

The sources and composition of organic matter in sediments of the Jiaozhou Bay: implications for environmental changes on a centennial time scale

KANG Xuming^{1,2}, SONG Jinming^{1,2,3*}, YUAN Huamao^{1,2,3}, LI Xuegang^{1,2,3}, LI Ning^{1,2,3}, DUAN Liqin^{1,2,3}

¹Key Laboratory of Marine Ecology and Environmental Sciences, Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, China

²Laboratory for Marine Ecology and Environmental Sciences, Qingdao National Laboratory for Marine Science and Technology, Qingdao 266237, China

³University of Chinese Academy of Sciences, Beijing 100049, China

Received 12 January 2017; accepted 8 February 2017

©The Chinese Society of Oceanography and Springer-Verlag Berlin Heidelberg 2017

Abstract

The Jiaozhou Bay is characterized by heavy eutrophication that is associated with intensive anthropogenic activities. Four core sediments from the Jiaozhou Bay are analyzed using bulk technologies, including sedimentary total organic carbon (TOC), total nitrogen (TN), the stable carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) isotopic composition to obtain the comprehensive understanding of the source and composition of sedimentary organic matter and further shed light on the environmental changes of the Jiaozhou Bay on a centennial time scale. Results suggest that the TOC and TN concentrations increase in the upper core, having indicated a probable eutrophication process since the 1920s in the inner bay and the 2000s in the bay mouth. The TOC and TN concentrations outside the bay have also changed since 1916 owing to the variation of terrigenous input. Considering TOC/TN ratio, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, it can be concluded there is a mixture of terrigenous and marine organic matter sources in the study area. A simple two end-member (terrigenous and marine) mixing model using $\delta^{13}\text{C}$ indicates that 45%–79% of TOC in the Jiaozhou Bay is from the marine source. The environmental changes of the Jiaozhou Bay are recorded by geochemical proxies, which are influenced by the intensive anthropogenic activities (e.g., extensive use of fertilizers, and discharge of sewage) and climate changes (e.g., rainfall).

Key words: organic matter, sources, anthropogenic activities, environmental changes, sediments, Jiaozhou Bay

Citation: Kang Xuming, Song Jinming, Yuan Huamao, Li Xuegang, Li Ning, Duan Liqin. 2017. The sources and composition of organic matter in sediments of the Jiaozhou Bay: implications for environmental changes on a centennial time scale. *Acta Oceanologica Sinica*, 36(11): 68–78, doi: 10.1007/s13131-017-1076-1

1 Introduction

The burial of organic matter in coastal and shelf sediments plays a key role in regulating the global carbon cycle, and up to 80% of organic matter is buried in shallow marine ecosystems (Bernier, 1982). The coastal margins, especially those under significant river influence, are characterized by complex biogeochemical patterns of sedimentary organic matter due to significant land-sea exchange of materials along with anthropogenic impact (Gao et al., 2012; Wang et al., 2013). Knowledge of the sources and composition of organic matter in estuarine and coastal sediments and factors in controlling its distribution is important for the understanding of global biogeochemical cycles (Wang et al., 2013; Li et al., 2015a, b). Moreover, the exploration of the geochemical behavior of sedimentary organic matter is important for a better understanding of its responses to regional climate changes and anthropogenic impact (Bianchi and Allison, 2009;

Wang et al., 2013; Hu et al., 2016).

As bulk parameters, TOC/TN ratios and the isotope compositions of carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) are reliable proxies in the study of the sources and composition of organic matter buried in marine sediments, which could help us to understand the environmental changes in coastal systems (Cohen and Fong, 2005; Henderson and Holmes, 2009; Wang et al., 2013; Hu et al., 2016; Ke et al., 2017). The use of these parameters relies on the differences among the natural abundance of $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and TOC/TN ratio in organic matter from different sources (Gao et al., 2012). In general, organic matter of the marine source and the terrigenous source had a TOC/TN ratio of approximately 4–10 and greater than 20, respectively (Meyers, 1994; Li et al., 2008). However, post-depositional changes in this ratio could occur (Meyers, 1994), which would result in the inaccuracy of source identification. In contrast to TOC/TN ratios, $\delta^{13}\text{C}$ only changed

Foundation item: The Joint Fund between Natural Science Foundation of China and Shandong Province under contract No. U1606404; the National Basic Research Program (973 Program) of China under contract Nos 2015CB452901 and 2015CB452902; the National Key Research and Development Plan Sino-Australian Centre for Healthy Coasts under contract No. 2016YFE0101500; the Program for Aoshan Excellent Scholars of Qingdao National Laboratory for Marine Science and Technology of China under contract No. 2015ASTP-OS13.

*Corresponding author, E-mail: jmsong@qdio.ac.cn

slightly during the sedimentation and degradation (Wang et al., 2013). Terrigenous organic matter generally exhibited more depleted $\delta^{13}\text{C}$ ($<-27\text{‰}$) relative to marine organic matter (-22‰) (Meyers, 1994). The $\delta^{13}\text{C}$ usually increased with increasing productivity (Hodell and Schelske, 1998). The $\delta^{15}\text{N}$ was commonly used to track anthropogenic nitrogen pollution, and varied significantly in different contaminants (Wang et al., 2013), ranging from -2‰ to 4‰ in nitrogen fertilizers and from 10‰ to 20‰ in human and animal manure (Ke et al., 2017). Moreover, $\delta^{15}\text{N}$ in sediments could be used to reflect the deposition rates of organic matter and origins of nitrogen in phytoplankton and mineralization process (Cohen and Fong, 2005; Wang et al., 2013). Therefore, the combination of these three parameters could help us better discriminate organic matter sources in coastal areas (Meyers, 1994).

Owing to the interference of the anthropogenic activities (e.g., rapid human population growth, rapid urbanization, excessive use of agricultural fertilizers, increasing sewage discharge, intensive mariculture and land reclamation) and climate changes, severe environmental problems including eutrophication, organic matter accumulation and heavy metal pollution occurred in China's coastal waters and lakes (Shen et al., 2005; Dai et al., 2007a; Liu et al., 2010b; Wang et al., 2013; Li et al., 2014, 2015a, b; Lin et al., 2015; Yuan et al., 2016). Consequently, the nature balance between the production and decomposition of organic matter has been disturbed in many coastal areas (Yang et al., 2011; Gao et al., 2012; Wang et al., 2013). Understanding the sources of anthropogenic inputs and the coupled impacts from the anthropogenic activities and the climate changes on ecosystems is therefore a major environmental concern.

Over the last 150 a, with the rapid economic and social development in Qingdao City, the Jiaozhou Bay has been largely affected by the anthropogenic activities, and increasing amounts of industrial, agricultural and aquaculture waste have been discharged into the Jiaozhou Bay (Li et al., 2008). Moreover, climate changes, including the temperature increase and the rainfall decrease were reported (Yuan et al., 2016). As a result of the anthropogenic activities and the climate changes, eutrophication and

harmful algal blooms occurred frequently (Liu et al., 2010b; Yuan et al., 2016). These changes, in turn, have the potential to alter the nature and content of organic matter of marine deposits and their TOC/TN ratio, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values (Gao et al., 2012). There are plenty of reports on eco-environment feedback of the Jiaozhou Bay to anthropogenic activities (Dai et al., 2007a; Liu et al., 2010b), such as the nutrient structure and phytoplankton community compositions (Shen, 2001), the heavy metal pollution (Li et al., 2011), the burial of biogenic element (Dai et al., 2007b; Wang et al., 2017) and the sedimentary dynamics (Zhao et al., 2015), etc. However, the study on organic matter sources and distribution in this region is scarce and the past study was simply based on the TOC/TN ratio or single core sediment (Li et al., 2008; Yang et al., 2011). Moreover, the impact of anthropogenic disturbance on environmental changes on a centennial time scale is still unclear in the Jiaozhou Bay. Therefore, in this study, the TOC/TN ratio, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values were combined to present a comprehensive picture of the sources and composition of organic matter buried in the Jiaozhou Bay sediments. In addition, the present study intended to further address the hypothesis that the environment is significantly influenced by intensive anthropogenic activities and climate changes.

