Ekoloji 27(106): 307-318 (2018)

# Air-water $CO_2$ Exchange Fluxes and Its Controlling Mechanism in Modaomen Estuary of the Pearl River, China

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**Abstract**

The seasonal and spatial characterization of dissolved $CO_2$ and its control mechanism in the Modaomen Estuary of the Pearl River (China) were determined by the four underway surveys in April, July, October 2013 and January 2014, respectively. The partial pressure of carbon dioxide ($pCO_2$) was various among different seasons, which may be attributed to the variational runoff among wet and dry seasons. The $pCO_2$ is wet season (April and July) was greatly higher than that of dry season (October and January). The runoff may be regarded as the mainly source of $CO_2$ in the estuary, while the contribution of *in situ* biologic respiration in the estuary may be limited. The outgassing fluxes of $CO_2$ in the Modaomen Estuary were approximately 30.80 mol C $m^{-2}$ $yr^{-1}$. Approximately 2% dissolved inorganic carbon (DIC) in the runoff was emitted into atmosphere during transportation processes in the estuary. The runoff was the key factor for the seasonal variation of $CO_2$ outgassing fluxes in the Modaomen Estuary.

**Keywords:** the partial pressure of $CO_2$, $CO_2$ outgassing flux, runoff, Modaomen Estuary, Pearl River

Tang W, Gao Q, Zheng X, Zhang Q, Ma Z, Zhang C, Ye L, Li Y, Zheng W (2018) Air-water $CO_2$ Exchange Fluxes and Its Controlling Mechanism in Modaomen Estuary of the Pearl River, China. Ekoloji 27(106): 307-318.

## INTRODUCTION

Estuary is known as the most sensitive area of terrestrial-ocean interaction and the important channel for the carbon exchange, which has a significant impact on global carbon cycling (Hossler and Bauer 2013). There is approximately 85% of continental substances entered in ocean through estuary. However, the fractionation and amount of these continental substances are changed greatly due to the complex hydrodynamic conditions and biochemical environment in the estuary (Liu Z et al. 2014). Therefore, identification of the estuarine impact to terrestrial-ocean transportation is of extremely important for the study of regional carbon balance response to climate change.

Many studies reported that the partial pressure of $CO_2$ ($pCO_2$) in the estuarine water was greatly higher than that of atmosphere, and suggested that $CO_2$ exchange in the water-air interfaces may be the important source for atmospheric $CO_2$ (Frankignoulle et al. 1998, Gupta et al. 2009, Hunt et al. 2014, Muduli et al. 2012, Noriega and Araujo 2014). There have been many investigations into the dissolved $CO_2$ exchange, the sources, and the mechanism in the estuary, and suggested that the transportation of carbon in the estuary were determined by various factors including biochemical processes, residence time, tidal and anthropogenic activities (Amann et al. 2012, Borges 2005, Borges et al. 2005, Cai 2011, Chen et al. 2012, 2013, Noriega et al. 2013, Reum et al. 2014). The outgassing fluxes of $CO_2$ in the estuary were approximately 0.1~0.5 Pg C $yr^{-1}$ (1 Pg = $10^{15}$ g), which were equivalent to the amount of dissolved carbon discharged from river to the ocean (Cai 2011, Chen et al. 2013). However, the $CO_2$outgassing fluxes were various among different estuaries for the complex environment, and finally resulted in the uncertainty of the global estimation from different types of estuaries (Bauer et al. 2013, Borges et al. 2005, Sarma et al. 2011). It has been reported that the $CO_2$ outgassing fluxes in of some great estuaries in China including the Changjiang (Yangtze River) Estuary (Yu et al. 2013, Zhai et al. 2007), the Lingdingyang bay of the Pearl

 Received: 21 Jun 2018 / Accepted: 19 Sep 2018

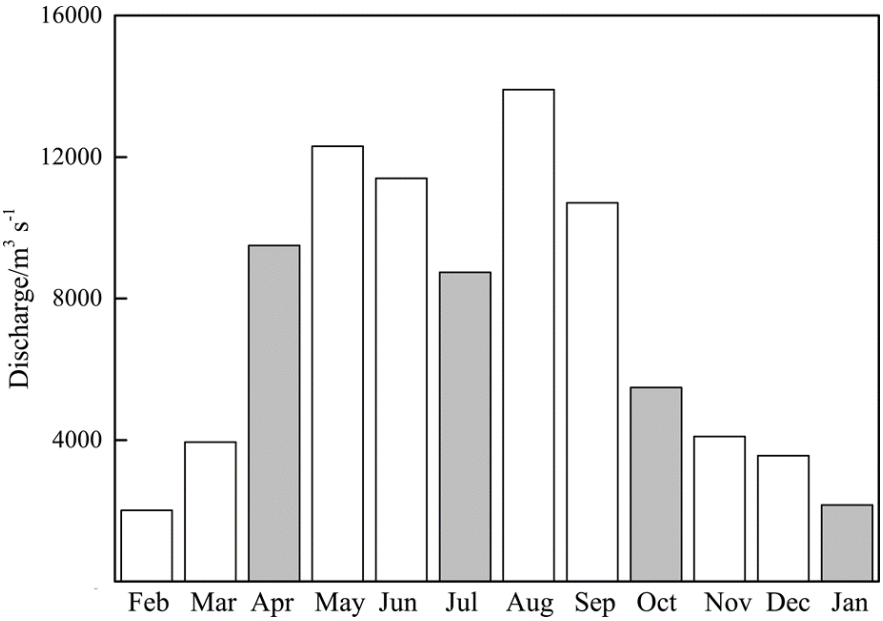


**Fig. 1.** Monthly mean discharges from February 2013 to January 2014 in the Makou hydrological stations of the Xijiang River (the grey bars represent the sampling months)

River (Guo et al. 2009) and the Jiulongjiang River Estuary (Chen et al. 2013), were lower than that of medium and small estuaries in Europe and America (Amann et al. 2015, Chen et al. 2013, Crosswell et al. 2012).

