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CO_2 flux and seasonal variability in a large subtropical estuarine system, the Pearl River Estuary, China

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[1] This paper presents the spatial distribution and seasonal changes of the carbonate system and CO_2 fluxes in a complex river-estuary system located in a subtropical region, the Pearl River Estuary, based on five surveys covering primarily a wet and dry seasonal cycle on two major subestuaries of the Pearl River, namely Lingdingyang and Huangmaohai. Significant spatial and seasonal variations of surface water partial pressure of CO_2 (pCO_2) were observable in these two subestuaries. While both Lingdingyang and Huangmaohai had higher pCO_2 in their upper estuaries, which quickly decreased downstream as seen in many estuarine settings elsewhere, significant differences occurred between the two subestuaries in terms of pCO_2 level, with much higher pCO_2 in the upper Lingdingyang than the upper Huangmaohai. In terms of seasonality, substantially higher pCO_2 was observed in warm and wet seasons in both upper estuaries (2100–8350 μatm in the Lingdingyang and 1040–3590 μatm in the Huangmaohai) than in cold and dry seasons (1100–7460 μatm and 560–970 μatm in the Lingdingyang and the Huangmaohai, respectively). As a consequence, CO_2 emission from the Pearl River Estuary system in summer was ~6 times of that in winter. At the same time, we observed a clear drawdown of pCO_2 in the lower estuary in both summer and winter, reaching a level of water pCO_2 which was below the atmospheric level. This seasonal and spatial contrast can also be seen in the distribution of dissolved inorganic carbon (DIC) and total alkalinity. On the basis of a seasonal and zonal distribution of pCO_2, the annual CO_2 emission from the Pearl River Estuary was estimated to be $\sim 3 \times 10^{10}$ mol C, which is equivalent to ~6% of the total DIC export flux to the South China Sea from the Pearl River system.

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1. Introduction

[2] The carbon cycle in river/estuarine systems is an important component of the global carbon budget. Export of carbon from rivers to the ocean is ~1 Gt C a^{-1} [*Degens et al.*, 1991], 40% of which is DIC (dissolved inorganic carbon) [*Degens et al.*, 1991; *Mackenzie et al.*, 2004]. Recent studies further demonstrate that direct river/estuarine efflux of CO_2 may also be substantial, even comparable to the riverine DIC export flux to the ocean. *Frankignoulle et al.* [1998] report that CO_2 emission from European estuaries is 0.03–0.06 Gt C a^{-1}, representing the same order of magnitude as the DIC flux from European rivers (0.05 Gt C a^{-1} [*Kempe et al.*, 1991]), or 5–10% of the total anthropogenic CO_2 emissions from Western Europe in 1995. *Borges et al.* [2005] further compile the available CO_2 efflux data from world estuaries, and reach an estimate of 0.34 Gt C a^{-1}, which is also comparable to the DIC input from continents to the ocean [*Degens et al.*, 1991; *Mackenzie et al.*, 2004]. It should be noted that, as correctly pointed out by *Borges et al.* [2005], the current estimate is based on a very limited data set, in particular, data from subtropical and tropical large river estuaries are scarce. It is also worth noting that the surface area of low-latitude estuaries is however overwhelming, much larger than the sum of midlatitude and high-latitude estuaries [*Borges et al.*, 2005].

[3] The Pearl River is a large river system located in the subtropical zone of Asia. This river system discharges a large amount of freshwater, nutrients and carbon into the northern South China Sea, affecting the carbon dynamics there [*Cai et al.*, 2004; *Dai et al.*, 2008b]. Prior research reveals a high partial pressure of CO_2 (pCO_2) up to 7000 μatm in the lower section of the river and in the upper Lingdingyang, one of the subestuaries of the Pearl River system [*Chen et al.*, 2008; *Dai et al.*, 2006; *Jiao et al.*, 2008; *Zhai et al.*, 2005]. The main source to maintain such a high pCO_2 in the low-salinity waters is believed to be aerobic respiration and nitrification [*Dai et al.*, 2008a, 2006; *Zhai et al.*, 2005]. However, there have not been

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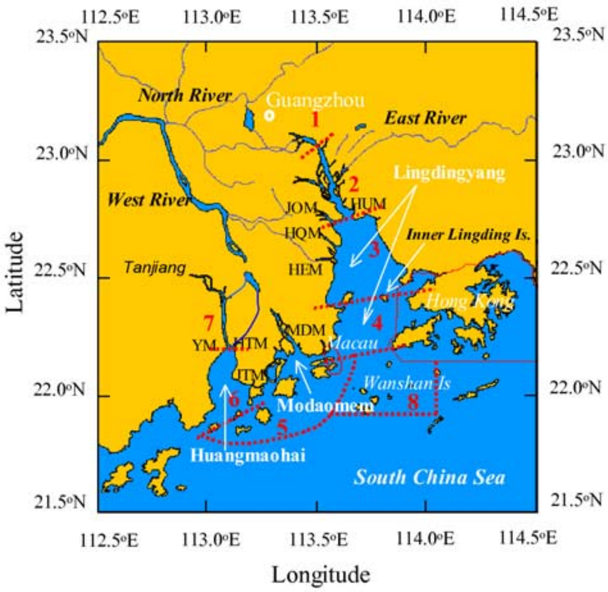

Figure 1. Map of the Pearl River Estuary. HUM, JOM, HQM, HEM, MDM, JTM, HTM, and YM denote Humen, Jiaomen, Hongqimen, Hengmen, Modaomen, Jitimen, Hutiaomen, and Yamen, respectively. Lingdingyang, Modaomen, and Huangmaohai are the three subestuaries of the Pearl River system. We divided the study area into 8 zones, numbered in red and separated with dotted lines.

thus far estimates of air-water CO_2 fluxes in this important subtropical estuarine system, in particular in the context of its relative importance to DIC export into the South China Sea. Questions also remain as to how the high pCO_2 in the upper estuary declines during the course of estuarine mixing. Furthermore, the majority of the prior studies have thus far focused on the Lingdingyang subestuary, especially the upper Lingdingyang subestuary, leaving other water areas unsampled.

[4] The Pearl River Estuary is such a complex system, which is composed of 3 subestuaries featured with different hydro-biogeochemistry (see below). The relatively well studied upper Lingdingyang subestuary is similar to European estuaries such as the Scheldt, in many ways showing the strong influence of anthropogenic activities [*Dai et al.*, 2006; *Frankignoulle et al.*, 1996]. At the same time, the other two subestuaries of the Pearl River system appear to be less impacted; rather they display characteristics of a carbonate-dominated system with high DIC and high TAlk (total alkalinity) [*Chen and He*, 1999].

[5] This study therefore sought to obtain a comprehensive understanding of the biogeochemistry of the CO_2 system of the Pearl River Estuary by extending our study area, for the first time, to almost the entire estuary system. We will present the surface water pCO_2 distribution in the estuary covering spring, summer, fall and winter. Water-air CO_2 fluxes will be determined based on the seasonal and zonal distribution of pCO_2 and further justified over a larger-scale context. Estuarine DIC and TAlk dynamics will also be discussed briefly. Emphasis will be placed on the seasonal variation in the CO_2 flux and the comparison between two of the subestuaries.

2. Materials and Methods

2.1. Study Area

[6] The Pearl River is located in a subtropical climate zone in southwestern China. It is the second largest river in China in terms of freshwater discharge, with an annual discharge of $\sim$3.26 $\times$ 10^{11} m^3, $\sim$80% of which takes place in the wet season from April to October driven by the Asian monsoon [*Zhao*, 1990].

[7] The Pearl River system has three main tributaries, namely the West River (Xijiang), the North River (Beijiang) and the East River (Dongjiang), as well as several small local rivers in the delta (Figure 1). The drainage basins of the West River and North River are rich in carbonate rocks, while the basin of the East River is dominated by weathering silicate rocks. Therefore the bicarbonate (HCO_3^-) content in the West and North Rivers is much higher than that in the East River [*Chen and He*, 1999]. All runoff from these tributaries discharges into the South China Sea via eight major outlets (the Humen, Jiaomen, Hongqimen, Hengmen, Modaomen, Jitimen, Hutiaomen and Yamen) through three subestuaries: the Lingdingyang, Modaomen and Huangmaohai (Figure 1).

[8] Both Lingdingyang and Huangmaohai are funnel-shaped subestuaries. The Modaomen subestuary is an arc-like siltation zone with its apex at the Modaomen and Jitimen outlets between Lingdingyang and Huangmaohai (Figure 1). The Lingdingyang subestuary mainly collects the discharge from the East, North Rivers, and some branches of the West River through the 4 eastern outlets (the Humen, Jiaomen, Hongqimen and Hengmen). The Modaomen subestuary receives most of the freshwater of the West River through the Modaomen and Jitimen outlets. The Huangmaohai subestuary collects the discharge from two branches of the West River and a local river (the Tanjiang) through the Hutiaomen and Yamen outlets.

