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Article

Analysis of Regional Differentiation and Sediment Provenance in the Lu'erhuan River Sea Area of Qinzhou Bay, Guangxi Province

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Abstract: Globally, coastal regions are vital areas of human activities and, as such, are centres of population growth and urban and economic development. Long-term human development has had a major impact on the ecological environment of coastal zones. Therefore, exploring the distribution and provenance of marine sediment types in coastal areas heavily influenced by human activities can provide scientific evidence and references for the current and future ecological management of these sensitive environments. For this reason, we have conducted an analysis on the sediment grain size, Endmember, organic matter content and geochemical elements in the Lu'erhuan River–Malan Island–Sandun Island area in the eastern part of Qinzhou Bay, a region heavily influenced by human activities. Sediment grain size clearly differs throughout the study site and the material provenances and hydrodynamic conditions are also varied, likely due to the local environmental conditions and the significant impact human activities have had on the area. The finest-grained sediment is imported from either inland or coastal areas via rivers and weak tidal currents, the next finest component is input from coastal areas through weak tidal currents, and the moderately coarse component mainly originates from nearby beaches. The two coarsest-grained sediment components are influenced by the combination of human activities, tidal currents and waves and enter the water via erosion. Organic matter provenance resembles that of the sediment components, exhibiting varied characteristics. This is due to the combination of natural and human activities in the bay. The organic matter in the upper reaches of the Lu'erhuan River originates from the river and coastal paddy fields, with obvious terrigenous characteristics; the organic matter in northern Malan Island mainly comes from external sources related to oyster farming; while organic matter in eastern Sandun Island is mainly produced endogenously by marine plankton. Al, Ti, Fe, Mg, K, Ga and other elements indicate that terrestrial sediments are significantly disturbed by human activities. However，Mn reflects the marine distribution of terrestrial sediments from the Lu'erhuan River to Jishuimen. Ca and Sr, indicators of marine sediments, are distributed in the eastern offshore area of Sandun Island, which is connected to the open waters. Due to the influence of human activities, As and Cd are highly enriched in the study area, while Cu is less affected by human activities.

Keywords: Qinzhou Bay; sediment provenance; human activities; endmember analysis

1. Introduction

Throughout the world, coastal regions are the areas with the largest concentrations of human, urban and economic activities. Over the years, high-intensity human activities have had a major impact on the ecological environment of coastal zones, making them among the world's most vulnerable ecosystems. A series of increasingly prominent ecological and environmental challenges, such as severely reduced coastal wetlands, reduced biodiversity, destroyed mangroves, environmental pollution, seawater eutrophication and coastal erosion, have all become topics of great concern. Under the guidance of the

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strategic decision of ecological civilization construction [1], the coastal ecological restoration project has been gradually implemented.

Among coastal zones, gulf regions most frequently bear the burden imposed by human activities; thus, they are prime areas for ecological restoration. Qinzhou Bay, located in the northern part of the South China Sea, is a major area for oyster breeding in China due to its uperior geographical location and abundant natural resources. It is known in China as the "hometown of oysters" [2] and promotes the social and economic development of the region. Over the years, to meet the needs of economic development, construction on structures such as ports, wharves, highways and bridges has consumed a large area of the shoals and beaches. This has caused damage to the ecological environment and has had serious impacts on the aquaculture[3].In the eastern part of Qinzhou Bay, the abundance of the human activities, such as the construction of coastal highways, the Sandun Marine Highway and SandunPort, has divided the marine area around Lu'erhuanRiver–Malan Island–Sandun Island from Qinzhou Bay. This has had a significant impact on coastal hydrological characteristics and surface sediments, which in turn pose serious problems for ecological safety and aquaculture. Therefore, by considering the larger regional context of intense human activities, analyses of the distribution characteristics and provenance of sediments in this bay can provide scientific evidence and a reference for current and future ecological construction projects in coastal areas.

Grain size analysis [4-5], Endmember analysis [6-7] and geochemical element analysis [8-9] of bay sediments are effective ways to explore sediment distribution characteristics and material provenance. Therefore, on the basis of these analytical methods and in combination with the characteristics of high-intensity human activities in the marine area of Lu'erhuanRiver–Malan Island–Sandun Island, this study seeks to explore the following: ①sediment types and their distribution characteristics; ②Endmember analysis and material provenance of sediments impacted by intense human activities; ③distribution characteristics and provenance of organic matter impacted by intense human activities; ④elemental analysis and the local impact of human activities. By addressing the above issues, we aim to provide reliable suggestion sand references for coastal development and ecological environment management.

2. Physical conditions of the study area and research methods

2.1. Physical conditions of the study area

Qinzhou Bay (21°33′20″-21°54′30″N, 108°28′20″-108°45′30″E) is located at the northern coast of the Beibu Gulf in the South China Sea (Figure 1.). The bay area is 380 km^2, of which the beach is approximately 200 km^2 in area. It is the largest bay in the coastal zone of the Guangxi province[3,10].However, with the construction of ports, docks, highways and bridges in coastal areas in recent years, the bay area has shrunk to 320km^2, and the areal extent of the tidal flats has also decreased correspondingly[3]. The Lu'erhuan River–Malan Island–Sandun Island marine area along the east side of Qinzhou Bay(21°35′18″-21°44′40″N, 108°40′53″-108°44′28″E) is narrow and runs from north to south. The Lu'erhuan River and Jinwo Reservoir are connected on the north side, and the river flows southward from Malan Island towards Sandun Island passing through Jishui Mountain. In recent years, the coastal environment in this area has been strongly disturbed by the construction of coastal roads, the Sandun Marine Road and Sandun Port. In addition, the hydrodynamic conditions, sediment transport and redistribution characteristics of the bay have undergone substantial change, which makes the comprehensive regulation and ecological restoration of the Lu'erhuan River–Malan Island marine area difficult and challenging.

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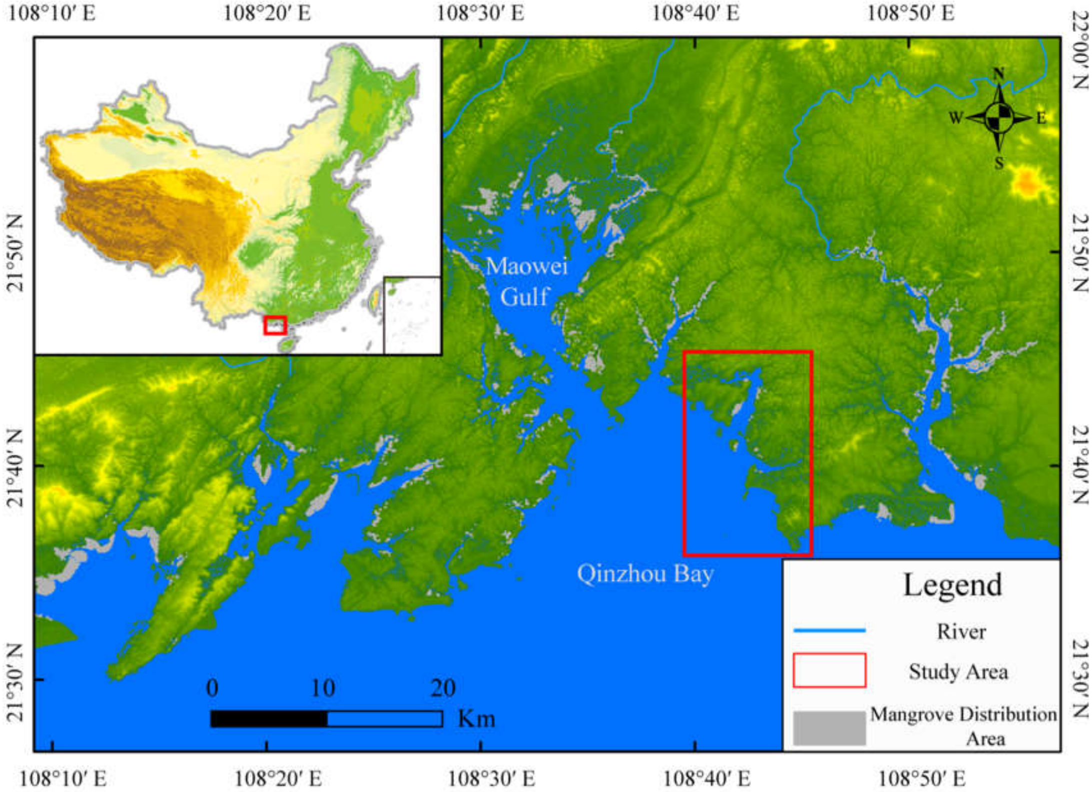

Figure 1. Geographical location of the study area.