Modaomen estuary is the most important outletfor the Pearl River, which contains the typical characteristics of Asian estuary. Meanwhile, the Modaomen Estuary is effected by subtropical monsoon climate, and its runoff is obviously different among wet and dry season. The previous study was mainly focused on investigate the Lingdingyang bay, where was known as the economically developed region in Pearl River (Han et al. 2010, Liu B et al. 2014). The substance fluxes, hydrodynamic and anthropogenic activities are quite different between Lingdingyang bay and Modaomen Estuary. Much effort has been expended in studying the hydrodynamic processes, sediment environment and water mixing processes in the Modaomen Estuary. Nevertheless, the study on the carbon cycle and its biogeochemistry is extremely scarce (Jiao et al. 2009). The main objectives of this study are to: (1) investigate the spatio-temporal characterization of dissolved $CO_2$, (2) analysis the sources and the factors of dissolved $CO_2$, (3) calculate the outgassing fluxes of $CO_2$ in the Modaomen Estuary.

## MATERIALS AND METHODS

### Study Area

The Pearl River is the largest river in the South China, which consists of Xijiang River, Beijiang River, Dongjiang River and other rivers. These watersheds are entered into South China Sea through eight estuaries including Humen, Jiaomen, Hongqimen, Hengmen, Modaomen, Jitimen, Hutiaomen and Yamen. Among them, the fluxes of Modaomen are the largest, which accounts approximately 37.9% of the Xijiang River (Han et al. 2010). According to the monitoring data obtained from Makou hydrological station, the runoff of Modaomen was approximately $2.32\times10^{11}$ m$^3$ (**Fig. 1**) from February 2013 to January 2014, and was equivalent to the average annual runoff. The runoff was highest in August, which accounts 16% of the annual runoff. The average discharge in wet season (from April to September) and dry season (October to March) were 11735 m$^3$ s$^{-1}$ and 3359 m$^3$ s$^{-1}$, respectively. The runoff in the wet season accounts 75.5% of the annual runoff.

The Modaomen Estuary is the typical weak tidal harbor formed by its strong runoff. The flood tidal volume and ebb tidal volume were $160\times10^8$ m$^3$ and $1083\times10^8$ m$^3$, respectively (Jiao et al. 2009). Meanwhile, the river and sea interactionwas stronger gradually with the increasing of river dredging.

### Sampling and Analysis

In order to investigate the spatio-temporal characterization of hydro-chemical parameters in the Modaomen Estuary, four research cruises were carried out in April 2013, July 2013, October 2013 and January 2014, respectively. The study area was presented in **Fig. 2**. The surface water (0.5-1m below surface) was collected by water pump. The alkalinity (TAlk) in situ

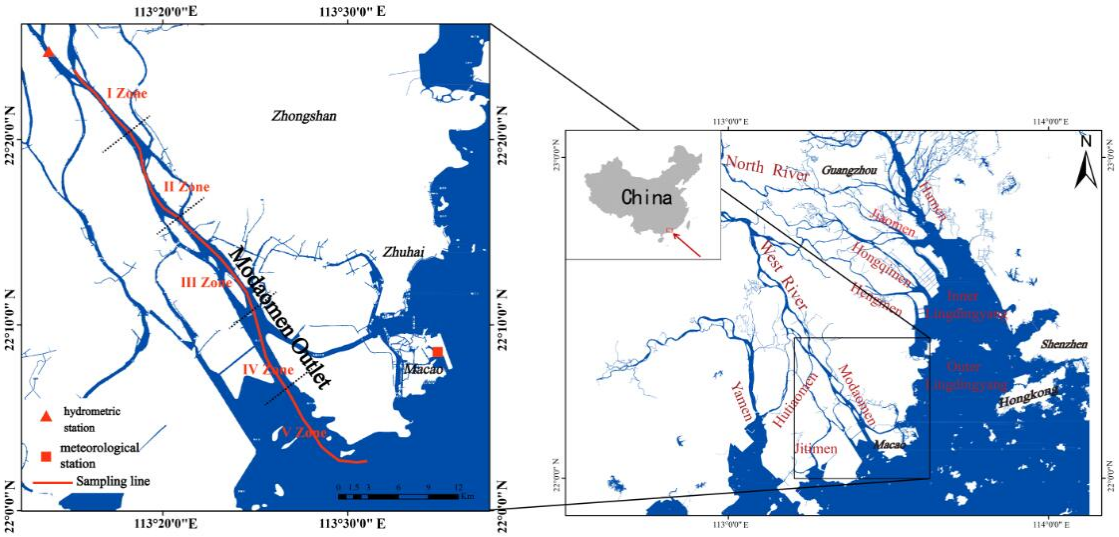


**Fig. 2.** Map of the Modaomen Estuary (the study area is divided into I~V zones and denoted by solid line) (generated by Arcgis 10.1, http://resources.arcgis.com/en/home/)

was determined by Titralab-865 automatic titrator. The temperature (T), salinity (S) and pH were measured by using Hydrolab DS5 multiparameter water analyser. The $pCO_2$ of the surface water was determined continuous by using AS-P2 $CO_2$ analysis system (produced by Apollo SciTech). The dissolved $CO_2$ in surface water was reach air-water balance in spray balancer and then dried by Nafion drying tube and anhydrone. Subsequently, the volume fraction of $CO_2$($xCO_2$) was measured by Licor 7000 $CO_2$/$H_2O$ non-dispersive infrared detector. The $CO_2$ analysis system was calibrated using standard $CO_2$ gas (National Research Center for Certified Reference Materials, China) with an uncertainty of $<$2%.

According to the temperature and salinity of the air-water balancer, the $pCO_2$ of the air-water balancer could be calculated as follows (Wanninkhof and McGillis 1999):

$$pCO_2(eq) = xCO_2 \times [P(eq) - Pw(eq)] \quad (1)$$

where $pCO_2$(eq) is the partial pressure of $CO_2$ in balancer (μatm), $xCO_2$ is the volume fraction of $CO_2$ (μmol mol$^{-1}$). $P_{(eq)}$ is the air pressure of the balancer, which was obtained by pressure probe (μatm). $P_{w(eq)}$ is the saturated vapor pressure (μatm), which was obtained by the equation of saturated vapor pressure. The $pCO_2$ of atmosphere was also measured by Licor 7000 $CO_2$/$H_2O$ non-dispersive infrared detector.

In order to avoid the effect of air escape and low water flow, the data obtained during $H_2O$ flow $<$1.0 L min$^{-1}$, vent flow$>$10 mL min$^{-1}$ and Licor flow deviated greatly from 100mL min$^{-1}$ were rejected. The effect of water temperature was neglected for the short diversion pipeline and the speedy water velocity in this study. In addition, the air $pCO_2$ was tested in four times to ensure the precision and accuracy.

