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High partial pressure of CO_2 and its maintaining mechanism in a subtropical estuary: the Pearl River estuary, China

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Abstract

We investigated distributions of surface water CO_2 partial pressure (pCO_2), dissolved oxygen (DO) and associated carbonate parameters in the Pearl River estuary, a large subtropical estuary under increasingly anthropogenic pressure in China, in the summer of 2000 and late spring of 2001. pCO_2 levels, measured underway using a continuous measurement system, were high during both seasons, with levels of >4000 μatm at salinity <0.5. pCO_2 distribution overall mirrored DO across the salinity gradient. Using the linear relationship between excess CO_2 and apparent oxygen utilization (AOU) in surface water, we conclude that aerobic respiration is the most important process in maintaining such high pCO_2 measured upstream. The material being respired is likely in a close association with the organic pollutants discharged into the system. Based on the measured excess CO_2 vs. AOU plots, we estimate that the upper limit of pCO_2 should be ~7000 μatm in the Pearl River estuary assuming that CO_2 was produced solely by aerobic respiration.

Keywords: Carbon dioxide; Carbon cycle; Respiration; Outgassing; Estuary; China; Pearl River estuary

1. Introduction

Recent observations have shown that river–estuary systems may release a significant amount of CO_2 into the atmosphere in addition to the commonly recognized fluvial export of inorganic/organic matter. Very high partial pressure of CO_2 (pCO_2, 2000–8000 μatm in the mainstream, >10 000 μatm in some tributaries) and significant outgassing of CO_2 have been reported for the Amazon River (Devol et al., 1987; Richey et al., 2002). In some U.S. estuaries, high pCO_2 values of 1000–6000 μatm were also reported (Cai and Wang, 1998; Raymond et al., 2000 and references therein). In Asia, aqueous pCO_2 of 800–2000 μatm was observed in mixing zones of the

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Changjiang (Yangtze) River estuary (Zhang et al., 1999), of the Mandovi–Zuari estuarine system (Sarma et al., 2001) and of Hooghly estuary on the Ganges Delta during the pre-monsoon season (Mukhopadhyay et al., 2002). Most significantly, Frankignoulle et al. (1998) estimated that CO_2 outgassed from European estuaries is equivalent to 5–10% of the present anthropogenic CO_2 emission from Western Europe, signifying the substantial contribution of estuarine systems to the global carbon cycle.

The mechanism(s) by which estuarine systems can sustain such high levels of pCO_2 are not well understood. Current knowledge of estuarine dynamics provides possible solutions to this problem. Firstly, estuarine tidal processes may increase water residence time in the estuarine mixing zone, which leads to more thorough decomposition of labile organic matter. Secondly, high turbidity, especially at the turbidity maximum zone, limits primary productivity and the associated CO_2 consumption. Lastly but not the least, anthropogenic organic matter can enhance the respiration rate and hence CO_2 production. All of these features increase the potential for biogenic gas production in estuaries (Frankignoulle and Middelburg, 2002). The negative correlation between pCO_2 and oxygen saturation in surface waters was observed in European (Frankignoulle et al., 1998) and U.S. estuaries (Cai et al., 1999). Cai and Wang (1998) argued that the combined effects of pelagic and benthic respiration, photodegradation, and the mixing of seawater and acidic river water were insufficient to sustain the high pCO_2 values and thereby high water-to-air fluxes in the estuaries they studied. They suggested that CO_2 input from organic carbon respiration in the tidally flooded salt marshes control the CO_2 concentration. This explanation is consistent with a subsequent mass balance study of biogenic gases (Cai et al., 1999).

In summary, the significance of riverine and estuarine CO_2 outgassing on a global scale needs to be investigated based upon regional studies. Tropical and subtropical river/estuary systems are expected to have high respiration rates and likely also the CO_2 outgassing fluxes due primarily to the high temperature therein. On the other hand, data are usually at paucity especially for Asian rivers. In this paper, we report for the first time direct measurements of high pCO_2 in the Pearl River estuary, a large subtropical estuarine system in China. Special attention will be given to examine processes that may be responsible for the observed high pCO_2.

2. Study area

The Pearl River has a drainage area of 4.5×10^5 km^2 and an annual water discharge of ~3.26×10^{11} m^3. It is the 13th largest river in the world and ranks the largest in southern China. The drainage area of the Pearl River has a sub-tropical climate, with a long summer and a short winter with annual rainfall of 1470 mm. Eighty percent of the river discharge takes place in the wet season from April to September (PRWRC/PRRCC, 1991).

The Pearl River has three major tributaries (Fig. 1a), Xijiang (West River), Beijiang (North River) and Dongjiang (East River). Both the East River and the North River are relatively small, contributing 22.8% of the total discharge, while the West River accounts for 68.5% (PRWRC/PRRCC, 1991). Since the upper reaches of the West River flow through an area characterized by carbonate rock weathering, its bicarbonate concentration is higher than that in other tributaries (Chen and He, 1999). These tributaries all pour into the netlike Pearl River Delta. All runoff of the three major tributaries and many other streams around the Pearl River Delta are distributed among numerous water channels and then discharged into the South China Sea (SCS) via eight major outlets. Although the mainstream of the West River discharge is released via the Modaomen outlet (Fig. 1a), previous investigations have focused on the four eastern outlets (namely Humen, Jiaomen, Hongqimen, and Hengmen). These four eastern outlets mainly collect the runoff from the East River and the North River and some other small rivers as well as a portion of the West River. These outlets account for >53% of the overall discharge of the Pearl River (PRWRC/PRRCC, 1991; Cheng, 2001). All discharges from the eastern four outlets pour into the largest sub-estuary in the Pearl River Delta, namely Lingdingyang Bay (Fig. 1b). The commonly called “Pearl River Estuary” refers to the Lingdingyang Bay and its outer water.

