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Sources and distribution of sedimentary organic matter in the Beibu Gulf, China: Application of multiple proxies

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ABSTRACT

Geochemical and biomarker methods were combined to investigate the sources of sedimentary organic matter (OM) and their spatial distribution in the Beibu Gulf, a subtropical estuary in southern China. We measured the total organic carbon (TOC) and total nitrogen (TN) content, the glycerol dialkyl glycerol tetraethers (GDGTs) concentration, as well as the isotopic composition of sedimentary OM ($\delta^{13}C_{org}$ and $\delta^{15}N$) in surface sediments collected from the Beibu Gulf. The spatial distribution of the bulk organic parameters (TOC, TN, C/N ratio, $\delta^{13}C_{org}$, and $\delta^{15}N$) revealed a generally decreasing trend in terrestrial OM from the Maowei Sea to the outer Qinzhou Bay, and from the tributary rivers to the outer bay. The BIT (branched/isoprenoid tetraether) indices also decreased seaward from the Maowei Sea to the Qinzhou Bay, and from rivers to the outer bay, showing that soil OM was mainly delivered to the bay by rivers. The spatial patterns of these bulk parameters suggest that the terrigenous OC is constrained to the coast and adjacent regions. The relatively high GDGT-0/Crenarchaeol ratios and increasing $\delta^{15}N$ values along the coast of the Maowei Sea indicate the anthropogenic nitrogen in the Beibu Gulf. Our results show how important a multiproxy approach can be to fully understand and quantify the relative contributions of terrestrial and marine OC components and the biogeochemical processes in the Beibu Gulf, especially in the context of growing anthropogenic activities.

1. Introduction

Estuaries are important locations for the transport, transformation, and burial of carbon and other biogenic elements (e.g., N, P, and S), exchanged between land and ocean environments (Canuel et al., 2012). Due to rapid population growth in coastal areas, as well as climatic changes in temperature and precipitation, estuarine ecosystems are vulnerable to serious ecological and environmental stresses (Canuel et al., 2012). Anthropogenic impacts, including agricultural and urban runoff, have increased nutrient concentrations in estuarine ecosystems, resulting in a dramatic increase in eutrophication and hypoxia on a global scale (Diaz and Rosenberg, 2008; Rabalais et al., 2010). These factors have the potential to influence the carbon cycle, through changes in organic matter (OM) production, degradation and export processes in estuaries (Lopes dos Santos and Vane, 2016). As a result, anthropogenic changes in the source(s) of OM in estuarine and coastal sediments can have a major impact on global biogeochemical cycles (Hedges and Keil, 1995).

Like other major estuarine systems worldwide, the Beibu Gulf has been increasingly impacted by human activity. Over the past decade, rapid industrialization and urbanization have led to increasing stresses on ecosystem structure and environmental quality (Xia et al., 2011; Zheng et al., 2012; Zhang et al., 2014). For example, eutrophication or even seasonal hypoxia occurs in the Qinzhou Bay, located in the northern Beibu Gulf (Lai et al., 2014). As one of the major aquaculture areas of China and Vietnam, the Beibu Gulf receives a massive flux of anthropogenic nutrients from fish farming. Also, the nutrient from agricultural activity and sewage are transported to the estuarine system. As a result, phytoplankton productivity is highly variable across the estuarine system. These changes may potentially alter the nature and OM content of marine sediments (Owen and Lee, 2004).

Bulk organic parameters, such as the carbon/nitrogen (C/N) ratio and the stable isotope ratios of carbon and nitrogen in OM, are typically used to track OM sources in coastal and estuarine systems (e.g. Hu

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et al., 2006; Ramaswamy et al., 2008; Goñi et al., 2013; Krishna et al., 2013). Generally, marine OM and terrestrial OM have C/N ratios of ~5–8 and > 15, respectively (Meyers, 1997). However, this ratio can be altered by postdepositional processes, and the presence of significant inorganic nitrogen (adsorbed on clay minerals) can limit the usefulness of the C/N ratio as a source indicator in marine sediments (Meyers, 1997; Schubert and Calvert, 2001).

The application of stable isotope ratios relies on an understanding of source-specific signatures. For example, the typical range of stable carbon isotopic ($\delta^{13}C$) values in terrestrial C_3 plants is −26‰ to −28‰, while the soil OM is a little more enriched in ^{13}C, with the $\delta^{13}C$ value around −24.0‰ in the southern China due to the degradation of the plant material (Yu et al., 2010). The $\delta^{13}C$ values in marine phytoplankton range from −19‰ to −21.9‰ (Fry and Sherr, 1984; Meyers, 1997). However, interpretation of such data can be complicated by multiple terrigenous sources of OM, such as the anthropogenic sewage and nutrient inputs (Kemp et al., 2010; Khan et al., 2013). The stable isotope signature of nitrogen ($\delta^{15}N$) can help to identify OM sources, and has been used successfully to trace anthropogenic OM sources, such as sewage and agricultural OM input (Costanzo et al., 2003; Abreu et al., 2006; Bao et al., 2013). Human activities generally result in increased nitrogen loading and enrichment in ^{15}N (Anderson and Cabana, 2006; Middelburg and Herman, 2007). The $\delta^{15}N$ of marine nitrate generally ranges from 3% to 6‰, but this can be significantly elevated by inputs of sewage and manure, to values of around 10–25‰ (Müller and Voss, 1999; McCutchan et al., 2003; Cole et al., 2004).

Several studies have suggested that the limitations of the bulk geochemical approach can be overcome by using specific biomarkers (Kim et al., 2012; Zhu et al., 2013; Li et al., 2017). Recently, a biomarker ratio based on the relative abundances of glycerol dialkyl glycerol tetraethers (GDGTs), the branched/isoprenoid tetraether (BIT) index (Hopmans et al., 2004), has been proposed as a proxy for the relative contribution of soil and marine OM to marine sediment. In soils, the BIT value is close to 1, while in purely marine OM, the BIT value is close to 0 (Kim et al., 2006; Weijers et al., 2006). This index has been used to constrain the input of soil OM in coastal and estuarine areas (Kim et al., 2006, 2010; Walsh et al., 2008; Strong et al., 2012). The index provides a general signal of soil OM, and is not restricted to specific types of terrestrial vegetation. Furthermore, the relatively high abundance of GDGT-0, indicating the presence of methanogenic archaea (Li et al., 2016), is a useful proxy for marine hypoxia (Lopes dos Santos and Vane, 2016). Therefore, a multi-proxy approach, using bulk geochemical signatures combined with targeted biomarkers, is applied to assess the anthropogenic influences in the estuarine systems.

In this study, we investigate the spatial distribution of TOC and TN content, stable isotopes of sedimentary OM, and GDGTs in surface sediments from the Beibu Gulf, a rapidly developing subtropical region. Our primary goal was to better constrain the sources, distribution and composition of sedimentary OC in this highly anthropogenic impacted estuarine system. In particular, we developed a three-end-member (soil, plant, and marine) mixing model based on the multivariate analysis on OC sources in the Beibu Gulf.

