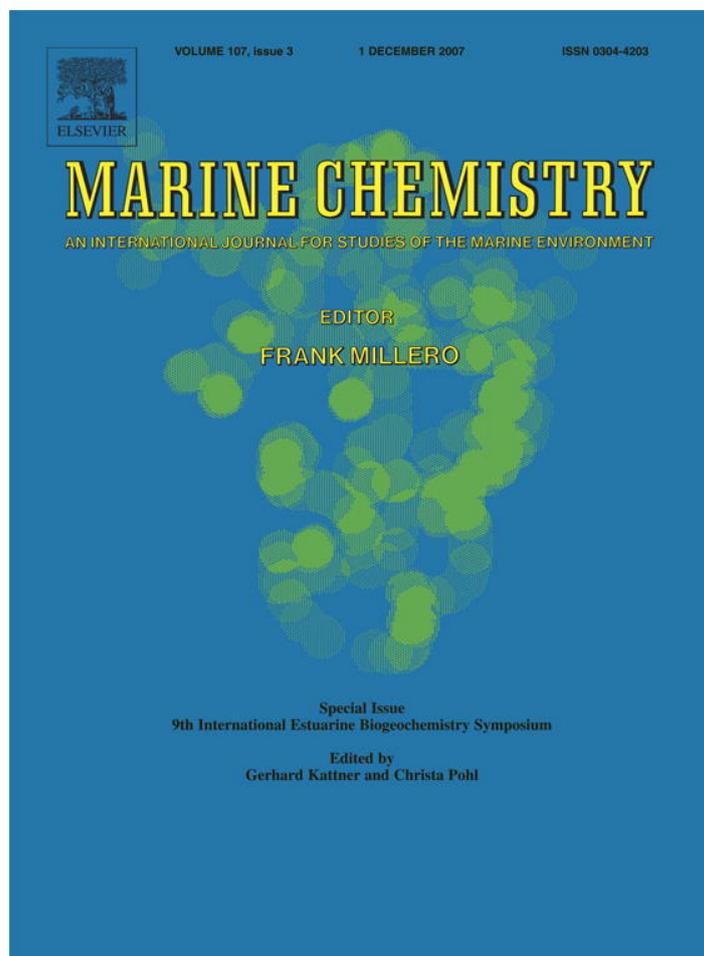


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Carbonate system and CO₂ degassing fluxes in the inner estuary of Changjiang (Yangtze) River, China

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Abstract

We examined the carbonate system, mainly the partial pressure of CO₂ (*p*CO₂), dissolved inorganic carbon (DIC) and total alkalinity (TAlk) in the Changjiang (Yangtze) River Estuary based on four field surveys conducted in Sep.–Oct. 2005, Dec. 2005, Jan. 2006 and Apr. 2006. Together with our reported *p*CO₂ data collected in Aug.–Sep. 2003, this study provides, for the first time, a full seasonal coverage with regards to CO₂ outgassing fluxes in this world major river–estuarine system. Surface *p*CO₂ ranged 650–1440 μatm in the upper reach of the Changjiang River Estuary, 1000–4600 μatm in the Huangpujiang River, an urbanized and major tributary of the Changjiang downstream which was characterized by a very high respiration rate, and 200–1000 μatm in the estuarine mixing zone. Both DIC and TAlk overall behaved conservatively during the estuarine mixing, and the seasonal coverage of these carbonate parameters allowed us to estimate the annual DIC export flux from the Changjiang River as $\sim 1.54 \times 10^{12}$ mol. The highly polluted Huangpujiang River appeared to have a significant impact on DIC, TAlk and *p*CO₂ in the lower reaches of the inner estuary. CO₂ emission flux from the main stream of the Changjiang Estuary was at a low level of 15.5–34.2 mol m⁻² yr⁻¹. Including the Huangpujiang River and the adjacent Shanghai inland waters, CO₂ degassing flux from the Changjiang Estuary may have represented only 2.0%–4.6% of the DIC exported from the Changjiang River into the East China Sea.

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Keywords: Carbon dioxide; Outgassing; Carbonate system; Changjiang Estuary

1. Introduction

CO₂ emission from rivers and their estuaries has been proposed as an important component of the global carbon cycle (Cai and Wang, 1998; Frankignoulle et al., 1998; Richey et al., 2002; Borges, 2005; Borges et al., 2005). Frankignoulle et al. (1998) argued that European estuaries emit 0.03–0.06 Gt C yr⁻¹, representing 5%–10% of the anthropogenic CO₂ emissions from Western

Europe in 1995. Borges et al. (2005) also made a first order estimate for global estuarine CO₂ emissions of >0.16 Gt C yr⁻¹ degassed from inner estuaries and >0.24 Gt C yr⁻¹ degassed from the ensemble of near-shore coastal ecosystems (mostly outer estuaries and/or river plumes). These studies might suggest that a substantial fraction of atmospheric carbon sequestered in the terrestrial system (transformed into either dissolved HCO₃⁻ or organic matter in continental waters) might be degraded and returned to the atmosphere on its route to the ocean, and thus on a relatively small time scale. For example, in the Scheldt estuary, a temperate and highly polluted European estuary, annually $\sim 10\%$ of inorganic

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carbon input (Hellings et al., 2001) or even $\sim 70\%$ of total carbon input in Mar. 1993 (Frankignoulle et al., 1996) was degassed within the estuarine mixing zone. According to Borges (2005), global estuaries and salt marshes may release CO_2 into the atmosphere at a level of $0.49 \text{ Gt C yr}^{-1}$, which is equivalent to $\sim 7\%$ of fossil-fuel associated carbon emissions or $\sim 60\%$ of global riverine carbon export ($\sim 0.8 \text{ Gt C yr}^{-1}$, based on Prentice et al., 2001).

However, different drainage areas (e.g. lime-rich vs. lime-poor) may exert a major control on the annual CO_2 cycle of different river-estuary systems, and this might exceed the changes due to biological processes (Thomas and Schneider, 1999). Borges et al. (2005) correctly pointed out that the current estimate of the global integrated CO_2 degassing fluxes from riverine-estuarine systems may be potentially subject to large uncertainties especially due to the data paucity for most large rivers/estuaries. For example, no data are so far available for the inner Amazon estuary, while the limited amount of data for the outer Amazon estuary (river plume) shows that it is a sink for atmospheric CO_2 (Ternon et al., 2000; Körtzinger, 2003), despite the fact that, in the Amazon River basin, CO_2 outgassing fluxes were estimated to be as high as 0.5 Gt C yr^{-1} , nearly one magnitude greater than the Amazonian fluvial export of total carbon to the ocean (Richey et al., 2002). Elsewhere in the inner Mississippi estuary, aqueous CO_2 partial pressure ($p\text{CO}_2$) as moderate as $1000\text{--}2100 \mu\text{atm}$ was reported for Aug.–Sep. 1998 (Cai, 2003).

It is also true, based on limited data sets however, that Asian rivers/estuaries overall have much lower $p\text{CO}_2$ levels as compared to the reported $p\text{CO}_2$ in those well-documented European estuaries. For example, the riverine/estuarine aqueous $p\text{CO}_2$ was moderate ($800\text{--}2500 \mu\text{atm}$) for two Indian estuaries, the Mandovi-Zuari (Sarma et al., 2001) and the Hooghly Estuary in the Ganges Delta (Mukhopadhyay et al., 2002), and for the Huanghe River/Estuary, China (Su et al., 2005). In the inner estuary of Gautami Godavari River, India, aqueous $p\text{CO}_2$ was reported as low as $300\text{--}500 \mu\text{atm}$ (Bouillon et al., 2003). Exceptions are seen in a mangrove ecosystem out of the Gautami Godavari Estuary, where aqueous $p\text{CO}_2$ as high as $\sim 6400 \mu\text{atm}$ was reported (Bouillon et al., 2003), and in the Zhujiang (Pearl) River Estuary, China, where aqueous $p\text{CO}_2$ as high as $4000\text{--}7500 \mu\text{atm}$ was observed persistently in its urbanized upper reaches (Zhai et al., 2005; Dai et al., 2006).

While it becomes clear that riverine-estuarine systems and their relevant carbon fluxes are vitally important to constrain global carbon fluxes, strong estuarine

CO_2 outgassing does not necessarily exist everywhere, especially in the large rivers of the world. Therefore, regional studies with better seasonal constraints are essential. In this study, we surveyed estuarine CO_2 in the largest Asian river, the Changjiang (Yangtze) River. To evaluate the influence of pelagic respiration on the carbonate system and water-air CO_2 flux in the river end of the Estuary, we also measured dissolved oxygen (DO) and the bulk oxygen consumption rate. Despite the fact that many research efforts have been devoted to this, one of the world major estuaries, only a few data reports are available on dissolved inorganic carbon (DIC) (Cauwet and Mackenzie, 1993) and aqueous $p\text{CO}_2$ (as summarized by Cole and Caraco, 2001; Chen et al., accepted for publication), including our first direct $p\text{CO}_2$ measurements in the summer of 2003 (Chen et al., accepted for publication). Only total alkalinity (TAlk) and pH are relatively well documented (Chen et al., 2002; Liu et al., 2002; Li and Zhang, 2003).