### Estimation of $CO_2$ Air-Water Exchanging Fluxes

Based on double membrane diffusion theory, the $CO_2$ air-water exchanging fluxes could be obtained by the following equation (Jiang et al. 2008):

$$F = k \times \alpha \times (pCO_2^{water} - pCO_2^{air}) \quad (2)$$

where α is the solubility coefficient of $CO_2$ in special salinity condition (mmol/(m$^3$atm)), which could be calculated by Weiss formula (Wanninkhof and McGillis 1999). $pCO_2^{water}$ and $pCO_2^{air}$ represent the partial pressure of $CO_2$ in surface water and air, respectively. $k$ is the transfer velocity of $CO_2$ (cm h$^{-1}$). The $CO_2$ is released from water when the F value is negative, while the $CO_2$ is absorbed by water once the F value is positive.

The transfer velocity ($k$) was calculated by the empirical equation of regression (Chen and Borges 2009) and widely applied for estimation of $CO_2$ fluxes in global (Crosswell et al. 2012, Laruelle et al. 2010, Takahashi et al. 1993). The transfer velocity ($k$) was defined by the following equation:

$$k = (0.314u^2 - 0.436u + 3.99) \times (600/S_C)^{1/2} \quad (3)$$

where μ is the wind speed, $S_c$ is the Schmidt number, which is the ratio of kinematic viscosity coefficient and diffusion coefficient and obtained by the equation

**Table 1.** The hydro-chemical parameters of the Modaomen Estuary surface water

| | | Salinity | Temperature (℃) | pH | TAlk(μmol·kg$^{-1}$) |
|---|---|---|---|---|---|
| 2013.4 | Range | 0.11~20.58 | 22.71~25.94 | 7.18~7.93 | 1326.6~2234.8 |
| | Mean | 3.39±6.22 | 23.53±1.00 | 7.70±0.13 | 1680.6±297.7 |
| 2013.7 | Range | 0.12~14.60 | 27.95~29.69 | 7.53~7.99 | 1614.6~1761.0 |
| | Mean | 1.54±3.62 | 29.32±0.43 | 7.69±0.09 | 1686.5±39.3 |
| 2013.10 | Range | 0.11~23.25 | 25.92~27.40 | 7.55~8.42 | 1444.5~2073.6 |
| | Mean | 5.43±7.12 | 26.58±0.34 | 7.98±0.16 | 1629.4±185.8 |
| 2014.1 | Range | 0.12~28.85 | 15.53~17.04 | 7.56~8.04 | 1461.4~1993.0 |
| | Mean | 5.32±8.13 | 16.08±0.47 | 7.82±0.09 | 1592.6±156.7 |

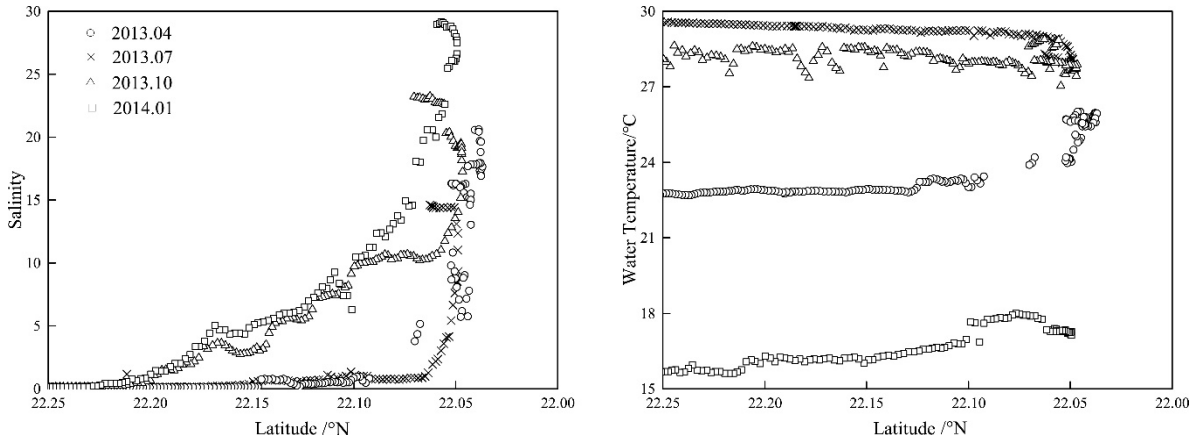


**Fig. 3.** Spatial-temporal distributions of salinity and temperature in the Modaomen Estuary

reported by Wanninkhof. The Modaomen Estuary was classified into five areas (I~V) to estimate the $CO_2$ exchanging fluxes accurately. The transfer velocity of air ($k_i$) and average $CO_2$ outgassing flux ($F_i$) of each area was calculated separately. Therefore, the total $CO_2$ outgassing fluxes of Modaomen Estuary could be calculated as (Chen and Borges 2009):

$$F_{area-average} = \frac{\sum F_i \times S_i}{\sum S_i} \quad (4)$$

where $S_i$ is the superficial area of each area (km$^2$).

## RESULTS

### The Spatial and Temporal Distribution Characterizations of Temperature and Salinity in the Estuary

The salinity in the surface water of Modaomen Estuary was listed in **Table 1** and **Fig. 3**, the salinity ranged from 0.11 to 28.85, the widely range may be attributed to the runoff and tidal. A large amount of freshwater was flowed into estuary in wet season (April and July) and controling the estuary water, resulted in the lower salinity in Modaomen Estuary. The mixing region of freshwater and seawater was located at the outlet (22.06°N). For the weak runoff and elevated tidal effect in dry season (October and January), the mixing region spread over the estuary region and the salinity was obviously higher than that of wet season. According to **Fig. 3**, the low salinity water was mainly located at 22.15°N~22.25°N, with the highest value of 5 in dry season. The seawater was primary distributed from outlet (22.06°N) to the sea, with the salinity ranged from 10 to 28. The salinity increasing sharply from 3~8 to 20 at 22.06°N~22.03°N, which may be explained by the existence of sand group around the harbor entrance.

According to **Table 1** and **Fig. 3**, the temperature of surface water in the Modaomen Estuary ranged from 15.53 to 29.69 °C, and decreased in the order of July > October > April > January. The aforementioned results suggesting that the temperature in wet season was higher than that of dry season. The widely variability of temperature at the upstream of the estuary may be attributed to the different specific heat between mainland and sea. The highest temperature of the upstream water was found in July, while the highest temperature of the downstream water was presented in October. The temperature of water increased with the flow direction in January and April, while the temperature shown an opposite tendency in July.