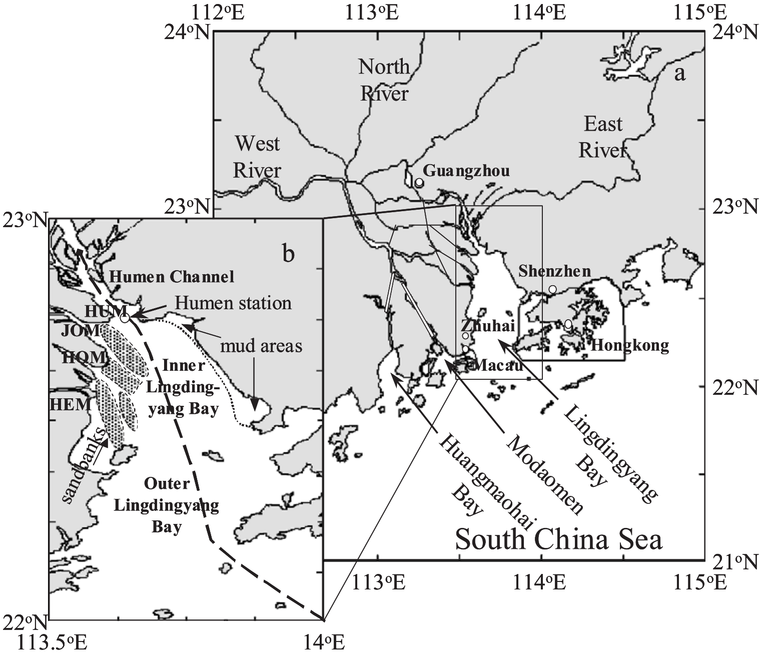

Fig. 1. Maps of the area under study (see text for detail explanations). Our main transect (dashed line) is shown in panel b, along which all underway pumping experiments and discrete water sampling were conducted. HUM—Humen Outlet; JOM—Jiaomen Outlet; HQM—Hongqimen Outlet; HEM—Hengmen Outlet.

The Pearl River Delta is one of the most highly developed regions in the world. It is surrounded by populated cities such as Hong Kong, Macau, Shenzhen and Zhuhai. Industrialization and urbanization that have been rapidly accelerated over the past two decades have created significant water pollution around the Delta. It is especially noteworthy that a highly industrialized metropolitan city, Guangzhou, has significant impact on Lingdingyang Bay through sewage discharge via the Humen water channel and outlet. Among the eastern four outlets, ~70% of organic pollutants are discharged into Lingdingyang Bay via Humen (Pang and Li, 2001). The oxygen-consuming pollutant is thereafter distributed in Lingdingyang Bay through hydrodynamic mixing (Chau and Jiang, 2002).

Over the past 30 years, Lingdingyang Bay has undergone extensive reclamation (Zhu, 2002) and/or silting (Cheng, 2001). Based on the latest navigation map (2002 edition), the area map plotted in Fig. 1b shows that some areas formerly underwater have become mud areas or sandbanks. According to Zhu (2002), from the 1970s through 1998 most of the sandbanks along the western side of Lingdingyang Bay were reclaimed as new lands. The updated total water area of the estuary is estimated to be 1350 km^2, much smaller than area datum cited by Han (1998) but consistent with that cited by Wong and Cheung (2000). Lingdingyang Bay is divided into two parts by two islands around the latitude of 22°25'N. The north part is designated Inner Lingdingyang Bay (Han, 1998). For the ease of discussion, we divide the estuary into three parts, namely Humen Channel, Inner Lingdingyang Bay and Outer Lingdingyang Bay (Fig. 1b). Navigation route of the Humen Channel (10–15 m) is deeper than the Inner Lingdingyang Bay (5–10 m). However, average water depth upstream the estuary is only 5–7 m (Wong and Cheung, 2000; Chau and Jiang, 2002).

3. Materials and methods

This study is a part of a CAR-TTT project (CARbon Transfer, Transport and Transformation) in the Pearl River estuary and the adjacent northern SCS.

Data were collected during two cruises on board the R/V Yanping II in the summer of 2000 (10 Jul–02 Aug) and late spring of 2001 (13 May–03 Jun). Both cruises took place during the wet season.

3.1. Sampling and analyses

During both cruises, we performed underway measurements for temperature, salinity, dissolved oxygen (DO) and $p\mathrm{CO}_2$ along a main transect (Fig. 1b).

Surface water was pumped from a side intake at a depth of ~2 m. Temperature and conductivity were measured continuously (recorded every 10 s, averaging to 1 min) using a SEACAT thermosalinograph system (CTD, SBE21, Sea-Bird) with an in situ temperature sensor. This underway CTD system was calibrated at Sea-Bird, just prior to our 2000 cruise. Surface water $p\mathrm{CO}_2$ and DO were determined using an underway system with continuous flow equilibrator (Fig. 2). YSI meters, YSI UPS600 (during the 2000 cruise) and YSI 6000UPG3-B-M-T (during the 2001 cruise) were used to continuously measure DO and temperature in the equilibrator (recorded every 1 min). The DO probe was calibrated against water-saturated air. Winkler DO samples encompassing different levels of DO were occasionally taken in order to ground truth the probe data. The precision of the DO probe was ~1%. Air $p\mathrm{CO}_2$ was determined every 6–12 h. The intake port from which atmospheric air was pumped was installed at ~15 m above the water surface to avoid contamination from the ship.

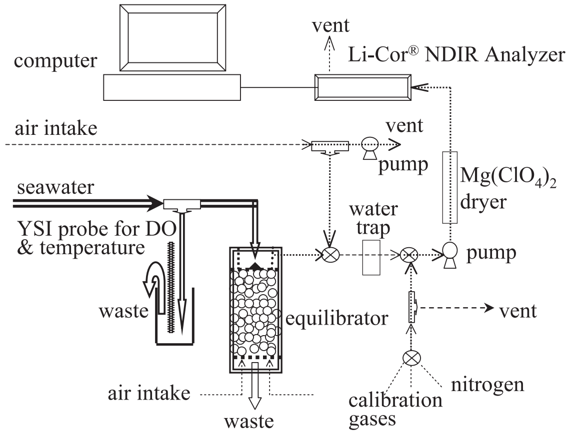

Fig. 2. Schematic plumbing diagram of the underway system and $p\mathrm{CO}_2$ analyzer.

