Marine Pollution Bulletin 64 (2012) 1148–1155

Contents lists available at SciVerse ScienceDirect

Marine Pollution Bulletin

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

Geochemistry of organic carbon and nitrogen in surface sediments of coastal Bohai Bay inferred from their ratios and stable isotopic signatures

Xuelu Gao [a,b], Yuwei Yang [a,b,c], Chuanyuan Wang [a,b,*]

[a] Key Laboratory of Coastal Zone Environmental Processes, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, China
[b] Shandong Provincial Key Laboratory of Coastal Environmental Processes, Chinese Academy of Sciences, Yantai 264003, China
[c] Graduate University of Chinese Academy of Sciences, Beijing 100039, China

ARTICLE INFO

Keywords:
Sediment
TOC/TN
Stable isotope
Organic matter sources
Coastal Bohai Bay

ABSTRACT

Total organic carbon (TOC), total nitrogen (TN) and their $\delta^{13}C$ and $\delta^{15}N$ values were determined for 42 surface sediments from coastal Bohai Bay in order to determine the concentration and identify the source of organic matter. The sampling sites covered both the marine region of coastal Bohai Bay and the major rivers it connects with. More abundant TOC and TN in sediments from rivers than from the marine region reflect the situation that most of the terrestrial organic matter is deposited before it meets the sea. The spatial variation in $\delta^{13}C$ and $\delta^{15}N$ signatures implies that the input of organic matter from anthropogenic activities has a more significant influence on its distribution than that from natural processes. Taking the area as a whole, surface sediments in the marine region of coastal Bohai Bay are dominated by marine derived organic carbon, which on average accounts for 62 ± 11% of TOC.

1. Introduction

Estuaries and coastal zones are the main channels between lands and oceans, which trap significant quantities of natural and anthropogenic organic matter under the interactions of a series of physical, chemical and biological processes. The organic matter in coastal marine sediments is a complex mixture of organic compounds originating from marine and terrestrial sources (Tesi et al., 2007). The preservation of organic matter in coastal marine sediments is an important link of the global carbon cycle and other bioactive elements as more than 90% of the organic carbon buried in the oceans occur in continental margin sediments (e.g. Emerson and Hedges, 1988; Hedges, 1992; Goni et al., 1997; Hu et al., 2006; Ramaswamy et al., 2008). Knowledge of the sources of organic matter in estuarine and coastal sediments and the factors controlling its distribution is essential to the understanding of global biogeochemistry.

Stable carbon and nitrogen isotopes ($\delta^{13}C$ and $\delta^{15}N$, respectively) and the elemental ratio of total organic carbon (TOC) to total nitrogen (TN), which is usually expressed as C/N or TOC/TN, have been widely used as proxies to elucidate the source and fate of organic matter in aquatic environments (e.g. Peters et al., 1978; Thornton and McManus, 1994; Gordon and Goni, 2003; Wu et al., 2007; Zhang et al., 2007; Ramaswamy et al., 2008). The use of these tracers relies on the existence of gross differences among natural abundances of stable carbon isotopes, stable nitrogen isotopes and C/N elemental ratios in organic matter from terrigenous and anthropogenic inputs and marine and freshwater in situ inputs (Liu et al., 2006).

In general, terrestrial organic matter has depleted $\delta^{13}C$ and $\delta^{15}N$ values when compared to marine organic matter (Vizzini et al., 2005). Typical isotopic composition of marine phytoplankton in temperate seas changes from −19.1‰ to −22‰ for $\delta^{13}C$ (Gearing et al., 1984) and from 3.0‰ to 12.0‰ for $\delta^{15}N$ (Wada and Hattori, 1991). Freshwater phytoplankton isotopic signatures mentioned in the literature have $\delta^{13}C$ from −35.0‰ to −25.0‰ (Boutton, 1991) and $\delta^{15}N$ around 5‰ (Wada and Hattori, 1991). Generally, marine organic matter and terrestrial organic matter have C/N of ~5–8 and >15, respectively (Meyers, 1997). The mixing of organic matter from different sources may result in $\delta^{13}C$, $\delta^{15}N$ and C/N values that fall out of the fields established for terrestrial land plants and phytoplankton, a situation particularly expected in coastal settings (Lamb et al., 2006).

Eutrophication and urban pollution have a major influence on the environmental quality of coastal areas. Sediments usually receive organic matter from autochthonous sources originating from diatoms, bacteria, green macroalgae, and fresh and decomposed litter. Anthropogenic inputs, however, originate from agricultural run-off, fertilisation, or livestock waste from sewage and domestic waste discharge. Consequently, the natural balance between production and decomposition of organic matter has been disturbed

* Corresponding author at: Key Laboratory of Coastal Zone Environmental Processes, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, China. Tel.: +86 0535 2109152.

E-mail addresses: xlgao@yic.ac.cn (X. Gao), cywang@yic.ac.cn (C. Wang).

0025-326X/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.marpolbul.2012.03.028

in many coastal areas (Mchenga and Tsuchiya, 2008). Understanding the sources of anthropogenic inputs and their impacts on ecosystems is therefore a major environmental concern.

Over the last decade in China, rapid economic development and urbanization have significantly impacted on its environments, especially along the coast. This is especially true for Bohai Bay coastal regions where the strong anthropogenic influence and various contamination sources exist. Bohai Bay is a large, semi-enclosed shallow water basin located along the western region of Bohai Sea in the northeastern part of China. There are a number of rivers along the east coast of Haihe Basin, through which a large amount of wastewater is being transported into Bohai Bay causing marine pollution. All the wastewater through rivers and channels drains into the near-shore waters of Bohai Bay directly. As a result of these activities, eutrophication and harmful algal blooms occurred frequently. These changes, in turn, have the potential to alter the nature and content of organic matter of marine deposits and their C/N, $\delta^{13}C$ and $\delta^{15}N$ values (Owen and Lee, 2004). There are plenty of reports on the environmental aspects of Bohai Bay (e.g. Ma et al., 2001; Hu et al., 2005; Gao and Chen, 2012). However, detailed information on organic matter distribution in this region remains scarcely documented, especially covering both the marine and riverine regions. The main objectives of the present study are to map the distribution of organic carbon and nitrogen in the surface sediments of coastal Bohai Bay and determine the factors controlling their distribution and accumulation. The relative contribution of allochthonous (terrigenous) and autochthonous (aquatic plankton) sources of organic matter is assessed by C/N ratios and isotopic signatures of carbon and nitrogen.