2. Materials and methods

2.1. Study area

The Changjiang River is the fourth largest river in the world by virtue of a water discharge of $\sim 944 \times 10^9 \text{ m}^3 \text{ yr}^{-1}$ at the estuary mouth (Dai and Trenberth, 2002). Its drainage area covers $1.8 \times 10^6 \text{ km}^2$, nearly 20% of the total terrestrial area of China (Chen et al., 2002). The Changjiang River flows from icy mountains in the Qinghai-Tibet Plateau and cuts through the Yun-Gui Plateau and the Sichuan Basin before it traverses the Three-Gorges region (Fig. 1a), where the basement rocks are abundant in carbonates (Chen et al., 2002). Then it runs through the subtropical plains in central and eastern China for $\sim 2000 \text{ km}$ and finally empties into the East China Sea (ECS). The Changjiang River is one of the most important solid transporting rivers (Gaillardet et al., 1999), although its downstream solid content has declined from $\sim 600 \text{ mg L}^{-1}$ in the 1960s to $<400 \text{ mg L}^{-1}$ in the 2000s (Li and Zhang, 2003). The Changjiang River is also a typical Himalayan river (Sarin, 2001), characterized by very high alkalinity (Chen et al., 2002) and carbonate weathering rate (Gaillardet et al., 1999) as compared with most other major rivers in the world. After entering the ECS, the Changjiang River plume, or so-called Changjiang Dilute Water, mixes with numerous ECS water masses (Chen and Wang, 1999). Since the Changjiang River discharges a large load of nutrients and sediments (Shen, 2001; Liu et al., 2002; Li and Zhang, 2003), much concern has been focused on the possible effect of damming in the upper part (e.g. the Three-Gorges Dam at $\sim 2000 \text{ km}$ upstream from the mouth of the Changjiang Estuary, the

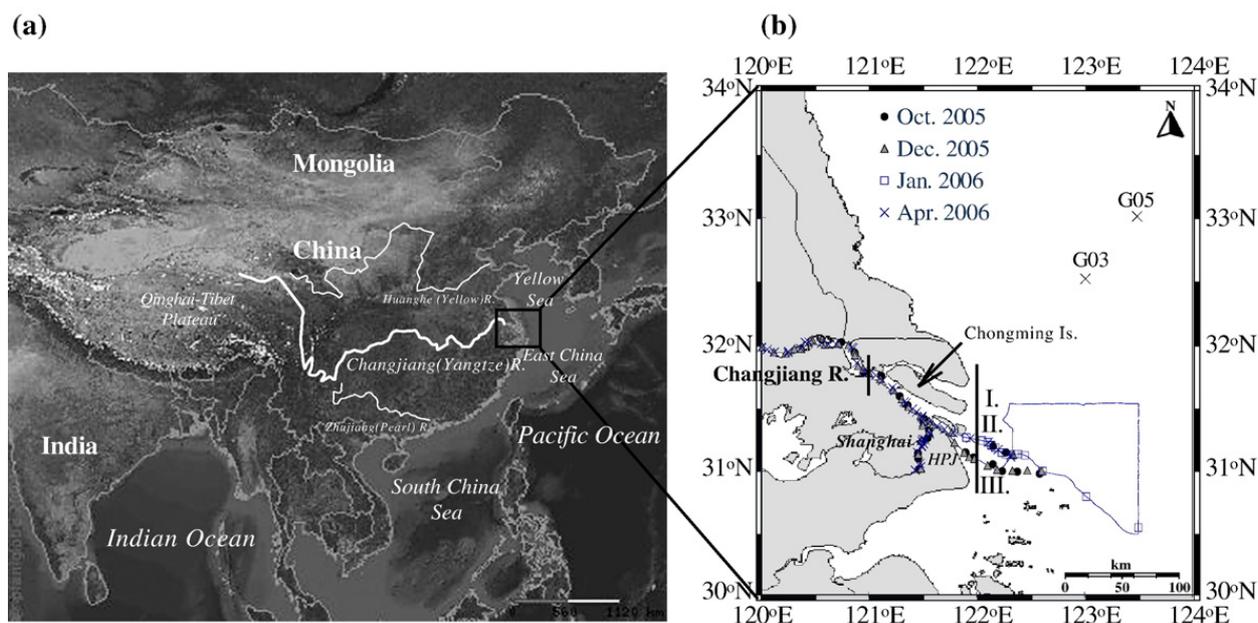


Fig. 1. Sketch maps of three major Chinese rivers (a) and the sampling map in the Changjiang River Estuary (b) and the Huangpujiang River (HPJ). Surface areas between the two longitudinal solid lines (located at 121°00'E and 122°00'E respectively) are regarded as the inner estuary. Outlet I. represents the North Branch, while outlets II. and III. indicate the North Passage and South Passage of the South Branch, respectively.

first filling stage of which started in Jun. 2003) on the biological and geochemical processes in the ECS (e.g. Gong et al., 2006).

The inner estuary of the Changjiang River is ~120 km long and >90 km wide at its estuary mouth, where it is divided into two branches by Chongming Island (Fig. 1b). Water is relatively well mixed in the inner estuary while it is partially stratified outside the estuary mouth in the river plume area (Shen and Pan, 2001). More than 95% of the river flow empties into the ECS through the South Branch (Shen, 2001). A highly industrialized metropolitan city, Shanghai, has a significant impact on the South Branch water through a large sewage load ($1.8\text{--}2.2 \times 10^9 \text{ m}^3 \text{ yr}^{-1}$ in the 2000s; Xu and Yin, 2003) mostly via the Huangpujiang River (HPJ), the farthest downstream tributary of the Changjiang River (Fig. 1b). This study focused on the South Branch of the Changjiang Estuary through its South Passage (Fig. 1b).

2.2. Sampling and analyses

Between late Sep. 2005 and early Apr. 2006, four cruises (Fig. 1b) were carried out in the Changjiang Estuary. Most of the cruises emphasized the inner estuary (including the neighboring HPJ), except for the 1–3 Jan. 2006 cruise, which mainly surveyed the outer estuary indicated by the triangular region marked in Fig. 1b. The cruises followed a major transect through

the South Branch (Fig. 1b), which was identical to our previous survey conducted in summer 2003 (Chen et al., accepted for publication). Surface water (at a depth of ~1–2 m) was continuously pumped from a side intake for measurements of $p\text{CO}_2$ and other hydrochemical parameters using an underway pumping system similar to that previously described in Zhai et al. (2005). With the data we have reported for summer 2003 (Chen et al., accepted for publication), we have the first set of direct measurements of $p\text{CO}_2$ with a full seasonal coverage. Also included in this study were TALK data obtained in summer 2003, and thus we were able to examine the seasonal variation of DIC and TALK in the Changjiang Estuary since the first filling stage of the Three-Gorges Dam began (Jun. 2003).

Aqueous $p\text{CO}_2$ was determined using a Li-Cor® 7000 NDIR spectrometer together with a continuous flow and cylinder-type equilibrator (see Zhai et al., 2005; Dai et al., 2006 for details). Since the Apr. 2006 cruise, we have employed a new and fully sealed equilibrator (designed and manufactured by W.-J. Cai and Y.C. Wang at the University of Georgia). For calibration, a wide range of CO_2 gas standards with $x\text{CO}_2$ values of 380×10^{-6} , 592×10^{-6} , 967×10^{-6} , 2.06×10^{-3} and 3.51×10^{-3} were applied in order to suit the wide range of $p\text{CO}_2$ in estuarine areas. The overall uncertainty of the contents of these standards was <1%. To transform the $x\text{CO}_2$ data into $p\text{CO}_2$, the associated air pressure records of the Li-Cor® 7000 were used. A set of meteorological sensors

(R.M. Young Company, USA) was also deployed to measure air pressure. Comparison between the two air pressure datasets revealed consistency at a relative error level of <0.1% (i.e. <1 hPa).

Atmospheric $x\text{CO}_2$ was typically determined every 1–3 h. The bow intake from which air was pumped was installed ~ 6 m above the water surface to avoid contamination from the ship. For the purpose of water–air flux estimation, the atmospheric $p\text{CO}_2$ was corrected to 100% humidity at in situ water surface temperature and salinity.

Salinity, temperature, DO and pH, were continuously measured with a YSI® 6600 meter and a WTW's CellOx® 325 DO probe. All these sensors were pre-calibrated and salinity/DO/pH were validated by simultaneous discrete chlorinity (for salinity verification), Winkler DO and pH data. These discrete samples (together with surface DIC and TALK) were all collected via a side vent of our pumping system. Within the estuarine mixing zone, sampling was primarily guided by salinity distribution. During the Sep.–Oct. 2005 cruise (30 Sep.–7 Oct.), vertical profiles of the water column were sampled at three selected stations, where water samples were obtained with 2.5-L Go-Flo bottles. During the Apr. 2006 cruise (3–10 Apr.), we surveyed only through to a salinity of ~ 14 due to rough sea conditions. To extend our DIC/TALK data range, two adjacent sampling stations (G03 and G05 shown in Fig. 1b, with surface salinity of 28 and 32.6) of a China–SOLAS cruise were included in this study. In that cruise, discrete water samples were obtained at three depths with 8-L Niskin bottles onboard the R/V Dongfanghong II on 26 Apr. 2006.

pH was measured on board with a Corning 350 pH/ion analyzer equipped with an Orion® Ross combination electrode against three NIST-traceable buffers at a precision of 0.005 pH. Water samples for DIC (unfiltered but allowed to settle before measurement) and TALK (pre-filtered with a 1 μm PE cartridge filter) analyses were preserved with HgCl_2 and determined within a time frame of 10 days upon sampling, except for the Aug. 2003 TALK samples, which were measured within five months after sampling. DIC was measured by infrared detection following acid extraction of a 0.5-mL sample with a KJoehn® digital syringe pump, as described in Cai et al. (2004). TALK was determined by Gran acidimetric titration on a 25-mL sample with a KJoehn digital syringe pump, using the Corning 350 pH/ion analyzer equipped with an Orion® Ross combination electrode for detection. Reference materials from Andrew G. Dickson's lab were used to calibrate the system at a precision of $\pm 2 \mu\text{mol kg}^{-1}$ for both DIC and TALK determinations (Cai et al., 2004).

Bulk oxygen consumption rates were determined at the upper reach of the Changjiang Estuary (110–130 km upstream of the estuary mouth) and in the HPJ. Both incubation and data integration followed Zhai et al. (2005) and Dai et al. (2006). Briefly, on-deck incubations were conducted using unfiltered water in a 20-L LDPE cubitainer (Fisher Scientific) under dark conditions, and a series of subsamples for DO measurements were taken via a stopcock pipe and measured using the Winkler method. A pseudo first order reaction quotient was calculated based on the assumption of constant concentration of oxygen consuming materials (Eqs. (1) and (2)).

$$\text{Differential equation: } -\frac{d[\text{O}_2]}{dt} = k \cdot [M] \cdot [\text{O}_2] = k' \cdot [\text{O}_2] \quad (1)$$

$$\text{Integral equation: } \ln[\text{O}_2] = -k' \cdot t + A \quad (2)$$

where $[\text{O}_2]$ is the DO concentration; $[M]$ is total concentration of oxygen consuming materials; t is incubation time; k is the integrated reaction quotient for all oxygen consumption reactions; k' is the pseudo first order reaction quotient based on the assumption of constant concentration of oxygen consuming materials; and A is a random constant. The in situ bulk oxygen consumption rate was then estimated using the pseudo first order reaction quotient and in situ DO based on Eq. (1).