### The Spatial and Temporal Distribution Characterizations of pH, Talk and $pCO_2$

The distribution characterization of pH in the Modaomen Estuary was presented in **Fig. 4**. The pH in the selected water ranged from 7.19 to 8.42. The pH in the upper estuary was higher than 7.5 and has a widely variability, while the pH in the lower estuary was relatively steady. The pH in the Modaomen Estuary water was mainly influenced by mixing processes, which was consistent with that of salinity. The pH at the

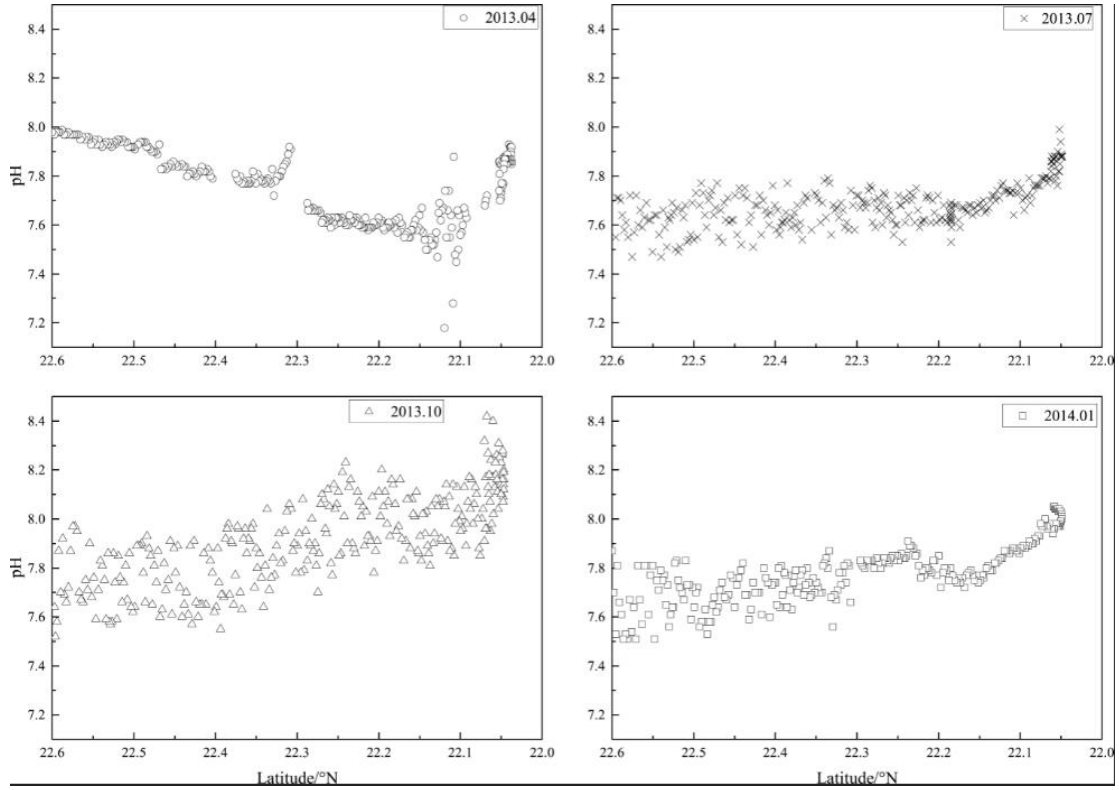


**Fig. 4.** Distribution of pH in the Modaomen Estuary

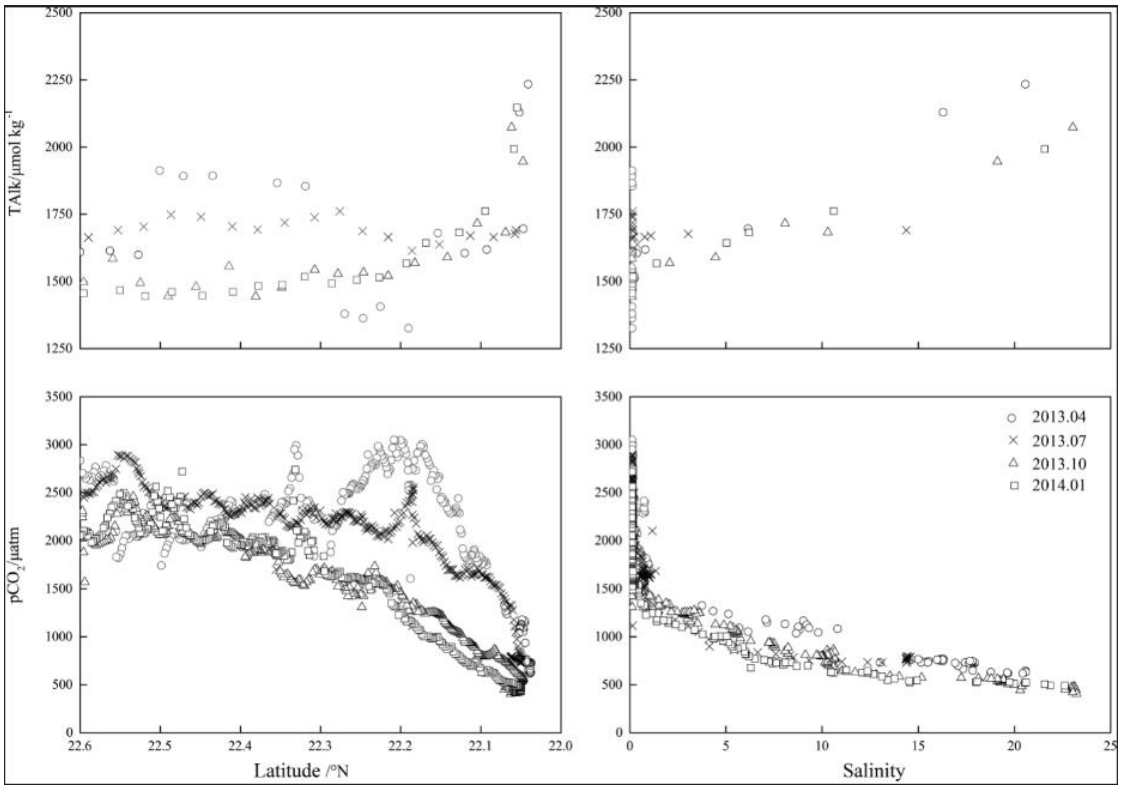


**Fig. 5.** Distribution of TAlk and $pCO_2$ in the Modaomen Estuary

outside of outlet was increased with the increasing of salinity in April and July, which may be attributed to the location of mixing region (around 22.06 °N). The pH at the inside of outlet was steady in April and July. For the weak runoff and the invasion of sea water, the pH in the whole estuary was increased gradually in October and January.

