



## Dissolved oxygen and O<sub>2</sub> flux across the water–air interface of the Changjiang Estuary in May 2003

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### ABSTRACT

The field observation of this study was carried out in the Changjiang Estuary from May 19 to 26, 2003, just a few days before the Three Gorges Dam began to store water. A total of 29 stations, including 2 anchor stations, were distributed through almost the whole salinity gradient. Based on the data gained from these stations, the biogeochemical characteristics of dissolved oxygen (DO) were examined. Spatial distribution of DO concentrations showed the pattern that it increased in a downriver direction. DO concentration generally varied within a narrow range of 7.33–8.10 mg l<sup>-1</sup> in the freshwater region and the west part of the mixed water region, and after that it increased rapidly. In vertical direction, the differences in DO concentrations between surface and 2 m above the bottom were big at the stations with water depths exceeding 20 m; DO concentration up to 14.88 mg l<sup>-1</sup> was recorded at the sea surface, while at 2 m above the bottom its concentration was only about 4 mg l<sup>-1</sup>. The fluctuation in DO concentrations was small during a period of 48 h in the mixed water region and 2 m above the bottom of the seawater region; while it was large during the same period in the seawater region for surface and 5 m below the surface layer, and a maximum variation from 8.77 to 12.66 mg l<sup>-1</sup> in 4 h was recorded. Oxygen fluxes also showed a marked spatio-temporal variation. As a whole, the freshwater region and mixed water region were an oxygen sink, while the seawater region was a source. Relationships between dissolved oxygen and some biogeochemical parameters which could markedly influence its spatio-temporal distribution were discussed in this paper.

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### 1. Introduction

Dissolved oxygen (DO) level in natural aquatic systems is a highly informative variable which can elucidate atmosphere–ocean interactions, water mass movements, net primary productivity and carbon remineralization processes. It is also strongly representative of an ecosystem's functionality and behavior (Ross et al., 2001). DO level indicates how well the water is aerated and is a commonly measured parameter because it is an immediate indicator—inadequate oxygen levels will quickly affect aquatic life. The atmosphere and aquatic plant photosynthesis are two main sources from which oxygen enters the water. Oxygen is essential not only for marine life but also for decomposition of organic matters, a process which consumes oxygen.

Estuaries are one of the important connections between land and sea and among the most productive natural systems on earth. With the rapid development of industry and agriculture in recent decades, huge amounts of nutrients from anthropogenic sources, together with other organic matters, have been discharged into shallow coastal waters each year through estuaries and other approaches such as atmospheric deposition (Wu, 1999; Liu et al., 2003; Zhang et al., 2004). Eutrophication, resulting from excess nutrient import, frequently causes a yearly harmful algae bloom, which gives a heavy stress on estuaries and the coastal environment (Rabalais and Turner, 2001). It has now become a major concern in shallow coastal waters (Turner and Rabalais, 1994; NRC, 2000). Hypoxic/anoxic conditions are usually the problematic symptoms accompanying eutrophication. Hypoxia can be a seasonal phenomenon, occurring during late summer and lasting for a few days in estuaries and fjords (Selberg et al., 2001) or months on the shelf (Rabalais and Turner, 2001).

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The Changjiang Estuary, which is currently about 120 km long and more than 90 km wide at its outer limit, is a mesotidal estuary and characterized by the complexity of morphology associated with multi-step bifurcations (Li and Zhang, 1998; Yang et al., 2003). It is a very important spawning and nursing ground for many commercially important fishes. After more than two decades of economic reform and booming industrial development, human activities have seriously impacted on its original features. Nowadays, it is presenting serious environmental problems due to excess nutrient import.

Since the China–U.S. joint study on sedimentation dynamics in the Changjiang Estuary and on the adjacent continental shelf in 1980–1981 first documented the existence of a low DO area (minimum value:  $2 \text{ mg l}^{-1}$ ) in the bottom waters of areas around the Changjiang Estuary, it has been confirmed by many researches (Limeburner et al., 1983; Chen, 1988; Tian et al., 1993; Li et al., 2002). Shanghai Comprehensive Survey of Coastal Zone Resources (SCSCZR) in 1981–1983 showed that low oxygen values appeared during summers around  $123^{\circ}00' \text{ E}$ ,  $30^{\circ}50' \text{ N}$  off the Changjiang Estuary at 20–40 m water depth (Chen, 1988). A hypoxic zone ( $<2 \text{ mg l}^{-1}$ ) of  $13,700 \text{ km}^2$  with an average thickness of 20 m at the bottom of the Changjiang Estuary with an oxygen minimum value of  $1 \text{ mg l}^{-1}$  was found in 1999, and its center was very similar to those observed during the China–U.S. joint study and SCSCZR (Li et al., 2002). The information for fully understanding DO biogeochemical behaviors in the Changjiang Estuary, however, is still insufficient. Furthermore, the Changjiang Three Gorges Dam, a project designed to generate power and improve flood control and navigation, has begun to store water since the 1st of June, 2003. Its construction has been causing widespread scientific controversy and worldwide concern, for it is expected that the construction will seriously change the primary characteristics of the Changjiang discharge and then have potential influence on the ecosystem in the Changjiang River and the East China Sea (Chen, 2000; Chen et al., 2003). The main objectives of this paper are to describe the DO spatial distribution in the Changjiang Estuary along almost the whole salinity gradient and diurnal variation at two representative sites, discuss the main factors impacting on them, and estimate the air–sea oxygen fluxes.