2.2. Sampling of surface sediments

Considering the geographical environment and the characteristics of human activity of the area around Lu'erhuan River–Malan Island–Sandun Island, the study area is divided into five partitions from north to south, called area A, area B, area C, area D and area E (Figure.2). Area B is surrounded by the other four areas; that is, it is separated from the other four areas by the east–west coastal highway, the north–south coastal highway, the islands and reefs along Jishui Mountain and the Sandun Marine Highway. Due to the impact of coastal roads, bridges, the Sandun Marine Highway and Sandun Island reclamation projects, the hydrological and sedimentary environment of each area differs slightly. Area A, which consists mostly of the Lu'erhuan River, is more clearly affected by the Jinwo Reservoir located upstream and terrestrial runoff from both banks, and the sediments here clearly have a terrigenous provenance. The north and east sides of area B are significantly affected by the Lu'erhuan and Dazao Rivers, while the south side is connected to area D and more significantly affected by ocean tides. Area C is mainly affected by the Dazao River flowing westward, which is similar to area A. The sediments indicate terrigenous origins. Areas D and E are connected with Qinzhou Bay and are mainly affected by ocean tides. In August 2020，a total of 24 surface sediment samples were obtained by a clam grab sampler, with eight, seven, one, six and two samples obtained from areas A, B, C, D, and E, respectively. The samples were sealed in plastic self-sealing bags and labelled according to their geographical location, number and other information and then returned to the laboratory for subsequent experimental analysis.

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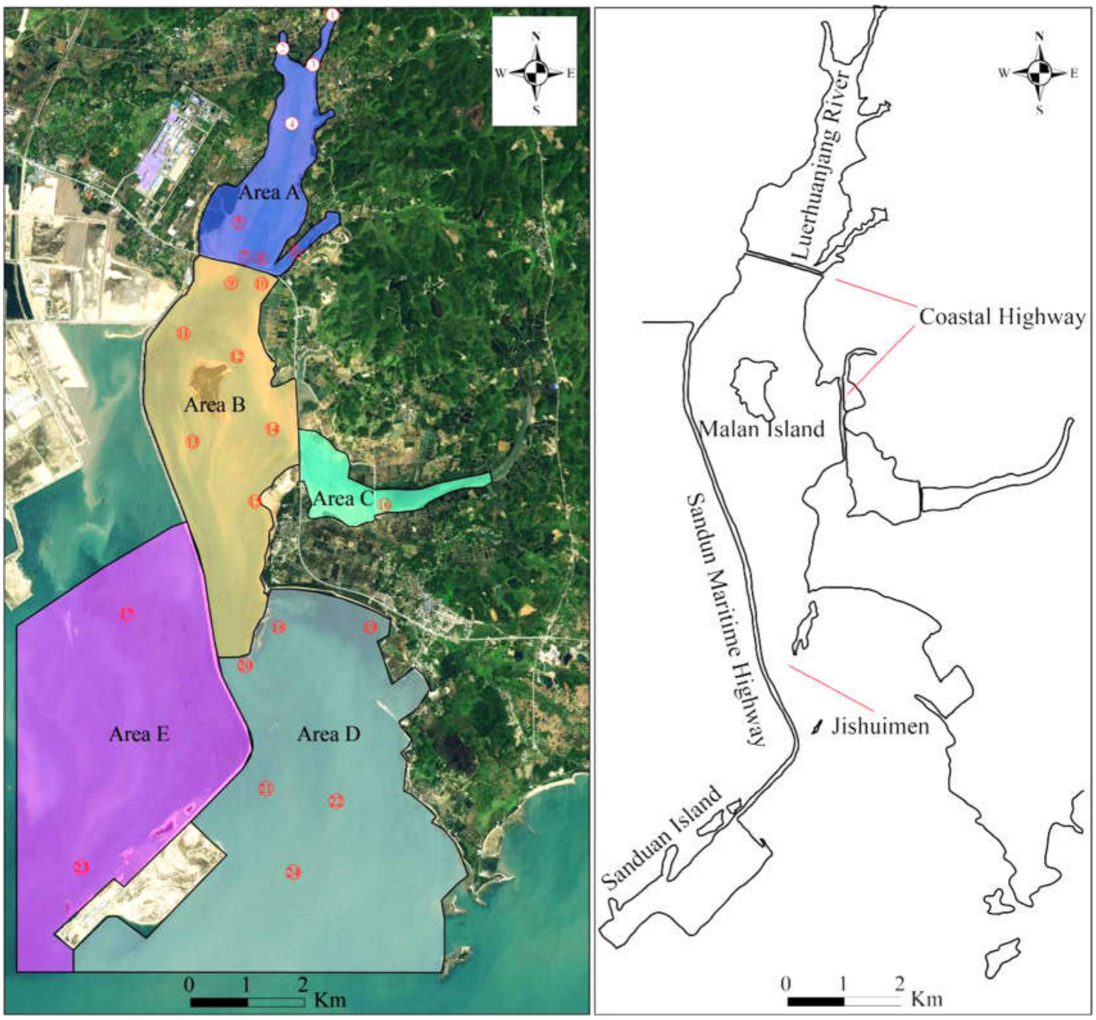

Figure 2. Map of the study area and sampling points.

2.3. Experimental analysis

Grain size, as one of the main physical sedimentary characteristics, is controlled by factors such as transport energy and transport mode and offers insight into the nature of the sedimentary environment [4]. In this study, according to the characteristics of the regional sedimentary environment, the grain size analysis was conducted with the following procedure: First, a suitable amount of each sediment sample was selected and placed into a centrifuge tube, and the samples were numbered appropriately. Next, a suitable amount of 10% HCl was added to the centrifuge tubes to acidify the calcium carbonate sediment in the sample. Distilled water was added to wash and neutralize the samples after the reactions had completed. Organic matter was removed from the samples with an appropriate amount of a 30% H_2O_2solution. After washing again with distilled water to neutralize the samples, 10 mL of a 0.05 mol/L $(NaPO_3)_6$ solutions was added, and the mixture was sonicated in an ultrasonic cleaner for 15 min. Finally, a laser particle size analyser (model: MicrotracS3500) was used to analyse the grain size of the processed samples. To reduce the error caused by uneven sampling, the measurement was repeated three times for each sample.

On the basis of grain size analysis, Endmember analysis was also carried out to accurately identify the sediment provenance. The analysis was performed using AnalySize1.2.1 software [11].After comparing the analysis results of the nonparametric and parametric model; this paper selects the fitting scheme of the general Weibull distribution parameter end member analysis [11].

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Organic matter refers to a variety of organic compounds in various forms within the sediments, and organic matter content is an important indicator in environmental research [12]. Loss-on-ignition 550℃ ($LOI_{550℃}$) is an effective method for measuring the organic content of sediment [13]. $LOI_{550℃}$ provides the percentage of the sample lost (organic matter) during high temperature combustion at 550℃. The specific experimental procedure is as follows: First, sediment samples of approximately 10-20g were ground into powder, placed in a beaker prepared in advance, and then dried in a drying oven at 105℃ together with the cleaned ceramic crucibles. Next, the empty weights of the dried ceramic crucibles were recorded. The dried samples were poured into the ceramic crucibles and dried again at 105°C. Then, the dried crucibles and samples were weighed to obtain the initial sample weights. Next, the ceramic crucibles were placed in a muffle furnace and burned at 550°C for 4-6 hours. Finally, when the temperature in the furnace dropped below 200°C, the ceramic crucibles were removed for final weighing, and the organic matter content was calculated (the drying oven was used to store the samples throughout the experiment). The formula for determining the organic matter content by the $LOI_{550℃}$ method is as follows:

$$\mathrm{LOI}_{550℃} = \frac{M_{105℃} - M_{550℃}}{M_{105℃} - m} \times 100\%$$

In the formula, m is the mass of the crucible; $M_{105℃}$ is the sum of the mass of the sample and crucible after drying at 105℃; and $M_{550℃}$ is the sum of the mass of the sample and crucible after combustion at 550℃.

