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Hypoxia off the Changjiang (Yangtze River) Estuary: Oxygen depletion and organic matter decomposition

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ABSTRACT

In an especially dry year (2006) in the Changjiang Estuary, three cruises were conducted between June and October, to study the process of oxygen depletion. Data for the hypoxic zone pooled for 1959 through 2006 suggest that a dramatic increase in the area of hypoxia has occurred in recent years, and that the center of hypoxia moved northwards in 2006. In August, the hypoxic area (dissolved oxygen, or DO, <62.5 μM) in the northern region was 15,400 km^2, which is comparable to that in the Gulf of Mexico. A large area of low DO (62.5 μM<DO<94 μM) also was found in the southern region. In near-bottom waters, particulate organic carbon (POC), dissolved inorganic phosphorus (DIP), dissolved inorganic nitrogen (DIN) and apparent oxygen utilization (AOU) showed coupled variation. For example, relationships can be found between AOU and POC/nutrients (POC/DIP: $r=-0.47$, POC/DIN: $r=-0.50$; $p<0.001$, $n=86$), and between AOU and $\Delta\sigma$ of the water column ($r=0.66$, $p<0.001$, $n=86$; $\Delta\sigma=\text{density}_{\text{near-bottom waters}}-\text{density}_{\text{surface waters}}$). It is interesting that oxygen depletion in the northern and southern regions developed separately, and they showed distinct differences. Oxygen depletion in the southern region is milder and relatively long lived, whereas in the northern region it is more pronounced and short lived. The different relationships between AOU and inorganic nutrients, indicates different mechanisms for the occurrence of oxygen depletion between the southern and northern regions, respectively. This can be due to 1) the influence of dissolved organic nutrients as another decomposition product besides inorganic forms, 2) and/or different chemical composition of organic matter that decomposed in the near-bottom waters.

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1. Introduction

Coastal hypoxia usually damages the coastal ecosystem and affects fisheries via food web interactions. Furthermore, a low dissolved oxygen (DO) level can change the natural redox condition of the marine environment and hence impact materials cycles (Turner et al., 2008; Bianchi and Allison, 2009). Hence, there has been increasing concern about coastal hypoxia in recent years.

The Changjiang (Yangtze River), one of the largest rivers in the world, strongly influences its estuary and adjacent shelf, forming stratified and turbid plumes, especially during summer. Like many other rivers in the world, the Changjiang has been suffering from eutrophication for the past few decades (Zhang et al., 1999). In addition to increased primary production and frequency of blooms in the estuary and adjacent area (Chen et al., 2003), a dramatic increase of oxygen depletion in the near-bottom waters off the estuary has occurred in recent decades (Li et al., 2002). DO<62.5 μM (usually defined as hypoxic) in the near-bottom waters was first reported in August 1959 (Office of integrated oceanographic survey of China, 1961). Li et al. (2002) described two regions of oxygen depletion off the estuary, one in the north and the other in the south (Fig. 1 in Li et al., 2002). The mechanism underlying the occurrence of hypoxia has been extensively discussed in previous reports. For example, elevated primary production promoted by terrestrial input and certain physical conditions (e.g. stratification) can lead to oxygen depletion in near-bottom waters (Li et al., 2002; Wei et al., 2007). Other influencing factors may include bottom water residence time (Rabouille et al., 2008) and temperature (Chen et al., 2007).

Although reports of hypoxia off the Changjiang Estuary exist, continuous observations (i.e. covering the hypoxia from its appearance to disappearance) of oxygen levels off the estuary are lacking. Thus, the duration of episodes of hypoxia off the Changjiang is unknown. It also is unclear how changes in river discharge affect hypoxia. For example, in a dry year with less terrestrial input, is the oxygen depletion off the estuary better or worse?

2006 was an especially dry year for the Changjiang. The river water level was so low that even in flood season (i.e. summer, August) there were problems with river shipping via the main channel. During this dry year, we conducted an investigation off the estuary in June, and then repeated it again in August and October. The study area covered the region in which hypoxia had been reported previously, including both the southern and northern oxygen depletion regions described

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in Li et al. (2002). Herein, we first briefly review hypoxia off the Changjiang Estuary, and compare a pooled hypoxic zone for a flood (derived from literature) versus a dry (based on this study) year. Next, the contribution of organic matter decomposition and stratification to oxygen depletion are discussed quantitatively. Finally, the two oxygen depletion areas (i.e., southern and northern) are compared in terms of behavior and mechanism.

2. Materials and methods

2.1. Study area

Data from previous studies provided background information about the study site. For example, the nitrogen flux at the Datong Hydrous Station (located in the lower river where the tide cannot impact) increased from 100×10^6 kg in 1968 to 1200×10^6 kg in 1997 (Yan and Zhang, 2003). Primary production off the Changjiang Estuary shows strong seasonal variation, with a maximum in summer that can reach >900 mg C m^{-2} d^{-1} (Gong et al., 2003). Although the Yellow Sea Cold Water mass (YSCW) is present in the bottom waters of the northern regions off the estuary, Changjiang Diluted Water (CDW) and Taiwan Current Warm Water (TCWW) are the main water masses in the estuary (Su, 1998; Chen, 2009), dominating in the surface and bottom layer, respectively (Fig. 1a). Because the Changjiang Estuary and the adjacent area are controlled by the East Asian Monsoon climate, they can be vertically well mixed in winter. In summer, the plume can be as wide as 85×10^3 km^2 and be strongly stratified. In years of low discharge, CDW tends to flow northeastward after leaving the estuary (Mao et al., 1963). Stronger YSCW in the north is conducive to its flowing northeastward (Zhu et al., 1998). TCWW it prevails in the bottom layer and flows northward.

As an operational term, hypoxia usually is defined as DO<2 mg L^{-1} or 62.5 μM (Diaz and Rosenberg, 1995), although in some studies it has been defined as DO<94 μM (e.g. Chen et al., 2007). In this study, we defined hypoxia as DO<62.5 μM, and we use the term low DO for DO concentration between 62.5 μM and 94 μM.

2.2. Sampling strategy and laboratory analysis

Three cruises (June, August, and October) were conducted in 2006 aboard the R/V Beidou. Each cruise lasted for ~11 days. The sampling stations (Fig. 1b), covered the areas where hypoxia had been previously reported (Li et al., 2002; Wei et al., 2007). To facilitate our description and discussion, the study area was divided into the northern region and the southern region (see the dashed line in Fig. 1b).