## 2. Materials and methods

This study was carried out from 19 to 26 May 2003 on board R/V *Zhe Hai Huan Jian*, just several days before the

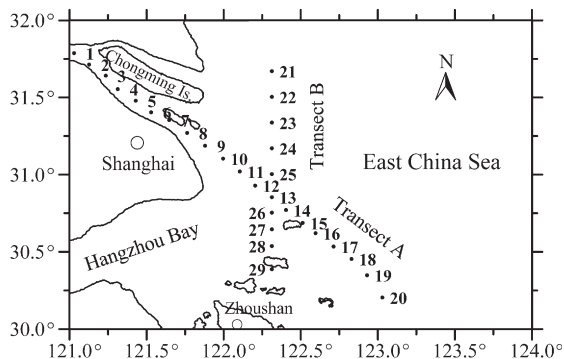


Fig. 1. Location of sampling stations in the Changjiang Estuary.

Three Gorges Dam began to store water. A total of 29 stations were established over two intersected transects identified as A and B (Fig. 1). Transect A extended from the freshwater river to the saltwater sea covering almost the whole salinity gradient; transect B ran across the edge of the bar area (Chen et al., 1999) covering the whole river mouth. At Stations 13 and 20 (two anchor stations), parameters were measured at 4-h intervals over a period of 48 h. Water sample collections were guided by a SeaBird CTD probe and carried out with a 5.0-l Niskin bottle. Water samples were taken at the depth of 0 m and 2 m above the bottom if water depth was  $<10 \text{ m}$ , and 0 m, 5 m, 10 m, 20 m and 2 m above the bottom if water depth was  $>10 \text{ m}$ . Some layers were not sampled when they were relatively near the 2 m above the bottom layer, but samples of 2 m above the bottom layer were taken in any case.

Physical parameters of seawater such as temperature, salinity and dissolved oxygen (DO) were determined using in situ instruments. DO was measured by traditional Winkler titration (Dickson, 1994). Just after sampling, sample for DO measurement was fixed by the addition of  $\text{MnCl}_2$  and alkaline KI solutions. After a period of time, sample was titrated with  $\text{Na}_2\text{S}_2\text{O}_3$  solution to a starch indicator (visual) endpoint after the addition of  $\text{H}_2\text{SO}_4$ . For measuring inorganic nutrient parameters, the water samples were filtered immediately after collection through pre-cleaned  $0.45 \mu\text{m}$  pore-size cellulose filters, and preserved deep frozen in the dark until analysis. Inorganic nutrients were determined by classical spectrophotometric methods (Grasshoff et al., 1983), and precisions were shown in Zhang et al. (1997). Water samples for chlorophyll *a* (Chl *a*) analysis were filtered through Whatman GF/F filters, which were immediately frozen until further analysis by a spectrophotometric method following the procedure outlined by Lorenzen (1967). Standard SPSS 11.0 for Windows software was used to calculate the correlation coefficients between DO concentrations and some biogeochemical parameters including salinity, water temperature, Chl *a*,  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  concentrations.

The water–air  $\text{O}_2$  flux ( $F$ ,  $\text{g m}^{-2} \text{ d}^{-1}$ ) was calculated using the following equation (Skjelvan et al., 2001; Olsen et al., 2002):

$$F = k([\text{O}_2]_{\text{m}} - [\text{O}_2]_{\text{s}})$$

where  $k$  is the gas transfer velocity for oxygen,  $[\text{O}_2]_{\text{m}}$  is measured oxygen content in the surface water and  $[\text{O}_2]_{\text{s}}$  is the corresponding saturation concentration calculated according to the equation of Weiss (1970). The magnitude of the flux is mainly imposed by the value of  $k$ , which is a function of various parameters and processes such as wind speed, turbulence at the interface, air bubbles, surface organic films, etc (Borges et al., 2004). However, wind speed is recognized as the main forcing factor on the  $k$  value and several algorithms to derive  $k$  from wind speed have been proposed in literature (e.g. Liss and Merlivat, 1986; Tans et al., 1990; Wanninkhof, 1992; Wanninkhof and McGills, 1999; Kuss et al., 2004). Among them, the relationships proposed by Wanninkhof (1992) have been widely used to calculate the gas flux across water–air interface of different marine areas including the areas around estuaries (Frankignoulle et al., 1998; Hellings et al., 2001; Borges and Frankignoulle, 2002). Field measurements on carbon dioxide had suggested that the

Wanninkhof (1992) quadratic relationship (for short-term winds) is reliable at low/moderate wind speeds, i.e.  $0\text{--}12\text{ m s}^{-1}$  (McGillis et al., 2001). This range of wind speed is consistent with the wind speeds we obtained from a standard meteorological station at Shengsi Island (a northern island of Zhoushan archipelago near Station 15 of this cruise), which ranged from  $2.5$  to  $11.1\text{ m s}^{-1}$  during the surveys. Since the  $k$  values for oxygen of the studied area measured on the spot are not available, the Wanninkhof (1992) quadratic relationship was used to calculate them. As a first attempt, this calculation is adequate for the purpose of tracing biogeochemical processes in this work. Positive  $F$  values indicate the transfer of oxygen from the waters to the atmosphere, while negative ones represent the reverse.

The gas transfer velocity of Wanninkhof (1992) quadratic relationship is expressed as:

$$k = 0.31 \times u^2 (Sc/Sc')^{-1/2}$$

where  $u$  is the wind speed;  $Sc$  and  $Sc'$  are Schmidt numbers.  $Sc$  was calculated using the algorithm proposed by Wanninkhof (1992). Its value under certain salinity was interpolated.  $Sc'$  is the Schmidt number of  $O_2$  in water of the same salinity as  $Sc$  at  $20\text{ }^\circ\text{C}$  (Wanninkhof, 1992).

