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CO_2 flux and seasonal variability in the turbidity maximum zone and surrounding area in the Changjiang River estuary*

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Abstract The turbidity maximum zone (TMZ) is one of the most important regions in an estuary. However, the high concentration of suspended material makes it difficult to measure the partial pressure of CO_2 (pCO_2) in these regions. Therefore, very little data is available on the pCO_2 levels in TMZs. To relatively accurately evaluate the CO_2 flux in an example estuary, we studied the TMZ and surrounding area in the Changjiang (Yangtze) River estuary. From seasonal cruises during February, August, November 2010, and May 2012, the pCO_2 in the TMZ and surrounding area was calculated from pH and total alkalinity (TA) measured in situ, from which the CO_2 flux was calculated. Overall, the TMZ and surrounding area acted as a source of atmosphere CO_2 in February and November, and as a sink in May and August. The average FCO_2 was -9, -16, 5, and 5 mmol/(m^2·d) in May, August, November, and February, respectively. The TMZ's role as a source or sink of atmosphere CO_2 was quite different to the outer estuary. In the TMZ and surrounding area, suspended matter, phytoplankton, and pH were the main factors controlling the FCO_2, but here the influence of temperature, salinity, and total alkalinity on the FCO_2 was weak. Organic carbon decomposition in suspended matter was the main reason for the region acting as a CO_2 source in winter, and phytoplankton production was the main reason the region was a CO_2 sink in summer.

Keyword: CO_2 flux; seasonal variability; turbidity maximum zone; Changjiang River estuary

1 INTRODUCTION

Numerous studies have shown that estuarine waters act as significant sources of CO_2 to the atmosphere (Zhai et al., 2007; Chen et al., 2008; Jiang et al., 2008; Guo et al., 2009; Zhai and Dai, 2009; Cai, 2011; Chen et al., 2013). Although globally, the surface area of estuaries only accounts for 4% of the continental shelf, its CO_2 degassing flux is as large as the CO_2 uptake of the entire continental shelf. Thus, both play important roles in global CO_2 flux (Borges, 2005; Borges et al., 2005; Cai et al., 2006; Li et al., 2007; Chen and Borges, 2009). Estimates for the global CO_2 degassing flux from estuaries varies, with Borges et al. (Borges, 2005; Borges et al., 2005) suggesting the flux is 0.34–0.43 pg C/a, while Cai (2011) and Chen (2012) suggested the flux is 0.25 and 0.26 pg C/a, respectively. However, there is no accepted accurate estuarine CO_2 degassing flux data, which indicates that our current knowledge of global estuarine CO_2 efflux is largely uncertain, for several reasons.

First, a limited number of estuaries have been investigated, and clearly studies do not include all estuaries globally. Second, in general, the amount of CO_2 released from water varies diurnally and seasonally, however, most investigations ignore these variations. Third, within the same estuary, different regions may act as sinks or sources of CO_2. In general, in large river, the upper regions of estuaries act as strong sources of CO_2, and wider regions in the mid- to lower estuaries act as weak sources or sinks. However, not all investigations of surface pCO_2 and

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air-water CO_2 flux cover the whole estuarine zone, especially the turbidity maximum zone (TMZ).

The Changjiang River estuary, which is about 120-km long and more than 90-km wide at its outer limit, has complex bottom topography. The TMZ is distributed widely across the estuary, and coincides locally with the mouth-bars. The pristine TMZ in the estuary was thought to be caused by sediment resuspension, which was primarily controlled by the interaction of tidal currents and river discharge (Li and Zhang, 1998; Pan et al., 1999). The TMZ was usually located at the edge of saline intrusion, and its magnitude and extent varies seasonally (Wu et al., 2012).

As one of the largest estuaries in the world, the partial pressure of CO_2 (pCO_2) and CO_2 flux of the Changjiang River estuary has recently gained increased attention. Chen et al. (2008) measured the surface pCO_2 in the environs of the estuary and the nearby Huangpu River outlet in the summer of 2003, using an underway-pumping system. However, their investigation was restricted to a measuring line. Zhai et al. (2007) examined the surface pCO_2, dissolved inorganic carbon and total alkalinity in the estuary, but their investigation focused on the inner and outer estuary, with only a few sampling stations in the middle. Zhai and Dai (2009) examined emphatically the surface pCO_2 and dissolved oxygen (DO) in the outer Changjiang River estuary. Li et al. (2006b) measured the surface pCO_2 in the estuary in May 2005, but only investigated five stations in the inner estuary. Gao et al. (2008) investigated pCO_2 in the estuary, Hangzhou Bay and surrounding areas in August 2004, but almost all sampling stations were in Hangzhou Bay. At present, most investigations of the surface pCO_2 in the estuary have not focused on the middle region of the estuary where the TMZ is situated. Thus, in this study, we focused on the air-sea CO_2 fluxes and influencing factors in the TMZ and surrounding area in the Changjiang River estuary.

2 MATERIAL AND METHOD

2.1 Sampling

Measures of TA, pH, and auxiliary data (salinity (*S*), temperature (*T*), wind speed, barometric pressure, etc.) were acquired in February, August, November 2010, and May 2012, representing winter, summer, fall and spring, respectively. Water column samples were collected with a Sea-Bird CTD rosette system equipped with 2.0-L Niskin bottles onboard the R/V

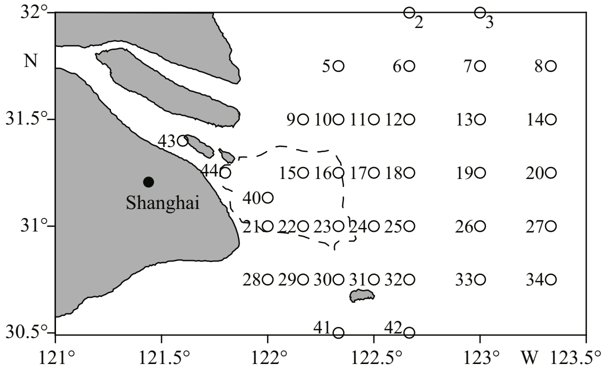

Fig.1 The study area and site deployment

The area surrounded by the broken line is the maximum turbidity zone from Shen and Pan (2001).