Water was continuously pumped into an efficient equilibrator that combines laminate-flow and shower-head equilibration (Körtzinger et al., 2000; Frankignoulle et al., 2001). During analysis, a small amount of air was withdrawn from the headspace and the resultant vacancy was replaced by laboratory air bubbled through column fillings. The headspace air (or atmospheric air divided from the intake air flow) was then pumped through a water trap and an external drier pipe with $\mathrm{Mg(ClO_4)_2}$ to remove water vapor. The CO_2 mole fraction in dry air ($x\mathrm{CO}_2$) was measured continuously (recorded every 15 s, averaging to 1 min) using a Li-Cor® non-dispersive infrared (NDIR) spectrometer, LI-6262 during the 2000 cruise and LI-6252 during the 2001 cruise. Using an induced acidification experiment similar to Frankignoulle et al. (2001), we obtained a 95% response time of the equilibration system of ~1 min.

The NDIR detectors were calibrated against a series of CO_2 gas standards and one N_2 reference. $x\mathrm{CO}_2$ of the standards ranged from 273×10^{-6} to 819×10^{-6}. These standard gases were provided by China National Research Center for Certificated Reference Materials of China as the First Class Standard Gases of China (GBW, the highest grade). The overall uncertainty of their contents is <1% (Wang, 1996 and their certificates). These GBW gas standards are also traceable to *Comit International des Poids et Mesures* (CIPM) Interlaboratory Study II in 1993 (Wang, 1996). Under our typical sampling conditions (span of the Li-Cor >3.5), calibrated instrumental response was linear. It should be noted that during our 2001 cruise, the LI-6252 reading was out of range for $x\mathrm{CO}_2$ $>4200\times10^{-6}$. We had to change the LI-6252 sensitivity by adjusting the "span". Under this circumstance, LI-6252 readings were not linear, causing our measurements with $x\mathrm{CO}_2$ $>4200\times10^{-6}$ a higher uncertainty than that within the linear range. Fortunately, only a few data points were out of this range over the course of the cruise.

In addition to continuous underway measurements, we took discrete samples via a side vent of the $p\mathrm{CO}_2$ pumping system for the determination of dissolved inorganic carbon (DIC), pH, and other parameters. pH was measured at ~28 °C using a Ross Orion combination electrode. Three NBS pH buffers were used for calibration. DIC was analyzed with 0.5 ml acidified sample following a method modified from Cai and Wang (1998). The measurements were conducted during and/or after the cruise within a time frame of 1 week. A standard DIC reference material provided by A. Dickson from the Scripps Institution of Oceanography was used for calibration. The method has a precision of 0.1% within typical seawater concentration range and ~0.2% for low DIC content (river) water samples.

3.2. Pelagic respiration rate

On-deck incubations were conducted using unfiltered water in a 20-L darkened LDPE cubitainer (Fisher Scientific), submerged in a flowing water tank for temperature regulation. A duplicate sample poisoned with saturated $HgCl_2$ (0.2‰ of the sample volume) was incubated concurrently as a control. Five subsamples for DO measurements were taken at an interval of 8 h and measured with the Winkler method. The rate of decrease in DO concentration of the non-poisoned water sample represents the pelagic respiration rate at that DO level.

3.3. pCO_2 data processing

Water saturated pCO_2 in the equilibrator was calculated from the xCO_2 in dry air, atmospheric pressure and equilibrium water vapor using the following equation (DOE, 1994):

$$\begin{aligned} &p\mathrm{CO_2}\ (\text{in the equilibrator}) \\ &\quad = (P - VP(\mathrm{H_2O, s/w})) \times x\mathrm{CO_2} \\ &\quad = p\mathrm{CO_2}\ (\text{in dry air}) - x\mathrm{CO_2} \\ &\qquad \times VP(\mathrm{H_2O, s/w}) \qquad (1) \end{aligned}$$

where P is atmospheric pressure; $VP(H_2O, s/w)$ is saturated water vapor pressure in the equilibrator according to the Weiss and Price (1980) formula.

Aqueous pCO_2 in the equilibrator was then corrected to in situ temperature via a temperature effect coefficient. Using carbonate dissociation constants (Millero, 1996) and the Weiss (1974) constant for CO_2 solubility along with the measured surface temperature range of 26–30 °C, surface DIC and alkalinity of the estuarine water under survey (obtained from Cai et al., 2004), we calculate the overall temperature coefficient of pCO_2 to range from ~2.5% $°C^{-1}$ at salinity of 0.1 to ~4.0% $°C^{-1}$ at seawater and mid-salinity water. The latter is close to the Takahashi et al. (1993) coefficient of 4.23% $°C^{-1}$. In this study, we use a constant temperature effect coefficient of 4% $°C^{-1}$ for overall salinity range. This may result in ±30 μatm an error of the freshwater pCO_2, representing the maximum errors due to the uncertainty of the temperature correction.

Finally, air pCO_2 was corrected to 100% humidity at surface water temperature and salinity at the time of sampling.

3.4. Excess CO_2 and apparent oxygen utilization

Note that the concentration of oxygen in the Pearl River estuary under study was generally under saturation, and the concentration of CO_2 was generally above it. To facilitate discussion, we define the departure of free dissolved CO_2 from atmospheric equilibrium as excess CO_2 (Eq. 2) and the departure of oxygen as apparent oxygen utilization (AOU) after Richey et al. (1988) as Eq. (3):

$$\text{Excess } \mathrm{CO_2} = [\mathrm{CO_2}^*] - K_{\mathrm{H}}^{\mathrm{CO_2}} \times p\mathrm{CO_2}\ (\text{in air}) \qquad (2)$$

where $[CO_2^*]$ is the concentration of total free CO_2 (i.e., $[CO_2^*]=[CO_2]+[H_2CO_3]=K_H^{CO_2} \times pCO_2$ in water); $K_H^{CO_2}$ is the solubility coefficient of CO_2.

$$\mathrm{AOU} = [\mathrm{O_2}]_{\mathrm{eq}} - [\mathrm{O_2}] \qquad (3)$$

where $[O_2]_{eq}$ is the DO concentration at equilibrium with the atmosphere, calculated from the Benson and Krause (1984) equation and local air pressure; $[O_2]$ is the in situ DO concentration.