2. Materials and methods

2.1. Study area and sampling

The Beibu Gulf, located in the northwest South China Sea, spans the Guangdong coast from Hainan Island to the border with Guangxi (Ma et al., 2010), covering an area of approximately 128,000 km^2 (Fig. 1). The water depth in the Beibu Gulf is typically < 100 m, with a mean depth of 50 m. The climate is subtropical and monsoonal (Chen et al., 2009). Annual air temperature ranges from −0.8 to 37.4 °C, with an average of 22.4 °C. Average annual rainfall is ~2100 mm, with 80–85% of rainfall occurring during the summer. The Beibu Gulf is fed by numerous tributary estuaries (hydrological details are shown in Table S1), where rivers discharge nutrients, and in some cases sewage, into the gulf (Zheng et al., 2012).

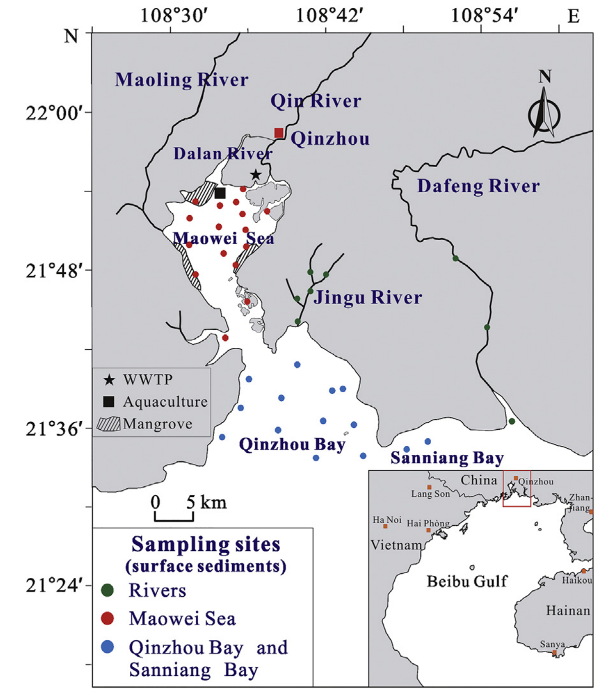

Fig. 1. The sampling sites from the Beibu Gulf and rivers, China. The location of the Beibu Gulf is shown in the inserted map. The locations of mangrove, aquaculture site, and waste water treatment plant (WWTP) are shown too.

A total of 38 marine surface sediment and river bed sediment (0–5 cm) samples were collected with a stainless steel grab sampler in July 2010. Sampling was carried out in the north of the Beibu Gulf and its tributary rivers, including the Maowei Sea, Qinzhou Bay, Sanniang Bay, Jingu River, and Dafeng River (Fig. 1). All samples were packed into pre-sterilized aluminum foil in polyethylene bags, and stored at −20 °C until further treatment.

2.2. Bulk organic matter

The sediment samples were freeze dried, homogenized, and powdered. Sub-samples selected for TOC, TN, and isotope analyses were treated with 6 N HCl for 24 h to remove carbonate, then rinsed with deionized water (Hu et al., 2006). The carbonate-free samples were dried, then analyzed for OC and TN content on a Thermo electron FLASH EA 1200 Series CNS elemental analyzer. Duplicate analyses were performed for every sample, with the mean of the two measurements reported in this study. Replicate analysis of one sample (n = 5) gave a 1σ precision of ± 0.02 wt%C and ± 0.003 wt%N.

Carbon and nitrogen isotope analyses were performed on carbonate-free sediment samples, using a FLASH2000 Elemental Analyzer connected to a Thermo MAT-253 isotope ratio mass spectrometer. Results are reported using standard delta notation in permil units (‰): $\delta (‰) = (R_{sample} - R_{reference})/R_{reference} \times 1000$, where δ (‰) stands for $\delta^{13}C$ (‰) or $\delta^{15}N$ (‰), and R_{sample} and $R_{reference}$ are the isotopic ratios of the sample and reference material, respectively. For carbon, the reference standard is Peedee belemnite (PDB); for N, the reference standard is atmospheric air ($\delta^{15}N$ = 0‰). Analytical precision for international and in-house reference materials was generally better than ± 0.2‰ for $\delta^{13}C$ and ± 0.3‰ for $\delta^{15}N$ (n = 5). Replicate measurements of samples yielded similar standard deviations.