Elemental geochemistry, an important component of marine sediment research, is one of the major indicators used to identify the elemental composition of sediment. Changes in sedimentary composition and distribution can reflect the provenance of the sediment [14-15]. In this study, some samples are subjected to elemental analysis. First, some of the sediment samples are dried at 105°C, and then the dried samples are ground into powder. Then, 0.1g of powdered sample was weighed and placed in a sealed clean thromboethylene digestion tank. Next, 5mL ofHNO_3 and 1mL of HF were added, and the solution was placed into a microwave digester. After the digestion was completed and the sample had cooled, it was moved to the acid evaporator to remove the excess acid, and 1mL of perchloric acid was added. Then, the processed sample was kept in a constant volume and placed in a 50mL volumetric flask for testing. Finally, an appropriate amount of the liquid to be measured was added to the inductively coupled plasma optical emission spectrometer (ICP–OES) and the carbon and nitrogen analyser to test the contents of metal elements (K, Ca, Mg, Al, Fe, Co, Ni, Cu, Zn, Ti, Mn, Cr, Ga, Cd, Sr, Sn, Ba, Pb) and nonmetal elements (P, As, N).

3. Results and discussion

3.1. Surface sediment types and grain size distribution characteristics

Since the sea area around Lu'erhuan River–Malan Island–Sandun Island is affected by intense human activities, the grain size of the sediments differs greatly. Here, the grain size analysis results of the 24 surface sediment samples are presented. According to Folk sediment classification method (Figure3.)[16], the surface sediments in the study area are divided into four types. The grain size categories are, from fine to coarse, mud (I), silt (II), sandy silt (III) and sand (IV). The finest mud is mainly from five samples from the northernmost Lu'erhuan River (area A). In addition to area A, silt is also present in the other four areas. Sandy silt is mainly present in areas B and D along the route from Malan Island to Sandun Island. However, there is one sample of sandy silt obtained from area a located near the water outlet of the bridge in the southernmost part of the area. This location is extremely vulnerable to the influence of area B during high tide. The sediment with the coarsest grain size is mainly distributed in areas B and D, with two samples each. One sample in area A and one in area E are identified as sand, and they were located near the coastal highway and Sandun artificial island, respectively.

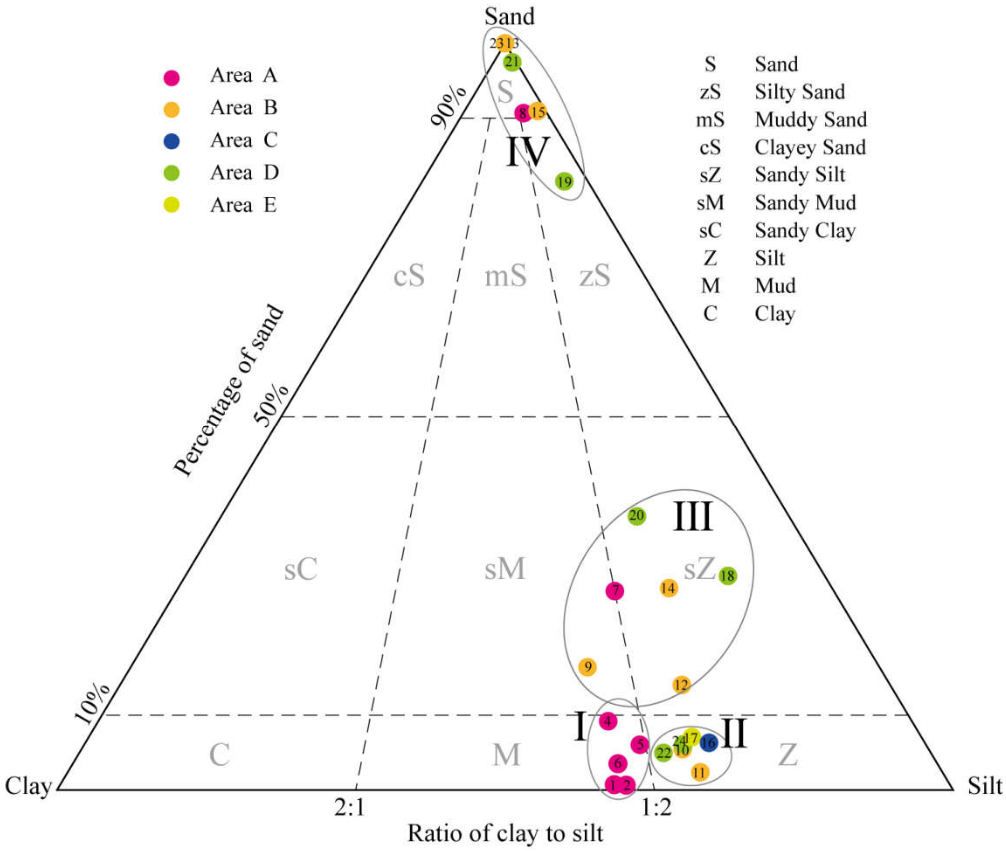

Figure 3. Folk sediment classification diagram.

The grain size frequency curve and average grain size of the four types of sediments in the study area, mud (I), silt (II), sandy silt (III) and sand (IV),differ significantly (Figure 4.). Types I and II show typical unimodal morphology with average grain sizes of 5.99μm and 7.89μm, respectively. Moreover, these sediments are not widely distributed, indicating that the sediment dynamics are localized. The sediment grain size frequency curve of type III is bimodal, and the frequency of the two peaks is close to 5%, indicating that the sediment dynamics of type III are distinctly different from those of types I and II and are more complex. The average grain size is between 9.94 and 22.74μm, with a mean value of 16.40μm, which is relatively broad (Figure 3.). The sediment grain size frequency curve of type IV is chaotic. There are two or more peaks, all of which exceed 100μm or even 1,000μm. The proportion is close to 40%, and the average grain size of sediments is scattered, ranging from 86.46 to 1,044.34μm, with an average of 628.34μm.