**Table 2.** The $pCO_2$ and $CO_2$ outgassing flux in the Modaomen Estuary surface water

| | | Acreage ($km^2$) | $pCO_2$ of air (μatm) | $pCO_2$ of water(μatm) | $k_{(CO2)}$/mol $L^{-1}$ $atm^{-1}$ | Air-water $CO_2$ flux (mmol C $m^{-2}$ $d^{-1}$) |
|---|---|---|---|---|---|---|
| 2013.4 | Part I | 9.87 | 415 | 2372 | 0.03592 | 140.57 |
| | Part II | 15 | 411 | 2418 | 0.03595 | 144.09 |
| | Part III | 22.17 | 417 | 2794 | 0.03605 | 170.80 |
| | Part IV | 22.39 | 427 | 2169 | 0.03576 | 124.61 |
| | Part V | 30.71 | 380 | 851 | 0.03172 | 30.73 |
| 2013.7 | Part I | 9.87 | 403 | 2299 | 0.02960 | 151.83 |
| | Part II | 15 | 400 | 2246 | 0.02968 | 147.70 |
| | Part III | 22.17 | 404 | 2185 | 0.03011 | 142.30 |
| | Part IV | 22.39 | 410 | 1732 | 0.03017 | 104.88 |
| | Part V | 30.71 | 420 | 1040 | 0.02976 | 47.66 |
| 2013.1 | Part I | 9.87 | 365 | 1877 | 0.03170 | 126.41 |
| | Part II | 15 | 364 | 1579 | 0.03132 | 101.14 |
| | Part III | 22.17 | 362 | 1459 | 0.03107 | 90.87 |
| | Part IV | 22.39 | 365 | 1019 | 0.03041 | 52.52 |
| | Part V | 30.71 | 372 | 599 | 0.02926 | 17.06 |
| 2014.1 | Part I | 9.87 | 364 | 1945 | 0.04387 | 120.87 |
| | Part II | 15 | 379 | 1816 | 0.04422 | 109.88 |
| | Part III | 22.17 | 378 | 1370 | 0.04402 | 75.42 |
| | Part IV | 22.39 | 372 | 805 | 0.04181 | 31.43 |
| | Part V | 30.71 | 371 | 502 | 0.03805 | 8.67 |

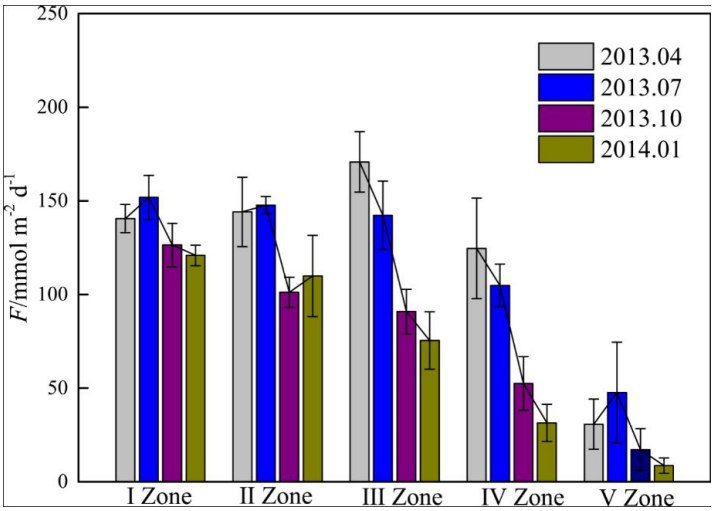


**Fig. 6.** Spatial and seasonal variability of area-averaged $CO_2$ fluxes in the Modaomen Estuary (the study area is divided into I~V zones and numbered in **Fig. 2**)

The content of TAlk in the Modanmen estuary was in the range of 1327~2235 μmol $kg^{-1}$ (**Fig. 5**). As illustrated in **Fig. 5**, the TAlk in the upper estuary was lower than that of the lower estuary. The conservative relationship between TAlk and salinity may be explained by the weak biological activity for TAlk. The widely variability of TAlk in April may be attributed to the complex sources of runoff.

The value of $pCO_2$ in the Modanmen estuary ranged from 434 to 3080 μatm, and with an annual mean value of 1449 μatm. The annual mean value of $pCO_2$ in air was approximately 389 μatm, which was lower than that in water. The $pCO_2$ in wet season was greatly higher than that in dry season. The average values of $pCO_2$ in April, July, October and January were 1906, 1680, 1120 and 1087 μatm, respectively. The elevated value of $pCO_2$ in wet season may be attributed to the strong runoff, while the lower value of $pCO_2$ in dry season was explained by the stronger mixing with seawater. The $pCO_2$ in the Modaomen Estuary decreased with the increasing of salinity, which was consistent with the results obtained from other estuaries.

### The Distribution Characteristic of $CO_2$ Outgassing Flux

The spatial and temporal distributions of $CO_2$ outgassing fluxes were presented in **Table 2** and **Fig. 6**. It could be obviously found that the seasonal difference was greatly higher than that of the spatial difference. The average $CO_2$ outgassing fluxes in April, July, October and January were 110.5 mmol C $m^{-2}$ $d^{-1}$, 106.7 mmol C $m^{-2}$ $d^{-1}$, 64.7 mmol C $m^{-2}$ $d^{-1}$ and 54.8 mmol C $m^{-2}$ $d^{-1}$, respectively. Meanwhile, the $CO_2$ outgassing fluxes were greatly different between July and October. The $CO_2$ outgassing fluxes in the upstream and midstream of the Modaomen Estuary (Part I-III) ranged from 43.86 to 49.28 mol C $m^{-2}$ $yr^{-1}$, with the highest in the Part III in April. The lowest $CO_2$ outgassing flux were 9.54 mol C $m^{-2}$ $yr^{-1}$ and found in Part V in January. The average annual $CO_2$ outgassing fluxes of the Modaomen Estuary were approximately 30.80 mol C $m^{-2}$ $yr^{-1}$.