4. Results and discussions

4.1. Spatial distribution of aqueous pCO_2

Typical distributions of temperature, salinity, pH, DIC, pCO_2 and DO across the estuary are presented in Fig. 3 for the 01 Jun 2001 survey. Upstream from the Humen outlet, pCO_2 ranged 3380–4785 μatm, while DO was 76–143 μmol O_2 kg^{-1}. DIC was ~1100 μmol kg^{-1} and pH was 7.0–7.2. Temperature was relatively high (28.1–28.5 °C). Between the Humen outlet and shortly before the Hongqimen outlet, i.e., in the Inner Lingdingyang Bay, temperature and pCO_2 rapidly declined while pH and DO substantially increased within a narrow salinity range (0.25–1.3). In this salinity range, DIC apparently increased. However, when we normalized DIC with salinity to S=5 (nDIC in Fig. 3b) according to Friis et al. (2003), nDIC declined and followed the similar trend of pCO_2. Note that the dramatic drop of nDIC in the low salinity range as compared to pCO_2 may be reflective of multiple inputs of DIC from the branches of Pearl River as we previously reported (Cai et al., 2004). Around the outlets of Hongqimen and Hengmen, both pCO_2 and DO fluctuated moderately, while DIC leveled

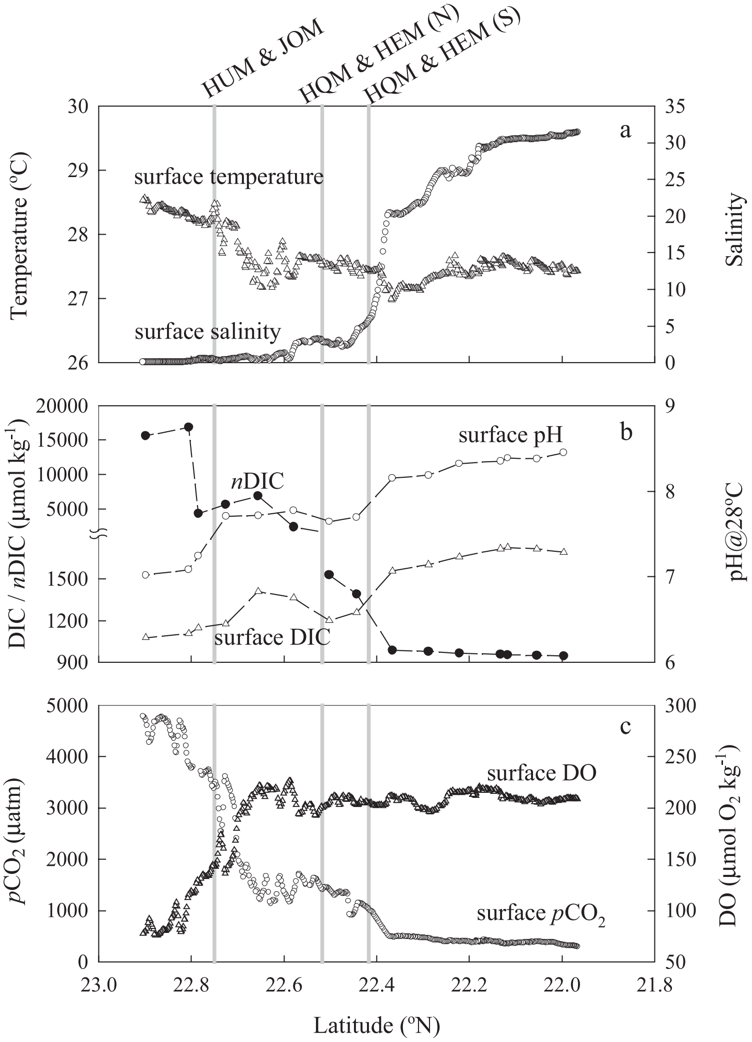

Fig. 3. Surface water pCO_2 and relevant parameters measured during underway pumping experiments in the Pearl River estuary on 01 June 2001. Vertical lines represent the major outlets. In (b), nDIC values are DIC being normalized to S=5 according to Friis et al. (2003). In (c), pCO_2 data of >3700 μatm have a higher uncertainty than the rest of our reported data due to the LI-6252 reading was out of range and we had to change its sensitivity. See text for details. (a) Temperature and salinity. (b) DIC, salinity normalized DIC (nDIC) and pH. (c) pCO_2 and DO.

off to <1200 µmol kg^{-1}, due to the additional freshwater input from these two outlets. Downstream from these two outlets, where the influence of fresh water starts to diminish, a salinity front was observable at salinity 3–20. Within the front, pCO$_2$ dropped rapidly, from >1000 to <500 µatm, and pH rose from ~7.8 to >8.0. DIC also rose to ~1600 µmol kg^{-1} while DO did not change significantly. In the Outer Lingdingyang Bay, pCO$_2$ remained at <500 µatm, while DO was ~210 µmol O$_2$ kg^{-1}, DIC was 1600–1700 µmol kg^{-1}, pH was 8.2–8.4, and temperature reached a relatively low value of 27.0–27.5 °C. The strong inverse relationship between pCO$_2$ and DO observed in the low salinity region (S<4) became less significant in the Outer Lingdingyang Bay (Fig. 3c).