2.3. DIC export flux estimation

DIC export fluxes were estimated based on the DIC concentration and water discharge at the river end-member, taking into consideration the seasonal variation of DIC and its biogeochemical behavior within the estuarine mixing zone. Since on-the-spot water discharge data were not available, we used water discharge measured at the Datong Station (the most downstream hydrological station, ~ 640 km upstream of the estuary mouth, <http://sqqx.hydroinfo.gov.cn/websq/>). Based on another on-the-spot study in the Changjiang Estuary (Wang et al., 2006), there was no significant difference between the Datong Station water discharge and that measured at the river end of the Estuary.

2.4. Water–air CO_2 flux estimation

Average net CO_2 fluxes (F) were estimated based on the formula: $F = k \times K_{\text{H}} \times \Delta p\text{CO}_2$, where k is the gas transfer velocity of CO_2 , K_{H} is the solubility of CO_2 (Weiss, 1974), and $\Delta p\text{CO}_2$ is the mean difference

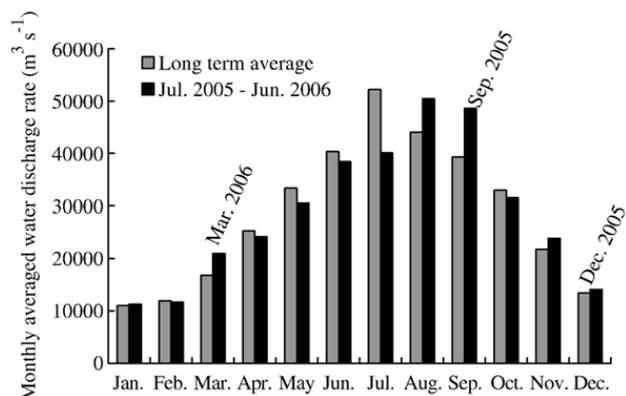


Fig. 2. Monthly water discharge at the Datong Station, the farthest and major downstream hydrological station in the Changjiang River. The long-term averages are from Liu et al. (2002) for the period 1963–1999. The Jul. 2005–Jun. 2006 data are from the Hydrological Information Centre of China (<http://sqqx.hydroinfo.gov.cn/websq/>).

between water and air $p\text{CO}_2$. A positive flux value represents the net CO_2 exchange from the water body to the atmosphere and a negative value refers to the net exchange from the atmosphere to the water body. Since the on site k value was not available, our calculations were based on a suit of empirical functions of wind speed, so as to determine the variation between different k values in this simple parameterization methodology for gas transfer velocity derived under complex hydrodynamical and geomorphological conditions (Abril et al., 2000; Raymond and Cole, 2001; Borges et al., 2004a,b).

2.4.1. Wanninkhof (1992) function

$$k(\text{cm h}^{-1}) = 0.31 \times (u/\text{m s}^{-1})^2 \times (\text{Sc}/600)^{-0.5} \quad (3)$$

2.4.2. Raymond and Cole (2001) function

$$k(\text{cm h}^{-1}) = 1.91 \times \exp[0.35 \times (u/\text{m s}^{-1})] \times (\text{Sc}/600)^{-0.5} \quad (4)$$

2.4.3. Borges et al. (2004a) function

$$k(\text{cm h}^{-1}) = [4.045 + 2.580 \times (u/\text{m s}^{-1})] \times (\text{Sc}/600)^{-0.5} \quad (5)$$

where k is the gas transfer velocity; u is the field-measured wind speed at 6 m/10 m height, here recorded by our onboard meteorological sensors; Sc is the Schmidt number of CO_2 in freshwater or seawater; 600 is the Sc value in freshwater at 20 °C and adjusted to 660 for seawater, according to Wanninkhof (1992).

3. Results

3.1. Hydrographic settings

Although the Three-Gorges Dam has been in its first filling stage since Jun. 2003 (Gong et al., 2006), water discharge of the Changjiang River at the Datong Station was still recorded as $911 \times 10^9 \text{ m}^3$ in the year under survey (Jul. 2005–Jun. 2006) (<http://sqqx.hydroinfo.gov.cn/websq/>), which is no less than the long-term average (over the period 1963–1999, Liu et al., 2002). Fig. 2 shows that, during Jul. 2005–Jun. 2006, both August and September were at the peak of river discharge, which is different from the long-term average scenario in the

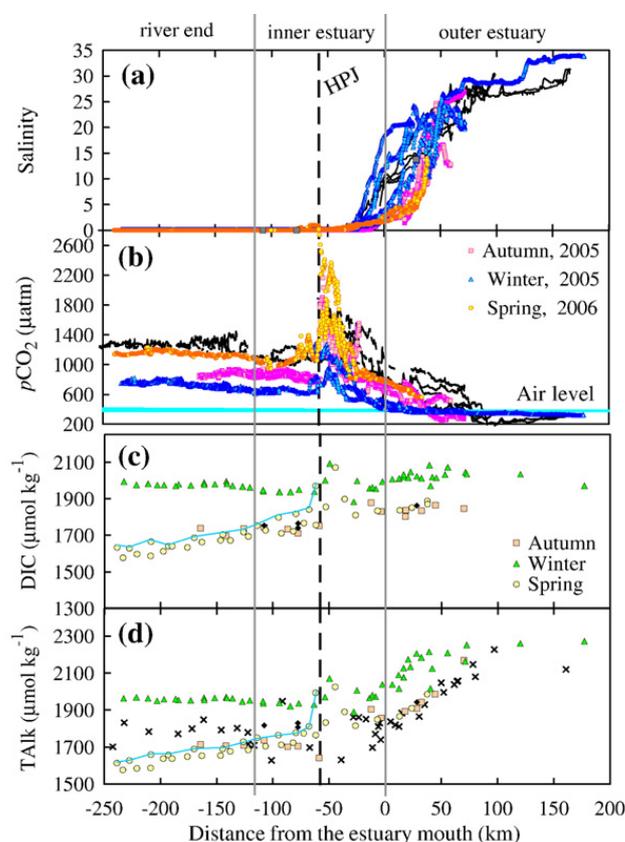


Fig. 3. Salinity (a), air/water $p\text{CO}_2$ (b), DIC (c) and TALK (d) along the transect surveyed in the Changjiang Estuary and adjacent waters. Data for 8–12 m depth during the Oct. 2005 cruise are also shown by grey squares in panel (a) and black diamonds in panels (c) and (d). Data for the Huangpujiang River (HPJ) are not included. Grey vertical lines show the estuary mouth (right) and the upper limit of the inner estuary (left, ~120 km upstream of the estuary mouth). The two boundaries are also referenced to Fig. 1b. The broken vertical line represents the location of the HPJ outlet. Thin curves in panels (a) and (b) show data for Aug.–Sep. 2003 (Chen et al., accepted for publication). The circles linked with blue lines in panels (c) and (d) show DIC/TALK data of samples in the first 2 days during the Apr. 2006 cruise, while the other Apr. 2006 DIC/TALK data are of later samples. Black \times symbols in panel (d) show TALK data for Aug.–Sep. 2003.

Table 1
Water temperature, salinity and $p\text{CO}_2$ in the Changjiang Estuary and adjacent Huangpujiang River (HPJ)

Survey dates	Water temperature (°C)	Salinity	Aqueous $p\text{CO}_2$ (μatm)	Air $p\text{CO}_2$ (μatm)
<i>River end (>120 km upstream of the estuary mouth)</i>				
28–31 Aug. 2003 ^a (~180 km)	28.3±0.13 (27.8–28.8)	0	1280±47 (1130–1445)	359±11 (344–382)
06–07 Oct. 2005 (~43 km)	22.9±0.16 (22.6–23.2)	0.03	870±25 (810–940)	400±19 (364–420)
26–28 Dec. 2005 (~110 km)	8.2±0.12 (7.9–9.2)	0.15	731±39 (642–822)	388±5 (383–399)
05–07 Apr. 2006 (~120 km)	14.9±0.3 (14.2–15.6)	0.01	1046±27 (1076–1230)	401±16 (386–435)
<i>Upper reach of the inner estuary (upstream of the HPJ outlet, ~600 km² b)</i>				
27–31 Aug. 2003 ^a	28.3±0.2 (27.9–28.7)	0	1105±70 (985–1250)	352±1.7 (349–355)
06–07 Oct. 2005	23.1±0.2 (22.8–23.4)	0.03	850±46 (752–940)	377±24 (360–412)
26–29 Dec. 2005	8.0±0.15 (7.4–8.4)	0.15	658±43 (607–837)	383.8±1.0 (383–386)
07–08 Apr. 2006	14.8±0.13 (14.4–15.1)	0.02	1093±93 (943–1395)	394±7 (383–402)
<i>Huangpujiang River (~60 km² c)</i>				
31 Aug.–02 Sep. 2003 ^a (~5 km)	(28.1–30.3)	0.02	(1500–4600)	(347–365)
30 Sep. 2005 (57 km)	26.9±0.3 (26.3–27.8)	0.15	3220±270 (2250–3710)	370±4 (363–376)
29 Dec. 2005 (56 km)	5.9±0.5 (5.3–8.0)	0.35	1410±190 (935–1865)	390±3 (387–393)
08–09 Apr. 2006 (60 km)	18.5±0.4 (17.3–20.8)	0.24	3900±280 (3260–4580)	397±7 (384–408)
<i>Lower reach of the inner estuary (downstream of the HPJ outlet, ~1000 km² a)</i>				
27 Aug. 2003 ^a	28.9±0.3 (28.4–29.5)	1.1±2.5 (0–9.9)	1100±280 (400–1510)	369±1.5 (367–371)
01–02 Sep. 2003 ^a	28.2±0.3 (27.5–28.7)	2.3±3 (0–10.4)	1250±350 (820–1890)	355±6 (349–364)
01 Oct. 2005	25.8±0.3 (25.4–26.8)	0.7±0.9 (0.03–3.2)	1000±240 (620–1800)	367±6 (361–375)
06 Oct. 2005	23.3±0.3 (22.8–23.9)	0.3±0.5 (0.02–2.1)	1043±380 (705–2160)	N/A
24–26 Dec. 2005	6.9±0.8 (5.3–8.8)	1.8±2.8 (0.18–12.1)	750±240 (410–1275)	386±5 (380–393)
03 Jan. 2006	7.8±0.4 (7.2–8.5)	5±6 (0.18–18.3)	630±130 (410–870)	387.4±0.9 (386–389)
08 Apr. 2006	15.1±0.5 (14.4–17.1)	0.7±0.6 (0.03–2.7)	1260±510 (770–3120)	385±9 (377–400)
<i>Outer estuary (river plume outside the estuary mouth, >3000 km² b)</i>				
26–27 Aug. 2003 ^a (~165 km)	28.2±1.0 (25.9–29.7)	24±6 (8.5–31.4)	380±160 (181–712)	364±4 (358–371)
01–02 Sep. 2003 ^a (~100 km)	26.5±0.6 (24.9–27.7)	20±6 (9.4–30.5)	640±190 (269–987)	358±4 (352–362)
01 Oct. 2005 (~60 km)	26.5±0.5 (25.5–27.8)	9±5 (2.7–16.6)	535±60 (446–653)	359±1.5 (358–361)
05 Oct. 2005 (~70 km)	23.3±0.6 (22.6–24.3)	13±10 (1.4–27.0)	490±190 (248–775)	370±2 (368–374)
25 Dec. 2005 (~70 km)	6.3±0.6 (5.2–7.5)	18±5 (5.2–24.5)	385±21 (356–450)	416±10 (407–437)

