



Spatiotemporal variations of biogenic elements and sources of sedimentary organic matter in the largest oyster mariculture bay (Maowei Sea), Southwest China

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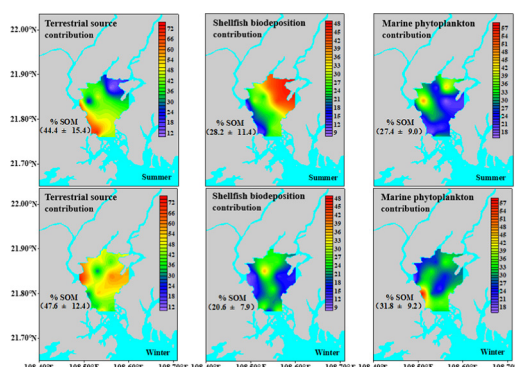
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HIGHLIGHTS

- TOC, TN and BSi relates to SOM sources, sediment texture and hydrodynamics.
- SOM is mostly dominated by terrestrial source in the Maowei Sea.
- SOM from marine phytoplankton generally exceeds that of shellfish mariculture.
- SOM from shellfish biodeposits is significantly impacted by seasons.
- More shellfish biodepositions are found in the intensive mariculture regions.

GRAPHICAL ABSTRACT



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ABSTRACT

China is the largest mariculture producer in the world, but detailed information on the spatiotemporal variations of biogenic elements and sources of sedimentary organic matter (SOM) via mariculture is limited. The primary objective of this study was to assess the influence of mariculture on the origin of SOM in relation with biogenic elements and geochemical parameters due to the importance of SOM as a potential source of nutrients and energy in coastal marine environments. Surface sediments from the Maowei Sea were collected in August (summer) and December (winter), 2016 for grain size, total organic carbon (TOC), total nitrogen (TN), organic phosphorus (OP), biogenic silica (BSi), $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ analyses. Significant correlation ($p < 0.01$) was observed between TOC and TN in summer and winter respectively, indicating that they have common source in both seasons. The spatiotemporal distributions of TOC, TN, OP and BSi were influenced by the sources and distribution of SOM, grain sizes and hydrodynamic conditions in the Maowei Sea. The overall ranges of $\delta^{13}\text{C}$ (-26.86% to -23.01%) and $\delta^{15}\text{N}$ (2.54% to 9.82%) and C/N ratio (5.83 to 18.67) showed that SOM is derived from mixed sources. The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ -based three-end-member mixing model results revealed that $>40\%$ of the deposited SOM originates from terrestrial source during two seasons. The SOM from shellfish mariculture was seasonal, mainly

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deposited in the intensive mariculture areas, and its proportions were only higher than contributions from marine plankton in summer. Generally, this study indicates that shellfish biodepositions can significantly influence the cycle of carbon and other biogenic elements in the intensive mariculture areas. Nevertheless, the overall dominance of terrestrial and marine SOM suggests that the sources of SOM and factors influencing carbon cycling in the Maowei Sea do not exclusively depend on the intensity of mariculture activities.

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1. Introduction

Continental shelves and coastal areas are among the most productive and exploited waters around the world. These coastal marine environments play significant roles in carbon cycle through the coupling of terrestrial, oceanic and atmospheric carbon reservoirs (Bianchi and Allison, 2009; Bauer et al., 2013). Marine sediments serve as the ultimate sink for sedimentary organic matter (SOM), sequestering carbon on a geologic time scale (Dickens et al., 2004). The SOM in these environments is composed of sinking particulate and colloidal materials originating from terrestrial or marine sources. Intense anthropogenic activities such as agriculture and aquaculture activities, including biological processing of SOM through bioturbation and remineralization (Gireeshkumar et al., 2013; Yang et al., 2015a; Gu et al., 2017) can affect the contents and distribution SOM. Moreover, hydrodynamics can induce deposition, resuspension and redistribution of fine-grained sediments (FGS), which plays important role in the preservation of SOM (Hu et al., 2006; Zhu et al., 2008). In addition, seasonal variations in marine primary productivity (Kubo and Kanda, 2017; Zhou et al., 2018) and riverine discharge may potentially affect the contents and distribution of SOM in coastal environments. Therefore, knowledge of the sources and factors influencing the distribution of SOM is necessary for understanding the global biogeochemical cycling of carbon and other biogenic elements, and also essential due to the importance of SOM as nutrient and energy sources which may ultimately influence carbon cycle in marine environments.

Stable carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) isotopes are widely used to trace and discriminate SOM from various sources including those from terrestrial and marine origins. The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ isotopic signatures can also be used to evaluate the mixing and transformation of SOM in different aquatic settings based on the distinct signatures of the sources (Guo and Macdonald, 2006; Ramaswamy et al., 2008; Liu et al., 2015; Dan et al., 2019). Generally, terrestrial organic matter (TOM) has depleted $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ isotopic values when compared to marine organic matter (MOM) (Lamb et al., 2006). Isotopic fractionation frequently occurring as a result of biological, physical and/or chemical processes during post deposition of organic matter (OM) can aid the understanding of the fate of SOM in marine environments because the enrichment of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ isotopic values may possibly result from the preferential degradation of $^{13}\text{C}/^{15}\text{N}$ -depleted compounds by bacteria (Lehmann et al., 2002; Middelburg and Herman, 2007). Thus, the application of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ isotopes together with the elemental carbon to nitrogen (C/N) ratios can improve the accuracy of source identification, due to the complex nature of SOM (Middelburg and Herman, 2007; Cai et al., 2015). Moreover, mapping of the geographical distributions of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ isotopic values can help validate the specific sources of SOM in coastal marine systems (Hu et al., 2006; Liu et al., 2015; Dan et al., 2019). Therefore, these methods were applied in studying the sources and distribution of SOM in a complex, highly changeable mariculture environment.

China is the largest mariculture producer in the world, with an annual production of >17 million tons (Mt) of shellfish and seaweed mariculture (MOAC, 2017). As one of the most significant anthropogenic activities in coastal regions, aquaculture can significantly influence carbon cycle, as well as the function, evolution, and structure of coastal ecosystem (Zhang et al., 2017). Loss of $3.79 \pm 0.37 \text{ Mt} \cdot \text{yr}^{-1}$ of carbon through photosynthetic and calcification processes, and 1.20 ± 0.11

Mt. yr^{-1} of carbon due to seaweed and shellfish mariculture have been reported for coastal ecosystems in China (Tang et al., 2011). Mariculture activities in China are implemented in shallow coastal regions, such as the Zhanjiang Bay and Sanggou Bay (Hu et al., 2013; Xia et al., 2019). The biodeposit excrement from fishes and shellfish mariculture, fish feed residues, and the dying off seaweed can increase SOM accumulation (Holmer et al., 2005; Ren et al., 2014; Yang et al., 2018a). Although the biological activity of the bivalves increases biodeposit sedimentation, the presence of bivalve themselves and cultivation structures favor sedimentation of fine-grain particulates by increasing turbulence and thus decreasing current speed. Therefore, understanding the sources of SOM in coastal mariculture bays play an important role in understanding the impact of the mariculture on the deposited SOM and carbon cycle (Yokoyama et al., 2006; Alongi et al., 2009; Zhang et al., 2009; Jiang et al., 2015; Gu et al., 2017; Zhang et al., 2017). The Maowei Sea, located in the southern Guangxi Province is a typical dense oyster (*Crassostrea hongkongensis*) seedling and mariculture areas for bivalve in China. Due to the importance of oyster seedling and mariculture for the local economy, the local government has no stringent regulations on mariculture activities, which have affected this coastal environment (Liao et al., 2018). Moreover, Maowei Sea is a typical tropical bay where high industrialization, urbanization and intense agriculture have simultaneously changed the marine ecological environment in recent years (Gu et al., 2015; Yang et al., 2017a; Zhang et al., 2019), which may result in complex SOM sources. However, lack of standard methods to quantify the sources of SOM in mariculture areas, especially in China, has been reported (Zhang et al., 2017). Nevertheless, there have been no previous studies to shed light on the discriminatory contributions of SOM from shellfish mariculture, terrestrial, marine sources in the study area, especially between the intensive mariculture area (IMA) and non-intensive mariculture area (NIMA), and between summer and winter seasons.

Study on the sources and composition of SOM may have important implications in the Maowei Sea, which is under the influence of many stressors including intense mariculture activities. Not only that it will contribute to the understanding of carbon cycle, but it is also important for the fact that SOM serves as sources of nutrient and energy in marine environments (Pancost and Boot, 2004; Moyer et al., 2013; Dan et al., 2019). The rationales for selecting the possible sources of SOM in the Maowei Sea, a typical intensive mariculture bay are as follows. First, Maowei Sea is relatively shallow. The flushing time is >40 days (Li et al., 2014), which is partly caused by the baggy bathymetry, the narrow channel linking the sea with Qinzhou Bay and suspended oyster rafts. Although partly dependent on the extent of post depositional processes affecting the SOM, it is apparent that the amount of SOM from terrestrial source in the sea would be relatively high due to lower biodegradability of terrestrial materials. Secondly, almost the entire Maowei Sea surface is covered by shellfish mariculture in the northern and southern regions. Because shellfish requires no additional feed and only depend on nutrients, phytoplankton and zooplanktons, we presume that the suspended shellfish culture may locally enhance the flux of OM to surface sediments through filter-feeding and subsequent deposition of faeces and pseudofaeces by the cultured organisms, which may account for SOM from shellfish mariculture. Thirdly, marine diatoms are the dominant primary producers in the Maowei Sea (Luo et al., 2019). Thus, even with the fact that planktons are the primary source of food for shellfish, they may account for the SOM sequestered

in the Maowei Sea, especially in less intensive mariculture areas. Therefore, the sources of SOM in surface sediments of the Maowei Sea could be divided into three bulk pools comprising of the terrestrial, marine and shellfish biodeposition sources.