Huchongyu 4936. These samples covered almost the entire salinity gradient (Fig.1).

2.2 Analysis

The pH, TA, *S* and *T* of the samples were measured in situ. Salinity and *T* were measured using a combined Sea-Bird SBE 19plus CTD probe on the Rosette sampler. The pH was measured using Thermo Scientific Orion 3-Star Plus pH Meters with resolutions of 0.001 and relative accuracies of 0.002, and a Rex E-201-D combination electrode with measurement accuracy of 0.001. The electrode was calibrated at the beginning of every survey day by a three-point calibration using homemade buffers, including phthalate ($C_8H_5KO_4$ 0.05 mol/L, pH=4.002 at 25°C), phosphate (KH_2PO_4 0.025 mol/L and Na_2HPO_4 0.025 mol/L, pH=6.864 at 25°C), and borate ($Na_2B_4O_7$ 0.01 mol/L, pH=9.182 at 25°C). The precision of pH measurements was 0.002 pH units. Measurement of pH was carried out within minutes of sampling, to prevent CO_2 evasion and biological modifications of the sample.

Samples for total alkalinity were filtered through Whatman GF/F filters and analyzed onboard by Gran titration as quickly as possible, with a precision of approximately 0.1%–0.3% (Gao et al., 2008). Dickson standard reference materials were used for quality control in the total alkalinity measurements.

The pCO_2 can be determined using either a direct or indirect method. The direct method first equilibrates the sample water with air in an equilibrator, and then the pCO_2 is measured using infrared spectrometry or gas chromatography. This method has been used in many surveys and was thought to be the most accurate method to determine pCO_2 in subsurface seawater. An underway pCO_2 measurement system is the most commonly used instrument for this measurement, and pCO_2 measurements from the Changjiang River estuary have mostly been acquired from this instrument. However, the direct method does not work well in the maximum turbidity zone, because most equilibrators are not designed for working in turbid waters (blockage by suspended material). This is the main reason that there is little pCO_2 data from TMZs. Therefore, an indirect method may be a better choice for measuring pCO_2. The indirect method calculates pCO_2 from at least two of the following parameters: pH, TA, and total dissolved inorganic carbon (DIC). pH and TA are the most commonly used parameters. Many studies have proved that pCO_2 can be accurately calculated from pH and TA (Frankignoulle and Borges, 2002; Gray et al., 2011). In this study, pCO_2 was computed from measurements of pH and TA using the carbonic acid constant sets proposed by Cai and Wang (1998), the borate acidity constant from Millero (1979) and the CO_2 solubility coefficient of Weiss (1974).

2.2.1 CO_2 fluxes (FCO_2)

The CO_2 flux across the sea-air interface was estimated at each station using the equation:

$$F=ks\,\Delta pCO_2,$$

where k is the gas transfer velocity (in cm/h), s is the solubility of CO_2 in seawater as a function of temperature and salinity taken from Weiss (1974), and ΔpCO_2 is the gradient in CO_2 partial pressure between the seawater and the atmosphere, in μatm.

In estuaries, and particularly in macrotidal estuaries, the relationship between k and wind speed is usually site-specific and can be significantly affected by wind, water current, fetch, and turbidity (Abril et al., 2009). Therefore, we applied the most recent parameterization of Abril et al. (2009) to compute k. Wind speed has been recognized as the main force driving turbulence and gas exchange at the air-sea interface. As wind speed at one site varied greatly with time, the CO_2 flux calculated by instantaneous wind speed was thus an instantaneous value, which may be an inaccurate representative of the region. The CO_2 flux calculated by the average wind speed over a long period may have better results for this region. Therefore, in this paper, we used the average annual wind speed in different seasons to calculate the seasonal CO_2 flux. The average wind speeds used were acquired from the pilot vessel station (122°04.12′E, 31°04.07′N) from 1979 to 1998 (Sui, 2003). Atmospheric pCO_2 ($pCO_{2\,air}$) was adopted from Zhai et al. (2007) and Zhai and Dai (2009). Tidal data for the periods of observations were collected at each station by a direct reading current meter (model SLC9-2).

Suspended particulate matter (SPM) concentration was determined as the weight of material retained on a Whatman GF/F membrane per volume unit after drying to constant weight at 60°C. The concentrations of chlorophyll *a* (Chl *a*) were determined spectrophotometry, after a 90% acetone extraction of the material retained on a Whatman GF/C membrane.

3 RESULT AND DISCUSSION

3.1 Spatial and temporal distributions of SPM

The SPM concentrations in the surface water of the TMZ and surrounding area in the Changjiang River estuary are shown in Fig.2 and Table 1. Similar to other investigations (Wu et al., 2012), the TMZ occurred in the south of the estuary. However, there were distinct seasonal differences in the magnitude and extent of the TMZ. The SPM concentration in the surface water of the TMZ and surrounding area was highest in February, with an average value of 177 mg/L. This peak may be related to the strong winds at the time of sampling, which caused high levels of sediment to be re-suspended. It is known that the SPM in the bottom layer is commonly diffused to the upper layer during the dry season (Wu et al., 2012). The SPM concentration was lower in May and August, than in February and August. This pattern related to differences in transported matter from the Changjiang River and sea conditions between winter and summer.

3.2 Spatial and temporal distributions of TA

The overall TA distribution pattern in the surface water of the TMZ and surrounding area in the estuary did not vary seasonally, with TA increasing from the river mouth to the offshore region (Fig.3). However, there were small-scale differences in TA distribution patterns between seasons. The average and range of TA was similar in February and May (2 056 μmol/L, Table 1). Minimum average TA was recorded in August (2 018 μmol/L), which was the Changjiang River flood season, with a large amount of fresh water entering the estuary and surrounding area. The TA was slightly higher in November than in August, but lower than in February and May.

