Marine Pollution Bulletin 60 (2010) 1591–1599

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Environmental change in Jiaozhou Bay recorded by nutrient components in sediments

Su Mei Liu [a,*], Bing De Zhu [a], Jing Zhang [b], Ying Wu [b], Guang Shan Liu [c], Bing Deng [b], Mei-Xun Zhao [a], Guan Qun Liu [d], Jin Zhou Du [b], Jing Ling Ren [a], Gui Ling Zhang [a]

[a] *Key Laboratory of Marine Chemistry Theory and Technology Ministry of Education, College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, China*
[b] *State Key Laboratory of Estuarine and Coastal Research, East China Normal University, Shanghai 200062, China*
[c] *Oceanography Department, Xiamen University, 422 Siming Road South, Xiamen 361005, China*
[d] *College of Environmental Science and Engineering, Ocean University of China, Qingdao 266100, China*

ARTICLE INFO

Keywords:
Carbon
Nitrogen
Phosphorus
Silicon
Environmental change
Jiaozhou Bay

ABSTRACT

Inorganic or bulk organic chemical indicators, including organic carbon (OC), total nitrogen, organic nitrogen (ON), fixed ammonium (N_{fix}), exchangeable ammonium, exchangeable nitrate, organic phosphorus (OP), inorganic phosphorus (IP), and biogenic silica (BSi), were examined in a 3-m core collected in Jiaozhou Bay (JZB) to decipher how the environment has changed during the preceding two centuries of increasing anthropogenic influence in this region. Concentrations of BSi, OC, and OP reveal overall increases to ca.30 cm (~1984), then decreased toward the surface, probably reflecting a decrease in the productivity of overlying waters since 1984. Aquaculture might play an important role in the decrease of nutrient elements in the upper layers recorded in sediments. The decreased molar BSi/OC ratios upcore may be due to a change in dominance from large- to small-sized diatoms, as shown in other research. However, the shift may also be related to changes from heavily-silicified to lightly-silicified diatoms or to non-siliceous forms such as dinoflagellates. ON concentrations increased towards the surface sediment, which is most likely consistent with the increase in fertilizer application and wastewater discharge. Concentrations of IP, total P, and N_{fix} all decreased conspicuously upcore at 41 cm depth (~1977), and were largely consistent with the decrease in rainfall and freshwater discharge to JZB. Our data suggest that the environment has significantly changed since the1980s. Anthropogenic activities in the watersheds may exert a substantial influence on carbon cycling processes in estuaries and potentially the coastal ocean.

1. Introduction

Global nutrient cycles have been greatly altered by land-use changes resulting from human disturbance over the last century (Vitousek et al., 1997; Bennett et al., 2001). Excessive nutrient discharges and changes in their relative concentrations have been known to result in eutrophication, hence modifying aquatic food webs and causing severe hypoxic events in coastal environments (Humborg et al., 1997; Ragueneau et al., 2002; Turner and Rabalais, 1994; Turner, 2002; Piehler et al., 2004). Even though monitoring programs and historical data are not sufficient to establish the anthropogenic effects on the ecology of coastal areas, stratigraphic records preserved in the sediments can be used to reconstruct environmental changes in coastal areas (e.g., anoxia and eutrophication) (Cooper and Brush, 1993; Gooday et al., 2009).

The objective of this study is to assess how human-induced activities and the impact of changing environmental conditions in JZB are recorded in sediments, and to elucidate the changing nature of nutrient composition including the forms of the nutrients deposited during the last century in order to understand changes in the trophic state of JZB in relation to changes in land use and water, sediment, and nutrient delivery to JZB. The results of sedimentary paleoindicator studies help validate the need for management of nutrient loads for a system where nutrient-related problems are difficult to identify, based on limited water quality data.

2. Study site

JZB is a typical semi-enclosed water body with a channel of 2.5 km width connected with the Yellow Sea, with an area of 390 km^2 and an average water depth of 6–7 m. Almost one fifth of the bay area is intertidal. The southeast and southwest shores

* Corresponding author. Tel.: +86 532 66782005; fax: +86 532 66781810.
E-mail address: sumeiliu@ouc.edu.cn (S.M. Liu).

0025-326X/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.marpolbul.2010.04.003

of the bay are rocky, and are the locations of two large ports. JZB is of semi-diurnal tide with an average tidal range of 2.7–3.0 m (Liu et al., 2007b). Strong turbulent mixing in JZB results in nearly homogeneous vertical profiles of temperature and salinity with weak stratification only in the summer when the land-source freshwater input reaches its maximum (Liu et al., 2004b). About 10 streams empty seasonally into the bay with various amounts of freshwater discharge and sediment loads. Most of these rivers, however, have become conduits of industrial and domestic waste discharges due to the region's rapid economic development and population growth.

Over the last half century, JZB has been affected by the ever-increasing anthropogenic perturbations. For example, the surface area and intertidal area of JZB has been reduced by 30% and 70%, respectively (Dai et al., 2007; Yang et al., 2003). Population increased from 4.1 million in 1949 to 7.3 million in 2004. In this period, the GDP per capita in Qingdao increased by ca. 400 times. The cultivation area was reduced by one-third from 657×10^3 ha to 423×10^3 ha, whereas crop productions increased from 723×10^3 tons yr^{-1} to 2.32×10^6 tons yr^{-1} (Qingdao Municipal Statistics Bureau, 2005). The application of chemical fertilizers increased from 1.9×10^3 tons yr^{-1} to 325×10^3 tons yr^{-1} (Zhang, 2007).

JZB has been affected by the ever-increasing anthropogenic perturbations. The dissolved inorganic nitrogen (DIN) levels increased from the 1960s to 1990s by about five times, the phosphate concentration increased from the 1960s to the 1980s by three times, then decreased by 30%, and $Si(OH)_4$ levels decreased from the 1980s to the 1990s by 17%, resulting in higher DIN/PO_4^{3-} and lower $Si(OH)_4/DIN$ molar ratios compared to four decades ago (Shen, 2001). Both silicon and phosphorus limitation have been proposed (Zhang and Shen, 1997; Shen, 2001; Liu et al., 2005a, 2008b; Zou, 2001). Since 1997, red tide events have been increasing in number, frequency, and intensity in JZB (Wu et al., 2005). Moreover, aquaculture has been present in this bay since the 1960s with some kelp culture, in the 1980s shrimp and shellfish aquaculture were promoted and in the 1990s, shellfish culture became more important, accounting for 64% of marine culture (Lu et al., 2001; Zhang, 2007; Zhu and Zhang, 2007). In addition to the strong tidal-driven exchange with the Yellow Sea, top-down pressure from shellfish aquaculture further contributes to systems low eutrophic conditions (Zhu and Zhang, 2007).

3. Materials and methods

3.1. Sample collection

Duplicate sediment cores (~270 cm) were collected at Station JZ using an inner diameter of 9 cm and length of 400 cm gravity-corer in the central part of JZB, in 17 m of water in September of 2002 (Fig. 1), with one for diatom community analysis and sediment dating, and the other for chemical parameter analyses. Disruption of the core during handling was reduced by the ability to remove one side of the core barrel, thus eliminating disruption and compaction caused by core extrusion. Meanwhile, another sediment core (~40 cm) was collected by a multi-corer of 9-cm diameter tubing. Both cores were sectioned immediately after collection. The gravity core was sub-sampled at 1-cm intervals, and the multi-core was sub-sampled at 0.5-cm intervals in the upper two centimeters and at 1-cm intervals in the remainder of the core. As the upper 10 cm of the gravity core may be disturbed during sampling and handling, it was discarded. The upper 10 cm of the multi-core was used instead. More than 10 sediment samples of gravity and multi-cores at 10–40 cm depth were used to simultaneously measure the chemical parameters, which show consistent values, average values were given in the figures. In the laboratory, sub-samples of the sediment core were freeze–dried, homogenized, and ground. A total of 272 sub-samples (0–270 cm) were analyzed for nitrogen forms, total and inorganic phosphorus, biogenic silica, and 158 sub-samples were analyzed for total organic carbon. Altogether 155 sub-samples were dated with sub-samples taken from the sediment core at 1 cm intervals between 0 and 40 cm and at 2 cm intervals below 40 cm.