2 Materials and methods

2.1 Study area

The Jiaozhou Bay is a semi-enclosed bay, located on the western coast of the Yellow Sea, which is adjacent to Qingdao City (Fig. 1). The bay has a total area of approximate 390 km^2 , with a mean depth of 6–7 m (Dai et al., 2007a, b). The Jiaozhou Bay lies in a warm temperature monsoon climate zone, with an average annual air temperature of 12.3°C and rainfall of 725–1 100 mm (Yuan et al., 2016). There are more than ten small rivers (e.g., Yanghe River, Dagou River, and Licun River) discharging into the Jiaozhou Bay with industrial and domestic sewage and sediments. Moreover, there are large coastal areas of mariculture ponds along the bay for fish, shrimp and shellfish culture. The annual discharge of terrigenous dissolved inorganic nitrogen in-

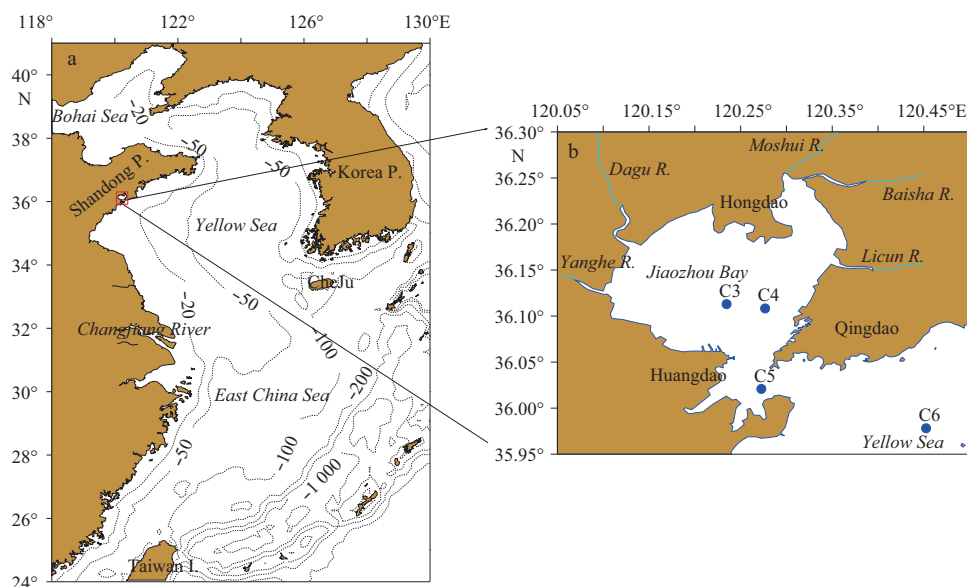


Fig. 1. Study area. a. East China marginal seas and the location of the Jiaozhou Bay (inside the red rectangle), and b. the sampling stations of the Jiaozhou Bay.

creased by ten times from the 1980s to the 2000s (Wang, 2009; Yuan et al., 2016), which induced the algae blooms, the depletion of fish biodiversity and ecosystem degradation in the Jiaozhou Bay in recent years (Li et al., 2008; Lu et al., 2017; Yuan et al., 2016).

2.2 Sampling

Field expeditions, aboard the R/V *Kexue 3*, were carried out in the Jiaozhou Bay during June 2015. Four gravity cores were retrieved from the inner, mouth and outside of the bay, respectively (Fig. 1). Cores C3 and C4 were collected in the inner bay, with the water depths of 13 and 10 m, respectively, and consisted of clay silt. Cores C5 and C6 were sampled in the mouth and outside of the bay, with the water depths of 21 and 22 m, respectively. The sediment type of them was sandy silt. The core was sliced into 2 cm-thick segments and immediately placed in plastic zip lock bags with air being excluded. All samples were stored in the dark at -20°C in the laboratory for further analysis.

2.3 Bulk parameters (TOC, TN, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and porosity)

Samples for TOC, TN, and stable carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) isotopes of organic matter were measured at Third Institute of Oceanography, State Oceanic Administration, China. TOC and TN of sediment samples were analyzed using a Vario El-III elemental analyzer, following the method of Hu et al. (2014). Briefly, sediment samples were ground in an agate mortar after being dried, and then soaked in $1\text{ mol/dm}^3\text{ HCl}$ at the room temperature for 1 d to remove carbonates. After rinsing with Milli-Q water several times and drying in an oven at 60°C , the carbonate-free samples were measured for the TOC and TN concentrations. Replicate analysis of well-mixed samples provided a standard deviation of 0.01% for the TOC and TN concentrations ($n=5$). The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ analysis was performed on inorganic carbon-free sediments, using a Thermo DeltaPlus XL continuous flow mass spectrometer. The values of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ were expressed in a standard delta notation relative to Pee Dee Belemnite (PDB) and air, respectively. The average standard deviations of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ based on the replicated analysis were 0.1‰ ($n=5$). Porosity was determined by a mass difference before and after the drying of the sediments.

2.4 Sediment ages and burial flux of organic carbon

Sediments of Core C4 were dated using ^{210}Pb radionuclide. ^{210}Pb was measured via its grandparent ^{210}Po . The method was described in detail in Huh et al. (1997). In brief, 0.5 g of sedi-

ments for each aliquot was digested with concentrated HNO_3 after adding an accurate ^{209}Po spike as yield monitor. Both ^{210}Po and ^{209}Po in solution were finally auto-deposited on a silver-plate under specific conditions. The activities of Polonium isotopes (i.e., ^{210}Po and ^{209}Po) were counted using α -spectrometry (ORTEC). The sedimentation rate of Core C4 was calculated by excess ^{210}Pb with a widely used constant initial concentration (CIC) model (Dai et al., 2007a). Considering locations of sediment Cores C3 (36.113°N , 120.235°E), C5 (36.020°N , 120.272°E) and C6 (35.978°N , 120.452°E) were close to the sampling stations of J37 (36.123°N , 120.222°E), D4 (36.019°N , 120.259°E) and J94 (35.977°N , 120.452°E) collected in the Jiaozhou Bay during 2003 in the published studies of our group (Qi, 2005; Dai et al., 2007a; Li et al., 2011). The sedimentation rate had been constant during these several years owing to the stable sedimentary environment in the Jiaozhou Bay (Liu et al., 2010a). Therefore, the sedimentation rates of J37, D4 and J94 in previous studies were employed in this study. The burial flux of organic carbon was calculated according to Li et al. (2008).

2.5 Statistical analyses

All statistical tests were performed using SPSS 16.0 software. Before each statistical analysis, Shapiro and Bartlett tests were performed to test the data set normality and homoscedasticity, respectively. One-way ANOVA was applied on data sets following normal distributions and showing homogeneous variances. The one-way ANOVA was used to determine the differences of the parameters between two stations. For all statistical tests, a probability (P) of 0.05 was used to show the statistical significance.

3 Results and discussion

3.1 Sedimentation rate

The ^{210}Pb and excess ^{210}Pb activities were plotted on a log scale against depth (Fig. 2). The excess ^{210}Pb values show a negative trend with an increasing depth for Cores C3 ($r=-0.82$, $P<0.05$), C4 ($r=-0.82$, $P<0.001$) and C6 ($r=-0.99$, $P<0.01$). While the excess ^{210}Pb values exhibit a fluctuating trend with the increasing depth for Core C5. According to the CIC model, the average sedimentation rate of Core C4 was calculated to 0.28 cm/a. The sedimentation rate from previous investigations was 0.64 cm/a for Core C3, 1.63 cm/a in the above 38 cm and 3.96 cm/a below 38 cm for Core C5, and 0.45 cm/a for Core C6, respectively. According to the sedimentation rates, the chronologies for Cores C3, C4, C5

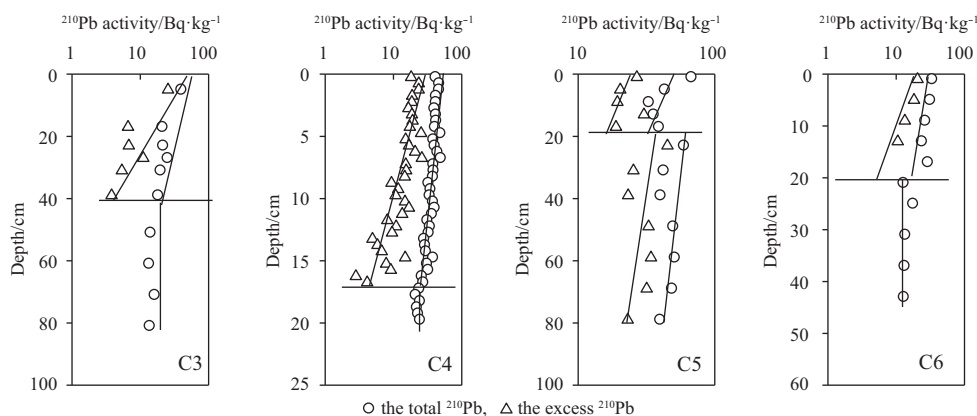


Fig. 2. ^{210}Pb activity in the sediment core of the Jiaozhou Bay.

and C6 were ca. 1923–2015, 1726–2015, 1980–2015 and 1777–2015, respectively.