Further summarized in Fig. 4 are pCO$_2$ and DO data from both the 2000 and 2001 cruises, plotted here against salinity. As a general feature described above, the pCO$_2$ level rapidly declined along with the increase in salinity, reaching <1000 µatm at salinity 2–3 (Fig. 4a), while the DO level rose along with the salinity increase, reaching near-saturation in saline waters (Fig. 4b). A significant difference in pCO$_2$ and DO distribution can be observed however, for the survey on May 23, where lower DO and higher pCO$_2$ signals were observed further downstream as compared with what we observed during other surveys (Fig. 4). This is most likely related to heavy precipitations immediately before the survey, which transported much more oxygen-consuming organic pollutants from upper stream of Human into the Inner Lingdingyang Bay and resulted in the high pCO$_2$ and low DO signal further downstream as compared to typical hydrological conditions. Indeed, the total precipitation in the upstream watershed was ~120 mm during 15–18 May 2001 and ~21 mm on 21–22 May 2001 according to the weather records from the Guangzhou Weather Observatory (the upriver station of our study area) (http://ccar.ust.hk/dataview/stnplot/current/).

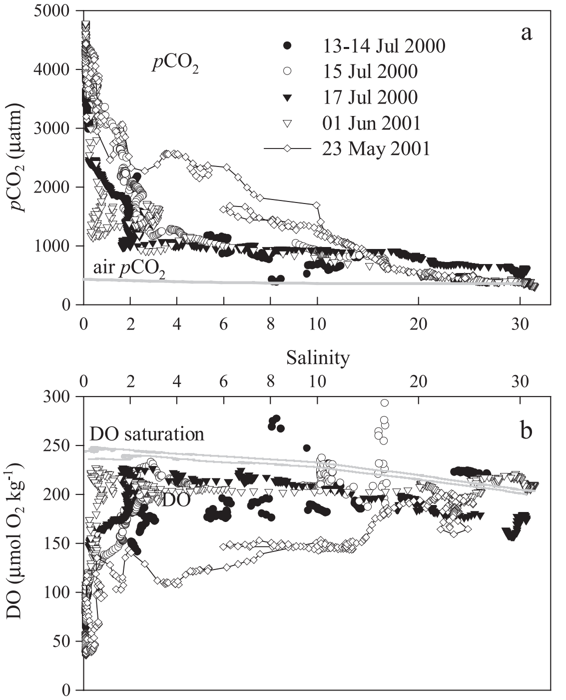

Fig. 4. Distributions of pCO$_2$ and DO concentration in the estuary. In (a), pCO$_2$ data of >3700 µatm of 2001 surveys have a higher uncertainty than the rest of our reported data due to the LI-6252 reading was out of range and we had to change its sensitivity. See text for details. (a) Surface water pCO$_2$ vs. salinity. (b) DO concentration vs. Salinity. The upper DO saturation line in panel b is of spring while the lower one is of summer.

4.2. Upstream high pCO$_2$ and the control by organic matter degradation

In the vicinity of the Humen outlet, we observed remarkably high surface water pCO$_2$ as 4230 µatm in the summer of 2000 and 4785 µatm in the late spring of 2001. These data along with DO, pH, salinity and temperature in the Humen Channel and/or at the Humen outlet are shown in Table 1. The high pCO$_2$ was apparently accompanied by a phenomenally low DO level of 30–50 µmol O$_2$ kg^{-1} (Fig. 4b). To ground truth the low DO values obtained from the YSI probe, we used Goflo bottles to collect discrete samples in the morning of 22 May 2001, then measured DO with the Winkler titration method. DO was determined to be 48.2±0.2 (n=3) µmol O$_2$ kg^{-1} at a depth of 0.6 m.

A number of biogeochemical processes may be associated with surface water pCO$_2$ in the estuary. The negative correlation between pCO$_2$ and DO observed during our cruises suggests that there may exist a dominant process controlling both the CO$_2$ production and oxygen consumption in the surface water of the inner estuary. In order to examine this

Table 1
$p\text{CO}_2$, pH, dissolved oxygen, water temperature and salinity in the Humen Channel and/or at the Humen outlet

Date	$p\text{CO}_2$ (μatm)	pH	DO (μmol O_2 kg^{-1})	Salinity	Water temperature (°C)
15 July 2000	2180–4230	7.18–7.61	99–177	0.11–1.82	30.27–30.83
17 July 2000	1815–2460	7.44–7.71	146–176	0.23–1.76	29.80–30.24
22 May 2001	1740–4660	6.89–7.12	30–190	0.07–0.56	26.37–27.81
23 May 2001	3940–4460	6.96–7.28	36–60	0.07–0.10	27.17–27.51
01 June 2001	3380–4785	7.01–7.70	76–143	0.09–0.60	28.14–28.56

process from a quantitative point of view, we plot excess CO_2 vs. AOU.

Excess CO_2 and AOU in the surface water are significantly correlated, with limited variation aside from the previously mentioned anomalous data from 23 May 2001 (Fig. 5). These plots strongly suggest that the high $p\text{CO}_2$ in the upstream water may be controlled by oxidation of organic matter. The difference in plot slopes shown in Fig. 5 might be reflective of different organic material yielding different ratios of excess CO_2 and AOU. At the same time, the acid–base reaction during the oxidation of organic matter (Redfield respiration) can also result in slope variations.

To quantify this Redfield respiration in an environment with abundant HCO_3^-, the following stoichiometric relationship (assuming traditional Redfield ratio and directly linking aqueous free CO_2 to O_2 consumption) may be used:

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138O_2 + 18HCO_3^- \rightarrow 124CO_2 + 140H_2O + 16NO_3^- + HPO_4^{2-} \qquad (4)$$

$$\Delta CO_2 : (-\Delta O_2) = (106 + 18)/138 = 0.90 \qquad (5)$$

The ΔCO_2:$(-\Delta O_2)$ is the planktonic respiration quotient (Taylor et al., 2003) plus contribution of HCO_3^- titration. Chen et al. (1996) pointed out that despite the various elemental compositions for marine plankton biomass proposed by various investigators, respiration quotients (also ΔPOC:ΔO_2) fell in the range of 0.62–0.79. This range includes the latest