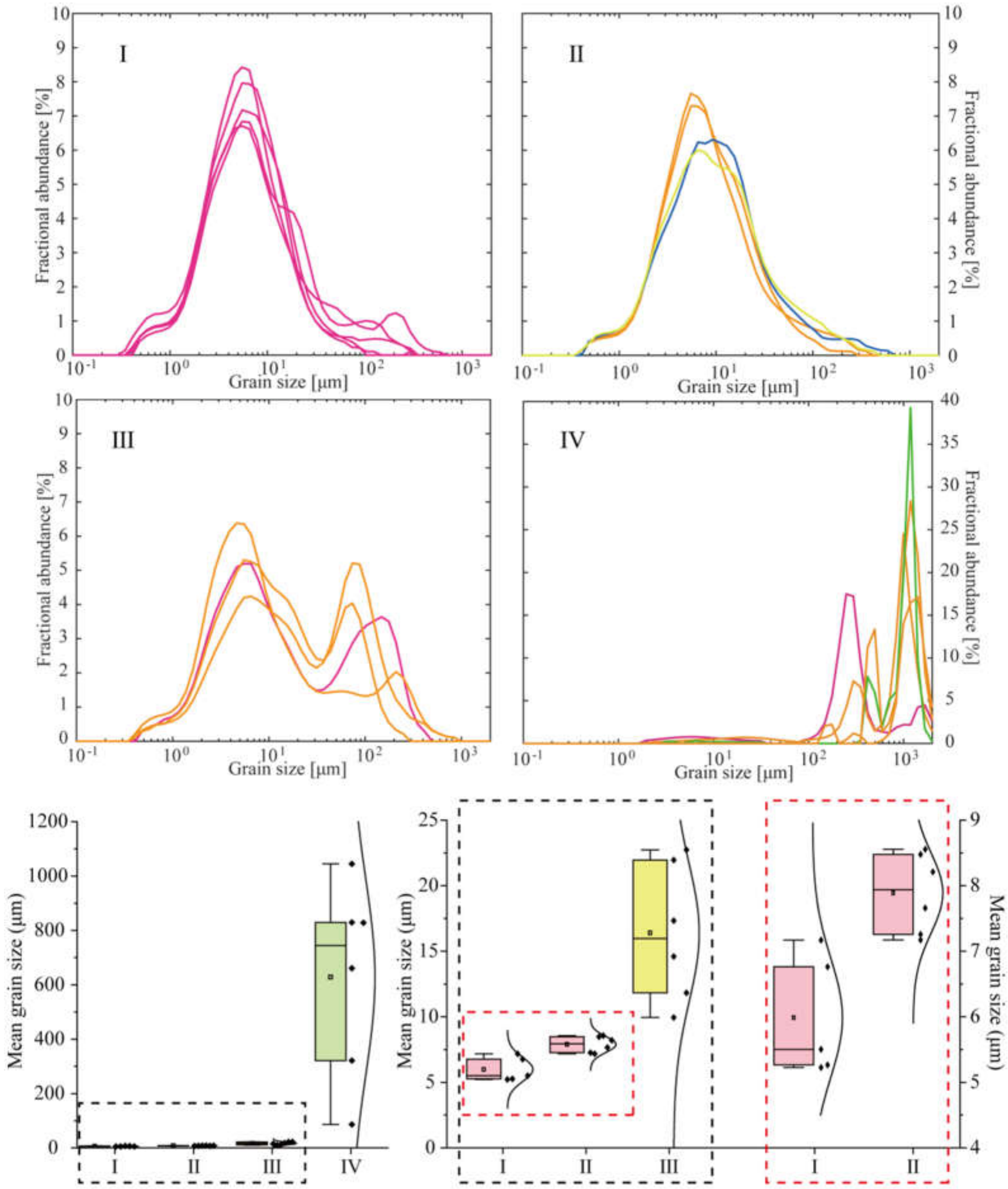

Figure 4. Sediment grain size frequency curve and average grain size distribution.

Next, the spatial distribution of sand (63–2,000μm), silt (4–63μm) and clay (<4μm) content in the sediment samples in the study area are analysed (Figure 5.). The average grain size of the sample exhibits an obvious positive correlation with the percentage content of sand and a negative correlation with those of silt and clay, showing either an exponential increase or decrease. The average grain size of the entire study area is fine, and there are several peaks on the north side of the coastal highway at the junction of areas A and B, the south side of Malantou Island in area B, and the east and west sides of Sandun Island. Due to the significant positive correlation with the average grain size, the percent sand distribution is very similar to the average grain size distribution. However, an area of high percent sand values appears near the easternmost coast of study area, and the six high value areas are also consistent with sampling point IV shown in Figure 3. In contrast, the distributions of fine sand and clay are relatively similar, mainly distributed along the route from the Lu'erhuan River to Malan Island in the north of the study area, and along the east and west offshore areas located far from SandunIsland and the Sandun Marine Highway.

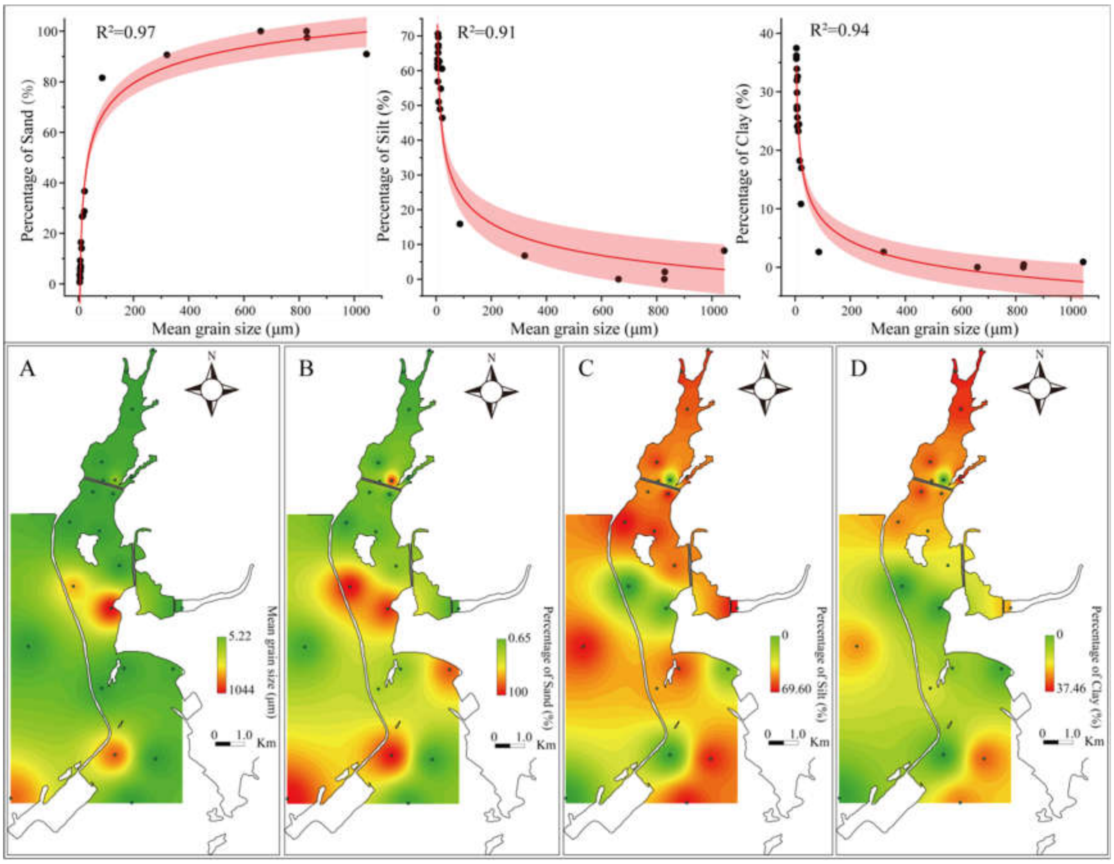

Figure 5. The correlation between mean grain sizes, sand and spatial distribution of silt and sand.

The grain size analysis and sediment type distribution of surface sediments in the study area suggest that the fine-grained sediments are mainly mud (I) and silt (II), with average grain sizes of only 5.99 and 7.89μm, respectively. They are mainly distributed along the route from the Lu'erhuan River to Malan Island (north of areas A, C and B), where a freshwater river enters the bay. In addition, the barrier between the Sandun Marine Highway and coastal highway makes this a relatively enclosed area. For these reasons, the area is less affected by tidal actions, and there are many fine-grained materials there. Moreover, the grain size distribution of sediments is unimodal, indicating stable hydrodynamic conditions and a weak sedimentary environment [17-18]. It is speculated that the surface sediments in this area mainly originate from terrestrial runoff, being transported by rivers or surface water, suspended in water bodies in estuaries and fluctuating tidal currents, and accumulated in a relatively stable hydrodynamic environment. Fine-grained clay and silt accumulation in the coastal area are common throughout the BeibuGulf[18-20], which differs significantly from the coastal areas subjected wave-induced scouring[21]. In addition, east of Sandun Island (area D), the fine-grained sediment component content is also high, yet the sediment grain size distribution shows multiple peaks, indicating that sediment from multiple sources and varied dynamic conditions are present. One possible reason for this is that this location is connected to the open sea, and it is thus affected by multiple tidal currents and waves [20]. The coarse-grained sediments are mainly sand, with an average grain size of 628.34μm. They are mainly distributed on the south side of Malan Island and near SandunIsland. This sampling point is connected to the open sea. Affected by tidal currents and breaking waves, coastal erosion is severe at this location. In addition, the large volume of debris produced by intense human activities, such as land reclamation, marine highway construction and oyster breeding, have caused the sediment distribution here to take on a chaotic multimodal shape in Figure 4.