Table 1 Environmental parameters, CO_2 system and CO_2 fluxes in surface waters of the TMZ and surrounding area

Item	May		August		November		February	
	Range	Average	Range	Average	Range	Average	Range	Average
TA (μmol/L)	1 646–2 315	2 056	1 681–2 147	2 018	1 729–2 241	2 034	1 780–2 381	2 056
pH	8.013–8.800	8.283	7.960–8.650	8.318	7.950–8.100	8.016	7.791–8.102	7.997
pCO_2 (μatm)	41–523	265	64–533	223	348–559	449	331–600	440
FCO_2 (mmol/(m^2·d))	-26–11	-9	-31–14	-16	-3–18	5	-5–20	5
Salinity	0.14–31.79	20.09	1.26–29.86	21.65	0.95–32.52	23.21	11.55–33.43	27.00
Water temperature (°C)	18.40–24.45	20.26	23.52–31.38	27.14	14.16–18.13	16.25	7.32–10.56	9.06
Wind speed (m/s)	-	5.47	-	5.54		5.02	-	5.22
Chl *a* (mg/m^3)	0.43–2.7	1.38	0.58–2.75	1.36	0.70–1085	1.06	0.37–1.27	0.68
DO (mg/dm^3)	7.48–16.34	9.34	5.61–8.43	7.21	-	-	8.98–10.30	9.63
Suspended matter (mg/dm^3)	0.6–241	35	19–247	46	8.6–316	67	8.5–997	177

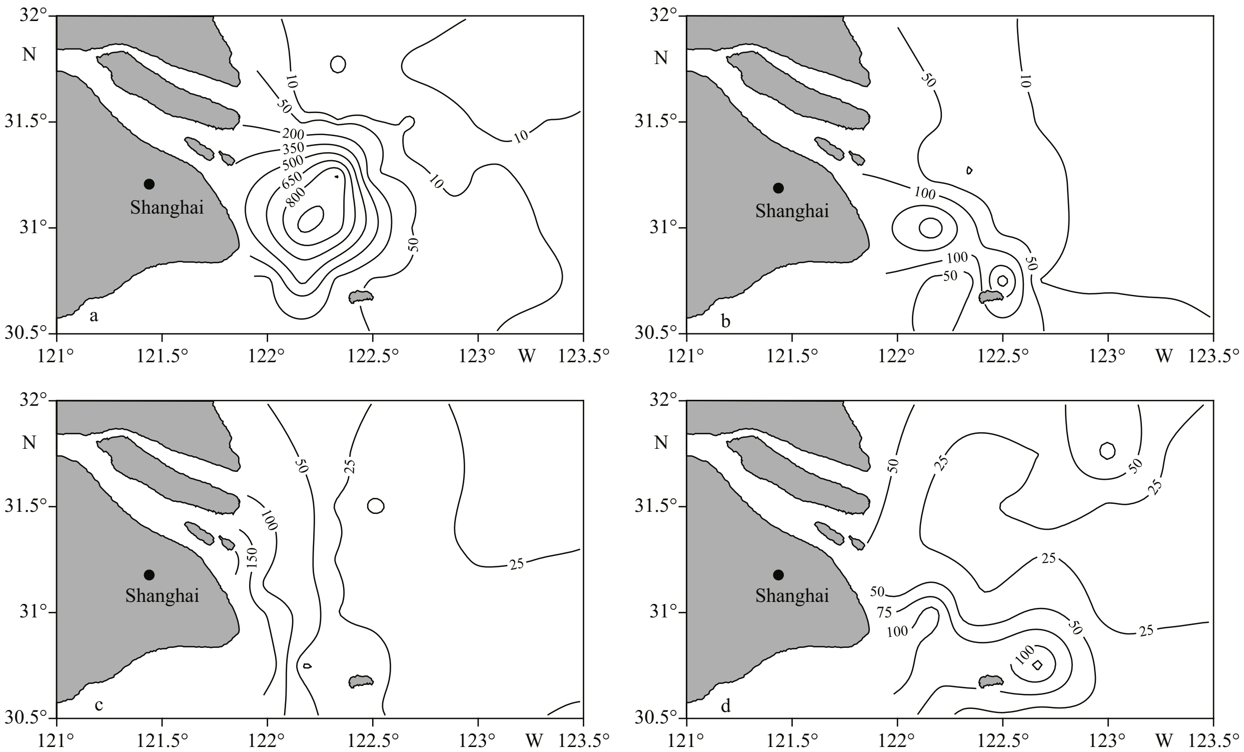

Fig.2 Horizontal distributions of SPM concentrations in surface water of the TMZ and surrounding area in different seasons

a. February; b. May; c. August; d. November.

3.3 Spatial and temporal distributions of pCO_2

The pCO_2 distribution pattern in the surface water of the TMZ and surrounding area was more complicated than that of TA, with pCO_2 highly variable both spatially and seasonally during the four cruises (Fig.4). During our investigation periods, the largest pCO_2 (600 μatm) appeared in February and the lowest in May (40 μatm). In February and November, the surface pCO_2 was highest in the southwest of the region surveyed, decreased to its lowest in the center, and then increased to the northwest. During fall and winter, surface pCO_2 was oversaturated with respect to the atmosphere in most regions. In February, pCO_2 ranged from 331 to 600 μatm with an average of 440 μatm in February. Similarly, in November, pCO_2 ranged from 348 to 559 μatm with an average of 449 μatm. In May and August, pCO_2 decreased from the southwest to the northeast of the region, and was unsaturated with respect to the atmosphere in most regions. In May, pCO_2 ranged from 41to 523 μatm with an average of 265 μatm, with a range of 64–