The sedimentation rates (0.28 cm/a) of Core C4 were relatively lower than those (0.64 cm/a) of Core C3 due to their different geographic positions. Core C4 occupies the cross of two main channels, namely Cangkou Channel and Hongdao Channel, where a current velocity is high during a tidal fluctuation. Fine sediments were difficult to deposit under the high current velocity (Qi, 2005). Compared with Cores C3, C4 and C6, Core C5 shows much higher sedimentation rates (1.63 cm/a above 38 cm and 3.96 cm/a below 38 cm). The higher sedimentation rates in Core C5 were related to large amounts of terrigenous material input and serious coastal erosion (Qi, 2005; Wang et al., 2006). The sedimentary environment changed in this area with the variation of terrigenous material input. The sedimentation rate decreased by 59% in recent decades owing to the decline of terrigenous material input (Qi, 2005).

3.2 Geochemical parameters in sediments of the Jiaozhou Bay

TOC and TN contents range from 0.14% to 0.41% and 0.02% to 0.05% in core C3, respectively. Both TOC and TN contents have displayed an increasing trend with time since 1923, with $r=0.92$ ($P<0.01$) for TOC and $r=0.91$ ($P<0.01$) for TN, respectively, especially in recent 15 a (upper 10 cm) (Figs 3a1 and a3), implying a heavy eutrophication in this site. The burial flux of TOC has ranged from 3.63 to 6.77 mmol/(m²-d), and displayed an increasing trend with time since 1923 ($r=0.91$, $P<0.01$) (Fig. 3a2). The TOC/TN ratios varied from 8.2 to 11.5, displaying an increasing trend with time since 1923 ($r=0.72$, $P<0.01$) (Fig. 3a4). $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ ranged from -22.2‰ to -20.4‰ and from 9.7‰ to 15.7‰ , respectively. Both of them have presented a decreasing trend with time since 1923 ($r=0.70$, $P<0.01$) (Figs 3a5 and a6).

Core C4 is also located in the inner bay and close to the eastern coast of the Jiaozhou Bay. TOC and TN contents in core C4 ranged from 0.34% to 0.74% and 0.03% to 0.05%, respectively, which are significantly higher than those in Core C3 (One-way ANOVA, $P<0.05$). Generally, a grain size is a major factor in controlling the spatial variations of TOC and TN (Gao et al., 2012). In this study, the porosity data were used to compare the differences of the grain size between these two cores, considering the fine-grained sediments tending to have higher porosities than coarser sediments (Buckingham, 2005). The results indicate that there is no significant difference in the porosity between Cores C3 and C4 (One-way ANOVA, $P>0.05$), implying that the grain size is not the main factor in determining organic matter contents in the Jiaozhou Bay. Besides, TOC/TN ratio of Core C3 (8.2–11.5) was significantly lower than that (11.4–16.4) in core C4 (One-way ANOVA, $P<0.05$). Babbín et al. (2014) suggested that organic matter could easily decompose under the relatively low TOC/TN ratio. The TOC contents in Core C4 vary with time before 1919 ($r=-0.32$, $P>0.05$) and then have presented an increasing trend since 1919 ($r=0.76$, $P<0.05$) (Fig. 3b1). The increasing TOC from 1748 to 1812 might be related to the increasing terrigenous input, which was proved by the decreased $\delta^{13}\text{C}$. The burial flux of TOC range from 2.39 to 5.75 mmol/(m²-d), and displayed an increasing trend with time since 1919 ($r=0.79$, $P<0.05$) (Fig. 3b2). TN presents a decreasing trend with time before 1919 ($r=-0.74$, $P<0.01$), but an increasing trend since that time ($r=0.79$, $P<0.05$) (Fig. 3b3). The TOC/TN ratio varies with time before 1919, but a decreasing trend has occurred since 1919 ($r=-0.88$, $P<0.01$) (Fig. 3b4). The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ range from -22.8‰ to -21.8‰ and from 7.2‰ to 17.6‰ , respectively. The $\delta^{13}\text{C}$ presents two decreasing trends with time before 1919 ($r=-0.72$, $P<0.05$)

and since 1983 ($r=-0.93$, $P<0.05$). An increasing trend of $\delta^{13}\text{C}$ occurred from 1919 to 1962 ($r=0.99$, $P<0.05$), suggesting the variation of terrigenous organic matter (Fig. 3b5). Moreover, the decreased $\delta^{13}\text{C}$ might be related to the wide growth of Core C3 plant with $\delta^{13}\text{C}$ of -26‰ to -27‰ (Wang et al., 2013) in northern China during this period. There were two increasing trends of $\delta^{15}\text{N}$ with time before 1919 ($r=0.79$, $P<0.01$) and since 1983 ($r=0.91$, $P<0.05$) (Fig. 3b6).

Station C5 is located in the mouth of the Jiaozhou Bay, which is more adjacent to Huangdao and Qingdao Cities than other three stations (Fig. 1). The TOC and TN contents are 0.30% to 0.82% and 0.03% to 0.07%, respectively. The relatively high TOC and TN contents might be related to the high sedimentation rate at this station, which is beneficial to the preservation of organic matter (Ingall and van Cappellen, 1990). Both TOC and TN contents vary with time before 2003, but an increasing trend occurred since 2003 ($r=0.74$, $P<0.05$ for TOC and $r=0.80$, $P<0.05$ for TN) (Figs 3c1 and c3). The burial flux of TOC ranges from 14.74 to 82.12 mmol/(m²-d), and displays a sharp decrease after 1992 (Fig. 3c2). The TOC/TN ratio ranges from 10.3 to 14.4, and has presented a decreasing trend with time since the 1980s ($r=-0.50$, $P<0.05$) (Fig. 3c4). The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values range from -22.2‰ to -18.6‰ and from 6.6‰ to 13.0‰ , respectively. The $\delta^{13}\text{C}$ presents a decreasing trend with time since the 1980s ($r=-0.72$, $P<0.01$), whereas the $\delta^{15}\text{N}$ presents an increasing trend with time after the 1980s ($r=0.56$, $P<0.05$) (Figs 3c5 and c6). The decreased $\delta^{13}\text{C}$ and increased $\delta^{15}\text{N}$ imply the intensive terrigenous input in this site. The high TN contents and a significant correlation between $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ ($r=-0.66$, $P<0.05$; Table 1) also indicated the high nitrogen loadings at this station.

Compared with Cores C3, C4 and C5, the lower and less variable TOC (0.18%–0.30%) and TN (0.02%–0.03%) contents were observed in core C6, which probably resulted from the little riverine input. Sediments in this area came from the Jiaozhou Bay, which were carried by the tidal and coastal current (Qi, 2005). The TOC and TN contents varied with the time before and since 1916 (Figs 3d1 and d3). The decrease of TOC and TN contents since 1916 might be related to the dilution by increased terrigenous material. It could be proved by the changed $\delta^{13}\text{C}$ signal (ranging from -22.6‰ to -21.3‰). Prior to 1916, $\delta^{13}\text{C}$ varies with time, but a decreasing trend have occurred since 1916 ($r=-0.72$, $P<0.05$) (Fig. 3d5). The burial flux of TOC ranges from 2.76–4.64 mmol/(m²-d), and displays a similar trend as TOC (Fig. 3d2). The TOC/TN ratio ranges between 9.6 and 11.9, which varies with time before 1942 and has decreased since 1942 ($r=-0.90$, $P<0.01$) (Fig. 3d4). The $\delta^{15}\text{N}$ ranges from 4.8‰ to 16.8‰ , which varies with time before 1916 and has decreased since 1916 ($r=-0.82$, $P<0.01$) (Fig. 3d6). The $\delta^{15}\text{N}$ shows higher values in Core C6 before 1950, implying a clear nitrogen input during that period. The high nitrogen input promoted the increase of productivity and consequently induced the high $\delta^{15}\text{N}$ before 1950. Teranes and Bernasconi (2000) suggest that the increasing productivity is likely to induce the decrease of surface dissolved inorganic nitrogen and the increase of $\delta^{15}\text{N}$ values. The decrease of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ since 1916 has indicated that the outside bay is suffering from an increasing influence from the terrigenous input.