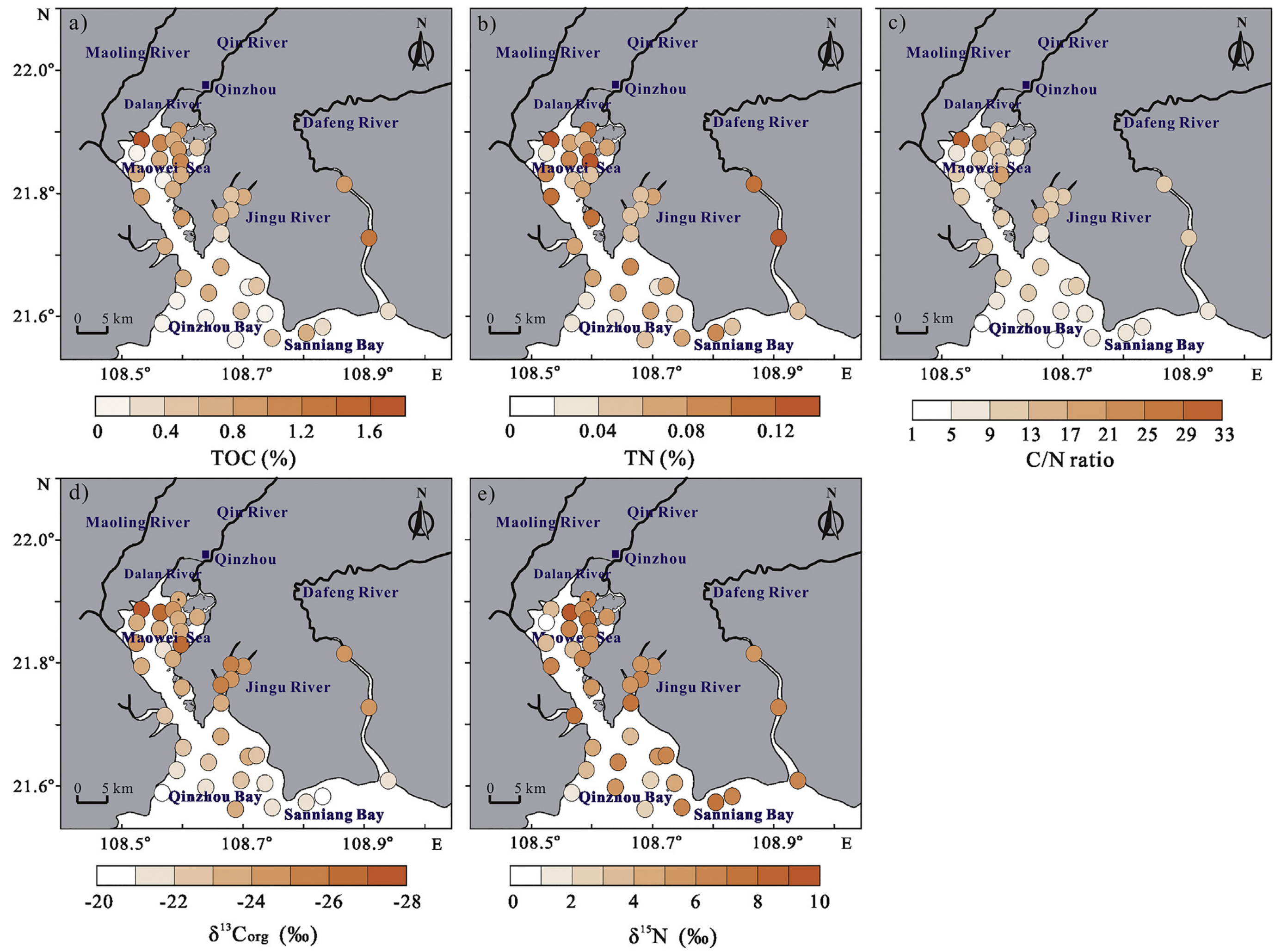

Fig. 2. The spatial distribution of a) TOC (%), b) TN (%), c) C/N ratios, d) $\delta^{13}C_{org}$, and e) $\delta^{15}N$ in surface sediments from the Beibu Gulf, China.

2.3. Glycerol dialkyl glycerol tetraethers (GDGTs)

A total of 10–15 g of each powdered sample was spiked with an appropriate amount of C_{46}–GDGT standard compound, then extracted via Soxhlet reflux for 48 h using a mixture of dichloromethane (DCM) and methanol (2:1, *v*/v). The resulting mixture was centrifuged, and the organic phase was separated from the aqueous phase using a separation funnel following an addition of 5% KCl solution. The aqueous phase was extracted with DCM (×3), and the collected organic material was concentrated by rotary evaporation. The total lipid extract was fractionated by column chromatography using neutral alumina. The non-polar and polar fractions were eluted with a hexane/DCM mixture (9:1, v:v) and a DCM/methanol mixture (1:1, v:v), respectively. The polar fraction (DCM/methanol) was condensed by rotary evaporation, re-dissolved in a hexane/isopropanol mixture (99:1, v/v), and filtered through a 0.45 μm polytetrafluoroethene filter prior to analysis.

High-performance liquid chromatography/atmospheric pressure chemical ionization-mass spectrometry (HPLC/APCI-MS) was used to analyze the GDGT content of all samples. Analyses were performed using an Agilent 1200 series liquid chromatograph, equipped with auto-injector and ChemStation chromatography management software. The specific parameters of the HPLC/APCI-MS analysis followed those described in Zhou et al. (2014). GDGTs were detected using selected ion monitoring (SIM) mode, following the methods described in Schouten et al. (2007). Integration of the peak area of $[M + H]^+$ ion traces was used to quantify GDGT content. Each sample was analyzed in duplicate, and the data presented are mean values. Replicate HPLC/APCI-MS analysis of one sample revealed the reproducibility of the BIT index is ± 0.035. Proxies based on the distribution of GDGTs were calculated as following:

$$\mathrm{BIT} = \frac{\mathrm{Ia + IIa + IIIa}}{\mathrm{(Ia + IIa + IIIa + Cren.)}}$$

(Hopmans et al., 2004);

$$\mathrm{MBT'} = \mathrm{(Ia + Ib + Ic)/(Ia + Ib + Ic + IIa + IIb + IIc + IIIa)}$$

(Peterse et al., 2012);

$$\mathrm{CBT} = -\log\left[\mathrm{(Ib + IIb)/(Ia + IIa)}\right]$$

(Peterse et al., 2012);

$$\#\mathrm{rings}_{tetra} = \mathrm{(Ib + 2^{*}Ic)/(Ia + Ib + Ic)}$$

(Sinninghe Damsté, 2016).where Ia–IIIc refer to branched GDGTs with various degrees of cyclisation and branches as shown in Fig. S1.

3. Results

3.1. Total organic carbon and total nitrogen content

Total organic carbon (TOC) and total nitrogen (TN) content range from 0.04% to 3.41% and 0.02% to 0.14% (% of dry weight) in the full sample set, respectively (Fig. 2, Table S2). TOC ranges from 0.04% to

3.41% in the Maowei Sea, from 0.06% to 0.75% in Qinzhou Bay and Sanniang Bay, and from 0.27% to 1.23% in the two tributary rivers (Fig. 2a). TN content is also relatively high in the Maowei Sea and Dafeng River, ranging from 0.02% to 0.13% and 0.10% to 0.14%, respectively. TN content ranges from 0.04% to 0.12% in Qinzhou Bay and Sanniang Bay, and from 0.04% to 0.08% in the Jingu River (Fig. 2b). The highest TOC and TN content occur in the Maowei Sea. TOC and TN content in the Jingu River and Dafeng River are generally higher than in Qinzhou Bay or Sanniang Bay (Fig. 2a and b).

The C/N ratio ranges from 2.2 to 33.3 in the full sample set (Fig. 2c, Table S2). More specifically, the ratio ranges from 2.4 to 33.3 in the Maowei Sea, 2.2 to 10.8 in Qinzhou Bay and Sanniang Bay, and 7.9 to 15.0 in the tributary rivers. The highest C/N ratio (33.3) occurs in the Maowei Sea (Fig. 2c).

3.2. Isotopic composition of sedimentary organic matter

Organic carbon isotope values in the complete set of samples range from −27.8 to −20.0‰ (Fig. 2d, Table S2). The most negative value (−27.8‰) occurs in a sample from the Maowei Sea. The relatively negative $\delta^{13}C_{org}$ values occur close to the river mouths, and in the rivers (Fig. 2d). The $\delta^{13}C_{org}$ values are relatively positive in the Qinzhou Bay and Sanniang Bay (Fig. 2d).

The $\delta^{15}N$ values of the sediment samples range from 0.8 to 9.0‰, with the least positive $\delta^{15}N$ value (0.8‰) and most positive $\delta^{15}N$ value (9.0‰) both occurring in the Maowei Sea (Fig. 2e, Table S2). The $\delta^{15}N$ values range from 5.1 to 7.7‰ in the tributary rivers, from 1.2 to 6.3‰ in the outer part of the Qinzhou Bay, and from 6.5 to 7.6‰ in the Sanniang Bay.

3.3. GDGTs and their derived proxies

All sediment samples were analyzed for branched and isoprenoid GDGTs. The concentrations of isoprenoid GDGTs range from 0.04 to 3.75 ng/g dry weight (dw) (Fig. 3a). Isoprenoid GDGT content normalized to TOC ranges from 0.01 μg/g TOC to 3.78 μg/g TOC (Fig. 3c). The higher isoprenoid GDGT contents (> 2.4 ng/g dw) occur in the Sanniang Bay, the outer part of the Qinzhou Bay, and the channel between the Maowei Sea and the outer Qinzhou Bay (Fig. 3a). After normalized to TOC, the highest content of isoprenoid GDGTs is found in the western margin of the outer Qinzhou Bay (Fig. 3c).