[9] In terms of surface area, the Lingdingyang and Huangmaohai subestuaries are the largest, with a surface area of $\sim$1400 km^2 for the Lingdingyang and 560 km^2 for the Huangmaohai (Figure 1). The Lingdingyang subestuary is a heavily perturbed area and surrounded by several metropolis such as Guangzhou, Shenzhen and Hong Kong. These metropolis have populations of several to >10 million and annual sewage discharge of $\sim$700–1000 million tons [*Bu and Ye*, 2007]. In contrast, the Huangmaohai and Modaomen subestuaries are surrounded by relatively less populated cities such as Jiangmen and Zhuhai (locations not shown). Populations of these two cities are 4 and 1.5 million and the sewage discharges are 150 and 120 million tons, respectively [*Bu and Ye*, 2007].

[10] This study focuses on Lingdingyang and Huangmaohai. The Modaomen subestuary was only partially covered, primarily in the coastal water off Modaomen Outlet because the water near the Modaomen Outlet is too shallow (1–2 m) to be accessible by research boats.

[11] For the convenience of CO_2 flux estimation and discussion, we divided the study area into 8 zones according to the pCO_2 level and the geometry of the estuary (Figure 1). These 8 zones are (1) the Guangzhou section, the channel

flowing through the city of Guangzhou; (2) the Huangpu Channel, from Guangzhou to Humen Outlet; (3) Inner Lingdingyang, from Humen Outlet to Inner Lingding Island; (4) Outer Lingdingyang, from Inner Lingding Island to the waters near Macau and Hong Kong; (5) the coastal region between Lingdingyang and Huangmaohai; (6) Huangmaohai; (7) Yamen and Hutiaomen upstream; (8) the outer estuary around Wanshan Islands (outer estuary hereafter, north of 21.8°N and west of 114°E) (Figure 1). Zones 1, 2, 3, and 4 belong to the Lingdingyang subestuary, and zones 6 and 7 belong to the Huangmaohai subestuary. Zone 5 includes the coastal waters off the Modaomen subestuary.

2.2. Sampling and Analysis

[12] In 5–11 November 2002, 12–16 February 2004, 18–25 January 2005, 1–8 August 2005 and 21–27 April 2007, five survey cruises were conducted. The November 2002 and February 2004 cruises were on board R/V *Yanping II* and January 2005, August 2005 and April 2007 cruises were on the boat *Yue-Dongguan-Yu 00589*. These five cruises covered spring, summer, fall and winter. February 2004 and January 2005 were in the cold and dry season (winter) and August 2005 was in the warm and wet season (summer), while April 2007 (spring) and November 2002 (fall) were transitional seasons.

[13] Underway pumping was performed for continuous measurements of surface water pCO_2, dissolved oxygen (DO), temperature and salinity as previously described by *Zhai et al.* [2005] and *Dai et al.* [2006]. Discrete DO samples were taken from the side vent of the pumping system and analyzed with the Winkler method for calibration. Data processing of pCO_2 was after *Zhai et al.* [2005]. For the purpose of air-sea CO_2 flux estimation, meteorological parameters were measured continuously with a series of shipboard sensors.

[14] In January 2005 and August 2005, besides the pCO_2 and DO measurements, discrete sampling was also conducted for DIC and TAlk. The analytical methods for DIC and TAlk are described by *Wang and Cai* [2004]. Each has a precision of ±2 μmol kg^{-1}. Certified reference materials from A. G. Dickson of Scripps Institution of Oceanography were used for calibration. DO saturation (%) was calculated from the observed DO and the DO saturation level calculated based upon the algorithm of *Benson and Krause* [1984].

[15] Bulk oxygen consumption incubations were conducted at the upper estuary of the Lingdingyang subestuary (~40 km upstream of the Humen Outlet) in April 2007, August 2005 and January 2005 after *Dai et al.* [2006] and *Zhai et al.* [2007].

2.3. Estimation of CO_2 Fluxes and Calculations of Conservative pCO_2 and Excess CO_2

[16] CO_2 fluxes ($F(CO_2)$) were estimated based on equation (1).

$$F(CO_2) = k(CO_2) \times K_H \times \Delta pCO_2 \quad (1)$$

where $k(CO_2)$ is the gas transfer velocity of CO_2, K_H is the solubility of CO_2 calculated after *Weiss* [1974], and ΔpCO_2 is the pCO_2 difference between surface water and the atmosphere. A positive value means net flux from water to air.

[17] Since direct measurements of gas transfer velocities are not available in the Pearl River Estuary, empirical formulae of gas transfer velocity as a function of wind speed were adopted. We thus used the *Wanninkhof* [1992] parameterization (equation (2)) to estimate the flux.

$$k(CO_2)(W92) = \left(0.31 \times U_{10}^2\right) \times (Sc/660)^{(-0.5)} \quad (2)$$

[18] U_{10} is the wind speed at 10 m above the sea surface and Sc is the Schmidt number calculated from temperature [*Wanninkhof*, 1992]. It should be pointed out that the gas transfer velocity in the inner estuaries is believed to be site specific [*Borges et al.*, 2004a].

[19] The expected conservative pCO_2 was calculated from the conservatively mixed DIC and TAlk with the CO2SYS program (Version 14) [*Lewis and Wallace*, 1998]. The dissolution constants of carbonic acid are from *Cai and Wang* [1998]. The CO_2 solubility coefficient is from *Weiss* [1974], and the sulfate dissociation constant is from *Dickson* [1990]. The PO_4^{3-} and SiO_2 data are Dai et al. (unpublished data).

[20] Excess CO_2 (ECO_2, also as CO_2^*) is the dissolved CO_2 in the water that can escape to the atmosphere [*Richey et al.*, 1988; *Zhai et al.*, 2005],

$$\text{Excess}\,CO_2 = [CO_2] - [CO_2]_{equ.} = K_H \times \Delta pCO_2 \quad (3)$$

In which, $[CO_2]$ and $[CO_2]_{equ.}$ are the concentrations of dissolved CO_2 in the water and that at equilibrium with the atmosphere.

3. Results

3.1. Hydrological Settings

[21] Freshwater discharge from the Pearl River system is high in summer and low in winter. The spatial distribution of salinity within the estuary is largely reflective of such a river discharge pattern.

[22] In August 2005 in the Lingdingyang subestuary, salinity at the Humen Outlet was very low (~0–3). Average salinity was ~6 in the Inner Lingdingyang and 17 in the Outer Lingdingyang. In the Huangmaohai subestuary, salinity was ~0 at the Yamen and Hutiaomen outlets and 15 in the Huangmaohai. Average salinity was 21 in the outer estuary (Figure 2b, left and Table 1).

[23] In contrast, in winter (February 2004 and January 2005), estuarine mixing moved upstream and salinity at the Humen Outlet of the Lingdingyang subestuary was ~18. Average salinity was ~20 in the Inner Lingdingyang and ~30 in the Outer Lingdingyang, which was much higher than that in summer. In the Huangmaohai subestuary, salinity was ~10 at the Yamen and Hutiaomen outlets and ~24 in Huangmaohai. Average salinity was 34 in the outer estuary (Figures 2d and 2e, left and Table 1).

[24] In the transitional season (April 2007), salinity at the Humen Outlet was ~2, slightly higher than that in summer but much lower than in winter. The salinity distribution pattern in the Inner Lingdingyang and Outer Lingdingyang was between that in summer and winter (Figure 2a, left and Table 1). Surface salinity in November 2002 was similar but