3.3 Sources and composition of organic matter in sediments of the Jiaozhou Bay

The TOC/TN ratio and $\delta^{13}\text{C}$ have been widely used to distinguish marine sources and terrigenous sources of organic matter (Hu et al., 2013; Ke et al., 2017). The TOC/TN ratios of organic matter >20 and between 4 and 10 were from terrigenous and

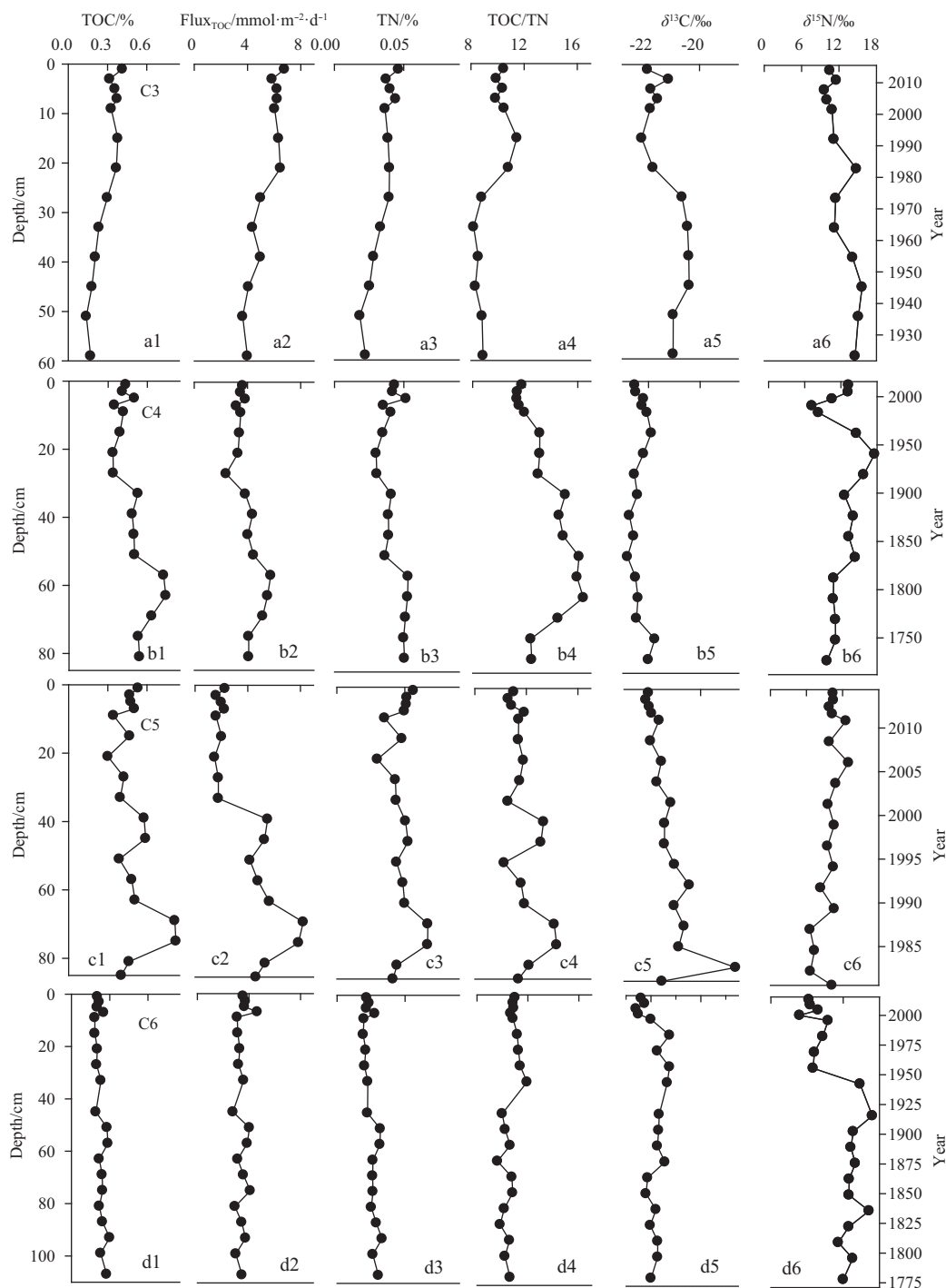


Fig. 3. The temporal variations of TOC contents, burial fluxes of TOC (Flux_{TOC}), TN contents, TOC/TN ratio, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in sediment cores of the Jiaozhou Bay. Note that the burial fluxes of TOC in Core C5 should be $\times 10$.

marine sources, respectively (Meyers, 1994; Li et al., 2008). The $\delta^{13}\text{C}$ for terrigenous and marine sources is -26‰ and -19‰ , respectively (Yang et al., 2011). Significant correlations exist between TOC and TN contents in four cores (Table 1), indicating that the influence of the sorption of inorganic nitrogen on organic matter was minimal (Hu et al., 2013; Li et al., 2015a, b). The significant correlations between the TOC/TN ratio and $\delta^{13}\text{C}$ in three studied cores ($P < 0.01$ for Core C3; $P < 0.05$ for Cores C4 and C6) indicate that these two parameters can be used to identify the sources of organic matter in Cores C3, C4 and C6. Organic mat-

ter in the Jiaozhou Bay exhibits a range of TOC/TN ratio (8.2–16.4) and $\delta^{13}\text{C}$ values (-18.6‰ to -22.8‰) indicative of mixed source inputs from marine and terrigenous materials. It was noteworthy that the single terrigenous input could also result in the corresponding $\delta^{13}\text{C}$ (-18.6‰ to -22.8‰). For example, the mixture of terrigenous C3 (-26‰ to -27‰) and C4 (-9‰ to -16‰) plants could result in a $\delta^{13}\text{C}$ value of -22‰ (Wang et al., 2013). However, although corn is the primary C4 plant in northern China, the influence of terrigenous C4 plant on organic matter could be neglected for its higher TOC/TN ratio (60–200) com-

Table 1. Pearson correlations between TOC content, TN content, TOC/TN ratio, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of samples in the four sediment cores

Factor	Core	TN	TOC/TN	$\delta^{13}\text{C}$	$\delta^{15}\text{N}$
TOC	C3	0.960**	0.831**	-0.799**	-0.732**
	C4	0.833**	0.668**	-	-
	C5	0.942**	0.817**	-	-0.707**
	C6	0.957**	-	-	-
TN	C3	-	0.644*	-0.615*	-0.788**
	C4	-	-	-	-0.573
	C5	-	0.582*	-	-0.700**
	C6	-	-0.502*	-	-
TOC/TN	C3	-	-	-0.962**	-
	C4	-	-	-0.510*	-
	C5	-	-	-	-0.514*
	C6	-	-	-0.538*	-0.481*
$\delta^{13}\text{C}$	C3	-	-	-	-
	C4	-	-	-	-
	C5	-	-	-	-0.663**
	C6	-	-	-	-

Note: * The correlation is significant at the 0.05 level (2-tailed); ** the correlation is significant at the 0.01 level (2-tailed).

pared with organic matter (TOC/TN ratio being less than 17) in the Jiaozhou Bay. Therefore, it was reasonable that organic matter in the Jiaozhou Bay was a mixture of marine and terrigenous origins, which was consistent with previous studies of the Jiaozhou Bay (Li et al., 2008; Yang et al., 2011).

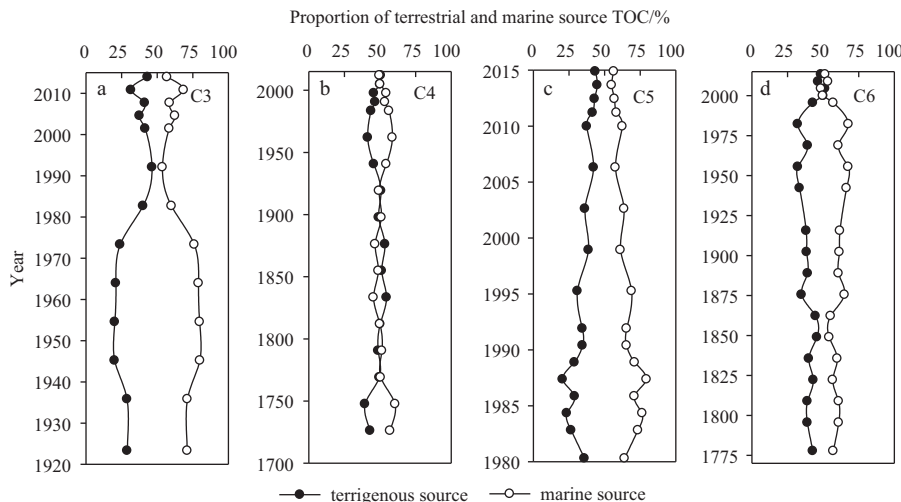
Various end-member mixing models have been successfully used to study the variation of different sources of organic matter inputs in aquatic systems (Yang et al., 2011; Li et al., 2015a, b). Here, we employed a two end-member mixing model using $\delta^{13}\text{C}$ as source markers to distinguish the relative contribution of terrigenous and marine organic carbon in the Jiaozhou Bay, which assumed discrete $\delta^{13}\text{C}$ values for terrigenous and marine end-member carbon (Liu et al., 2015). Another important assumption here is that end-member values have not changed significantly over the period of time examined in this study. The calculation of terrigenous and marine source (f_{T} and f_{M}) organic carbon contribution (Yang et al., 2011) was gained based on the following equations:

$$f_{\text{T}} = \frac{\delta^{13}\text{C}_{\text{M}} - \delta^{13}\text{C}_{\text{S}}}{\delta^{13}\text{C}_{\text{M}} - \delta^{13}\text{C}_{\text{T}}}$$

$$f_{\text{M}} = 1 - f_{\text{T}}$$

On the basis of a previous study of the Jiaozhou Bay (Yang et al., 2011), the end-members values of $\delta^{13}\text{C}$ for terrigenous and marine source ($\delta^{13}\text{C}_{\text{T}}$ and $\delta^{13}\text{C}_{\text{M}}$) were -26‰ and -19‰ , respectively. $\delta^{13}\text{C}_{\text{S}}$ was the values in the core samples.