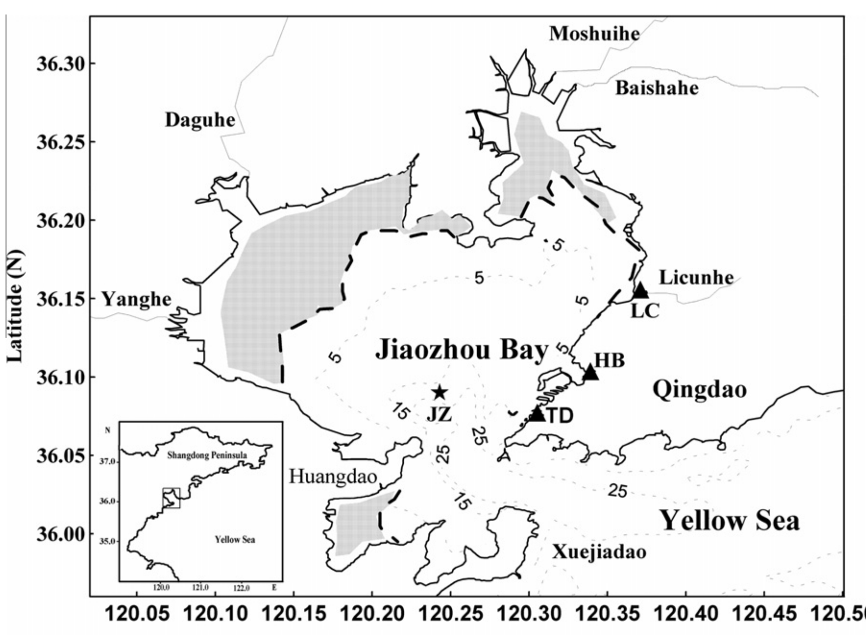

Fig. 1. Map of Jiaozhou Bay, which shows location of sediment core site JZ (★), the Haibohe (HB), Licunhe (LC) and Tuandao (TD) wastewater disposal plants (▲) and the major streams surrounding the bay: Daguhe, Yanghe, Moshuihe, Baishahe and Licunhe. The inset at the lower left is the location map. The dashed bold line indicates the 0-m isoline and the dashed line indicates the isobaths of 5, 15 and 25 m.

3.2. Analytical methods

The sediment core was dated at Xiamen University, China, using ^{210}Pb and ^{137}Cs radiometric-dating techniques with a HPGe γ spectrometer (from Canberra Company, US). The detector was a model GX3020 (Liu et al., 2007a).

BSi was analyzed using a combined alkaline leaching method of Mortlock and Froelich (1989) and DeMaster (1981) (c.f. Liu et al., 2002, 2005b, 2008b). Briefly, BSi was dissolved in 2 M Na_2CO_3 at 85 °C. The extraction solution was centrifuged and the supernatant was analyzed to determine the amount of silicic acid. The CV for five parallel extractions was 1.9%. Quality control of BSi-analyses was carried out by using the same reference samples used in an interlaboratory comparison (Conley, 1998). All values are reported as weight percent as opal with assumed water content of ca. 10% (Mortlock and Froelich, 1989).

Organic carbon (OC) was measured using a CHNOS Elemental Analyzer (Model: Vario EL III, Elementar Analysensysteme GmbH) after acidification of the sediment sample with HCl to remove carbonates. The precision was <6%, estimated by repeated analyses of sediment samples.

Sedimentary nitrogen forms were separated using modifications adapted from Silva and Bremner (1966) into ON and inorganic nitrogen (IN). The latter can be separated into fixed ammonium (N_{fix}), exchangeable ammonium ($NH_{4\,ex}^+$), and exchangeable nitrate ($NO_{3\,ex}^-$). $NH_{4\,ex}^+$ and $NO_{3\,ex}^-$ in the sediments were leached by 20 ml 0.5 M KCl per 40 mg sediments for 5 min. The problem of analytical artifacts resulting from redistribution of NH_4^+ onto residual solid surfaces during extraction has been resolved by leaching the sediment at the appropriate solid-solution ratio. The extracted NH_4^+ and NO_3^- were determined using an Auto-Analyzer Skalar SAN^{plus} (Liu et al., 2005a). N_{fix} was extracted by mixed acid of 5 M HF plus 1 M HCl (25 °C for 24 h) after pretreatment with KBrO (25 °C for 2 h, boiling for 5 min) and then KCl solution to wash the residue solids (Silva and Bremner, 1966), in which NH_4^+ in the extract was measured with the dilution spectrophotometry method instead of the original distillation–titration method, as there was no significant difference between these two methods (Zhu, 2007). The extracted ammonium was measured by manual spectrophotometry (Liu et al., 2003). Total nitrogen (TN) was measured using a CHNOS Elemental Analyzer. ON was determined by the difference between TN and IN. The analytical precision for the N extractions was better than 2.7% for $NH_{4\,ex}^+$, 4.7% for $NO_{3\,ex}^-$, 1.0% for N_{fix}, and 1.2% for TN.

IP was measured by 1 M HCl extraction (25 °C for 24 h), and total P (TP) was measured by 1 M HCl extraction after ignition of the sediment (550 °C for 2 h). OP was obtained by subtracting IP from TP (Liu et al., 2004a). The extracted PO_4^{3-} was measured by spectrophotometry (Liu et al., 2003). The analysis of the Chinese standard of coastal sediment (GBW 07314) gave the TP concentrations of $19.68 \pm 0.08\ \mu mol\ g^{-1}$, which compared well with the certified value ($20.85 \pm 1.97\ \mu mol\ g^{-1}$). The analytical precision for the P extractions was better than 0.1% for IP and 0.5% for TP (Liu et al., 2004a).

4. Results

4.1. Sediment dating

Sediments at this station have been dated using excess ^{210}Pb and fallout nuclide ^{137}Cs using the constant sedimentation rate model (Appleby and Oldfield, 1992; Liu et al., 2007a, 2008a). Fig. 2 shows the depth distribution of $^{210}Pb_{ex}$, ^{210}Pb and ^{226}Ra, in which $^{210}Pb_{ex} = {}^{210}Pb - {}^{226}Ra$. Based on the $^{210}Pb_{ex}$ activity profile, the sedimentation rate for the core estimated from the slope of the linear regression of the ln $^{210}Pb_{ex}$ versus depth is 1.64 cm yr^{-1} with a constant sediment mass accumulation rate of 1.49 g cm^{-2} yr^{-1}.

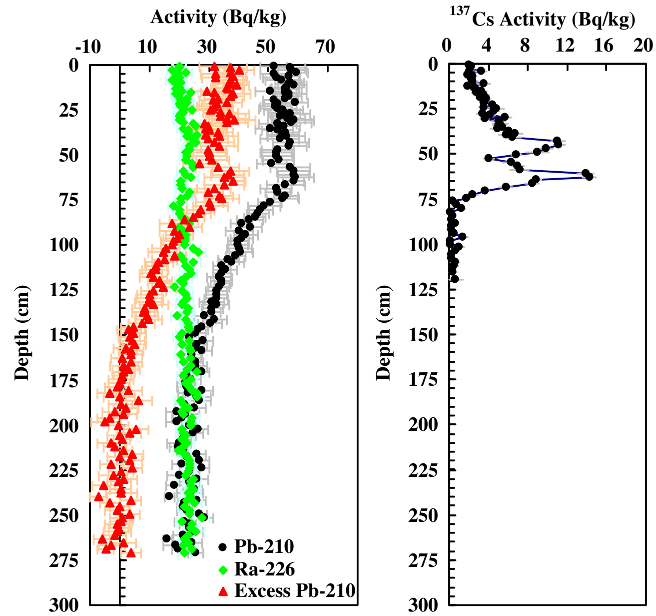

Fig. 2. The profiles of total ^{210} Pb, ^{226}Ra, excess ^{210}Pb, and ^{137} Cs activities in sediment core.