Temperature and salinity profiles were obtained using a Sea-Bird 911 plus CTD. In every cruise, generally four layers of water samples were obtained: surface waters (1 m beneath sea surface), near-bottom waters (about 3–4 m above seabed), the other two layers depth were designed on board according to the CTD profiles of the station. In case of too shallow stations (e.g. water depth<12 m), or station vertically well mixed in terms of CTD profile, then only three layers were sampled (i.e. 1 m beneath sea surface, middle depth, and 3–4 m above the seabed as bottom layer). In some deep stations (e.g. water depth>60 m), up to five or six layers were sampled. Seawater samples were collected with Niskin bottles. Immediately after sample collection, DO was measured, both polarographically and using the traditional Winkler titration method (Bryan et al., 1976). DO results from both methods agreed well and showed a strong linear relationship ($r^2 = 0.96$, $p<0.001$, $n = 184$).

Particulate organic carbon (POC) and particulate nitrogen (PN) were concentrated onto Whatman GF/F membranes (pore size: 0.7 μm, pre-combusted under 500 °C for 5 h) by filtering 0.5–20 L of seawater under mild vacuum. Filters then were stored in a −20 °C freezer until analysis. Similarly, particles were collected for the measurement of chlorophyll *a* (Chla). The filtration procedure was performed in dim light. For nutrient analysis [PO_4^{3-} (as dissolved inorganic phosphorus, DIP), NH_4^+, NO_3^-, NO_2^-, and SiO_3^{2-}], seawater was filtered through acid-cleaned acetate cellulose filters (pore size: 0.45 μm). Filtrates were then poisoned with $HgCl_2$ and stored in the dark at 4 °C until analysis. Seawater was also filtered through weighed cellulose acetate filters for the determination of total suspended matter (TSM), and salt was washed away with distilled water.

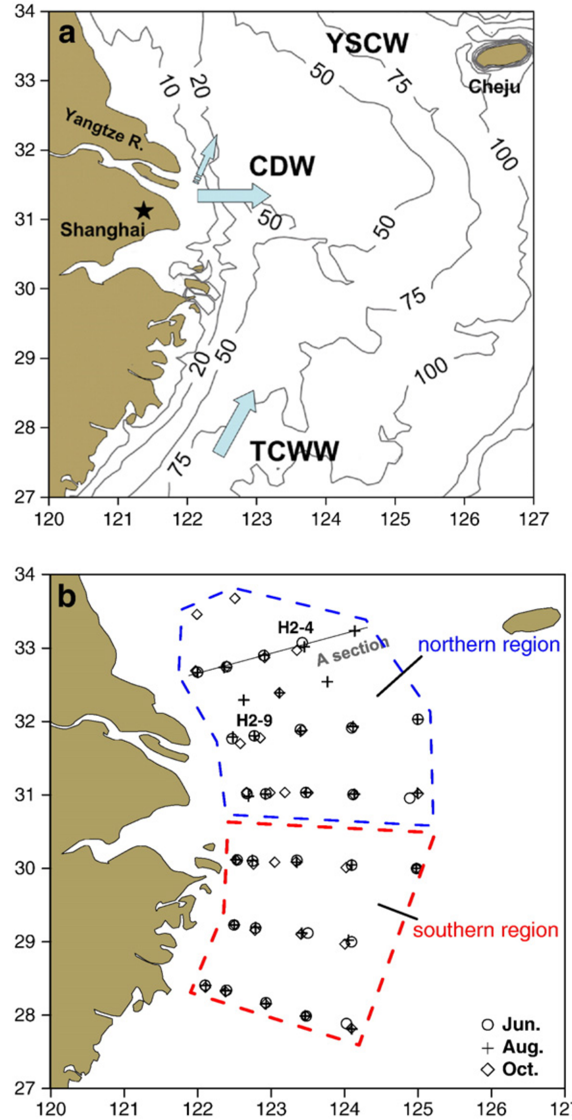

Fig. 1. Study area and sampling stations off the Changjiang Estuary. (a) Background: the dashed arrow indicates the spreading direction of CDW in year of lower riverine discharge; CDW: Changjiang Diluted Water; TCWW: Taiwan Current Warm Water; YSCW: Yellow Sea Cold Water. (b) Sampling stations in 2006. To facilitate our description and discussion, the study area is divided by a dashed line into southern and northern regions.

In the laboratory, POC samples were dried in a freeze dryer and analyzed with a CHNOS analyzer (Elementar® Vario EL III) after removing the inorganic carbon by reaction with HCl (Ehrhardt and Koeve, 1999). Analysis of PN followed a procedure similar to that of POC, but it excluded reaction with acid. The precision of this analysis is better than 6% based on repeated determinations (Zhu et al., 2006). Chla concentration was determined with HPLC (Agilent® 1100 series) following the method described by Zapata et al. (2000) with a slight modification. Milli-Q water was added to the extract (5:1, v/v) immediately before injection to avoid the shape distortion of earlier eluting peaks (Zapata and Garrido, 1991). Chla in samples was quantified based on the comparison of retention time and spectra (at 440 nm) with authentic standards purchased from Sigma-Aldrich Company. Nutrient concentrations in the seawater samples were analyzed using a continuous flow analyzer (SKALAR®, SAN[plus]). Details about the methods used for nutrients analysis are described by Zhang et al. (2007). The cellulose acetate filters were dried at 50 °C and weighed for TSM determination.

3. Results

In June, no hypoxia was observed, and only a small zone in the southwest corner of the study area showed low DO (Fig. 2a). In August, a hypoxic area of 15,400 km^2 was observed in the near-bottom waters of the northern region (Fig. 2b), at water depth ranging from 28 m to 39 m. The DO minimum (27.5 μM) occurred at 20 m depth (not the bottom layer) of station H2-4 (Fig. 1b) in the northern region. The DO value of the near-bottom waters increased at the eastern end of section A (Figs. 1b and 3), where salinity was 32–33 and temperature was ~14 °C (Fig. 3). These physical characteristics are very close to those of the YSCW (Chen, 2009), which is rich in DO (Gu, 1980). In the southern region, a large area of oxygen depletion also was observed. The low DO area covered an area of 15,500 km^2 (water depth ranged from 20 to 63 m), thus it was as large as the northern hypoxic zone (Fig. 2b). In October, DO depletion in the near-bottom waters was alleviated and the hypoxic zone in the northern region totally disappeared (Fig. 2c). Table 1 provides a comparison of the main parameters for the near-bottom waters in the northern and southern study regions.