The results of the two end-member model show that marine organic carbon is the dominant component of sedimentary TOC in four cores, and vary from 54% to 80%, 45% to 61%, 55% to 79% and 49% to 68% in Cores C3, C4, C5 and C6, respectively. Generally, the relative contributions from different sources were generally stable before the 1960s in the inner bay. After the 1960s, the contribution of terrigenous TOC has showed an increasing trend in Cores C3 and C4 since 1964 ($r=0.67$, $P<0.05$) and 1962 ($r=0.88$, $P<0.05$), respectively (Figs 4a and b). The relative contributions from marine TOC decreased (Figs 4a and b). The terrigenous TOC has presented an increasing trend in Cores C5 and C6 since 2003 ($r=0.76$, $P<0.05$) and 1955 ($r=0.71$, $P<0.05$), respectively (Figs 4c and d). The increasing TOC/TN ratio and decreasing $\delta^{13}\text{C}$ in the same period also imply an increase in the input of terrigenous organic matter (Fig. 3). Moreover, depleted sedimentary $\delta^{13}\text{C}$ corresponds to higher TOC contents, and a clear negative rela-

**Fig. 4.** Historical variations of proportion of terrigenous and marine source TOC content.

relationship is observed in Core C3 ($r=-0.799$, $P<0.01$). In a semi-enclosed system, the increased terrigenous input related to the intensive anthropogenic activities was the main contributor to the elevated sedimentary TOC contents.

The $\delta^{13}\text{C}$ composition of organic matter in marine ecosystems was controlled by several factors, including the source of organic matter, changes in community structure of phytoplankton and productivity, and the input of dissolved inorganic carbon into the ocean (Meyers, 1994; Yu et al., 2012; Finkenzindler et al., 2015). Our results indicate a significant seaward increase in $\delta^{13}\text{C}$ when comparing $\delta^{13}\text{C}$ at the inshore station (Core C4) with that in the offshore stations (Cores C3, C5 and C6) (One-Way ANOVA, $P<0.01$). According to the previous study, the seaward increase in $\delta^{13}\text{C}$ of marine sediment might be related to the seaward increase in marine photosynthetic organic matter relative to terrigenous organic matter (Gao et al., 2012). However, there was a significant seaward decrease in $\delta^{13}\text{C}$ when $\delta^{13}\text{C}$ at Stas C3 and C5 was compared with that in C6. The high $\delta^{13}\text{C}$ at Stas C3 and C5 might have resulted from CO_2 limitation due to eutrophication and high primary production of phytoplankton (Voß and Struck, 1997; Ke et al., 2017). In the inner area of the Jiaozhou Bay, we did not find a typical riverine $\delta^{13}\text{C}$ signal (i.e., depleted $\delta^{13}\text{C}$ with value being less than 24.3‰). Actually, the Jiaozhou Bay is a typical eutrophic bay, where blooms frequently occur (Yuan et al., 2016), which can increase $\delta^{13}\text{C}$ (Ke et al., 2017). Moreover, it was reasonable that the riverine TOC was partly diluted by the in situ produced TOC (Zhu et al., 2014). And hence there was no typical depleted $\delta^{13}\text{C}$ in the inner bay. In addition, the surface partial pressure of carbon dioxide in the Jiaozhou Bay was below atmospheric partial pressure of carbon dioxide (Zhang et al., 2012), which indicated that the input of watershed respiration products had no effect on $\delta^{13}\text{C}$ of dissolved inorganic carbon into the Jiaozhou Bay (Finkenzindler et al., 2015). Furthermore, the community structure of phytoplankton has changed obviously in the Jiaozhou Bay since 1954 (Wu et al., 2005), which can also influence the $\delta^{13}\text{C}$ value (Yu et al., 2012).

The $\delta^{15}\text{N}$ variation could reflect the change of productivity, the source of organic matter and the isotopic composition of the nitrogen input into the sea water (Yang et al., 2011; Yu et al., 2012; Wang et al., 2013). Our results indicate that $\delta^{15}\text{N}$ in the inner bay (Cores C3 and C4) was significantly higher than that in the bay mouth (Core C5) (One-Way ANOVA, $P<0.01$). The lower $\delta^{15}\text{N}$ in the bay mouth might be explained by a lower input of $\delta^{15}\text{N}$ -enriched sewage and organism manure (Ruiz-Fernández et al., 2002; Cao et al., 2015; Ke et al., 2017). In addition, there was no significant correlation between TOC/TN ratio and $\delta^{13}\text{C}$ in Core C5, whereas significant correlations were observed between the TOC/TN ratio and $\delta^{15}\text{N}$, and between $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ ($P<0.05$) (Table 1). It was because the diagenesis or anthropogenic disturbances might modify the organic composition in this area (Teranes and Bernasconi, 2000; Gao et al., 2012; Yu et al., 2012; Li et al., 2015a, b). The anthropogenic disturbances might be a more probable reason, which would be further proved by the $\delta^{15}\text{N}$ data. More significantly enriched $\delta^{15}\text{N}$ in Cores C3, C4 and C5 than in C6 were observed after 1942 (One-Way ANOVA, $P<0.01$), which might be related to the increased input of $\delta^{15}\text{N}$ -depleted nitrogen fertilizers and ammonia in the industrial waste water or other factors.

The element and stable isotope composition of sediment samples in this study were summarized and compared with those of other marginal seas and bays (Fig. 5). The majority of sediment samples collected from these areas display intermediate TOC/TN ratios between 6 and 16 and relatively enriched $\delta^{13}\text{C}$ sig-

natures between -20.0‰ and -24.0‰ (Fig. 5), suggesting that organic matter may be originated from the mixture of various sources (Hu et al., 2016). The average TOC/TN ratio in the Jiaozhou Bay (11.48) was much higher than that in marginal seas, such as the Bohai Sea (8.33) (Liu et al., 2015), the Yellow Sea (7.99) (Hu et al., 2013) and the inner shelf of the East China Sea (7.14) (Li et al., 2015a; Hu et al., 2012) (Fig. 5). The TOC/TN ratio was also higher than that in those areas with obvious anthropogenic loadings, such as the Sishili Bay (9.36) (Wang et al., 2013) and the Gulf of Mexico (7.13) (Goñi et al., 1998), owing to the increasing TOC contents in the Jiaozhou Bay (Fig. 3). However, it should be mentioned that although the discharge of sediments from small rivers around the Jiaozhou Bay was relatively lower than those large rivers (e.g., the Changjiang River, the Huanghe River), the observed $\delta^{13}\text{C}$ values in this area were more in line with a partly marine signature and comparable with those of other marginal seas and bays summarized in Fig. 5.

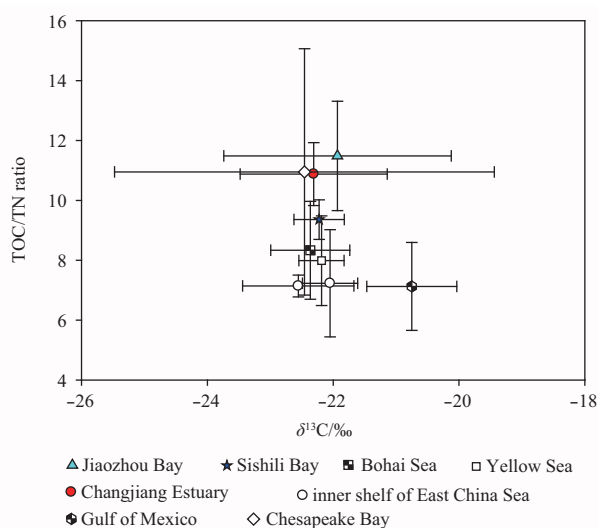


Fig. 5. The TOC/TN ratio versus $\delta^{13}\text{C}$ of the sediments in the Jiaozhou Bay and the comparison with other marginal seas and bays around the world such as the Sishili Bay (Wang et al., 2013), the Bohai Sea (Liu et al., 2015), the Yellow Sea (Hu et al., 2013), the Changjiang Estuary (Hu et al., 2012), the inner shelf of East China Sea (Li et al., 2015a; Hu et al., 2012), the Gulf of Mexico (Goñi et al., 1998), and the Chesapeake Bay (Zimmerman and Canuel, 2001).

