples for the determination of total inorganic carbon were collected into plastic flasks from



FIG. 1. - Sampling stations in the Jiaozhou Bay

10 L Niskin bottles, and then preserved with 0.5ml 10%  $HgCl_2$  per 100 ml of sample, immediately sealed and stored in the refrigerator at a constant temperature of  $3\pm1^{\circ}C$ . All samples were brought into the base laboratory and analysed within 2 days.

#### Determination of DIC and calculation of pCO<sub>2</sub>

DIC in seawater was measured by a simple and rapid method with an airproof device designed by the authors (Fig. 2; Song *et al.*, 2004). Between 100 and 150 ml of the seawater sample was placed in a conical flask, and then 10% H<sub>3</sub>PO<sub>4</sub> was added to it. Therefore, the DIC from the sample was extracted as CO<sub>2</sub> gas by acidification and stripped by N<sub>2</sub> gas purified through two grades of NaOH solution (30%), and then CO<sub>2</sub> gas was absorbed by two grades of 0.1 mol/L NaOH solutions. Finally, the absorbed solution was titrated with a HCl standard solution of 0.01000 mol/L and the end points were detected with the indicators phenolphthalein and bromocre-



FIG. 2. – A new pre-treatment device for DIC determination in seawater.

sol green-methyl red mixture. The method was tested by analysing a primary standard of Na<sub>2</sub>CO<sub>3</sub>, which showed a satisfactory rate of recovery (about 99.8~100.2%). The analytical results were completely consistent with those of a TCO<sub>2</sub> analyser with an infrared detector. The standard deviation of replicate measurements was less than 0.3% and the accuracy was 5  $\mu$ mol<sup>-1</sup>.

pCO<sub>2</sub> can be calculated from DIC and pH, and the first and second dissociation constants of the carbonic acid,  $k_1$  and  $k_2$ .  $k_1$  and  $k_2$  were calculated according to Lueker *et al.* (2000). The estimated standard deviation of the computed pCO<sub>2</sub> values was 1.4% and the accuracy was ±6 µatm.

#### CO<sub>2</sub> fluxes

In order to determine whether the Jiaozhou Bay constitutes a net  $CO_2$  sink or source on an annual basis,  $CO_2$  air-sea fluxes had to be obtained. The flux of  $CO_2$  across the sea-air interface was estimated in June, July and November 2003 and February 2004 at each station using the equation:

$$F = ks \Delta pCO_2$$

where k is the gas transfer velocity (in cm h<sup>-1</sup>), s is the solubility of  $CO_2$  in seawater as a function of temperature and salinity taken from Weiss (1974).  $\Delta pCO_2$  is the gradient in  $CO_2$  partial pressure between the seawater and the atmosphere, in µatm. Values for  $pCO_2$  in seawater are readily calculated

mont	h	DIC µmol -1	salinity	water temperature (°C)	wind speed m s <sup>-1</sup>	Chlorophyll <i>a</i> * mg m <sup>-3</sup>	pCO <sub>2</sub> µatm	CO <sub>2</sub> flux mmol m <sup>-2</sup> d <sup>-1</sup>
2	range	1765-2465	32.37-32.97	3.87-4.63	5.1-6.8	2.0-20.0	92-595	-25.6-21.6
~	average	2044	32.71	4.10	5.9	1565	31/	-2.91
0	average	2027	32.03-32.01	15.22-19.21 17.5	4.3-5.8 5.1	1.3-0.3	452-864 640	5.55-50.6 16.9
7	range	1856-2414	29.19-31.11	20.22-22.22	4.2-5.3	1.5-6.0	500-903	7.23-28.8
	average	2042	30.60	21.20	4.6	1015	695	17.7
11	range average	1642-2318 2025	29.07-30.64 30.01	10.52-14.79 12.43	5.8-7.1 5.9	1.0-4.5	279-593 419	-8.57-22.6 5.40

TABLE 1. – Carbon dioxide system concentrations and CO<sub>2</sub> fluxes in Jiaozhou Bay surface waters

\* chlorophyll *a* data form Li C L *et al*. (2005a)

from DIC. The transfer velocity equation of Wanninkhof (1992) was used to obtain the  $CO_2$  fluxes. The wind speed at 10 m above the sea surface  $(u_{10}, \text{ in m s}^{-1})$  was used to calculate the gas transfer velocity (k), which was gathered at every station from the anemometer on top of the ship. Air  $pCO_2$ was determined using a Li-Cor non-dispersive infrared (NDIR) spectrometer (LI-6262) every day. The NDIR detectors were calibrated once a day with two CO<sub>2</sub> gas standards and an N<sub>2</sub> reference. The overall uncertainty of the pCO<sub>2</sub> measurements was less than 1% .The bow intake from which atmospheric air was pumped was installed at ~10 m above the sea surface to avoid contamination from the ship. Air pCO<sub>2</sub> measurements were corrected to 100%humidity at in situ temperature.

