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Research Article

Sources of sedimentary organic carbon in coastal ecosystems from the Tien Yen Bay, Quang Ninh

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Abstract: Mangroves in Tien Yen Bay, Quang Ninh province are considered typical mangrove ecosystems in Northern Vietnam. Mangroves play a significant role in carbon storage, and mangrove sediment is the largest carbon pool in this ecosystem. The present study aims to determine the role of the carbon source from mangroves to provide the organic matter in intertidal sediments by the stable isotopes approach. The $\delta^{13}C$ of sediments ranged from –27.36 ± 0.28‰ in mangrove forest (RNM) to –26.28 ± 0.05‰ in the tidal flat with seagrass (SG1). Stable isotope mixing model results showed that mangrove materials are an important source of sedimentary organic carbon (OC), providing 64.6 ± 14.9%, 38.4 ± 14.9%, 39.8 ± 15%, and 48.8 ± 14.9% for the site RNM, SG1, SG2, and SG3, respectively. The second OC source in mangrove sediment is suspended particulate organic matter (POM). The POM in this area includes fine mangrove materials, which are exchanged with coastal waters through the tidal dynamics. The present results suggested that mangroves are important in accumulating organic carbon and fine–grained sediments in the Tien Yen Bay, contributing important values to climate change mitigation and maintaining biodiversity in this area.

Keywords: Carbon sources; Mangroves; Stable isotopes; Sediment; Tien Yen.

1. Introduction

Mangrove forests play an important role in preventing climate change, natural disasters, catastrophes such as storms, floods, coastal erosion, saline intrusion, etc. [1–2]. They also provide critical ecological functions and services such as nursing habitat, feeding zone, breeding grounds for aquatic species, waterbirds, migratory birds, and providing high economic benefits for humans [3–5]. Recently, mangrove forests have been degraded globally due to human activities such as aquaculture, urbanization, industry, and agriculture [6–7]. The Kyoto Protocol (1997) and the Paris Agreement on Climate Change (2016) were signed by 191 members of the United Nations Framework Convention on Climate Change to reduce greenhouse gas emissions. These agreements are the legal basis for implementing greenhouse gas reductions through various solutions and mechanisms such as the Clean

Development Mechanism (CDM) and the Greenhouse Gas Emission Reduction Initiative. The Reducing Emissions from Deforestation and Forest Degradation program (REDD+) plays essential roles in reducing deforestation and forest degradation, enhancing conservation, sustainable management of forests, and maintaining forest carbon stocks [8–9]. Mangroves are considered a rich carbon pool in coastal areas, with higher carbon storage than other forests on Earth [10–11]. Currently, the total global area of mangroves is 139170 km^2, from which mangroves accumulate about 6.5 billion tons of carbon, equivalent to 24 billion tons of potential CO_2 gas [12].

The largest C stock of mangrove forests is sedimentary organic carbon, which have trapped CO_2 for thousands of years [10, 13–15]. Thus, carbon accumulation in mangrove sediments plays a vital role in the global carbon cycle and reduces Greenhouse gas. In Vietnam, mangrove forests are also large carbon sinks in coastal areas and can store more than 900 tons of C/ha [14, 16, 17]. In mangrove research, the stable isotope carbon ($\delta^{13}C$) is applied to trace organic carbon sources for animals and deposited sediments [18]. Study results from the Red River Delta and Thanh Hoa province highlighted that mangrove materials are important carbon sources in mangrove sediments [19–20]. Therefore, understanding the roles of mangroves on carbon accumulation in the sediment will provide valuable information for conserving and coastal ecosystems and climate change mitigation. In the present study, we hypothesize that the mangrove materials are the primary sources of organic carbon accumulation in mangrove sediments and adjacent habitats in Tien Yen Bay, Northern Vietnam. We investigated the transect analysis of sediment grain size, total organic carbon (TOC), total Nitrogen (TN) and $\delta^{13}C$ values of sediment samples through a natural mangrove forest to seagrass beds to examine the roles of mangrove forest in organic carbon accumulation and to determine the sources of organic carbon in sediments.