Strong stratification was observed in August, as shown by $\Delta\sigma$, (the difference between surface and bottom water density). $\Delta\sigma$ was greatest in August [4.9 kg m^{-3} (1.2–11.4 kg m^{-3})] relative to June [2.2 kg m^{-3} (0.01–5.7 kg m^{-3})] and October [1.3 kg m^{-3} (−0.01–4.4 kg m^{-3})]. A typical stratified water column profile (from station H2-9) in August (Fig. 4) revealed that above the pycnocline, seawater was characterized by high POC and low nutrients, whereas beneath the pycnocline, near-bottom waters were depleted in POC and elevated in nutrients.

4. Discussion

4.1. Re-assessment of hypoxia off the Changjiang Estuary

On one hand, the area of the hypoxic zone off the Changjiang Estuary increased from 1900 km^2 in 1959 to 15,400 km^2 in 2006. The largest areas of hypoxia have occurred in recent 10 years, indicating that the extent of oxygen depletion has become more severe recently (Fig. 5a). The area we observed in August 2006 is comparable to that of other large hypoxic zones in the world (e.g., Gulf of Mexico, 20,000 km2; Turner et al., 2005). On the other hand, DO in the near-bottom waters can be stable on the order of days (Gao and Song, 2008), but on a longer time scale (e.g. month), hypoxia off the estuary becomes rather unstable (i.e., easy to disappear), relative to other well known hypoxic area such as the Black Sea. In the summer of 2006, severe hypoxia took place in August, but 1 month later much of hypoxia had disappeared (Fig. 5b).

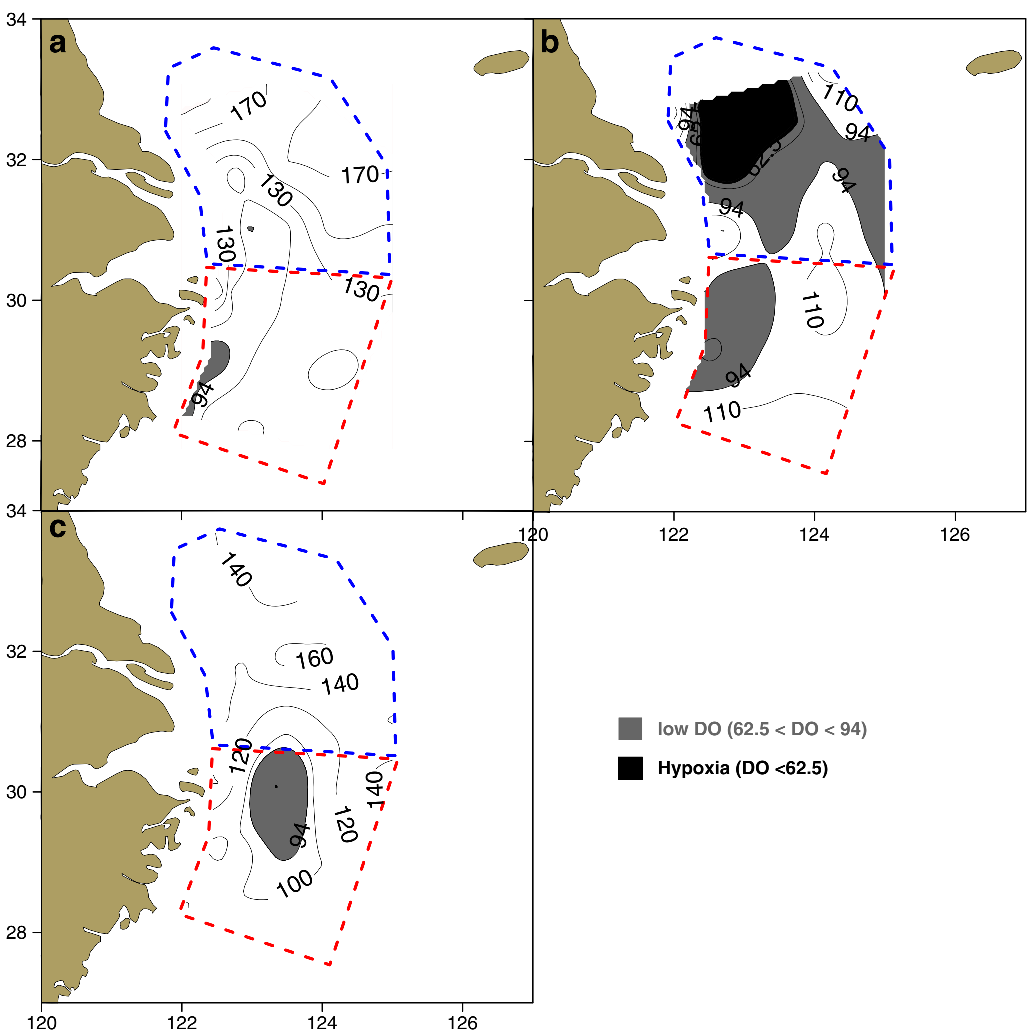

Fig. 2. DO (μM) distribution of near-bottom waters in (a) June, (b) August, and (c) October of 2006.

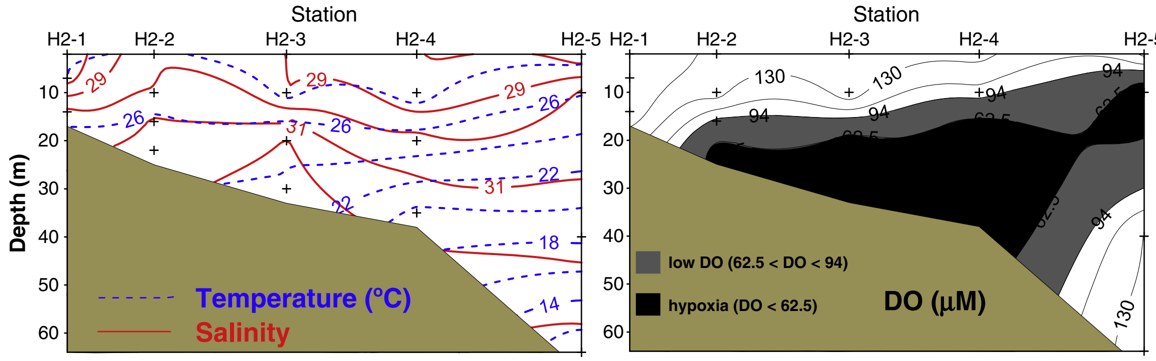

Fig. 3. Temperature, salinity, and DO distribution along the section A in August, 2006.

Using DO values and hypoxic area, the volume of hypoxic water and the amount of oxygen that was depleted can be estimated. The thickness of hypoxic water masses in August averaged 20 m. Given that the hypoxic area was 15,400 km^2, the volume of hypoxic water was 308 km^3. The apparent oxygen utilization (AOU, the difference between the measured DO concentration and its equilibrium saturation concentration in water with the same physical and chemical properties) of the hypoxic waters averaged 171 μM, resulting in an estimate of 1.69×10^6 t for oxygen depletion. In August, 1999, the hypoxic water volume was 274 km^3 and oxygen depletion was 1.59×10^6 t (Li et al., 2002).