To bridge the gaps in our understanding of the influence of mariculture activities and terrestrial inputs on biogenic elements cycling, the objectives of this study were to 1) characterize the spatiotemporal variations of biogenic elements and their relationship with bulk sediment textural characteristics, 2) examine the distributions of stable isotopic compositions, elemental ratios and their implications for tracing SOM sources, 3) apply a three end-member mixing model to provide estimates of SOM from terrestrial, marine and shellfish biodeposition sources, and 4) evaluate seasonal variability of SOM signatures and implications.

2. Materials and methods

2.1. Study area

The Maowei Sea, a semi-enclosed and shallow sea, covering an area of $\sim 135 \text{ km}^2$, with a water depth range of 0.1–5 m, is situated at the landward region of Qinzhou Bay, which connects to Beibu Gulf in the northwestern part of South China Sea (Fig. 1) (Yang et al., 2019a; Zhang et al., 2019). The mean annual rainfall in this region is 2140 mm of which 80–85% falls during the wet rainy season (May to September). An irregular diurnal tide is dominant in this region, with average tidal range of 2.5 m and maximum of 5.5 m (Meng et al., 2016; Chen et al., 2018). The weaker water exchange with Beibu Gulf is partly caused by the baggy geomorphology as well as the narrow outlet channel linking the Maowei Sea with Qinzhou Bay (Zhang et al., 2019). The surface water circulation in the Maowei Sea is anti-cyclonic, and the water current from Qinzhou Bay enters and exit from the eastern and western coastal areas, respectively (Yang et al., 2012). The Maowei Sea is also influenced by the major riverine inputs of the Maolingjiang River and Qinjiang River that annually discharges $27.73 \times 10^9 \text{ m}^3$ freshwater with accompanied 8.64×10^4 tons of suspended sediments supply into the sea (Wang et al., 2014a). Natural mangrove reserve wetlands occupy an area of $\sim 2784 \text{ hm}^2$ along the coastline of the Maowei Sea (Wang et al., 2017; Chen et al., 2018). Because of its unique ecological environment and resources of freshwater and saltwater, the Maowei Sea has been used for mariculture for over

50 years, and presently is the largest natural oyster spawning and breeding area ($\sim 2340 \text{ hm}^2$) in China (Gu et al., 2018; Yang et al., 2019a). Generally, the floating raft culture of *Crassostrea hongkongensis* represents unique mariculture modes that cover almost the whole sea surface. The oyster is usually cultivated between May and October, and harvested from November to April. In addition, the recovery period after oyster spawning is from July to October.

2.2. Sampling collection

According to the hydrological characteristics and different environmental functions in the Maowei Sea, surface sediment samples (0–5 cm) were collected from 15 stations during high tide within one day (Fig. 1) with a stainless-steel Peterson grab sampler (Volume: 3 L; Opening area: $10 \text{ cm} \times 20 \text{ cm}$) in August (summer) and December (winter) in 2016, respectively. Multiple samples were collected at each station in order to have sufficient samples and representative data for the research. Sampling stations 1–8 are located in the NIMA, while stations 9–15 are located in the IMA. Between these areas, station 9, 10 and 15 are located at different estuaries. Because nearly all of the SOM in coastal marine systems are derived from the sinking particulates from the water column, adequate amount of suspended particulate matter was collected below the raft cultures in the IMA regions. After collection, all samples were sealed in high-density polyethylene bags, and immediately placed in an insulation can filled with ice cubes ($< 4^\circ \text{C}$), and were transported to the laboratory and stored frozen at -20°C until further analysis. The sediment grain size, total organic carbon (TOC), organic phosphorus (OP), biogenic silica (BSi), $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ isotopes were measured in surface sediments for both summer and winter seasons sampling campaign in the Maowei Sea. The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values were also measured in the suspended sediment samples collected from the IMA regions, and only the average data, which were used for mariculture end-member are reported (Section 2.4 below).

2.3. Analytical methods

In the laboratory, surface sediment samples were freeze-dried and pre-treated with 10% H_2O_2 to remove organic matter for grain size measurement. The particles were further dispersed with 0.05% $(\text{NaPO}_3)_6$ solutions, and different grain sizes were measured with a laser particle

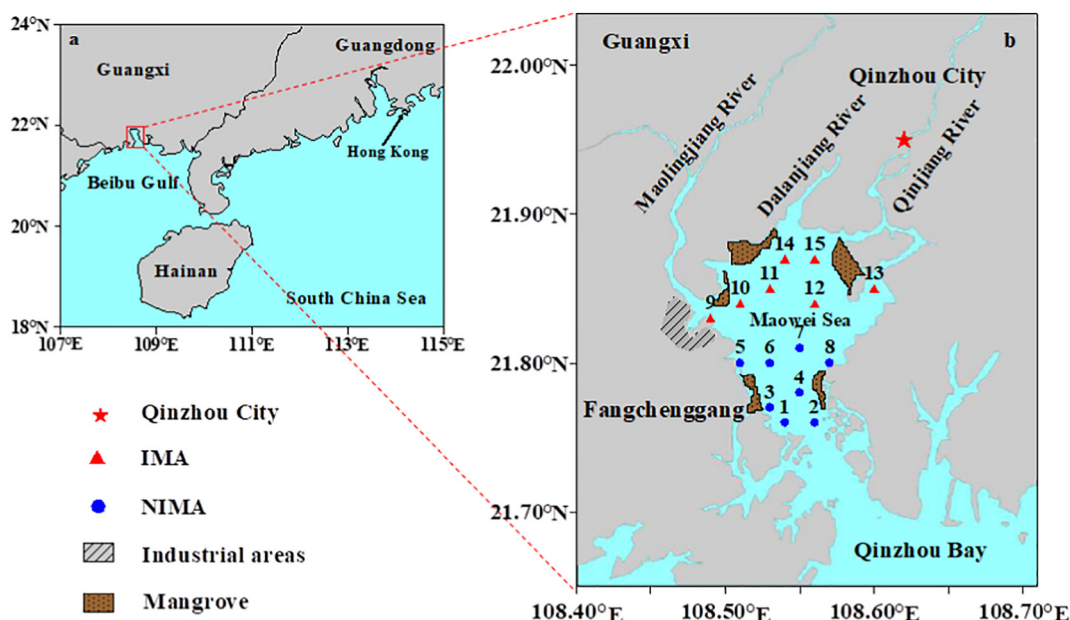


Fig. 1. Map of the Maowei Sea showing (a) the study location and (b) sampling stations.

size analyzer (Mastersizer 3000; Malvern Instruments Ltd., Worcestershire, UK), capable of analyzing grain sizes ranging from 0.02 to 2000 μm (Yang et al., 2018b). The analytical precision was <2%, and according to standard nomenclature, grain sizes were divided into FGS (<63 μm , including clay and silt) and sand (>63 μm) (Folk et al., 1970).

Aliquot freeze-dried samples were homogenized, ground and sieved through 200 mesh screen. About 2 g of each sub-sample was treated with 50 mL 1 M HCl for 24 h to remove inorganic carbon for the determination of TOC, while TN was measured in untreated sediment samples (Liu et al., 2015). Both the concentrations of TOC and TN were detected using a Vario EL-III CHNOS Elemental Analyzer. Based on duplicate measurements, the precision for the analysis of TOC was <6%, and 1.2% for TN (Yang et al., 2015a, 2017b). Measurements of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ isotopic values were carried out using the isotope ratio mass spectrometer (DELTA^{plus} XL). The results were expressed in parts per thousand (‰), calculated as follows:

$$\delta (\text{‰}) = (R_{\text{sample}} - R_{\text{reference}}) / R_{\text{reference}} \times 1000$$

where $\delta (\text{‰})$ denotes $\delta^{13}\text{C}$ (‰) and $\delta^{15}\text{N}$ (‰), while R_{sample} and $R_{\text{reference}}$ are the isotopic ratios of the sample and reference, respectively. The $\delta^{13}\text{C}$ was reported from the isotopic composition of the Pee Dee Belemnite (PDB) standard, while that of $\delta^{15}\text{N}$ was atmospheric air standard ($\delta^{15}\text{N} = 0\text{‰}$). The analytical precision was $\pm 0.2\text{‰}$ for $\delta^{13}\text{C}$ and $\pm 0.4\text{‰}$ for $\delta^{15}\text{N}$ ($n = 6$), based on analytical duplicates.

Exactly 0.2 g of sub sediment samples were extracted by applying the combined wet alkaline leaching method of DeMaster (1981) and Mortlock and Froelich (1989) for BSi analysis. The contents of BSi were expressed as weight percent as opal with assumed water content of approximately 10% (Liu et al., 2005; Dan et al., 2019), and the analytical precision was <2% based on duplicate analyses of the same sample (Yang et al., 2015a). Organic phosphorus (OP) was calculated as the difference between measurements of 1 M HCl extractable P for 24 h prior to and following the high temperature combustion of the sediments at 550 °C for 2 h (Aspila et al., 1976). The relative standard deviation was <3% based on replicate analyses of the same sample (Yang et al., 2016).