### 3. Results and discussion

#### 3.1. Spatial distribution of DO concentration

Dynamic patterns of DO emerge in estuaries from complex interactions among physical, chemical, and biological processes (Turner et al., 1987; Kemp et al., 1992; Diaz and Rosenberg 1995; Borsuk et al., 2001). The DO concentration of a water mass is largely determined by a balance between: the exchange of atmospheric oxygen with the upper mixed layer, net increases due to photosynthetic processes and net decreases due to respiratory demands and heterotrophic processes. Variations in temperature, freshwater discharge, saltwater intrusion, bathymetry, circulation, meteorology, and biological production and respiration combine to produce strong estuarine DO gradients (Falkowski et al., 1980; Stanley and Nixon 1992; Stanley 1993).

In the Changjiang Estuary, the tidal wave reaches as far as  $640\text{ km}$  inland (Chen et al., 1999); the freshwater influence extends ca.  $200\text{ km}$  into the sea (Milliman et al., 1986). The saline interface shows considerable variability in depth and width owing to the balance between river discharge and marine driving forces. Mixing of fresh and saline water occurs from the head of the mouth bar to the mouth of the Estuary (Chen et al., 1999).

Generally, waters around the Changjiang Estuary can be classified as three principal water masses: (1) freshwater from the Changjiang River; (2) seawater (continental shelf waters) entering the East China Sea, either with the Yellow Sea longshore current from the north or with the Taiwan Warm Current and its branches from the south; and (3) the transition zone between freshwater and seawater, resulting in estuarine mixed water (Chen et al., 1999).

Based on the salinity data gained during the field investigation, salinity between Stations 10 and 16 changed quickly, indicating that the freshwater and seawater interacted with

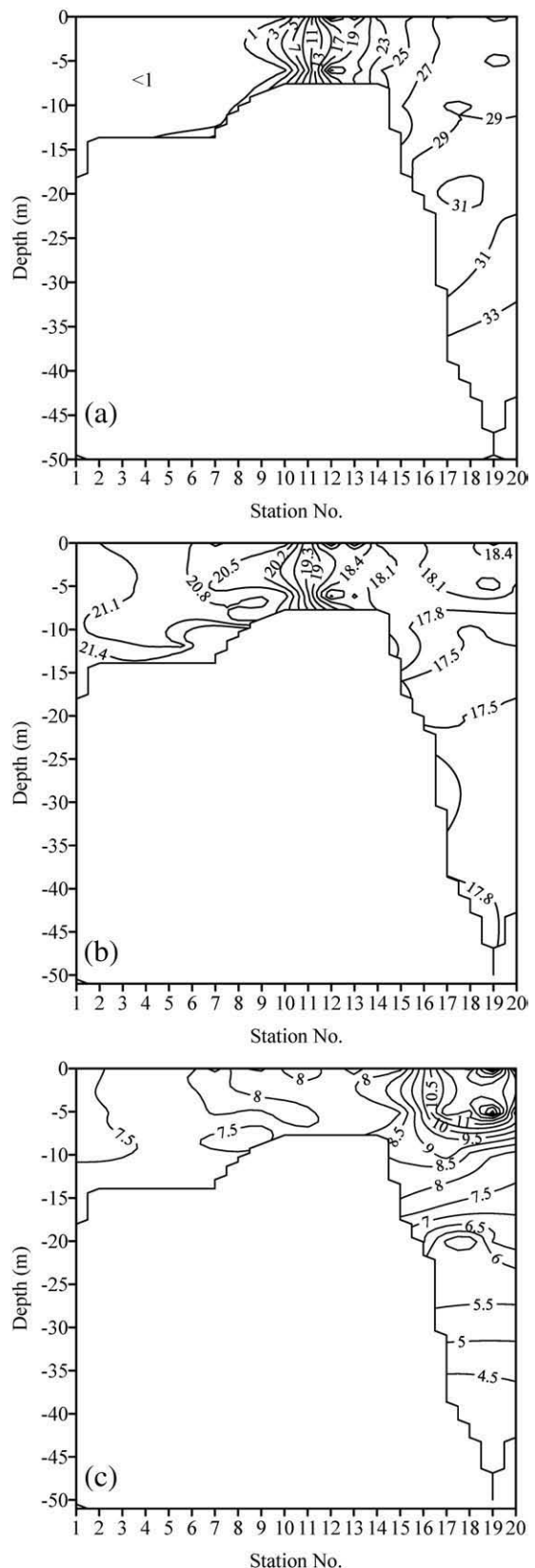


Fig. 2. The spatial distributions of salinity (a), temperature (b,  $^\circ\text{C}$ ) and DO (c,  $\text{mg l}^{-1}$ ) isolines along Transect A.

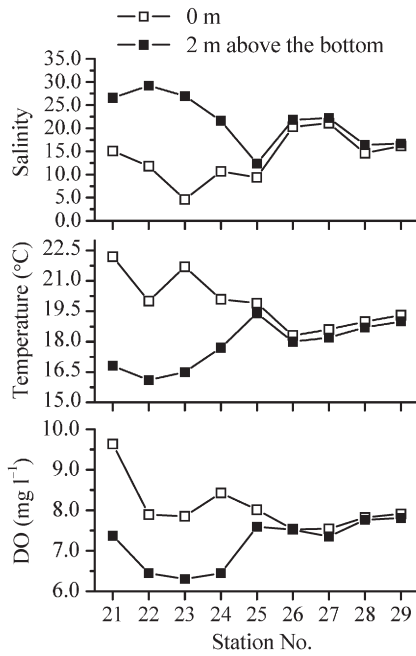


Fig. 3. The distributions of salinity, temperature and DO along Transect B.

each other in this area (Fig. 2). Basically, Station 10 could be regarded as the salt-wedge (Chen et al., 1999) and waters ahead of and behind it could be classified as freshwater mass and estuarine mixed water mass, respectively; Station 16 could be regarded as the estuarine front (Chen et al., 1999) and waters ahead of and behind it could be classified as estuarine mixed water mass and seawater mass. Variation of water temperature exhibited a trend that it decreased with the increase of salinity in a downriver direction, which meant that salinity and temperature in the Changjiang Estuary during this investigation showed the summer characteristic, i.e. seawater is cooler than river water (Fig. 2).