The sedimentation rate estimated with ^{137}Cs was determined using the peak position of the maximum deposition during 1963 from nuclear weapons testing. The maximum ^{137}Cs activity was measured at 62 cm depth of the core, from which a linear accumulation rate of 1.65 cm yr^{-1} can be retrieved. The ^{137}Cs-derived accumulation rate is in agreement with the ^{210}Pb-derived rate.

4.2. Nutrients in sediment core

Concentrations of BSi were at the long-term average level from the bottom to 108 cm sediment horizon, and then increased gradually to above the mean at 30 cm, and followed by a decrease at ca. 30-cm depth, with lower values than the mean for the top 30 cm (Fig. 3). OC concentrations increased gradually from lower than the long-term average at the bottom of the core to above the mean at 30 cm depth (~1984), decreased abruptly upcore (by 59%) across the 30 cm (~1984) sediment horizon and then changed slightly at the mean level (Fig. 4).

TN concentrations were generally at the mean levels at depths below 53 cm, then decreased upward below the mean at sediment horizons of 53–12 cm, and remained generally at the low values for the upper 12 cm. ON concentrations were at the mean levels and slightly increased from the bottom to 12 cm and then were above the mean for the upper 12 cm. The concentrations of N_{fix} remained generally at the mean levels below a depth of 41 cm (~1977), and then decreased upcore below the mean to the top. $NO_{3\,ex}^-$ concentrations were at low levels below 12 cm depth, and increased in the upper 12 cm of the core (not shown). $NH_{4\,ex}^+$ concentrations were generally above the mean at depths below 117 cm, and decreased upcore below the mean until 12 cm (~1995) and then remained at low levels in the upper 12 cm of the core (Fig. 5).

N_{fix} represented 30–45% of TN below a depth of 12 cm and decreased upcore to 15% at the sediment surface. $NH_{4\,ex}^+$ accounted for 12–15% of the TN in the lower depth of the core and decreased to less than 5% in the upper 12 cm of the core. $NO_{3\,ex}^-$ represented less than 0.2% of TN. IN accounted for 45–60% of TN in the lower layer and decreased to 20% in the upper layer (not shown). In com-

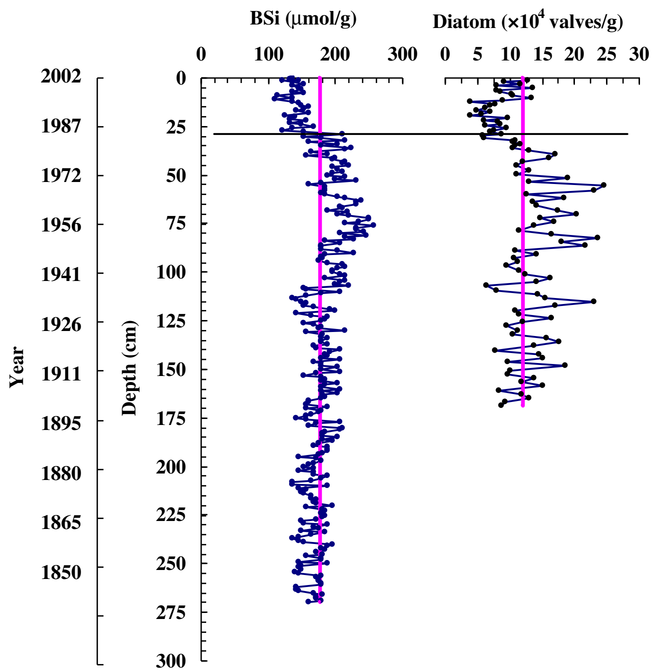

Fig. 3. Concentrations of biogenic silica (μmol/g) and diatom ($\times 10^4$ valves/g) in sediment core (diatom data taken from Liu et al. (2008a); courtesy of D. Liu). Vertical solid lines represent the mean values for all the data points.

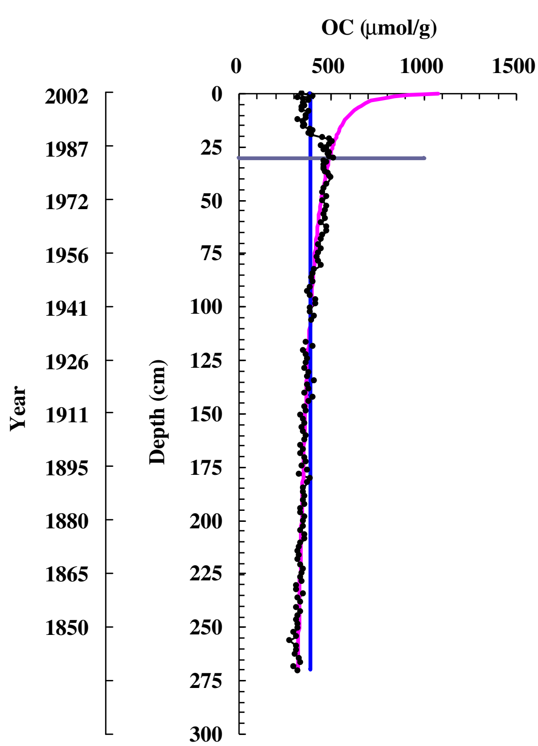

Fig. 4. Concentrations of OC (μmol/g) in sediment core. The solid line is the output of the Middelburg (1989) diagenetic model of organic matter decomposition; initial values of organic carbon were selected to match the data at depth. Vertical solid line represents the mean value for all the data points.

parison, ON represented 45–55% in the lower layer and increased to 80% of TN in the upper layer (Fig. 5).

Both IP and TP concentrations increased from lower or nearly the mean at the bottom to above the mean at 41 cm and then decreased by 25–30% with values below the mean to the sediment surface (Fig. 6). OP concentrations fluctuated at the mean in the lower depth, decreased to below the mean for the upper 30 cm (Fig. 6). IP represented 68–84% of TP and OP accounted for 16–32% of TP.

5. Discussion

5.1. Historic record of environment change

Changes in land use, economic development and population increase may have altered the nature and nutrient loading of JZB. The changes of nutrients deposited in sediment of JZB suggest that C, N, P, and Si are most likely affected by anthropogenic activities to different extents and by different factors. The observed changes of nutrients in sediment core can result from several factors including a steady-state input-decomposition balance, inputs of organic matter to the sediment–water interface, and altered decomposition pathways and sediment organic matter preservation associated with changing redox conditions (Cornwell et al., 1996). The normalized OC to Al profile (Fig. 7) and the normalized nutrients to Al (not shown) are similar to those found for OC and nutrients themselves, suggesting that grain size does not likely appear to be a major cause of changes in OC and nutrient profiles. Moreover, OC is predicted by the diagenetic model of Middelburg (1989), which assumes constant OC accumulation and a time-dependent decomposition rate. Below a depth of 30 cm, the derived OC by the model corresponds to the measured values, showing that the observed change in organic matter concentrations can be most likely accounted for by steady input and is shaped strongly by decomposition. While in the upper 30 cm depth, the derived OC is in excess of that OC preserved in sediment (Fig. 4), might indicating the effects of top-down pressure from shellfish aquaculture (Zhu and Zhang, 2007) (see discussion below). The effects of changes in carbon preservation rates associated with changes in the degree of oxygen depletion could not be a major cause as strong turbulent mixing results in nearly homogeneous vertical profiles of temperature and salinity in JZB (Liu et al., 2004b).