The isoprenoid GDGT fraction is dominated by crenarchaeol (cren.) and GDGT-0, accounting for 6.5–59% and 23–77% of total isoprenoid GDGTs, respectively. The molecular composition of the isoprenoid GDGTs is spatially variable. The highest GDGT-0 content occurs in the Maowei Sea, and the lowest content is found in the Sanniang Bay. The GDGT-0/Crenarchaeol ratios range from 0.4 to 12.0, with the highest value occurring in the Maowei Sea (Fig. 4a).

Branched GDGT contents in sediments range from 0.01 to 9.40 ng/g dry weight (Fig. 3b), accounting for 15.0–86.9% of total GDGTs. Branched GDGT content normalized to TOC ranges from 0.004 to 3.50 μg/g TOC (Fig. 3d). The branched GDGT fraction is dominated by GDGT-I compounds (i.e., GDGT-Ia, Ib, and Ic, accounting for 62–75% of branched GDGTs) and GDGT-II (21–32% of branched GDGTs). The percentage of total branched GDGTs is relatively high in the Maowei Sea and rivers.

The BIT ratios range from 0.19 to 0.98 in the full set of sediment samples (Fig. 4b). BIT ratios range from 0.37 to 0.98 in the Maowei Sea, 0.19 to 0.86 in the Qinzhou Bay and Sanniang Bay, and 0.60 to 0.95 in the tributary rivers. Showing a spatial distribution similar to that of branched GDGTs, the highest BIT index values occur in the Maowei Sea and the tributary rivers (Fig. 4b), with progressive decreases seaward toward the Qinzhou Bay and Sanniang Bay.

The MBT' and CBT indices (methyl branched and cyclized branched tetraethers; Peterse et al., 2012) arise from the degree of branching and cyclisation of soil bacterial GDGTs and together reflect the mean annual air temperature (MAT) in which the branched GDGTs were synthesised (Weijers et al., 2007).

The MBT' values range from 0.62 to 0.74 and the CBT values range from 0.33 to 0.84 (Fig. S2 & S3). The calculated mean annual air temperatures (MAT) range from 17.0 to 20.3 °C (Fig. S4), with an average of 18.6 °C as calculated according to the equation below:

$MAT = 0.81 - 5.67 \times CBT + 31.0 \times MBT'$ (Peterse et al., 2012).

Since the chromatographic method used does not allow the separation of 5- and 6-methyl brGDGTs (De Jonge et al., 2014), the accuracy of the reconstructed MAT might be controversial, however, the spatial trend of the MAT is authentic.

4. Discussion

4.1. TOC and TN contents

TOC and TN content are both seen to decrease seaward, from the Maowei Sea into the outer Qinzhou Bay, and from tributary rivers into the Qinzhou Bay and Sanniang Bay (Fig. 2). This spatial distribution of sedimentary OC is similar to other subtropical estuarine systems, such as the Pearl River Estuary (Hu et al., 2006). The most likely explanation for this phenomenon is the high concentration of terrestrial OM in rivers draining into the Maowei Sea. The river input terrestrial OM might partially derive from industrial and municipal wastewater, or from rivers affected by agricultural activity. The Qin River flows through the Qinzhou City, which have a population of 1 million people and discharge plenty of wastewater. Furthermore, fertilization during agricultural activities is common along the Qin River and Maoling River. These anthropogenic activities have caused abundant nutrient to enter the Maowei Sea. In that case, the nutrient might promote the primary production in the Maowei Sea (Harding, 1994; Glé et al., 2008), which is supported by the relatively high concentration of chlorophyll *a* (14.0 μg/L) in the water column (Liao et al., 2004; Yang et al., 2015).

Outside the Maowei Sea, TOC and TN content decreases seaward. The main mechanism is that terrigenous material mainly settled closer to the coast. Meanwhile, the high energy of currents and waves along the coastline of the Beibu Gulf may transport some terrigenous material to the open sea (Zhang et al., 2011; Kaiser et al., 2014). The tide and wave may easily resuspend the sediments and transport them toward the open sea, as the water depth is below 5 m in the Qinzhou Bay. Alternatively, high turbidity at the mouths of the Jingu and Dafeng rivers may limit the primary productivity in the outer Qinzhou Bay and Sanniang Bay. The relatively low water column chlorophyll *a* concentration (< 2.0 μg/L) also suggests low primary productivity in Qinzhou Bay and Sanniang Bay (Liao et al., 2004; Yang et al., 2015). Another possibility is the preservation and degradation of OM during the process of transportation (Bao et al., 2016). The spatial variation patterns of the TOC and TN contents are similar to the tide direction in the outer Qinzhou Bay and Sanniang Bay (Zhang et al., 2011), which supports the idea that hydrodynamic processes play a critical role in the dispersal and distribution of sedimentary OM on the continental margins (Bao et al., 2016).

The coast of the Maowei Sea is lined by mangrove forests, and senescent mangrove leaves could contribute to the sedimentary OC pool. According to Meng et al. (2016), the TOC content and C/N ratio of senescent mangrove leaves can be as high as 44.2% and 37.4%, respectively. Consequently, mangrove leaves may contribute to the high TOC values observed in the Maowei Sea sediments. In contrast, low TOC values suggest that the outer part of Qinzhou Bay and Sanniang Bay do not receive a significant input of mangrove-derived OM. This may be because the Maowei Sea is connected to Qinzhou Bay just through a narrow channel, which limits water exchange between the Maowei Sea and the outer part of Qinzhou Bay (Meng et al., 2016). Without significant input from coastal mangrove forests, the spatial distributions of TOC in the Qinzhou Bay and Sanniang Bay show the