## **RESULTS AND DISCUSSIONS**

#### Spatial and temporal distributions of DIC

The seasonal variation of DIC was not clear, and it ranged from 2025 to 2044 µmol kg<sup>-1</sup> (Table 1). Although the horizontal distributions showed different patterns in different seasons, in general the DIC in the inner bay was higher than in the outer bay except in July (Fig. 3). The characteristics of the DIC distributions are mainly determined by the plankton growth and the hydrographic conditions in the Jiaozhou Bay (Li et al., 2004). Particularly, Haibo River, Licun River and Loushan River receive the industrial waste and sewage from Qingdao City on the northeastern shore of the Jiaozhou Bay. Dagu River receives industrial waste and sewage from urban districts on the northwestern shore, the western and northern shores are mollusc cultivation regions, and the southeastern and southwestern shores are occupied by port facilities. Therefore, seawater in the

inner bay receives a large mount of industrial and domestic sewage, which is ultimately decomposed into  $CO_2$ . Furthermore, the water exchange with the Yellow Sea is slow and the average water residence time is about 80 days in the inner bay (Zhao *et al.*, 2002). For these reasons, DIC in the inner bay was higher than that in the outer bay. The reason for DIC in the outer bay being higher than that in the inner bay in July might be related to phytoplankton blooming. In July, phytoplankton grows faster in Jiaozhou Bay and decreases from the inner to the outer bay (Wu *et al.*, 2004), so the DIC consumed in the inner bay was higher, causing the DIC in the inner bay to be lower than that in the outer bay.

#### Seasonal variability of pCO<sub>2</sub>

Strong seasonal variation in pCO<sub>2</sub> was evident, with the lowest value of 311 µatm in February and the highest value of 695 µatm in July (Fig. 4 and Table 1). The  $CO_2$  content of most waters was oversaturated with respect to the atmospheric  $CO_2$ . However, undersaturated waters were found in the southern inner bay during February and in the bay mouth during November. To discuss such a seasonal variation of  $pCO_2$ , three major processes can be invoked: (i) the river inputs; (ii) the variation in temperature; and (iii) the biological activity in the water column. Because the annual change of river input and DIC in the Jiaozhou Bay is small, the river input should not be the main reason for the seasonal variation in  $pCO_2$ . However, the average pCO<sub>2</sub> decreased from July, June and November to February. The higher the surface seawater temperature was, the higher pCO<sub>2</sub> was. Water temperature shows a strong seasonal change (Fig. 5). Temperature affects the equilibrium constants of dissolved inorganic carbon and, in particular, the solubility coefficient of CO<sub>2</sub>. The seasonal change



FIG. 3. - Horizontal distributions of sea surface DIC in the different seasons in the Jiaozhou Bay



FIG. 4. – Horizontal distributions of sea surface pCO<sub>2</sub> in the different seasons in the Jiaozhou Bay.

in  $pCO_2$  shows that the increase of solubility of  $CO_2$ , which was caused by the decrease in seawater temperature, was an important reason for the behaviour of the bay as a  $CO_2$  source/sink. Therefore, temperature plays a key role in  $pCO_2$  variation. Like DIC, phytoplankton may also influ-

ence  $pCO_2$  in its bloom season. Although salinity in the inner bay was a bit lower than in the outer bay because of river-water input in all seasons, its distribution was clearly different from DIC and  $pCO_2$ (Fig. 6), which showed that salinity has no influence on DIC and  $pCO_2$ .



FIG. 5. - Horizontal distributions of sea surface temperature in the different seasons in the Jiaozhou Bay.



FIG. 6. - Horizontal distributions of sea surface salinity in the different seasons in the Jiaozhou Bay.