3.4 Environmental responses to anthropogenic activities and climate changes in the Jiaozhou Bay

Previous studies indicated that the anthropogenic activities including fertilizer use, sewage discharge, shipment, mariculture and deforestation had an obvious influence on the distribution of TOC, TN and its isotopic composition (Shen et al., 2005; Wang et al., 2013). With the reform and opening up of China since 1978, various anthropogenic activities (e.g., shipment, mariculture, sewage discharge, ammonia discharge and fertilizer use) have been performed dramatically around the Jiaozhou Bay, resulting in an increase in population and gross domestic production (GDP) (Figs 6a–h). The increase of population, Qingdao Port throughput, fishery and mariculture brought large amounts of industrial, agricultural and domestic sewage into the Jiaozhou Bay (Figs 6a–h). Although the data of the sewage discharge were not available before 1999, we speculated that the sewage discharge

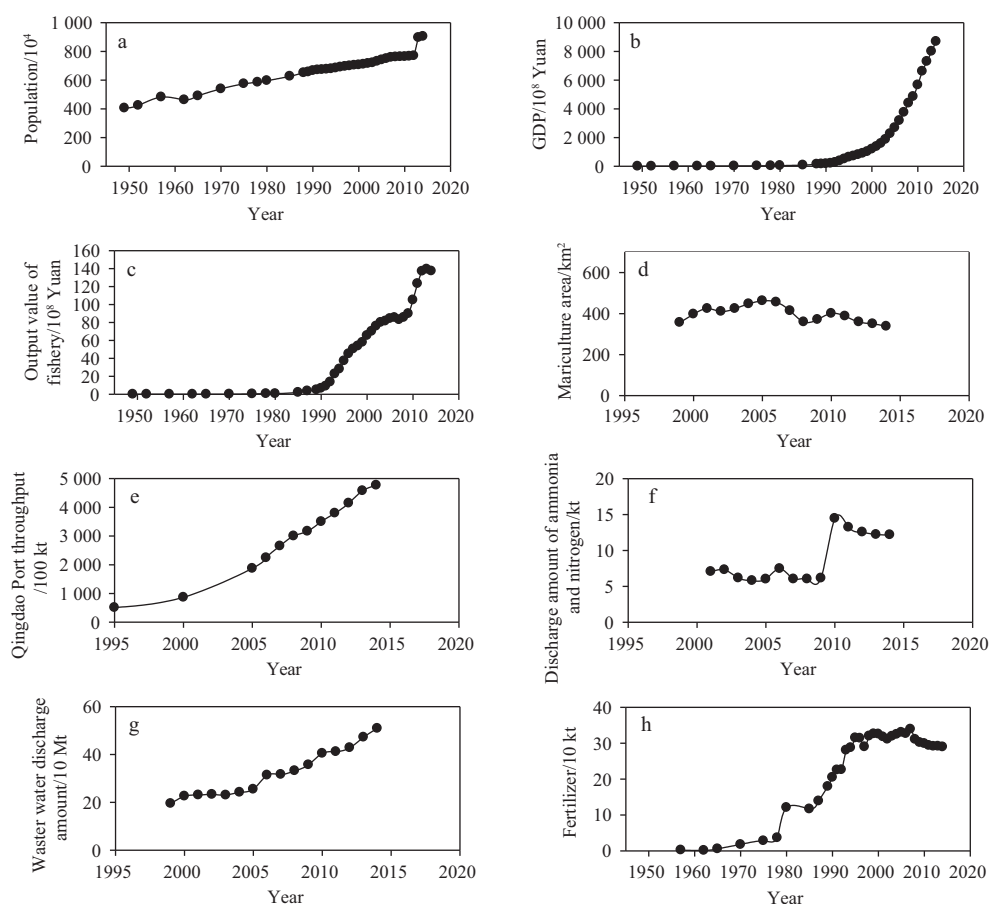


Fig. 6. Long-term variations of human activity factors in Qingdao, China (SSY, 2001–2015; QSY, 2001–2015).

increased significantly with population increase. Our data suggest that the sewage discharge in 2015 increases to be 2.6 times that in 1999 (Fig. 6g). The discharge of ammonia into the bay was about 15.0 kt during 2015 (Fig. 6f). Moreover, with the rapid development of agriculture and fishery, large amounts of fertilizers were used for fast growth of plants and animals. The application of nitrogen fertilizers in 2015 increases to be 152 times that in 1957 (Fig. 6h).

All of the above changes were recorded by the geochemical proxies in the Jiaozhou Bay. For example, TOC and TN contents have presented an increasing trend with time in Cores C3, C4 and C5 since 1923, 1919 and 2003, respectively, implying the Jiaozhou Bay has been suffering from a heavy eutrophication since that time. However, after a statistical analysis, it could be concluded that the increase of TOC and TN contents in Cores C3 and C4 was not significantly influenced by a single anthropogenic activity ($P > 0.05$). We speculated that the increase of TOC and TN contents in Cores C3 and C4 was the result of combined impacts from various anthropogenic activities and climate changes. The correlation analysis ($r = 0.77$, $P < 0.05$) indicates that the increase of TOC contents in Core C5 is significantly influenced by the ammonia discharge. Moreover, a significant positive correlation ($r = 0.74$, $P < 0.05$) of terrigenous TOC with sewage discharge amount, ammonia discharge amount ($r = 0.80$, $P < 0.05$) and Qingdao Port throughput ($r = 0.77$, $P < 0.05$) was observed in this area, indicating that the increase of TOC contents should be related to these anthropogenic activities, while the increase of TN contents was significantly influenced by the ammonia discharge amount

($r = 0.78$, $P < 0.05$) and the sewage discharge amount ($r = 0.74$, $P < 0.05$). In addition, a significant positive correlation ($P < 0.01$) between TOC and TN and a negative correlation ($P < 0.01$) between TOC and $\delta^{15}\text{N}$ ($P < 0.01$) suggested that the increasing TOC content was induced, at least partly, by the acute nitrogen pollution in the inner bay and the mouth of the bay. Although the impact of the anthropogenic activities on sediments in the outside bay (Core C6) was not significant ($P > 0.05$), the sedimentary environment in this area has also changed since 1916. For example, the increase of terrigenous TOC content was significantly influenced by the increase of fertilizer utilization ($r = 0.74$, $P < 0.05$). Moreover, the impact of the anthropogenic activities on the burial flux of TOC was complex. For example, there was a significant positive correlation of the burial flux of TOC with fertilizer utilization in Core C3 ($r = 0.67$, $P < 0.05$) and a significant negative correlation of the burial flux of TOC with fertilizer utilization ($r = -0.89$, $P < 0.05$) in Core C5. However, the burial flux of TOC content in Cores C4 and C6 was not significantly influenced by a single anthropogenic activity. That was because the burial flux of TOC was mainly influenced by the TOC concentration, the sedimentation rate and the sediment porosity (Li et al., 2008).

Similarly, the anthropogenic activities also exerted a significant influence on the isotope composition of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$. For example, fertilizer utilization produced a significant influence on $\delta^{13}\text{C}$. The statistical analysis indicates that there is a significant negative correlation of $\delta^{13}\text{C}$ with fertilizer utilization in Cores C3 ($r = -0.66$, $P < 0.05$), C4 ($r = -0.90$, $P < 0.05$), C5 ($r = -0.65$, $P < 0.05$) and C6 ($r = -0.85$, $P < 0.05$). That is because with the increase of fertil-

izer utilization, the terrigenous TOC content increased and consequently results in the low $\delta^{13}\text{C}$ value. In addition, the $\delta^{13}\text{C}$ in Core C5 is significantly influenced by sewage discharge amount ($r=-0.78$, $P<0.05$), ammonia discharge amount ($r=-0.76$, $P<0.05$) and Qingdao Port throughput ($r=-0.87$, $P<0.05$). That is because this area is influenced by the intensified anthropogenic activities from Qingdao City and Huangdao City. Moreover, the Qingdao Port is also located in this area. Previous studies indicate that $\delta^{15}\text{N}$ can be influenced by the sewage discharge and fertilizer utilization (Ruiz-Fernández et al., 2002; Zhu et al., 2014). However, after the statistical analysis we found that the variation of $\delta^{15}\text{N}$ in the Jiaozhou Bay was not significantly influenced by the sewage discharge and nitrogen fertilizer utilization ($P>0.05$). That is not to say the sewage discharge and nitrogen fertilizer utilization have no influence on the $\delta^{15}\text{N}$ variation. The increase of the $\delta^{15}\text{N}$ values with time in Cores C4 and C5 since the 1980s might be a result of various anthropogenic activities. The high $\delta^{15}\text{N}$ (ranging from 9.7‰ to 17.6‰) in Core C4 during 1726–1941 might be related to the discharge of sewage (10‰ to 20‰) and the human or animal manure (7‰ to 25‰) (Ruiz-Fernández et al., 2002; Cao et al., 2015). However, $\delta^{15}\text{N}$ in Cores C3 and C6 has decreased since 1923 and 1916, respectively, which is because the less effects of the sewage discharge on Cores C3 and C6 than Cores C4 and C5.