(continued on next page)

Table 1 (continued)

Survey dates	Water temperature (°C)	Salinity	Aqueous $p\text{CO}_2$ (μatm)	Air $p\text{CO}_2$ (μatm)
<i>Outer estuary (river plume outside the estuary mouth, >3000 km²^b)</i>				
01 Jan. 2006 (~180 km)	11±2.8 (7.1–15.5)	27±7 (7.5–34.0)	350±30 (316–477)	384.2±0.9 (382–386)
08 Apr. 2006 (~40 km)	15.1±0.3 (14.6–15.7)	5.1±2.6 (1.7–14.0)	690±70 (560–800)	381±4 (377–385)

^a Field data in the Aug.–Sep. 2003 cruise are cited from Chen et al. (accepted for publication).

^b Modified from Shen (2001).

^c The Huangpujiang River is ~110 km long (Zhu et al., 2004) and ~600 m wide (based on the 2005 edition 1:60,000 navigation map).

period 1963–1999, characterized by a single high water discharge peak in July (Liu et al., 2002). This may have resulted from the manipulation of water discharge from the Three-Gorges Dam. In the current context, our Sep.–Oct. cruise (30 Sep. 2005 for the HPJ and 1–7 Oct. 2005 for the Changjiang Estuary) may represent a flood season; our Dec.–Jan. cruises (24–29 Dec. 2005 and 1–3 Jan. 2006) a drought period of the year; and the Apr. cruise (5–9 Apr. 2006) a transitional season between the dry/cold season and the wet/warm season.

A significant salinity front was observable persistently around the estuary mouth, where freshwater at 10–50 km upstream of the estuary mouth mixed with outside saline water (Fig. 3a). However, the salinity at this mouth (1.4–2.7) in the present flood/transitional seasons (Oct. 2005/Apr. 2006) was much lower than in Aug.–Sep. 2003, which was supposed to be in a flood season but reduced by the Dam immediately after the Jun. 2003 start of filling ($S \sim 10$, see Table 1). Even in the typical dry/cold season (Jan. 2006), the salinity was no more than 31 around 120 km away from the estuary mouth along our major transect (Fig. 3a), which suggests that the so-called Changjiang Dilution Water reached farther offshore than in the initial filling years of the Dam (Gong et al., 2006).

3.2. Aqueous $p\text{CO}_2$

Table 1 shows the average $p\text{CO}_2$ and its range in the river end, inner estuary and outer estuary. Due to the influence of the HPJ, a highly polluted river channel and thus with extremely high $p\text{CO}_2$ (see below), we further divided the inner estuary into two parts, i.e. upstream and downstream of the HPJ outlet.

Upstream of the HPJ outlet, the Changjiang River or its inner estuary had a surface $p\text{CO}_2$ range of 610–1445 μatm with the highest level in summer and lowest in winter (Fig. 3b; Table 1). The peak $p\text{CO}_2$ (which varied between 800 and 3120 μatm depending on the season and tide) along the main transect appeared 30–60 km upstream of the estuary mouth, i.e. a region around the outlet of the HPJ with its high

level of pollution (location shown in Fig. 1). Following the peak, $p\text{CO}_2$ rapidly dropped from 600–1200 μatm inside the estuary mouth to 400–700 μatm around 20 km outside and nearly reached equilibrium with the air $p\text{CO}_2$ around 35 km away from the estuary mouth (Fig. 3b). Further offshore (~60 km away from the estuary mouth) and with an increase in salinity, aqueous $p\text{CO}_2$ reached its lowest level and even fell below saturation in winter (Fig. 3a and b), despite the fact that water temperature increased from ~10 °C at 60–120 km offshore to ~15.5 °C at >160 km (data not shown). The lowest winter $p\text{CO}_2$ (~320 μatm) was observed at >160 km and, although this is higher than summer bloom $p\text{CO}_2$ values (as low as ~200 μatm as reported by Chen et al. accepted for publication, and references therein), it is consistent with the general ECS shelf water, where drawdown of $p\text{CO}_2$ is typical (Wang et al., 2000). In summary, surface $p\text{CO}_2$ showed a general trend to decrease in the order: inner estuary downstream HPJ > river end > inner estuary upstream HPJ > outer estuary.

3.3. Dissolved inorganic carbon

Surface DIC, TAlk and pH upstream of the HPJ outlet (also upstream of the estuarine mixing zone) are summarized in Table 2. Due to the impact from the HPJ, both DIC and TAlk had peak values of 1750–2090 $\mu\text{mol kg}^{-1}$ (DIC) and 1640–2070 $\mu\text{mol kg}^{-1}$ (TAlk) at the area 30–60 km upstream of the estuary mouth (Fig. 3c, d). Beyond this HPJ impacted region, the variation of DIC/TAlk in the Changjiang River and its estuary was relatively smooth.

In the typical cold/dry season (from Dec. 2005 to Jan. 2006), DIC at both the river end and the sea end varied within a narrow range, between 1930 and 2080 $\mu\text{mol kg}^{-1}$, while in contrast, TAlk increased substantially, from 1920–1970 $\mu\text{mol kg}^{-1}$ at the river end to 2250–2270 $\mu\text{mol kg}^{-1}$ at the sea end (Fig. 3c, d).

In the previous flood season (Oct. 2005), DIC varied from 1695–1765 $\mu\text{mol kg}^{-1}$ at the river end to

Table 2

Surface DIC, TALK, pH and DO in the Changjiang River upstream of the Huangpujiang outlet and the estuarine mixing zone (>60 km upstream of the estuary mouth)

Survey dates	Water discharge (m ³ s ⁻¹)	DIC (μmol kg ⁻¹)	TALK (μmol kg ⁻¹)	pH	DO saturation (%)	Ref.
27–31 Aug. 2003	39,150 ^a	N/A	1630–1950	7.81–7.98	72–93	Chen et al. (accepted for publication)
06–07 Oct. 2005	40,050 ^a	1695–1750	1700–1740	N/A	85–90	This study
26–28 Dec. 2005	12,700 ^a	1935–1995	1920–1970	7.92–8.04	93–97	This study
05–07 Apr. 2006	22,600 ^a	1575–1840	1575–1810	7.76–8.03	84–91	This study

^a Average water discharge between the prior and the succeeding months.

1800–1865 μmol kg⁻¹ 20–70 km outside the estuary mouth (Fig. 3c), and TALK increased from 1700–1740 μmol kg⁻¹ at the river end to ~2170 μmol kg⁻¹ around 70 km outside the estuary mouth (Fig. 3d). In another flood season (Aug.–Sep. 2003), TALK mostly ranged from 1700–1850 μmol kg⁻¹ at the river end (though it could be as low as 1630 μmol kg⁻¹ or as high as 1950 μmol kg⁻¹, Table 2) and increased to 2120–2230 μmol kg⁻¹ at >90 km outside the estuary mouth (Fig. 3d). Note that DIC was not available from this Aug.–Sep. 2003 cruise.

Complex variability was observed in the transitional period. During the Apr. 2006 cruise, both DIC and TALK steadily increased from 1600±30 μmol kg⁻¹ at >200 km upstream of the estuary mouth to ~1870 μmol kg⁻¹ (DIC) and ~1985 μmol kg⁻¹ (TALK) around 40 km outside the estuary mouth (Fig. 3c, d). Even in 3 days during the survey period, we observed a significant decline of DIC/TALK upstream of the estuarine mixing zone (Fig. 3c, d). Such unsteady distributions are consistent with the characteristics of a transitional season as discussed below (Section 4.1).

The limited number of subsurface / bottom samples we collected in the inner estuary for DIC and TALK during Oct. 2005 (Fig. 3c, d) showed that, although salinity profiles suggested a well mixed system (Fig. 3a) and DIC had only a minor enhancement (10–55 μmol kg⁻¹ more as compared with the surface water) in subsurface and bottom waters (8 m/12 m) (Fig. 3c), significant TALK increases of 80–120 μmol kg⁻¹ were observed in the subsurface/bottom waters (Fig. 3d).

3.4. Dissolved oxygen and bulk oxygen consumption rate

Fig. 4 shows that surface DO varied to a large extent, from as low as 55% to 100%, in the region influenced by the HPJ. Upstream of the HPJ outlet region, DO ranged 84%–91% in transitional and flood seasons and 93%–97% in the dry season (Dec. 2005) (Fig. 4, Table 2). The limited vertical profiles in Oct. 2005 (see Fig. 3 for location reference) showed that DO was vertically homogeneous in the upper reaches of the Changjiang Estuary (data not

shown). Outside the estuary mouth, DO gradually increased to ~95%–105% in Dec. 2005, Jan. 2006 and Apr. 2006. In Oct. 2005, DO in the outer estuary varied significantly but still was not higher than 107% (Fig. 4a).