On the whole, DO concentrations increased downriver with the rise of salinity and reached their high values in the area between Stations 17 and 20 (Fig. 2). In the freshwater and

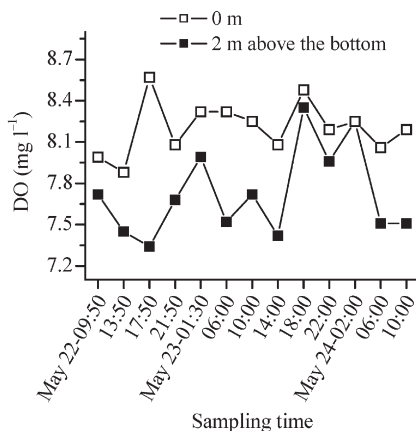


Fig. 4. Temporal variations in DO within 48 h for Station 13.

mixed water before Station 14, DO concentrations were relatively stable and fluctuated basically within the narrow range of 7.33–8.10 mg l<sup>-1</sup>, and after that they increased rapidly. In the relatively deeper water column between Stations 17 and 20, DO concentrations decreased with water depth from the highest of 14.88 mg l<sup>-1</sup> at the 0 m layer of Station 19 to the lowest of ~4 mg l<sup>-1</sup> at the 2 m above the bottom layer of the same station.

Transect B was situated among estuarine mixed water mass, and water depths of stations located along it were shallow, only three of them a bit deeper than 10 m. So, for most stations, only water samples of 0 m layer and 2 m above the bottom layer were carried. Results indicated that at the four northern stations, namely Stations 21 to 24, DO concentrations at 0 m layer were markedly higher than those at 2 m above the bottom layer. Even for Station 22, where the difference between the two layers was the smallest among the four northern stations, the DO concentration at 0 m layer was still 1.44 mg l<sup>-1</sup> higher than it was at the 2 m above the bottom layer; while the differences between the two layers were small and all were <0.5 mg l<sup>-1</sup> at each of the other five stations (Fig. 3). Average DO concentrations were 8.07±0.65 (mean± standard deviation) and 7.18±0.60 mg l<sup>-1</sup> for 0 m and 2 m above the bottom layer, respectively. The variation pattern of DO along Transect B was similar to that of temperature, while it was to some extent inverse to that of salinity (Fig. 3). All these three parameters indicated that water in the south part of Transect B mixed better than that in the north part.

Dissolved oxygen is of concern in aquatic ecosystems because depressed levels can be stressful for fish and other limnetic or marine organisms. A minimum level of 5.0 mg l<sup>-1</sup> is considered crucial for aquatic life. When DO levels drop to 3

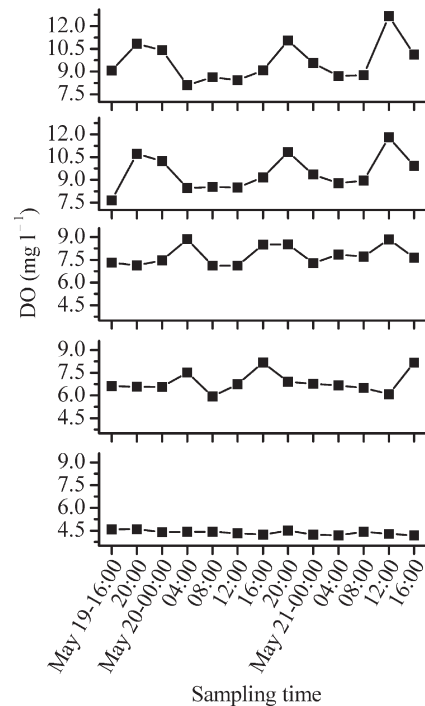


Fig. 5. Temporal variations in DO within 48 h for Station 20 (from top to bottom: 0 m, 5 m, 10 m, 20 m and 2 m above the bottom).

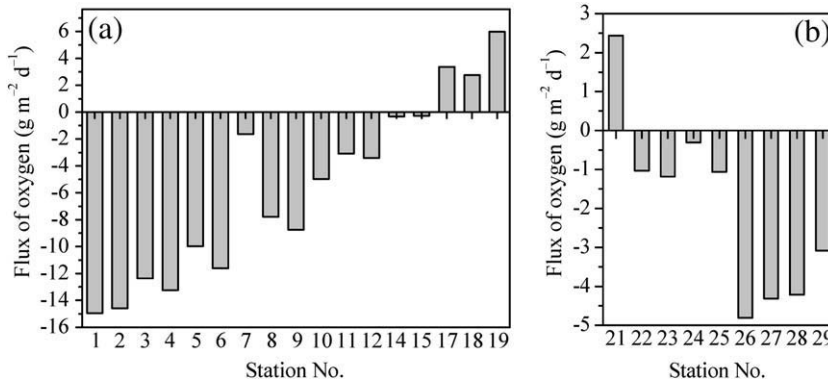


Fig. 6. Variations of oxygen flux strength along Transects A (a) and B (b).

to 5 mg l<sup>-1</sup>, most organisms become stressed, and mobile species must move to areas with higher oxygen concentrations to survive, while immobile species often perish. Below 3 mg l<sup>-1</sup>, a condition called hypoxia sets in. Hypoxic levels are regularly seen in the area around the Changjiang Estuary, particularly in the summer time (Li et al., 2002).