Results of different studies covering a similar area off the Changjiang Estuary (e.g. Li et al., 2002; Wang, 2009, and this study) show that hypoxia appeared in different locations from year to year. Many hypoxia centers were found around 123°E, 30.8°N (Wang, 2009). It is interesting that in recent years, hypoxia in the northern region seemed to be increasing, as indicated by the hypoxic zone in 2003 and especially in 2006, a large area over the shelf from 32°N to 33°N became hypoxic (Fig. 5c). The location of the hypoxic zone indicates that the occurrence of hypoxia in the Changjiang Estuary seems to be regulated by complex factors, including the spreading pathway of CDW (Fig. 5c; Zhou et al., 2010), which varies from year to year due to discharge variation and other factors (e.g. winds and YSCW). In high discharge year, hypoxic zone can be found far away from the river mouth, whereas in low discharge year, hypoxic zone took place northwards off the estuary. For example, during a destructive flood in August 1998 (the Changjiang River discharge in 1998: $12{,}440 \times 10^8$ m^3), the CDW traveled eastwards over 400 km and salinity of the surface water close to the Cheju Island was <30 (Lie et al., 2003). Hypoxia occurred over 200 km offshore (Fig. 5c) (Wang and Wang, 2007), just in the pathway of the spreading CDW, simultaneously, a large area of low DO was present in the near-bottom waters along the pathway (figure not shown). In August 2006, the Changjiang water discharge (the Changjiang River discharge in 2006: 6886×10^8 m^3) was extremely low, accounting for only 60% of the long-term average value (data from the report of the Changjiang Water Resources Commission of the Ministry of Water Resources of China; please also see: http://yu-zhu.vicp.net/ and http://www.grdc.sr.unh.edu/html/Polygons/P2181900.html). Under such a low discharge background, the CDW tends to spread northeastwards off the estuary. Indeed, we observed brackish water (27.3<salinity<29.9) along the surface of section A (Fig. 3), indicating the existence of the CDW in the northern region. Simultaneously, hypoxia occurred in the region north of 32°N (Figs. 2b and 5c). The Changjiang River discharge is only one of the factors that influencing the location of bottom hypoxic zone and there is not a simple relationship between the Changjiang River discharge and hypoxic zone (e.g., distance to river mouth or area, figure not shown). It should be noted that back in 1960s, the Changjiang River nitrogen flux was on the level of 12×10^7 kg (Zhang et al., 1999; Yan and Zhang, 2003) and between 1999 and 2006, the nitrogen flux has increased to $100{\sim}120 \times 10^7$ kg (based on our unpublished routine observation data). Besides the ten times increase of nitrogen flux for the past 50 years, the hypoxic area increased almost ten times, too (from 1.9×10^3 km^2 to $13.7{\sim}20 \times 10^3$ km^2 (Fig. 5a)). Water discharge changed slightly for the past a few decades while carrying much more nutrients. Therefore the CDW can play a more important role in hypoxic zone location, relative to 50 years ago.

Table 1
Comparison of the near-bottom waters between the northern and southern region in August, 2006. [mean value (minimum–maximum)].

Parameter	Unit	Northern	Southern
DO	μM	73 (29–164)	99 (65–120)
DO	%	33 (13–78)	43 (27–55)
AOU	μM	144 (47–203)	134 (100–172)
DIP	μM	0.45 (0.12–0.92)	0.94 (0.45–1.3)
Nitrate	μM	8.99 (2.98–15.58)	10.67 (3.37–15.77)
Nitrite	μM	1.39 (0.07–4.68)	0.41 (0.11–1.75)
POC	μM	14.5 (1.2–30)	10.2 (2.9–21)
Chla	$\mu g\ L^{-1}$	1.18 (0.19–3.38)	0.39 (0.11–0.85)
TSM	$mg\ L^{-1}$	26 (10.4–56.1)	21 (5.3–51)
pH		8.16 (7.89–8.38)	8.19 (7.64–8.77)

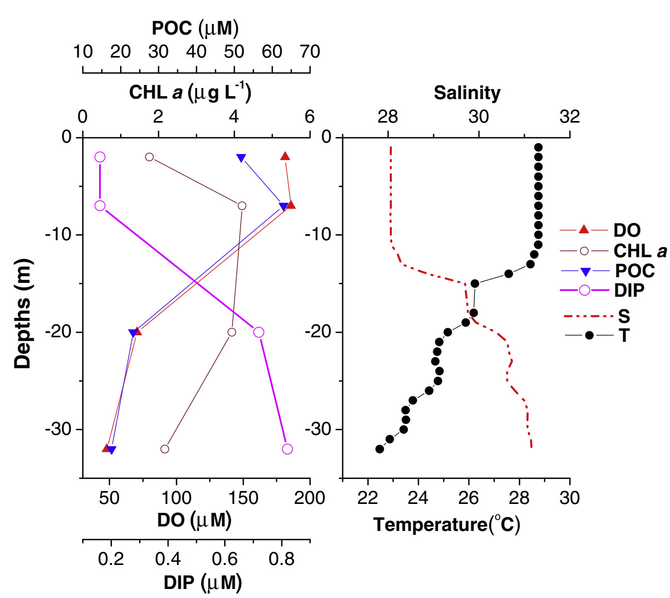

Fig. 4. Typical profile of hypoxia in the near bottom waters (station H2-9, August, 2006).

Organic matter decomposition and stratification are among the most frequently discussed processes in studies of estuarine and/or coastal hypoxia. Hypoxia off the Changjiang Estuary, organic matter decomposition in the near-bottom waters and stratification in the water column are generally suggested in former literature.