On the whole, the off shore area around Lu'erhuan River–Malan Island–Sandun Island is subject to intense human activities, and the grain sizes of sediments in this location are obviously varied. Taking the vicinity of Malan Island as the boundary, the sediments on the north side have a singular provenance, are subjected to stable hydrodynamic conditions, and the sediment grain size is relatively small. Finally, the sediment on the south side is complex, and the average grain size is relatively large due to the combined impacts of human activities, tidal currents and waves.

3.2. Endmember analysis of sediments and discussion of material provenances

To more accurately explore the sedimentary environment and sediment provenances in the Lu'erhuan River–Malan Island–Sandun Island area, Endmember analysis of sediment grain size data in the study area was also conducted. Regarding the selection of the Endmember analysis model, after comparing the analysis results of the nonparametric and parametric model, we ultimately selected the fitting scheme of the general Weibull distribution parameter for end member analysis [11]. It can be seen from the grain size Endmember fitting results (Figure 6.) that the Endmember numbers 2, 3, 4, 5 and 6 correspond to R^2values (linear correlation；>0.8 indicates that the fitting requirements are basically met) of 0.794, 0.904, 0.923, 0.957 and 0.957, respectively, and the angular deviation corresponds to 24.0, 14.3, 13.0, 9.3 and 9.2, respectively. The R^2 and angular deviation values tend to be stable as the number of Endmembers increases. Through comparison, the best fitting results can be obtained in the case of five end members. Each Endmember presents a single peak, and the correlation is 0.013, indicating that the separation effect between end members is excellent. The composition data of each Endmember (Table 1.) show that EM1 (1.69–13.37μm) and EM2 (5.99–74μm) are primarily composed of clay and silt, while EM3 (55.9–132.24μm), EM4 (144.66–336.53μm) andEM5 (705.20–1335.68μm) are mainly composed of sand (subdivided into very fine sand (63–125μm), fine sand (125–250μm), medium sand (250–500μm), coarse sand (500–1,000μm) and very coarse sand (1,000–2,000μm)).

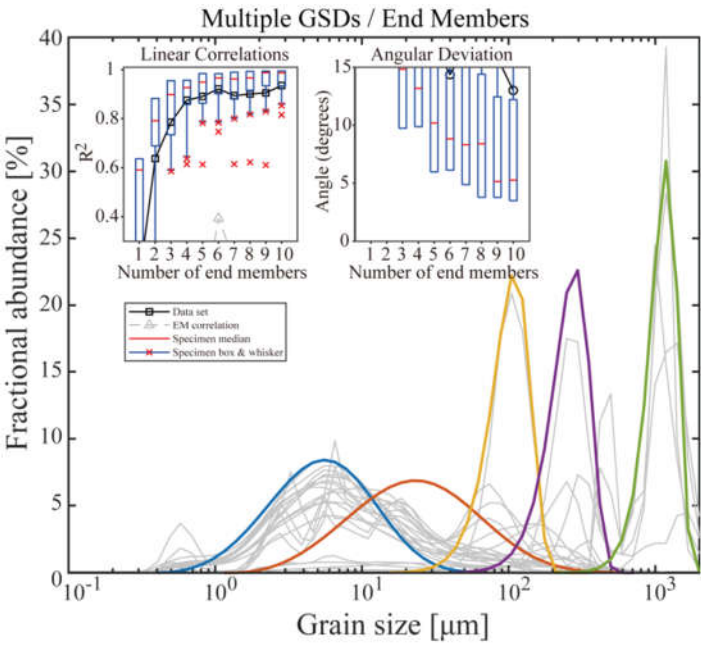

Figure 6. Endmember analysis Diagram.

Table 1. Endmember analysis Chart.

End-Member	P10(μm)	P25(μm)	P50(μm)	P75(μm)	P90(μm)
EM 1	1.69	2.78	4.89	8.43	13.37
EM 2	5.99	10.74	21.11	41.40	74.00
EM 3	55.94	72.99	92.72	113.42	132.24
EM 4	144.66	187.01	237.54	288.48	336.53
EM 5	705.20	856.34	1025.70	1178.83	1335.68

It can be seen from the comparison between the component distribution of each Endmember and the spatial distribution of the average grain size (Figure 7.) that there is a significant inverse relationship between the distribution of fine-grained EM1 and EM2 components and the distribution of the average grain size. An area of high values is formed in the region ranging from the Lu'erhuan River to Malan Island, while the east and west sides of the Sandun Marine Highway, from Malan Island to Sandun Island, exhibit the inverse trend. The distribution of EM5 components with the coarsest grain size is consistent with the average grain size distribution, and five relatively significant high value centres are formed in the study area. The distribution of other coarse-grained EM3 and EM4 components bears no obvious relationship with the average grain size distribution, and two high value centres are formed in the easternmost coastal area of area D and in the northern part of the southernmost Marine Highway in area A.

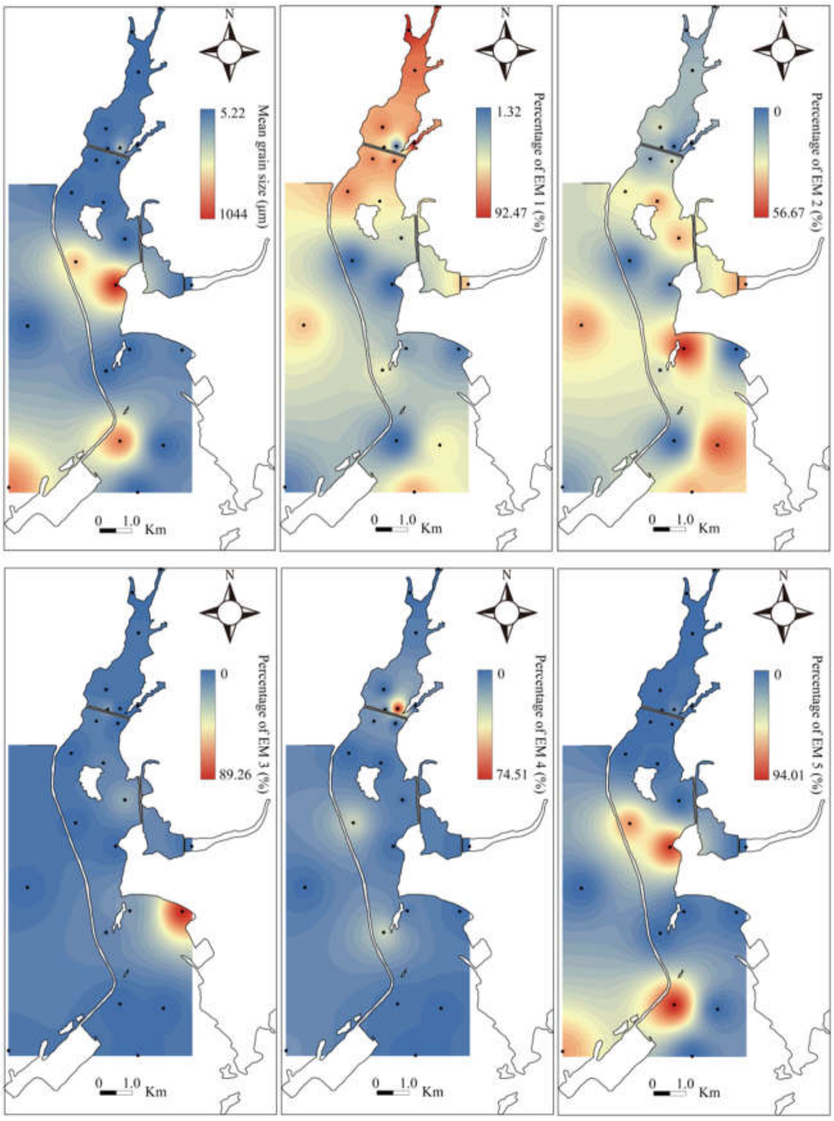

Figure 7. Distribution of average grain size and Endmember components in the study area.