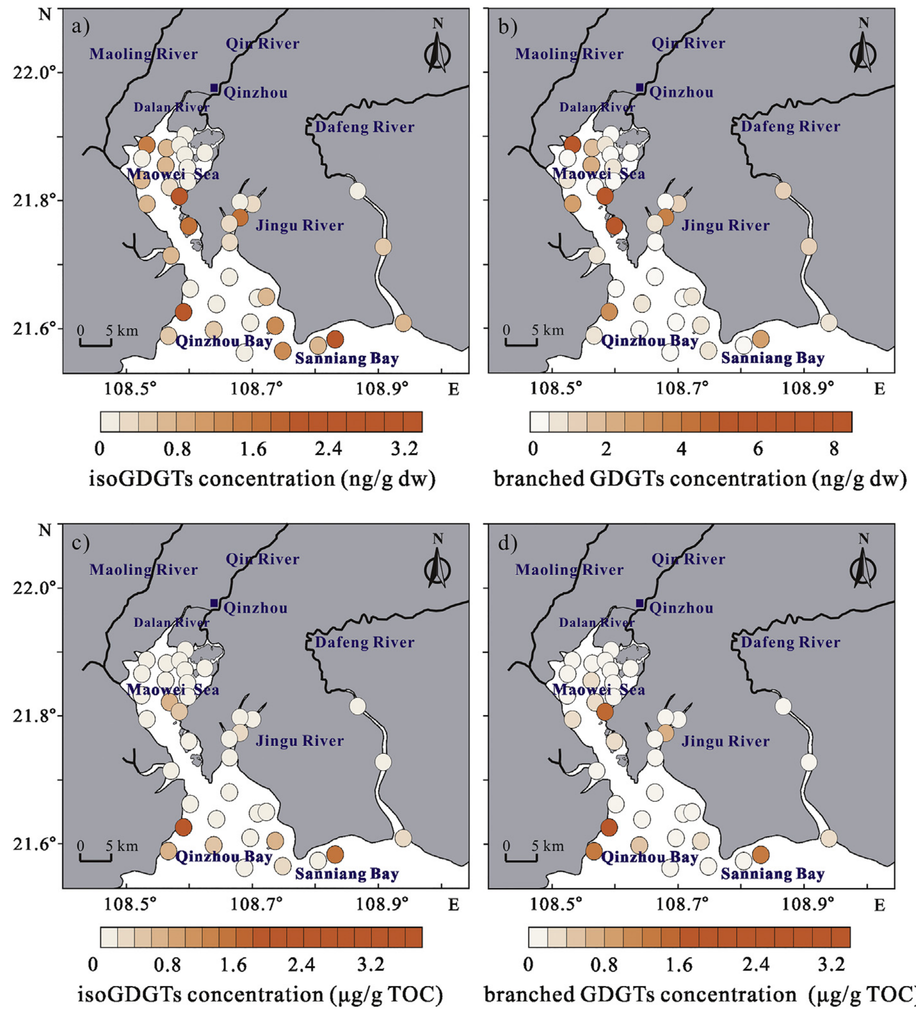

Fig. 3. The spatial variation in a) isoprenoid GDGTs (ng/g dw), b) branched GDGTs (ng/g dw), c) isoprenoid GDGTs (μg/g TOC), and d) branched GDGTs (μg/g TOC) in surface sediments in the Beibu Gulf, China.

similar patterns as those in the Pearl River estuary, which decreased seaward (Hu et al., 2006).

4.2. Implications of C/N ratios and $\delta^{13}C_{org}$ values

The C/N ratio of degraded marine phytoplankton is generally close to 6–7 (Meyers, 1994; Hedges and Oades, 1997), while the widespread vascular plants around the Beibu Gulf, Eucalyptus, have C/N ratios

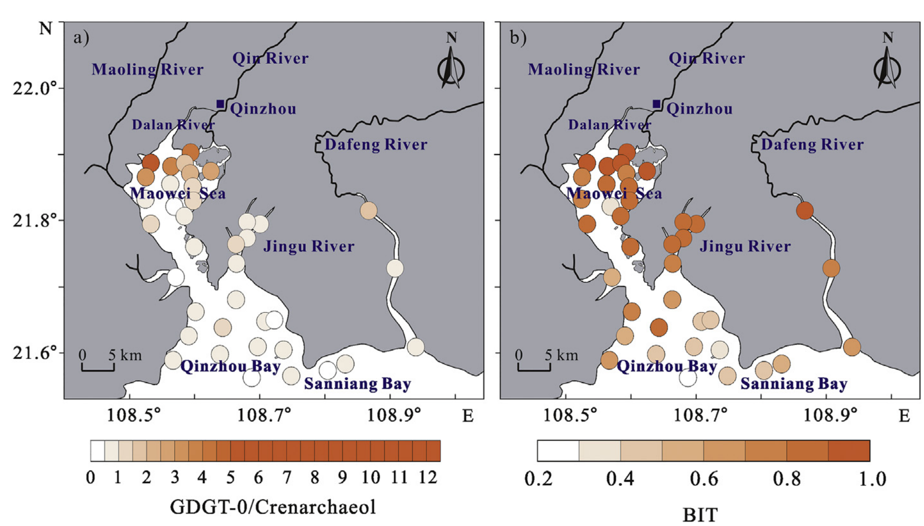

Fig. 4. The spatial variation in a) GDGT-0/Crenarchaeol ratios and b) the BIT index in surface sediments in the Beibu Gulf, China.

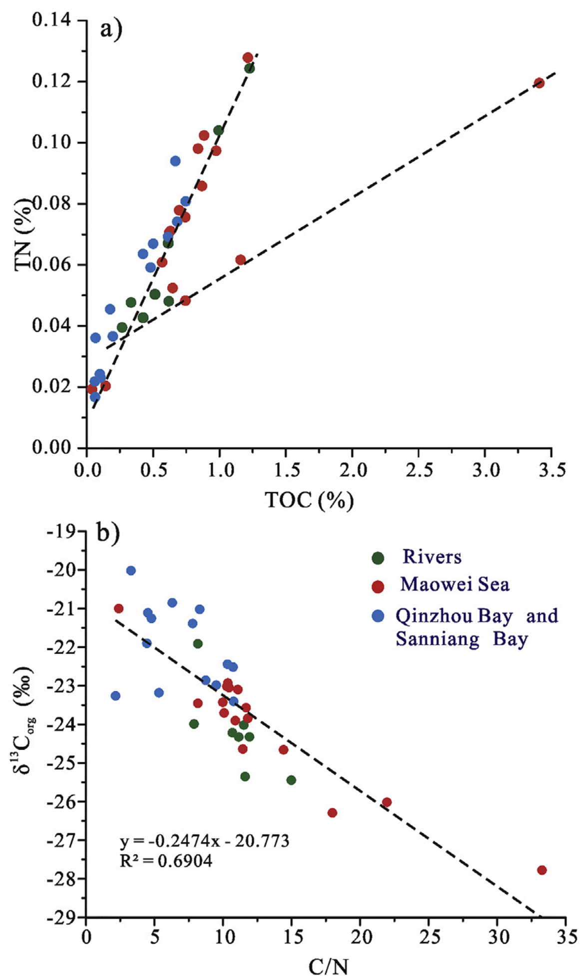

Fig. 5. Correlation between a) TOC and TN and b) $\delta^{13}C_{org}$ and C/N in surface sediments in the Beibu Gulf, China.

around 36 (Kaiser et al., 2014). The C/N ratios range from 2.2 to 33.3 in the Beibu Gulf, which are mainly between the value of marine phytoplankton and vascular plants. Similarly, the measured $\delta^{13}C_{org}$ values range from −27.8 to −20.0‰ in the Beibu Gulf, which overlap with the values seen in terrestrial C_3 plants (−33 to −22‰; Bender, 1971) and marine phytoplankton (−23 to −17‰; Bouillon et al., 2008). Therefore, the range of C/N ratios and $\delta^{13}C_{org}$ values suggest that the OM is derived from both marine and terrestrial sources in the Beibu Gulf sediments (Fig. 2c and d).