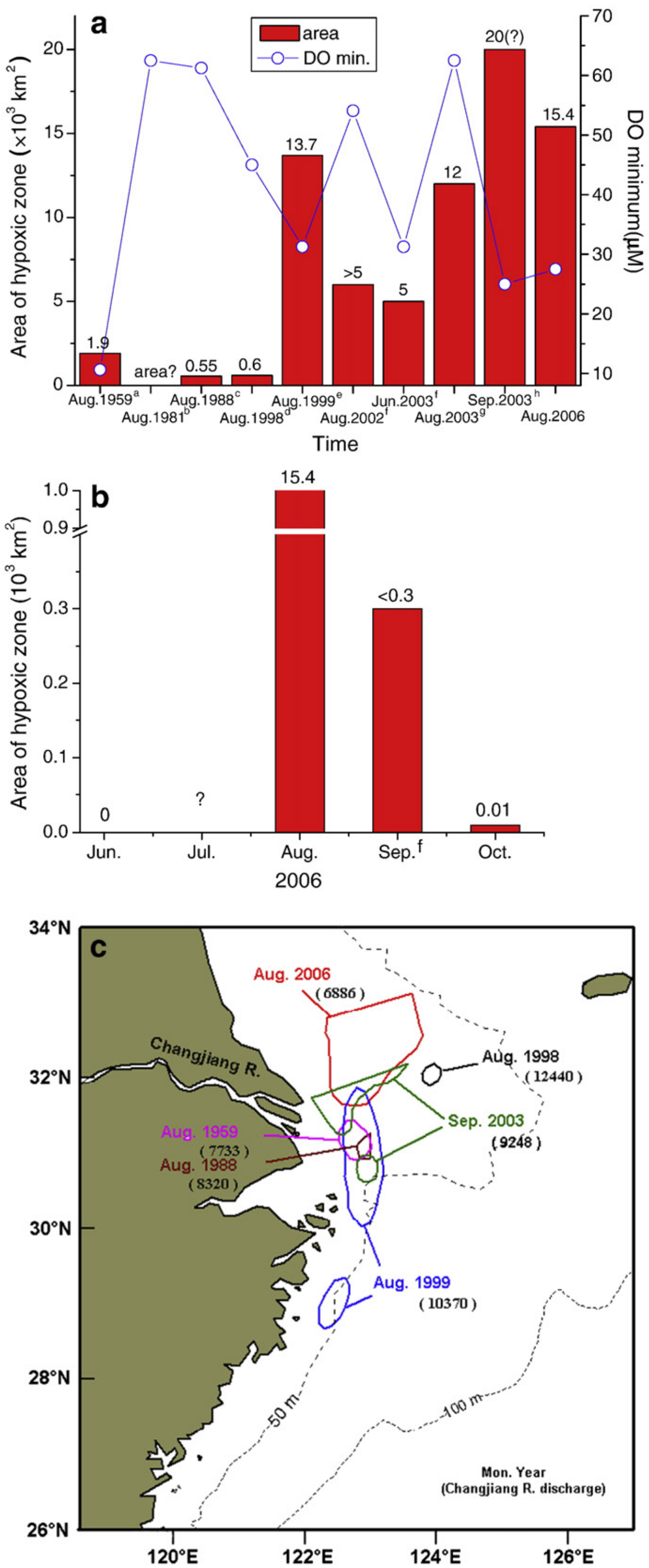

Fig. 5. Overview of hypoxia off the Changjiang Estuary (References: a: Office of Integrated Oceanographic Survey of China, 1961; b: Limeburner et al., 1983; c: Tian et al., 1993; d: Wang and Wang, 2007; e: Li et al., 2002; f: Wang, 2009 and references therein; g: Chen et al., 2007; h: Wei et al., 2007.) (a) Reported area of hypoxic zone and DO concentration minimum based on literature and this study. Note that there is not a continuous timeline along the x-axis due to lack of historical observation data. (b) Monthly variation of the hypoxic area from June to October 2006 (July is not shown due to lack of data). (c) Pooled bottom hypoxic zone from 1959 to 2006. This is a conservative estimate, only showing area of DO<62.5 μM exactly within literature's investigation zone. As a result, the area for September 2003 (reference h) is much smaller (~5000 km^2) when compared to the reported area (i.e. 20,000 km^2). It is very difficult to extract hypoxic zone data from references b, f, and g, so no corresponding hypoxic zones were shown. The Changjiang River water discharge ($\times 10^8$ m^3, recorded at the Datong station) is shown below every year, in brackets. Discharge data is from the report of the Changjiang Water Resources Commission of the Ministry of Water Resources of China.

4.2. Evidence of organic matter decomposition during periods of hypoxia

The coupling of organic matter decomposition and regeneration of nutrients is a complex process that involves physical, chemical, and biological interactions. When the process as a whole reaches its thermodynamic reaction balance, the chemical composition concerned can be expressed as follows (Redfield et al., 1963):

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138O_2 \rightarrow 106CO_2 + 122H_2O + 16HNO_3 + H_3PO_4 \qquad (1)$$

The Changjiang Estuary and the adjacent coastal sea are highly dynamic areas with various origins of materials. Former studies suggest that organic matter decomposition plays an important role in oxygen depletion in this area (Li et al., 2002; Chen et al., 2007; Wei et al., 2007; Rabouille et al., 2008; Wang, 2009).

The source of estuarine and coastal organic carbon is direct terrestrial input and in situ production, whereas the source of nutrients is terrestrial input and organic matter decomposition. The terrestrial input off the Changjiang Estuary can be quite high (e.g. Yang et al., 2007). However, strong stratification in the water column in summer (e.g. Fig. 4) can strongly prevent vertical dissolved materials exchange and hence nutrients in the near-bottom waters are mainly influenced by water masses nutrients background level and organic matter decomposition. If we take the POC or nutrients as a whole, regardless of their various origins, and the organic matter decomposition/nutrient regeneration process is significant enough, we should be able to observe a decreasing of bulk POC and an increase in nutrients, or namely a decreasing POC/nutrients ratio (i.e. POC/nutrients is used here as a simple proxy to quantitatively indicate the degree of action for the organic matter decomposition processes), correlating with a increasing AOU, according to Eq. (1). For all of the bottom samples, POC and nutrients showed corresponding negative relationships with bottom AOU (Fig. 6). The relationship between AOU and POC/nutrients of all the samples (i.e. including Jun. Aug. and Oct.) from the near-bottom waters is clear ($r = -0.47$ for POC/DIP and $r = -0.50$ for POC/DIN, $p < 0.001$, $n = 86$, Fig. 6). Tightness of the relationship is, however, not good (i.e. $|r|$ is not very big). This can be due to the complexity of organic matter decomposition and oxygen depletion in marine environment. Anyway, as is shown, high AOU is mainly corresponding to low POC/nutrients ratios, whereas low AOU is mainly corresponding to high POC/nutrients ratios. In other words, for the near-bottom waters, oxygen-depleted waters were all related to relatively lower POC concentration and a higher nutrient level; when relatively higher POC concentration and lower nutrient levels occurred, DO conditions of the near-bottom waters are often better.