Fig. 5 presents our on-deck incubation results for the Changjiang River water. Compared with nearly constant DO concentration in the control, all the non-poisoned samples showed DO consumption during the 27–28 hours of incubation. Logarithmic DO declined linearly with incubation time (Fig. 5), which suggests that our assumption for pseudo first order DO consumption was valid. The slopes presented in Fig. 5 are pseudo first order reaction quotients for the incubations, i.e. -0.012 day⁻¹ in Dec. 2005 (dry/cold season) and -0.029 day⁻¹ in Oct. 2005 (wet/warm season). Based on the pseudo first order reaction quotients and field DO concentration, we further estimated field bulk oxygen consumption rates for the river water in these three seasons as 6.9 (Oct. 2005) and 4.2 (Dec. 2005)

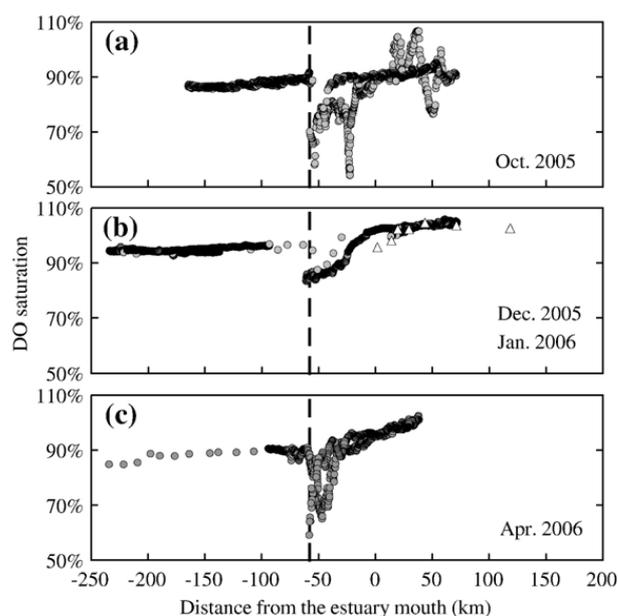


Fig. 4. Saturation of surface DO in Oct. 2005 (a), Dec. 2005/Jan. 2006 (b) and Apr. 2006 (c) along the transect surveyed in the Changjiang Estuary and adjacent waters. Data for the Huangpujiang River are not included.

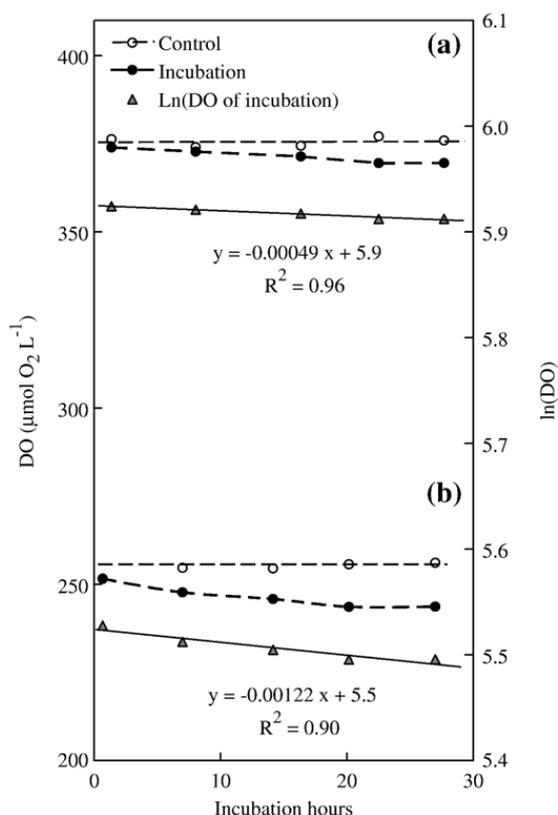


Fig. 5. Changes in DO concentration with time during incubation for river end bulk oxygen consumption rate conducted in Dec. 2005 (a) and Oct. 2005 (b).

$\text{mmol O}_2 \text{ m}^{-3} \text{ day}^{-1}$. These measurements gave us a first-order estimation of the weak/moderate respiration rate in the region.

In the HPJ, surface DO saturation ranged mostly from 20%–40% (although it could be as low as $\sim 8\%$) in the Sep.–Oct. 2005 survey, 70%–87% in the Dec. 2005 survey and 40%–60% in the Apr. 2006 survey. The pseudo first order oxygen consumption quotients for incubation experiments in the HPJ were -0.27 day^{-1} in Sep.–Oct. 2005 and -0.06 day^{-1} in the Dec. 2005 surveys, i.e. 5–10 times higher than the Changjiang River but lower than the upper reach of the Pearl River Estuary (-0.29 day^{-1} in May 2001, Zhai et al., unpublished data; -0.72 day^{-1} in Feb. 2004, Dai et al., 2006). The in situ oxygen consumption rates were calculated as 16–17 $\text{mmol O}_2 \text{ m}^{-3} \text{ day}^{-1}$ in both Sep.–Oct. 2005 (DO $\sim 60 \mu\text{mol O}_2 \text{ kg}^{-1}$) and Dec. 2005 (DO $\sim 285 \mu\text{mol O}_2 \text{ kg}^{-1}$) surveys.

4. Discussion

4.1. Carbonate system during water mixing

When DIC and TALK were plotted against salinity (Fig. 6), we observed overall conservative behavior in

the dry season for both parameters, with much less data variability as compared to prior measurements (e.g. Cauwet, 1990; Cauwet and Mackenzie, 1993). In transitional and flood seasons, DIC vs. salinity plots did not follow a straight conservative mixing curve (Fig. 6a), due likely to water end-member shift given the fact that DO was nearly in equilibrium (Fig. 4) and thereby did not support the biological uptake of inorganic carbon. Note that as high as $\sim 190\%$ DO saturation was observed outside the estuary mouth in Aug.–Sep. 2003 (Chen et al., accepted for publication), which was apparently induced by an algal bloom in the Changjiang Estuary occurring typically in May through August (Chen et al., 2003) and probably accompanied with substantially biological uptake of inorganic carbon (Dai et al., accepted for publication). A significant shift of the TALK mixing curve was also shown for the Aug.–Sep. 2003 cruise, during which the seawater end-member of the Sep. 2003 survey was $>100 \mu\text{mol kg}^{-1}$ higher than the Aug. 2003 survey (Fig. 6b). This reveals the complexity of water mixing in the outer estuary of

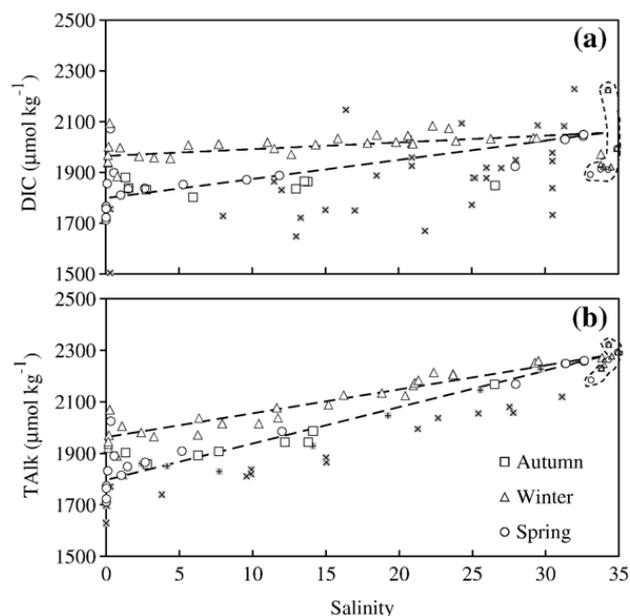


Fig. 6. DIC vs. salinity (a) and TALK vs. salinity (b) in the estuarine mixing zone. Shaded \times in panel (a) show data from Jul. 1986 (Cauwet and Mackenzie, 1993). Shaded \times and $+$ in panel (b) show data from two outer estuary surveys conducted on Aug. 2003 and Sep. 2003, respectively. Broken straight lines indicate conservative mixing lines of recent cruises based on a simple two end-member mixing model. The upper lines in both panels correspond to the Dec. 2005 and Jan. 2006 cruises, while the lower lines correspond to Oct. 2005 and Apr. 2006 cruises. Mixing lines of the Aug.–Sep. 2003 cruise are not shown. Plots in broken curves are DIC/TALK in different ECS water masses in summer (circles) and in winter (triangles) based on Chen and Wang (1999).

the Changjiang River among different water masses in the shelf region (Chen and Wang, 1999).

To further analyze the carbonate system during estuarine mixing, especially for the inner estuary (inside the estuary mouth) and the river end where salinity was ~ 0 , we plotted DIC against TALK (Fig. 7). Within this region, surface DIC was generally conservative. DIC vs. TALK mostly followed a linear 1:1 relationship and scarcely departed from the 1:1 line. The exceptions were in the HPJ impacted area (DIC:TALK > 1) and in subsurface / bottom waters (DIC:TALK < 1). Since free CO_2 concentration should be several times higher than CO_3^{2-} ions in the fresh waters at pH ~ 8 , the fact that the DIC signal was close to that of TALK shown in Fig. 7 may demonstrate notable non-carbonate alkalinity in the river end and inner estuary. Based on the surface DIC, TALK and pH data shown in Table 2, using carbonate dissociation constants compiled by Cai and Wang (1998), and re-examined by field $p\text{CO}_2$, we estimated that the non-carbonate alkalinity may be in the order of $20\text{--}60 \mu\text{mol kg}^{-1}$ (representing 1.0%–3.5% of TALK) in the river end and the inner estuary. Note that the ratio of DIC increase to TA increase ($55/120 \sim 0.5$) of depth

samples during Oct. 2005 (Fig. 3c, d) may have been a signal related to CaCO_3 dissolution in the sediment of this turbid estuary, which needs further investigation however. In the outer estuary, DIC mixing was much more complicated as noted above.

It is fairly obvious that DIC–TALK plots in the HPJ were different from those in the Changjiang Estuary. The differences between DIC and TALK varied from ~ 0 at locations near the Changjiang River to a maximum of $\sim 120 \mu\text{mol kg}^{-1}$ (Fig. 7), which was basically (but not exactly) consistent with the high $p\text{CO}_2$ of $1000\text{--}4500 \mu\text{atm}$ in the HPJ (Table 1). Although we did not actually get the upstream end-member of the HPJ, we observed significant addition of DIC during the mixing in Dec. 2005 (Fig. 7).