2. Materials and methods

2.1. Sampling location

Sediments used in this study were collected from 42 sites of coastal Bohai Bay in May 2008 (Fig. 1). The sampling stations were arranged along the major rivers of this area extending from the land to the sea and formed four transects. Sampling sites started from the freshwater end-member in upper riches of the river estuaries to saltwater sea covering the whole salinity gradient. The surface sediments from the marine region were collected using a Van Veen style stainless steel grab sampler, and the surface sediments from rivers were collected using a plastic spatula. The top 5–10 cm sediment was collected at each sampling site. After collection, the samples were homogenized and placed into sterile polyethylene bags, sealed and stored at ~4 °C in the dark until further analysis.

2.2. Sample preparation and analysis

The sediments were freeze-dried, homogenized and ground in an agate mortar prior to elemental and isotopic analysis. Total carbon (TC) and total nitrogen (TN) were analyzed via high temperature combustion on an Elementar vario MACRO cube CHNS analyzer. Total inorganic carbon (TIC) analysis was carried out on a Shimadzu TOC-V_{CPH}/SSM-5000A analyzer. Total organic carbon (TOC) in sediments was obtained by subtracting TIC from TC. Duplicate analyses of every sample were run, and the mean of the two measurements are reported here. Replicate analysis of one sample ($n = 5$) gave a 1 σ precision of ±0.02 wt.% C and ±0.003 wt.% TN. For isotope analysis, samples were treated with hydrochloric acid to remove carbonate and subsequently rinsed with deionized water to remove salts before drying overnight at 60 °C (Huon et al., 2002; Hu et al., 2006).

The carbonate free sediments were analyzed by a Finnigan DELTA^{plus} XL isotope ratio mass spectrometer, and the results were expressed in δ notation as the deviation from standard reference material in parts per mil (‰):

$$\delta^{13}C \text{ or } \delta^{15}N(‰) = (R_{sample}/R_{reference} - 1) \times 1000$$

where R_{sample} and $R_{reference}$ are the heavy to light isotopic ratios (i.e. $^{13}C/^{12}C$ and $^{15}N/^{14}N$) of the sample and reference, respectively. For $\delta^{13}C$, the reference is PeeDee Belemnite (PDB), and for $\delta^{15}N$, it is atmospheric nitrogen. The samples were run in duplicate and the analytical precision was ±0.2‰ for $\delta^{13}C$ and ±0.3‰ for $\delta^{15}N$.

The sample granulometry was analyzed on fresh sediments using a Malvern Mastersizer 2000 laser diffractometer capable of analyzing particle sizes between 0.02 and 2000 μm. The percentages of the following three groups of grain sizes were determined: <4 μm (clay), 4–63 μm (silt), and >63 μm (sand).

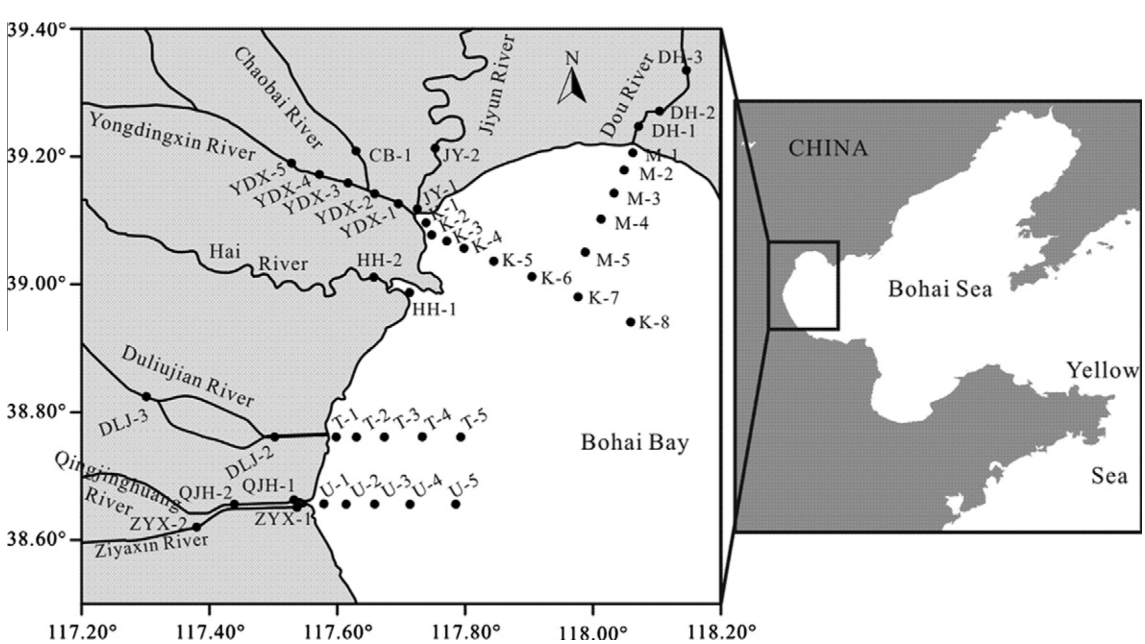

Fig. 1. Location of sampling sites in coastal Bohai Bay.

2.3. Statistical analysis

Statistical analyses were performed with the Microsoft Excel 2010 for Windows. The relationships between variables were based on Pearson's correlation coefficients.

3. Results and discussion

3.1. TOC and TN in coastal Bohai Bay surface sediments

As shown in Fig. 2, it is clear that TOC and TN concentrations decrease seaward along all the studied transects except the Duliujian River-T one, implying that the anthropogenic waste input through river discharge is a key source for the accumulation of organic matter in coastal Bohai Bay surface sediments. TOC concentrations vary in a wide range of 0.85–7.24% (mean 2.30 ± 1.27%). The spatial difference of TOC contents among riverine sediments is significant. The average TOC concentration in sediments from riverine sites is 3.18 ± 1.38%. Three samples, HH-1, DH-2 and DH-3, from Hai River and Dou River, have the TOC contents of 7.24%, 4.89% and 5.90%, respectively, being obviously higher than that of the rest samples. The TOC contents in sediments from marine sites fluctuate between 1% and 2% with only a few exceptions, averaging 1.62 ± 0.32%. It was reported that the TOC contents in surface sediments of Bohai Sea ranged broadly from 0.04% to 0.69% with a mean of 0.38 ± 0.17% (Hu et al., 2009). Compared with Bohai Sea, the TOC contents in surface sediments of coastal Bohai Bay are apparently higher, which may be due to the fact that the organic matter input to Bohai Bay sediment is strongly influenced by both terrestrial and anthropogenic sources. Like TOC, the TN values also show a wide variation range of 0.03–0.47% with a mean of 0.14 ± 0.08% in surface sediments of coastal Bohai Bay, which are wider and higher than the reported Bohai Sea's 0.01–0.10% and 0.06 ± 0.02% (Hu et al., 2009). The average TN concentrations in riverine and marine sediments are 0.19 ± 0.09% and 0.09 ± 0.02%, respectively. The spatial distribution of TN contents is similar to that of sedimentary organic carbon (Fig. 2). There is a good linear relationship being significant at $P < 0.001$ between TOC% and TN% as shown in Fig. 3.