BSi, OP, and OC decreased at ~30 cm (~1984), probably reflecting a decrease in water column productivity. In JZB, diatom species represented 60–82% of phytoplankton, and the diatom cell abundance accounted for >95% of phytoplankton (up to 5.8×10^6 cell m^{-3}) (Li et al., 2005; Liu, 2004). Data on the phytoplankton community in the water column of JZB show that the diatom cell abundance decreased from the 1980s to the 1990s (Jiao, 2001; Liu, 2004; Wu et al., 2005). BSi variations in deposited sediments can be probably regarded as an indicator of diatom productivity and phytoplankton community change, which agree with water column studies. Microfossil evidence further supports the conclusion that a major environmental change most likely occurred beginning in the early 1980s. Liu et al. (2008a) examined the diatom record in duplicate core and mentioned that the total diatom cell abundance declined abruptly by 37% beginning at 30 cm and there was a concurrent decrease in diatom diversity, suggesting environmental change. There might be a change in dominant species from large diatoms to small-sized diatoms rather than in the biomass (Liu et al., 2008a). In the northern Gulf of Mexico, silicon limitation also affects the community composition, with shifts from heavily-silicified diatoms to more lightly-silicified diatoms (Rabalais et al., 1996, 2007; Dortch et al., 2001).

High grazing pressure caused by large-scale aquaculture of filter-feeders might have been one important factor in the decrease of phytoplankton biomass after the early 1980s (Liu et al., 2008a; Zhu and Zhang, 2007). The decrease of BSi and OC concentrations in the upper 30 cm is likely related to top-down pressure from

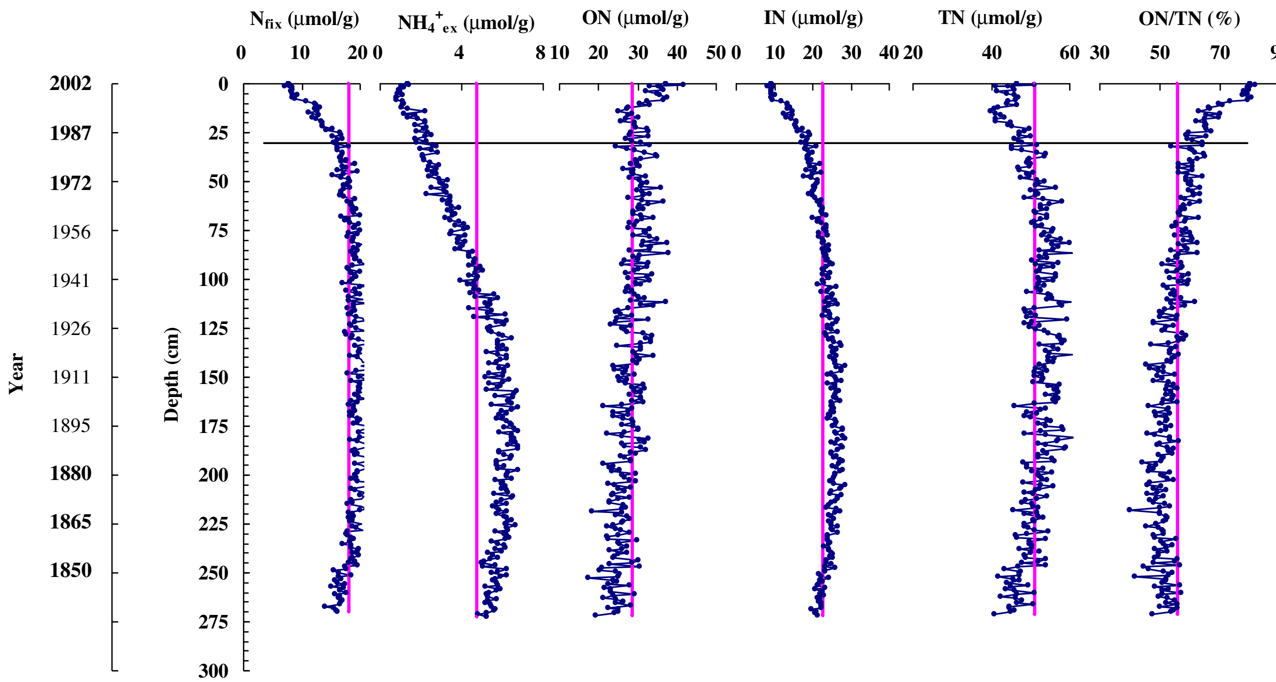

Fig. 5. Concentrations of nitrogen forms (μmol/g), and percentage of ON in TN as well in sediment core. Vertical solid lines represent the mean values for all the data points.

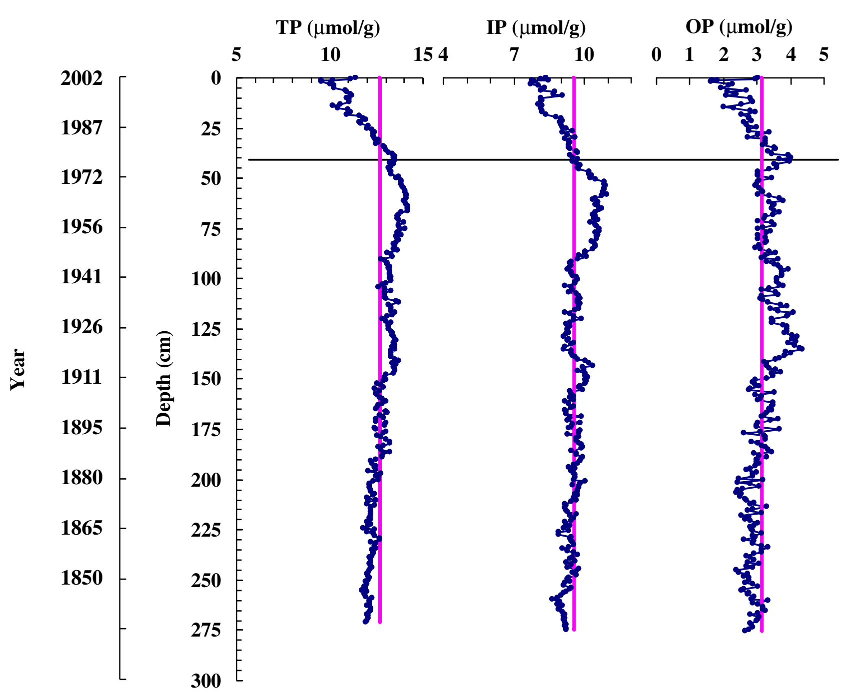

Fig. 6. Concentrations of IP, TP and OP (μmol/g) in sediment core. Vertical solid lines represent the mean values for all the data points.

shellfish aquaculture. It was indicated that the total areas of JZB used for marine culture increased by 10 times from 1330 ha in 1978 to 13737 ha in 2001 (Wu et al., 2005). The production of scallops in JZB increased dramatically from 540 tons yr^{-1} in 1980 to 81,000 tons yr^{-1} in 1995 (Lu et al., 2001). However, an epidemic disease of scallops occurred at the end of the 1990s due to intensive culturing and pollution, resulting in the extensive death of scallops; the population was restored several years later (Wang and Xiang, 1999; Wang et al., 2002). Similar results have been observed in Miaodao Strait: phytoplankton abundance decreased by one-sixth from the early 1980s to the end of the 1980s due to scallop culturing (Xiang et al., 1996). In Lake Mendota, zebra mussel reduced cyanobacterial blooms and increased water clarity (Reed-Andersen et al., 2000). The feeding activity of cultivated clams may also greatly influence the phytoplankton and primary production of JZB (Zhang et al., 2005). Moreover, the production