The sediments in the area around the Lu'erhuan River–Malan Island–Sandun Island area have been deeply affected by long-term human activities, such as the land reclamation projects, marine highway construction, oyster breeding, marine fishery infrastructure, and other projects. The material provenances and hydrodynamic conditions are varied. Among the five Endmember components fitted by the Endmember analysis, the spatial distribution of the finest EM1 component is essentially consistent with the clay distribution in the grain size analysis. These finer sediments are mainly distributed in the area

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from the Lu'erhuan River to Malan Island in the northern part of the study area, while the EM1 component content to the south of Malan Island is generally low. In general, such fine-grained sediments are typically suspended in the water column and enter the system via the river and weak tidal currents and are gradually deposited under relatively stable hydrodynamic conditions [17-20]. The area from the Lu'erhuan River to Malan Island is enclosed due to the construction of the Sandun Marine Highway and coastal highway, which simply creates a relatively stable sedimentary environment leading to the deposition of fine-grained materials in this area. In addition, the mangroves distributed on the east and west sides of the Lu'erhuan River dampen the disturbance of the tidal current [22] while also providing muddy sediments for the shoals from the Lu'erhuan River to Malan Island. In short, the materials of EM1 mainly originate from inland or coastal areas and are transported by rivers and weak currents. The spatial distribution of the finer EM2 component is basically consistent with the distribution of silt from the grain size analysis, but its content is relatively low; thus, it is not the main sediment type in the study area. Silt is mainly distributed near Malan Island and in areas D and E, far from Sandun Island and the Sandun Marine Highway. The sediment with this grain size is widely distributed in the coastal area of the Beibu Gulf [20] and is deposited under relatively stable hydrodynamic conditions. It is speculated that this sediment is mainly imported from the near shore through a weak tidal current. The rather coarse EM3 component is concentrated in only one location in the study area, near the beach on the northeast side of area D and connected with the vast inland sea of Qinzhou Bay. It is speculated that the sediment of the EM3 component mainly originates from the nearby beach and is input through the erosion of the coast by weak waves and tidal currents. Coarse-grained EM4 and EM5 are unevenly distributed in the study area (mainly distributed in areas with intense human activities, such as Sandun Island and the Sandun Marine Highway and coastal highway). It is speculated that these components are affected by the combination of human activities, tidal currents and waves and were deposited by ocean water after coastal erosion.

3.3. Organic matter provenance influenced by intense human activities

The organic matter content in the study area was measured by the loss-on-ignition 550°C method ($LOI_{550°C}$). Overall, the organic matter content is low (Figure 8.), with an average of only 4.26%, ranging between 0.72% and 9.49%. In terms of spatial distribution, the organic matter is mainly distributed in the off shore areas from the Lu'erhuan River to Malan Island and the eastern marine area of Sandun Island. Two high value centres are formed in the upper reaches of the Lu'erhuan River and the north-western side of Malan Island. Near Sandun Island, the Sandun Marine Highway and coastal highway, which have undergone intense human activities, the organic matter content is relatively low.

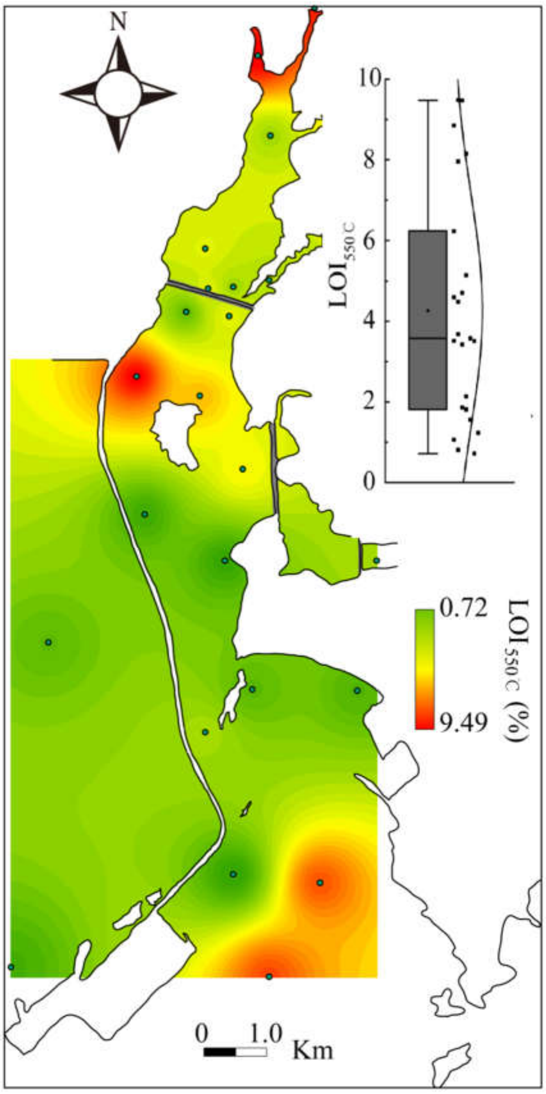

Figure 8. Organic matter content and its spatial distribution.

The content of organic matter in the sediment is closely related to its provenance [23-24]. It can be seen from the correlations between the organic matter content, grain size and Endmember components that the organic matter content of the sediments in the study area has a relatively significant negative correlation with the average grain size of sediment, the percentage content of sand, and the percentage content of coarse-grained EM5(respective R^2: 0.32, 0.46 and 0.30) in Figure 9.Meanwhile, it has a relatively significant positive correlation with the percentage content of silt, clay and fine-grained EM1 sediments (respective R^2: 0.42, 0.445 and 0.42), but there is no significant correlation with the components of EM2, EM3 and EM4 (R^2values of 0.11, 0.05 and 0.06, respectively).

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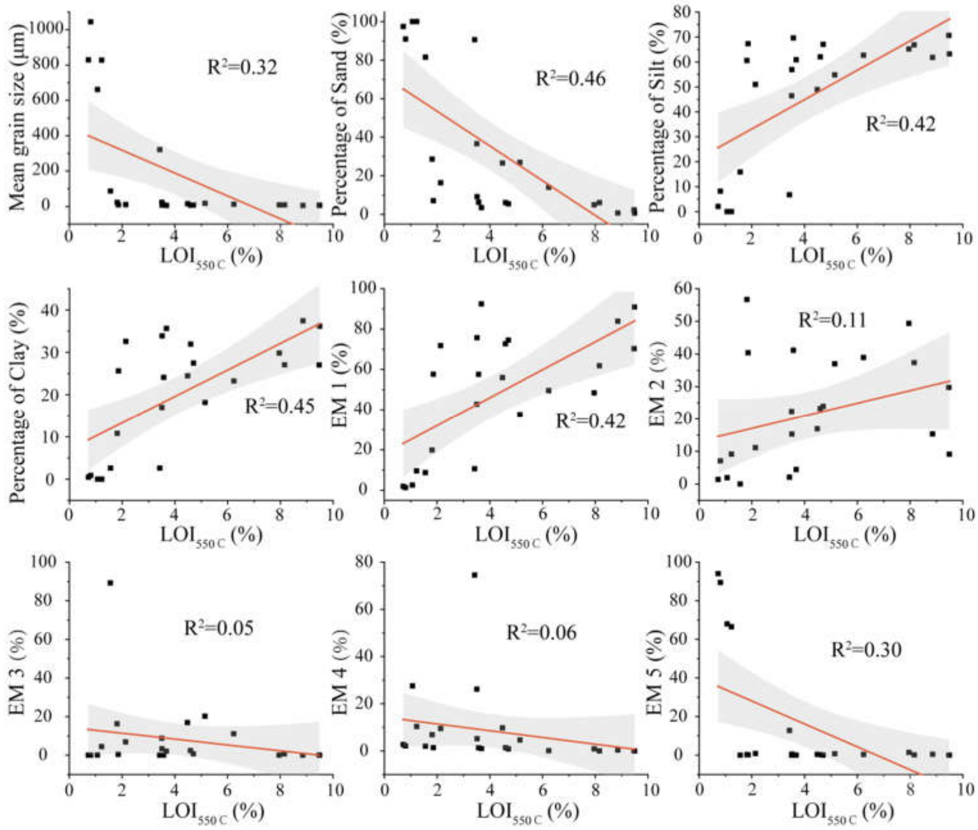

Figure 9. Correlation between organic matter content and grain size along with Endmember components.