The National Standard number GB3097-1997, which is established by the Standardization Administration of China (SAC), has defined four grades of seawater. Grade I is suitable for nature reserves with DO concentration of ≥6 mg l<sup>-1</sup>; Grade II is suitable for mariculture and leisure activities such as swimming with DO concentration of ≥5 mg l<sup>-1</sup>; Grade III is suitable for tourism and industrial purpose except food processing with DO concentration of ≥4 mg l<sup>-1</sup>; Grade IV is harbour quality with DO concentration of ≥3 mg l<sup>-1</sup>. Based on this standard, DO concentrations measured up to Chinese seawater quality grade I in the brackish water region off the Changjiang mouth.

### 3.2. Temporal distribution of DO concentration

To investigate the trend of DO variation with time, two representative anchor stations viz Stations 13 and 20 were monitored over a period of 48 h in mixed water and seawater regions, respectively. Parameters were measured at about 4-h intervals.

Water depth of Station 13 was only 8 m. Two layers, namely 0 m and 2 m above the bottom, were studied. The plot of DO against time variation shows that, there is only one time that the two layers were recorded with the same DO concentration, and apart from that 0 m layer had a higher DO concentration than that of 2 m above the bottom layer; the biggest difference between the two layers, which was recorded at 17:50, May 22, was 1.23 mg l<sup>-1</sup> (Fig. 4). This indicates that the waters were not well mixed most of the time despite the shallow depth. The same conclusion could also be drawn from salinity data (not shown). DO concentrations fluctuated more widely at 2 m above the bottom layer than at 0 m layer, but at both of the two layers the magnitude of the fluctuations was usually less than 0.5 mg l<sup>-1</sup>, namely 6%, from one sampling time to the next. The average DO concentrations were 8.20±0.19 and 7.72±0.32 mg l<sup>-1</sup> for 0 m and 2 m above the bottom layer, respectively.

Anchor Station 20 was located near the estuarine front. Its depth was 43 m, according to which a total of five layers, namely 0 m, 5 m, 10 m, 20 m and 2 m above the bottom, were investigated. For the five samples collected at the same time, DO concentration decreased gradually with the increase of water depth except for only a few cases; the maxima nearly always appeared at the top two layers, especially at the 0 m layer, while the minima appeared at the 2 m above the bottom layer with no exception (Fig. 5). The biggest difference among

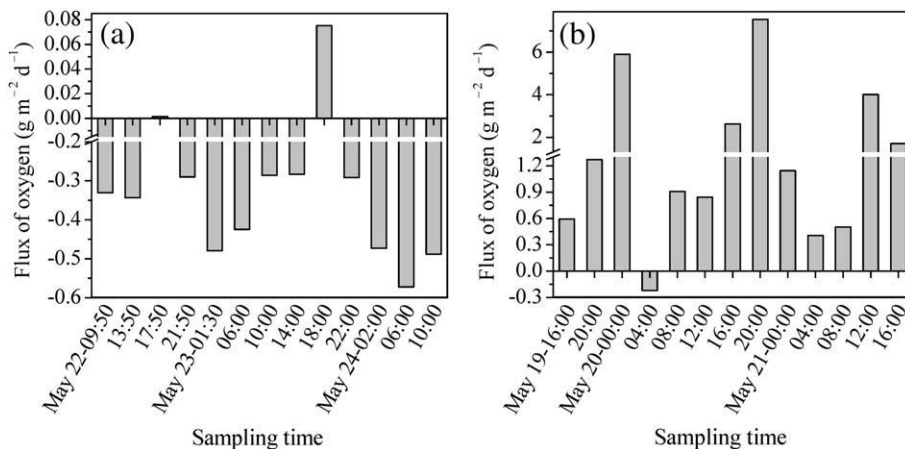


Fig. 7. Variations of oxygen flux strength within 48 h for Stations 13 (a) and 20 (b).

**Table 1**

Correlation coefficients between DO and some biogeochemical parameters

	Data of anchor Station 13			Data of anchor Station 20			Data of other stations		
	Data of 0 m layer (n=13)	Data of 2 m above the bottom (n=13)	Whole data (n=26)	Data of 0 m layer (n=13)	Data of other layers (n=52)	Whole data (n=65)	Data of 0 m layers (n=26)	Data of other layers (n=52)	Whole data (n=78)
DO vs. S	ns	-0.912***	-0.866***	-0.741**	-0.909***	-0.907***	0.527**	ns	ns
DO vs. T	ns	0.899***	0.764***	ns	0.478***	0.517***	ns	ns	ns
DO vs. Chl <i>a</i>	ns	-	-	0.787**	-	-	0.896***	0.688***	0.726***
DO vs. NO <sub>3</sub> <sup>-</sup>	ns	0.619*	0.501**	ns	ns	ns	-0.501**	ns	ns
DO vs. PO <sub>4</sub> <sup>3-</sup>	ns	ns	ns	ns	-0.863***	-0.852***	-0.688***	ns	-0.244*

S: salinity; T: water temperature ns: not significant; \*: significant at  $P < 0.05$ ; \*\*: significant at  $P < 0.01$ ; \*\*\*: significant at  $P < 0.001$ .

the five samples collected at the same time was  $8.38 \text{ mg l}^{-1}$  (12:00, May 21), more than twice the smallest  $4.04 \text{ mg l}^{-1}$  (04:00, May 20), which means the average vertical oxygen gradient reached  $0.20 \text{ mg l}^{-1} \text{ m}^{-1}$  at that time. Compared with other layers, DO concentration was more variable from one sampling time to the next at the 0 m layer and a variation from  $8.77$  to  $12.66 \text{ mg l}^{-1}$  was recorded during the period of 08:00 to 12:00, May 21. That means the DO concentrations varied 44.4% in 4 h. The variation trends of DO concentration at the top two layers were very similar and showed a significant correlation ( $R^2=0.8734$ ,  $P < 0.001$ ). Among the five layers studied, DO concentrations at 2 m above the bottom layer were the most stable, and their variation ratios were  $\leq 6.1\%$  for any two sequent sampling times. From 0 m to 2 m above the bottom layer, the average DO concentrations were  $9.65 \pm 1.31$ ,  $9.45 \pm 1.18$ ,  $7.80 \pm 0.67$ ,  $6.86 \pm 0.69$ ,  $4.37 \pm 0.14 \text{ mg l}^{-1}$ , respectively. DO differences between the top two layers for the samples collected at the same time were usually  $< 0.3 \text{ mg l}^{-1}$ , namely  $< 3.1\%$  of the averaged DO concentration at these two layers, which means that water in the upper 5 m was well mixed in terms of DO concentration. This could also be proved by the salinity data gained at the same time (not shown).