4.3. Evidence of stratification during the occurrence of hypoxia

Although stratification does not directly consume DO, the formation of a stable water column structure prohibits vertical DO exchange and promotes pelagic phytoplankton growth, resulting in

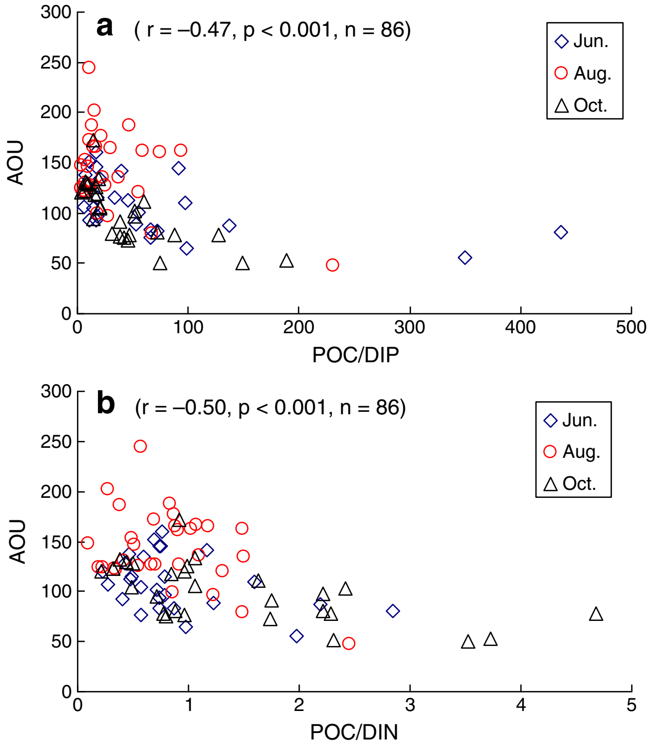

Fig. 6. Bottom AOU plotted against bottom (a) POC/DIP and (b) POC/DIN ratios (AOU: μM; POC/nutrients: μM/μM).

excess organic matter being delivered to the benthic system. This usually plays a role in occurrence of hypoxia in estuaries and coasts where stratification is common (e.g. Diaz, 2001; Bianchi et al., 2010). Unlike in the open ocean, stratification in shallow estuaries occurs not only because of the thermocline, but also because of the strong vertical salinity gradient. For example, at station H2-9, a strong pycnocline existed at 15 m depth, making the pelagic and benthic systems distinctly different (Fig. 4).

The water depth of the study area (average 50 m) is not very deep compared to the open ocean. Thus, we used $\Delta\sigma$ to quantitatively stand for the strength of stratification ($\Delta\sigma = \text{density}_{\text{near-bottom waters}} - \text{density}_{\text{surface waters}}$). From June to October, $\Delta\sigma$ ranged from -0.01 kg m^{-3} to 11.4 kg m^{-3}. The minimum value means that the water column was well mixed vertically and the maximum means that the water column was strongly stratified. $\Delta\sigma$ was positively related to the bottom AOU (including samples from Jun. Aug. and Oct.; $r = 0.66$, $p < 0.001$, $n = 86$, Fig. 7). When $\Delta\sigma$ was >5 kg m^{-3}, bottom AOU did not increase so fast or remained stable (Fig. 7). This indicates that, as a non-direct oxygen-depletion process, when

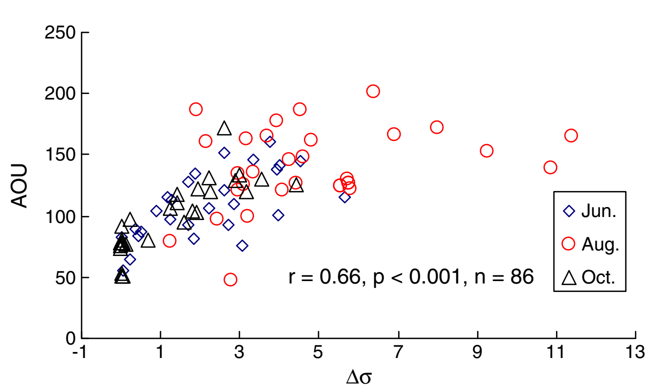

Fig. 7. Every station's $\Delta\sigma$ (kg m^{-3}) of the water column plotted against its AOU in the near-bottom waters (μM) ($\Delta\sigma = \text{water density}_{\text{bottom}} - \text{water density}_{\text{surface}}$).

strong stratification exists ($\Delta\sigma > 5$ kg m^{-3}), it is not the main limiting factor for oxygen depletion. Other oxygen consumption process (e.g. organic matter decomposition) then determines the bottom AOU.

4.4. A comparison of the southern and northern region

An investigation conducted in August 1999 suggested that the oxygen depletion area off the Changjiang Estuary has two parts, one in the northern region and the other in the southern region (Li et al., 2002). In 2006, we also observed these two regions of oxygen depletion (Fig. 2b). The occurrence of hypoxia (or oxygen depletion) was not consistent between the two regions. Instead, oxygen depletion in the two regions seemed to take place separately. For example, low DO in the southern region was repeatedly observed in June, August, and October, but the area seldom became hypoxic. In contrast, in the northern region, obvious oxygen depletion (i.e. DO<94 μM) was only observed in August, but it was very severe in both area and extent (Fig. 2b). However, one month later the area of oxygen depletion was dramatically reduced to <300 km^2 (Fig. 5b). Thus, oxygen depletion in the southern region is milder and longer lived, whereas oxygen depletion in the northern region is more severe and shorter lived.

Strong stratification occurs in the water column (especially in August) and hence prevents the vertical dissolved material exchange. Therefore, direct terrestrial nutrients input cannot be the reason for elevated nutrients concentration in the near-bottom waters. Elevated nutrients concentration in the near-bottom waters are mainly due to organic matter decomposition. It should be noted that, organic matter decomposition involves various biochemical degradation processes. Besides inorganic forms, nitrogen and phosphorus can also be released in organic forms. Furthermore, influenced by strong terrestrial input, organic matter decomposition in the near-bottom waters may not follow the formulae proposed by Redfield et al. (1963), although oxygen demand in near-bottom waters appears to be fueled by delivery of autochthonous carbon from phytoplankton blooms rather than by allochthonous carbon input (Anderson and Taylor, 2001). Therefore, a linear relationship following the classical Redfield ratio between AOU and inorganic nutrients is not expected. Although nitrogen is complex due to potential nitrification/denitrification processes, majority of the northern region plots (for both phosphorus and nitrogen) were above the classical Redfield slop, whereas AOU and DIP for the southern region seemed to follow Eq. (1) (Fig. 8a). A further quantitative calculation based on bottom DIP concentration (Table 1) and Eq. (1) (i.e., 1 μM AOU corresponds to 1/138 μM DIP) suggests that bottom-AOU-related DIP for the northern and southern region should be 1.0 μM and 0.97 μM, respectively. The calculated 1.0 μM DIP for the northern region is over twice that of the observed value, 0.45 μM (Table 1).