Climate changes can be better recorded by geochemical proxies including TOC, TN, TOC/TN ratios and $\delta^{13}\text{C}$ (Shen et al., 2005, 2006; Li et al., 2015a; Rao et al., 2017). In this study, as the most important climatic factor, rainfall was used for the discussion of the impact of climate changes on environment changes. Rainfall in Qingdao City decreased concurrently from 792 mm during 1950–1976 to 642 mm during 1977–2015 (Fig. 7). Rao et al. (2017) indicate that there is a significant negative correlation between rainfall and the $\delta^{13}\text{C}$ value. However, the significant negative correlation of $\delta^{13}\text{C}$ with rainfall was only observed in Core C5 ($r=-0.48$, $P<0.05$). That might be because of the dam construction having weakened the influence of rainfall on the inner bay. In addition, the correlation analysis indicates that there is no significant correlation of TOC content, burial flux of TOC, terrigenous TOC content, TN content and $\delta^{15}\text{N}$ with rainfall ($P>0.05$). The most likely reasons for weak statistical linkages between our proxies and rainfall are the multitude of other anthropogenic changes (e.g., river discharge, dam construction) that have occurred in the Jiaozhou Bay. Moreover, sectioning precision and possible errors of core chronology also contributed to these weak statistical linkages (Li et al., 2015a).

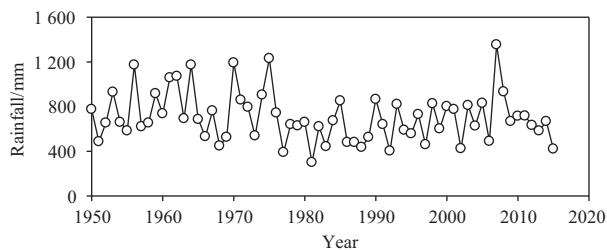


Fig. 7. Changes of rainfall in the Jiaozhou Bay for the last 65 a. The data of rainfall from 1950 to 2001 were cited from Liu Zhu et al. (2010b) and the data from 2002 to 2015 were cited from QSY (2001–2015).

4 Conclusions

Sedimentary organic carbon and nitrogen including isotopes

are effective for historical trend reconstruction. In this study, TOC, TN and their isotope composition in four sediment cores were used to reflect the historical environmental changes in the Jiaozhou Bay on a centennial time scale. The increase of TOC and TN contents in Cores C3 and C4 since the 1920s was the result of combined impacts from various anthropogenic activities and climate changes, which indicated the probable eutrophication in the inner bay. The $\delta^{13}\text{C}$ was significantly influenced by the fertilizer utilization. The $\delta^{15}\text{N}$ might be influenced by sewage discharge and fertilizer utilization. In addition, the influence of rainfall on the isotopic composition of carbon and nitrogen in the inner bay was little. The increase of TOC and TN content in Core C5 since the 2000s was the result of ammonia and sewage discharge, which indicated the probable eutrophication in the mouth of the bay. The $\delta^{13}\text{C}$ in Core C5 was significantly influenced by the fertilizer utilization, ammonia and sewage discharge, the Qingdao Port throughput and rainfall. The $\delta^{15}\text{N}$ variation in Core C5 might be the result of various anthropogenic activities. The variation of terrigenous input in Core C6 suggested that the environments of the outside bay also have changed since 1916. The $\delta^{13}\text{C}$ in Core C6 was significantly influenced by the fertilizer utilization, while the $\delta^{15}\text{N}$ might be related to the sewage discharge or other anthropogenic activities. The source analysis indicates that organic matter of the Jiaozhou Bay is a mixture of terrigenous and marine sources. The results of two end-member $\delta^{13}\text{C}$ isotopic mixing model indicate the organic matter is mainly from the marine source in the Jiaozhou Bay. The increased terrigenous TOC content illustrated an increased terrigenous loading and was associated to anthropogenic activities. As mentioned above, the environmental changes of the Jiaozhou Bay are the complex results of both anthropogenic activities and climate changes. There is much work to do to quantitatively discriminate the impacts from anthropogenic activities and climate changes in the near future.

Acknowledgements

The authors thank Chen Min for providing the sediment rate data of Core C4. They also thank the colleagues in Key Laboratory of Marine Ecology and Environmental Sciences of Institute of Oceanology for their assistance in sample collection.

References

- Babbitt A R, Keil R G, Devol A H, et al. 2014. Organic matter stoichiometry, flux, and oxygen control nitrogen loss in the ocean. *Science*, 344(6182): 406–408
- Berner R A. 1982. Burial of organic carbon and pyrite sulfur in the modern ocean: its geochemical and environmental significance. *American Journal of Science*, 282(4): 451–473
- Bianchi T S, Allison M A. 2009. Large-river delta-front estuaries as natural “recorders” of global environmental change. *Proceedings of the National Academy of Sciences of the United States of America*, 106(20): 8085–8092
- Buckingham M J. 2005. Compressional and shear wave properties of marine sediments: comparisons between theory and data. *The Journal of the Acoustical Society of America*, 117(1): 137–152
- Cao Wenzhi, Huang Zheng, Zhai Weidong, et al. 2015. Isotopic evidence on multiple sources of nitrogen in the northern Jiulong River, Southeast China. *Estuarine, Coastal and Shelf Science*, 163: 37–43
- Cohen R A, Fong P. 2005. Experimental evidence supports the use of $\delta^{15}\text{N}$ content of the opportunistic green macroalga *Enteromorpha intestinalis* (chlorophyta) to determine nitrogen sources to estuaries. *Journal of Phycology*, 41(2): 287–293
- Dai Jicui, Song Jinming, Li Xuegang, et al. 2007a. Environmental changes reflected by sedimentary geochemistry in recent hundred years of Jiaozhou Bay, North China. *Environmental Pollution*, 145(3): 656–667