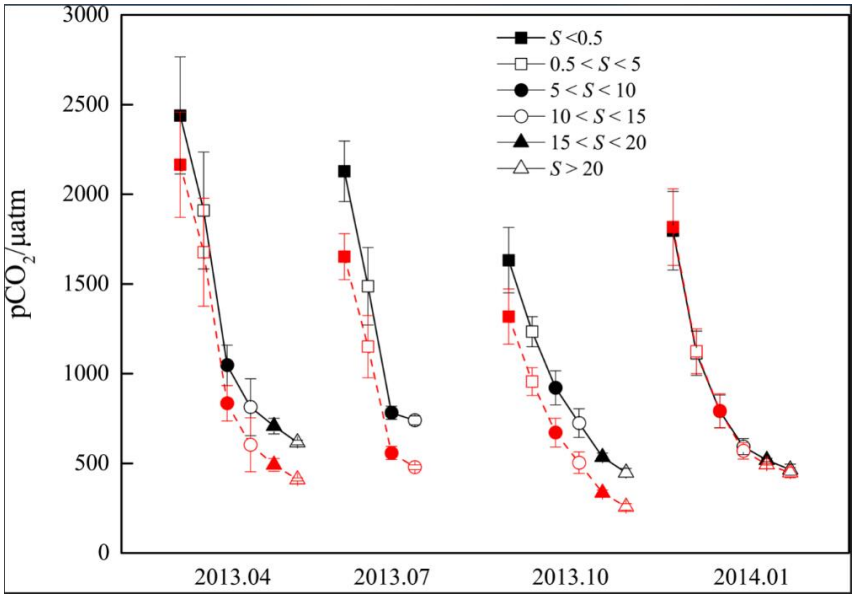


**Fig. 7.** Monthly mean values of $pCO_2$ at in situ temperature (black lines) and temperature-normalized $pCO_2$ (at 16.08°C, red lines) in April, July, October 2013 and January 2014, grouped into salinity bins

## DISCUSSION

### Effect of Temperature on The $pCO_2$

The $pCO_2$ in the estuary was not only controlled by runoff, freshwater-seawater mixing and biological processes, but also influenced by the water temperature directly (Takahashi et al. 2002). Based on the laws of thermodynamics, the $pCO_2$ increased with the increasing of temperature. In order to avoid the effect of temperature on the $pCO_2$, the temperature modified coefficient of $pCO_2$ was set as 4.23 %/°C in the ocean (Raymond et al. 2000, Takahashi et al. 2002). Nevertheless, the temperature modified coefficient was not an absolute constant under different saline conditions. According to previous studies (Weiss and Price 1980), the temperature coefficient of $pCO_2$ in the Pearl River Estuary was calculated by the equation of (0.125×S+1.875)%/°C and ranged from 2.5 to 4.0 %/°C. Therefore, the modified $pCO_2$ could be calculated as follows:

$$pCO_2@T = pCO_2 \times exp[(0.125 \times S + 1.875)(T - T_{obs})/100] \quad (5)$$

where S is the salinity, $pCO_2$@T is the modified $pCO_2$, $T_{obs}$ and T represent the observed temperature and the mean temperature in January, respectively. The mean temperature in January was 16.08 °C, and with a small deviation. Therefore, the observed $pCO_2$ in situ in other sampling seasons should be modified to investigate the effect of temperature on $pCO_2$. Once the water temperature was the single factor to control $pCO_2$, the modified $pCO_2$@16.08°C should be maintaining a constant in the same salinity condition.

The $pCO_2$@16.08°C in April, July and October decreased in the range of 6.5~38.8% (**Fig. 7**). Nevertheless, trends of the modified $pCO_2$ *vs* salinity were consistent with that of the observed $pCO_2$, suggesting that the spatial distribution of $CO_2$ in the Modaomen Estuary was not influenced by the water temperature. According to **Fig. 7**, although the modified $pCO_2$was lower than the observed $pCO_2$ insitu, the $pCO_2$@16.08°C in April under the same salinity condition was higher than that of other sampling seasons.

For the higher temperature in July and October, the $pCO_2$@16.08°Cwas greatly lower than that of the observed$pCO_2$. The modified $pCO_2$@16.08°C in July and October were similar to the $pCO_2$ in January. For example, the modified and observed $pCO_2$ in July were 1652 and 2128 μatm, respectively. It is indicating that the water temperature was an important factor for the higher $pCO_2$in July and October.

### The Sources of $CO_2$ in the Estuary

The dissolved $CO_2$ in the estuary may be derived from sea, runoff and internal process. For the decomposition of organic matter, the $CO_2$ in the runoff was generally supersaturation (Yao et al. 2007). The $pCO_2$ in Xijiang River ranged from 590 to 7100 μatm (Jiang et al. 2013). For the highly primary productivity in the sea, the $pCO_2$ in seawater was equivalent to the air $pCO_2$. The dissolved $CO_2$ sources of internal process