4.2. DIC export from the Changjiang River

In order to evaluate DIC export from the Changjiang River, we needed to examine the relationship between DIC and water discharge rate. Although Chen et al. (2002) reported that the long-term variation of TALK concentration upstream of the Changjiang Estuary (at the Datong Station) has a negative correlation with the water discharge, the minimum monthly average TALK at the station actually occurs in April, i.e. three months before the water discharge peak in July (Chen et al., 2002). Fig. 8 shows that our upstream TALK and DIC data were not a monofonic function of water discharge. If we plotted monthly average TALK at the Datong Station against the monthly water discharge rate (Fig. 8a) based on Liu et al. (2002), the intra-annual variation of TALK was found to be significantly controlled by the annual hydrological cycle in the overall drainage basin.

The most likely reason for such a pattern is that melt waters from the upriver Qinghai–Tibet mountains (Fig. 1a) played a major role on chemical properties of the river. As indicated by Shen (2001), a time lag exists between the flood seasons in the upper river part (limestone rich) and the flood seasons in the central and lower river parts (limestone poor). The peak flood months of the central and lower parts of the Changjiang River watershed are mostly in May and June, while the peak flood months of the upper part are always in July and August. As shown in Fig. 8a, from January to April, TALK (also DIC) concentrations declined along with the water discharge increase, which may have resulted from the dilution effect of runoff from the limestone-lacking central and lower parts of the Changjiang River watershed. From May to July, the riverhead region supported more and more runoff together with abundant carbonate into the Changjiang River. Therefore TALK and DIC

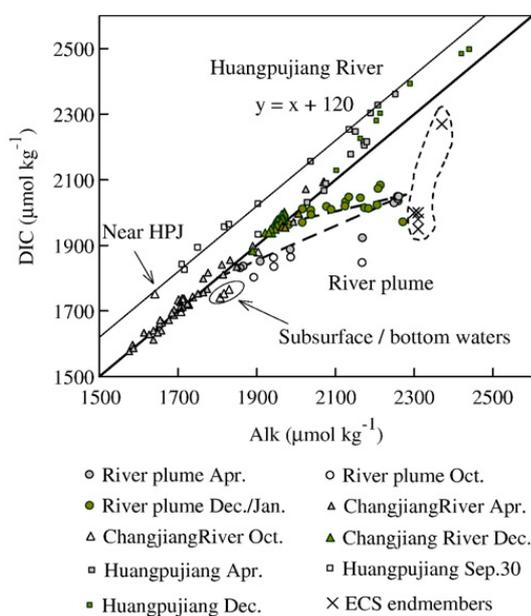


Fig. 7. DIC vs. TALK in the Changjiang Estuary and the adjacent Huangpujiang River. Circles denote seasonal data outside the estuary mouth, i.e. in the outer estuary/river plume. Triangles show the seasonal data in the inner estuary and river end of the Changjiang River, while squares represent seasonal data in the Huangpujiang River. Cross symbols in the broken circle sketch characteristics of different ECS water masses reported by Chen and Wang (1999). The thin solid line parallel to the thick 1:1 line provides a mark of DIC–TALK = $120 \mu\text{mol kg}^{-1}$. The two broken straight lines indicate conservative mixing lines of two end-members, which are also referenced to Fig. 4.

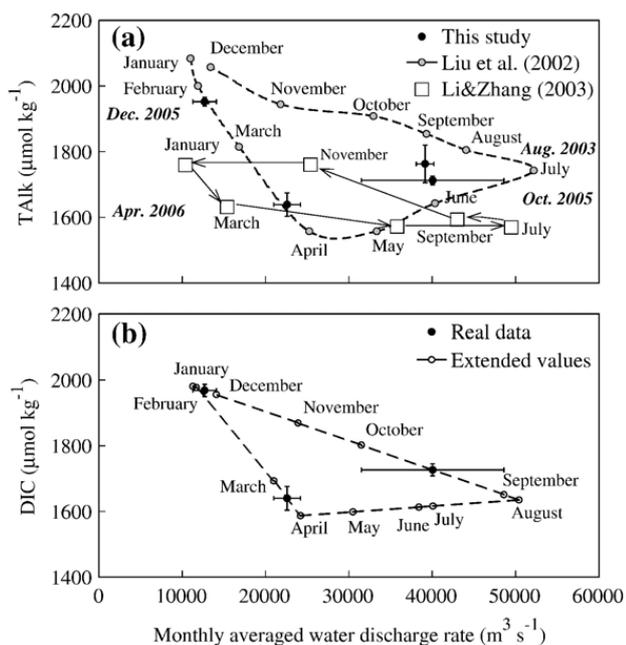


Fig. 8. Monthly TALK vs. water discharge rate (a) and DIC concentration vs. water discharge rate (b) in a year. Black circles with error bars are upstream TALK (a) and DIC (b) data in this study (refer to Table 2). Error bars for water discharge rate are extreme differences between the neighboring monthly averaged water discharge rates. Error bars for TALK/DIC are standard errors. In panel (a), the grey circles connected with a broken line are long-term averaged TALK data from the Datong Station (~640 km upstream of the estuary mouth) during the period 1963–1999 (Liu et al., 2002), which is as a whole consistent with Chen et al. (2002), while the squares are averaged TALK data from another sampling site around Nantong (~180 km upstream of the estuary mouth) during the period 1996–2001 (Li and Zhang, 2003). Grey circles connected with broken lines in panel (b) show the inferred monthly data for the hydrological year Jul. 2005–Jun. 2006.

slightly increased along with water discharge until the water discharge rose to its highest value. From July to December, both chemical weathering and dilution were important in modulating TALK and DIC in the Changjiang River.

TALK data collected from another sampling site around Nantong (~180 km upstream of the estuary mouth) during the period 1996–2001 (Li and Zhang, 2003) also show a similar seasonal cycle of TALK (Fig. 8a), although the data of Li and Zhang (2003) are generally lower than those from Liu et al. (2002). Such a seasonal pattern of DIC vs. water discharge may be typical for Himalayan rivers. For example, in India, a similar DIC variation of low flow > high flow > median flow has been reported in some Himalayas-rooted tributaries of the tropical Godavari River (Sarin et al., 2002).

Our data were overall consistent with the long-term average for the Datong Station (Liu et al., 2002), despite the fact that our more recent TALK data for flood seasons were lower (Fig. 8a). Based on the relationship between

TALK (also DIC) and water discharge shown in Fig. 8a, and using the updated monthly water discharge dataset from the Hydrological Information Centre of China, we extended our DIC dataset from three cruises to twelve months of the year (Jul. 2005–Jun. 2006; Fig. 8b), which was consistent with the Aug. 2003 data. The major uncertainty may come from the three peak flood months between July and September. Since the Three-Gorges Dam project modulated the peak flood month(s) from what was previously July to currently August–September (Fig. 2), TALK and DIC in these peak flood months may be different from what they used to be (Fig. 8). If the extrapolated data in Fig. 8b are valid for the hydrological year under survey, the DIC export flux of the Changjiang River should have been $\sim 1.54 \times 10^{12} \text{ mol yr}^{-1}$, which was consistent with the Liu et al. (2002) long-term TALK export estimate of $1.6 \pm 0.4 \times 10^{12} \text{ mol yr}^{-1}$ for the Datong Station during the period 1963–1999 and the estimated TALK export of $1.53 \times 10^{12} \text{ mol yr}^{-1}$ by Li and Zhang (2003) for the Nantong site during the period 1996–2001.

4.3. Water–air CO₂ flux estimation

In order to estimate water–air CO₂ fluxes in the Changjiang Estuary, we divided the water areas in the region into five parts (Table 1). Although the most significant variation of water–air $\Delta p\text{CO}_2$ may have been as large as $\pm 50\%$ (Table 1), the greatest uncertainty for the water–air CO₂ flux estimation came from the gas exchange coefficient. The reported formulae gave significantly different transfer coefficients under the same wind speed. At low to moderate wind speed ($< 4 \text{ m s}^{-1}$), Wanninkhof (1992) gives a lower to moderate value, Raymond and Cole (2001) give a moderate to higher

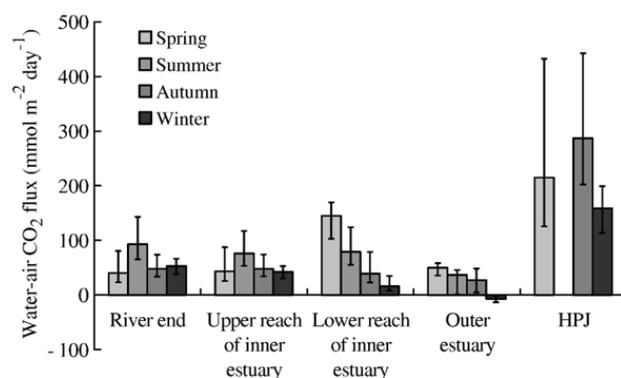


Fig. 9. Seasonal water–air CO₂ flux estimates for different zones in the Changjiang Estuary and the adjacent Huangpujiang River under survey. Note that the flux estimate for the outer estuary may be subject to larger errors given the fact that the river plume is a very heterogeneous environment that was not fully covered by the present surveys.

Table 3
CO₂ degassing flux estimation in the river end of the Changjiang Estuary

Survey dates	Averaged $\Delta p\text{CO}_2$ (μatm)	Wind speed u (m s^{-1})	k_{600} (cm h^{-1})			CO ₂ degassing flux ($\text{mmol m}^{-2} \text{day}^{-1}$)		
			W92 (0.31 u^2)	R&C01 (1.91 $e^{0.35u}$)	B04 (4.045 + 2.580 u)	W92	R&C01	B04
27–31 Aug. 2003	921 ^a	5 (0–8.0)	7.7 (0–19.8)	11.0 (1.9–31.4)	16.9 (4.0–24.7)	65.5 (0–168)	92.9 (16–266)	143.2 (34–209)
06–07 Oct. 2005	470	5 (1.7–8.2)	7.7 (0.9–20.8)	11.0 (3.5–33.7)	16.9 (8.4–25.2)	33.7 (3.9–91)	47.8 (15–147)	73.8 (36–110)
26–28 Dec. 2005	343	6 (2.4–9.0)	11.2 (1.8–25.1)	15.6 (4.4–44.6)	19.5 (10.2–27.3)	37.8 (6.0–85)	52.9 (15–151)	66.2 (34–93)
05–07 Apr. 2006	645	3.5 (2.7–7.2)	3.8 (2.3–16.1)	6.5 (4.9–23.7)	13.1 (11.0–22.6)	23.5 (14–99)	40.2 (30–147)	80.9 (68–140)

^a Based on Chen et al. (accepted for publication).

value, while Borges et al. (2004a) give a maximum. This is based on the fact that gas transfer velocities in riverine/estuarine environments are mostly higher than those in the ocean for a same wind speed due to the higher level of near-surface turbulence (Abril et al., 2000; Zappa et al., 2003; Borges et al., 2004a,b). So, generally (but not always) we used Wanninkhof (1992) gas transfer velocities to provide the minimum estimates of the fluxes in the riverine and inner estuary environments, while those of Raymond and Cole (2001) and Borges et al. (2004a) were used to offer the middle and maximum estimates, respectively.