- Dai Jicui, Song Jinming, Li Xuegang, et al. 2007b. Geochemical records of phosphorus in Jiaozhou Bay sediments-Implications for environmental changes in recent hundred years. *Acta Oceanologica Sinica*, 26(4): 132–147
- Finkenbinder M S, Abbott M B, Finney B P, et al. 2015. A multi-proxy reconstruction of environmental change spanning the last 37000 years from Burial Lake, Arctic Alaska. *Quaternary Science Reviews*, 126: 227–241
- Gao Xuelu, Yang Yuwei, Wang Chuanyuan. 2012. Geochemistry of organic carbon and nitrogen in surface sediments of coastal Bohai Bay inferred from their ratios and stable isotopic signatures. *Marine Pollution Bulletin*, 64(6): 1148–1155
- Goñi M A, Ruttnerberg K C, Eglinton T I. 1998. A reassessment of the sources and importance of land-derived organic matter in surface sediments from the Gulf of Mexico. *Geochimica et Cosmochimica Acta*, 62(18): 3055–3075
- Henderson A C G, Holmes J A. 2009. Palaeolimnological evidence for environmental change over the past millennium from Lake Qinghai sediments: a review and future research prospective. *Quaternary International*, 194(1–2): 134–147
- Hodell D A, Schelske C L. 1998. Production, sedimentation, and isotopic composition of organic matter in Lake Ontario. *Limnology and Oceanography*, 43(2): 200–214
- Hu Bangqi, Li Jun, Zhao Jingtao, et al. 2014. Late Holocene elemental and isotopic carbon and nitrogen records from the East China Sea inner shelf: implications for monsoon and upwelling. *Marine Chemistry*, 162: 60–70
- Hu Limin, Shi Xuefa, Bai Yazhi, et al. 2016. Recent organic carbon sequestration in the shelf sediments of the Bohai Sea and Yellow Sea, China. *Journal of Marine Systems*, 155: 50–58
- Hu Limin, Shi Xuefa, Guo Zhigang, et al. 2013. Sources, dispersal and preservation of sedimentary organic matter in the Yellow Sea: the importance of depositional hydrodynamic forcing. *Marine Geology*, 335: 52–63
- Hu Limin, Shi Xuefa, Yu Zhigang, et al. 2012. Distribution of sedimentary organic matter in estuarine-inner shelf regions of the East China Sea: implications for hydrodynamic forces and anthropogenic impact. *Marine Chemistry*, 142–144: 29–40
- Huh C A, Piasias N G, Kelley J M, et al. 1997. Natural radionuclides and plutonium in sediments from the western Arctic Ocean: sedimentation rates and pathways of radionuclides. *Deep-Sea Research: Part II. Topical Studies in Oceanography*, 44(8): 1725–1743
- Ingall E D, van Cappellen P. 1990. Relation between sedimentation rate and burial of organic phosphorus and organic carbon in marine sediments. *Geochimica et Cosmochimica Acta*, 54(2): 373–386
- Ke Zhixin, Tan Yehui, Huang Liangmin, et al. 2017. Spatial distributions of $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and C/N ratios in suspended particulate organic matter of a bay under serious anthropogenic influences: Daya Bay, China. *Marine Pollution Bulletin*, 114(1): 183–191
- Li Fengye, Li Xuegang, Qi Jun, et al. 2011. Accumulation of heavy metals in the core sediments from the Jiaozhouwan Bay during last hundred years and its environmental significance. *Journal of Marine Sciences (in Chinese)*, 29(2): 35–45
- Li Hongmei, Tang Hongjie, Shi Xiaoyong, et al. 2014. Increased nutrient loads from the Changjiang (Yangtze) River have led to increased harmful algal blooms. *Harmful Algae*, 39: 92–101
- Li Dong, Yao Peng, Bianchi T S, et al. 2015a. Historical reconstruction of organic carbon inputs to the East China Sea inner shelf: implications for anthropogenic activities and regional climate variability. *The Holocene*, 25(12): 1869–1881
- Li Xuegang, Yuan Huamao, Li Ning, et al. 2008. Organic carbon source and burial during the past one hundred years in Jiaozhou Bay, North China. *Journal of Environmental Sciences*, 20(5): 551–557
- Li Junlong, Zheng Binghui, Hu Xupeng, et al. 2015b. Terrestrial input and nutrient change reflected by sediment records of the Changjiang River estuary in recent 80 years. *Acta Oceanologica Sinica*, 34(2): 27–35
- Lin Lei, Liu Zhe, Xie Lian, et al. 2015. Dynamics governing the response of tidal current along the mouth of Jiaozhou Bay to land reclamation. *Journal of Geophysical Research: Oceans*, 120(4): 2958–2972
- Liu Dongyan, Li Xin, Emeis K C, et al. 2015. Distribution and sources of organic matter in surface sediments of Bohai Sea near the Yellow River Estuary, China. *Estuarine, Coastal and Shelf Science*, 165: 128–136
- Liu Yunling, Wang Yaping, Gao Jianhua, et al. 2010a. Specific activity distribution patterns of lead-210 and sediment accumulation rates in the Jiaozhou Bay in Shandong Province, China. *Haiyang Xuebao (in Chinese)*, 32(1): 83–93
- Liu Sumei, Zhu Bingde, Zhang Jing, et al. 2010b. Environmental change in Jiaozhou Bay recorded by nutrient components in sediments. *Marine Pollution Bulletin*, 60(9): 1591–1599
- Lu Dongliang, Li Keqiang, Liang Shengkang, et al. 2017. A coastal three-dimensional water quality model of nitrogen in Jiaozhou Bay linking field experiments with modelling. *Marine Pollution Bulletin*, 114(1): 53–63
- Meyers P A. 1994. Preservation of elemental and isotopic source identification of sedimentary organic matter. *Chemical Geology*, 144(3–4): 289–302
- Qi Jun. 2005. Modern sedimentation rate and heavy metal accumulation in Jiaozhou Bay sediments (in Chinese) [dissertation]. Qingdao: Institute of Oceanology, Chinese Academy of Sciences
- QSY. 2001–2015. Qingdao Statistical Yearbook (in Chinese). <http://www.stats-qd.gov.cn/statsqd/Columns/tjyb.shtml?typeid=943&parentid=942&videos&jms230>
- Rao Zhiguo, Guo Wenkang, Cao Jiantao, et al. 2017. Relationship between the stable carbon isotopic composition of modern plants and surface soils and climate: a global review. *Earth Science Reviews*, 165: 110–119
- Ruiz-Fernández A C, Hillaire-Marcel C, Ghaleb B, et al. 2002. Recent sedimentary history of anthropogenic impacts on the Culiacan River Estuary, northwestern Mexico: geochemical evidence from organic matter and nutrients. *Environmental Pollution*, 118(3): 365–377
- Shen Ji, Wang Yong, Liu Xingqi, et al. 2006. A 16 ka climate record deduced from $\delta^{13}\text{C}$ and C/N ratio in Qinghai Lake sediments, northeastern Tibetan Plateau. *Chinese Journal of Oceanology and Limnology*, 24(2): 103–110
- Shen Ji, Yang Liyuan, Yang Xiangdong, et al. 2005. Lake sediment records on climate change and human activities since the Holocene in Erhai catchment, Yunnan Province, China. *Science in China Series D Earth Sciences*, 48(3): 353–363
- Shen Zhiliang. 2001. Historical changes in nutrient structure and its influences on phytoplankton composition in Jiaozhou Bay. *Estuarine, Coastal and Shelf Science*, 52: 211–224
- SSY. 2001–2015. Shandong statistical yearbook. http://xxgk.stats-sd.gov.cn/xxgk/jcms_files/jcms1/web1/site/col/col33/index.html
- Teranes J L, Bernasconi S M. 2000. The record of nitrate utilization and productivity limitation provided by $\delta^{15}\text{N}$ values in lake organic matter-A study of sediment trap and core sediments from Baldeggersee, Switzerland. *Limnology and Oceanography*, 45(4): 801–813
- Voß M, Struck U. 1997. Stable nitrogen and carbon isotopes as indicator of eutrophication of the Oder river (Baltic sea). *Marine Chemistry*, 59(1–2): 35–49
- Wang Gang. 2009. Study on the pollutant of point source and maritime fluxes flowing into Jiaozhou Bay (in Chinese)[dissertation]. Qingdao: Ocean University of China
- Wang Zhaohui, Guo Xin, Zhang Ke, et al. 2017. Environmental changes in Jiaozhou Bay of northern China during the past 90 years using metals and biogenic elements in sediments. *Journal of Environmental Sciences*, 53: 301–312, doi: 10.1016/j.jes.2016.06.002
- Wang Yujue, Liu Dongyan, Richard P, et al. 2013. A geochemical record of environmental changes in sediments from Sishili Bay, northern Yellow Sea, China: anthropogenic influence on organic matter sources and composition over the last 100 years. *Mar-*

- ine Pollution Bulletin, 77(1–2): 227–236
- Wang Wei, Zhang Shiqi, Ji Youliang. 2006. Evolution and controlling factor of the circum-Jiaozhou Bay coastline. *Marine Geology Letters (in Chinese)*, 22(9): 7–10
- Wu Yulin, Sun Song, Zhang Yongshan. 2005. Long-term change of environment and its influence on phytoplankton community structure in Jiaozhou Bay. *Oceanologia et Limnologia Sinica (in Chinese)*, 36(6): 487–498
- Yang Liyang, Wu Ying, Zhang Jing, et al. 2011. Burial of terrestrial and marine organic carbon in Jiaozhou Bay: different responses to urbanization. *Regional Environmental Change*, 11(3): 707–714
- Yu Yu, Song Jinming, Li Xuegang, et al. 2012. Indicative significance of biogenic elements to eco-environmental changes in waters. *Acta Ecologica Sinica (in Chinese)*, 32(5): 1623–1632
- Yuan Yuan, Song Dehai, Wu Wen, et al. 2016. The impact of anthropogenic activities on marine environment in Jiaozhou Bay, Qingdao, China: a review and a case study. *Regional Studies in Marine Science*, 8: 287–296
- Zhao Ke, Qiao Lulu, Shi Jinghao, et al. 2015. Evolution of sedimentary dynamic environment in the western Jiaozhou Bay, Qingdao, China in the last 30 years. *Estuarine, Coastal and Shelf Science*, 163: 244–253
- Zhang Longjun, Xue Ming, Liu Qizhen. 2012. Distribution and seasonal variation in the partial pressure of CO₂ during autumn and winter in Jiaozhou Bay, a region of high urbanization. *Marine Pollution Bulletin*, 64(1): 56–65
- Zhu Zhuoyi, Wu Ying, Zhang Jing, et al. 2014. Reconstruction of anthropogenic eutrophication in the region off the Changjiang Estuary and central Yellow Sea: from decades to centuries. *Continental Shelf Research*, 72: 152–162
- Zimmerman A R, Canuel E A. 2001. Bulk organic matter and lipid biomarker composition of Chesapeake Bay surficial sediments as indicators of environmental processes. *Estuarine, Coastal and Shelf Science*, 53(3): 319–341