Grain size composition is an important factor that greatly influences the geochemical behaviors of elements in sediments. The ternary diagram in Fig. 4 categorizes the sediments of intertidal Bohai Bay according to the classification of Shepard (1954). Sediments in the studied area mainly consisted of fine particles with the grain size <63 μm (silt + clay). All samples except two are clayey silt sediments. The sand content in most of the samples is <5%. Organic matter is known to be closely associated with fine-grained sediments because of the larger surface area which provides good binding sites for organic matter (Mayer, 1994). A good negative correlation is seen between the median grain size (D50)

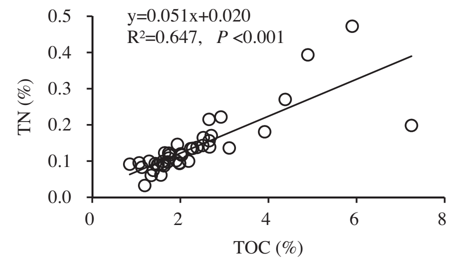

Fig. 3. Relationship between TN and TOC in surface sediments of coastal Bohai Bay.

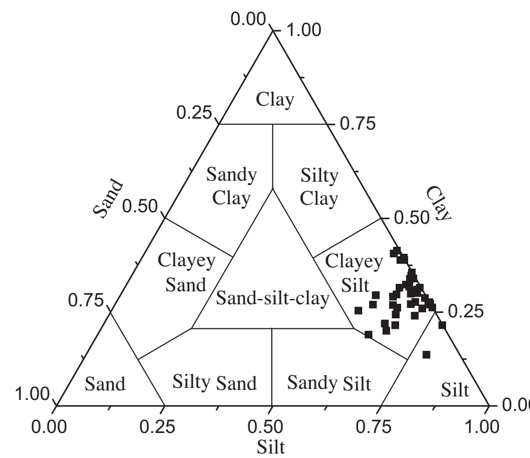

Fig. 4. Ternary diagram showing the sediment classification and deposition patterns.

and TOC content for samples from the marine region (Fig. 5). The balance between industrial and human waste discharge and current dispersal of fine sediments is a critical determinant of pollution (Owen and Sandhu, 2000). The relationship in Fig. 5 indicates the influence of hydrodynamics on the distribution of sedimentary organic matter (SOM) in the marine region of coastal Bohai Bay. No such relationship is found for the D50 and TOC data of riverine sediments implying the dominance of anthropogenic influence on SOM distribution in the riverine region.

3.2. Source of organic matter in coastal Bohai Bay surface sediments

3.2.1. C/N ratios

The C/N elemental ratio often acts as an indicator of predominant sources of organic matter in aquatic ecosystems (e.g. Meyers, 1994; Hedges and Oades, 1997; Graham et al., 2001; Lamb et al.,

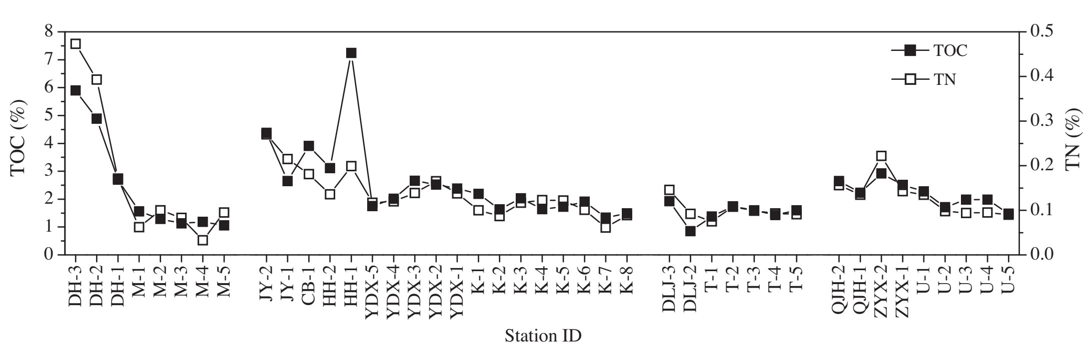

Fig. 2. Spatial variations of TOC and TN in surface sediments of coastal Bohai Bay.

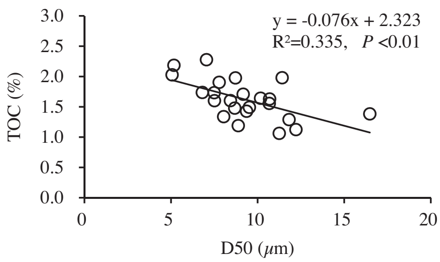

Fig. 5. Relationship between TOC and median grain size (D50) in surface sediments from the marine region.

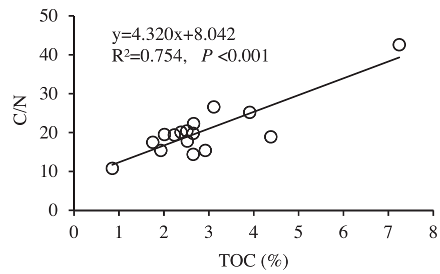

Fig. 7. Relationship between C/N and TOC in surface sediments from rivers except Dou River.