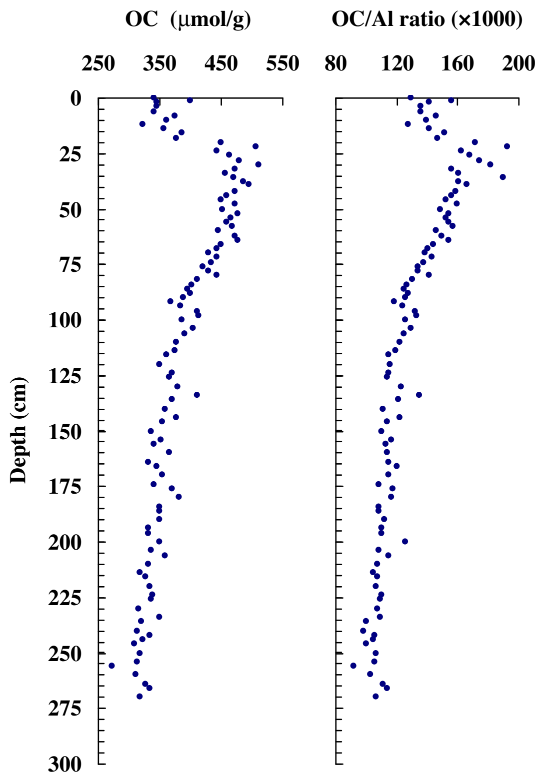

Fig. 7. Concentrations of OC (μmol/g) in sediment core and the same OC data normalized by dividing it by the concentration (μmol/g) of total aluminum. The other nutrient elements have the similar results and not shown. Note that only OC data with Al data measured at the same horizon are shown.

of one important clam, *Ruditapes philippinarum*, decreased in the early 1990s. Therefore, phytoplankton abundance probably recovered and increased again with nutrient enrichment.

ON deposited in sediments shows changes different from OC, OP, and BSi. JZB is characterized by high concentrations of dissolved nitrogen in the water column. *Paralia sulcata*, an indicative species of high dissolved nitrogen concentrations, may significantly increased after the 1980s (30 cm) in JZB (Liu et al., 2008a), which is consistent with ON profile related to anthropogenic activities (such as fertilizer application and wastewater discharge). The wastewater discharge characterizing by high nitrogen in JZB watersheds increased by ~35% from 1993 to 2004 (Liu et al., 2005a; Zhang, 2007). The application of chemical fertilizers has increased by 150–200 times with nitrogen fertilizer accounting for 38% (Zhang, 2007). In comparison, the cultivation area was reduced by one third over the last five decades, whereas the crop production increased by more than three times (Qingdao Municipal Statistics Bureau, 2005).

The decrease of IP, TP, and N_{fix} at 41 cm depth (~1977) can be argued to be related to riverine input. While it is difficult to quantify the changing inputs of nutrients into the bay, the data for IP and TP are even more limited, and there are no data for N_{fix} and IN in particulate matter in the major rivers emptying into JZB. Over the last half century, Daguhe, which represents more than 80% of total freshwater discharge emptying into JZB, has shown an abrupt decrease by more than six times in freshwater discharge from $7.4 \times 10^8\ m^3\ yr^{-1}$ during 1951–1976 to $1.2 \times 10^8\ m^3\ yr^{-1}$ during 1977–2001 owing to exhaustive consumption of water resources and damming over the watersheds (Fig. 8). Although long-term sediment load data are not available, the total riverine sediment discharge decreased from 2×10^6 tons yr^{-1} before the 1970s to less than 3×10^4 tons yr^{-1} after the 1980s due to the construction of reservoirs and dams (State Oceanographic Administration, 1993). Urban waste residue is another dominant source of sediment in JZB, which was 1.0×10^6 tons yr^{-1} before 1980, comparable to riverine sediment input. It increased to 1.6×10^6 tons yr^{-1} in the 1980s due to rapid economic development, and decreased significantly after 1990 due to government control (Gao and Wang, 2002). Rainfall decreased concurrently from 805 mm during 1951–1976 to 617 mm during 1977–2001 (Fig. 8). A decrease in both freshwater discharge and rainfall induced an increase in the seawater surface salinity in JZB (Liu et al., 2005a).

Questions still remain, however, concerning geochemical changes that occur immediately across the 30–41 cm (~1978–1984) sediment horizon. Apparently, the decrease in phytoplankton and microbially-derived OM was proportional to the decrease in OC at this time. The timing and magnitude of the change in productivity are consistent with long-term trends in surface chlorophyll, which decreased during the early 1980s to 1990s and increased later (Wu et al., 2005). Accordingly, BSi, OP, and OC decreased at ~30 cm, might reflecting a decrease in water column productivity. The organic and inorganic geochemical changes that we observed indicate that a single 'cause and effect' relationship should not be made, because other probable changes such as increases in sewage input, urbanization, and aquaculture, all linked with the increasing human population growth rate, occurred at the same time in JZB. Furthermore, this work was based upon the geochemical record of a single core in JZB; additional work will be undertaken to extend these findings to other portions of the bay.

5.2. Changes in sediment organic matter composition and diagenesis

The elemental ratios of organic matter provide useful indices of sediment provenance (i.e., terrestrial versus estuarine) dominance and differential rates of sediment decomposition for C, N, P, and BSi (Fig. 9). The C/N ratio is often indicative of the predominant source of organic matter in a system. Phytoplankton C/N ratios range from 6 to 9 (Holligan et al., 1984). Bacterioplankton is nitrogen-rich and has C/N ratios from 2.6 to 4.3 (Lee and Fuhrman, 1987). The terrestrial organic matter can have significantly higher C/N ratios (>12) (Hedges and Mann, 1979). The decreases of OC/ON ratios in the upper 30 cm of the core largely indicate decreases in terrestrial organic matter input. However, it should be noted that the C/N ratio can be changed due to decomposition of OC and ON by microorganisms (Hedges and Oades, 1997). The $\delta^{13}C$ values were −21.9‰ to −19.7‰ in the sediment core and varied from −21.7‰ to −21.1‰ in the upper 30 cm of the core, suggesting that organic matter was primarily marine source (Wu et al., unpublished data). Different results may be obtained when different OC/nitrogen ratios are used to identify the source of organic matter. For example, major terrestrial organic matter and mixing source is suggested based on the OC/ON ratios, while a phytoplankton source and mixing source of organic matter is suggested based on the OC/TN ratios. It is important to separate nitrogen into organic and inorganic parts; inorganic nitrogen might represent 20% at the sediment surface to 50% in the lower portion of the core.

The molar ratios of OC/OP ranged from 82 to 239 with an average of 127. The values were above the mean (127) in the upper 30 cm, decreased downcore to at or slightly lower than the mean below 80 cm. The molar ratios of ON/OP ranged from 6 to 12 at depths below 12 cm, and increased to 14–20 at the sediment surface (Fig. 9), with ratios similar to the Redfield ratio near the sediment–water interface. The increased ON/OP ratios in the upper 12 cm of the core may be ascribed to the preferential remineralization of OP or greater nitrogen input relative to phosphorus input. The latter may be the case, as ON concentrations increased but OP concentrations decreased in the upper 12 cm of the core, as

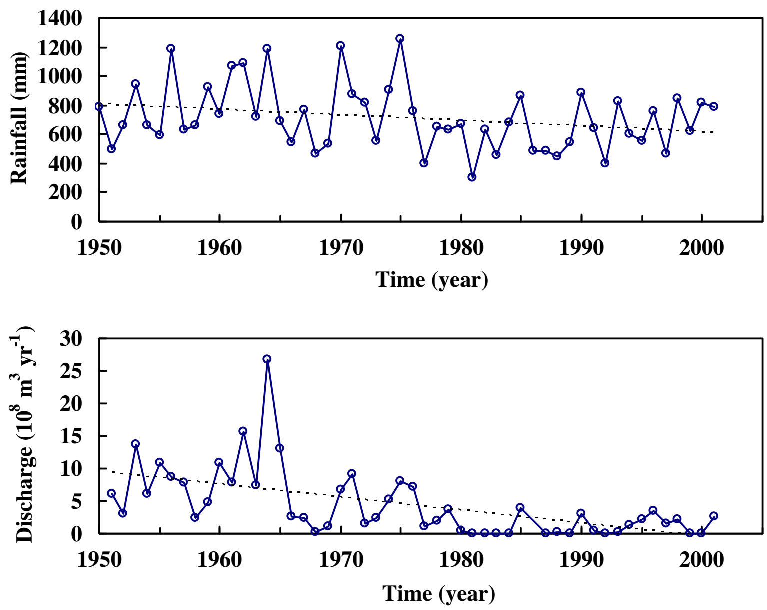

Fig. 8. Changes of precipitation (mm) in Jiaozhou Bay and freshwater discharge (10^8 m^3 yr^{-1}) of the Daguhe for the last 50 years.