2. Materials and Methods

2.1. Study site

The study was conducted in the Hai Lang and Dong Rui communes, Tien Yen District, Quang Ninh province. Sampling sites are located between the Voi Lon and the Ba Che Rivers, with natural mangrove forests and seagrass bed growth in the tidal flat along the coastline. Tien Yen Bay is a large semi-closed Bay in the Northeast of Quang Ninh Province [21], which has a high biodiversity with specific ecosystems such as mangroves, seagrass beds and estuaries. Recently, the wetlands in Hai Lang have been converted into cultivated land and aquaculture, causing the degradation of coastal ecosystems. Human activities such as exploiting marine resources, farming, sea transportation, seafood harvesting strongly affected the environment and ecosystem in this area. The mangrove forest in Hai Lang commune covered 770.81 ha, which is considered a typical mangrove ecosystem in Northern Vietnam. The mangroves have good forest quality, dominated by *Kandelia obovata*, *Avicennia marina*, *Aegiceras corniculatum*, and *Bruguiera gymnorrhiza* and *Rhizophora stylosa* [21]. Mangrove forests in this area are rich in biodiversity with high–value seafood products such as peanut worms, octopus, flower crabs, and penaeid shrimps. However, the mangrove forest ecosystem in the study area has been degraded due to the less sustainable exploitation activities. The remaining forest area is still under threat of destruction and degradation due to infrastructure and economic development impacts.

2.2. Field Sampling

Sediment samples were collected following three transects from mangrove forest to seagrass beds in Hai Lang–Dong Rui tidal flat, Tien Yen Bay, Quang Ninh (Figure 1). Four sediment samples were collected at each transect by a stainless-steel spatula in the low tide and kept in polyethylene bags. Samples were stored in a cool box with ice immediately then transported to the laboratory for further analysis. We also recorded additional information of dominant vegetation and sediment characteristics in each sampling site. The seagrass species *Halophila ovalis* and *Halophila beccarii* are distributed in tidal mudflat (SG1, SG2, SG3) adjacent to mangrove forest (RNM). Total 12 sediment samples were collected for analysis, with 09 samples in seagrass beds and 03 samples in mangrove forests. SG 01 is the sampling zone with a distance of 300 m from the mangrove forest, SG 02 is located between the estuary and mangrove forests, SG 03 is adjacent to the mangrove forest, and the RNM zone is inside mangrove forests. The distance between each transect was approximately 200 m in length.