2.4. Relative proportions of SOM in the Maowei Sea

The different source proportions of SOM were estimated based on $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ three-end-member mixing model (Phillips, 2001; Dan et al., 2019) as follows:

$$\delta^{13}\text{C}_{\text{sample}} = (\delta^{13}\text{C}_{\text{ter}} \times f_{\text{ter}}) + (\delta^{13}\text{C}_{\text{mar}} \times f_{\text{mar}}) + (\delta^{13}\text{C}_{\text{bio}} \times f_{\text{bio}})$$

$$\delta^{15}\text{N}_{\text{sample}} = (\delta^{15}\text{N}_{\text{ter}} \times f_{\text{ter}}) + (\delta^{15}\text{N}_{\text{mar}} \times f_{\text{mar}}) + (\delta^{15}\text{N}_{\text{bio}} \times f_{\text{bio}})$$

$$f_{\text{ter}} + f_{\text{mar}} + f_{\text{bio}} = 1$$

where f_{ter} , f_{mar} and f_{bio} are the fractions for terrestrial, marine and shell-fish biodeposition sources relative to the total SOM. It is noteworthy

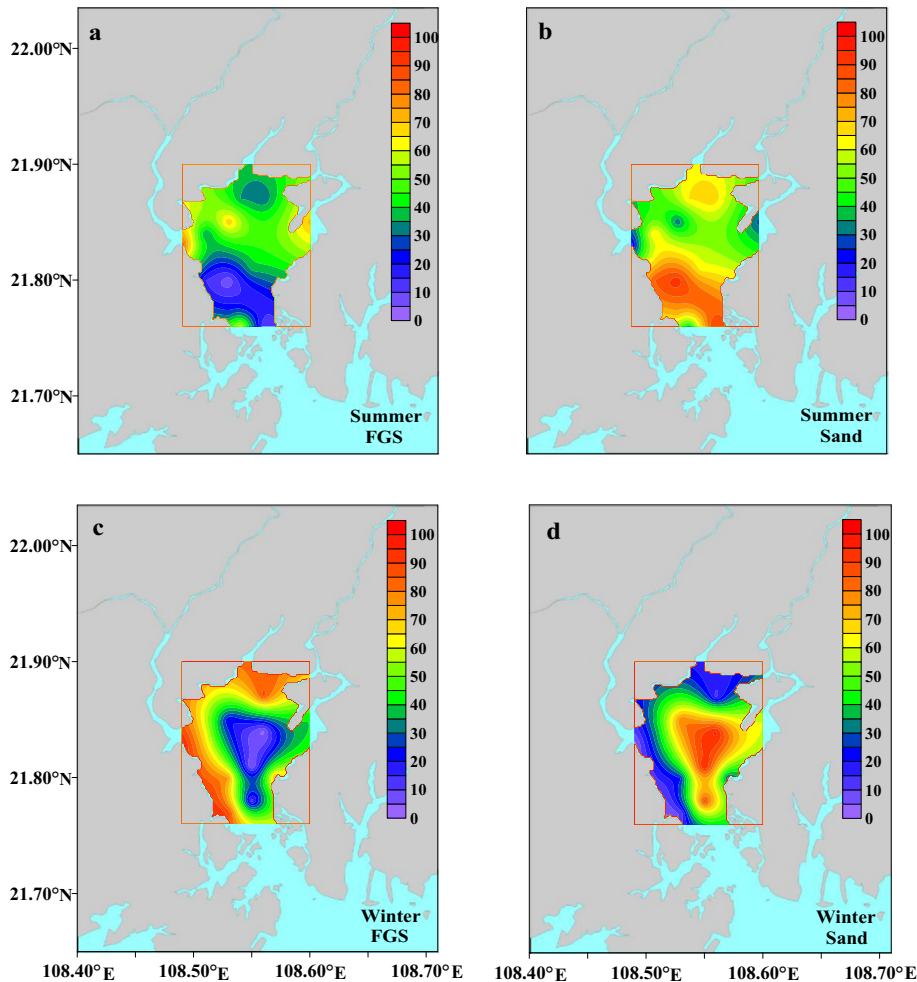


Fig. 2. Spatial distributions of FGS and sand fractions (unit: %) in the Maowei Sea during summer and winter seasons.

that isotopic fractionation may affect sources calculation. However, it should be noted that almost all of the SOM are derived from the sinking particulates from the water column. Although not reported in this study, the average $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of suspended particulate matter of near bottom water samples below the raft cultures in IMA were -20.5% and 6.5% , respectively, and were used as end-members representing shellfish biodeposition in this study. The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ isotopic values representing terrestrial end-member were -27.1% and 2.3% , respectively, while those for marine end-member were -23.1% and 4.2% , respectively. These values are within the SOM end-member range reported for terrestrial C_3 plants and marine plankton in coastal marine systems, and mariculture bays (Vizzini and Mazzola, 2006; Carlier et al., 2009; Guerra et al., 2013; Lamb et al., 2006; Gao et al., 2012; Zhao et al., 2019; Dan et al., 2019; Pan et al., 2019; Xia et al., 2019). The variation of the mean value for each end-member was $<0.3\%$ at almost all the investigated sites by randomly sampling each parameter value 5 times, ensuring the stability of our calculation.

2.5. Statistical analysis and graphing

In this study, Pearson correlation analysis was used to discuss the relationship between the measured parameters, and the interaction effect between seasons and mariculture activities on the measured variables was analyzed using a 2-way MANOVA. These programs were computed using SPSS version 22.0 (SPSS Inc., IBM, Armonk NY, USA). The bi-plots were created using Origin Pro 9 statistical software (OriginLab, USA), while the maps were produced using Surfer 12.0 (Golden Software, USA), and kriging method was used for creating contours.

3. Results and discussion

3.1. Sediment textural properties and biogenic elements

Sediment texture is among of the major factors influencing the geochemical behavior of biogenic elements in sedimentary environments (Badin et al., 2008; Martinez-Garcia et al., 2015). The distributions of

surface sediments textures in the Maowei Sea are shown in Fig. 2 (a–d), and detailed information about the sediment properties in the investigated sites have been previously reported (Yang et al., 2019b). Generally, the average proportion of sand in surface sediments was 17.3% higher in summer than in winter. Moreover, sediments in NIMA was coarser (average sand $\sim 74.1 \pm 17.3\%$) than in IMA (average sand $\sim 46.9 \pm 21.7\%$) in summer, while in winter, the surface sediments in NIMA were slightly finer (average FGS = $\sim 58.6 \pm 32.4\%$) than in IMA (average FGS = $\sim 52.9 \pm 33.6\%$). The distributions of sediment grain sizes appeared to be impacted by both seasons and mariculture activities. For example, previous studies have shown that $>80\%$ freshwater from the rivers draining into the Maowei Sea is annually discharged between April and September, while the remaining 20% is discharged between October and March (Meng et al., 2016). Apparently, most of the finer suspended particle, which eventually become deposited in sediments, can be delivered through riverine discharge. Additionally, the biodeposits of faecal pellets and pseudofaeces from intense shellfish cultures can increase the fine-grained texture of surface sediments (Franzo et al., 2014), especially in winter where the riverine freshwater discharge is low in the Maowei Sea. However, none of these factors had a significant impact on the distributions of sediment grain sizes during this study. This was supported by the 2-way MANOVA results which showed that the textural composition of surface sediments in the investigated sites was not impacted by seasons ($p = 0.114$) and mariculture ($p = 0.289$) (Table 5). Nevertheless, the observed differences in the distributions of sediment grain sizes may be attributed to other factors including hydrodynamic conditions in the Maowei Sea.

The contents of TOC ranged from 0.10% to 1.19% (average, $0.48 \pm 0.29\%$) in summer (Table 1; Fig. 3a), and 0.18–1.02% (average, $0.54 \pm 0.24\%$) in winter (Table 1; Fig. 3b). The TOC levels in the Maowei Sea was within the range reported for other coastal marine systems used for mariculture, such as the Zhelin Bay (Gu et al., 2017), Sanggou Bay (Xia et al., 2019) and Ailian Bay (Pan et al., 2019), but higher than those reported for systems with non-mariculture such as the Yellow River estuary and adjacent shelf (Liu et al., 2015) and East China Sea shelf in China (Zhou et al., 2018) (Table 2). The differences in the levels

Table 1
Composition of sedimentary organic matter parameters and grain size in the Maowei Sea during summer and winter seasons.