2006). The C/N ratios of undegraded marine phytoplankton is generally close to 6.7, while vascular plants are N-depleted and have the ratios exceeding 12 (Meyers, 1994; Hedges and Oades, 1997; Lamb et al., 2006). As shown in Fig. 6, C/N ratios ranging from 10.8 to 42.6 with an average of 21.3 ± 6.1 in this study indicate that the terrestrial materials from rivers could be an important source for organic matter in surface sediments of coastal Bohai Bay. The C/N ratios at most of the sampling sites vary in the range of 15–25. Three exceptionally higher values are found in the sediments from sites M-1, M-4 and HH-1. Comparatively, the measured TOC/TN ratios in sediments of Bohai Sea vary from 3 to 9 with a mean of 6.7 ± 1.0 suggesting a predominant marine origin (Hu et al., 2009). The C/N ratios of sedimentary organic matter in coastal Bohai Bay are much higher than that of Bohai Sea. Except for the influence from the input of terrestrial sources, the higher C/N ratios could also be ascribed to the anthropogenic influence. Anthropogenic activities such as the widespread use of organic chemicals may alter the C/N ratios of organic matter from natural origins. As shown in Fig. 7, C/N values have a significant positive relationship with TOC concentrations for sediments from all the sampled rivers except Dou River, which indicates that the variation of C/N ratios at these riverine sites is controlled by TOC concentrations. For the sediments from the marine region, no such relationship is found between C/N ratios and TOC concentrations reflecting a weak disturbance from the anthropogenic TOC input. The spatial variation in TN concentrations seems to have no influence on the distribution of C/N ratios, because there is no significant relationship between them no matter considering the data from riverine and marine regions separately or together.

Given that the C/N ratio strongly reflects the sources of organic matter, it is expected that there exists a significant negative correlation between δ13C and C/N ratios (i.e., organic matter with high C/N ratio has much light δ13C value) (Wu et al., 2002). However, it is shown that C/N ratios against δ13C have no pronounced relationship at the studied areas (Fig. 9a). This should be attributed to the decomposition processes (e.g., autolysis, leaching and microbial mineralization) of organic matter (Wu et al., 2003). Indeed, during sediment diagenesis, the C/N ratio can be altered by the selective degradation of organic matter components (Meyers et al., 1996). Typically, the C/N ratios tend to decrease over time due to the release of CO2 or CH4 as degradation products, ammonia preservation and addition of microbially-associated nitrogen. On the contrary, organic-rich sediments from high surface productivity areas can register elevated values of the C/N ratio, higher than typical algal values (Meyers, 1997) because during organic matter settlement a delayed loss of carbon relative to nitrogen occurs, proteinaceous organic matter decomposing more easily (Meyers, 1997; Nijenhuis and de Lange, 2000). Accordingly, in the area studied differential decomposition rates for carbon and nitrogen-rich compounds may account for the increasing profiles for the C/N ratio in the coastal zone.

3.2.2. Distribution of $\delta^{13}C$ values of TOC

The values of $\delta^{13}C$ measured for TOC in the surface sediments from coastal Bohai Bay range from −18.23‰ to −25.69‰ with an average of −22.86 ± 1.43‰, lower than the $\delta^{13}C$ values of marine-derived organic matter (−18‰∼−22‰) (Ramaswamy et al., 2008). The sample from HH-1 has the highest TOC content (7.24%) and C/N ratio (42.6), with $\delta^{13}C$ value being less negative than the values measured for sediments from other locations. Moreover, the spatial variation of $\delta^{13}C$ in the marine area of coastal Bohai Bay is relatively weaker (−22.96 ± 0.73‰) than that of its adjacent rivers (−22.75 ± 1.96‰) (Fig. 8).

Stable carbon isotopic composition has been widely used to distinguish marine sources and terrestrial plant sources of organic matter (e.g. Middelburg and Nieuwenhuize, 1998; Schubert and Calvert, 2001; Hu et al., 2005; Ramaswamy et al., 2008). Terrestrial plants with C_3 pathway have an average $\delta^{13}C$ value of −27‰, ranging from −22‰ to −33‰, while for the C_4 pathway it is from −9‰ to −16‰, with a mean value of −13‰ (Pancost and Boot, 2004). Riverine algae are usually more depleted than terrestrial organic matter as they assimilate carbon with low $\delta^{13}C$ values (Middelburg and Hermann, 2007). The distribution features of $\delta^{13}C$ suggest that

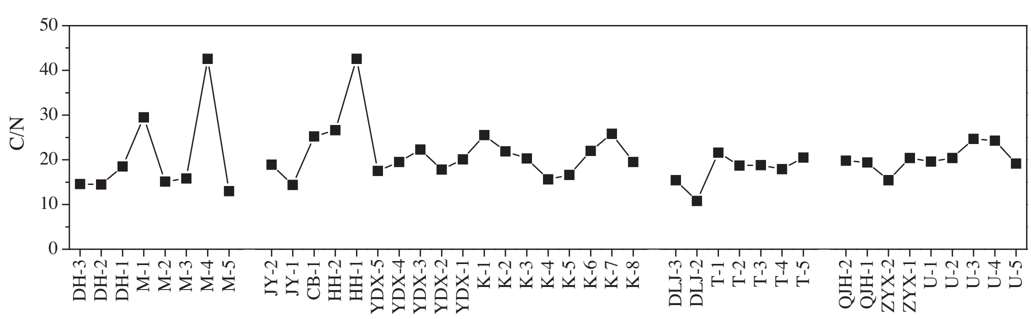

Fig. 6. Spatial variations of C/N ratios in surface sediments of coastal Bohai Bay.

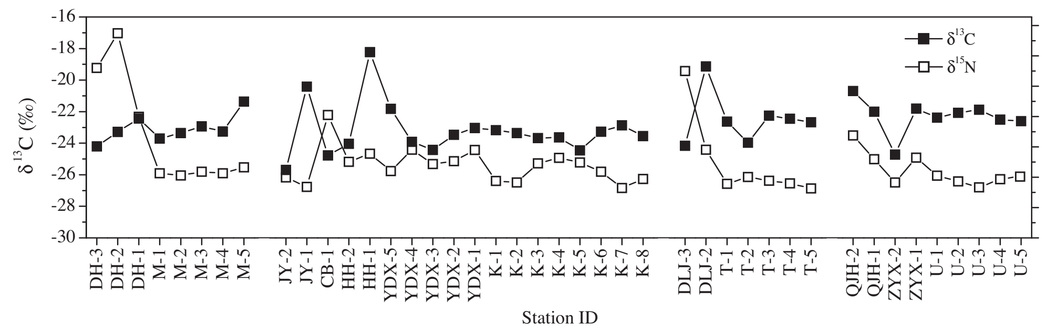

Fig. 8. Spatial variations of $\delta^{13}C$ and $\delta^{15}N$ in surface sediments of coastal Bohai Bay.

organic matter in surface sediments of coastal Bohai Bay is basically the mixture of continental derived material and marine material. In addition, the apparent fluctuation of $\delta^{13}C$ values in the samples from rivers reflects that some local additional factors probably exert an important influence on the $\delta^{13}C$ signatures of SOM. Guo et al. (2006) reported that C_3 plant ecosystem dominated North China; therefore, the portion of organic matter with terrestrial higher plant origin in surface sediments of the studied area is mainly derived from C_3 vascular plants.