Fig. 9 summarizes the estimated water–air CO₂ fluxes based on field $p\text{CO}_2$ (Table 1) and wind speed data, and Table 3 presents the details for the river end including the temporal variability of these flux estimates potentially caused by the wind speed variation. Generally, the Changjiang Estuary was a significant source for atmospheric CO₂, except for the outer estuary in winter and during the summer bloom period. The riverine/estuarine CO₂ degassing fluxes in the Changjiang Estuary ranged mostly from 0 to 100 $\text{mmol m}^{-2} \text{day}^{-1}$. Exceptions existed in the HPJ, where the CO₂ degassing fluxes were estimated as 100–400 $\text{mmol m}^{-2} \text{day}^{-1}$ and were close to some European inner estuaries (100–760 $\text{mmol m}^{-2} \text{day}^{-1}$, 170 $\text{mmol m}^{-2} \text{day}^{-1}$ on average) (Frankignoulle et al., 1998). Based on these flux estimates and surface area data modified from Shen (2001), the total CO₂ degassing flux in the inner estuary of the Changjiang River ranged 2.5–5.5 $\times 10^{10}$ mol yr^{-1} in the inner estuary, representing 1.6%–3.6% of the DIC export from the Changjiang River into the ECS.

4.4. Contribution of the Huangpujiang River and Shanghai waters

The HPJ is a highly urbanized tributary of the Changjiang Estuary collecting most of the sewage and

runoffs from the metropolitan Shanghai. This region is highly polluted and was characterized by 1000–4600 $\mu\text{atm } p\text{CO}_2$ (Table 1) and higher DIC than the Changjiang River (Fig. 7). Annually, the HPJ has an $\sim 11 \times 10^9$ m^3 water discharge (Zhu et al., 2004) carrying $\sim 2.3 \times 10^{10}$ mol DIC into the Changjiang River, representing $\sim 1.5\%$ of the DIC export from the Changjiang River, and leading to the significant $p\text{CO}_2$ /DIC peaks along our main transect around the HPJ outlet (Fig. 3), and $<20\%$ increase in the average $p\text{CO}_2$ in the Changjiang Estuary (Table 1). However, both the $p\text{CO}_2$ and DIC peaks were quickly diluted by the huge amount of Changjiang water (Fig. 3).

We have surveyed ~ 60 km (~ 600 m wide) of the HPJ, which accounts for $\sim 55\%$ of the whole length and $\sim 30\%$ of the total surface area of Shanghai waters (~ 122 km^2 according to Management Zoning 2005 for Sea Areas in Shanghai, <http://www.eastsea.gov.cn/>). Simply extrapolating the CO₂ degassing flux from the HPJ (Fig. 9) to the entire inland waters of Shanghai, a CO₂ emission flux of 0.65–1.6 $\times 10^{10}$ mol yr^{-1} was obtained, which was equal to 20%–30% of the CO₂ degassing from the inner Changjiang Estuary.

4.5. Biogeochemical processes influencing the river end carbonate system and water–air CO₂ fluxes

It is obvious that net respiration during a two end-member mixing will result in a positive departure from the DIC–TALK linear relationship and net photosynthesis will result in a negative departure (Dai et al., accepted for publication). During these surveys both respiration and photosynthesis may have been at a steady state at the river end and inner estuary (Fig. 7). Aqueous photosynthesis should have been at a low level given the highly turbid environment of the Changjiang downstream waters, with a suspended solid content of 240–400 mg L^{-1} (Li and Zhang,

2003), while the surface bacterial respiration rate around the estuary mouth mostly ranged between $4 \text{ mmol O}_2 \text{ m}^{-3} \text{ day}^{-1}$ (in winter) and $11 \text{ mmol O}_2 \text{ m}^{-3} \text{ day}^{-1}$ (in summer) (Courties et al., 1990, with uncertainties of 50%–150%), which was also a very low level and consistent with our bulk oxygen consumption rates in Oct. 2005 and in Dec. 2005. Assuming that aqueous organic carbon was aerobically respired at a rate of $4\text{--}11 \text{ mmol O}_2 \text{ m}^{-3} \text{ day}^{-1}$ and using the Redfield ratio, the daily DIC production should have been at the very low level of $3\text{--}8.5 \text{ mmol m}^{-3} \text{ day}^{-1}$. If we use the average upstream water depth of $\sim 8 \text{ m}$ (Shen, 2001) and assume again that the aqueous primary production was negligible, the water column integrated DIC production rate would be $24\text{--}68 \text{ mmol m}^{-2} \text{ day}^{-1}$, which was almost in equilibrium with the CO_2 degassing fluxes in Oct. 2005, Dec. 2005 and Apr. 2006 (Table 3). Therefore, aerobic respiration was overall sufficient to support CO_2 degassing fluxes in the upper reaches of the Changjiang Estuary, although other processes may also have contributed to the Aug. 2003 CO_2 degassing (Table 3).

In the HPJ, the in situ oxygen consumption rate of $16\text{--}17 \text{ mmol O}_2 \text{ m}^{-3} \text{ day}^{-1}$ in both the Sep.–Oct. 2005 and Dec. 2005 surveys led to an aerobic respiration induced DIC production of $12\text{--}13 \text{ mmol m}^{-3} \text{ day}^{-1}$ (based on the Redfield ratio), or a water column integrated value of $60\text{--}130 \text{ mmol C m}^{-2} \text{ day}^{-1}$ (given an average water depth of $5\text{--}10 \text{ m}$). This was substantially lower than the degassing fluxes of $100\text{--}400 \text{ mmol m}^{-2} \text{ day}^{-1}$ (Fig. 9). This fact suggested that, although aerobic respiration in the water column may have acted as an important CO_2 supplier of the HPJ, other processes must have contributed to the CO_2 production and the DIC addition in Dec. 2005 as shown in Fig. 7. Since the surface DO was still 20%–90% saturated in the field, sediment anaerobic processes may have contributed, but this needs further investigation.

5. Conclusions

This study showed that the annual average CO_2 degassing flux from the Changjiang inner estuary, exclusive of the highly urbanized HPJ and inland Shanghai waters, was at a moderate level of $15.5\text{--}34.2 \text{ mol m}^{-2} \text{ yr}^{-1}$, which was higher than in some Indian inner estuaries ($5\text{--}14 \text{ mol m}^{-2} \text{ yr}^{-1}$) but lower than in many polluted European inner estuaries ($31\text{--}76 \text{ mol m}^{-2} \text{ yr}^{-1}$) as summarized by Borges et al. (2005). The total CO_2 degassing flux in the inner estuary of the Changjiang River ranged $2.5\text{--}5.5 \times 10^{10} \text{ mol yr}^{-1}$ representing 1.6%–3.6% of the DIC export from the Changjiang River into the ECS. Even if we considered

the contribution of the highly urbanized HPJ and all of the inland Shanghai waters, this ratio only increased to 2.0%–4.6%.

In a global context, $\sim 0.4 \text{ Gt C yr}^{-1}$ (i.e. $33 \times 10^{12} \text{ mol yr}^{-1}$) of terrestrial DIC derived mostly from the weathering of limestone is exported by riverine systems (Prentice et al., 2001; Richey et al., 2002). This study shows that, although the Changjiang DIC export was significant and accounted for $\sim 5\%$ of the global terrestrial DIC export, its estuarine CO_2 degassing level was much lower than some well-documented urbanized riverine–estuarine systems. This study demonstrates again that riverine/estuarine CO_2 degassing may vary in different systems and/or under different environmental conditions and that much remains to be investigated in order to quantitatively evaluate the significance of riverine and estuarine CO_2 outgassing on a global scale.

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References

- Abril, G., Etcheber, H., Borges, A.V., Frankignoulle, M., 2000. Excess atmospheric carbon dioxide transported by rivers into the Scheldt estuary. *C. R. Acad. Sci., II A* 330, 761–768.
- Borges, A.V., 2005. Do we have enough pieces of the jigsaw to integrate CO_2 fluxes in the coastal ocean? *Estuaries* 28, 3–27.
- Borges, A.V., Vanderborcht, J.-P., Schiettecatte, L.-S., Gazeau, F., Ferrón-Smith, S., Delille, B., Frankignoulle, M., 2004a. Variability of gas transfer velocity of CO_2 in a macrotidal estuary (the Scheldt). *Estuaries* 27, 593–603.
- Borges, A.V., Delille, B., Schiettecatte, L.-S., Gazeau, F., Abril, G., Frankignoulle, M., 2004b. Gas transfer velocities of CO_2 in three European estuaries (Randers Fjord, Scheldt, and Thames). *Limnol. Oceanogr.* 49, 1630–1641.
- Borges, A.V., Delille, B., Frankignoulle, M., 2005. Budgeting sinks and sources of CO_2 in the coastal ocean: diversity of ecosystems counts. *Geophys. Res. Lett.* 32, L14601. doi:10.1029/2005GL023053.
- Bouillon, S., Frankignoulle, M., Dehairs, F., Velimirov, B., Eiler, A., Abril, G., Etcheber, H., Borges, A.V., 2003. Inorganic and organic carbon biogeochemistry in the Gautami Godavari estuary (Andhra