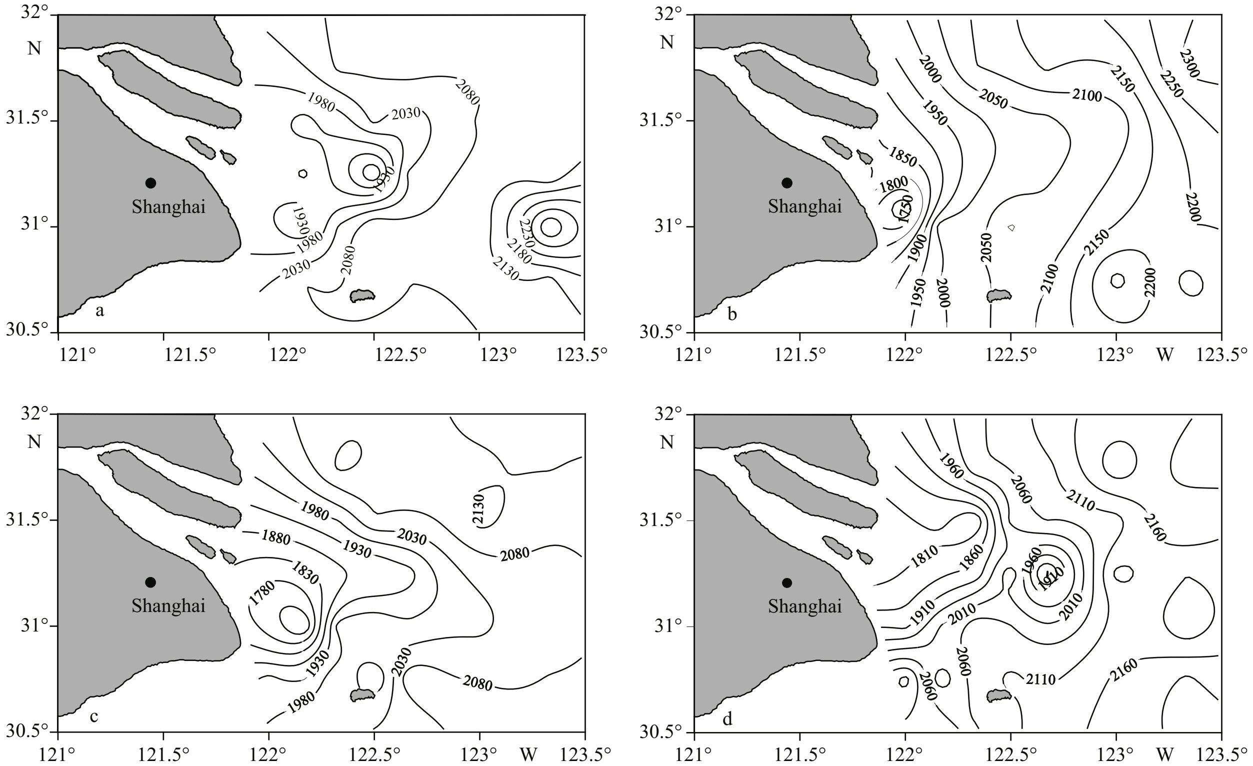

Fig.3 Horizontal distributions of TA in surface water of the TMZ and surrounding area in different seasons

a. February; b. May; c. August; d. November.

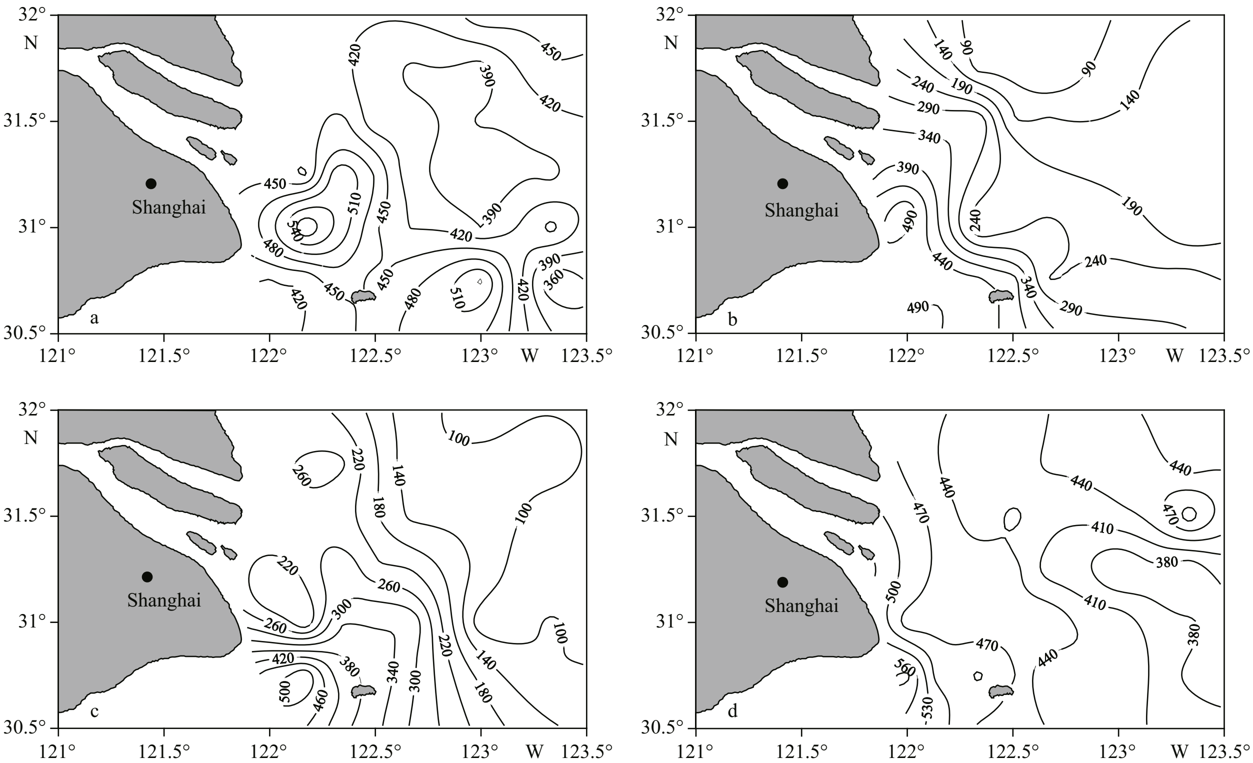

Fig.4 Horizontal distributions of pCO_2 in surface water of the TMZ and surrounding area in different seasons

a. February; b. May; c. August; d. November.