Season	Station	Longitude (°E)	Latitude (°N)	TOC (%)	TN (%)	C/N	$\delta^{13}\text{C}$ (‰)	$\delta^{15}\text{N}$ (‰)	BSi (%)	Clay (%)	Silt (%)	Sand (%)
Summer	1	108.54	21.76	0.49	0.06	9.53	−24.81	3.29	0.48	26.5	32.8	40.7
	2	108.56	21.76	0.16	0.01	18.67	−24.33	3.90	0.43	5.2	6.0	88.8
	3	108.53	21.77	0.48	0.03	18.67	−26.69	2.88	0.29	13.6	15.5	70.9
	4	108.55	21.78	0.26	0.02	15.17	−25.64	3.53	0.34	7.3	8.1	84.6
	5	108.51	21.80	0.15	0.02	8.75	−25.95	3.16	0.32	5.3	9.9	84.8
	6	108.53	21.80	0.10	0.02	5.83	−25.67	3.38	0.32	2.8	4.4	92.8
	7	108.55	21.81	0.35	0.03	13.61	−24.84	3.59	0.56	16.2	21.2	62.6
	8	108.57	21.80	0.45	0.04	13.13	−24.41	3.30	0.51	15.0	17.7	67.3
	9	108.49	21.83	1.19	0.10	13.88	−26.86	3.95	0.50	34.0	50.1	15.9
	10	108.51	21.84	0.49	0.05	11.43	−25.17	5.64	0.30	9.6	24.4	66.0
	11	108.53	21.85	0.89	0.08	12.98	−25.28	5.67	0.90	31.0	38.2	30.8
	12	108.56	21.84	0.63	0.06	12.25	−23.99	6.18	0.57	18.7	28.3	53.0
	13	108.60	21.85	0.70	0.08	10.21	−23.01	5.13	0.82	30.7	41.2	28.1
	14	108.54	21.87	0.50	0.04	14.58	−24.51	5.89	0.29	9.8	25.0	65.2
	15	108.56	21.87	0.41	0.04	11.96	−24.56	6.26	0.40	9.8	20.8	69.4
Winter	1	108.54	21.76	0.50	0.05	11.67	−24.91	4.99	0.38	8.1	64.2	27.7
	2	108.56	21.76	0.62	0.05	14.47	−24.28	4.02	0.40	7.9	52.2	39.9
	3	108.53	21.77	0.60	0.05	14.00	−24.23	3.59	0.39	13.6	74.7	11.7
	4	108.55	21.78	0.24	0.03	9.33	−24.58	9.23	0.25	1.4	10.6	88.0
	5	108.51	21.80	0.58	0.05	13.53	−24.68	2.54	0.44	13.4	71.2	15.4
	6	108.53	21.80	0.42	0.04	12.25	−24.73	5.12	0.27	9.7	65.3	25.0
	7	108.55	21.81	0.18	0.02	10.50	−25.08	8.85	0.36	0.6	3.4	96.0
	8	108.57	21.80	0.42	0.04	12.25	−24.59	3.45	0.32	15.4	56.9	27.7
	9	108.49	21.83	0.90	0.08	13.13	−26.51	2.55	0.53	12.3	84.4	3.3
	10	108.51	21.84	1.02	0.07	17.00	−25.54	3.07	0.25	5.4	57.3	37.3
	11	108.53	21.85	0.68	0.08	9.92	−23.67	9.62	0.31	3.4	17.0	79.6
	12	108.56	21.84	0.24	0.02	14.00	−25.63	9.82	0.25	0.4	3.5	96.1
	13	108.60	21.85	0.36	0.03	14.00	−25.33	3.88	0.31	6.5	33.9	59.6
	14	108.54	21.87	0.55	0.04	16.04	−25.28	3.65	0.30	9.8	50.2	40.0
	15	108.56	21.87	0.74	0.06	14.39	−23.72	3.41	0.36	15.4	70.7	13.9

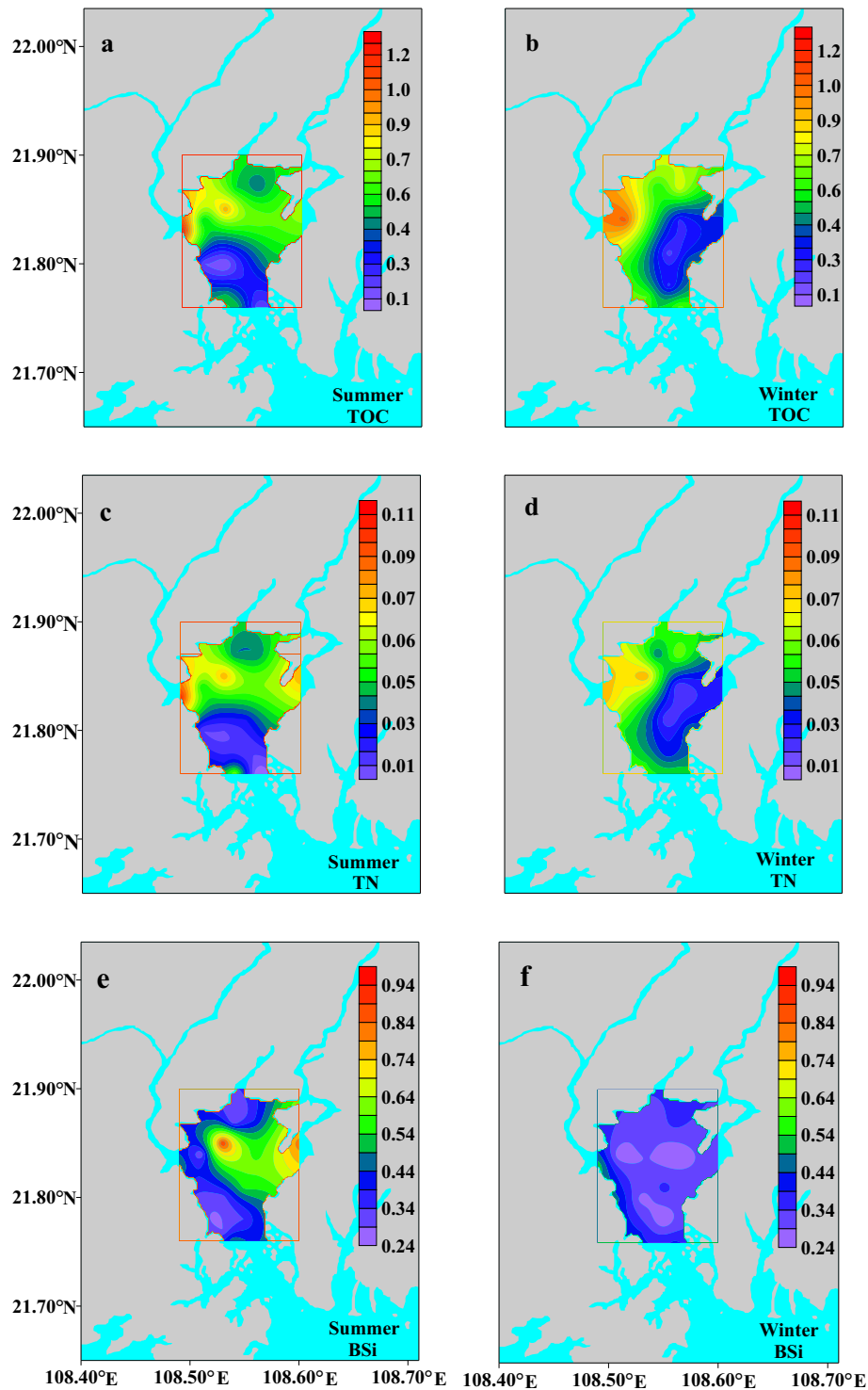


Fig. 3. Spatial distributions of TOC, TN and BSi (unit: %) in surface sediments of the Maowei Sea during summer and winter seasons.

of TOC between these bays are partly related to the type and intensity of mariculture among other factors. As observed in this study, the average TOC values in summer (0.69%) and winter (0.64%) seasons were higher in IMA compared to NIMA with the average values in summer (0.31%) and winter (0.45%). Although the seasonal variability in bulk TOC in the study area was not statically significant ($p = 0.567$), the differences in the spatial distribution between IMA and NIMA was statistically significant ($p = 0.001$) (Table 5). This indicates that the accumulation of SOM may be impacted by oyster seedling and mariculture activities (Andrews et al., 1998). Moreover, seawater temperature drops

gradually as the winter season sets in with gradual decline in biological activity. The reduction in biological productivity can result in lower SOM degradation rate, which favors the accumulation of OM in surface sediments and increase the content of TOC in winter, which was higher than that in summer, consistent with the reports in other study areas (e.g., Zhou et al., 2018). Nevertheless, the distributional patterns of TOC in summer was similar to the trend of progressive southward decline of FGS (Fig. 3a), but in winter more TOC were found in the north-western regions of the sea (Fig. 3b). Significant positive relationships were found between TOC and FGS both in summer ($r = 0.92$,

Table 2

Bulk TOC, TN and BSi contents (% , rang (mean)) in surface sediments from worldwide estuaries and bays and Chinese coastal sea areas.

	Location	TOC (%)	TN (%)	BSi (%)	Reference
Mariculture areas	Maowei Sea, China	0.10–1.19	0.01–0.10	0.25–0.9	This study
	Chesapeake Bay, USA	0.75–3.46	0.33–0.47	–2.8	Zimmerman and Canuel, 2000
	Jiaozhou Bay, China	0.07–0.45	0.16–0.48	0.94–2.00	Dai et al., 2007; Wu et al., 2015
	Pearl River Estuary, China	0.88–1.15	0.03–0.05	1.04–2.16	Qi et al., 2010; Wang et al., 2015
	Zhelin Bay, South China Sea, China	0.15–0.75	0.022–0.151	1.83–2.98	Feng et al., 2011; Zhou et al., 2018
	Ailian Bay, China	0.58–1.21	0.06–0.17	Na	Pan et al., 2019
	Sangou Bay, China	0.2–1.08	0.018–0.142	Na	Xia et al., 2019
Non-mariculture areas	East China Sea, China	Na	Na	0.2–0.9	Wang et al., 2014b
	Yellow River estuary and adjacent shelf, China	0.08–0.91	0.01–0.11	0.1–1.1	Liu et al., 2015
	East China Sea shelf, China	0.46–1.23	0.08–0.2	Na	Gu et al., 2017
	Cross River estuary system and adjacent shelf, Nigeria	0.47–5.28	0.08–0.33	0.09–0.74	Dan et al., 2019

Na means not available.

$p < 0.001$) and winter ($r = 0.63$, $p < 0.001$) seasons as shown in the regression plot (Fig. 4a). This suggests that FGS is among the factors influencing the distributions of TOC in the study area due to its characteristic large surface area for organic matter adsorption (Gireeshkumar et al., 2013; Kennedy et al., 2014; Sun et al., 2018).