Organic matter contained within shallow sea sediments can be primarily divided into endogenous and exogenous material [12]. The former is the accumulation of organic matter produced by organism within the water body (microorganisms, animals, plants, plankton, etc.), while the latter is mainly the particulate or dissolved organic matter imported by rivers and terrestrial runoff. Through research on the spatial distribution of organic matter content and the correlation between organic matter and grain size Endmembers in the offshore area around Lu'erhuan River–Malan Island–Sandun Island, it has been found that the organic matter content has a significant positive correlation with the fine-grained sediments and a negative correlation with the coarse-grained sediments. The organic matter content in the study area may be affected by the provenance of sediments. The organic matter content in the relatively enclosed area from the Lu'erhuan River to Malan Island is relatively high. In particular, the upper reaches of the Lu'erhuan River (the northernmost side of area A) are replenished by inland rivers and the upstream Jinwo Reservoir. Large areas of paddy fields are distributed along the coast, which can input a large amount of granular or dissolved organic matter into the river. This is the primary factor causing the high organic matter content in the surface sediments of this area, thus indicating the enrichment of organic matter as the combined result of natural and human activities. In addition, the content of organic matter on the north side of Malan Island is also high. This area is less affected by the Lu'erhuan River and tidal currents. The relatively weak hydrodynamic environment is conducive to the sedimentation of fine-grained sediments [17-20] and promotes the accumulation of organic matter. Moreover, the large-scale oyster culture in this area [25-26] will also inevitably lead to the input of exogenous organic matter and plankton enrichment [27-29]. This is the main reason for the increase in organic matter in the sediments of the off shore area. In the area connected with the open sea to the east of Sandun Island, the sediment grain size is relatively fine due to the action of tidal currents and waves. In addition, the organic matter content in this area is obviously affected by marine plankton, which is basically consistent with previous research results in the Beibu Gulf [30].

In summary, the provenance of organic matter in the study area resembles that of the sediment Endmember components, exhibiting diversified characteristics resulting from the combined impact of natural and human activities. The organic matter in the upper reaches of the Lu'erhuan River originates from the river and the paddy fields along it and has obvious terrigenous characteristics. The organic matter to the north of Malan Island mainly originates from the external input produced by oyster culture, while the organic matter to the east of Sandun Island is mainly produced internally by marine plankton.

3.4. Elemental analysis and discussion about provenances

In shallow marine sediments, the species, abundance and regional distribution of elements are significantly affected by their provenance [31]. In this study, after analysing 15 heavy metal elements, four common metal elements, and two nonmetal elements, it is found that the distributions of Pb and Cr are similar and are mainly found in the offshore areas from the Lu'erhuan River to Malan Island (Figure10.). The distributions of Fe, Ti, Ga, Co, Sn, Zn, Ni, P, K, Al and Mg are similar and are mainly located near Malan Island and the off shore area to the east of Sandun Island(Figure11.). The distributions of As and Cd are similar, and they are concentrated near the Lu'erhuan River (area A) and Jishuimen (a narrow channel at the junction of areas B and D).Both Cu and Ba have similar distribution characteristics and are concentrated in the offshore area from the Lu'erhuan River to Malan Island and the offshore area to the east of Sandun Island (area D).Two biophilic elements, Sr and Ca, as markers of nonterrigenous sedimentation, show the same distribution characteristics and are mainly distributed in the offshore region to the east of Sandun Island, which is connected to the open sea. The abundance of Mn may be affected by rivers, and is mainly distributed in areas A, B and C from the Lu'erhuan River to Jishuimen. In addition, the change in N is not obvious throughout the study area, but Nis relatively concentrated along the east coast of Sandun Island.

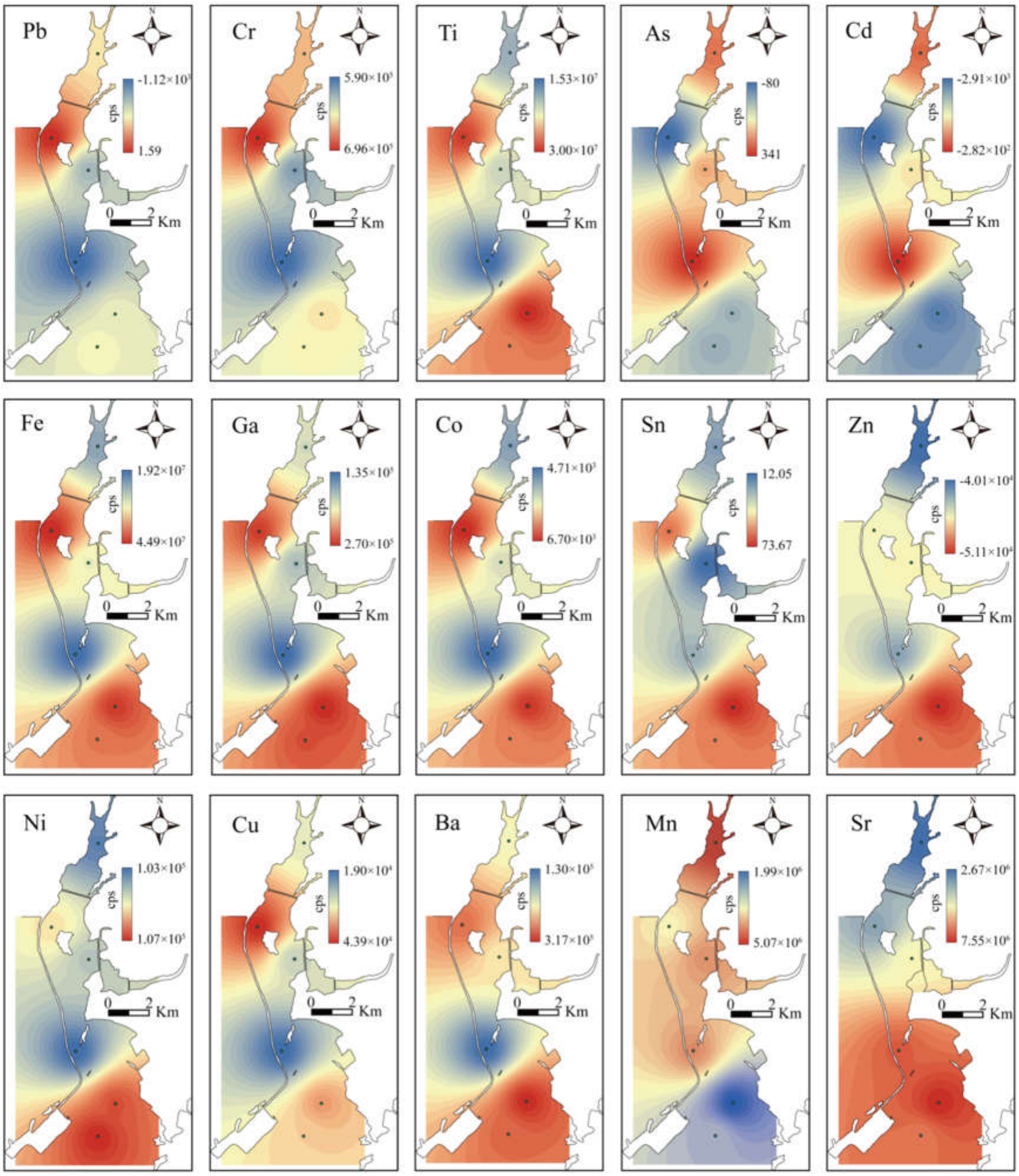

Figure 10. Spatial distribution of heavy metal elements.