According to previous studies, there is a net seaward increase in $\delta^{13}C$ in marine sediments (Ramaswamy et al., 2008; Hu et al., 2009). A straightforward explanation for this trend is a progressive seaward decrease in the proportions of terrigenous organic matter relative to marine autogenous organic matter. This explanation is also consistent with the seaward decrease in $\delta^{15}N$ and C/N. However, such a distribution pattern is not distinct in the marine region of coastal Bohai Bay except at transect M, which may be due to that the hydrodynamic condition and flat sea-floor of this area make organic matter from different sources well mixed.

Given that the C/N ratio is also an indicator for the sources of organic matter, it is expected that there exists a significant negative correlation between $\delta^{13}C$ and C/N ratios, i.e. organic matter with high C/N ratio has much lighter $\delta^{13}C$ value (Wu et al., 2002). However, it is shown that $\delta^{13}C$ against C/N ratios has no pronounced relationship at the studied areas no matter analyzing the data from riverine and marine regions separately or together (Fig. 9a). This should be attributed to the decomposition processes (e.g. autolysis, leaching and microbial mineralization) of organic matter (Thornton and McManus, 1994; Wu et al., 2003) and/or the anthropogenic disturbances. The anthropogenic disturbances might be a more probable reason because the samples of this study are surface sediments experiencing a short period of degrading, and the $\delta^{15}N$ data which are discussed below will provide further evidence of this.

3.2.3. Distribution of $\delta^{15}N$ values of TN

Similar to that of $\delta^{13}C$, the spatial variation of $\delta^{15}N$ in the riverine region of coastal Bohai Bay is greater than in the marine region (Fig. 8). Apparently higher $\delta^{15}N$ values of >7‰ were measured in samples from Dou River, Chaobai River and Duliujian River. For each transect M, T and U, the $\delta^{15}N$ difference among marine samples is small. The samples from riverine sites have an average $\delta^{15}N$ value of 6.06 ± 2.81‰, which is heavier than that of the marine sediments' 4.05 ± 0.53‰.

Marine organic matter usually has the $\delta^{15}N$ value of 3–12‰ with the mean of 5–7‰ as derived from phytoplankton which normally use dissolved nitrate (Brandes and Devol, 2002; Lamb et al., 2006). Organic matter derived from nitrogen fixing land plants has $\delta^{15}N$ values around zero, whereas plants using only mineral N from soil (NO_3^- or NH_4^+) have usually positive $\delta^{15}N$ values. Generally, river suspension has quite variable $\delta^{15}N$ values that are mostly lower than oceanic values (Maksymowska et al., 2000; Gaye-Haake et al., 2005). Low $\delta^{15}N$ in rivers could be due to contributions from forest and soil nitrogen as terrestrial plant ecosystems have low $\delta^{15}N$. Unlike that of natural origins, generally, the waste that experienced anthropogenic disturbances is isotopically rich in heavy nitrogenous components (Cole et al., 2006; Bănaru et al., 2007). Compared with atmospheric deposition ($\delta^{15}N$ of +2‰ to +8‰) and commercial, inorganic fertilizers ($\delta^{15}N$ of −3‰ to +3‰), nitrogen derived from human wastewater and livestock ($\delta^{15}N$ of +10‰ to +22‰) is relatively enriched in N^{15} (McClelland et al., 1997). In this study, as mentioned above, the $\delta^{15}N$ values in surface sediments from many riverine sampling sites are apparently higher than that from the marine region reflecting that the input of organic matter from anthropogenic activities has a more significant influence on its spatial distribution than from natural processes. As just mentioned, the terrigenous detrital organic matter is generally characterized by a low $\delta^{15}N$ signature while the marine component has a relatively higher $\delta^{15}N$ value. Based on this, some distinct progressive

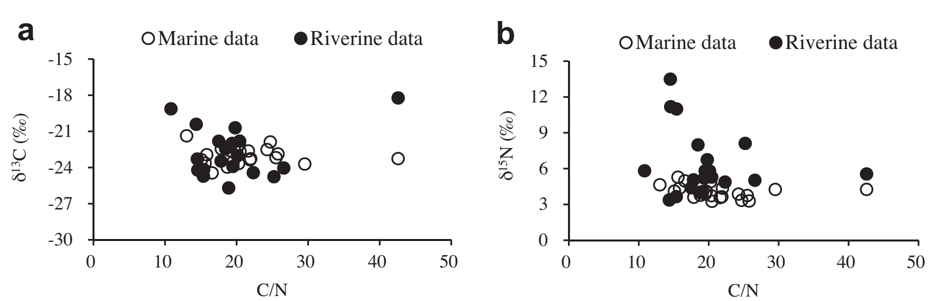

Fig. 9. Relationship between $\delta^{13}C$ and C/N ratios (a) and $\delta^{15}N$ and C/N ratios (b) in surface sediments of coastal Bohai Bay.

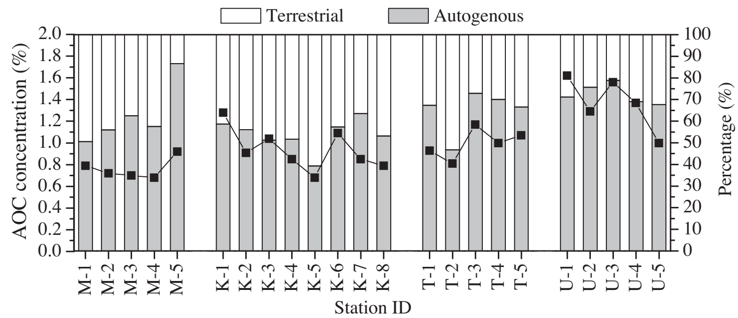

Fig. 10. AOC concentration and relative contribution of terrestrial and autogenous organic carbon in surface sediments from marine sampling stations.