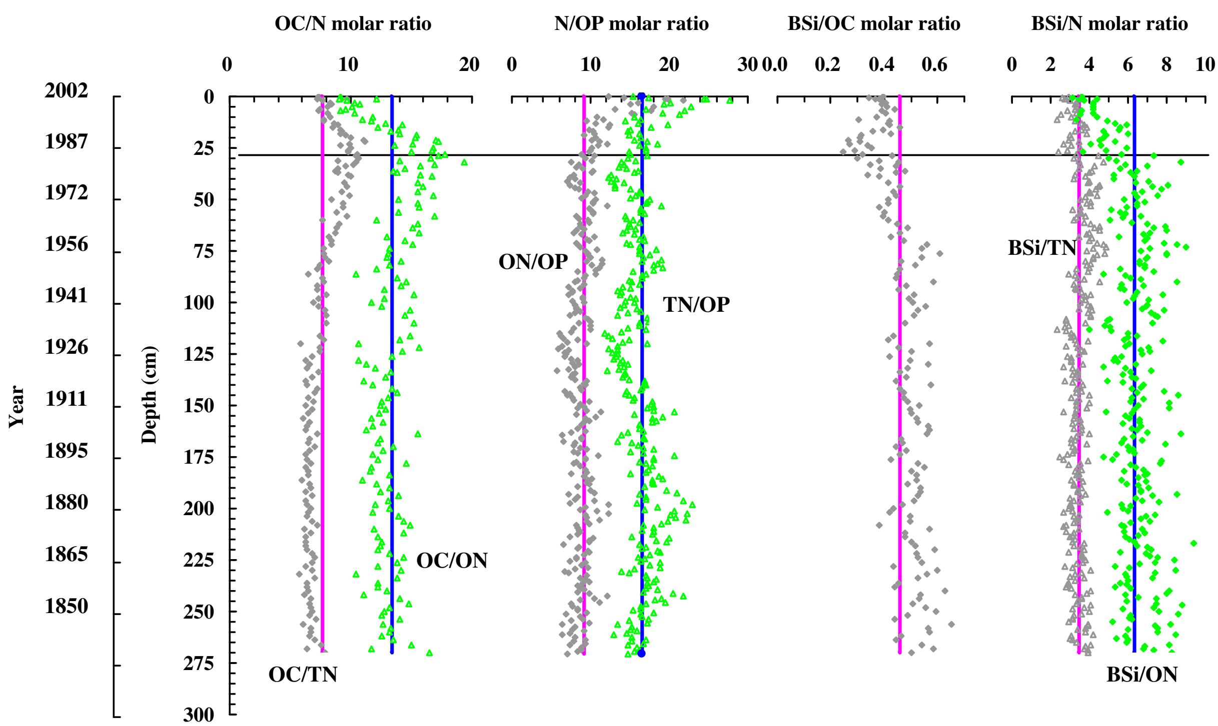

Fig. 9. Molar ratios of OC/N, N/OP, BSi/OC, and BSi/N in sediment core. Vertical solid lines represent the mean values for all the data points.

mentioned above (Figs. 5 and 6). In JZB, the total wastewater drainage increased from 1.8×10^8 tons yr^{-1} in 1993 to 2.4×10^8 tons yr^{-1} in 2004, of which the emission from the industrial sector amounted to 35–55% and only ca. 1/3 was processed by waste treatment facilities before being drained off (Zhang, 2007). The wastewater is characterized by high nitrogen, with DIN/PO_4^{3-} molar ratios of 60–134 (Liu et al., 2005a).

The BSi/ON molar ratios remained constant at 6.6 ± 0.9 in the lower portion of the core (below 30 cm) and decreased to ~3.2 at the surface sediment. The BSi/OC ratios decreased upcore (Fig. 9). This is likely ascribed to a change in dominant species from large diatoms to small-sized diatoms in JZB (Liu et al., 2008a) caused by the decrease of Si(OH)$_4$/DIN ratio in the nutrient loading (Liu et al., 2005a; Shen, 2001). Accordingly, the large dominant diatom species *Th. anguste-lineatus* (45–60 μm), *Th. eccentria* (35–110 μm), *C. excentricus* (36–72 μm), *C. concinnus* (390–464 μm) and *D. gorjanovici* (48–65 μm) below 30 cm of the core were replaced by the small species *Cy. stylorum* (30–66 μm) and *P. sulcata* (15–36 μm) in the upper 30 cm of the core related to anthropogenic activities and climate change. Moreover, the Shannon-Wiener index of diatom floral diversity fluctuated with depth, with a slight, gradual increase above 30 cm ($r^2 = 0.09$) (Liu et al., 2008a). However, the shift may also be related to changes from heavily-silicified to lightly-silicified diatoms or to non-siliceous forms such as dinoflagellates.

Correlation analysis among nutrients forms indicates that there are significant linear correlations between OC and ON, ON and OP, BSi and ON, and BSi and OC, with correlation coefficients of $r = 0.616$, 0.374, 0.412, and 0.548 at $p = 0.001$, respectively, for sediments below 30 cm. However, there are no significant linear relationships between them in the upper 30 cm of the core. This largely suggests that the environment significantly changed after the 1980s. In comparison, correlation analysis among nutrient elements in suspended particulate matter of the water column in 2001–2003 indicates that there are significant linear relationships between POC and PN, BSi and POC, and BSi and PN, with correlation coefficients of $r = 0.922$, 0.632, and 0.539 at $p = 0.001$ ($n = 136$) respectively. However, there are no significant correlations between PN and POP or POC and POP.

There is a continuous decrease in the reactivity of organic matter over more than eight orders of magnitude of time since burial, although their reactivity at the sediment–water interface is different (Middelburg, 1989). Organic matter could be divided into various groups of compounds of different reactivity, each of which undergoes first-order decomposition. This multi-G model can be expressed as (Berner, 1980; Westrich and Berner, 1984; Zimmerman and Canuel, 2000):

$$\ln(G_i/G_0) = -kt + \ln(G_\infty/G_0) \quad (1)$$

where G_i is the concentration of metabolizable organic carbon in each group, G_0 is the concentration of metabolizable organic matter at the sediment surface, G_∞ is the asymptotic organic matter concentration, k is the first-order decay constant for each group, and t is time. In the core of JZB, it is largely apparent that there are two distinct portions of the organic matter profile (Fig. 10). Non-steady-state conditions are most likely suggested by the mismatch in the upper portion of the core. Anthropogenic activities (aquaculture) are probably the major reason for this case, as discussed above.