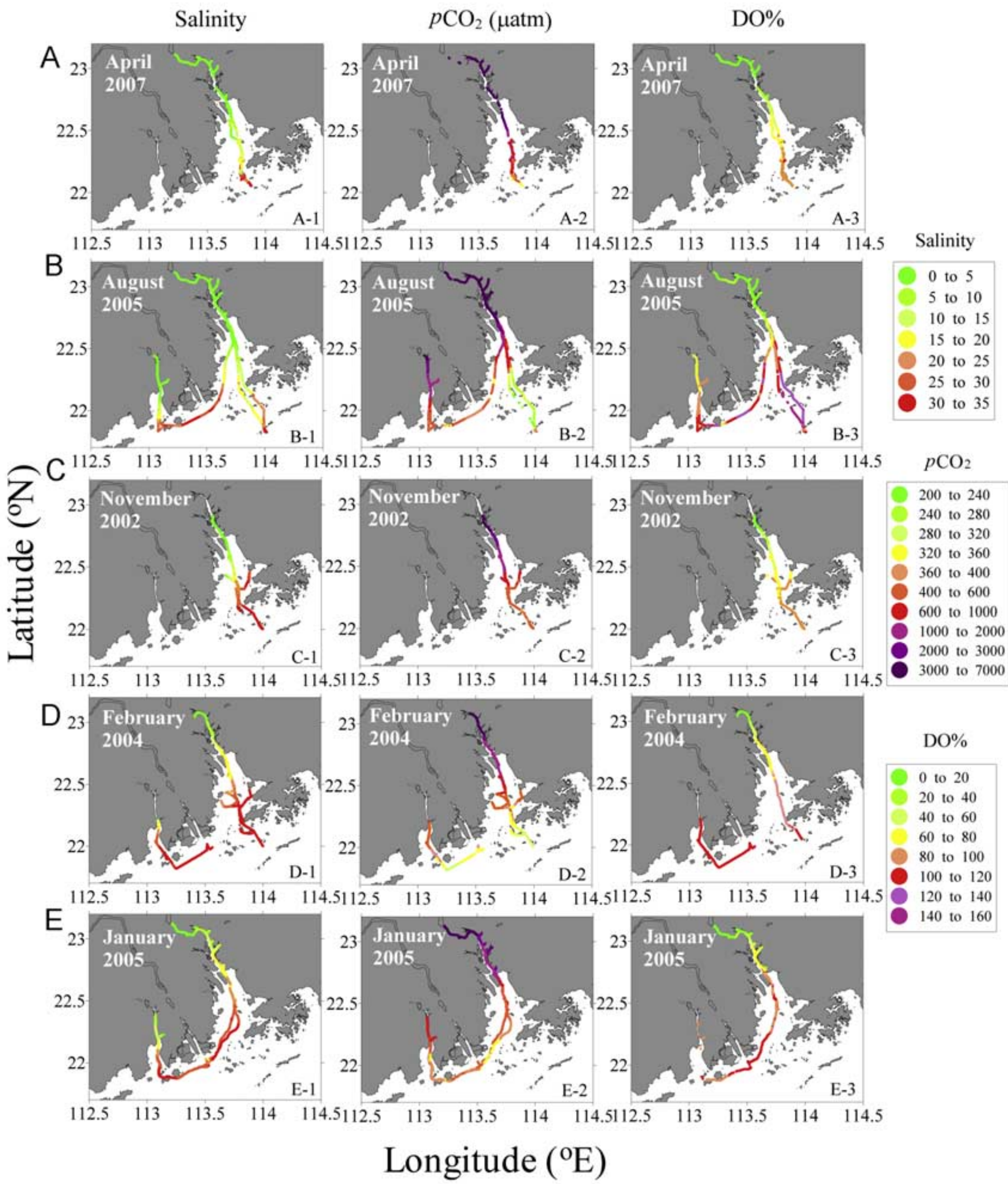

Figure 2. Spatial distribution of salinity, pCO_2 and DO saturation (%) in the Pearl River Estuary in (a) April 2007, (b) August 2005, (c) November 2002, (d) February 2004, and (e) January 2005. The pCO_2 and DO data in the upstream Humen of the Lingdingyang subestuary in February 2004 were cited from *Dai et al.* [2006].

slightly higher than that in April 2007 (Figure 2c, left and Table 1).

[25] Average surface water temperature in April 2007, August 2005, November 2002, February 2004 and January 2005 was 23.9, 30.4, 22.4, 15.2 and 16.3°C. In general, the temperature in summer was ~15°C higher than that in winter.

3.2. Spatial and Seasonal Variations of pCO_2, DO, and CO_2 Fluxes

3.2.1. Spatial and Seasonal Variations in pCO_2 and DO

[26] The general pattern of pCO_2 was that it was higher at the upper estuaries in both Lingdingyang and Huangmaohai and decreased downstream. The upper Lingdingyang had much higher pCO_2 than the upper Huangmaohai. At the same time, pCO_2 in summer was higher than that in winter (Figures 2a–2e, middle).

[27] In the Lingdingyang subestuary, the Guangzhou section (zone 1) had very high pCO_2 (3900–8364 μatm), similar to the level reported by *Dai et al.* [2006]. pCO_2 in the Huangpu Channel (zone 2) was higher in spring and summer (2096–7633 μatm) than fall and winter (1123–6775 μatm). pCO_2 decreased in the Inner Lingdingyang (zone 3) to 322–4600 μatm in summer and 362–1764 μatm in winter. pCO_2 in the Outer Lingdingyang (zone 4) was

Table 1. Surface Water pCO_2 and CO_2 Flux in the Pearl River Estuary

			Area[a]	Salinity				pCO_2 (μatm)				CO_2 Flux[b] ($mmol\ m^{-2}\ d^{-1}$)				CO_2 Emission[c] ($10^6\ mol\ d^{-1}$)	
Season	Survey	Zone	(km^2)	Average	SD	Maximum	Minimum	Average	SD	Maximum	Minimum	Average	SD	Maximum	Minimum	Average	SD
Spring	Apr 2007	1	35	0.2	0.0	0.3	0.2	7366	364	8364	6465	112.41	5.74	128.25	97.94	3.9	0.2
		2	72	1.4	1.5	4.8	0.1	6309	751	7274	4079	346.27	44.96	403.85	214.93	25.0	3.3
		3	582	12.5	5.8	26.0	2.4	1798	1317	6009	613	79.35	75.67	322.53	12.22	46.2	44.1
		4	699	22.3	6.2	31.3	9.2	570	215	1463	358	12.17	15.63	63.55	−2.38	8.5	10.9
		5	1012	-	-	-	-	-	-	-	-	-	-	-	-	-	-
		6	552	-	-	-	-	-	-	-	-	-	-	-	-	-	-
		7	11	-	-	-	-	-	-	-	-	-	-	-	-	-	-
		8	1400	31.2	2.5	33.1	22.0	368	39	517	332	−1.22	4.53	16.25	−5.35	−1.7	6.3
Summer	Aug 2005	1	35	0.1	0.0	0.2	0.1	5299	641	6638	3900	347.23	219.88	801.35	145.17	12.1	7.7
		2	72	0.6	0.7	3.0	0.1	5348	982	7633	2096	342.21	206.38	2293.58	16.69	24.7	14.9
		3	582	5.6	3.1	15.3	0.6	1184	821	4600	322	108.23	96.24	398.54	−2.78	63.0	56.0
		4	699	16.7	4.1	26.2	11.1	356	71	501	256	5.27	15.74	45.39	−12.39	3.7	11.0
		5	1012	29.5	2.5	33.5	23.6	418	61	668	341	10.77	11.22	54.88	−3.67	10.9	11.4
		6	552	14.8	9.8	30.4	0.2	649	301	1526	378	60.01	84.36	304.97	−0.14	33.1	46.6
		7	11	0.1	0.1	0.9	0.1	2200	808	3589	1042	249.57	127.36	515.91	48.84	2.7	1.4
		8	1400	20.8	5.9	32.8	12.7	254	59	372	168	−13.30	6.81	1.50	−25.82	−18.6	9.5
Fall	Nov 2002	1	35	-	-	-	-	-	-	-	-	-	-	-	-	-	-
		2	72	1.0	1.0	4.1	0.1	3772	1196	5487	1366	99.60	52.09	252.86	23.46	7.2	3.8
		3	582	12.0	6.7	25.8	1.4	1205	592	2919	533	24.88	30.24	123.39	1.39	14.5	17.6
		4	699	29.8	2.8	32.0	19.4	484	98	773	409	15.37	10.52	52.12	5.94	10.7	7.4
		5	1012	-	-	-	-	-	-	-	-	-	-	-	-	-	-
		6	552	-	-	-	-	-	-	-	-	-	-	-	-	-	-
		7	11	-	-	-	-	-	-	-	-	-	-	-	-	-	-
		8	1400	32.4	1.1	33.0	28.6	411	19	471	392	10.11	7.00	51.32	2.56	14.2	9.8
Winter	Feb 2004	1	35	2.4	0.9	4.1	0.8	6677	533	7465	5329	66.62	76.61	273.46	0.02	2.3	2.7
		2	72	9.0	3.8	17.1	3.4	3239	1315	6091	1238	47.69	44.44	228.50	0.06	3.4	3.2
		3	582	17.0	3.4	27.4	9.4	1168	372	1764	516	37.92	44.27	178.49	0.13	22.1	25.8
		4	699	29.9	3.5	33.9	20.4	428	60	604	314	1.33	4.09	18.90	−9.96	0.9	2.9
		5	1012	33.2	0.7	33.8	30.5	331	24	384	289	−11.36	3.58	−5.02	−22.72	−11.5	3.6
		6	552	25.8	5.6	32.6	11.6	426	65	627	298	−0.14	3.82	7.53	−22.24	−0.1	2.1
		7	11	-	-	-	-	-	-	-	-	-	-	-	-	-	-
		8	1400	33.9	0.2	34.2	33.1	320	10	354	305	−5.07	4.49	−0.42	−17.59	−7.1	6.3
	Jan 2005	1	35	2.0	1.6	6.3	0.7	5174	381	6101	3915	337.85	241.63	907.71	35.10	11.8	8.4
		2	72	11.6	3.7	18.7	4.1	2538	1387	6775	1123	120.34	64.75	289.08	9.67	8.7	4.7
		3	582	21.3	5.3	30.3	11.6	773	324	1641	362	22.60	23.23	79.21	−3.04	13.2	13.5
		4	699	29.7	1.5	32.3	27.8	405	35	458	347	−1.09	0.92	0.12	−4.05	−0.8	0.6
		5	1012	27.7	3.3	32.8	17.4	396	35	514	333	−0.37	3.02	9.97	−10.47	−0.4	3.1
		6	552	23.9	6.2	31.2	10.8	436	90	669	316	6.15	16.07	75.44	−8.25	3.4	8.9
		7	11	8.9	2.8	13.7	3.5	763	84	965	567	66.83	47.60	177.61	9.82	0.7	0.5
		8	1400	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Winter																	
Lingdingyang					-	-		-	-	-	-	22.22	11.20	-	-	-	-
Huangmaohai					-	-		-	-	-	-	4.24	8.15	-	-	-	-
Entire estuary					-	-		-	-	-	-	4.63	3.95	-	-	-	-