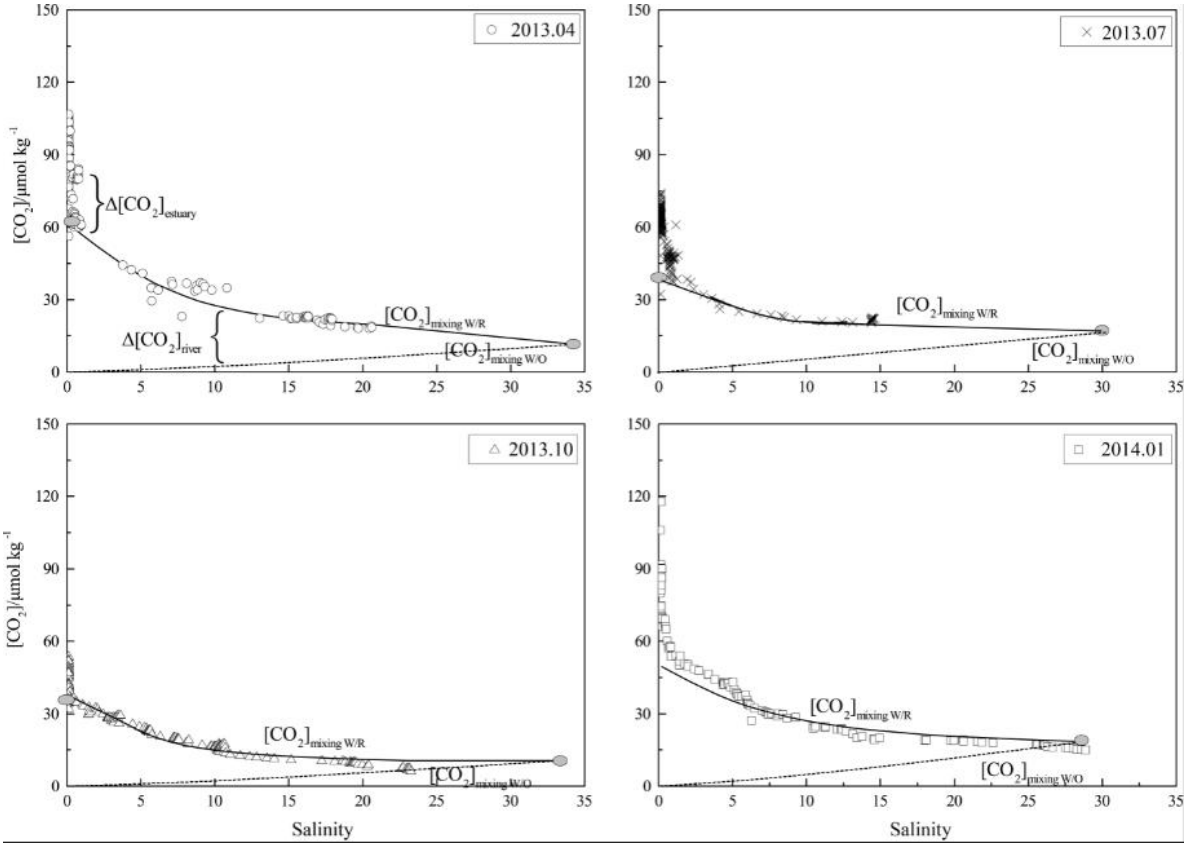


**Fig. 8.** Inputs of area averaged dissolved $CO_2$ in April, July, October 2013 and January 2014, normalized to 16.08°C, from river and estuary sources

in the estuary include the biological activities, air-water exchanging, and deposition and dissolution of carbonate minerals. The dissolved $CO_2$ ($\Delta[CO_2]_{estuary}$) contributed by internal process of the estuary could be calculated by the following equation (Chen and Borges 2009).

$$\Delta[CO_2]_{estuary} = [CO_2]_i - [CO_2]_{mixingw/R} \quad (6)$$

where $[CO_2]_i$ is the concentration of dissolved $CO_2$ in water, $[CO_2]_{mixing\ w/R}$ is the theoretical concentration of $CO_2$ in the runoff and seawater mixing.

The dissolved $CO_2$ ($\Delta[CO_2]_{river}$) contributed by runoff could be defined as Equation (7) (Chen and Borges 2009, Cai and Wang 1998):

$$\Delta[CO_2]_{river} = [CO_2]_{mixingw/R} - [CO_2]_{mixingw/O} \quad (7)$$

where $[CO_2]_{mixing\ w/0}$ is the theoretical concentration of $CO_2$ in the seawater only diluted by freshwaterthat contains nodissolved $CO_2$. For the higherTAlk and lower $pCO_2$ in the seawaterthan runoff, the dissolved $CO_2$ could is affected by both physical mixingand chemical processes. Therefore, the conservative mixing processes of $[CO_2]$ were non-linear. The $[CO_2]_{mixing\ w/R}$ and $[CO_2]_{mixing\ w/0}$ were indirectly obtained by carbonate dissociation constant reported by Cai et al (1998).

According to **Fig. 8**, the $\Delta[CO_2]_{estuary}$ ranged from -3.48 to 13.73μmol $kg^{-1}$, the $[CO2]_i$ was distributed along the runoff-seawater mixing line, suggesting that $[CO2]_i$in theestuary was mainly determined by runoff-seawater mixing processes. The contribution of internal process ($\Delta[CO_2]_{estuary}$)for the dissolved $CO_2$ in Modaomen Estuary was unconspicuous.The $\Delta[CO_2]_{river}$ was always higher than that of $\Delta[CO_2]_{estuary}$ during mixing processes, suggesting that runoff may be the mainly source for $CO_2$ in Modaomen Estuary water.

In general, the $CO_2$ from internal process of the estuary was mainly influence by both biological activities and air-water exchanging processes. For the highly content of DO (> 4.9 mg $L^{-1}$), the effects of nitrification, denitrification and sulfate reduction may be negligible (Borges et al. 2006, He et al. 2010). The $CO_2$ produced by respiratory degradation was proportional to the residence time of water in the estuary (Borges et al. 2004). It has been suggested that the respiratory may be the mainly source for $CO_2$ in the estuary when the residence time more than 20 days (Jiao et al. 2007). However, for the highly runoff in the

**Table 3.** The $CO_2$ outgassing characterizations in Modaomen Estuary and Humen Estuary of Pearl River

| | Modaomen Estuary | Humen Estuary |
|---|---|---|
| Anthropogenic activities | Small | Serious |
| Estuary type | Channel | Reactor |
| Source of fresh water | Runoff of Xijiang River | Runoff of whole Dongjiang River, and part of Xijiang River and Beijing River |
| Tidal | Weak | Strong |
| Residence time of water | 3 d | 7 d |
| pH | 7.5 in the upstream, | 4.81~6.43 in the upstream |
| Hypoxic condition | Inconspicuous | Frequent |
| $pCO_2$ of water | 434~3080 μatm | 3000~7260 μatm |
| Air-water $CO_2$ flux | 30.8 mol C $m^{-2}$ $yr^{-1}$ | 81.7 mol C $m^{-2}$ $yr^{-1}$ |
| The percentage of $CO_2$ outgassing flux to DIC output flux | 2% | 12% |
| $CO_2$ control mechanism | Runoff | Biological process |

Modaomen Estuary, the residence time was only 0.5~7 days and results in reduce of biogeochemistry of the internal estuary (Jiao et al. 2009). Jiao et al. found that the residence time of Modaomen Estuary water was extended in the dry season, but the $pCO_2$ in water was uncorrelated to the oxygenation (Jiao et al. 2009, Xiao et al. 2013). Meanwhile, Xiao et al reported that the dissolved organic matter was mainly influence by physical mixing process by sea water (Ludwig et al. 1996).