The C/N ratios in the Maowei Sea and the tributary rivers are mostly fall in the range of 7–12 (Fig. 2c). Meanwhile, the soil microbes have C/N ratios of 5–15 (Hedges and Oades, 1997), which suggests that the sedimentary OC in the Maowei Sea might also be derived from soil. As the fine fraction of soil could deposit close to the river mouth, the sedimentary OC in the Maowei Sea might contain significant amount of soil OC. Furthermore, the plot of the TOC and TN contents indicates that several samples in the Maowei Sea result in a line that intersects at 0.03 of N and zero values of OC (Fig. 5a), suggesting that these samples contain significant amounts of inorganic nitrogen (presumably as NH_4^+ adsorbed on clays, Meyers, 1997). Since the inorganic nitrogen is usually associated with fine-grained soil, the relatively high inorganic nitrogen in the Maowei Sea indicates the input of soil OC.

The $\delta^{13}C_{org}$ values of sediments in the Qin River and Maoling River are −23.6‰ and −24.8‰ on average, respectively (Meng et al., 2016), While the average $\delta^{13}C_{org}$ value of sediments in the Maowei Sea is −24.0‰, which is the same as the $\delta^{13}C_{org}$ value of soil OM close to the Nanliu systems (Kaiser et al., 2014). Therefore, the C/N ratios and the $\delta^{13}C_{org}$ values reflect relatively higher contribution of soil OM in the Maowei Sea.

As the Beibu Gulf is undergoing rapid economic development, sewage derived from human activities should be considered as a third source of organic material. The C/N ratio of sewage-derived suspended particulate matter (SPM) is higher than 11 (Thornton and McManus, 1994; Andrews et al., 1998). However, the C/N ratio in the sample taken close to the outlet of the waste water treatment plant (WWTP) in the Qin River is 10.1, suggesting limited influence from sewage in the river. Moreover, the average C/N ratio in sediments taken from the Qin River is 14.1 (Meng et al., 2016), indicating little contribution of sewage-derived SPM from the WWTP. The $\delta^{13}C_{org}$ values of sewage range from −28 and −23‰ (Andrews et al., 1998), within the range of $\delta^{13}C_{org}$ values observed in the Beibu Gulf. However, the $\delta^{13}C_{org}$ value at site near the sewage treatment discharge outlet (e.g., the mouth of the Qin River) is −23.8‰, which is similar to those seen elsewhere in the gulf (avg. −23.3‰). Thus, the C/N ratio and the $\delta^{13}C_{org}$ values are not good tracers for sewage influence in the Maowei Sea systems.

As shown in Fig. 2c and d, the C/N ratios are higher and $\delta^{13}C_{org}$ values are more negative in the Maowei Sea (average 12.9‰ and −24.0‰) relative to the outer Qinzhou Bay and Sanniang Bay (average 6.9‰ and −22.0‰), indicating that the proportion of terrigenous OM relative to marine OM decreases seaward. The most negative $\delta^{13}C_{org}$ value and highest C/N ratio are found in the Maowei Sea. Furthermore, C/N ratios are higher and the $\delta^{13}C_{org}$ values are more negative along the coastline of the Maowei Sea than those in the neighboring rivers (avg. 11.4 and −24.8‰, Meng et al., 2016), suggesting that OM in the Maowei Sea is not solely derived from terrestrial OM delivered via rivers, but also an additional OM source with higher C/N ratio and more negative $\delta^{13}C_{org}$ value. As discussed above, mangrove leaves likely contribute OM to the sediment in the Maowei Sea, since the $\delta^{13}C_{org}$ values of mangrove leaves are very negative (−30.0‰, Meng et al., 2016) and C/N ratios are high (37.4, Meng et al., 2016). Thus, given the distribution of mangrove forests around the Maowei Sea (Fig. 1), mangrove leaves could potentially be the source of depleted $^{13}C_{org}$ along the coastline of the Maowei Sea. The $\delta^{13}C_{org}$ values are relatively positive in the center of the Maowei Sea, likely due to enhanced marine primary production (Liao et al., 2004). In summary, the C/N ratios and $\delta^{13}C_{org}$ values indicate that the sedimentary OM is mixtures of terrestrial plant, soil, and marine OM. The terrestrial OM contribution decreases seaward. Moreover, the mangrove leaves contribute to the sedimentary OM in the coast of the Maowei Sea.

The $\delta^{13}C_{org}$ values are more positive (mean: −22.0‰) and the C/N ratios are lower (mean: 6.9) in the outer Qinzhou Bay and Sanniang Bay (Fig. 2d), indicating a greater proportional contribution of marine OM compared to the Maowei Sea and the tributary rivers. Also, the $\delta^{13}C_{org}$ values along the coastline of the outer Qinzhou Bay are similar, suggesting that the transport of OM by tides and waves shows similar influences on the preservation of marine and terrestrial OM. In other words, sedimentary OM is not substantially influenced by the terrestrial OM flux in the outer part of Qinzhou Bay and Sanniang Bay.

As shown in Fig. 5b, the $\delta^{13}C_{org}$ values and C/N ratios of sedimentary OM exhibit a strong correlation in the Beibu Gulf, which indicates that the sedimentary OM in the Beibu Gulf was hardly altered by the postdepositional processes, or the presence of little inorganic nitrogen in the sediment. The correlation is different in different regions. For example, the $\delta^{13}C_{org}$ and C/N ratios vary at a wide range and fluctuate close to the correlation line in the Maowei Sea. The higher C/N ratios as well as the lower $\delta^{13}C_{org}$ values indicate the local input of plant detritus, especially the input of mangrove leaves. Moreover, the correlation of samples from the Qinzhou Bay and Sanniang Bay show a broad scatter, suggesting that the degradation of OC in these regions is relatively obvious. This can be explained by the resuspension of sediments due to the strong current and wave toward the open sea.

4.3. $\delta^{15}N$ values and their implications

The spatial distribution of $\delta^{15}N$ displays an interesting pattern in the Beibu Gulf (Fig. 2e). In general, $\delta^{15}N$ values are more positive at the river mouths. Sedimentary $\delta^{15}N$ values are highly variable in the Maowei Sea, with the most negative $\delta^{15}N$ value (0.8‰) and most positive $\delta^{15}N$ value (9.0‰) both occurring in this part of the gulf.