seaward enrichment of $\delta^{15}N$ value could also be seen. Nevertheless, similar to stable carbon isotope, $\delta^{15}N$ in surface sediments of coastal Bohai Bay has more complex spatial fluctuations (Fig. 8), which indicates that additional factors have significant influences on the distributions of $\delta^{15}N$ in sedimentary organic matter. Nitrogen isotopic compositions could be easily modified by a series of complex biogeochemical processes on some time scales. Dynamic cycling of nitrogen is subject to kinetic isotope fraction effects especially during the biogenic transformation and recycling of dissolved and particulate nitrogen compounds (Cifuentes et al., 1988, 1996; Wu et al., 2003). Liu et al. (2006) reported that heavier $\delta^{15}N$ values significantly corresponded with higher C/N ratios in intertidal sediments from the Yangtze Estuary, China, and the authors ascribed this relationship to the result of organic matter diagenesis. It has also been reported that nitrogen isotopic enrichment during organic decomposition was relative to heterotrophic microorganisms (Macko and Estep, 1984). The effects of heterotrophs were documented by Caraco et al. (1998) who found that the $\delta^{15}N$ of microbially reworked terrestrial particulates increased from −4‰ to 9‰. As microbial mineralization proceeds, the total amount of nitrogen present in the organic substrates reduces with ^{14}N being preferentially lost. Consequently, higher decomposed organic matter will contain little nitrogen enriched in $\delta^{15}N$. However, it is shown that, like $\delta^{13}C$, $\delta^{15}N$ against C/N ratios also has no pronounced relationship in this study (Fig. 9b). Although $\delta^{13}C$ and $\delta^{15}N$ of sediments can be modified by microbial rearrangement, isotopic fractionation specifically associated with early diagenesis is negligible (Lehmann et al., 2004) and the isotopic composition of sedimentary organic matter is fairly conservative, mirroring the isotopic signatures of the sources (Di Leonardo et al., 2009). Thus, it implies that organic matter in surface sediments of the studied area is relatively fresh and the nitrogen cycling in early diagenesis processes has no obvious effect on the nitrogen isotopic composition.

3.2.4. Contribution of terrigenous and autogenous organic carbon

To assess the relative proportions of terrigenous and marine autogenous organic carbon (AOC) present in the sediments, a simple $\delta^{13}C$-based two end-member mixing model based on the work of Calder and Parker (1968) and adopted by other researchers such as Schlunz et al. (1999) and Hu et al. (2006) was applied to this area. We took −27.0‰ as the $\delta^{13}C$ value of terrestrial end-member ($\delta^{13}C_{terrestrial}$) based on the $\delta^{13}C$ value of coastal sediments of Bohai Bay. This value is close to that of C_3 plants. Likewise, we assumed −20.5‰ as the $\delta^{13}C$ value of marine end-member ($\delta^{13}C_{marine}$) (Jia and Peng, 2003). The calculation of terrestrial organic carbon contribution (*f*) was gained by the following equation:

$$f(\%) = (\delta^{13}C_{marine} - \delta^{13}C_{measured})/(\delta^{13}C_{marine} - \delta^{13}C_{terrestrial}) \times 100$$

Then the contribution of marine algae (f') to the TOC could be estimated by the following expression:

$$f'(\%) = 100 - f$$

The content of AOC was obtained from the following equation:

$$AOC = TOC \times f'\%$$

Considering the obvious anthropogenic disturbance to the organic matter composition in the riverine region as discussed above, only the data of the marine region were calculated. As shown in Fig. 10, the AOC concentrations generally descend seaward along transects M, K and U. This might be explained by the flourish of marine primary producers responding to the input of nutrients from land to this area by surrounding rivers. The resulting estimates for the contribution of the terrestrial and autogenous organic carbon in marine sediments of coastal Bohai Bay are also summarized in Fig. 10. Taking as a whole, the surface sediments in the marine region of coastal Bohai Bay are dominated by marine derived organic carbon, which on average accounts for 62 ± 11% of their TOC concentrations. Although the highest proportion of AOC up to 87% of TOC is recorded at site M-5, the contribution of AOC to TOC in nearly all samples from the northern two transects is lower than that in a majority of samples from the southern two transects. Except for site T-2, AOC accounts for 67–79% of TOC in surface sediments from the rest sites of transects T and U, while it accounts for <60% of TOC in most surface sediments from the sites at transects M and K. The contribution of AOC to TOC increases from 51% to 87% seaward along transect M; the contribution of AOC to TOC decreases seaward along the transect K from site K-1 to K-5 and increases thereafter and then decreases again at site K-8. The relative proportion autogenic and terrestrial organic carbon in sediments is the integrated results of any natural and anthropogenic processes that influence the biogeochemical cycle of TOC such as waste discharge, hydrodynamics, primary production in the overlying water body and early diagenesis.

4. Conclusions

In this study, spatial variations of total organic carbon, total nitrogen and their isotopes were observed in surface sediments of coastal Bohai Bay. Our findings indicate that the spatial distributions of TOC, TN, $\delta^{13}C$ and $\delta^{15}N$ in surficial sediments from the coastal Bohai Bay are broadly similar with their average values being higher in riverine sediments than in marine ones. The average TOC concentrations in riverine and marine sediments are 3.18 ± 1.38% and 1.62 ± 0.32%, respectively, and the corresponding values for TN is 0.19 ± 0.09% and 0.09 ± 0.02%, respectively. The high TN concentrations correspond well with high TOC concentrations in the sediments from rivers, which serve as the main pathway for urban runoff, sewage and industrial waste water discharge to Bohai Bay. In general, there is evidence suggesting that anthropogenic activities have a significant influence on the geochemistry of organic matter in riverine sediments besides natural processes; the spatial distributions of TOC, TN and their isotopic signatures in marine sediments are mainly controlled by the mixing inputs of terrigenous and marine components. The organic matter in marine sediments of coastal Bohai Bay is predominated by autogenous source and the estimated autogenous organic carbon is about 51–87% of TOC. The results of this study imply qualitatively that, in coastal Bohai Bay, particulate organic matter from anthropogenic sources is mainly trapped in riverine sediments. As sedimentary organic carbon is the most important carrier for persistent organic pollutants, the spatial distribution pattern of organic carbon indicates that much attention should be paid to the riverine sediments for environmental monitoring and risk assessment of coastal Bohai Bay.

Acknowledgements

This study was co-supported by the Chinese Academy of Sciences (KZCX2-YW-Q07-03, KZCX2-YW-JC203), the National Natural Science Foundation of China (Grant No. 40806048) and the CAS/SAFEA International Partnership Program for Creative Research Teams (Representive environmental processes and resources effects in coastal zone).