Table 1. (continued)

Season	Survey	Zone	Area[a] (km^2)	Salinity				pCO_2 (μatm)				CO_2 Flux[b] ($mmol\ m^{-2}\ d^{-1}$)				CO_2 Emission[c] ($10^6\ mol\ d^{-1}$)	
				Average	SD	Maximum	Minimum	Average	SD	Maximum	Minimum	Average	SD	Maximum	Minimum	Average	SD
Summer																	
	Lingdingyang			-	-	-	-	-	-	-	-	74.61	42.88	-	-	-	-
	Huangmaohai			-	-	-	-	-	-	-	-	63.68	82.77	-	-	-	-
	Entire estuary			-	-	-	-	-	-	-	-	30.18	17.65	-	-	-	-

[a]The surface area of zone 1 was calculated based on the average length and width of the Pearl River flowing through Guangzhou recorded in Guangzhou Record (Natural Geology Record) (http://www.gzsdfz.org.cn). The area of other zones was calculated based on the Navy Map of the Pearl River Estuary (1:150000) (2002 edition). Zone 5 only includes the waters shallower than 10 m (those with water depth > 10 m are included in zone 8). The Yamen upstream only includes the part south of 22.25°N, and the Hutiaomen upstream only includes the part south of 22.23°N.

[b]Annual average CO_2 flux ($mol\ C\ m^{-2}\ a^{-1}$) is 6.92 ± 2.63.

[c]Annual CO_2 emission ($10^{10}\ mol\ C\ a^{-1}$) is 3.02 ± 1.15.

256–501 μatm and 314–604 μatm in summer and winter, respectively.

[28] In the Huangmaohai subestuary, pCO_2 in both zones 7 and 6 were lower than that of zones 1–3 of the Lingdingyang subestuary. pCO_2 in upstream of the Yamen and Hutiaomen Outlets (zone 7) was 1042–3589 μatm in summer, which was higher than that in winter (567–965 μatm). pCO_2 in the Huangmaohai (zone 6) was also higher in summer (378–1526 μatm) than in winter (298–669 μatm) (Table 1).

[29] pCO_2 in the outer estuary (zone 8) was lower than the atmospheric level in both summer (168–372 μatm) and winter (305–354 μatm), while it was higher than the atmospheric pCO_2 during fall and nearly in equilibrium with the atmosphere in spring.

[30] Zonal average pCO_2 values in the eight zones are summarized in Table 1 and further presented in Figure 3. Average pCO_2 was highest in the Guangzhou section (zone 1). It was 7366 μatm in spring, 5299 μatm in summer and 5174 (January 2005) to 6677 (February 2004) μatm in winter. pCO_2 in the Huangpu Channel (zone 2) was 6309 μatm in spring and 5348 μatm in summer, but lower during fall (3772 μatm) and winter (3239 μatm in February 2004 and 2538 μatm in January 2005). Average pCO_2 in the Inner Lingdingyang (zone 3) was 1798 μatm during spring, 1184 μatm in summer, 1205 μatm in fall, and 773 μatm (January 2005) to 1168 μatm (February 2004) in winter. In the Outer Lingdingyang (zone 4), average pCO_2 was 570 μatm in spring, 484 μatm in fall, 405 μatm (January 2005) to 428 μatm (February 2004) in winter and much lower in summer (356 μatm). Average pCO_2 in the outer estuary (zone 8) was higher during spring (368 μatm) and fall (411 μatm) than that of summer (254 μatm) and winter (356 μatm).

[31] The Huangmaohai subestuary (zones 6 and 7) and the coastal waters between Lingdingyang and Huangmaohai (zone 5) were surveyed only in summer and winter. In Huangmaohai (zone 6), average pCO_2 was 649 μatm in summer and 426 μatm (February 2004) to 436 μatm (January 2005) in winter. Upstream of the Yamen and Hutiaomen Outlets (zone 7), average pCO_2 was 2200 μatm atm in summer and 763 μatm in winter. Average pCO_2 in zone 5 was 418 μatm in summer and 331 μatm (February 2004) to 396 μatm (January 2005) in winter.

[32] The distribution pattern of DO saturation (%) generally mirrored that of pCO_2 (Figures 2a–2e, right). In the Lingdingyang subestuary, the upstream of the Humen Outlet had low DO saturation in all seasons (0–60% in fall and winter and 0–40% in spring and summer). During spring and fall, DO was undersaturated in most of the estuary. In contrast, in summer, DO saturation in the outer estuary (zone 8) was up to >150%, where pCO_2 was as low as 170 μatm.

[33] As seen above, pCO_2 in the upper Lingdingyang subestuary was significantly higher than that in the upper Huangmaohai. For example, in August 2005, average pCO_2 at the Huangpu Channel (zone 2) of the Lingdingyang subestuary was 5348 μatm, which was more than twice the 2200 μatm in upstream of the Yamen and Hutiaomen Outlets (zone 7) of the Huangmaohai subestuary. This might be due to the stronger respiration and nitrification rates in

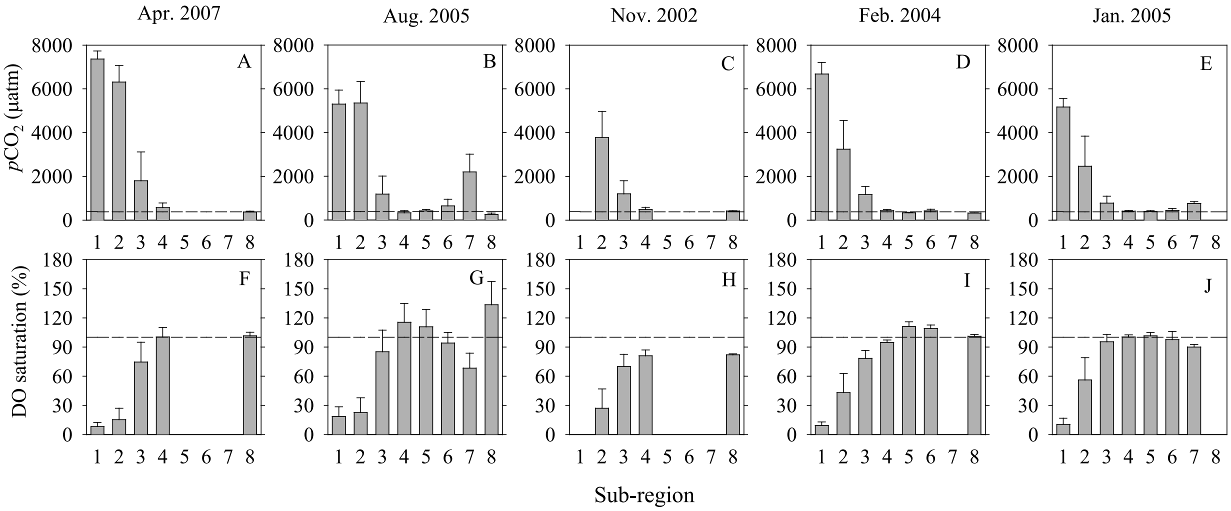

Figure 3. Zonal average of surface water (a–e) pCO_2 and (f–j) DO saturation in the Pearl River Estuary in April 2007, August 2005, November 2002, February 2004, and January 2005. The horizontal dashed lines are the atmospheric pCO_2 or DO 100% saturation. Data in the upstream Humen of the Lingdingyang subestuary in February 2004 were cited from *Dai et al.* [2006].

the upper Lingdingyang than the upper Huangmaohai subestuary [*Dai et al.*, 2008a].