533 μatm and an average of 223 μatm in August. Thus, the surface pCO_2 was higher in February and November, but lower in May and August, which is in contrast to the outer estuary, where there was much less seasonal variability (Zhai and Dai, 2009). Specifically, the outer estuary pCO_2 winter range was 320–380 μatm (average ~345 μatm), spring range 180–450 μatm (average ~330 μatm), summer range 150–620 μatm (average ~310 μatm), and autumn range 120–540 μatm (average ~375 μatm).

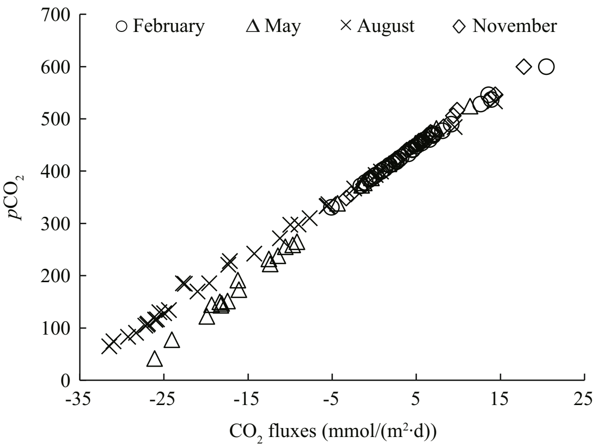

Fig.5 Correlation of FCO_2 and pCO_2 in the TMZ and surrounding area

3.4 Spatial and temporal distributions of FCO_2

In the TMZ and surrounding area of the Changjiang River estuary, FCO_2 and pCO_2 were significantly correlated (Fig.5). Therefore, FCO_2 distribution in this region was similar to that of pCO_2, showing clear seasonal variations (Fig.6). Overall, the TMZ and surrounding area acted as a source of atmosphere CO_2 in February and November, but as a sink in May and August. FCO_2 ranged between -5 and 20 mmol/(m^2·d) in February and -3 and 18 mmol/(m^2·d) in November. In the east central region, FCO_2 was negative throughout the study period. In May and August, FCO_2 was greatest in the northwestern region, then decreased in the northeastern region, and reached its lowest value in the north in May, or in the east in August. The sink or source characteristic of atmosphere CO_2 in the TMZ was quite different to the outer estuary. First, in winter, the TMZ and surrounding area in the Changjiang River estuary was a source, but the outer estuary was a sink of atmosphere CO_2 (Zhai and Dai, 2009). Second, in spring and summer, the TMZ and surrounding area was a stronger sink of atmosphere CO_2 than the outer estuary. Third, the TMZ and surrounding area was a stronger source of atmosphere CO_2 than the outer estuary in the autumn.

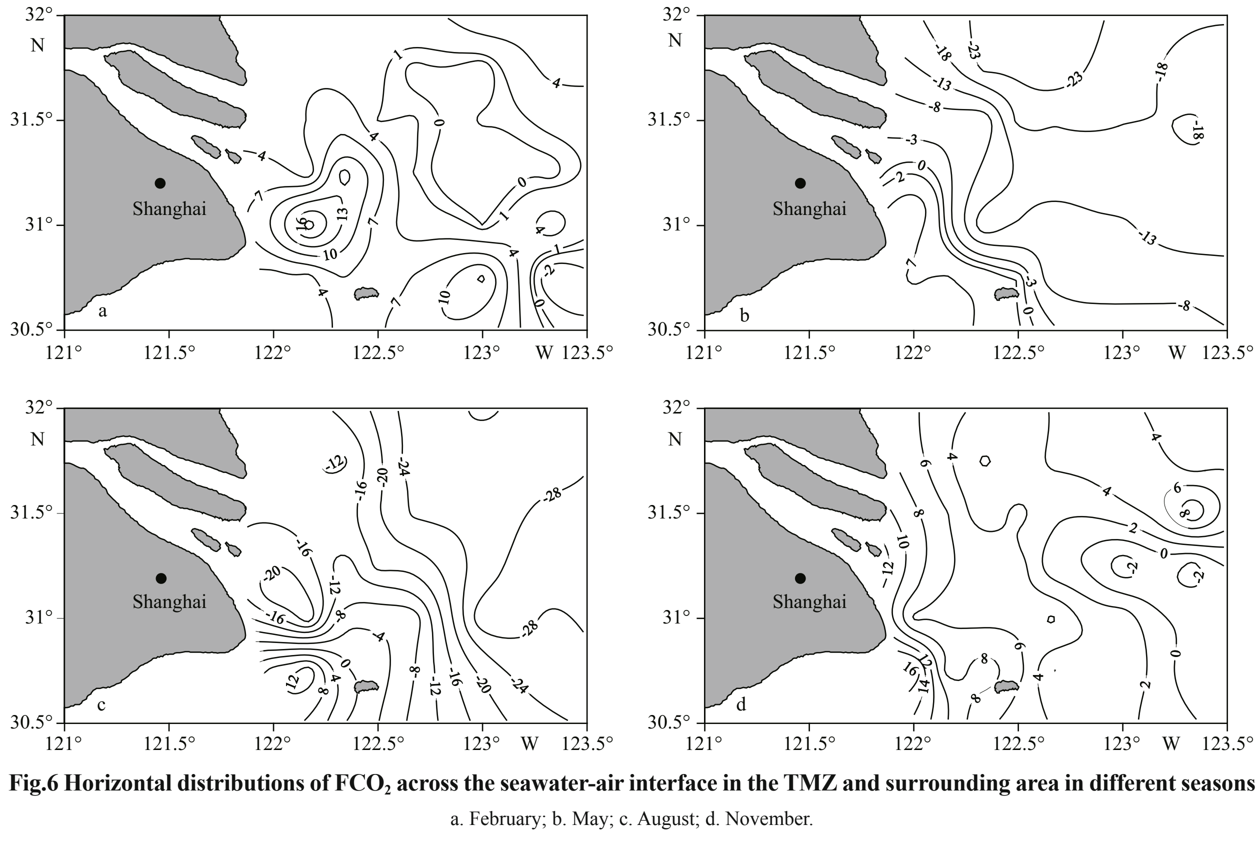

Fig.6 Horizontal distributions of FCO_2 across the seawater-air interface in the TMZ and surrounding area in different seasons

a. February; b. May; c. August; d. November.