References

Bănaru, D., Harmelin-Vivien, M., Gomoiu, M.-T., Onciu, T.-M., 2007. Influence of the Danube River inputs on C and N stable isotope ratios of the Romanian coastal waters and sediment (Black Sea). Mar. Pollut. Bull. 54, 1385–1394.

Boutton, T.W., 1991. Stable carbon isotope ratios of natural materials: II. Atmospheric, terrestrial, marine, and freshwater environments. In: Coleman, D.C., Fry, B. (Eds.), Carbon Isotopes Techniques. Academic Press, San Diego, pp. 173–185.

Brandes, J.A., Devol, A.H., 2002. A global marine-fixed nitrogen isotopic budget: implications for Holocene nitrogen cycling. Glob. Biogeochem. Cy. 16, 1120–1134.

Calder, J.A., Parker, P.L., 1968. Stable carbon isotope ratios as indices of petrochemical pollution of aquatic systems. Environ. Sci. Technol. 2, 535–539.

Caraco, N.F., Lampman, G., Cole, J.J., Limburg, K.E., Pace, M.L., Fisher, D., 1998. Microbial assimilation of DIN in a nitrogen-rich Estuary: implication for food quality and isotope studies. Mar. Ecol. -Prog. Ser. 167, 59–71.

Cifuentes, L.A., Sharp, J.H., Fogel, M.L., 1988. Stable carbon and nitrogen isotope biogeochemistry in the Delaware Estuary. Limnol. Oceanogr. 33, 1102–1115.

Cifuentes, L.A., Coffins, R.B., Slolrzano, L., Cardenas, W., Espinoza, J., Teilley, R.R., 1996. Isotopic and elemental variations of carbon and nitrogen in a mangrove Estuary. Estuar. Coast. Shelf Sci. 43, 781–800.

Cole, M.L., Kroeger, K.D., McClelland, J.W., Valiela, I., 2006. Effects of watershed land use on nitrogen concentrations and δ^{15}N nitrogen in groundwater. Biogeochemistry 77, 199–215.

Di Leonardo, R., Vizzini, S., Bellanca, A., Mazzola, A., 2009. Sedimentary record of anthropogenic contaminants (trace metals and PAHs) and organic matter in a Mediterranean coastal area (Gulf of Palermo, Italy). J. Mar. Syst. 78, 136–145.

Emerson, S., Hedges, J.I., 1988. Processes controlling the organic carbon content of open ocean sediments. Paleoceanography 3, 621–634.

Gao, X.L., Chen, C.T.A., 2012. Heavy metal pollution status in surface sediments of the coastal Bohai Bay. Water Res. 46, 1901–1911.

Gaye-Haake, B., Lahajnar, N., Emeis, K.-Ch., Unger, D., Rixen, T., Suthhof, A., Ramaswamy, V., Schulz, H., Paropkari, A.L., Guptha, M.V.S., Ittekkot, V., 2005. Stable nitrogen isotopic ratios of sinking particles and sediments from the northern Indian Ocean. Mar. Chem. 96, 243–255.

Gearing, G.N., Gearing, P.L., Rudnick, D.T., Requejo, A.G., Hutchins, M.J., 1984. Isotope variability of organic carbon in a phytoplankton based temperate estuary. Geochim. Cosmochim. Acta 48, 1089–1098.

Goni, M.A., Ruttenberg, K.C., Eglinton, T.I., 1997. Sources and contribution of terrigenous organic carbon in the Gulf of Mexico. Nature 389, 275–278.

Gordon, E.S., Goni, M.A., 2003. Sources and distribution of terrigenous organic matter delivered by the Atchafalaya river to sediments in the northern gulf of Mexico. Geochim. Cosmochim. Acta 67, 2359–2375.

Graham, M.C., Eaves, M.A., Farmer, J.G., Dobson, J., Fallick, A.E., 2001. A study of carbon and nitrogen stable isotope and elemental ratios as potential indicators of source and fate of organic matter in sediments of the Forth Estuary, Scotland. Estuar. Coast. Shelf Sci. 52, 375–380.

Guo, Z.G., Li, J.Y., Feng, J.L., Fang, M., Yang, Z.S., 2006. Compound-specific carbon isotope compositions of individual long-chain n-alkanes in severe Asian dust episodes in the North China coast in 2002. Chinese Sci. Bull. 51, 2133–2140.

Hedges, J.I., 1992. Global biogeochemical cycles—progress and problems. Mar. Chem. 39, 67–93.

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

Hu, J., Peng, P., Jia, G., Mai, B., Zhang, G., 2006. Distribution and sources of organic carbon, nitrogen and their isotopes in sediments of the subtropical Pearl River estuary and adjacent shelf, Southern China. Mar. Chem. 98, 274–285.

Hu, J.Y., Wan, Y., Shao, B., Jin, X.H., An, W., Jin, F., Yang, M., Wang, X.J., Sugisaki, M., 2005. Occurrence of trace organic contaminants in Bohai Bay and its adjacent Nanpainu River, North China. Mar. Chem. 95, 1–13.

Hu, L., Guo, Z., Feng, J., Yang, Z., Fang, M., 2009. Distributions and sources of bulk organic matter and aliphatic hydrocarbons in surface sediments of the Bohai Sea. China. Mar. Chem. 113, 197–211.

Huon, S., Grousset, F.E., Burdloff, D., Bardoux, G., Mariotti, A., 2002. Sources of fine-sized OM in North Atlantic Heinrich layers: δ^{13}C and δ^{15}N tracers. Geochim. Cosmochim. Acta 66, 223–239.

Jia, G.D., Peng, P.A., 2003. Temporal and spatial variations in signatures of sedimented organic matter in Lingding Bay (Pearl estuary), Southern China. Mar. Chem. 82, 47–54.

Lamb, A.L., Wilson, G.P., Leng, M.J., 2006. A review of coastal palaeoclimate and relative sea-level reconstructions using δ^{13}C and C/N ratios in organic material. Earth-Sci. Rev. 75, 29–57.

Lehmann, M.F., Sigman, D.M., Berelson, W.M., 2004. Coupling the ^{15}N/^{14}N and ^{18}O/^{16}O of nitrate as a constraint on benthic nitrogen cycling. Mar. Chem. 88, 1–20.