The contents of TN ranged from 0.01% to 0.10% (average, $0.05 \pm 0.03\%$) in summer. Although the mean TN ($0.05 \pm 0.02\%$) in winter was similar to that in summer, the concentration range (0.02–0.08%) was relatively narrow as with TOC (Table 1; Fig. 3c–d). Comparatively, the range of TN in surface sediments of the study area is higher than that reported for the Pearl River Estuary (Qi et al., 2010). On the other hand, TN range in this study was lower than that reported for the Zhelin Bay (Gu et al., 2017), Ailian Bay (Pan et al., 2019) Jiaozhou Bay (Dai et al., 2007) and Cross River estuary system and adjacent shelf (Dan et al., 2019), but comparable to the values reported in the Sanggou Bay (Xia et al., 2019), which are systems with and without mariculture practices (Table 2). The distributions of TN were similar to the spatiotemporal distribution patterns of TOC in both seasons (Fig. 3c–d). Moreover, the spatial variation in the distributions of TOC and TN in summer and winter seasons was statistically significant ($p < 0.001$) (Fig. 4b), indicating that they were derived from common source during the study period. The intercepts of the bi-plot (Fig. 4b) in both seasons were near zero (i.e., 0.004% in summer and 0.008% in winter), suggesting that TN may be dominated by organic nitrogen (Goñi et al., 2003; Liu et al., 2015) in surface sediments of the Maowei Sea. Specifically, approximately 8% and 16% of the TN in summer and winter represents inorganic nitrogen, respectively. Subtracting these fractions from TN, the average content of organic nitrogen would be 0.04% in both seasons, which is comparable the average TN values in this study. Similar to TOC, the average TN values in both summer (0.06%) and winter (0.05%) seasons were higher in IMA compared to NIMA with average values in summer (0.03%) and winter (0.04%). Although the seasonal variability in bulk TN in this study was not also statically significant ($p = 0.858$) as with TOC, however, the differences in the contents between IMA and NIMA was statistically

significant ($p = 0.002$) (Table 5), implying that the distribution of TN in SOM may be significantly impacted by the intensity of mariculture activities. Most intense oyster rafts are distributed around the Maolingjiang River estuary regions where salinity condition is favourable for oyster breeding and growth. The highest TOC and TN were also found in this region. Therefore, the significant relationship between TOC and TN and the statistical significance in their spatial distribution between IMA and NIMA during this study underlines the impact of mariculture activities in the distribution of biogenic elements (Zhou et al., 2006; Zhang et al., 2012) in the study area.

Concentrations of OP in surface sediments of the investigated sites ranged from $1.79 \mu\text{mol g}^{-1}$ to $11.83 \mu\text{mol g}^{-1}$ in summer and $1.10 \mu\text{mol g}^{-1}$ to $11.26 \mu\text{mol g}^{-1}$ in winter. Detailed information about the temporal and spatial variation characteristics of OP in the study area were previously reported by Yang et al. (2019b). Dissolved silicate (DSi) is a key macronutrient required plankton growth (e.g. diatoms) and food web (Wang et al., 2014b; Ran et al., 2016). DSi is consumed in the photic zone of the water column by diatoms to generate frustule, which consists of amorphous hydrated silica described as BSi or opal (Ragueneau et al., 2005). Thus, BSi in surface sediments can be used as an indicator of the contributions of siliceous organisms, such as planktonic diatoms, microphytobenthos and radiolarians that are closely correlated with primary productivity in the marine ecosystem (Liu et al., 2015; Krause et al., 2011; Li et al., 2018). In this study, BSi contents ranged from 0.29% to 0.90% (average, $0.47 \pm 0.19\%$) in summer, and 0.25–0.53% (average, $0.34 \pm 0.08\%$) in winter (Table 1). In general, the contents of BSi in the study area were $< 1\%$ in both seasons (Fig. 3e–f; Table 1). However, the range of BSi in surface sediments of the Maowei Sea was higher than those reported for some non-mariculture systems such as the Cross River estuary system and adjacent shelf (Dan et al., 2019), Yellow River estuary and adjacent shelf (Liu et al., 2015) but comparable to those of the East China Sea (Wang et al., 2014b), but less than values reported for other mariculture bays such as Chesapeake Bay (Zimmerman and Canuel, 2000), the Guishan Island in Pearl River

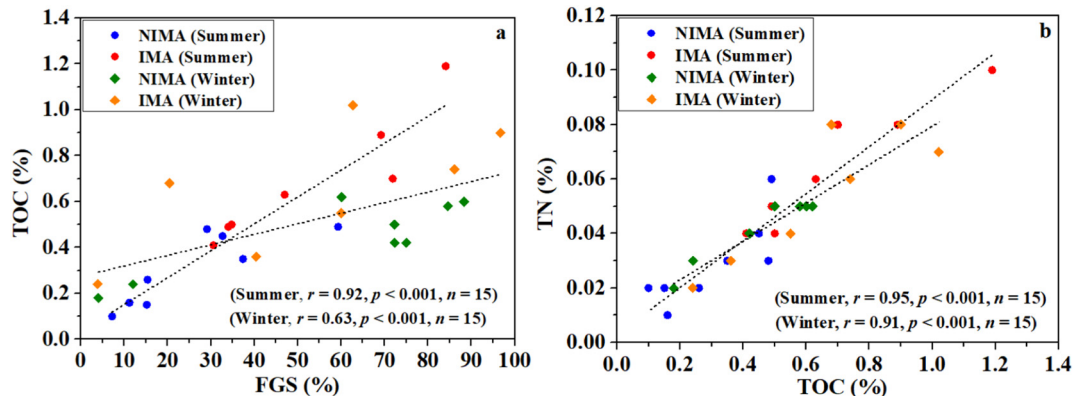


Fig. 4. Linear correlations between TOC and FGS (<63 μm) content and between TOC and TN in surface sediments of the Maowei Sea during summer and winter seasons.

estuary (Wang et al., 2015), Jiaozhou Bay (Dai et al., 2007) and Zhelin Bay, South China Sea (Zhou et al., 2018). Although the BSi values were not reported for other systems as shown in Table 2, the differences in the BSi contents between the study area and other cited mariculture and non-mariculture bays may be dependent the level of primary productivity in relation to nutrient bioavailability, feeding selectivity of shellfish on diatom, sources of BSi, as well as deposition and dissolution rates of diatom cells (Wang et al., 2014b; Lan et al., 2018; Dan et al., 2019). Unlike TOC and TN, the contents of BSi appeared to be more impacted by seasons ($p = 0.016$) other than mariculture activities ($p = 0.282$) (Table 5). The lack of significant spatial variation in the distribution between IMA and NIMA may be related in part to the abundance of diatoms in the Maowei Sea. Highest BSi values were found in the central and eastern coastal area during summer (Fig. 3e), and in the western coastal areas during winter (Fig. 3f), consistent with regions of high TOC and TN contents (Fig. 3a–d), indicating significant contributions to SOM from marine organisms.

Results of Pearson correlation analysis are shown in Table 3. Apparently, there were significant positive correlations between TOC, TN, OP and FGS both in summer and winter (Table 3). This indicates that the spatial distribution of SOM in the investigated sites is partly related with the distributions of fine-grained sediments, due to the large specific surface area for OM adsorption (Gao et al., 2012; Sanchez-Vidal et al., 2012), especially for the adsorption of the finer composition of shellfish faeces and pseudofaeces collectively referred to as biodeposits, which are rich in OM (Zhang et al., 2009; Franzo et al., 2014). The relationships between BSi and TOC ($r = 0.56$, $p < 0.05$), TN ($r = 0.65$, $p < 0.01$), OP ($r = 0.70$, $p < 0.01$) in summer, and OP ($r = 0.76$, $p < 0.001$) in winter were also positive and significant (Table 3), indicating the coupling between BSi production and cycling of SOM in the study area during the study period (Dan et al., 2019), especially in summer. Moreover, there were significant positive correlations between BSi and FGS in both seasons (Table 3), indicating that distributions of fine-grained is among the factors responsible for the variations of BSi in the study area (Ran et al., 2015).

3.2. Distribution and implication of $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ and elemental ratios

As reliable makers, the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ isotopic compositions have been widely used to trace the sources of SOM in coastal marine environments (Lamb et al., 2006; Ramaswamy et al., 2008; Gao et al., 2012; Dan et al., 2019). The $\delta^{13}\text{C}$ values of terrestrial plants with C_3 pathway ranged from -33‰ to -24‰ (average, -27‰), and -16‰ to -9‰ (average, -13‰) for those with C_4 pathway (Pancost and Boot, 2004). The $\delta^{13}\text{C}$ values for sewage derived from human activities ranges

from -28‰ to -23‰ (Andrews et al., 1998), -26‰ to -22‰ for soil OM (Thorp et al., 1998; Xia et al., 2019), -24‰ to -17‰ for marine phytoplankton (Bouillon et al., 2008), and -23‰ to -17‰ for marine shellfish biodeposition (Xia et al., 2014; Pan et al., 2019). In this study, no seasonal influence was found in the variability of average $\delta^{13}\text{C}$ ($p = 0.617$) isotopic values in the study area. Moreover, the changes in the average $\delta^{13}\text{C}$ between IMA and NIMA were not also statistically significant ($p = 0.925$) (Table 5). However, the spatial distributional patterns of $\delta^{13}\text{C}$ values in surface sediments were different between the summer and winter seasons, and between IMA and NIMA (Fig. 5a and b). The $\delta^{13}\text{C}$ ranged from -26.86‰ to -23.01‰ (average, $-25.05 \pm 1.01\text{‰}$) in summer, and -26.51‰ to -23.67‰ (average, $-24.85 \pm 0.75\text{‰}$) in winter (Table 1). While the $\delta^{13}\text{C}$ increased gradually from the west coast to the east coast with elevated values near the Qinjiang River estuary in summer (Fig. 5a), much depleted values were found near the Maolingjiang River estuary in summer, which progressively increased towards the NIMA outlet sites in winter, (Fig. 5b). This suggests gradual decrease in the relative proportions of SOM from terrestrial source from the estuarine regions with increase in the proportions of marine sourced SOM in both seasons, respectively. Moreover, more positive $\delta^{13}\text{C}$ isotopic values (average, $-24.77 \pm 1.20\text{‰}$) were found in IMA, while the average $\delta^{13}\text{C}$ in NIMA was slightly depleted ($-25.29 \pm 0.83\text{‰}$), suggesting contributions to SOM from shellfish biodeposition as well as marine plankton sources in the study area. Additionally, the relative positive $\delta^{13}\text{C}$ values in the north-central and southern sea areas may also likely due to elevated marine primary productivity (Yang et al., 2015b).