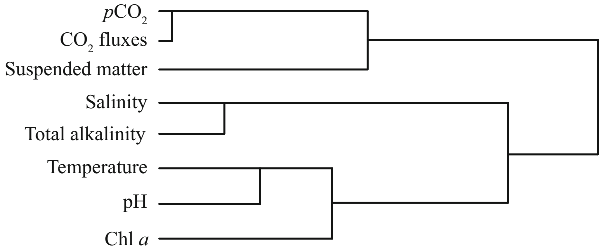

Fig.7 Cluster analysis of the influencing factors in the TMZ and surrounding area of the Changjiang River estuary

3.5 The influencing factors of FCO_2

According to our study, the sink or source characteristics of atmosphere CO_2 were quite different in the TMZ and surrounding area, compared with the outer estuary. In an estuarine area, the TMZ acts as a filter between the terrestrial and marine realms, with most suspended particle carried by rivers deposited in the TMZ. Lisitsyn (1995) calculated that, worldwide, about 93%–95% of the suspended and 20%–40% of the dissolved riverine materials are deposited in what he calls the "marginal filter". Shen et al. (2008) thought that the chemical behavior, transfer, and fate of organic matter might be affected by the TMZ. Therefore, it is not surprising that the characteristics of FCO_2 are different in the TMZ, compared with other regions. However, FCO_2 can be influenced by several factors, including the biological production or respiration of organic matter, calcification/dissolution of calcium carbonate, thermodynamic effects, physical mixing, and nitrification. However, the influences of these various factors are not isolated, rather they are interlinked. To identify the main influencing factors of CO_2 fluxes in the TMZ, we discuss seven of the said factors.

Cluster analysis of CO_2 fluxes and its influencing factors was used to determine which factor had the closest relationship with CO_2 flux (Fig.7). Cluster analysis classified the factors into three homogenous clusters, with each cluster influencing CO_2 fluxes in similar ways. Overall, pCO_2 concentration had the closest relationship with CO_2 fluxes, with a direct strong effect of pCO_2 on CO_2 flux, which accorded with the calculation of CO_2 fluxes from pCO_2 differences between seawater and air. Suspended matter concentration was also closely linked to CO_2 fluxes. The other influencing factors all had an indirect effect on CO_2 fluxes.

Factor analysis examined the influencing factors of CO_2 fluxes in the TMZ and surrounding area (Table 2). All of the influencing parameters can be represented by two factors, which contribute 74% of all information. Factor 1 contributed far more than factor 2. Table 3 presents a factor-loading matrix for the factor analysis. Factor 1 mainly includes temperature, pCO_2, and pH, suspended matter, and Chl *a*, with these factors having the greatest influence on CO_2 fluxes in the TMZ of the estuary. Factor 2 mainly includes salinity and alkalinity, which have a smaller impact on CO_2 fluxes. The importance of each influencing factor is discussed in the following section.

Table 2 Factor analysis on the influencing factors of FCO_2 in the TMZ and surrounding area

Factor	Eigenvalue	Percentage of variance	Percentage of accumulated variance
1	3.902	48.774	48.774
2	2.023	25.282	74.056
3	0.814	10.179	84.235
4	0.683	8.543	92.778
5	0.377	4.709	97.487
6	0.172	2.145	99.632
7	0.025	0.311	99.943
8	0.005	0.057	100.000

Table 3 Factor loading matrix of factor analysis (after rotation)

Parameter	1	2
Temperature	0.813	-0.213
Salinity	-0.061	0.950
Total alkalinity	0.067	0.895
pCO_2	-0.946	-0.215
pH	0.950	0.101
Suspended matter	-0.396	-0.336
Chl *a*	0.586	-0.320
CO_2 flux	-0.949	-0.190

3.5.1 Suspended matter in the TMZ

The TMZ is the region with higher suspended matter concentration than its surrounding area, and generally appears in estuaries. The location and strength of the TMZ usually changes with the estuarine circulation pattern. The TMZ, which is characterized by high suspended-matter concentrations, is an ideal site for physical, chemical, and biological reactions between dissolved and particulate species (Gebhardt et al., 2005). Therefore, the TMZ should play an important role in CO_2 degassing in estuaries.

Table 4 Correlation between FCO_2 and its influencing factors

Season	SST[a]	Salinity	Alkalinity	pCO_2	pH	Suspended particle	Chl *a*
February	0.150	-0.572**	-0.347	0.998**	-0.937**	0.621**	0.398*
May	0.251	-0.641**	-0.651**	0.999**	-0.931**	0.555**	-0.582**
August	0.031	-0.312	-0.280	0.998**	-0.969**	0.521**	0.052
November	-0.525**	-0.609**	-0.270	0.996**	-0.798**	0.504**	0.455**
Total year	-0.654**	-0.149	-0.203*	0.993**	-0.956**	0.349**	-0.403**

[a]: SST: sea surface temperature. *: Correlation is significant at the 0.05 level (2-tailed). **: Correlation is significant at the 0.01 level (2-tailed).