DO variation with time indicates that, at Station 13 and the upper 20 m of Station 20, its concentrations were significantly  $> 6.0 \text{ mg l}^{-1}$  except for a very few cases, and measured up to Chinese seawater quality grade I; at the 2 m above the bottom layer of Station 20, its concentrations only measured up to Chinese seawater quality grade III.

### 3.3. Air–water oxygen flux

Dissolved oxygen concentration in the upper layer of the ocean is affected by the transport of oxygen into and out of this layer. Oxygen will be transported horizontally by advective forces and vertically by air–sea gas exchange as well as by mixing in the water column. In addition, biological production and remineralization will also alter the oxygen concentration in the water column.

To understand the status of air–water oxygen exchange in the Changjiang Estuary area, the oxygen fluxes across the air–water interface were calculated. Spatial data indicate that an oxygen sink gradually shifted to a source in a downriver direction, and the strength of oxygen fluxes ranged from  $-14.95$  to  $5.98 \text{ g m}^{-2} \text{ d}^{-1}$  (Fig. 6). Stations 1 to 15 of Transect A and all the stations of Transect B except Station 21 were sinks for atmospheric oxygen, and their average strength was  $-5.77 \pm 5.00 \text{ g m}^{-2} \text{ d}^{-1}$  during this cruise; the rest were sources for atmospheric oxygen, and their mean strength was  $3.64 \pm 1.61 \text{ g m}^{-2} \text{ d}^{-1}$ .

Temporal data indicate that, for both Stations 13 and 20, the strength of oxygen flux varied within a wide range, and even the direction changed from one sampling time to another (Fig. 7). Considering the whole studied period, Station 13 was a net sink for atmospheric oxygen and the average  $F$  value was  $-0.32 \pm 0.19 \text{ g m}^{-2} \text{ d}^{-1}$ , while Station 20 was a net source and the average  $F$  value was  $2.10 \pm 2.34 \text{ g m}^{-2} \text{ d}^{-1}$ .

### 3.4. Factors influencing DO concentration

The ability of water to hold oxygen is dependent on salinity, temperature, time of day, season and so on. Oxygen is not very soluble in water, and is even less soluble in salt water. Temperature also plays a big role. Water at higher temperatures cannot hold as much oxygen as colder water. DO levels vary greatly during a diurnal cycle. Generally, the water at noon holds high levels of DO due to oxygen generated from photosynthesis; once night falls, photosynthesis stops and plants consume oxygen as they respire, decreasing DO levels.

DO levels are also affected by depth. Temperature differences at different depths affect how much oxygen the water can hold. Waters can become stratified in late spring and summer, which means a layer of warmer, fresher water forms over a colder, saltier layer. Thus, oxygen is unable to reach the lower depths, resulting in lower DO levels at deeper depths and higher near the surface.

Nutrient availability can impact on DO levels in several ways. Excess nutrients lead to an increase in phytoplankton and other types of algae. When the algae die and decompose, they use up oxygen in the estuary, resulting in low DO conditions. In some cases, living phytoplankton or algae can also cause low DO conditions.

Historically Chl *a* has been used as a measure of phytoplankton standing stock. Also, when related to photosynthetic carbon production, the concentration of Chl *a* and its distribution in water column allow one to estimate an index of the efficiency of phytoplankton in harvesting light, consuming CO<sub>2</sub> and releasing oxygen.

Obviously, based on the whole spatial data obtained in this study, the highly significant correlation between DO and Chl *a* indicates that phytoplankton photosynthesis was a major factor influencing DO spatial distribution (Table 1). In the Changjiang Estuary, nutrient concentrations generally decreased seaward, which is mainly because they were diluted by seawater and consumed by autotroph especially phytoplankton during their export to sea. When only the data obtained at water surface are considered, significant negative correlations exist between DO and the parameters of NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup> concentrations, which seems to further prove the

conclusion that phytoplankton photosynthesis has a significant influence on DO spatial distribution from another aspect (Table 1). The influence of phytoplankton photosynthesis on DO spatial distribution must be rather strong at water surface resulting in a positive correlation between DO and salinity, for they should be negatively correlated under normal conditions (Table 1).

Data obtained from Station 13 show that DO variation with time can be mainly attributed to the influence of physical factors in the mixed water region (Table 1). The influence of salinity on DO variation with time was greater than that of temperature based on the correlation coefficients between DO and them. The significant positive correlation between DO and water temperature is inconsistent with thermodynamic knowledge, which suggests that the influence of other factors on DO variations with time is more significant than the thermodynamic factor. When only the data obtained at water surface are considered, none of the five parameters has significant correlation with DO viz salinity, water temperature, Chl *a*, NO<sub>3</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup> concentrations.

Data obtained from Station 20 show that DO variation with time can be attributed to the conjunct influence of physical and biological factors in seawater region (Table 1). Advective transport, namely the movement of water body with higher DO concentration from other regions to Station 20, must have an important influence on DO variations with time in the upper two layers, because two of the three marked peak values appeared at nighttime when the influence of photosynthesis stopped (Fig. 5). It seems that PO<sub>4</sub><sup>3-</sup> concentration is more likely to become a limiting factor of phytoplankton photosynthesis than NO<sub>3</sub><sup>-</sup> considering the whole water column, since it had a significant negative correlation with DO while NO<sub>3</sub><sup>-</sup> did not. This coincides with other reports (e.g. Harrison et al., 1990; Pu et al., 2000, 2001).