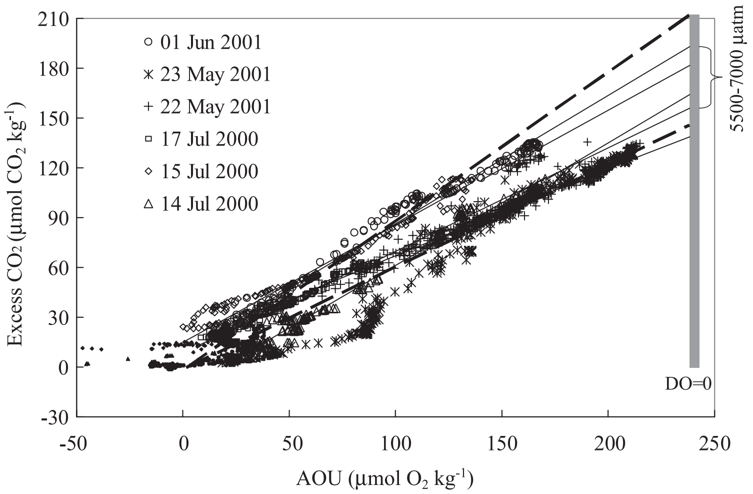

Fig. 5. Excess CO_2 vs. AOU in the Pearl River estuary. Excess CO_2 data of >120 μmol kg^{-1} of 2001 surveys have a higher uncertainty than the rest of our reported data due to the LI-6252 reading was out of range and we had to change its sensitivity. See text for details. The regression lines, fitted by minimizing the sum of the squares of the y-offsets, are: 14 July 2000—y=0.752x−14.09, R^2=0.982; 15 July 2000—y=0.706x+14.74, R^2=0.967; 17 July 2000—y=0.624x+8.05, R^2=0.985; 22 May 2001—y=0.527x+14.28, R^2=0.966 (at the Humen station and upstream); 01 June 2001—y=0.778x+8.27, R^2=0.984. The two dashed lines show the upper limit (slope=0.90) and the lower limit (slope=0.62) for stoichiometric ratio of aerobic biological respiration in the environment with abundance of HCO_3^-. The grey region at right side represents anoxic condition, i.e., DO=0.

estimation of 0.69 (Hedges et al., 2002). The Redfield-based respiration quotient (106/138=0.77) is close to the highest value of the range summarized by Chen et al. (1996) since the traditional Redfield composition did not take the lipids into account (Fraga et al., 1998). The consensus is that for heterotrophic breakdown of phytodetritus, not taking into account the titration of HCO_3^-, respiration quotients for the remineralization lie around ~0.71 (Laws, 1991; Anderson, 1995; Fraga et al., 1998; Taylor et al., 2003). Therefore, we use 0.90 from Eq. (5) as the theoretical upper limit of ΔCO_2:($-\Delta O_2$). At the same time, although ΔCO_2:($-\Delta O_2$) should be slightly higher than the respiration quotient, we regard 0.62 as the theoretical lower limit of ΔCO_2:($-\Delta O_2$) in the estuary based on the assumption that estuarine organic carbon may include more reduced molecules than typical average organic matter. Thus, most of measured slopes of the excess CO_2 vs. AOU plots (Fig. 5), ranging between 0.624 and 0.778, are consistent with the reported stoichiometric ratios. It is worthwhile to note that this slope declines to ~0.527 around the most oxygen depleted station near Humen (Fig. 5). That is, CO_2 production was less than expected. This may be due to in situ organic matter degradation that might produce low molecular weight organic matter instead of the final biochemical product (CO_2).

In this analysis, it is appropriate to directly link aqueous free CO_2 to DO consumption. This is because in low salinity regions of the estuary, nearly 100% of the respiratory DIC addition will exist in the form of CO_2*. For example, for estuarine water with S=1, DIC=1100 μmol kg^{-1} and total alkalinity (TAlk)=1000 μmol kg^{-1}, the following parameters can be calculated based on Dickson and Millero (1987) constants: pCO_2=2614 μatm, [CO_2*]=101.8 μmol kg^{-1}, [HCO_3^-]=996.5 μmol kg^{-1}, [CO_3^{2-}]=1.6 μmol kg^{-1} and pH=7.3. With a respiratory addition of 106 μmol kg^{-1} DIC and 18 μmol kg^{-1} reduction in TAlk (see Eq. (4)), one obtains that pCO_2=5768 μatm, [CO_2*]=224.7 μmol kg^{-1}, [HCO_3^-]=980.6 μmol kg^{-1}, [CO_3^{2-}]=0.7 μmol kg^{-1} and pH=7.0. Therefore, all the respiratory CO_2, plus some extra CO_2 converted from HCO_3^- due to the pH decline, exist as CO_2* molecules although HCO_3^- is still the dominant species in the water. This is consistent with what Richey et al. (1988) suggested for the Amazon River but is quite different from the situation in seawater where DIC (sum of CO_2*, HCO_3^- and CO_3^{2-}) should be used to determine the stoichiometric relationship between CO_2 and O_2 (DeGrandpre et al., 1997).

Another piece of evidence for organic matter oxidation supporting the high pCO_2 in the upper reaches of the estuary is from the pelagic respiration rate of Humen water, as determined by an on-deck incubation experiment. A high respiration rate of 48 mmol O_2 m^{-3} day^{-1} was measured. A single measurement though, this gives us a first-order estimation of a very large respiration rate in the region, as compared to, for example, 6.0–28.6 mmol O_2 m^{-3} day^{-1} in some U.S. marsh-dominated estuaries (Cai et al., 1999). This respiration rate can also be compared to CO_2 evasion fluxes. For excess pCO_2=4000 μatm, and given the gas transfer velocity k(T)=1.4 m day^{-1} (calculated based on Wanninkhof, 1992) at a water temperature of 26–30 °C, wind speed of 4 m s^{-1}, and $K_H^{CO_2}$=32 mol m^{-3} atm^{-1}, CO_2 outgassing fluxes can be estimated as 180 mmol m^{-2} day^{-1}. Given 6 m as an average depth upstream the estuary (Wong and Cheung, 2000; Chau and Jiang, 2002), we calculated a water column CO_2 production rate as 180/6=30 mmol m^{-3} day^{-1}. Dividing this value by the respiration rate that we measured (48 mmol O_2 m^{-3} day^{-1}), we have a ratio of 30/48=0.63. This ratio is consistent with our [CO_2*]/AOU (0.62–0.78). It is thus reasonable to hypothesize that the high respiration rate leads to the low DO and in turn high pCO_2.