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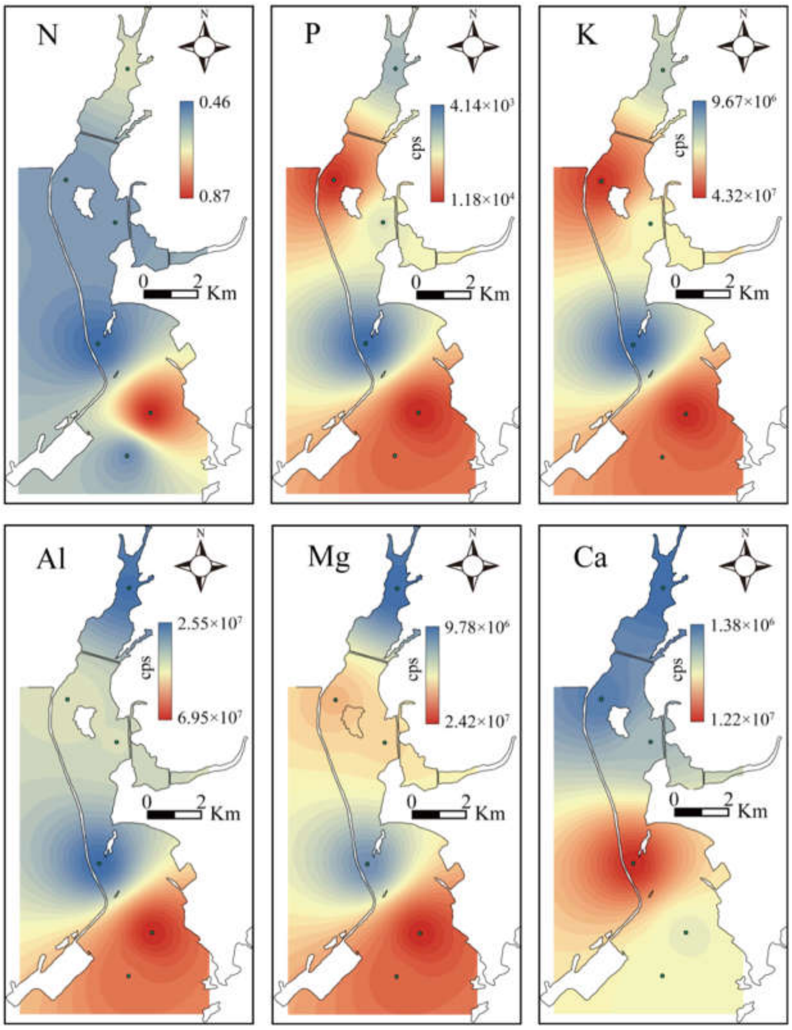

Figure 11. Spatial distribution of N, P and other metal elements.

Compared with all heavy metals, other metals, N and P elements, Al mainly appears in the crystal lattice of clay mineral sand is the characteristic element of clay minerals. As an indicator of terrigenous components in offshore sediments, it is relatively stable during the transportation process from the mainland to the sea [31-33]. Inert elements Ti, Fe, Mg and K and other elements with a positive correlation to Al [31] can also indicate terrigenous input. In addition, Ga is very sensitive to weathering processes and can be transported and deposited with the particles. Classified as lithophilic elements, almost all Ga is derived from clastic materials and can also indicate terrigenous clastic deposits. In this study, the above elements are mainly distributed near Malan Island and the eastern off shore area of Sandun Island. However, there is no obvious increase in the elements in the Luerhuan River (area A) that could be attributed to riverine input. The north side of Malan Island is an area of dense oyster breeding. A popular breeding method in this area is to place rough cement columns or cement plates under oyster rows to create a living environment for the oysters [34]. Due to being submerged in corrosive seawater, Al, Fe and other elements in rough cement columns will gradually leach out and lead to local enrichment. It is speculated that this is the main reason for the high content of these elements near Malan Island. In the offshore area on the eastern side of Sandun Island, human activities, such as high-intensity land reclamation, have introduced many terrestrial sediments [34]. Combined with erosional forces of waves and rainstorms, the sediments enter the bay mouth with the tide and cause the enrichment of Al, Fe, Ga and other elements. In other words, as human activities intensified in the region, there has been a clear deviation in the terrestrial indicator elements within the sediments in the study area. However,

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it is worth noting that the heavy metal element Mn, which mainly originates from river input and oxidation precipitation in shallow sea sediments [32], can partially indicate terrigenous sediments. The Mn in the study area is mainly distributed along the route from the Lu'erhuan River to Jishuimen (areas A, B and C). This area is subject to the confluence of river discharge and terrestrial runoff, and portions of the terrestrial materials are deposited here.

Unlike Al, Ti and other terrestrial indicator elements, Ca and Sr are characteristic elements and biophilic elements of marine sediments, respectively [31-32], and represent the provenance of marine sediments. In this study, the spatial distributions of Ca and Sr bear some similarities. They are mainly distributed in the off shore area to the east of Sandun Island, which connects with the open sea. Under the action of tides and waves, it is easy to carry marine sediments to this location. Additionally, this location is also affected by human activities, especially near Jishuimen (the narrow waterway at the junction of areas B and D), and Ca is significantly enriched here. It is speculated that the cement used in oyster breeding and engineering construction decomposes and is deposited here by the tides. In general, although the Ca and Sr in the study area are affected by human activities, they can still indicate the provenance of marine sediments in the area.

The existence form and enrichment degree of transition elements (Cr, Mn, Fe, Co, Ni, Cu, Zn and Cd) in the study area represent, to a certain extent, the input flux of organic matter in the corresponding depositional period [31]. As and Cd are clearly affected by human activities, while Cu is less affected by human activities [8]. The enrichment degree of As and Cd is quite apparent, especially in the vicinity of the Luerhuan River (area A) and Jishuimen. The reason for this may be related to industrial and agricultural wastewater and other human activities [35-36].

In general, although the sediments in the study area are strongly affected by human activities, Ca and Sr, as indicative elements of the provenance of marine sediments, may still be distributed in the eastern sea area of Sandun Island, which is connected to the open sea. Meanwhile， Al, Ti, Fe, Mg, K, Ga and other elements are significantly impacted by human activities when used as terrigenous indicators. However, the distribution of Mn in this area compensates for this defect and can better indicate the distribution of terrigenous sediments. Mn is mainly distributed in the off shore area from the Luerhuan River to Jishuimen.The influence of human activities on the enrichment of As and Cd in the study area is very obvious, while Cu is less affected by human activities.

4. Conclusions

The following conclusions can be drawn from the grain size analysis, Endmember analysis and geochemical element analysis of surface sediments in the Luerhuan River–Malan Island–Sandun Island area currently influenced by intense human activities.

The offshore area around Lu'erhuan River–Malan Island–SandunIsland is affected by intense human activities; thus, the sediment grain sizes differ significantly. Taking the vicinity of Malan Island as the boundary, the sediment on the north side has a single provenances, hydrodynamic conditions vary little, and the sediment grain size is relatively small. However, the sediment on the south side is complex, and the average grain size is relatively large due to the multiple impacts of human activities, tidal currents and waves.

The Endmember analysis shows that, due to long-term intense human activities, the material provenances and hydrodynamic conditions in the offshore area around Lu'erhuan River–Malan Island–Sandun Island are varied. The EM1 component is mainly transported by rivers and weak tidal currents from inland or coastal areas; the EM2 component is mainly input from near shore sources through the weak tidal current; and the rather coarse EM3 component mainly comes from the nearby beach and is input through coastal erosion by weak waves and tidal currents. However, the coarse-grained EM4 and EM5 are unevenly distributed in the study area. They are affected by human activities, tidal currents and waves and are deposited by marine transport after coastal erosion.

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The provenance of organic matter in the waters around Lu'erhuan River–Malan Island–SandunIsland resembles that of the sediment Endmember components, exhibiting diversified characteristics as a result of the superposed impact of natural and human activities. The organic matter in the upper reaches of the Lu'erhuan River originates from the river and the paddy fields along it and exhibits obvious terrigenous characteristics. Meanwhile, the organic matter to the north of Malan Island mainly comes from the external input produced by oyster breeding, while organic matterto the east of Sandun Island mainly comes from the internal input produced by marine plankton.

In the elemental analysis, although Al, Ti, Fe, Mg, K, Ga and other elements are significantly disturbed by human activities when used as indicators ofter rigenous sediments, Mn can still sufficiently indicate the distribution characteristics of terrigenous sediments, which are mainly distributed in the offshore area from the Lu'erhuan River to Jishuimen.In addition, Ca and Sr, as indicative elements of marine sediment provenance, are located in the eastern off shore area of Sandun Island, which connects with the open sea. Finally, affected by human activities, the enrichment of As and Cd in the study area is clearly a result of human activities, while Cu is less affected by human activities.

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