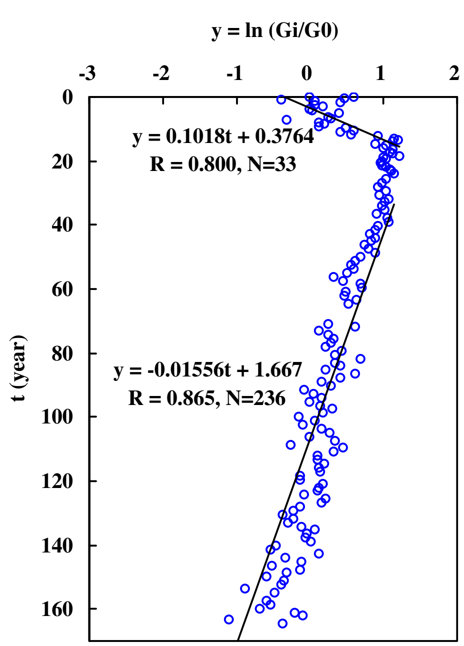

Fig. 10. Plot of $\ln(G_i/G_0)$ versus time. G_∞ was set at 270 μmol g^{-1} sediment for the whole core. G_i values are the difference between measured OC and G_∞. Linear relationships are shown for the upper 30 cm and below 30 cm portions of the core.

6. Summary

Increased inorganic fertilizer application and human population growth in the watershed of JZB are coincident with changes in the trophic state of JZB, suggesting that anthropogenic activities within estuarine watersheds may exert a substantial influence on carbon cycling processes in estuaries and potentially the coastal ocean. Variations in BSi and OC profiles are largely consistent with changes in the productivity of overlying waters, suggesting a reduction since the 1980s. Aquaculture probably plays an important role in the decrease of nutrient elements in the upper layers recorded in sediments. Decreases in the molar BSi/OC ratios upcore were most likely ascribed to changes in dominant species from large diatoms to small-sized diatoms and/or changes from heavily-silicified to lightly-silicified diatoms or to non-siliceous such as dinoflagellates. IP, TP, and fixed nitrogen profiles are likely consistent with the decrease in rainfall and freshwater discharge to JZB. The ON profile is largely consistent with increases in fertilizer application and wastewater discharge. Our data might suggest that the environment has significantly changed since the 1980s.

Acknowledgements

The authors would like to thank Xiao Shi Xu, Kui Xuan Lin, Guo Sen Zhang, Xi Wen Ye, Wen Qing Cao, Yuan Yuan Zhu, Xiao Hong Qi, Ying Fei Zhao, Liang Xie, Xiu Huan Ou-Yang, Lei Gao, and the crews of R/V "Dong Fang Hong 2" for their assistance in field and laboratory work, and the facilities for POC/N determination by SKLEC/ECNU. This study was funded by the Natural Sciences Foundation of China (Nos. 40925017 and 40876054), the Ministry of Education (108081), the Ministry of Science and Technology of PR China (No. 2006CB400602).

References

Appleby, P.G., Oldfield, F., 1992. Application of ^{210}Pb to sedimentatin studies. In: Ivanovich, M., Harmon, R.S. (Eds.), Uranium-series Disequilibrium: Applications to Earth, Marine, and Environmental Sciences, second ed. Oxford, Clarendon, pp. 731–778.

Bennett, E.M., Carpenter, S.R., Caraco, N.F., 2001. Human impact on erodable phosphorus and eutrophication: a global perspective increasing accumulation of phosphorus in soil threatens rivers, lakes, and coastal oceans with eutrophication. Bioscience 51, 227–234.

Berner, A., 1980. A rate model for organic matter decomposition during bacterial sulfate reduction in marine sediments. Biogeochemistry of organic matter at the sediment–water interface. CNRS Int. Colloq. 293, 35–44.

Conley, D.J., 1998. An interlaboratory comparison for the measurement of biogenic silica in sediments. Mar. Chem. 63, 39–48.

Cooper, S.R., Brush, G.S., 1993. A 2500-year history of anoxia and eutrophication in Chesapeake Bay. Estuaries 16, 617–626.

Cornwell, J.C., Conley, D.J., Owens, M., Stevenson, J.C., 1996. A sediment chronology of the eutrophication of Chesapeake Bay. Estuaries 19, 488–499.

Dai, J., Song, J., Li, X., Yuan, H., Li, N., Zheng, G., 2007. Environmental changes reflected by sedimentary geochemistry in the last hundred years of Jiaozhou Bay, North China. Environ. Pollut. 145, 656–667.

DeMaster, D.J., 1981. The supply and accumulation of silica in the marine environment. Geochim. Cosmochim. Acta 45, 1715–1732.

Dortch, Q., Rabalais, N.N., Turner, R.E., Qureshi, N.A., 2001. Impacts of changing Si/N ratios and phytoplankton species composition. In: Rabalais, N.N., Turner, R.E. (Eds.), Coastal Hypoxia: Consequences for Living Resources and Ecosystems. Coastal and Estuarine Studies, vol. 58. American Geophysical Union, Washington, DC, pp. 37–48.

Gao, S., Wang, Y.-P., 2002. Characteristics of sedimentary environment and tidal inlet evolution of Jiaozhou Bay. Adv. Mar. Sci. 20, 52–59 (in Chinese with English abstract).

Gooday, A.J., Jorissen, F., Levin, L.A., Middelburg, J.J., Naqvi, S.W.A., Rabalais, N.N., Scranton, M., Zhang, J., 2009. Historical records of coastal eutrophication-induced hypoxia. Biogeosciences 6, 1707–1745.

Hedges, J.I., Mann, D.C., 1979. The characterization of plant tissues by their lignin oxidation products. Geochim. Cosmochim. Acta 43, 1803–1807.

Hedges, J.I., Oades, J.M., 1997. Comparative organic geochemistries of soils and marine sediments. Org. Geochem. 27, 319–361.

Holligan, S.G., Montoya, J.P., Nevins, J.L., McCarthy, J.J., 1984. Vertical distribution and partitioning of organic carbon in mixed, frontal and stratified waters of the English Channel. Mar. Ecol. Prog. Ser. 14, 111–127.