A simple and direct connection between bottom nutrients and AOU via Eq. (1) may be lack of consideration, but it is true that difference of the bottom AOU between the northern and southern regions is ~7% while differences of bottom nutrients (i.e., DIP, Table 1) can be as high as 70%. In other words, near-bottom waters in the northern region have a slightly higher AOU and obviously lower inorganic nutrient content, relative to the southern region. This high-AOU and low-nutrients cannot be due to lateral advection in the bottom layer, as TCWW flows northwards, or to interaction of DIP in the water and sediment phase. Transport and transformation of sediment phosphorus in large river estuaries can be complex (e.g. Sutula et al., 2004). But the accumulation rate in the southern region (2.90–17.2 μmol cm^{-2} yr^{-1}) (Fang et al., 2007) is estimated to be higher than that in the northern region (0.54–6.19 μmol cm^{-2} yr^{-1}) (Liu et al., 2004). Further, lower DO conditions in the near-bottom waters can lead to the release of phosphorus from sediments back into the water (Conley et al., 2002). Adsorption processes in the near-bottom waters represent another potential removal pathway for DIP,

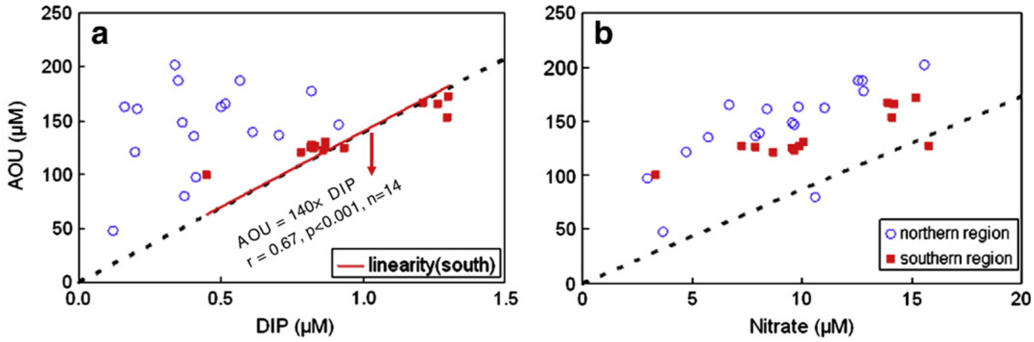

Fig. 8. AOU plotted against (a) DIP and (b) nitrate for the near-bottom waters in August 2006. Dashed lines represent the classical Redfield slope.

but because the bottom TSM and pH are comparable, the influence of this process should be limited (Zhang, 2007).

Other oxygen depletion processes are at work as well. Nitrification (EPA, 1993; Eqs. (2) and (3)) should play a minor role, as nitrate and nitrite concentration are very low relative to the DO level, (N_2O is not considered here for its much lower concentration).

$$NH_3 + 1.5O_2 \rightarrow NO_2^- + H^+ + H_2O \qquad (2)$$

$$NO_2^- + 0.5O_2 \rightarrow NO_3^- \qquad (3)$$

For example, even given that all of the nitrate and nitrite were derived from nitrification process, and regardless of the contribution from any other sources (e.g. Eq. (1), and/or terrestrial input), 1 μM nitrite and nitrate would then means consuming 1.5 μM and 2 μM DO, respectively (Eqs. (2) and (3)). Considering the nitrate and nitrite concentration (Table 1), such processes would result in AOU of less than 22 μM. If contribution from organic matter decomposition (Eq. (1)) and any other sources are considered, nitrification would contribute to a much less AOU in the near-bottom waters (probably <6 μM). Possible oxygen depletion can occur due to sedimentary process, but biogenic silica content of surface sediments in the northern region was lower than that in the southern region (Liu et al., 2005), indicating the lower content of labile organic matter in the northern region surface sediments.

For the near-bottom waters, DIN/DIP ratio of the nutrients can drop to 10–20 (or even <10) in the Kuroshio impacted regions, whereas along the coast and inner shelf, DIN/DIP ratio can reach up to over 100 (Zhang et al., 2007). In the Yellow Sea where YSCW impacted, DIN/DIP ratio of the near-bottom waters tend to be around 10–20 (Liu et al., 2003; Chen, 2009). Under such water masses background, within the oxygen-depletion-area that concerned in this study, DIN/DIP ratio of the near-bottom waters in August are relatively low for the southern region, whereas are relatively high for the northern region (Fig. 9).

In the southern region, the observed AOU, DIN, DIP, and DIN/DIP ratio in the near-bottom waters seems to be well coupled following the classic Redfield ratio, whereas in the northern region, the high-AOU and low-nutrients pattern does not follow the classic Redfield ratio, and further shows an elevated DIN/DIP ratio (Figs. 8 and 9). There can be two reasons: 1) complex biomineralization process that yields much organic nutrients, instead of inorganic nutrients, and/or 2) differences in the chemical composition of organic matter that degraded within the near-bottom waters. For the first reason, in the northern region, DOP concentration were generally higher than DIP and DOP concentration can increase 2 to 3 fold from surface to bottom (Liu et al., 2003). This is also proved by our former investigations, which suggested that bottom DOP in the northern region was 0.4 to 1.1 μM whereas DIP remained 0.09 to 0.24 μM (our unpublished data). Actually, DOP is found to be a very important species for phosphorus (representing 50% of the total phosphorus) in the northern region off the Changjiang Estuary) (Liu et al., 2003). Therefore, when considering the AOU level, relatively lower DIP in the near-bottom waters of the northern region may be due to contribution from bottom DOP. It is interesting that even in the condition of lower AOU for the near-bottom waters, higher Chla was founded in the near-bottom waters of northern region, relative to the southern region (Table 1). Although water depth off the Changjiang Estuary is not very deep (only ~50 m), turbid CDW makes the euphotic layer very shallow (Zhu et al., 2009). In shallow systems such as estuaries and coasts, large algal species (especially diatoms) are very common and usually are the main species present. They may settle out of surface waters and sink to the aphotic bottom layer if turbulence is insufficient to buoy them up as individuals or if they sink within aggregates (Sarthou et al., 2005). Therefore, biomineralization (e.g., respiration of living phytoplankton in the aphotic layer) of organic matter in the near-bottom waters can play an important role in oxygen depletion (Hopkinson, 1985; Anderson and Taylor, 2001). For the second reason, on one hand in the coastal zone and inner shelf of the southern region, DIN/DIP ratio of near-bottom waters are much higher than Redfield ratio (Zhang et al., 2007), but in August when large area of oxygen depletion occurs, the ratio are then much closer to the Redfield ratio (~20, Fig. 9). On the other hand, in the northern region where hypoxia happens, DIN/DIP ratio is higher (over 60, Fig. 9) in the near-bottom waters. Strong stratification prohibits the vertical exchange of dissolved materials and hence the shift of DIN/DIP ratio from its background value of its water masses is mainly due to the organic matter decomposition. Besides other sinking organic matter, fecal pellet is another important organic matter that sinks into the near-bottom waters, resulting in notable oxygen demand (Dagg et al., 2008; Shek and Liu, 2010). As an important source for nitrogen, it is possible that the sinking of fecal pellet induces observed elevated DIN/DIP ratios in the near-bottom waters.