Various N sources have distinct ranges of $\delta^{15}N$ values. For example, the $\delta^{15}N$ values of OM derived from marine phytoplankton (which grow via marine nitrate uptake) range from 5.0 to 7.0‰ (Brandes and Devol, 2002; Lamb et al., 2006). The nitrate delivered from agricultural runoff and human sewage is enriched in ^{15}N, with $\delta^{15}N$ values ranging from 10 to 25‰ (Kendall, 1998). The typical $\delta^{15}N$ values of terrestrial vascular plants range from −5 to +18‰ with an average value of ~3‰ (Wada and Hattori, 1991). The $\delta^{15}N$ values near the Maoling River mouth are lower than the ranges of $\delta^{15}N$ values of marine phytoplankton and sewage, indicating the terrestrial input from the River. However, this is complicated by the input of wastewater from Qinzhou City to the Qin River, which ultimately discharges into the Maowei Sea. Nitrogen from urban sewage and aquaculture pollute the semi-enclosed Maowei Sea, yielding relatively high $\delta^{15}N$ values (10–22‰) (Cole et al., 2004). Thus, our most positive observed $\delta^{15}N$ value (9.0‰) reflects the impact of anthropogenic nitrogen pollution in the Maowei Sea. Previous research found that eutrophication indeed caused high $\delta^{15}N$ values near a river mouth (Voβ and Struck, 1997). Therefore, the high $\delta^{15}N$ can be used as a good tracer for the anthropogenic impact in the Maowei Sea systems.

Measured $\delta^{15}N$ values range from 1.2 to 6.3‰, with most values between 4‰ and 5‰ in the outer part of Qinzhou Bay (Fig. 2e). These values are lower than the expected $\delta^{15}N$ values of OM derived from marine nitrate (5–6‰). Specifically, the lowest $\delta^{15}N$ value is 1.2‰, indicating some contribution by nitrogen-fixing phytoplankton. The phosphate in the Beibu Gulf mostly comes from the river input and the nitrogen comes from both river input and coastal current along the Guangxi coast (Ma et al., 2013). The phytoplankton utilizes phosphate in the Maowei Sea, which lead to the depletion of P in the Qinzhou Bay, and a transition from N to P limitation (Ma et al., 2013). Incomplete utilization of nitrate due to a transition from N to P limitation might also explain the relatively low $\delta^{15}N$ values in the outer part of Qinzhou Bay.

The $\delta^{15}N$ values (6.5–7.6‰) in the Sanniang Bay are within the typical range for OM produced from assimilation of the marine nitrate pool (Brandes and Devol, 2002; Lamb et al., 2006), suggesting no significant anthropogenic nitrogen pollution in this part of the gulf. In addition, these values are in agreement with the $\delta^{15}N$ values (6.1‰) of POC in the Beibu Gulf (He et al., 2014).

4.4. Signatures of GDGTs

Isoprenoid GDGTs in marine sediments originate mainly from Archaea, one of the dominant prokaryote groups in modern oceans (Herndl et al., 2005). Crenarchaeol is an isoprenoid GDGT derived from marine Thaumarchaeota (Hopmans et al., 2004; Pearson et al., 2004; de la Torre et al., 2008), while GDGT-0 can be produced in large amount by methanogenic archaea (Pancost et al., 2001; Villanueva et al., 2014). It has been suggested that a GDGT-0/Crenarchaeol ratio > 2 indicates substantial methanogenesis in the sediments (Blaga et al., 2009). In the Qinzhou Bay and Sanniang Bay, GDGT-0/Crenarchaeol ratios are uniformly < 2, indicating that GDGT-0 is not primarily derived from methanogen biomass. However, in the northern Maowei Sea, GDGT-0/Crenarchaeol ratios are > 2 (maximum = 12.2; Fig. 4a). Such high ratios indicate a substantial methanogenic component of GDGT-0 in the northern Maowei Sea, and suggest extensive sedimentary methanogenesis (Inglis et al., 2015). GDGT-0 is produced in high abundances by methanogenic archaea, and is thus a useful proxy for hypoxia, which is a common effect of anthropogenic nitrogen input (Lopes dos Santos and Vane, 2016). These results are in agreement with the highly positive $\delta^{15}N$ values of the same samples, indicative of an anthropogenic nitrogen input (Vizzini and Mazzola, 2004). Both GDGT-0/Crenarchaeol ratios and $\delta^{15}N$ values suggest that there is a substantial anthropogenic impact on the ecology in the Maowei Sea.

Branched GDGTs occur ubiquitously in soils and peat worldwide (Weijers et al., 2006), and thus represent soil OM input to marine systems (Fietz et al., 2011). However, marine *in situ* production of branched GDGTs has been observed in recent studies (Zhu et al., 2011; Hu et al., 2012; Weijers et al., 2014; Zhou et al., 2014), raising concerns about the applicability of BIT as a terrigenous proxy. Sinninghe Damsté (2016) proposed the $\#rings_{tetra}$ value to distinguished soil-derived brGDGTs and *in situ* produced brGDGTs. In our study, the $\#rings_{tetra}$ values are all lower than 0.7, indicating that the brGDGTs are mostly derived from soil erosion. Meanwhile, weak correlation between brGDGTs and crenarchaeol concentrations ($r^2 = 0.31$), suggesting that brGDGTs and crenarchaeol come from different sources, that is to say, insignificant *in situ* production of brGDGTs in the estuarine systems. Furthermore, the averaged MAT reconstructed by MBT and CBT proxies is 18.6 °C, which is close to the measured MAT (22.0 °C) in the Qinzhou weather station. Thus, the brGDGTs are mostly derived from soil in the study area.

The high concentration of branched GDGTs in the Maowei Sea suggests a major influx of soil OM, which then decreases in the seaward direction toward outer Qinzhou Bay. Moreover, the composition of branched GDGTs in the Maowei Sea is similar to that seen in the outer Qinzhou Bay and in Sanniang Bay, indicating that the branched GDGTs derive from the same source(s).

The branched/isoprenoid tetraether (BIT) index is based on the relative abundance of branched GDGTs and crenarchaeol, representing soil OM and aquatic OM, respectively (Hopmans et al., 2004). BIT indices decreased from the Maowei Sea to the outer Qinzhou Bay, and from the tributary rivers to the sea (Fig. 4b). BIT indices, representing the proportion of branched GDGTs, are relatively high in the Maowei Sea, with the exception of the central part. This suggests that soil OM is mainly deposited along the coasts. In the outer Qinzhou Bay, BIT indices decrease in the seaward direction, indicating that soil OM in the Qinzhou Bay is mainly delivered via riverine transport. A decrease in BIT indices from the Dafeng River to Sanniang Bay is also observed, indicating that soil OM in the Sanniang Bay is mostly derived from the Dafeng River.

4.5. Quantification of different OC sources

It has been suggested that continental margins account for over 90% of total organic carbon (OC) burial in the ocean (Berner, 1982; Hedges and Keil, 1995). In order to improve the estimates of OC sources in the Beibu Gulf, a rapidly developing subtropical region, we quantified the relative proportion of terrestrial soil OC, plant OC, and marine OC in the total OC pool. This has important implications for understanding global coastal carbon budgets (Cui et al., 2016). The relative proportions of terrestrial soil OC (OC_{soil}), plant OC (OC_{plant}), and marine OC (OC_{mar}) present in the sediment are estimated using the three-end-member mixing model. Since the C/N ratio is affected by degradation and/or absorption of inorganic nitrogen, we used the BIT index and the $\delta^{13}C_{org}$ in the three-end-member model, similar to that described by Weijers et al. [2009]. The two equations on which the three-end-member mixing model was based are as following:

$$BIT_{Sample} = (BIT_{Mar} \times f_{Mar}) + (BIT_{Soil} \times f_{Soil})$$

$$\delta^{13}C_{Sample} = (\delta^{13}C_{Mar} \times f_{Mar}) + (\delta^{13}C_{Soil} \times f_{Soil}) + (\delta^{13}C_{Plant} \times f_{Plant})$$

With the additional mass balance equation of:

$$f_{Mar} + f_{Soil} + f_{Plant} = 1$$

where the f_{Mar}, f_{Soil}, and f_{Plant} are the fractions of marine, soil, and plant OC, respectively.