#### 4. Conclusions

In the Changjiang Estuary, spatial DO distribution showed a clear pattern that its concentration increased in a downriver direction in May 2003. The significant positive correlation between DO and Chl *a* indicates that the phytoplankton photosynthesis was a major factor for DO spatial distribution. In the south–north direction, DO difference between 0 m and 2 m above the bottom layer was more significant in the north part than in the south part. The average DO concentration in the region out of the Changjiang mouth was significantly >6 mg l<sup>-1</sup>, measured up to Chinese seawater quality grade I.

The fluctuation in DO was small during a period of 48 h in the mixed water region and 2 m above the bottom of the seawater region; while it was large during the same period in the seawater region for surface and 5 m below the surface layer, and a variation from 8.77 to 12.66 mg l<sup>-1</sup> in 4 h was recorded. DO variations with time are mainly attributed to the influence of physical factors in the mixed water region and the conjunct influence of physical and biological factors in the seawater region.

Oxygen fluxes also showed a marked spatio-temporal variation. As a whole, fresh water and mixed water region was an oxygen sink, while the seawater region was a source.

DO is one of the parameters widely used to indicate seawater quality. Since it shows highly dynamic character-

istics in the Changjiang Estuary, sufficient spatial and temporal DO data are needed for estimating its annual flux accurately.

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#### References

- Borges, A.V., Frankignoulle, M., 2002. Distribution and air-water exchange of carbon dioxide in the Scheldt plume off the Belgian coast. *Biogeochemistry* 59, 41–67.
- Borges, A.V., Delille, B., Schiettecatte, L.-S., Gazeau, F., Abril, G., Frankignoulle, M., 2004. Gas transfer velocities of CO<sub>2</sub> in three European estuaries (Randers Fjord, Scheldt, and Thames). *Limnology and Oceanography* 49, 1630–1641.
- Borsuk, M., Stow, C.A., Luettich Jr., R.A., Paerl, H.W., Pinckney, J.L., 2001. Probabilistic prediction of hypoxia in the Neuse River Estuary using an empirical model of oxygen dynamics. *Estuarine, Coastal and Shelf Science* 52, 33–49.
- Chen, J.Y., 1988. Report of Shanghai Comprehensive Survey of Coastal Zone Resources. Shanghai Science and Technology Press, Shanghai, pp. 114–116.
- Chen, C.T.A., 2000. The Three Gorges Dam: reducing the upwelling and thus productivity in the East China Sea. *Geophysical Research Letters* 27, 381–383.
- Chen, J., Li, D., Chen, B., Hu, F., Zhu, H., Liu, C., 1999. The processes of dynamic sedimentation in the Changjiang Estuary. *Journal of Sea Research* 41, 129–140.
- Chen, C., Zhu, J., Beardsley, R.C., Franks, P.J.S., 2003. Physical–biological sources for dense algal blooms near the Changjiang River. *Geophysical Research Letters* 30, 1515–1518.
- Diaz, R.J., Rosenberg, R., 1995. Marine benthic hypoxia: a review of its ecological effects and the behavioural responses of benthic macrofauna. *Oceanography and Marine Biology: An Annual Review* 33, 245–303.
- Dickson, A.G., 1994. Determination of dissolved oxygen in sea water by Winkler titration. *WOCE Hydrographic Program, Operations and Methods Manual*. Woods Hole, Massachusetts, pp. 1–11.
- Falkowski, P.G., Hopkins, T.S., Walsh, J.J., 1980. An analysis of factors affecting oxygen depletion in the New York Bight. *Journal of Marine Research* 38, 479–506.
- 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.
- Grasshoff, K., Ehrhardt, M., Kremling, K., 1983. *Methods of Seawater Analysis*, Second Ed. Verlag Chemie GmbH D6940, Weinheim. 419 pp.
- Harrison, P.J., Hu, M.H., Yang, Y.P., Lu, X., 1990. Phosphate limitation in estuarine and coastal waters of China. *Journal of Experimental Marine Biology and Ecology* 140, 79–87.
- Hellings, L., Dehairs, F., Damme, S.V., Baeyens, W., 2001. Dissolved inorganic carbon in a highly polluted estuary (the Scheldt). *Limnology and Oceanography* 46, 1406–1414.
- Kemp, W.M., Sampou, P.A., Garber, J., Tuttle, J., Boynton, W.R., 1992. Seasonal depletion of oxygen from bottom-waters of Chesapeake Bay: roles of benthic and planktonic respiration and physical exchange processes. *Marine Ecology Progress Series* 85, 137–152.
- Kuss, J., Nagel, K., Schneider, B., 2004. Evidence from the Baltic Sea for an enhanced CO<sub>2</sub> air–sea transfer velocity. *Tellus* 56B, 175–182.
- Li, J., Zhang, C., 1998. Sediment resuspension and implications for turbidity maximum in the Changjiang Estuary. *Marine Geology* 148, 117–124.
- Li, D., Zhang, J., Huang, D., Wu, Y., Liang, J., 2002. Oxygen depletion off the Changjiang (Yangtze River) Estuary. *Science in China Series D* 45, 1137–1146.
- Limeburner, R., Beardsley, R.C., Zhao, J., 1983. Water masses and circulation in the East China Sea. *Proceedings of International Symposium on Sedimentation on the Continental Shelf, with Special Reference to the*