Suspended matter had a significant influence on the CO_2 fluxes in the TMZ and surrounding area, according to cluster analysis and the significant positive correlation between CO_2 fluxes and the concentration of suspended particles in this region (Table 4). The most conspicuous feature of the TMZ is its high concentration of suspended particles. The decomposition of organic carbon in suspended particles was the main reason that suspended particles had a significant influence on FCO_2 levels. For example, in the Seine estuary TMZ, about 20% of both POC and DOC were degraded by organisms (Garnier et al., 2008). In the Changjiang River estuary, organic carbon content in suspended particles was higher, with a range of 0.48%–0.69% (Li et al., 2006a). Organic carbon content was highest in the TMZ, decreasing upstream of the river mouth and lowest in the outer sea of the river mouth (Lin et al., 2009). Therefore, the large amount of organic carbon being decomposed in the TMZ of the Changjiang River estuary must affect the exchange of CO_2 between water and the atmosphere. The influence of organic carbon decomposition on FCO_2 was most significant in winter, when phytoplankton abundance was at its annual minimum, and thus the influence of phytoplankton on FCO_2 was limited. This low phytoplankton abundance might be the reason that the TMZ acted as a source in winter, but the outer estuary acted as a sink.

3.5.2 Sea surface temperature (SST)

Temperature is one of the most important thermodynamic factors controlling the fluxes of CO_2. Many researchers have reported that sea surface temperature (SST) has a positive correlation with seawater pCO_2 and CO_2 fluxes. This is because SST affects the equilibrium constants of dissolved inorganic carbon and, in particular, the solubility coefficient of CO_2. Solubility of CO_2 in seawater decreases with an increase in SST, so pCO_2 rises with an increase in SST. It is reported that pCO_2 may rise by ~4% when temperature increases by 1°C (Borge and Frankignoulle, 2002). However, in the TMZ and surrounding area, SST had a significant negative correlation with CO_2 fluxes on intra-annual timescales (Table 4; Fig.8), suggesting that other factor(s) might overwhelm temperature in controlling the annual fluxes of CO_2. Similar negative relationships between temperature and pCO_2 have been reported by Zhang et al. (2010) in the southern Yellow Sea in March, and by Chou et al. (2011) in the East China Sea during winter. Zhang et al. (2010) suggested that this correlation strongly indicated that the seasonal variations in pCO_2 were controlled by biological activity. There were no significant correlations between SST and FCO_2 during spring, summer, and autumn in the TMZ of the estuary in our study (Table 1; Fig.8). The results concur with Zhai and Dai's (2009) investigations in the outer estuary, where the relationship between SST and pCO_2 was generally random. In the outer estuary, SST changed very little but CO_2 flux was greatly variable during the study period, which indicated that temperature had not significantly influenced FCO_2. However, SST had a significant positive correlation with Chl *a* on intra-annual timescales (Table 1; Fig.9). The SST could have influenced the FCO_2 by controlling phytoplankton growth; phytoplankton biomass may increase as SST

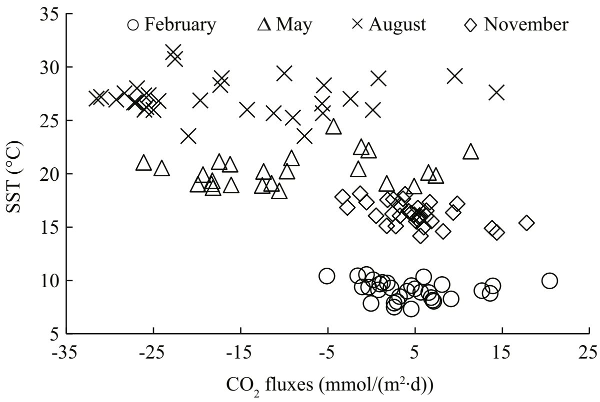

Fig.8 Relationship between SST and FCO_2 in the TMZ and surrounding area

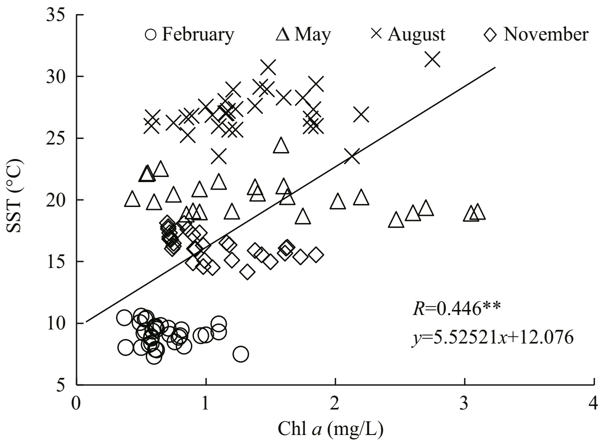

Fig.9 Relationship between SST and Chl *a* in the TMZ and surrounding area

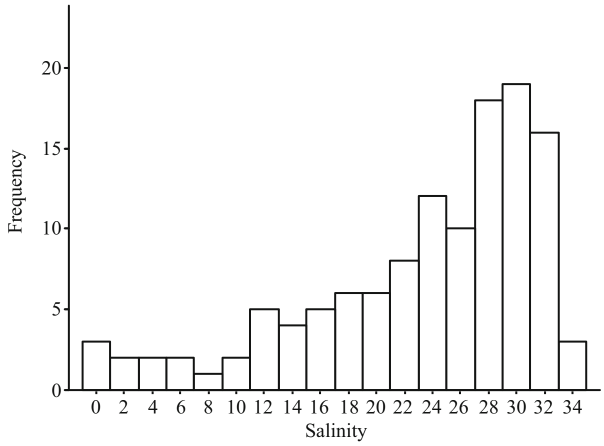

Fig.10 Surface water salinity frequencies in the TMZ and surrounding area

increases, and thus use more CO_2 in seawater. The pCO_2 in seawater may thus decrease, leading to a negative relationship between SST and FCO_2.