Various nitrogen sources have distinct $\delta^{15}\text{N}$ values. For example, the $\delta^{15}\text{N}$ values of SOM from marine phytoplankton ranges from 4‰ to 10‰ with average values in the range of $5\text{--}7\text{‰}$ (Brandes and Devol, 2002; Lamb et al., 2006), while the average $\delta^{15}\text{N}$ for SOM from shellfish biodeposition is approximately $5.12 \pm 0.20\text{‰}$ (Pan et al., 2019). The SOM from terrestrial source has relatively wide $\delta^{15}\text{N}$ values (range, -10‰ to 10‰), but lower average (-2‰) (Gao et al., 2012), and that of soil OM ranges from 6‰ to 16‰ (Liu et al., 2009). Unlike the SOM from natural sources, the anthropogenic SOM is isotopically rich in heavy nitrogenous constituents (Cole et al., 2004; Bănarău et al., 2007). For example, the nitrate delivered from anthropogenic sewage and agricultural runoff is enriched in $\delta^{15}\text{N}$ with isotopic values ranging from 10‰ to 25‰ (Kendall, 1998; Dan et al., 2019). In this study, the $\delta^{15}\text{N}$ isotopic values in SOM ranged from 2.88‰ to 6.26‰ (average, $4.38 \pm 1.25\text{‰}$) in summer, and 2.54‰ to 9.82‰ (average, $5.18 \pm 2.72\text{‰}$) in winter (Table 1). In summer, the $\delta^{15}\text{N}$ values decreased gradually from the northern IMA regions to the southern NIMA regions (Fig. 5c), whereas relatively high $\delta^{15}\text{N}$ values were observed in the central areas with lower values around the coastal areas in winter (Fig. 5d). In summer, the $\delta^{15}\text{N}$ values in the estuarine areas, especially around the Qinjiang River estuary region in IMA were relatively lower than values reported for sewage (Kendall, 1998, and references therein), but comparable to the mean $\delta^{15}\text{N}$ of marine phytoplankton and shellfish biodeposition reported in the literature (Brandes and Devol, 2002; Lamb et al., 2006; Pan et al., 2019), indicating that SOM around this estuary region is likely derived from marine and shellfish biodeposition sources, with limited influence from sewage. Despite the differences in the spatial distributions, both the seasons ($p = 0.338$), and mariculture activities ($p = 0.177$) did not statistically influence the average $\delta^{15}\text{N}$ isotopic values in the study area (Table 5). However, the $\delta^{15}\text{N}$ values in NIMA were within the range of $3\text{--}3.6\text{‰}$ (Fig. 5c) in winter. These values were lower than the typical $\delta^{15}\text{N}$ values ($5\text{--}7\text{‰}$) for SOM derived from marine plankton, which feed on ammonium and nitrate, suggesting some contributions from nitrogen-fixing phytoplankton (Liao et al., 2018). As earlier mentioned, the average $\delta^{15}\text{N}$ values for SOM from terrestrial sources are generally low, while SOM derived from marine sources is generally characterized by relatively higher $\delta^{15}\text{N}$ values. The lower $\delta^{15}\text{N}$ values along the coastal area in winter were within the range reported terrestrial derived SOM, suggesting

Table 3
Result of correlation analysis of geochemical parameters in surface sediments of the Maowei Sea during summer and winter seasons.

	FGS	TOC	TN	OP	BSi	C/N	$\delta^{13}\text{C}$
Summer	FGS						
	TOC	0.93 ^a					
	TN	0.97 ^a	0.95 ^a				
	OP	0.91 ^a	0.90 ^a	0.87 ^a			
	BSi	0.70 ^a	0.56 ^b	0.65 ^a	0.70 ^a		
	C/N	−0.05	0.12	−0.15	0.09	−0.09	
	$\delta^{13}\text{C}$	0.10	−0.10	0.06	−0.14	0.44	−0.13
	$\delta^{15}\text{N}$	0.31	0.36	0.40	0.11	0.30	−0.05
Winter	FGS						
	TOC	0.63 ^b					
	TN	0.53 ^b	0.91 ^a				
	OP	0.82 ^a	0.67 ^a	0.64 ^b			
	BSi	0.58 ^b	0.37	0.43	0.76 ^a		
	C/N	0.44	0.53 ^b	0.16	0.30	0.01	
	$\delta^{13}\text{C}$	0.00	−0.07	0.09	−0.18	−0.15	−0.30
	$\delta^{15}\text{N}$	−0.90 ^a	−0.60 ^b	−0.38	−0.66 ^a	−0.49	−0.65 ^a

^a Correlation is significant at the 0.01 level (two-tailed).
^b Correlation is significant at the 0.05 level (two-tailed).

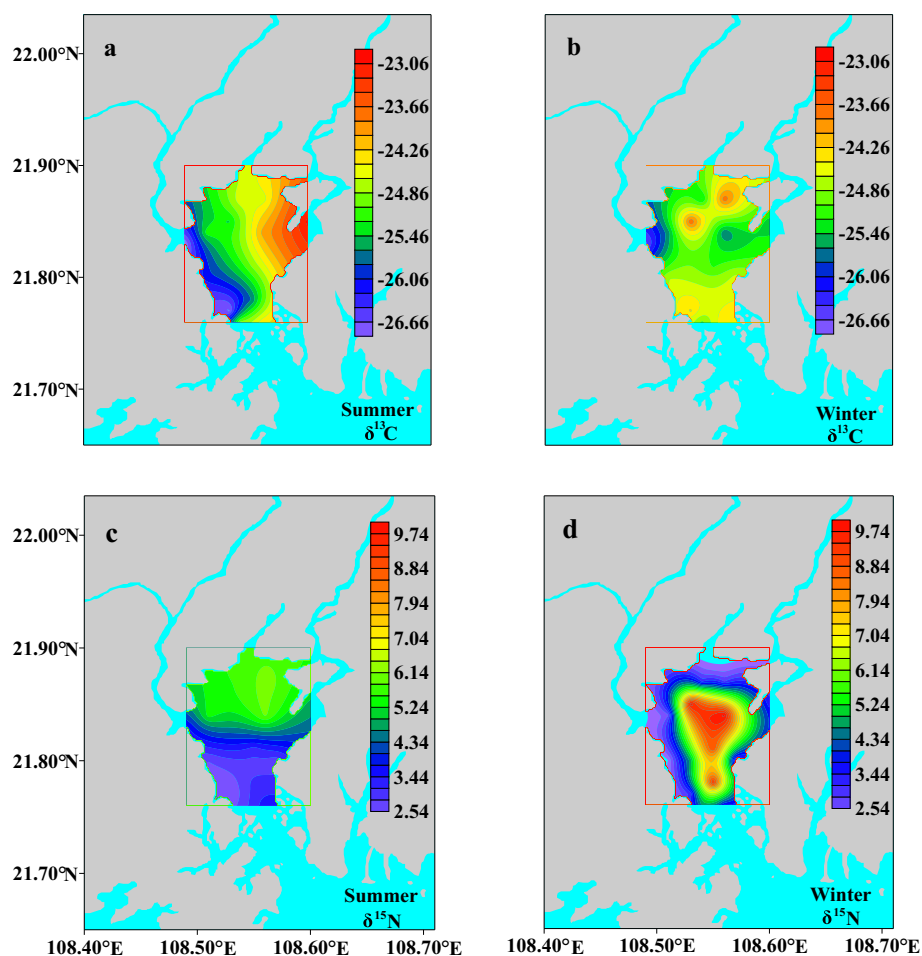


Fig. 5. Spatial distributions of stable $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ isotopes (unit: ‰) in surface sediments of the Maowei Sea during summer and winter seasons.

that the coastal areas may likely received elevated amount of SOM from terrestrial source in winter. However, the elevated $\delta^{15}\text{N}$ values in the central regions, which cut cross the IMA and NIMA reveals proportional input of SOM from both shellfish biodeposition and marine plankton sources during the winter season (Fig. 5d). Moreover, the average $\delta^{15}\text{N}$ was 4.38‰ in summer and 5.18‰ in winter, which may suggest possible nitrogen fractionation because of the decomposition of SOM. For example, isotopically enriched nitrogen can be produced in particulate OM through remineralization during nitrogen cycling in the bottom water (Wu et al., 2003), and most of the particulate OM can be deposited in surface sediments.