[34] The upper Lingdingyang subestuary was similar to the case of the upper Scheldt Estuary ~10 years ago, where strong aerobic respiration and nitrification dominated the levels of DO and pCO_2 [*Frankignoulle et al.*, 1996]. In the upper Lingdingyang subestuary, aerobic respiration and nitrification are the major processes maintaining the high pCO_2 and low DO levels [*Dai et al.*, 2008a, 2006; *Zhai et al.*, 2005]. In contrast, in the upper Huangmaohai subestuary, net aerobic respiration dominates the CO_2 production and hence the pCO_2 level, since the nitrification rate was too low to be detected [*Dai et al.*, 2008a]. DO at the upper Huangmaohai was higher than 80% (compared with 0–40% in the upper Lingdingyang), therefore the respiration rate in the upper Huangmaohai should be much lower than that in the upper Lingdingyang.

3.2.2. Seasonal Variation in CO_2 Flux and Annual CO_2 Emission

[35] Assuming that the average CO_2 flux of February 2004 and January 2005 was representative of winter, CO_2 flux from the Lingdingyang subestuary was 22.22 mmol C m^{-2} d^{-1}, which is ~5 times the 4.24 mmol C m^{-2} d^{-1} for the Huangmaohai subestuary. The average CO_2 flux from the entire Pearl River Estuary was 4.63 mmol C m^{-2} d^{-1} in winter.

[36] Similarly, assuming August 2005 represented summer, CO_2 flux from the Lingdingyang subestuary was 74.61 mmol C m^{-2} d^{-1}, which was slightly higher than that from the Huangmaohai subestuary (63.68 mmol C m^{-2} d^{-1}). The smaller difference in CO_2 flux between the Lingdingyang and Huangmaohai subestuaries in summer compared with that in winter was due mainly to the lower CO_2 flux from the Outer Lingdingyang in summer, which is the largest zone in the Lingdingyang subestuary. The average CO_2 flux from the entire Pearl River Estuary was 30.18 mmol C m^{-2} d^{-1} in summer, which was ~6 times that in winter.

[37] We did not survey the Modaomen subestuary, but a value for pCO_2 (~2400 μatm) calculated from TAlk and pH near the Modaomen Outlet in September 2006 is available [*Jiao et al.*, 2008]. This value is similar to that in the Yamen and Hutiaomen Outlets of the Huangmaohai subestuary in August 2005 (~2200 μatm). In addition, the Modaomen and Huangmaohai subestuaries have an almost common source of freshwater (the West River). We thus assumed that the CO_2 flux per unit area of the Modaomen subestuary was similar to that of the Huangmaohai subestuary. Therefore the CO_2 emission from the Modaomen subestuary could be estimated as $0.19 \pm 0.23 \times 10^{10}$ mol C a^{-1} (150 km^2).

[38] Since our surveys covered a complete seasonal cycle, it was possible to estimate the annual average CO_2 flux from the entire Pearl River Estuary. In November 2002, we did not survey the Guangzhou section, and so we assumed that the CO_2 flux from this zone in November 2002 was similar to the average of February 2004 and January 2005. In addition, we surveyed the Huangmaohai subestuary and the coastal area between Lingdingyang and Huangmaohai only in August 2005, February 2004 and January 2005, and so we used August 2005 to represent the wet season from April to September and the average of February 2004 and January 2005 to represent the dry season from October to March. The annual average CO_2 flux from the entire Pearl River Estuary was 6.92 (±2.63) mol C m^{-2} a^{-1}. The annual CO_2 emission from the Pearl River Estuary was 3.02 (±1.15) $\times$ 10^{10} mol C a^{-1}, accounting for ~6% of the DIC flux from the Pearl River system to the South China Sea (478 $\times$ 10^9 mol C a^{-1} [*Guo et al.*, 2008]). The estimated CO_2 flux from the Modaomen subestuary was ~4% of the CO_2 emission from the entire Pearl River Estuary calculated above, and therefore the absence of the CO_2 flux data from the Modaomen subestuary had little influence on the results of this study.

[39] In estuaries, gas transfer velocity is influenced by tidal current, bottom stress and fetch, etc., besides wind speed, and is thus suggested to be site specific [*Borges et al.*, 2004a, 2004b; *Raymond and Cole*, 2001; *Zappa et al.*, 2003, 2007]. The Pearl River Estuary is microtidal [*Zhao*, 1990], and wind speed in the Pearl River Estuary is usually

<10 m s^{-1}. Under these conditions, it is expected that if we use the *Borges et al.* [2004b] model, we would obtain a much higher gas transfer velocity for the Pearl River Estuary as compared to using other models [*Carini et al.*, 1996; *Clark et al.*, 1995; *Cole and Caraco*, 1998; *Kremer et al.*, 2003; *Marino and Howarth*, 1993; *Nightingale et al.*, 2000; *Sweeney et al.*, 2007]. Consequently, by using the *Borges et al.* [2004b] model, the calculated CO_2 flux is ~twice that of *Wanninkhof* [1992] in the upper estuary and up to 1.4 times of that *Wanninkhof* [1992] in the lower estuaries.

3.3. Distributions of DIC and TAlk

3.3.1. Summertime Scenario

[40] In the Lingdingyang subestuary, the freshwater endmember had low DIC and TAlk values (Figure 4a), which was the result of dilution by the low-carbonate East River. DIC and TAlk increased abruptly with salinity at S < 5. At S > 5, TAlk remained almost conservative, while DIC had a significant apparent removal at salinities 10–25. In this area, the measured pCO_2 (200–340 μatm) was much lower than the expected conservative pCO_2 (400–550 μatm) and DO saturation was up to 120–170% (Figure 4b). DIC removal, together with low pCO_2 and high DO saturation in this area indicated net biological uptake of DIC.

[41] In contrast, in the Huangmaohai subestuary, both DIC and TAlk showed conservative distributions (Figure 4c), suggesting that mixing was the dominant process. DO was almost constant at 80–100% and the observed pCO_2 was in reasonable agreement with the calculated conservative pCO_2 (Figure 4d).

[42] Net community production (NCP) is the difference between the gross primary production (GPP) and the community respiration (R) [*Gattuso et al.*, 1998], which is the net DIC uptake rate through organic carbon production. NCP can be estimated by the difference of effective DIC based on the mixing curve and the standard estuarine mixing model [*Boyle et al.*, 1974; *Kaul and Froelich*, 1984; *Officer*, 1979]. The effective DIC in the Lingdingyang and outer estuary was 1628 μmol kg^{-1} (C_1* in Figure 4a), while it was 984 μmol kg^{-1} in the DIC depleted zone (C_2^* in Figure 4a). Since the water discharge of the Pearl River system in August 2005 was 8600 m^3 s^{-1}, the DIC input flux from the river into the DIC depleted area (zones 4 and 8) and the export flux out of the area were 12.1 × 10^8 and 7.3 × 10^8 mol C d^{-1}, respectively. Therefore the DIC removal was 4.8 × 10^8 mol C d^{-1}. Knowing the surface area of the DIC depleted waters (2100 km^2), the NCP rate (NCP rate = DIC removal/surface area) was estimated to be 0.23 mol C m^{-2} d^{-1} or 2.73 g C m^{-2} d^{-1}.

3.3.2. Wintertime Scenario

[43] In the Lingdingyang subestuary, the freshwater endmember had very high DIC and TAlk values (>3000 μmol kg^{-1}) and they decreased with salinity at S < 10 (Figure 4e). The apparent drop of DIC and TAlk at S < 18 was mainly the result of the complicated mixing in the Humen upstream and was demonstrated in detail by *Guo et al.* [2008]. Further downstream in the Lingdingyang (S > 18), both DIC and TAlk were almost conservative. Observed pCO_2 was consistent with the expected conservative values and DO saturation was 80–100% (Figure 4f).

[44] In the Huangmaohai subestuary, both DIC and TAlk had a depletion of 0–50 μmol kg^{-1} (Figure 4g) at salinities of 15–25, the reason for which is yet not clear. However, the overall distribution of DIC was almost conservative compared to the case of the Outer Lingdingyang and the outer estuary in August 2005 (up to 280 μmol kg^{-1} of DIC removal). pCO_2 had a minor drawdown and DO saturation was 90–110% at a salinity zone of 15–25 (Figure 4h).