- Pradesh, India) during pre-monsoon: the local impact of extensive mangrove forests. *Glob. Biogeochem. Cycles* 17, 1114. doi:10.1029/2002GB002026.
- Cai, W.-J., 2003. Riverine inorganic carbon flux and rate of biological uptake in the Mississippi River plume. *Geophys. Res. Lett.* 30, 1032. doi:10.1029/2002GL016312.
- Cai, W.-J., Wang, Y.C., 1998. The chemistry, fluxes and sources of carbon dioxide in the estuarine waters of the Satilla and Altamaha Rivers, Georgia. *Limnol. Oceanogr.* 43, 657–668.
- Cai, W.-J., Dai, M.H., Wang, Y.C., Zhai, W.D., Huang, T., Chen, S.T., Zhang, F., Chen, Z.Z., Wang, Z.H., 2004. The biogeochemistry of inorganic carbon and nutrients in the Pearl River estuary and the adjacent Northern South China Sea. *Cont. Shelf Res.* 24, 1301–1319.
- Cauwet, G., 1990. Distribution and behaviour of organic and inorganic carbon in the Changjiang Estuary. In: Yu, G.H., Martin, J.M., Zhou, J.Y. (Eds.), *Biogeochemical Study of the Changjiang Estuary — Proceedings of the International Symposium on Biogeochemical Study of the Changjiang Estuary and Its Adjacent Coastal Waters of the East China Sea*, Mar. 21–25, 1988 (Hangzhou). China Ocean Press, Beijing, pp. 570–588.
- Cauwet, G., Mackenzie, F.T., 1993. Carbon input and distribution in estuaries of turbid rivers: the Yang Tze and Yellow rivers (China). *Mar. Chem.* 43, 235–246.
- Chen, C.T.A., Wang, S.L., 1999. Carbon, alkalinity and nutrient budget on the East China Sea continental shelf. *J. Geophys. Res.* 104, 20675–20686.
- Chen, J.S., Wang, F.Y., Xia, J.H., Zhang, L.T., 2002. Major element chemistry of the Changjiang (Yangtze River). *Chem. Geol.* 187, 231–255.
- Chen, C., Zhu, J., Beardsley, R.C., Franks, P.J.S., 2003. Physical–biological sources for dense algal blooms near the Changjiang River. *Geophys. Res. Lett.* 30, 1515. doi:10.1029/2002GL016391.
- Chen, C.T.A., Zhai, W.D., Dai, M.H., accepted for publication. Riverine input and air–sea CO₂ exchanges near the Changjiang (Yangtze) River Estuary: status quo and implication on possible future changes in metabolic status. *Cont. Shelf Res.*
- Cole, J.J., Caraco, N.F., 2001. Carbon in catchments: connecting terrestrial carbon losses with aquatic metabolism. *Mar. Freshw. Res.* 52, 101–110.
- Courties, C., Shi, J., Ning, X., Chen, Z., 1990. Seasonal variations in the respiration rates at the Changjiang Estuary and the adjacent East China Sea — Relations with bacterial numbers and chlorophyll a concentrations. In: Yu, G.H., Martin, J.M., Zhou, J.Y. (Eds.), *Biogeochemical Study of the Changjiang Estuary — Proceedings of the International Symposium on Biogeochemical Study of the Changjiang Estuary and Its Adjacent Coastal Waters of the East China Sea*, Mar. 21–25, 1988 (Hangzhou). China Ocean Press, Beijing, pp. 156–172.
- Dai, A.G., Trenberth, K.E., 2002. Estimates of freshwater discharge from continents: latitudinal and seasonal variations. *J. Hydrometeorol.* 3, 666–687.
- Dai, M.H., Guo, X.H., Zhai, W.D., Yuan, L.Y., Wang, B.W., Wang, L.F., Cai, P.H., Tang, T.T., Cai, W.-J., 2006. Oxygen depletion in the upper reach of the Pearl River estuary during a winter drought. *Mar. Chem.* 102, 159–169.
- Dai, M.H., Zhai, W.D., Cai, W.-J., Callahan, J., Huang, B.Q., Shang, S.L., Huang, T., Li, X.L., Lu, Z.M., Chen, W.F., Chen, Z.Z., accepted for publication. Effects of an estuarine plume-associated bloom on the carbonate system in the lower reaches of the Pearl River estuary and the coastal zone of the northern South China Sea. *Cont. Shelf Res.*
- Frankignoulle, M., Borge, I., Wollast, R., 1996. Atmospheric CO₂ fluxes in a highly polluted estuary (the Scheldt). *Limnol. Oceanogr.* 41, 365–369.
- Frankignoulle, M., Abril, G., Borges, A., Bourge, I., Canon, C., Delille, B., Libert, E., Théate, J.-M., 1998. Carbon dioxide emission from European estuaries. *Science* 282, 434–436.
- Gaillardet, J., Dupré, B., Louvat, P., Allègre, C.J., 1999. Global silicate weathering and CO₂ consumption rates deduced from the chemistry of large rivers. *Chem. Geol.* 159, 3–30.
- Gong, G.C., Chang, J., Chiang, K.P., Hsiung, T.M., Hung, C.C., Duan, S.W., Codispoti, L.A., 2006. Reduction of primary production and changing of nutrient ratio in the East China Sea: effect of the Three Gorges Dam? *Geophys. Res. Lett.* 33, L07610. doi:10.1029/2006GL025800.
- Hellings, L., Dehairs, F., Van Damme, S., Baeyens, W., 2001. Dissolved inorganic carbon in a highly polluted estuary (the Scheldt). *Limnol. Oceanogr.* 46, 1406–1414.
- Körtzinger, A., 2003. A significant CO₂ sink in the tropical Atlantic Ocean associated with the Amazon River plume. *Geophys. Res. Lett.* 30, 2287. doi:10.1029/2003GL018841.
- Li, J.Y., Zhang, J., 2003. Variations of solid content and water chemistry at Nantong station and weathering processes of the Changjiang watershed. *Resour. Environ. Yangtze Basin* 12, 363–369 (in Chinese).
- Liu, X.C., Shen, H.T., Huang, Q.H., 2002. Concentration variation and flux estimation of dissolved inorganic nutrient from the Changjiang River into its estuary. *Oceanol. Limnol. Sin.* 33, 332–340 (in Chinese).
- Mukhopadhyay, S.K., Biswas, H., De, T.K., Sen, S., Jana, T.K., 2002. Seasonal effects on the air–water carbon dioxide exchange in the Hooghly estuary, NE coast of Bay of Bengal, India. *J. Environ. Monit.* 4, 549–552.
- Prentice, I.C., Farquhar, G.D., Fasham, M.J.R., Goulden, M.L., Heimann, M., Jaramillo, V.J., Khesghi, H.S., Le Quééré, C., Scholes, R.J., Wallace, D.W.R., 2001. The carbon cycle and atmospheric carbon dioxide. In: Houghton, J.T., Ding, Y., Griggs, D.J., Noguer, M., van der Linden, P.J., Dai, X., Maskell, K., Johnson, C.A. (Eds.), *Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, Cambridge, pp. 185–237.
- Raymond, P.A., Cole, J.J., 2001. Gas exchange in rivers and estuaries: choosing a gas transfer velocity. *Estuaries* 24, 312–317.
- Richey, J.E., Melack, J.M., Aufdenkampe, A.K., Ballester, V.M., Hess, L.L., 2002. Outgassing from Amazonian rivers and wetlands as a large tropical source of atmospheric CO₂. *Nature* 416, 617–620.
- Sarma, V.V.S.S., Kumar, M.D., Manerikar, M., 2001. Emission of carbon dioxide from a tropical estuarine system, Goa, India. *Geophys. Res. Lett.* 28, 1239–1242.
- Sarin, M.M., 2001. Biogeochemistry of Himalayan rivers as an agent of climate change. *Curr. Sci.* 81, 1446–1450.
- Sarin, M.M., Sudheer, A.K., Balakrishna, K., 2002. Significance of riverine carbon transport: a case study of a large tropical river, Godavari (India). *Sci. China Ser. C* 45, 97–108 (suppl).
- Shen, H.T., 2001. Material flux of the Changjiang Estuary. China Ocean Press, Beijing. 176 pp (in Chinese).
- Shen, H.T., Pan, D.A., 2001. A Turbidity Maximum in the Changjiang Estuary. China Ocean Press, Beijing. 194 pp (in Chinese).
- Su, Z., Zhang, L.J., Wang, X.J., 2005. Influencing factors of partial pressure of CO₂ in Huanghe (Yellow) River. *Mar. Sci.* 29 (4), 41–44 (in Chinese).
- Ternon, J.F., Oudot, C., Dessier, A., Diverres, D., 2000. A seasonal tropical sink for atmospheric CO₂ in the Atlantic Ocean: the role of the Amazon River discharge. *Mar. Chem.* 68, 183–201.

- Thomas, H., Schneider, B., 1999. The seasonal cycle of carbon dioxide in Baltic Sea surface waters. *J. Mar. Syst.* 22, 53–67.
- Xu, Z.X., Yin, H.L., 2003. Study on Huangpu River pollution amelioration. *Shanghai Environ. Sci.* 22, 167–170 (in Chinese).
- Wang, S.L., Chen, C.T.A., Hong, G.H., Chung, C.S., 2000. Carbon dioxide and related parameters in the East China Sea. *Cont. Shelf Res.* 20, 525–544.
- Wang, Y.P., Pan, S.M., Wang, H.V., Gao, J.H., Yang, C., Wang, A.J., Li, Z.H., Wu, Z., 2006. Measurements and analysis of water discharges and suspended sediment fluxes in Changjiang Estuary. *Acta Geogr. Sin.* 61 (1), 35–46 (in Chinese).
- Wanninkhof, R., 1992. Relationship between wind speed and gas exchange over the ocean. *J. Geophys. Res.* 97, 7373–7382.
- Weiss, R.F., 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Mar. Chem.* 2, 203–215.
- Zappa, C.J., Raymond, P.A., Terray, E.A., McGillis, W.R., 2003. Variation in surface turbulence and the gas transfer velocity over a tidal cycle in a macro-tidal estuary. *Estuaries* 26, 1401–1415.
- Zhai, W.D., Dai, M.H., Cai, W.-J., Wang, Y.C., Wang, Z.H., 2005. High partial pressure of CO₂ and its maintaining mechanism in a subtropical estuary: the Pearl River estuary, China. *Mar. Chem.* 93, 21–32.
- Zhu, Z.Y., Zhang, L.H., Zhou, J.Z., Zhang, J., 2004. Variation of nutrients in Suzhou and Huangpu River in spring and summer of 2002. *Mar. Environ. Sci.* 23 (4), 19–23 (in Chinese).