The C/N ratios can often be used as a potential proxy for distinguishing SOM from marine autogenic and terrestrial sources, which generally ranges from 4 to 9 and >12, respectively (Meyers, 1994; Graham et al., 2001). The C/N molar ratios of marine phytoplankton enriched with protein are reported in the range of 4–10 with averages between 5 and 7 (Goñi et al., 2013; Krishna et al., 2015), while the average C/N ratio of eucalyptus vascular plant distributed around the northern Beibu Gulf is ~36 (Kaiser et al., 2014), and that of soil microbes ranged from 5 to 15 (Hedges and Oades, 1997). The range of TOC/TN (C/N) ratios in this study was 5.83 to 18.67 (average, 12.71 ± 3.43) in summer, and 9.33–17.00 (average, 13.10 ± 2.15) in winter (Table 1), and were similar to those in Ailian Bay, which is also largely influenced by shellfish mariculture activities (Pan et al., 2019). Similar to the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ isotopic compositions, the average C/N ratios in this study was not affected by both seasons ($p = 0.664$) and mariculture activities ($p = 0.522$) during the study period (Table 5). Although the mean C/N ratios in both seasons were somewhat comparable, the spatial distributions were relatively different in the Maowei Sea during

the summer and winter seasons. Elevated C/N ratios were found both in the northern IMA regions and at the NIMA outlet stations in summer, but was relatively high in the northern IMA areas with a gradual decreasing trend towards the outlet NIMA regions in winter (Fig. 6a and b). In summer, the low C/N ratios (<12) in the Qinjiang River estuary along IMA (Fig. 6a) indicate negligible influence from sewage effluents. The urbanization centers are located in the upstream regions and the depositions of pollutants from this river were likely reduced by tidal dilution. The average C/N ratio in surface sediments from this river was previously reported as 14.1, which showed limited influence from sewage effluents (Meng et al., 2016). Elevated C/N ratios (average, 37.4) were also previously reported in the outlet stations of NIMA (Meng et al., 2016), located near the Maowei Sea Mangrove Reserve (Fig. 6a). The elevated C/N ratios around the sites in implied that OM in surface sediments of the southernmost regions is potentially derived from mangrove vegetation.

Elemental ratios can indicate nutrient enrichment conditions in marine environments (Ruiz-Fernández et al., 2002). In summer, the molar TN/OP, BSi/TN and BSi/OP ratios ranged from 3 to 12 (average, 7), 3–22 (average, 7) and 15–72 (average, 41) respectively, and also ranged 5–21 (average, 9), 2–9 (average, 4) and 17–117 (average, 36), respectively in winter. Obviously, the average BSi/TN and BSi/OP ratios in both seasons were generally higher than the typical Redfield ratio (N:P:Si = 16:1:16, Redfield et al., 1963), while the molar TN/OP ratios were lower than the Redfield ratio, suggesting that the Maowei Sea surface sediments are enriched with Si and P (Yang et al., 2015a). Moreover, the average TOC and OP were 0.48% and 4.89 $\mu\text{mol g}^{-1}$ in summer, and 0.54% and 4.47 $\mu\text{mol g}^{-1}$ in winter (Yang et al., 2019b), respectively. On the premise of zero intercept (Fig. 4b), TN could be used to replace the content

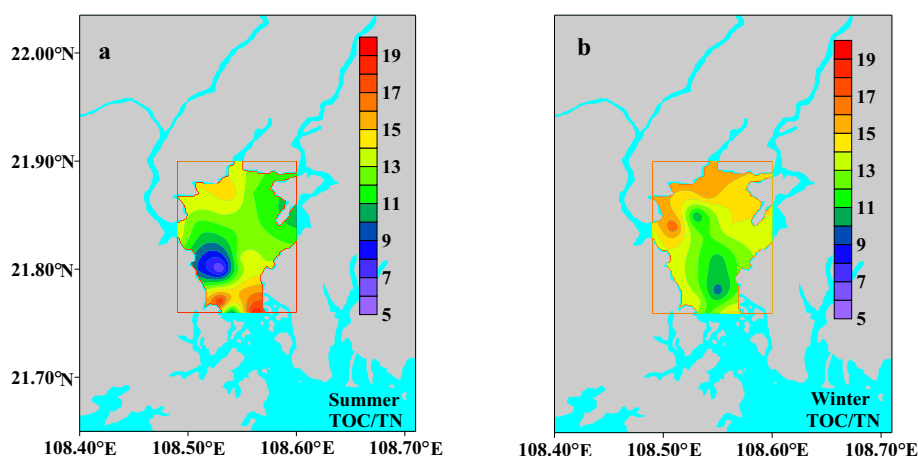


Fig. 6. Spatial distributions of TOC/TN (C/N) molar ratios in surface sediments of the Maowei Sea during summer and winter seasons.

of organic nitrogen (ON). However, ~8% and 16% of the TN in summer and winter represents inorganic nitrogen (IN), respectively. If these fractions of IN are subtracted from the TN, the average contents of ON were 0.04% in both seasons. If these values are converted into the same unit, the atomic ratios for TOC, ON, and OP will be 82:6:1 in summer and 101:6:1 in winter, respectively. These ratios are different from the Redfield ratio (C:N:P = 106:16:1, Redfield et al., 1963), indicating that the decomposition of OM in surface sediments of the mariculture bay could supply more P during summer and winter for the growth of marine phytoplankton in the overlying water.

3.3. Fractional contributions of SOM in the Maowei Sea estimated from $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ -based three-end-member mixing model

The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ three-end-member mixing model results revealed that the surface sediments in the Maowei Sea are enriched with SOM from terrestrial source both seasons, which accounted for 11.0–69.5% (average, $44.4 \pm 15.4\%$) in summer and 28.5–73.5% (average, $47.6 \pm 12.4\%$) in winter of SOM (Table 4). The dominance of terrestrial SOM in this sea may result from the fact that OM from terrestrial sources may be less susceptible to biodegradation (Anderson et al.,

Table 4

Summary of the contributions (%) of different SOM sources in the Maowei Sea during summer and winter seasons.

Station	Summer			Winter		
	Terrestrial	Shellfish biodeposition	Marine plankton	Terrestrial	Shellfish biodeposition	Marine plankton
1	41.7	25.3	33.0	55.2	13.6	16.8
2	44.6	25.6	29.8	37.4	30.5	22.1
3	69.5	12.3	18.2	34.9	28.5	25.4
4	50.8	28.5	20.7	42.4	20.6	25.5
5	59.4	18.6	22.0	28.5	14.1	27.2
6	47.5	21.4	31.1	53.2	19.6	28.3
7	47.0	24.6	28.4	52.0	25.9	31.2
8	46.2	29.2	24.6	46.7	15.8	31.3
9	68.2	8.3	23.5	73.5	9.7	32.1
10	21.5	30.8	47.8	56.1	12.6	33.6
11	47.8	24.1	28.0	29.5	36.8	35.0
12	39.1	43.9	17.0	60.2	14.4	36.6
13	32.7	46.5	20.8	56.6	15.0	37.0
14	38.7	39.9	21.4	49.0	25.5	37.5
15	11.0	44.5	44.4	38.9	26.1	57.4
Average $\pm$ SD	44.4 15.4	28.2 11.4	27.4 9.0	47.6 12.4	20.6 7.9	31.8 9.2

Table 5

Summary of a 2-Way MANOVA results for the Maowei Sea during summer and winter seasons.

Variables	Mean square			F-value			P-value		
	IF1	IF2	IF3	IF1	IF2	IF3	IF1	IF2	IF3
FGS	1964.091	859.573	2012.829	2.681	1.173	2.747	0.114	0.289	0.109
TOC	0.017	0.625	0.064	0.336	12.647	1.303	0.567	0.001	0.264
TN	0.00001167	0.004	0.001	0.033	12.288	2.637	0.858	0.002	0.116
BSi	0.131	0.024	0.045	6.692	1.206	2.290	0.016	0.282	0.915
$\delta^{13}\text{C}$	0.202	0.007	1.815	0.256	0.009	2.305	0.617	0.925	0.141
$\delta^{15}\text{N}$	3.960	8.012	9.313	0.954	1.930	2.244	0.338	0.177	0.146
C/N	1.610	3.496	9.607	0.193	0.420	1.155	0.664	0.522	0.292
Terrestrial%	117.132	59.664	905.228	0.673	0.343	5.198	0.420	0.563	0.031
Shellfish biodeposition%	483.751	177.515	263.150	5.574	2.045	3.032	0.026	0.165	0.093
Marine Plankton%	124.369	32.010	192.783	1.549	0.399	2.401	0.224	0.533	0.133

Notes: IF1, IF2, and IF3 represents different influencing factors of seasonal, mariculture activity, and the interaction effect between seasonal and mariculture activity, respectively.

2001) than those from marine or shellfish culture sources, and for the fact that much of the terrestrial SOM may have been supplied to the Maowei Sea through runoff. Nevertheless, the 2-way MANOVA results revealed that the contents of SOM from terrestrial source was significantly impacted by the interaction of the seasons and mariculture activities ($p = 0.031$) (Table 5). The seasonal effect may have been related in part to seasons of high riverine input, especially in summer and on the biodegradability of SOM, which may be low in winter. Generally, terrestrial SOM was low in the northern (IMA) regions, but gradually increased towards the southern (NIMA) regions of the Maowei Sea in

summer (Fig. 7a). In winter, elevated depositions were found along the coastal areas, especially at the outlet stations of both the Qingjiang River and Maolingjian River with minor deposition in the north-central and southern regions in winter (Fig. 7b), and may have resulted from changes in river discharge between season.