- East China Sea, April 12–16, 1983, Hangzhou, China, vol. 1. Ocean Press, Beijing, pp. 285–294.
- Liss, P.S., Merlivat, L., 1986. Air–sea gas exchange rates: introduction and synthesis. In: Buat-Ménard, P. (Ed.), *The Role of Air–sea Exchange in Geochemical Cycling*. Reidel, Dordrecht, Netherlands, pp. 113–127.
- Liu, S.M., Zhang, J., Chen, S.Z., Chen, H.T., Hong, G.H., Wei, H., Wu, Q.M., 2003. Inventory of nutrient compounds in the Yellow Sea. *Continental Shelf Research* 23, 1161–1174.
- Lorenzen, C.J., 1967. Determination of chlorophyll and phaeopigments: spectrophotometric equations. *Limnology and Oceanography* 12, 343–346.
- McGillis, W.R., Edson, J.B., Ware, J.D., Dacey, J.W.H., Jeffrey, E.H., Fairall, C.W., Wanninkhof, R., 2001. Carbon dioxide flux techniques performed during GasEx-98. *Marine Chemistry* 75, 267–280.
- Milliman, J.D., Shen, H., Yang, Z., Meade, R.H., 1986. Transport and deposition of river sediment in the Changjiang estuary and adjacent continental shelf. *Continental Shelf Research* 4, 37–45.
- NRC, 2000. *Clean Coastal Waters: Understanding and Reducing the Effects of Nutrient Pollution*. National Academy Press, Washington, 405 pp.
- Olsen, A., Anderson, L.G., Johannessen, T., 2002. The impact of climate variations on fluxes of oxygen in the Barents Sea. *Continental Shelf Research* 22, 1117–1128.
- Pu, X., Wu, Y., Zhang, Y., 2000. Nutrient limitation of phytoplankton in the Changjiang Estuary. I. Condition of nutrient limitation in autumn. *Acta Oceanologica Sinica* 22 (4), 60–66.
- Pu, X., Wu, Y., Zhang, Y., 2001. Nutrient limitation of phytoplankton in the Changjiang Estuary. II. Condition of nutrient limitation in spring. *Acta Oceanologica Sinica* 23 (3), 57–65.
- Rabalais, N.N., Turner, R.E., 2001. Hypoxia in the northern Gulf of Mexico: description, causes and change. In: Rabalais, N.N., Turner, R.E. (Eds.), *Coastal Hypoxia: Consequences for Living Resources and Ecosystems*. American Geophysical Union, Washington, pp. 1–36.
- Ross, S.W., Dalton, D.A., Kramer, S., Christensen, B.L., 2001. Physiological (antioxidant) responses of estuarine fishes to variability in dissolved oxygen. *Comparative Biochemistry and Physiology Part C* 130, 289–303.
- Selberg, C.D., Eby, L.A., Crowder, L.B., 2001. Hypoxia in the Neuse River Estuary: responses of blue crabs and crabs. *North American Journal of Fisheries Management* 21, 358–366.
- Skjelvan, I., Falck, E., Anderson, L.G., Rey, F., 2001. Oxygen fluxes in the Norwegian Atlantic Current. *Marine Chemistry* 73, 291–303.
- Stanley, D.W., 1993. Long-term trends in Pamlico River Estuary nutrients, chlorophyll, dissolved oxygen, and watershed nutrient production. *Water Resources Research* 29, 2651–2662.
- Stanley, D.W., Nixon, S.W., 1992. Stratification and bottom-water hypoxia in the Pamlico River Estuary. *Estuaries* 15, 270–281.
- Tans, P.P., Fung, I.Y., Takahashi, T., 1990. Observational constraints on the global atmospheric CO<sub>2</sub> budget. *Science* 247, 1431–1438.
- Tian, R.C., Hu, F.X., Martin, J.M., 1993. Summer nutrient fronts in the Changjiang (Yangtze River) Estuary. *Estuarine, Coastal and Shelf Science* 37, 27–41.
- Turner, R.E., Rabalais, N.N., 1994. Coastal eutrophication near the Mississippi River delta. *Nature* 168, 619–621.
- Turner, R.E., Schroeder, W.W., Wiseman, W.J., 1987. The role of stratification in the deoxygenation of Mobile Bay and adjacent shelf bottom-waters. *Estuaries* 10, 13–19.
- Wanninkhof, R., 1992. Relationship between wind speed and gas exchange over the ocean. *Journal of Geophysical Research* 97 (C5), 7373–7382.
- Wanninkhof, R., McGillis, W.R., 1999. A cubic relationship between air–sea CO<sub>2</sub> exchange and wind speed. *Geophysical Research Letters* 26, 1889–1892.
- Weiss, R.F., 1970. The solubility of nitrogen, oxygen and argon in water and seawater. *Deep-Sea Research* 17, 721–735.
- Wu, R.S.S., 1999. Eutrophication, water borne pathogens and xenobiotic compounds: environmental risks and challenges. *Marine Pollution Bulletin* 39, 11–22.
- Yang, S.L., Belkin, I.M., Belkina, A.I., Zhao, Q.Y., Zhu, J., Ding, P.X., 2003. Delta response to decline in sediment supply from the Yangtze River: evidence of the recent four decades and expectations for the next half-century. *Estuarine, Coastal and Shelf Science* 57, 689–699.
- Zhang, J., Yu, Z.G., Liu, S.M., Xu, H., Liu, M.G., 1997. Dynamics of nutrient elements in three estuaries of North China: the Luanhe, Shuangtaizihe and Yalujiang. *Estuaries* 20, 110–123.
- Zhang, J., Yu, Z.G., Raabe, T., Liu, S.M., Starke, A., Zou, L., Gao, H.W., Brockmann, U., 2004. Dynamics of inorganic nutrient species in the Bohai seawaters. *Journal of Marine Systems* 44, 189–212.