[45] There was no DIC removal in the Outer Lingdingyang (zone 4) in January 2005. We did not survey the outer estuary (zone 8) in this cruise, but we observed a DIC removal of ~45 μmol kg^{-1} during the February 2004 cruise (Dai. et al., unpublished data), where pCO_2 was 305–355 μatm (Figures 2d and 3). Using a mixed layer depth of 5 m and water travel time of 5 days, the NCP rate was estimated to be 46 mmol m^{-2} d^{-1} (0.55 g C m^{-2} d^{-1}).

4. Discussion

4.1. Controlling Factors of Seasonal Variations in pCO_2 and CO_2 Fluxes

[46] Significant seasonal variation in pCO_2 and hence CO_2 flux between warm seasons and wintertime was observed in the Pearl River Estuary. In this section, we will discuss the possible controlling factors. As water from the upper estuary is the source of freshwater with high pCO_2 for the midestuary, we will deal with the upper estuary and midestuary separately. The lower estuary will also be addressed briefly.

4.1.1. Upper Estuary (Zones 2 and 7)

[47] Water from upstream of the Humen Outlet is the freshwater source for the Lingdingyang. High pCO_2 in this area is the result of high rates of oxygen consumption processes (aerobic respiration and nitrification) [*Dai et al.*, 2008a, 2006; *Zhai et al.*, 2005].

[48] Bulk oxygen consumption rates measured onboard at the Huangpu Channel (~40 km upstream of the Humen Outlet) showed that the oxygen consumption rate was 51, 55 and 15 mmol O_2 m^{-3} d^{-1} in April 2007, August 2005 and January 2005. Taking an average depth of the Huangpu Channel as 6.64 m (Guangzhou Record, http://www.gzsdfz.org.cn), the O_2 consumption rate could be translated into 340, 370 and 100 mmol O_2 m^{-2} d^{-1} during April 2007, August 2005 and January 2005. The observed CO_2 flux from this area in the three seasons was 346, 342 and 120 mmol C m^{-2} d^{-1} based on the formula of *Wanninkhof* [1992] (Table 2). Therefore in general, the CO_2 flux had a similar seasonal pattern with that of the bulk oxygen consumption rate, which indicated that the rates of the oxygen consuming processes may dominate the CO_2 flux in this area.

[49] *Xu et al.* [2005] and *Chen et al.* [2008] report oversaturated concentrations of N_2O (by-product of nitrification and intermediate production of denitrification) in the waters of the Pearl River Estuary, especially at the upper Lingdingyang. Although no denitrification rate in waters has been reported for the Pearl River Estuary, denitrification cannot be excluded as a possible process that contributed to the high CO_2 flux. Furthermore, denitrification which occurs in the sediment [*Xu et al.*, 2005] might be transferred to the surface water as the water column was vertically well mixed in this area. In addition, benthic sulfate reduction may also contribute to the CO_2 production in coastal regions [*Smith and Hollibaugh*, 1997]. However, these processes

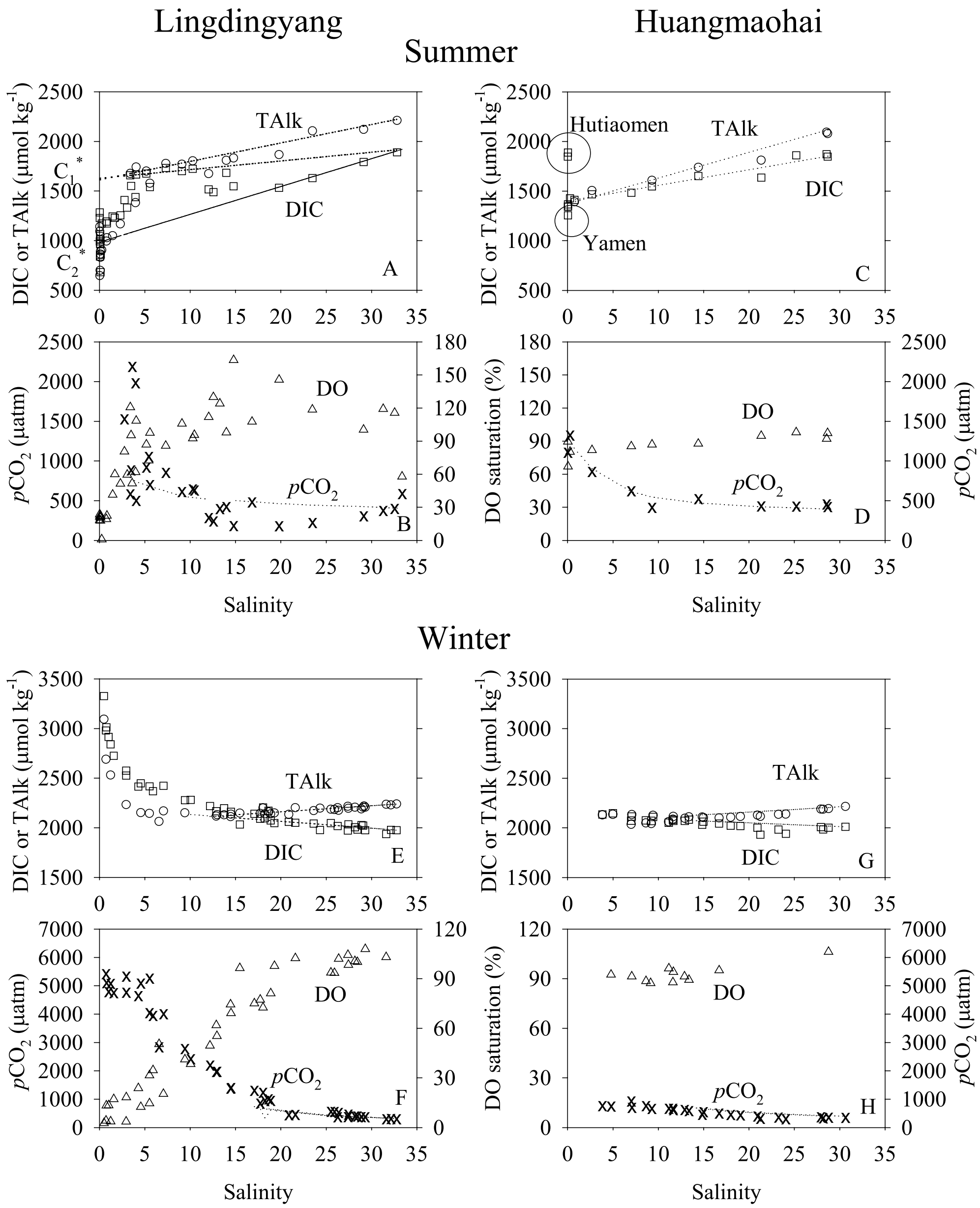

Figure 4. Distributions of (a, c, e, and g) DIC and TAlk and (b, d, f, and h) pCO_2 and DO% in the Lingdingyang and Huangmaohai subestuaries in summer (August 2005) and winter (January 2005). The outer estuary is included in the Lingdingyang subestuary in August 2005 (Figures 4a and 4b). The dotted lines in all the plots denote conservative mixing lines, which are for downstream of the Humen and Yamen/Hutiaomen Outlets. In Figure 4a, the solid line is the tangent line in the DIC depleted zone; C_1^* and C_2^* are the effective DIC of the entire Lingdingyang/outer estuary and the DIC depleted area, respectively. In Figures 4b, 4d, 4f, and 4h, the cross denotes the observed pCO_2, and the dotted curves represent the expected conservative pCO_2. The values of DIC and TAlk in the upper Huangmaohai were calculated based on the DIC and TAlk values upstream of the Yamen and Hutiaomen Outlets and the freshwater discharge through the two outlets. DIC in the freshwater at the Hutiaomen Outlet was significantly higher than that in the Yamen Outlet (Figure 4c), which is due to the fact that Hutiaomen is the outlet of a branch of the HCO_3^- rich West River [*Chen and He*, 1999]. DIC and TAlk data in the Lingdingyang subestuary in January 2005 are cited from *Guo et al.* [2008].

might not be as important as aerobic respiration and nitrification and they were hard to quantify in this study.