In addition, $\Delta[CO_2]_{estuary}$ decreased was negative value in the highly salinity region in October, which may be explained by the photosynthesis of aquatic organisms. The stronger tidal and light transmittance, and weak runoff and velocity of flow may promote the increase of aquatic phytoplankton.

### In Comparison the $CO_2$Outgassing Flux with Other Regions

The acreage of estuary in the lower latitudes was approximately $0.56\times10^6$ $km^2$, which accounts for 60% of the global estuaries (Dai et al. 2006). Meanwhile, more than 60% of the organic and inorganic carbon were transported into estuaries in the lower latitudes. Therefore, identification of the $CO_2$ outgassing fluxes of lower latitudes estuaries was of extremely significant for the calculation of $CO_2$ outgassing fluxes of global estuaries. The $CO_2$ outgassing fluxes in Modaomen Estuary were proportional to the change of seasons, the $CO_2$ outgassing fluxes in wet season (April and July) were 1.8 times than that of dry season (October and January). Meanwhile, the $CO_2$ outgassing fluxes in the Modaomen Estuary have a positive relation with runoff ($R^2$=0.93, $p<0.001$), suggesting that the runoff plays important role for the $CO_2$ outgassing fluxes in the Modaomen Estuary. The average wind speed and gas transfer velocity ($k$) were 4.8 m $s^{-1}$ and 7.3-11.8 cm $h^{-1}$, respectively. The $CO_2$ transfer velocity ($k$) in April was 8.6 cm $h^{-1}$, which was lower than that in July and October. Nevertheless, for the strongly runoff in April, a large amount of $CO_2$ was entered into the Modaomen Estuary and results in the highly $CO_2$ air-water exchanging fluxes. The $CO_2$outgassing fluxes in July were second only to April for the highly $CO_2$ transfer velocity ($k$). With the stronger incursion of seawater in January, the $CO_2$ outgassing fluxes were lowest.

The $CO_2$ outgassing fluxes in Modaomen Estuary were approximately 30.80 mol C $m^{-2}$ $yr^{-1}$, which were located at the middle level of global estuaries. This study was mainly focused on investigate the low salinity region of Modaomen Estuary, and the $CO_2$ outgassing fluxes were greatly higher than that of adjacent Lingdingyang bay (6.92 mol C $m^{-2}$ $yr^{-1}$) [20] and the estuaries in lower latitudes (23.9 mol C $m^{-2}$ $yr^{-1}$) (Chen et al. 2013). The $CO_2$ outgassing fluxes in the Modaomen Estuary were obviously lower when compared to Humen Estuary (the upstream of Lingdingyang bay) (81.7 mol C $m^{-2}$ $yr^{-1}$). The $CO_2$ outgassing fluxes in Modaomen Estuary were in the range of the Yangtse Riverestuary (15.5~34.2 mol C $m^{-2}$ $yr^{-1}$) (Yu et al. 2013, Zhai et al. 2007).

Although both Modaomen Estuary and Humen Estuary are located at Pearl River, the $CO_2$ outgassing mechanism were different (**Table 3**). Much effort has been expended in studying the air-water $CO_2$ outgassing flux in HumenEstuary, and suggested that the highly $pCO_2$ (> 3000 μatm) was attributed to the discharge of municipal sewage. The organic matter in municipal sewage could be decomposed by microorganism and results in low DO and pH in the Humen Estuary (Borges et al. 2006, Cai et al. 2008). However, for the weak anthropogenic activities, the $CO_2$ in Modaomen Estuary water was mainly derived from runoff and primary controlled by physical mixing processes (**Table 3**).

The study on $CO_2$ outgassing fluxes in global estuaries and beach are increasing concerns in recently years. Based on incomplete estimation, approximately 0.329~0.41 Pg DIC was entered into ocean from global rivers, nearly equivalent to the annual $CO_2$ outgassing fluxes (0.34 Pg C $yr^{-1}$) from global estuaries (Borges et al. 2005, Dai et al. 2006). In addition, the $CO_2$ outgassing fluxes in Europe estuaries (0.03~0.06 Pg C $yr^{-1}$) equivalent to the DIC fluxes of Europe rivers (0.05

Pg C $yr^{-1}$) (Frankignoulle et al. 1998). According to the amount of DIC in the runoff of Modaomen Estuary, the annual DIC output fluxes were approximately $2.07\times10^6$ t $yr^{-1}$. Therefore, 2% DIC was emitted into atmosphere during the transportation process in Modaomen Estuary, which was greatly lower than that in the Europe estuaries and the average value of global estuaries. The $CO_2$ outgassing fluxes in Yangtze River estuaries were also account 2-5% of the DIC fluxes (Zhai et al. 2007). These results may be explained by the higher DIC and runoff, and lower $CO_2$ outgassing fluxes in Pearl River and Yangtze River. Therefore, it may be hypothesized that the $CO_2$ outgassing fluxes in great river estuary were much lower than DIC output fluxes.

## CONCLUSIONS

The $pCO_2$ in the Modaomen Estuary water was controlled by runoff and seawater mixing processes. The $pCO_2$ in wet season (April and July) was greatly higher than that in dry season (October and January). The $pCO_2$ in the upstream of the Modaomen Estuary was higher than that in the downstream. The runoff was the primary $CO_2$ source for the Modanmen Estuary water. With the longer residence time and suitable temperature, the biogeochemistry in the internal estuary made important contribution for $CO_2$ in estuary in dry season. As a typical river-dominated estuary, the annual $CO_2$ outgassing fluxes in the Modaomen Estuary were approximately 30.80 mol C $m^{-2}$ $yr^{-1}$. Approximately 2% of DIC was emitted into atmosphere during transportation in the Modaomen Estuary, which was greatly lower than that in Europe and global estuaries.

## ACKNOWLEDGEMENTS

This work was financially supported by the Natural Science Foundation of Guangdong Province (2014A030311003) and the National Natural Science Foundation of China (41071054).

## AUTHOR CONTRIBUTIONS

Q.G. conceived and designed the experiments; W.T., Q.G., X.Z., Q.Z., Z.M., C.Z., L.Y., Y.L. and W.Z. performed the experiments; W.T. and X.Z. analyzed the data; Q.G. contributed reagents and analysis tools; W.T. wrote the paper.

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