4.3. *The upper limit of pCO_2 in Pearl River estuary and its implication*

From plots in Fig. 5, we extrapolate to an anoxic condition (i.e., DO=0) and estimate an upper limit of pCO_2 to be ~7000 μatm. The agreement of this prediction with field measurements provides us more confidence that the pCO_2 in this system (upstream region, near zero salinity) is indeed controlled by DO consumption through organic carbon oxidation.

pCO_2 values of >10 000 μatm were reported in the Amazon River (Richey et al., 1988, 2002) and European Scheldt River (Abril et al., 2000; Hellings et al., 2001). The source processes, however, are different from the Pearl River case. In the Amazon

River, much more CO_2* was produced than predicted by a theoretical ΔCO_2:($-\Delta O_2$) of 0.83. The "extra" CO_2 was presumably produced anaerobically, mostly from methanogenesis (Richey et al., 1988). In upper estuarine waters of some southeastern U.S. rivers, very high pCO$_2$ values of >6000 μatm have been shown to be the result of humic-rich, acidic river water, in situ respiration, and DIC supplied from the anaerobic degradation of organic matter from adjacent salt marshes (Cai and Wang, 1998). In the water column of the Pearl River estuary, DO never reached zero, thus anaerobic processes are not expected to be major.

Elsewhere in the Scheldt estuary, water pCO$_2$ ranges from 2200 μatm to a maximum of 15 500 μatm at salinity <10% (Hellings et al., 2001). Despite quasi-symmetrical distributions of DO and pCO$_2$, biological respiration only partly contributes to the upstream high pCO$_2$. In the freshwater zone, DO remains 25–30% of the saturation (Hellings et al., 2001). The AOU of 200–350 μmol O_2 kg^{-1} is at any rate not enough to support calculated excess CO_2 of 300–450 μmol kg^{-1} (based on Hellings et al., 2001). Moreover, the most reduced tributary has relatively low pCO$_2$ and a moderate excess CO_2 as compared to the other tributaries (Abril et al., 2000). On the other hand, the Scheldt estuary is characterized by higher DIC in the freshwater end-member than the marine end-member with DIC being significantly removed during mixing, and the freshwater zone is always 1.5–15 times oversaturated for calcite (Hellings et al., 2001), thus $CaCO_3$ precipitation needs to be investigated as a potential mechanism to consume alkalinity and DIC and release CO_2 in the Scheldt estuary.

5. Concluding remarks

Our observed correlation between excess CO_2 and AOU is consistent with stoichiometric ratios deduced from theoretical elemental composition on the basis of classic Redfield ratios. This suggests that the upstream high pCO$_2$ may be dominated by aerobic respiration. Pollution-related CO_2 emission had been observed in European estuaries (Frankignoulle et al., 1998) and the Pearl River estuary system discussed here may represent another example. Based on the measured CO_2 vs. AOU plots, we estimate that the upper limit of pCO$_2$ should be ~7000 μatm in spring and summer in the Pearl River estuary, assuming that CO_2 was produced solely by aerobic respiration.

In a global context, terrestrial ecosystems, especially those of the North American and Eurasian continents, can act as a sink of anthropogenic CO_2 under the current climate regime (Schimel et al., 2001). ~1×10^{12} kg year^{-1} of terrestrial carbon is transported by riverine systems on a global scale (Richey et al., 2002 and references therein). This flux represents only a small component of the global carbon budget, yet it is significant as compared to the net uptake of anthropogenic CO_2 (Richey et al., 2002). In addition to fluvial transport to the sea, many unpolluted river systems are overall heterotrophic (Thorp and Delong, 2002) and release a significant amount of CO_2 (and CH_4) into the atmosphere (Hope et al., 2001 and references therein; Richey et al., 2002 and references therein).

Our analysis shows that, although high pCO$_2$ in world rivers and estuaries is ubiquitous, factors controlling pCO$_2$ within estuaries may vary in different systems and/or under different environmental conditions. pCO$_2$ in the Pearl River estuary is no higher than 7000 μatm in spring and summer, but in the Amazon River and the Scheldt River estuary, pCO$_2$ reached >10 000 μatm. Therefore, simple extrapolation from these well-studied river and estuarine systems to a global scale may result in inaccurate global estimates. We thus contend that much remains to be investigated in order to 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.

Anderson, L.A., 1995. On the hydrogen and oxygen content of marine phytoplankton. Deep-Sea Res. 42, 1675–1680.

Benson, B.B., Krause, D., 1984. The concentration and isotopic fractionation of oxygen dissolved in fresh water and seawater in equilibrium with the atmosphere. Limnol. Oceanogr. 29, 620–632.

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., Pomeroy, L.R., Moran, M.A., Wang, Y.C., 1999. Oxygen and carbon dioxide mass balance in the estuarine/intertidal marsh complex of five rivers in the Southeastern US. Limnol. Oceanogr. 44, 639–649.

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.

Chau, K.W., Jiang, Y.W., 2002. Three-dimensional pollutant transport model for the Pearl River Estuary. Water Res. 36, 2029–2039.

Chen, J.S., He, D., 1999. Chemical characteristics and genesis of major ions in the Pearl River basin. Acta Scientiarum Naturalium Universitatis Pekinensis 35, 786–793 (in Chinese).

Chen, C.-T.A., Lin, C.M., Huang, B.T., Chang, L.F., 1996. Stoichiometry of carbon, hydrogen, nitrogen, sulfur and oxygen in the particulate matter of the western North Pacific marginal seas. Mar. Chem. 54, 179–190.

Cheng, Z.L., 2001. Decadal variation of hydrological status in stream network area and the eight outlets of Pearl River Delta. Acta Scientiarum Naturalium Universitatis Sunyatseni 40 (Suppl. 2), 29–31 (in Chinese).