Humborg, C., Ittekkot, V., Cociasu, A., Bodungen, B.V., 1997. Effect of Danube River dam on Black Sea biogeochemistry and ecosystem structure. Nature 386, 385–388.
Jiao, N., 2001. Ecological processes and sustainable development of typical coastal water ecosystems in China. Science Press, Qingdao, China (in Chinese).
Lee, S.H., Fuhrman, J.A., 1987. Relationships between biovolume and biomass of naturally derived marine bacterioplankton. Appl. Environ. Microbiol. 53, 1298–1303.
Li, Y., Li, R.X., Wang, Z.L., Zhu, M.Y., Sun, P.X., Xia, B., 2005. A preliminary study on the phytoplankton community structure and its changes in Jiaozhou Bay. Adv. Mar. Sci. 23 (3), 328–334 (in Chinese with English abstract).
Liu, D., 2004. Community Structure Succession Study of Phytoplankton and Sediment Diatoms in Jiaozhou Bay. PhD Thesis. Ocean University of China, Qingdao, China (in Chinese with English abstract).
Liu, D., Sun, J., Zhang, J., Liu, G., 2008a. Response of the diatom flora in Jiaozhou Bay, China to environmental changes during the last century. Mar. Micropaleontol. 66, 279–290.
Liu, G.S., Liu, S.M., Zhang, J., Huang, Y.P., Chen, M., 2007a. Sedimentary processes of the Qingdao nearshore traced using a multi-radionuclide approach. Water Air Soil Pollut. Focus 7, 693–701.
Liu, S.M., Li, X.N., Zhang, J., Wei, H., Ren, J.L., Zhang, G.L., 2007b. Nutrient dynamics in Jiaozhou Bay. Water Air Soil Pollut. Focus 7, 625–643.
Liu, S.M., Zhang, J., Chen, H.T., Xiong, H., Wu, Y., Zhang, Z.F., 2003. Nutrients in the Changjiang and its tributaries. Biogeochemistry 62, 1–18.
Liu, S.M., Zhang, J., Li, D.J., 2004a. Phosphorus cycling in sediments of the Bohai and Yellow Sea. Estuar. Coast. Shelf Sci. 59, 209–218.
Liu, S.M., Zhang, J., Chen, H.T., Zhang, G.S., 2005a. Factors influencing nutrient dynamics in the eutrophic Jiaozhou Bay, North China. Progr. Oceanogr. 66, 66–85.
Liu, S.M., Zhang, J., Li, R.X., 2005b. Ecological significance of biogenic silica in the East China Sea. Mar. Ecol. Progr. Ser. 290, 15–26.
Liu, S.M., Ye, X.W., Zhang, J., Zhao, Y.F., 2002. Problems with biogenic silica measurement in marginal seas. Mar. Geol. 192, 383–392.
Liu, S.M., Ye, X.W., Zhang, J., Zhang, G.S., Wu, Y., 2008b. The silicon balance in Jiaozhou Bay, North China. J. Mar. Syst. 74, 639–648.
Liu, Z., Wei, H., Liu, G., Zhang, J., 2004b. Simulation of water exchange in Jiaozhou Bay by average residence time approach. Estuar. Coast. Shelf Sci. 61, 25–35.
Lu, J., Wu, Y., Zhang, F., 2001. Fishery resource analysis and ecological fishery management. In: Jiao, N.Z. et al. (Eds.), Ecological Processes and Sustainable Development of Typical Coastal Water Ecosystems in China. Science Press, Beijing, pp. 88–95 (in Chinese).
Middelburg, J.J., 1989. A simple model for organic matter decomposition in marine sediments. Geochim. Cosmochim. Acta 53, 1577–1581.
Mortlock, R.A., Froelich, P.N., 1989. A simple method for the rapid determination of biogenic opal in pelagic marine sediments. Deep-Sea Res. 36, 1415–1426.
Piehler, M.F., Twomey, L.J., Hall, N.S., Paerl, H.W., 2004. Impacts of inorganic nutrient enrichment on phytoplankton community structure and function in Pamlico Sound, NC, USA. Estuar. Coast. Shelf Sci. 61, 197–209.
Qingdao Municipal Statistics Bureau, 2005. Qingdao Statistical Yearbook-2004. Statistics Press, Beijing, China (in Chinese).
Rabalais, N.N., Turner, R.E., Justić, D., Dortch, Q., Wiseman Jr., W.J., Sen Gupta, B.K., 1996. Nutrient changes in the Mississippi River and system responses on the adjacent continental shelf. Estuaries 19, 386–407.
Rabalais, N.N., Turner, R.E., Sen Gupta, B.K., Platon, E., Parsons, M.L., 2007. Sediments tell the history of eutrophication and hypoxia in the northern Gulf of Mexico. Ecological Applications, Special Issue, Nutrient Enrichment of Estuarine and Coastal Marine Environments 17 (5), S129–S143.
Ragueneau, O., Lancelot, C., Egorov, V., Vervlimmeren, J., Cociasu, A., Déliat, G., Krastev, A., Daoud, N., Rousseau, V., Popovitchev, V., Brion, N., Popa, L., Cauwet, G., 2002. Biogeochemical transformations of inorganic nutrients in the mixing zone between the Danube River and the Northwestern Black Sea. Estuar. Coast. Shelf Sci. 54, 321–336.
Reed-Andersen, T., Carpenter, S.R., Padilla, D.K., Lathrop, R.C., 2000. Predicted impact of zebra mussel (*Dreissena polymorpha*) invasion on water clarity in Lake Mendota. Can. J. Fish. Aquat. Sci. 57, 1617–1626.
Shen, Z.-L., 2001. Historical changes in nutrient structure and its influences on phytoplankton composition in Jiaozhou Bay. Estuar. Coast. Shelf Sci. 52, 211–224.
Silva, J.A., Bremner, J.M., 1966. Determination and isotoperation analysis of different forms of nitrogen in soils: 5. Fixed ammonium. Soil Sci. Soc. Am. Proc. 30, 587–594.
State Oceanographic Administration, 1993. China's Estuaries and Embayments (Vol. 4) – Southern Shandong Peninsula and Jiangsu Province. China Ocean Press, Beijing, pp. 157–258 (in Chinese).
Turner, R.E., Rabalais, N.N., 1994. Coastal eutrophication near the Mississippi River delta. Nature 368, 619–621.
Turner, R.E., 2002. Element ratios and aquatic food webs. Estuaries 25, 694–703.
Vitousek, P.M., Mooney, H.A., Lubchenco, J., Melillo, J.M., 1997. Human domination of earth's ecosystems. Science 277, 494–499.
Wang, X., Wang, C., Li, Y., 2002. Epidemiological study on massive death of the cultured scallop Chlamys farreri in Jiaozhou Bay. J. Fish. China 26, 149–154 (in Chinese).
Wang, Y., Xiang, J., 1999. Studies on causation of the mass mortality of Chlamys farreri. Oceanologia Limnologia Sinica 30, 770–774 (in Chinese).
Westrich, J.T., Berner, R.A., 1984. The role of sedimentary organic matter in bacterial sulfate reduction: the G-model tested. Limnol. Oceanogr. 29, 236–249.
Wu, Y.L., Sun, S., Zhang, Y.S., 2005. Long-term change of environment and its influence on phytoplankton community structure in Jiaozhou Bay. Oceanologia et Limnologia Sinica 487–498 (in Chinese with English abstract).
Xiang, F.T., Qu, W.G., Zhang, Y.E., Xu, B.Y., 1996. On aquaculture structure adjustment in Shallow Sea East to Miaodao Strait. Shandong Fish. 13 (2), 1–4 (in Chinese).
Yang, S.L., Chen, Q.M., Zhu, J., Zhang, J., 2003. Computation of storage capacity for tidal water of semiclosed bays where the intertidal zone is partly embanked-taking Jiaozhou Bay as an example. Mar. Sci. 27, 43–47 (in Chinese).
Zhang, J.H., Fang, J.G., Sun, S., Zhao, J.M., 2005. Clearance rate, ingestion rate and absorption efficiency of cultivated clam *Ruditapes philippinarum* in Jiaozhou Bay, China. Oceanologia et Limnologia Sinica 36, 548–555 (in Chinese with English abstract).
Zhang, J.S., Shen, Z.L., 1997. A study of changes in the nutrient structure of Jiaozhou Bay. Oceanologia et Limnologia Sinica 28, 529–535 (in Chinese).
Zhang, J., 2007. Watershed nutrient loss and eutrophication of marine recipients: a case study of the Jiaozhou Bay. Water Air Soil Pollut. Focus 7, 583–592.
Zimmerman, A.R., Canuel, E.A., 2000. A geochemical record of eutrophication and anoxia in Chesapeake Bay sediments: anthropogenic influence on organic matter composition. Mar. Chem. 69, 117–137.
Zhu, B.D., 2007. Study on the forms of nitrogen in the sediments of the Yellow Sea and Jiaozhou Bay. Master's Dissertation. Ocean University of China (in Chinese with English abstract).
Zhu, M., Zhang, X., 2007. Jiaozhou Bay, China: threats from eutrophication to large scale aquaculture stimulate nutrient management. In: Bricker, S., Longstaff, B., Dennison, W., Jones, A., Boicourt, K., Wicks, C., Woerner, J. (Eds.), Effects of Nutrient Enrichment in the Nation's Estuaries: A Decade of Change, National Estuarine Eutrophication Assessment Update. NOAA Coastal Ocean Program Decision Analysis Series No. 26. National Centers for Coastal Ocean Science, Silver Spring, MD, pp. 124–126.
Zou, L., 2001. An experimental study on the relationship between nutrients and phytoplanktons in the coastal waters of North China. PhD Dissertation. Ocean University of China (in Chinese with English abstract).