5. Summary and concluding remarks

In recent decades, an increase in the area of the hypoxic zone has been a seasonally recurrent event off the Changjiang Estuary. A large area of hypoxia (15,400 km^2) was detected off the Changjiang Estuary in August 2006, and this area is comparable to that in the Gulf of Mexico. In August, the water column was well stratified and $\Delta\sigma$ reached 11.4 kg m^{-3}. Above the pycnocline, higher Chla and POC and lower nutrient concentrations were observed, whereas a decreased POC concentration and an increase of nutrients occurred below the pycnocline. Clear relationships are further found when AOU in the near-bottom waters was plotted against bottom POC/nutrients (POC/DIP: $r = -0.47$, POC/DIN: $r = -0.50$; $p < 0.001$, $n = 86$) and against $\Delta\sigma$ of the water column ($r = 0.66$, $p < 0.001$, $n = 86$). Such relationships indicate that hypoxia is highly related to organic matter decomposition and stratification.

A comparison of the hypoxia off the Changjiang Estuary with former reports suggests that, besides increasing hypoxic area, severe hypoxia can occur in the northern region. Data collected at our three times of observation (June, August, and October) showed that oxygen depletion in the southern region is milder and long lived, whereas

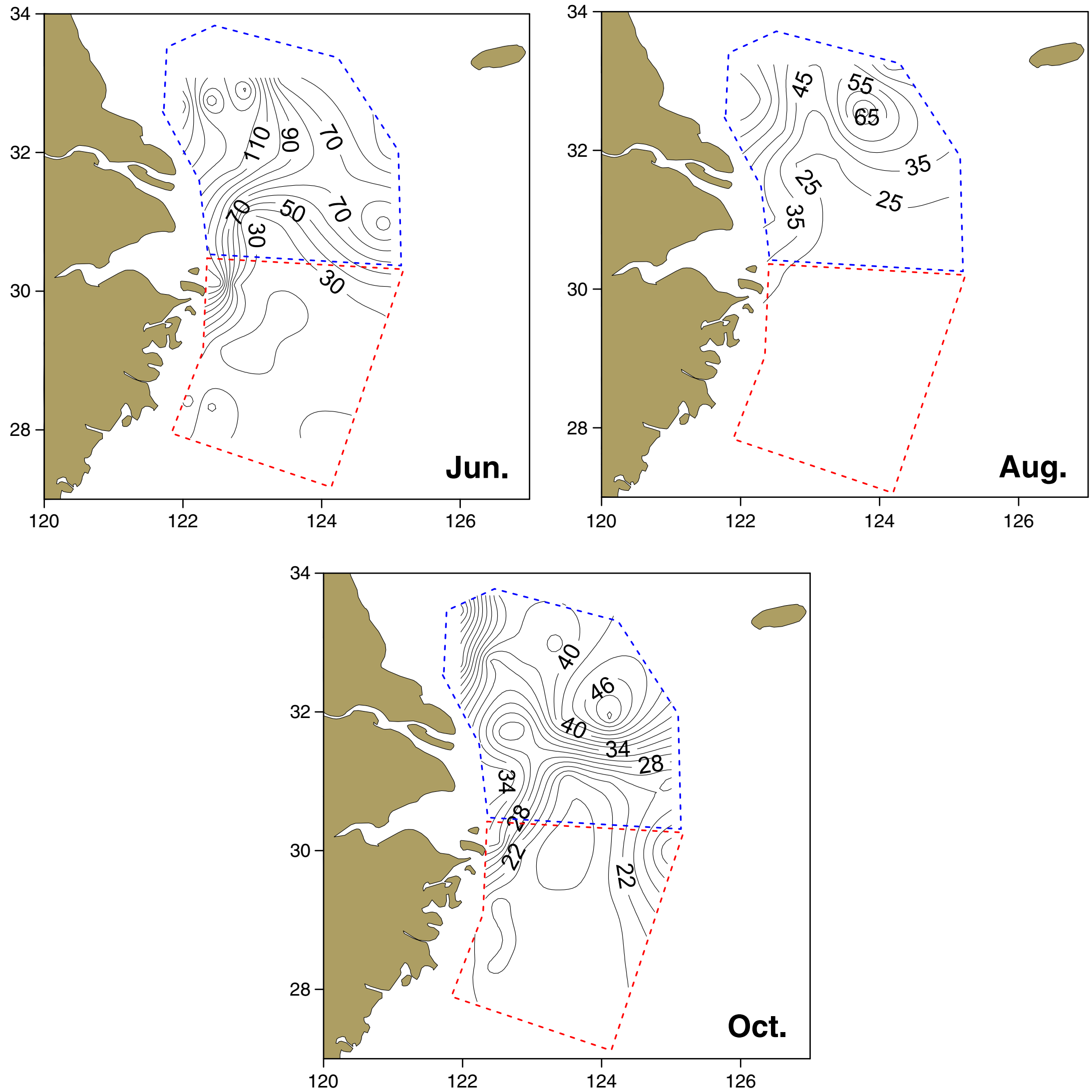

Fig. 9. DIN/DIP ratios of the samples from near-bottom waters in (a) June, (b) August, and (c) October, 2006.

oxygen depletion in the northern region is more pronounced and short lived. It is interesting to compare the coupling of observed bottom AOU and bottom organic matter decomposition between the northern and southern region. When bottom AOU was plotted against bottom inorganic nutrients, bottom AOU was higher in the northern region (with a much lower bottom inorganic nutrient concentration) compared to the southern region. This can be due to 1) the influence of dissolved organic nutrients as another decomposition product besides inorganic forms, 2) and/or different chemical composition of organic matter that decomposed. Hence, further work (for example, the dissolved organic nutrients, community respiration, and fecal pellets) is needed on the mechanisms that drive hypoxia to better explain linkages between AOU and bottom nutrient cycling in the northern and southern regions of the Changjiang estuary.

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