DeGrandpre, M.D., Hammar, T.R., Wallace, D.W.R., Wirick, C.D., 1997. Simultaneous mooring-based measurements of seawater CO_2 and O_2 off Cape Hatteras, North Carolina. Limnol. Oceanogr. 42, 21–28.

Devol, A.H., Quay, P.D., Richey, J.E., Martinelli, L.A., 1987. The role of gas exchange in the inorganic carbon, oxygen, and ^{222}Rn budgets of the Amazon River. Limnol. Oceanogr. 32, 235–248.

Dickson, A.G., Millero, F.J., 1987. A comparison of the equilibrium constants for the dissociation of carbonic acid in the seawater media. Deep-Sea Res. 34, 1733–1743.

DOE, 1994. Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water, ver. 2. In: Dickson, A.G., Goyet, C. (Eds.). ORNL/CDIAC-74.

Fraga, F., Ríos, A.F., Pérez, F.F., Figueiras, F.G., 1998. Theoretical limits of oxygen:carbon and oxygen:nitrogen ratios during photosynthesis and the mineralisation of the organic matter in the sea. Sci. Mar. 62, 161–168.

Frankignoulle, M., Middelburg, J.J., 2002. Biogases in tidal European estuaries: an introduction to the BIOGEST project. Biogeochemistry 59, 1–4.

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.

Frankignoulle, M., Borges, A., Biondo, R., 2001. A new design of equilibrator to monitor carbon dioxide in highly dynamic and turbid environments. Water Res. 35, 1344–1347.

Friis, K., Körtzinger, A., Wallace, D.W.R., 2003. The salinity normalization of marine inorganic carbon chemistry data. Geophys. Res. Lett. 30 (2), 1085.

Han, W., 1998. Marine Chemistry in the South China Sea. Science Press, Beijing, China (in Chinese).

Hedges, J.I., Baldock, J.A., Gélinas, Y., Lee, C., Peterson, M.L., Wakeham, S.G., 2002. The biochemical and elemental compositions of marine plankton: a NMR perspective. Mar. Chem. 78, 47–63.

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.

Hope, D., Palmer, S.M., Billett, M.F., Dawson, J.J.C., 2001. Carbon dioxide and methane evasion from a temperate peatland stream. Limnol. Oceanogr. 46, 847–857.

Körtzinger, A., Mintrop, L., Wallace, D.W.R., Johnson, K.M., Neill, C., et al., 2000. The international at-sea intercomparison of fCO_2 systems during the R/V Meteor Cruise 36/1 in the North Atlantic Ocean. Mar. Chem. 72, 171–192.

Laws, E.A., 1991. Photosynthetic quotients, new production and net community production in the open oceans. Deep-Sea Res. 38, 143–167.

Millero, F.J., 1996. Chemical Oceanography, 2nd ed. CRC Press, Boca Raton.

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.

Pang, Y., Li, Y.X., 2001. Effects of discharged pollutants from Pearl River Delta on east outlets. J. Hohai U. 29 (4), 50–55 (in Chinese).

PRWRC/PRRCC, 1991. The Pearl River Records 1 (Zhujiang Zhi). Guangdong Science & Technology Press, Guangzhou, China (in Chinese).

Raymond, P.A., Bauer, J.E., Cole, J.J., 2000. Atmospheric CO_2 evasion, dissolved inorganic carbon production, and net heterotrophy in the York River estuary. Limnol. Oceanogr. 45, 1707–1717.

Richey, J.E., Devol, A.H., Wofsy, S.C., Victoria, R., Riberio, M.N.G., 1988. Biogenic gases and the oxidation and reduction of carbon in Amazon River and floodplain waters. Limnol. Oceanogr. 33, 551–561.

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 CO_2. 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.

Schimel, D.S., House, J.I., Hibbard, K.A., Bousquet, P., Ciais, P., et al., 2001. Recent patterns and mechanisms of carbon exchange by terrestrial ecosystem. Nature 414, 169–172.

Takahashi, T., Olafsson, J., Goddard, J.G., Chipman, D.W., Sutherland, S.C., 1993. Seasonal variation of CO_2 and nutrients in the high-latitude surface ocean: a comparative study. Glob. Biogeochem. Cycles 7, 843–878.

Taylor, G.T., Way, J., Scranton, M.I., 2003. Planktonic carbon cycling and transport in surface waters of the highly urbanized Hudson River estuary. Limnol. Oceanogr. 48, 1779–1795.

Thorp, J.H., Delong, A.D., 2002. Dominance of autochthonous autotrophic carbon in food webs of heterotrophic rivers. Oikos 96, 543–550.

Wang, L.Z., 1996. On accuracy and consistency of the standard gases. In: Wang, G., Wen, Y. (Eds.), Greenhouse Gases and Their Emission Monitoring and Some Relative Processes. China Environmental Science Press, Beijing, China, pp. 24–31 (in Chinese).

Wanninkhof, R., 1992. Relationship between wind speed and gas exchange over the ocean. J. Geophys. Res., C: Oceans 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.

Weiss, R.F., Price, R.A., 1980. Nitrous oxide solubility in water and seawater. Mar. Chem. 8, 347–359.

Wong, M.H., Cheung, K.C., 2000. Estuarine systems of the South China Sea region: carbon, nitrogen and phosphorus fluxes. In: Smith, S.V., Dupra, V., Marshall Crossland, J.I., Crossland, C.J. (Eds.), Pearl River Estuary and Mirs Bay, South China, LOICZ Reports & Studies vol. 14. LOICZ IPO, Texel, Netherlands, pp. 7–16.

Zhang, L.J., Wang, B.Y., Zhang, J., 1999. pCO_2 in the surface water of the East China Sea in winter and summer. J. Ocean U. Qingdao (suppl.), 149–153 (in Chinese).

Zhu, X.G., 2002. Remote sensing monitoring of coastline changes in Pearl River Estuary. Mar. Environ. Sci. 21 (2), 19–22 (in Chinese).