3.5.3 Phytoplankton

In theory, phytoplankton can absorb CO_2 and release O_2, and thus phytoplankton blooms will decrease the CO_2 concentration in seawater. Therefore, the relationship between phytoplankton and pCO_2 in seawater should be negative. In the TMZ and surrounding area, FCO_2 had a significant negative relationship with Chl *a* throughout the year (Table 4). As shown in Table 1, in the TMZ and surrounding area, Chl *a* concentration was high in May and August and low in November and February. The results are consistent with those of Song et al. (2009) and Wu et al. (2004). Song et al. (2009) showed that Chl *a* concentration in the estuary changed seasonally, with higher levels in spring and summer and lower levels in autumn and winter. Wu et al. (2004) showed that the peak period of phytoplankton abundance coincided with that of Chl *a*, which occurred during summer, but the abundance of phytoplankton was very low during the winter (dry season). Therefore, the TMZ and surrounding area acted as a sink of atmospheric CO_2 in summer and spring, but as a source in winter and autumn. However, there was no clear negative correlation between phytoplankton abundance and FCO_2 in every month, bar August (Table 4), which may be linked to phytoplankton distribution in the TMZ of the estuary and surrounding area.

The phytoplankton distribution in the TMZ and surrounding area was obviously influenced by the tides. The abundance of phytoplankton was larger during the spring tide than the neap tide, in both the flood and dry seasons. The abundance of phytoplankton was larger in the tidal flood than the tidal ebb, both during spring and neap tides (Gu et al., 1995). Additionally, phytoplankton are known to have patchy distributions in the TMZ of estuaries (Gu et al., 1995). The variable correlation between Chl *a* and FCO_2 may be caused by the asymmetric distribution of phytoplankton and the inconsistent tide time during sampling.

3.5.4 Salinity

In estuaries, salinity is one of the important factors controlling the flux of CO_2, especially in the mixed zone, where FCO_2 decreases with increasing salinity. The TMZ of the estuary was located in the freshwater-seawater mixing zone. Further, salinity was less than 32 in most sampled sites throughout the four sampling seasons (Fig.10). Thus, the salinity in the TMZ and surrounding area should play an important role in the exchange of CO_2 across the sea-air interface. Table 4 shows the relationship between sea surface salinity (SSS) and the flux of CO_2. There is a clear negative correlation between FCO_2 and SSS in February, May and November, suggesting that low FCO_2 values were mainly influenced by seasonal variations in SSS. No such correlation was observed in August. In February, May, and November, mixing between the low-temperature/high-pCO_2 estuarine or coastal water and high-temperature/low-pCO_2 water of the East China Sea influenced the FCO_2. However, the weak relationship between FCO_2 and salinity revealed that salinity was not the major influencing factor on FCO_2 in summer. According to the seasonal variation in primary production, low FCO_2 in summer was controlled by high primary production.

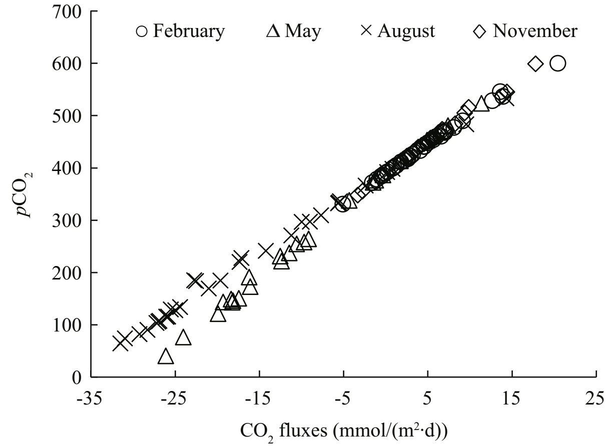

Fig.11 The relationship between CO_2 fluxes and pH in the TMZ in surface water of the TMZ and surrounding area

3.5.5 Total alkalinity and pH

The weak negative relationship between FCO_2 and total alkalinity indicated that total alkalinity was not the major controlling factor of FCO_2 in the TMZ and surrounding area (Fig.11 and Table 4). However, the pH in the surface water had a significant negative correlation with FCO_2, which indicated pH had a significance influence on FCO_2. The main alkaline compounds in the water are bicarbonate, carbonate, and hydroxide, which remove H^+ ions, and more than 90% of them are bicarbonates (Song, 2009). The pH is measured on a logarithmic scale and measures the amount of hydrogen ions (H^+) in the water; a 0.1 reduction means that the quantity of H^+ ions has increased by 30%. The carbonate system exists in the following equilibrium in water:

$H_2O+CO_2 \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO^{3-}$.

When the [H^+] or [HCO^{3-}] increase, the equilibrium may move to the left, the pCO_2 in the seawater will increase, and the uptake capacity of atmospheric CO_2 will reduce. As bicarbonate concentration is higher in seawater than the atmosphere, the pCO_2 variation caused by its change is not significant, and thus total alkalinity has a weak correlation with FCO_2. However, any little increase (or decrease) of pH may lead to a notable decrease (or increase) in [H^+] and cause a similar variation in pCO_2 with it. Therefore, pH has a strong negative correlation with FCO_2. In the TMZ and surrounding area, total alkalinity was mainly between 2 000 and 2 200 μmol/L throughout the four seasons, so any changes in total alkalinity were relatively small. Thus, although total alkalinity had a weak influence on FCO_2, the large change in pH from 7.791 to 8.800, indicates a large change in [H^+], so pH had a significant negative correlation with FCO_2.

4 CONCLUSION

The turbidity maximum zone (TMZ) in estuaries can differ in terms of its role as a source or sink of atmospheric CO_2 because of its high concentration of suspended matter. The TMZ and surrounding area in the Changjiang River estuary acted as a source of atmosphere CO_2 in February and November, and as a sink in May and August. The average FCO_2 was -9, -16, 5, and 5 mmol/(m^2·d) in May, August, November, and February, respectively. However, the source/sink characteristic differed in the TMZ compared with the outer estuary, especially in the winter, when the TMZ and surrounding area was a source, but the outer estuary was a sink of atmospheric CO_2. In addition to suspended matter, phytoplankton production and pH were the main factors influencing FCO_2 in the TMZ and surrounding area. The influence of temperature, salinity and total alkalinity on the FCO_2 was weak in the TMZ and surrounding area. Organic carbon decomposition in suspended matter was the main reason the TMZ and surrounding area was a CO_2 source in winter, and phytoplankton production was the main reason it was a CO_2 sink in summer.

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