## Seasonal variability of $CO_2$ fluxes

In order to assess the  $CO_2$  seasonal cycle, the monthly  $CO_2$  fluxes in June, July and November 2003 and February 2004 were calculated. The uncertainty of the fluxes was less than 15% due to the variability of pCO<sub>2</sub>. In February 2004, the average CO<sub>2</sub> flux in the Jiaozhou Bay was  $-2.91\pm0.44$  mmol C m<sup>-2</sup> d<sup>-1</sup>, which indicated that the Jiaozhou Bay absorbed atmospheric CO<sub>2</sub>. However, it was a weak sink compared with the adjacent Yellow Sea CO<sub>2</sub> flux of -14.79 mmol C m<sup>-2</sup> d<sup>-1</sup> in winter (Song, 2004). In

June 2003, the average CO<sub>2</sub> flux was  $16.9\pm2.5$  mmol C m<sup>-2</sup> d<sup>-1</sup>, which indicated that the Jiaozhou Bay released  $CO_2$  to the atmosphere. It was a strong source for atmospheric CO<sub>2</sub> and similar to the Yellow Sea in spring (Song, 2004). In July 2003, the average CO<sub>2</sub> flux was 17.7±2.6 mmol C m<sup>-2</sup> d<sup>-1</sup>, which indicated that the Jiaozhou Bay released CO<sub>2</sub> to the atmosphere at higher rates than the Yellow Sea in summer (Song, 2004). In November 2003, the CO<sub>2</sub> flux was 5.4±0.81 mmol C m<sup>-2</sup> d<sup>-1</sup>, which indicated that the Jiaozhou Bay released CO<sub>2</sub> to the atmosphere. This was consistent with the flux in the Yellow Sea in autumn (about 3 mmol C m<sup>-2</sup>d<sup>-1</sup>; Song, 2004), but weaker than in summer. Although the Jiaozhou Bay released  $CO_2$  to the atmosphere in summer and autumn and absorbed atmospheric CO<sub>2</sub> in winter, which was consistent with the Yellow Sea, the difference in strength was very large. In addition, the Jiaozhou Bay released  $CO_2$  to the atmosphere in spring, when the Yellow Sea is a CO<sub>2</sub> sink. The reason for this difference is that seawater temperature in spring increases faster than in the Yellow Sea because of the shallower waters of the Jiaozhou Bay.

Although the Jiaozhou Bay acted as a source or sink of atmospheric  $CO_2$  as a whole, spatial differences were obvious, especially in February and November (Fig. 7). The behaviour as a carbon source or sink was opposite in different regions of the Jiaozhou Bay. In February, atmospheric  $CO_2$  was absorbed in the inner bay, but  $CO_2$  was released to the atmosphere in the bay mouth and the outer bay. The distributions in June and July were similar. The whole region released  $CO_2$  to the atmosphere and the strength decreased from the inner bay to the bay mouth and to the outer bay. In November,  $CO_2$  was released to the atmosphere in the inner bay and the outer bay, and atmospheric  $CO_2$  was absorbed in the bay mouth.

# Factors determining the behaviour as a CO<sub>2</sub> source or sink

Using the CO<sub>2</sub> fluxes mentioned above and considering the surface area of the Jiaozhou Bay as 340 km<sup>2</sup>, its strength as a carbon source/sink for the 4 study months was calculated as follows: it released  $1.53 \times 10^{11}$  mmol C in June,  $1.61 \times 10^{11}$  mmol C in July and  $4.90 \times 10^{11}$  mmol C in November, and absorbed  $2.65 \times 10^{11}$  mmol C in February.

Many researchers have reported that the sea surface temperature (SST) is the primary factor that con-