Liu, M., Hou, L.J., Xu, S.Y., Ou, D.N., Yu, J., Wang, Q., 2006. Organic carbon and nitrogen stable isotopes in the intertidal sediments from the Yangtze Estuary, China. Mar. Pollut. Bull. 52, 1625–1633.

Ma, M., Feng, Z., Guan, C., Ma, Y., Xu, H., Li, H., 2001. DDT, PAH and PCB in sediments from the intertidal zone of the Bohai Sea and the Yellow Sea. Mar. Pollut. Bull. 42, 132–136.

Macko, S.A., Estep, M.L.F., 1984. Microbial alteration of stable nitrogen and carbon isotopic composition of organic matter. Org. Chem. 6, 787–790.

Maksymowska, D., Richard, P., Piekarek-Jankowska, H., Riera, P., 2000. Chemical and isotopic composition of the organic matter sources in the Gulf of Gdansk (Southern Baltic Sea). Estuar. Coast. Shelf Sci. 51, 85–598.

Mayer, L.M., 1994. Surface area control of organic carbon accumulation in continental shelf sediments. Geochim. Cosmochim. Acta 58, 1271–1284.

McClelland, J.W., Valiela, I., Michener, R.H., 1997. Nitrogen-stable isotope signatures in estuarine food webs: a record of increasing urbanization in coastal watersheds. Limnol. Oceanogr. 42, 930–937.

Mchenga, I.S.S., Tsuchiya, M., 2008. Nutrient dynamics in mangrove crab burrow sediments subjected to anthropogenic input. J. Sea Res. 59, 103–113.

Meyers, P.A., 1994. Preservation of elemental and isotopic source identification of sedimentary organic matter. Chem. Geol. 144, 289–302.

Meyers, P.A., Silliman, J.E., Shaw, T.J., 1996. Effects of turbidity flows on organic matter accumulation, sulphate reduction, and methane generation in deep sea sediments on the Iberia Abyssal Plain. Org. Geochem. 25, 69–78.

Meyers, P.A., 1997. Organic geochemical proxies of paleoceanographic, paleolimnologic, and paleoclimatic processes. Org. Geochem. 27, 213–250.

Middelburg, J.J., Hermann, P.M.J., 2007. Organic matter processing in tidal estuaries. Mar. Chem. 106, 127–147.

Middelburg, J.J., Nieuwenhuize, J., 1998. Carbon and nitrogen stable isotopes in suspended matter and sediments from the Schelde Estuary. Mar. Chem. 60, 217–225.

Nijenhuis, I.A., de Lange, G.J., 2000. Geochemical constraints on Pliocene sapropel formation in the eastern Mediterranean. Mar. Geol. 163, 41–63.

Owen, R.B., Lee, R., 2004. Human impacts on organic matter sedimentation in a proximal shelf setting, Hong Kong. Cont. Shelf Res. 24, 583–602.

Owen, R.B., Sandhu, N., 2000. Heavy metal accumulation and anthropogenic impacts on Tolo Harbour, Hong Kong. Mar. Pollut. Bull. 40, 174–180.

Pancost, R.D., Boot, C.S., 2004. The palaeoclimatic utility of terrestrial biomarkers in marine sediments. Mar. Chem. 92, 239–261.

Peters, K.E., Sweeney, R.E., Kaplan, I.R., 1978. Correlation of carbon and nitrogen stable isotopes in sedimentary organic matter. Limnol. Oceanogr. 23, 598–604.

Ramaswamy, V., Gaye, Birgit., Shirodka, P.V., Rao, P.S., Chivas, Allan R., Wheeler, David, Thwin, Swe, 2008. Distribution and sources of organic carbon, nitrogen and their isotopic signatures in sediments from the Ayeyarwady (Irrawaddy) continental shelf, northern Andaman Sea. Mar. Chem. 111, 137–150.

Schlunz, B., Schneider, R.R., Muller, P.J., Showers, W.J., Wefer, G., 1999. Terrestrial organic carbon accumulation on the Amazon deep sea fan during the last glacial sea level low stand. Chem. Geol. 159, 263–281.

Schubert, C.J., Calvert, S.E., 2001. Nitrogen and carbon isotopic composition of marine and terrestrial organic matter in Arctic Ocean sediments: implications for nutrient utilization and organic matter composition. Deep-Sea Res. Part I 48, 789–810.

Shepard, F.P., 1954. Nomenclature based on sand–silt–clay ratios. J. Sediment. Petr. 24, 151–158.

Tesi, T., Miserocchi, S., Goñi, M.A., Langone, L., Boldrin, A., Turchetto, M., 2007. Organic matter origin and distribution in suspended particulate materials and surficial sediments from the western Adriatic Sea (Italy). Estuar. Coast. Shelf Sci. 69, 225–245.

Thornton, S.F., McManus, J., 1994. Application of organic carbon and nitrogen stable isotope and C/N ratios as source indicators of organic matter provenance in estuarine systems: evidence from the Tay Estuary, Scotland. Estuar. Coast. Shelf Sci. 38, 219–233.

Vizzini, S., Savona, B., Caruso, M., Savona, A., Mazzola, A., 2005. Analysis of stable carbon and nitrogen isotopes as a tool for assessing the environmental impact of aquaculture: a case study from the western Mediterranean. Aquacult. Int. 13, 157–165.

Wada, E., Hattori, A., 1991. Nitrogen in the Sea: Forms, Abundances and Rate Processes. CRC Press, Boca Raton, 208 pp.

Wu, Y., Zhang, J., Zhang, Z.F., Ren, J.L., Cao, J.P., 2002. Seasonal variability of stable carbon and nitrogen isotope of suspended particulate matter in the Changjiang River. Oceanol Limnol Sin 33, 546–552 (in Chinese).

Wu, Y., Zhang, J., Li, D.J., Wei, H., Lu, R.X., 2003. Isotope variability of particulate organic matter at the PN in the East China Sea. Biogeochemistry 65, 31–49.

Wu, Y., Zhang, J., Liu, S.M., Zhang, Z.F., Yao, Q.Z., Hong, G.H., Cooper, L., 2007. Sources and distribution of carbon within the Yangtze River system. Estuar. Coast. Shelf Sci. 71, 13–25.

Zhang, J., Wu, Y., Ittekkot Jennerjahn, V., He, Q, 2007. Distribution of organic matter in the Changjiang (Yangtze River) Estuary and their stable carbon and nitrogen isotopic ratios: implications for source discrimination and sedimentary dynamics. Mar. Chem. 106, 111–126.