[50] In addition, stronger mixing with seawater might also contribute to the lower pCO_2 in winter. The surface salinity at the Humen Outlets was ~18 in winter, compared with 0–4 in other seasons (Table 1, the maximum salinity of zone 2), indicating that seawater intrusion was much stronger in winter than in other seasons. Therefore the lower pCO_2 in winter at the Huangpu Channel was partially resulted from the dilution by seawater with lower pCO_2. CO_2 system

Table 2. Bulk O_2 Consumption Rate and CO_2 Flux in the Upper Estuary and Freshwater Discharge, ECO_2 Load to, and CO_2 Emission From the Midestuary

	Upper Estuary (Huangpu Channel)			Midestuary (Inner Lingdingyang)						
		CO_2 Flux ($mmol\ m^{-2}\ d^{-1}$)			ECO_2 ($\mu mol\ kg^{-1}$)		ECO_2 Load ($10^6\ mol\ d^{-1}$)		CO_2 Emission ($10^6\ mol\ d^{-1}$)	
Season	O_2 Consumption Rate ($mmol\ m^{-2}\ d^{-1}$)	Average	SD	Water Discharge[a] ($m^3\ s^{-1}$)	Average	SD	Average	SD	Average	SD
Spring	340	346	45	2100	209	28	38.0	5.1	46.2	44.1
Summer	370	342	206	4600	140	32	55.7	12.7	63.0	56.0
Fall	-	100	52	2820	116	55	28.2	13.4	14.5	17.6
Winter	100	120[b]	65	1250	108[c]	41	11.6	4.5	17.6[c]	14.6

[a]The water discharge to Lingdingyang was estimated from monthly average discharge of the rivers in the surveyed month, and data came from the Department of Hydrology of China (http://sqqx.hydroinfo.gov.cn). The freshwater discharging into the Lingdingyang accounts for ~53% of the Pearl River system [*Zhao*, 1990].
[b]January 2005 when the bulk oxygen consumption incubation was conducted.
[c]Average of February 2004 and January 2005.

calculation showed that mixing between fresher water with pCO_2 of 5800 μatm (S = 1, DIC = 3300 $\mu mol\ kg^{-1}$, TAlk = 3050 $\mu mol\ kg^{-1}$) and seawater with pCO_2 of 380 μatm (S = 34, DIC = 2000 $\mu mol\ kg^{-1}$, TAlk = 2220 $\mu mol\ kg^{-1}$) produced water with pCO_2 of ~1840 μatm at salinity 18 (dissociation constants from *Cai and Wang* [1998], temperature at 16°C). This number was reasonably consistent with the observed pCO_2 values in the vicinity of the Humen Outlet in winter (Table 1). In other seasons, drawdown of pCO_2 due to mixing with seawater was negligible since salinity in this section was not significantly different from 0 (~0 in summer and <4 in spring and fall).

[51] Water from upstream of the Yamen and Hutiaomen Outlets (zone 7) is the freshwater source of the Huangmaohai. The observed zonal average pCO_2 in zone 7 was 2200 in summer and 760 μatm in winter. Temperature in summer was ~15°C higher than that in winter, therefore the temperature effect could increase pCO_2 by ~460 μatm to 1220 μatm (from 760 μatm) in summer [*Takahashi et al.*, 2002]. But it was still 1000 μatm lower than the observed pCO_2 in summer. In this section, excess CO_2 and oxygen depletion was linearly correlated (slope = 0.72, R^2 = 0.95) in summer. Therefore, aerobic respiration was the dominant process that produced CO_2 and consumed DO, since the observed nitrification rate was very low [*Dai et al.*, 2008a]. Although no bulk O_2 consumption incubation was conducted in this area, it would be reasonable to speculate that the respiration rate in winter would be much lower than that in summer because of the much lower temperature, and hence lower bacterial activities.

4.1.2. Midestuaries (Zones 3 and 6)

[52] Both Inner Lingdingyang (zone 3) and Huangmaohai (zone 6) are located in midestuaries. Higher pCO_2 and CO_2 flux in these two zones in summer may have resulted mainly from the higher CO_2 load from the upper estuaries and outgassing.

[53] Excess CO_2, which was very high (>100 $\mu mol\ kg^{-1}$) in the low-salinity waters of the upper subestuary, was discharged to the Lingdingyang together with the freshwater. Excess CO_2 was not greatly different in the seasons surveyed although spring had a slightly higher value (209, 140, 116 and 108 $\mu mol\ kg^{-1}$ in spring, summer, fall and winter) (Table 2). However, water discharge to the Lingdingyang had significant seasonal variation, with its highest value in summer (4600 $m^3\ s^{-1}$) and lowest in winter (1250 $m^3\ s^{-1}$). Therefore the excess CO_2 load to the Lingdingyang from the upper estuary had similar seasonal variation with that of the water discharge, and the values were 38×10^6, 56×10^6, 28×10^6 and 12×10^6 mol C d^{-1} in spring, summer, fall and winter (Table 2).

[54] During the estuarine mixing process, biological processes may influence pCO_2. In the midestuaries, the conservative mixing of DIC and TAlk (salinities 5–10 in the Lingdingyang and the entire Huangmaohai, Figures 4a and 4c) suggested that the net biological effect on pCO_2 was negligible compared with mixing and mixing should be the main process influencing pCO_2 in the midestuaries of the Pearl River.

[55] On the other hand, the average depth of the Lingdingyang subestuary is ~5 m. Taking an average gas transfer velocity of 7 cm h^{-1}, we can estimate the 50% equilibrium time [*Raymond et al.*, 2000] to be 3 days, which is similar with the water travel time in the Inner Lingdingyang (3 days in summer and 5 days in winter in the entire Lingdingyang [*Wong and Cheung*, 2000]). That is to say, most of the excess CO_2 should be released to the atmosphere when the water traveled through the estuary. Therefore the CO_2 emission should have a similar seasonal pattern and values with the excess CO_2 load to the Lingdingyang. The CO_2 emission from the Inner Lingdingyang (zone 3) was 46×10^6, 63×10^6, 15×10^6 and 18×10^6 mol d^{-1} in the four seasons, which agreed reasonably with the excess CO_2 load to the Lingdingyang given the uncertainties of the estimates (Table 2).

[56] Note that the above estimation is to help understand the seasonal variation in CO_2 flux rather than to make exact calculations, since the solubility of CO_2 (K_H) in water is a function of salinity and temperature rather than a constant [*Weiss*, 1974]. Seasonal variation in CO_2 flux from zone 6 had a similar mechanism to that of zone 3, and will not be repeated here.

4.1.3. Lower Estuary (Zones 8 and 4)

[57] Taking the outer estuary (zone 8) as an example, the average pCO_2 was 254, 411 and 320 μatm in summer, fall and winter, respectively (Table 1). At the same time, the estimated NCP rate was 2.73 in summer, ~0 in fall (conservative distribution of DIC in November 2002 [*Guo et al.*, 2008]), and 0.55 g C $m^{-2}\ d^{-1}$ in winter. Therefore,

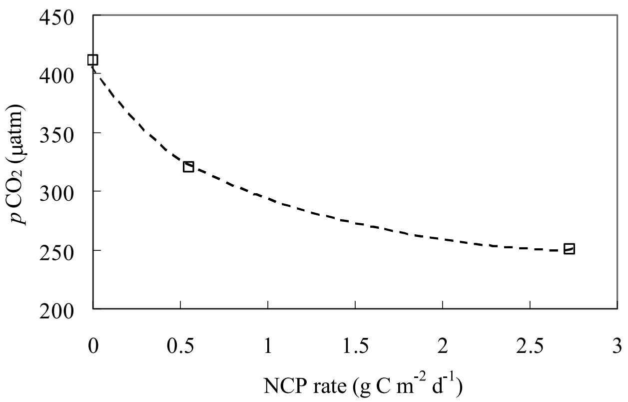

Figure 5. pCO_2 versus net community production (NCP) rate estimated from DIC in the outer estuary of the Pearl River. The dashed line shows the trend.

the NCP rate seemed to be the dominant factor influencing the pCO_2 level in the outer estuary (Figure 5), since net biological uptake of DIC through net community production drives the water to intake CO_2 from the atmosphere.

[58] Productivity in the Pearl River Estuary is believed to be light limited [*Cai et al.*, 2002]. TSS (total suspended solids) < 10 mg L^{-1} is the trigger for high productivity in the Amazon and Changjiang plumes [*DeMaster et al.*, 1986; *DeMaster and Pope*, 1996; *Ning et al.*, 1988]. In the Pearl River Estuary, *Huang et al.* [2005] report that the average TSS in the Lingdingyang is 38.4 mg L^{-1} in summer and 13.6 mg L^{-1} in spring. Even in the outer Pearl River Estuary, TSS was often still higher than 10 mg L^{-1} (Dai et al., unpublished data). During the November 2002 cruise, TSS was ~14 mg L^{-1} and chlorophyll a concentration was as low as 0.3–0.5 μg L^{-1} (Dai et al., unpublished data), therefore there was almost no net biological uptake of CO_2 and the average pCO_2 was 411 μatm. In sharp contrast in August 2005 (summer), TSS was only ~4 mg L^{-1} and the NCP rate was up to 2.73 g C m^{-2} d^{-1}. In February 2004, TSS was ~5 mg L^{-1} and the NCP rate was 0.55 g C m^{-2} d^{-1}. Phosphate may be another limiting factor of productivity in the lower Pearl River Estuary [*Yin et al.*, 2000; *Yin and Harrison*, 2008]. Although the limiting factor of productivity is still an open question, which is beyond the scope of this study, it appears that NCP rate is dominating the pCO_2 level in the lower Pearl River Estuary.