FIG. 7. - Average CO2 fluxes in difference regions of the Jiaozhou Bay

trols the variability of sea surface pCO<sub>2</sub> (Bates *et al.*, 2000; Takahashi et al., 2002; Olsen et al., 2004; Wang et al., 2005). Between  $40^{\circ}$  and  $60^{\circ}$  latitude in both the northern and southern hemispheres, heat flux resulting in low temperature has long been recognised to be a major mechanism that causes the area to be a net sink of atmospheric CO<sub>2</sub> (Sarmiento and Gruber, 2002; Takahashi et al., 2002). Therefore, SST should play a key role in CO<sub>2</sub> fluxes across the seawater-air interface. Long-term observations of the hydrography, wind and salinity, which are the important factors influencing the CO<sub>2</sub> fluxes, indicate that they change little in one season, and only the temperature changes considerably (Table 2). Therefore, the variability of temperature may be a major factor in the seasonal variation of the CO<sub>2</sub> flux in the Jiaozhou Bay. The good correlation between  $CO_2$  fluxes and the measured temperature in June, July and November 2003 and February 2004 indicates that temperature was the most important factor influencing CO<sub>2</sub> flux variations in the Jiaozhou Bay (Fig. 8). Based on the statistical results, the Jiaozhou Bay was a source of atmospheric  $CO_2$  when SST was higher than 6.6°C, and a sink when it was lower. SST also affects the equilibrium constants of dissolved inorganic carbon and, in particular, the solubility coefficient of CO<sub>2</sub>. Solubility, and the first and second apparent ionisation constants of H<sub>2</sub>CO<sub>3</sub> decrease with the increase in SST, so pCO<sub>2</sub> rises. It is reported that  $pCO_2$  may rise by ~4% when temperature increases 1°C (Borges and Frankignoulle, 2002). In the



FIG. 8. - Relationship between CO2 fluxes and SST in the Jiaozhou Bay.

Season	winter				spring		summer			autumn		
Month	1	2	3	4	5	6	7	8	9	10	11	12
*wind speed (m/s)	6.1	6.0	5.5	5.8	5.3	5	4.7	4.7	5.1	5.5	6.4	6.3
**SST (°C) ***Salinity	4.9	4.3 31.9	6.0	9.6	13.9 31.55	18.2	22.0	24.7 30.80	24.5	20.0	14.8 31.63	10.0
$CO_2$ fluxes (mmol m <sup>-2</sup> d <sup>-1</sup> ) Total $CO_2$ fluxes(10 <sup>7</sup> mol C)	-2.17 -2.03	-2.66 -2.50	-0.84 -0.79	3.86 3.51	9.39 8.83	15.0 13.7	19.9 18.7	23.5 22.1	23.2 21.1	17.3 16.3	10.7 9.67	4.38 4.11

TABLE 2. - Hydrographic and meteorological parameters and CO<sub>2</sub> fluxes in the Jiaozhou Bay during one year.

\*From China bay records (The edit committee of china bay records, 1992), average wind speed between 1960 and 1979; \*\*average SST was observed at a fixed station every day by the Jiaozhou Bay Marine Ecosystem Research Station between 2002 and 2004; \*\*\*From Yang and Wu (1999)

Jiaozhou Bay, 6.6°C was the critical temperature:  $pCO_2$  in seawater was higher than atmospheric  $CO_2$  partial pressure when the temperature was higher than 6.6°C; otherwise,  $pCO_2$  was lower than atmospheric  $CO_2$  partial pressure.

To assess the annual variability of the behaviour as a carbon source/sink,  $CO_2$  fluxes were calculated from January to December using the regression equation mentioned above and average SST between 2002 and 2004 (Table 2 and Fig. 9).

The Jiaozhou Bay was a  $CO_2$  sink in winter due to the low temperature and absorbed about  $5.32 \times 10^{10}$  mmol C. In spring, it was a  $CO_2$  source and released  $2.60 \times 10^{11}$  mmol C. In summer, it was a strong source and released  $6.18 \times 10^{11}$  mmol C. In autumn, as in spring, it was a source and released  $3.01 \times 10^{11}$  mmol C. Over the year, The Jiaozhou Bay acted a net  $CO_2$ source and released  $1.13 \times 10^{12}$  mmol C.

On a global scale, some researchers have reported that ocean margins act as  $CO_2$  sinks (Boehme *et al.*, 1998; Tsunogai *et al.*, 1999; Frankignoulle and Borges, 2001; Miller *et al.*, 2002; Thomas *et al.*, 2004), while some others consider that they are  $CO_2$  sources (Borges and Frankignoulle, 2002; Cai *et al.*, 2003; Olsen *et al.*, 2004; Ito *et al.*, 2005). For example, the Caribbean Sea was a  $CO_2$  source throughout 2002, but the northern and eastern parts were a net  $CO_2$  sink of around 0.5-1 mol C m<sup>-2</sup> y<sup>-1</sup>, and the



FIG. 9. - Monthly CO<sub>2</sub> fluxes in the Jiaozhou Bay.