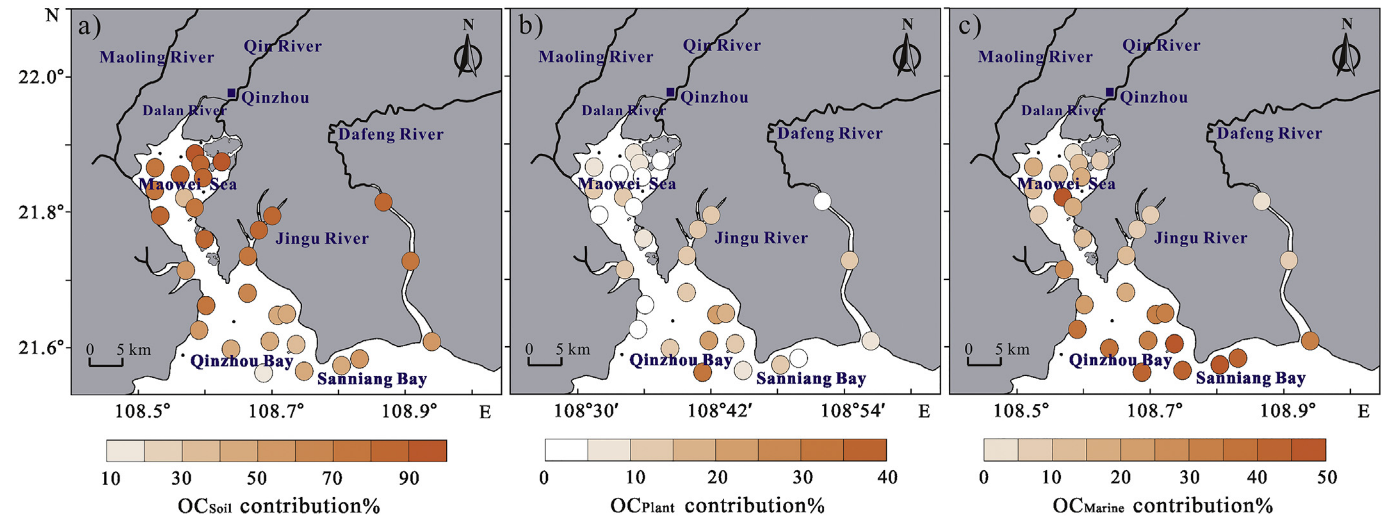

Fig. 6. The spatial distibution of the relative proportion of a) OC_{soil}, b) OC_{plant} and c) OC_{marine} based on the three-end-member mixing model in surface sediments in the Beibu Gulf, China.

For the marine end-member, the average $\delta^{13}C$ value of phytoplankton in the Beibu Gulf is −16.1‰ (Yang et al., 2013; Meng et al., 2016). Due to the lack of $\delta^{13}C$ value for the soil end-member around the Beibu Gulf, we choose the average $\delta^{13}C$ value of soil (−24‰) in the nearby Nanliu River drainage area as the soil end-member value (Kaiser et al., 2014). For the plant end-member, the average $\delta^{13}C$ value (−30.7‰) of the most widespread plant (Eucalyptus) in the drainage area is chosen (Kaiser et al., 2014). The BIT index of marine phytoplankton and plant are 0 (Hopmans et al., 2004), while the BIT index of soil is 1 (Hopmans et al., 2004; Yang et al., 2014).

Before starting to calculate the contribution of different sources of OC, some exceptional samples need to be rule out, as the end-member values might be inappropriate for them. For example, the samples located near the mangrove area in the Maowei Sea are influenced strongly by the input of mangrove soil, which has an average $\delta^{13}C$ value of −26.5‰ (Kaiser et al., 2014). Thus, the soil end-member $\delta^{13}C$ value of −24.2‰ is not applicable to them. For the samples in the Qinzhou Bay which have $\#rings_{tetra} > 0.5$, the *in situ* brGDGTs is not negligible. Thus, the use of marine end-member BIT value of 0 will overestimate the soil OC contribution for these samples. So, six samples in the Maowei Sea and two samples in the Qinzhou Bay are ruled out.

The calculated f_{soil}, f_{plant}, and f_{marine} ranges from 19% to 95%, 0% to 39%, and 0% to 48%, respectively, based on the three-end-member mixing model (Fig. 6). The OC_{soil} mainly deposits in the Maowei Sea, Jingu River and Dafeng River, and decreases seaward, indicating that the OC_{soil} mainly comes from river delivery. The OC_{marine} mostly deposits in the Qinzhou Bay and the central Maowei Sea, where the influence of river and wave-tide is less. The contribution of OC_{plant} is relatively low, which is < 20% in the Maowei Sea and rivers (Fig. 6b). The highest OC_{plant} contribution occurs in the Qinzhou Bay. The different spatial pattern of OC_{soil} and OC_{plant} could be explained by the difference of their transportation and preservation processes. In the study area, 80% of rainfall happens in the summer season, the intact and detrital plants are transported far away from the river mouth by the rain floods and are deposited in the Qinzhou Bay. In contrast, the more gradual upland flow of soil erosion and riverine input allow the accumulation of OC_{soil} in the shallower regions near the river mouths, like the Maowei Sea. This phenomenon was also observed in other estuarine systems (Smith et al., 2010; Strong et al., 2012). Therefore, the soil OM is an important contributor to the subtropical continental margin (Holtvoeth et al., 2005), which mainly deposits close to the river mouths. These findings have important implications for terrestrial OC burial in subtropical coastal regions under the influence of small rivers and mangrove forests.

5. Conclusions

Patterns of TOC and TN concentrations, $\delta^{13}C_{org}$ and $\delta^{15}N$ isotope ratios, and the BIT index in sediments allow us to trace the sources of OM in the Beibu Gulf, China. The results show that:

1) Terrestrial OM flux decreases from the Maowei Sea to outer Qinzhou Bay, and also from the inflowing rivers to the outer Beibu Gulf, suggesting that terrigenous OC input is restricted to coastal regions.
2) The three-end-member model shows that soil OC contributes significantly in the sedimentary OC pool in the northern Beibu Gulf and mainly deposits in the Maowei Sea and tributary rivers.
3) The increasing $\delta^{15}N$ values and high GDGT-0/Crenarchaeol ratios in sediments adjacent to mangrove forest in the Maowei Sea indicate the increasing contribution of anthropogenic nitrogen and influence from human impacted on the Beibu Gulf, China.

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