[59] In summary, the controlling factors of the CO_2 flux in the Pearl River Estuary are shown diagrammatically in Figure 6. In the upper estuaries, CO_2 flux was dominated by the respiration and nitrification rates. In the midestuaries, the excess CO_2 load from the upper estuaries dominated the CO_2 flux and mixing was the main process decreasing the pCO_2 level. However, in the lower estuary, net community production seemed to be the dominant process regulating the pCO_2 level.

4.2. How Significant Is the CO_2 Efflux From the Pearl River Estuary?

[60] Although the upper Lingdingyang subestuary has very high pCO_2, it covers only a very small area (~100 km^2

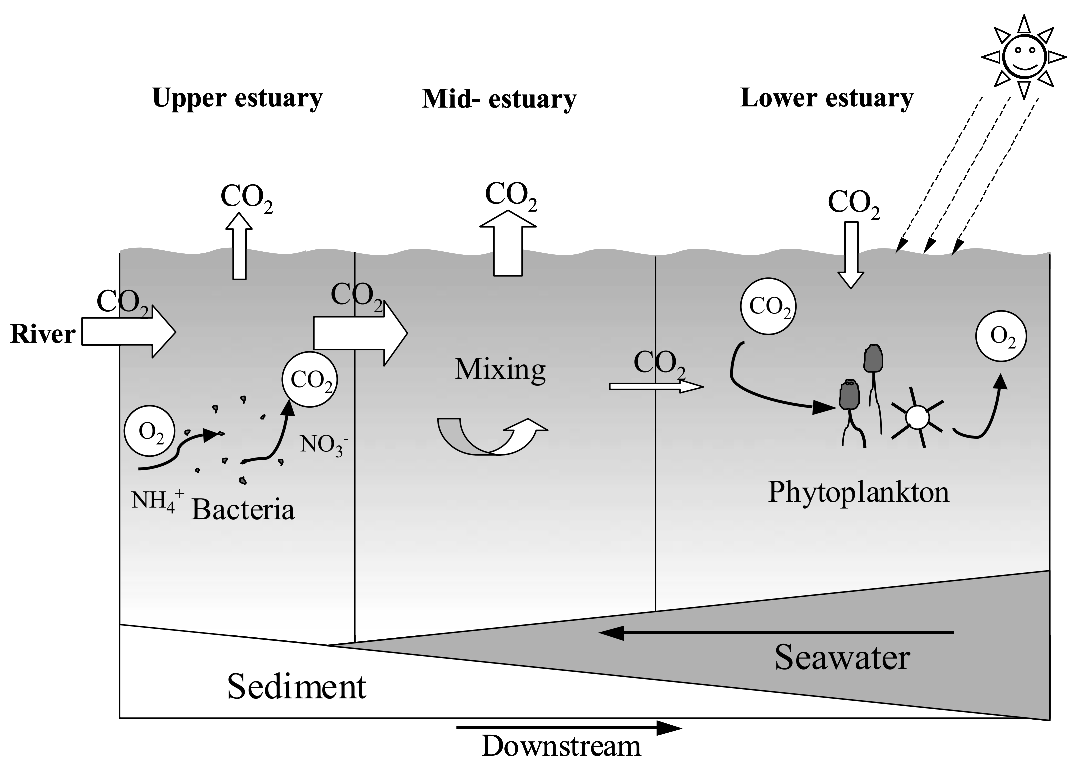

Figure 6. A simplified paradigm describing the controls on CO_2 flux in the Pearl River Estuary. The upper estuary was dominated by aerobic respiration and nitrification; the midestuary was dominated by mixing between freshwater and seawater; and the lower estuary was dominated by net community productivity. The width of the open arrow shows the relative amount of the total CO_2 exchange in the zone, but is not exactly proportional to the real data.

out of 4300 km^2). For the entire Pearl River Estuary system, CO_2 degassing flux was 6.92 mol C m^{-2} a^{-1}, which is significantly lower than that from temperate European estuaries, such as the Scheldt, Thames etc., which is up to 100 mol C m^{-2} a^{-1} [*Frankignoulle et al.*, 1998]. It should be noted that some of the CO_2 flux data in European estuaries were from floating-dome based measurements [*Borges*, 2005; *Frankignoulle et al.*, 1998]. The CO_2 degassing flux from the Pearl River Estuary is also lower than that from the inner Changjiang Estuary, which is 15.5–34.2 mol C m^{-2} a^{-1} [*Zhai et al.*, 2007]. However, it is similar to the CO_2 flux from tropical and subtropical Indian estuaries (the Godavari, Hoogly, and Mandovi-Zuari Estuaries), where CO_2 flux ranges from 2.9 to 24.3 mol C m^{-2} a^{-1} [*Bouillon et al.*, 2003; *Mukhopadhyay et al.*, 2002; *Sarma et al.*, 2001].

[61] The relatively lower CO_2 flux from the Pearl River Estuary may be similar with the cases of the Hoogly, Godavari and Mandovi-Zuari estuaries. The lower stretch of the Hoogly River receives ~400 million tons of sewage and wastes annually, but CO_2 flux from the Hoogly Estuary is only ~8.1 mol C m^{-2} a^{-1} [*Mukhopadhyay et al.*, 2002]. The relatively lower CO_2 flux from the low-latitude large river estuaries may be due to the large freshwater discharge, weak tide and thus short residence time of water in these estuaries [*Rao*, 2001; *Shetye*, 1999; *Sundar and Shetye*, 2005; *Zhao*, 1990], since high river flow decreases flushing time, while strong tidal influence increases residence time [*Dyer*, 1997].

[62] On the basis of the available literature, *Borges et al.* [2005] calculate that the average CO_2 flux from low-latitude (0–30°) and midlatitude estuaries is 16.83 and 46.00 mol C m^{-2} a^{-1}. However, the CO_2 flux from the Pearl River Estuary was significantly lower than that of the average low-latitude estuarine CO_2 flux known at the time of *Borges et al.* [2005]. Similarly, CO_2 flux from the inner Changjiang Estuary is also lower than that of the currently estimated global average for the midlatitude estuarine CO_2 flux and several times lower than that for the European estuaries of 36.5–182.5 mol C m^{-2} a^{-1} [*Borges et al.*, 2005; *Frankignoulle et al.*, 1998; *Zhai et al.*, 2007]. In the *Borges* [2005] data set, 11 of the 16 estuaries are European estuaries with high CO_2 fluxes and data for many large river estuaries were not available at that time. It is clear therefore that more data are mandatory, in particular from large river estuaries to better constrain the global estuarine CO_2 effluxes.

[63] As stated in section 1, CO_2 emission from European estuaries is in the same order of magnitude as the DIC export from European rivers; the currently estimated global estuarine CO_2 emission is also comparable with the DIC export flux from the total global rivers. However, the CO_2 emission from the Pearl River and Changjiang estuaries accounts for only ~6% and 2–5% of the DIC fluxes from the Pearl River (0.48 × 10^{12} mol C a^{-1}) and Changjiang (1.54 × 10^{12} mol C a^{-1}) [*Guo et al.*, 2008; *Zhai et al.*, 2007], which is more than an order of magnitude lower than the European estuaries and the global average. On the one hand, CO_2 flux from large Chinese river estuaries (Changjiang and Pearl River) is lower than that from European estuaries and the currently estimated global average. On the other hand, DIC export fluxes from large Chinese rivers are high since both DIC concentration and discharge are high [*Cai et al.*, 2008].

5. Concluding Remarks

[64] CO_2 outgassing flux from the Pearl River Estuary in summer is ~6 times that in winter. Average CO_2 flux and annual CO_2 emission from the Pearl River Estuary is 6.9 mol C m^{-2} a^{-1} and 3.0 × 10^{10} mol C a^{-1}, respectively. CO_2 flux from the Pearl River Estuary was similar to tropical and subtropical Indian estuaries and much lower than temperate European estuaries. Compared to DIC export flux, CO_2 emission from the large Chinese river estuaries was also significantly lower than both the global average and that for European estuaries.

[65] The much higher CO_2 flux in warm and wet seasons than in cold and dry seasons was due mainly to the stronger microbial processes in the upper estuary, and the outgassing of the higher loaded excess CO_2 from upper estuaries in warm and wet seasons.

[66] While it is known that CO_2 is supersaturated in many estuarine systems, along with many prior researches in world estuaries, this study has demonstrated that there exist substantial differences in CO_2 emission fluxes among estuaries at different latitudinal regions. Better understanding of the major low-latitude estuaries in tropical and subtropical regions such as the Pearl River Estuary is important in order to better constrain the global estuarine CO_2 emission and understand its role in the global carbon cycling.

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