The contributions of SOM from shellfish culture were higher in summer ranging from 8.3% to 46.5% with an average of $28.2 \pm 11.4\%$ than in winter where the proportions were 9.7–36.8% with an average of $20.6 \pm 7.9\%$ (Table 4). The results of 2-way MANOVA revealed that the SOM from shellfish culture were significantly impacted by seasons

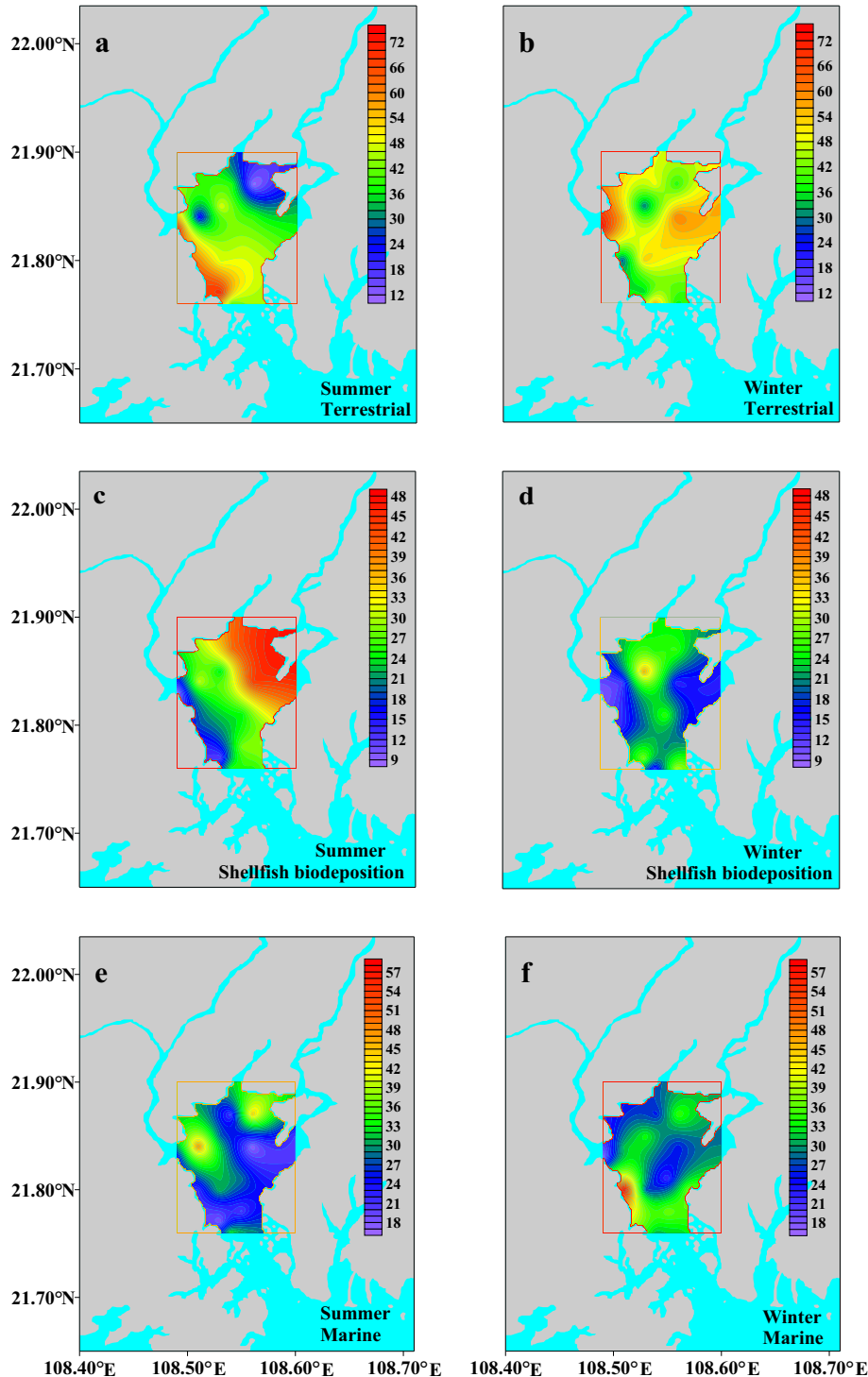


Fig. 7. Spatial distributions in the relative proportions of SOM from terrestrial, marine, and shellfish biodeposition sources, based on the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ three-end-member mixing model in surface sediments of the Maowei Sea during summer and winter seasons.

($p = 0.026$) (Table 5). The summer sampling month was within the spawning months of *Crassostrea hongkongensis*. Besides the influence of rainfall and primary productivity on the particulate transport to sediments, it is expected that more mature *Crassostrea hongkongensis* would produce considerable amount of excrements, and since because the Maowei Sea is relatively shallow, the biodeposition would eventually become incorporated in surface sediments resulting in elevated shellfish biodeposition relative to SOM from marine plankton. On the other hand, lower proportions of SOM from shellfish culture would also be expected during the winter sampling month whereby shellfish are harvested, suggesting possible increase in the proportions of SOM from marine phytoplankton as found in this study. The spatial distributions of SOM from shellfish culture were almost completely opposite to terrestrial source SOM in summer and winter (Fig. 7a–d). In generally, the SOM from shellfish culture was elevated at the northern (IMA) regions in summer (Fig. 7c), but lower in the southern (NIMA) regions. In winter, it decreased from the central regions towards the coastal areas with more depositions in the northern (IMA) regions than in the southern (NIMA) regions (Fig. 7d). This shows that the mixing of freshwater with saltwater in the northern (IMA) regions is quite suitable for oyster growth, and thus corroborates well the shellfish biodeposition patterns.

The summer SOM contributions from marine plankton ranged from 17.0% to 47.8% with an average of $27.4 \pm 9.0\%$, and were lower than the contributions from terrestrial sources as well as those from shellfish culture, but in winter, it ranged from 16.8% to 57.4% with an average of $31.8 \pm 9.2\%$ (Table 4), exceeding those from shellfish culture discussed in the preceding paragraph. The 2-way MANOVA revealed that the SOM from marine plankton was neither affected by seasons ($p = 0.224$) nor mariculture activities ($p = 0.533$) (Table 5). However, the distributions of SOM from marine plankton were somewhat patchy (Fig. 7e and f). The elevated depositions at the outlets stations of both the Qinjiang River and Maolingjina River in summer (Fig. 7e) partly reflects the eutrophic conditions due to elevated phytoplankton production resulting from the influx of the riverine nutrients (Hu et al., 2006; Zhang et al., 2019). In winter, more accumulation of SOM from marine plankton was found in the southern (NIMA) regions (Fig. 7f). The winter season is the period of reduced freshwater input; therefore, marine plankton may depend on nutrients brought in through the Qinzhou Bay by tides, which may result in the production and accumulation in the southern regions. Shellfish culture activities may significantly influence the cycling of biogenic elements and SOM in the Maowei Sea, especially as there were differences in the dominance of SOM from shellfish biodeposition and marine phytoplankton in both summer and winter seasons. However, the overall data during this study revealed that SOM from terrestrial sources was the highest and averagely accounted for $46.0 \pm 13.9\%$, followed by $29.6 \pm 9.2\%$, for marine plankton, and the least ($24.4 \pm 10.4\%$) from shellfish biodeposition; the contents changed locally between NIMA and IMA (Table 5). It is worth mentioning that SOM contributions from shellfish biodeposition averagely accounted for $27.0 \pm 11.8\%$ in IMA and higher than that in NIMA which was $22.2 \pm 6.1\%$ (Table 5). This reveals that the main source of SOM in the Maowei Sea, a typical intense mariculture bay is not exclusively related to the functions or usefulness this marine system as reported for other mariculture bays such as the Sanggou Bay in China (Xia et al., 2019) where mariculture was the main sources of SOM.

4. Conclusion

Knowledge of the sources and composition of SOM in coastal marine systems contributes to the understanding of global carbon cycle, and important for the fact that SOM act as sources of nutrient and energy in marine environments. The temporal and spatial pattern of TOC, TN, OP, and BSi contents, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ isotopic signatures, and sediment grain sizes were studied in the Maowei Sea, a typical mariculture bay in Southwest China. The spatial distributions of biogenic elements

were influenced by the sources of SOM in relation to interactions between seasons and mariculture activities, sediment textural characteristics and hydrodynamic conditions in the study area. The atomic ratios of biogenic elements suggested that surface sediments were enriched with BSi and OP in summer and winter seasons. The range of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ isotopes, and elemental C/N ratios showed that SOM was derived from mixed sources comprising of terrestrial, marine and shellfish biodeposition in summer and winter. The three-end-member mixing model using the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ isotopic values revealed that SOM was dominantly derived from terrestrial sources. Although significantly impacted by seasons, the proportions of SOM from shellfish mariculture were elevated in the intensive mariculture areas, which highlight that mariculture can significantly influence the cycling of carbon in coastal ecosystems. Besides, the overall dominance of SOM from terrestrial and marine sources underlines that the sources of SOM in an intensive mariculture bay does not exclusively relate to the intensity of mariculture activities. It is important to that the conclusions from this study are based on intensive mariculture vs non-intensive mariculture areas but their locations are not randomly distributed, and mariculture stations are also closer to the estuaries and further to open sea, which may hinder confounding factors between estuarine influence and mariculture. Therefore, future monitoring of mariculture sediments to evaluate the influence and risk of shellfish culture on the benthic marine environments is encouraged.

CRedit authorship contribution statement

Cheng Xu: Writing - original draft, Writing - review & editing. **Bin Yang:** Methodology, Writing - review & editing. **Solomon Felix Dan:** Writing - review & editing. **Dong Zhang:** Investigation. **Riquan Liao:** Investigation. **Dongliang Lu:** Investigation. **Ruihuan Li:** Formal analysis. **Zhiming Ning:** Formal analysis. **Shiqiu Peng:** Formal analysis.

Declaration of competing interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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