southwestern part was a net CO<sub>2</sub> sources of about 0.5-1 mol C m<sup>-2</sup> y<sup>-1</sup> (Olsen et al., 2004). The South Atlantic Bight is a strong CO<sub>2</sub> source with an average rate of 2.5 mol C m<sup>-2</sup> y<sup>-1</sup> (Wang et al., 2005). The northern South China Sea acts as a source with an average sea-to-air CO<sub>2</sub> flux of 7 mmol CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> in summer and 1-3 mmol CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> in spring and autumn (Zhai et al., 2005). Compared to these regions, The Jiaozhou Bay is a strong CO<sub>2</sub> source on the whole. Figure 9 shows the annual change in the behaviour of the Jiaozhou Bay as a carbon source/sink, indicating that it was a CO<sub>2</sub> sink from January to March, and acted strongest in February. Then, it was a source from April to December and especially from July to September. In one year, the Jiaozhou Bay changed from a source to a sink between December and January of the following year, and it changed from a sink to a source between March and April.

Although part of the carbonate in sediments may be released to the overlying water and participate in the pelagic carbon cycle (Li, 2005b), its influence on  $CO_2$  exchange across the air-water interface is indirect, and we do not discuss it here. We only focus on seawater temperature that influences  $CO_2$  solubility and abundance of phytoplankton that can consume  $CO_2$  in seawater.

The growth of phytoplankton will continuously consume CO<sub>2</sub> in seawater, and then CO<sub>2</sub> in atmosphere is propitious to be transported into seawater (Carrillo and Karl, 1999). The growth of phytoplankton shows a marked seasonal variability in the Jiaozhou Bay (Qian *et al.*, 1983). Long-term observations show that the peak of chlorophyll *a* frequently occurs in winter and summer, with a mean of  $4.72\pm3.15$  and  $4.33\pm2.57$  mg m<sup>-3</sup>, respectively. In spring, the mean chlorophyll *a* drops to  $2.78\pm2.43$ mg m<sup>-3</sup> and the lowest concentration is obtained in autumn, only  $1.95\pm0.80$  mg m<sup>-3</sup> (Wu *et al.*, 2004). The highest phytoplankton concentration is in February, and then it decreases gradually. From May, chlorophyll a increases again with the water temperature increase, and reaches its second peak in August, but the values are only half those in February. The seasonal changes in chlorophyll a are higher in the northern shallow area than in the southern area and the outer bay. The highest value occurs in February (monthly average concentration,  $15.52 \text{ mg m}^{-3}$ ), when it is nearly 30 times higher than in December  $(0.55 \text{ mg m}^{-3})$  in the northern area of the bay (Li et al., 2005a). The horizontal distribution patterns show that the concentration of chlorophyll a decreases from the northern to the southern inner bay, and it is higher in the inner bay than in the outer bay. The distributions of chlorophyll a and pCO<sub>2</sub> were completely consistent with each other in February. However, the strength as a carbon source/sink was not correlated with the total phytoplankton biomass. For example, the Jiaozhou Bay was a strong source in September but the phytoplankton bloom did not turn it from a source to a sink. Therefore, it is obvious that the influence of phytoplankton is limited in months when the carbon source is strong, and it does not determine the strength as a carbon source in the high temperature season. Nevertheless, phytoplankton might still play an important role in the switch from carbon source to sink in regions where the source or sink is weaker. For example, phytoplankton abundance in the inner bay is higher than that in the bay mouth. Moreover, the inner bay was a sink of atmospheric  $CO_2$  and the bay mouth was a weaker source in February.

The monthly variability as a carbon source/sink was consistent with the change in seawater temperature, which shows high annual variation in the Jiaozhou Bay, being highest in August and lowest in February. According to the clear correlation between the distribution of SST and strength as a carbon source/sink, the Jiaozhou Bay is a strong carbon source in August and a sink in February. The strength as a carbon source continually decreases and the area ultimately becomes a carbon sink as the temperature falls from the highest to the lowest level. It is clear that the influence of temperature on behaviour as a carbon source/sink is very great in the Jiaozhou Bay. Under the condition of global warming, seawater temperature will increase and the increase in the strength of seawater as a carbon source will be inevitable. The Jiaozhou Bay may therefore turn from a sink to a source even in the months with the lowest temperatures.

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