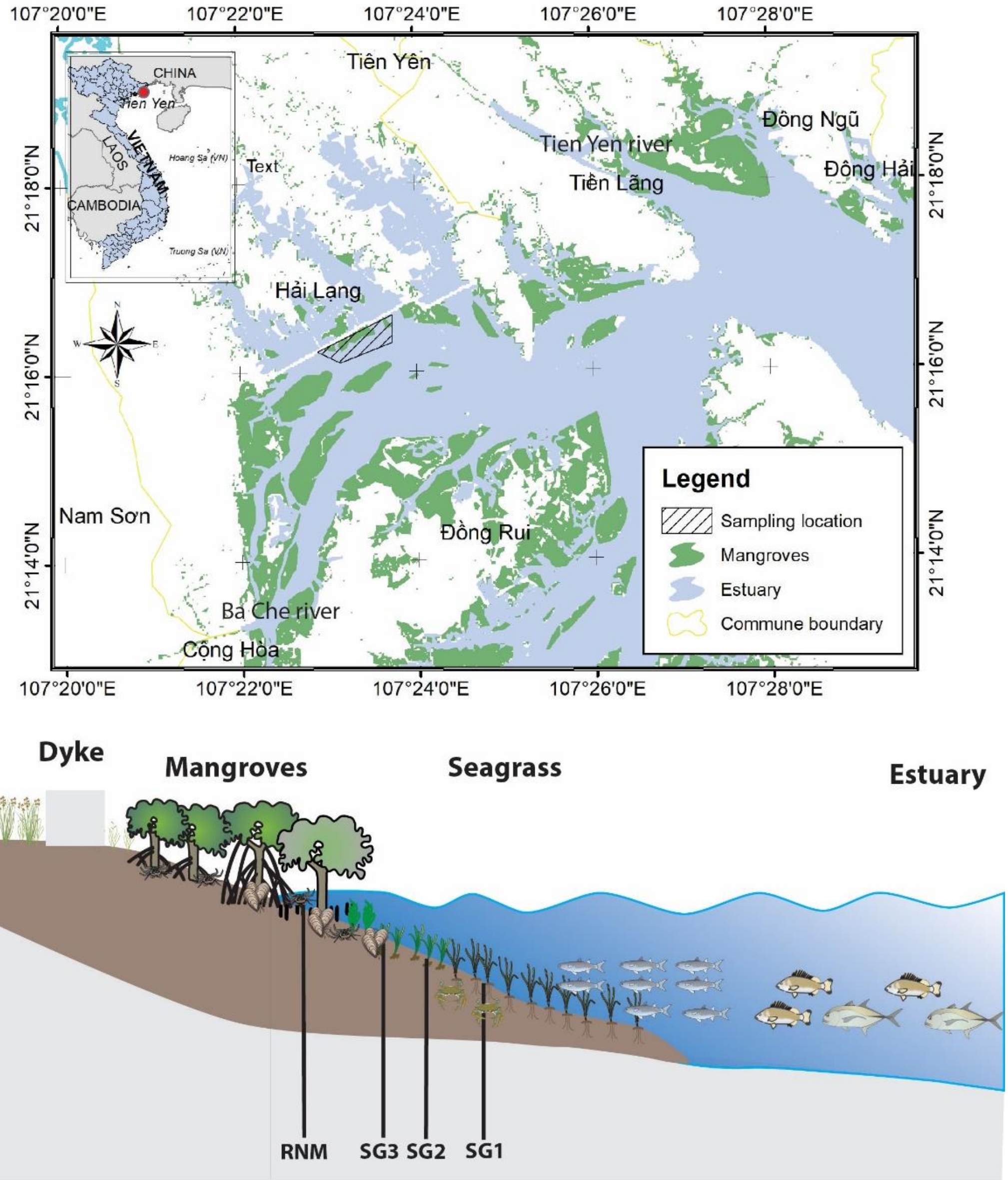


Figure 1. Map of the study area and sampling location.

2.3. Sediment grain size and organic matter content analysis

For sediment grain size analysis, approximately 1g of wet sediment sample was weighed and transferred to ceramic cups, then removed all visible root debris, shells, organic litter with a stainless steel clamp. Then 10% H_2O_2 solution was added to remove organic matter in sediment, and H_2O_2 solution was added to samples until no air bubbles existed. The remaining sample was put in the electric oven to remove the residual H_2O_2 and distilled water was added during the H_2O_2 removal process to ensure the sample was not dried. The laser particle analysis Horiba LA950 was used to determine sediment grain size, ranging from 0.01 to 3000 µm. Each sediment sample was analyzed repeatedly three times with a relative error <10%.

The organic matter (OM) content in sediment was measured by loss on ignition methods. Approximately ten cubic centimeters of fresh sediment samples were also collected to determine bulk sediment density. Fresh sediment samples were dried at 60°C in an electric oven until constant weight for bulk density measurement. Then, the dried samples were ground until fine powder by an agate mortar and pestle. All visible branches, roots, crumbs, and other organic materials are removed during the grinding process. Approximately 2 g of finely ground sediment sample will be burned at 550°C for 3 hours to estimate OM content [14, 19].

2.4 Total organic carbon (TOC), total nitrogen (TN), and stable isotope analysis

Approximately 0.2 g of finely ground sediment sample was placed in an Eppendorf tube for stable isotope analysis. Then, 2 ml of 1N HCl were added to remove the carbonate content in 24h. After acid treatment, the milli–Q deionized water was used to wash and remove any acid residuals in the sample. This process was repeated four times in each sample before the subsample was dried at 60°C for 48 hours. Powdered samples were weighed about 10–30 mg for stable isotopes analysis depending on organic matter content. Then the samples were wrapped in 6×8 mm tin capsules before analysis by stable isotope ratio mass spectrometry (IRMS) by the method of connecting elemental analysis system (Elemental Analyzer – Euro Vector) and the stable isotope ratio mass spectrometry system (Nu – Perspective IRMS) at Key laboratory of Geoenvironment and Climate Change Response, VNU University of Science.

Analytical samples were placed in the automatic sample tray and dropped into the elemental analyzer combustion chamber. In the combustion chamber, the sediment sample was converted to CO_2 and NO_2. Then, these gases were passed through the reducing chamber and reduced to CO_2 and N_2 gas. These gases were passed through the gas chromatographic column and separated for a stable isotope mass spectrometry system. Here, the gases are ionized and pass through the isotope ratio mass spectrometry (IRMS) where carbon and nitrogen isotopes are counted by Faraday cups. The IRMS determines the stable isotopes values of the sample by comparison with standard gases. The values $\delta^{13}C$ and $\delta^{15}N$ of the sample were calculated using the formula:

$$\delta X(‰) = \left(\frac{R_{sample}}{R_{standard}} - 1\right) \times 100 \quad (1)$$

where δX is $\delta^{13}C$ or $\delta^{15}N$, R is the ratio of a heavy isotope to a light isotope ($^{13}C/^{12}C$ or $^{15}N/^{14}N$), R_{sample} is the ratio of the sample analyzed, and $R_{standard}$ is the stable isotope standards of limestone Pee Dee Belemnite (PDB).

2.5. Stable isotope mixing model and statistical analysis

The source of organic matter can come from both local and phylogenetic sources. Locally–sourced organic matter is provided by mangrove or benthic plants that settle into the sediment. Organic matter has phytoplankton origin transport of organic matter from other places too, from the mainland by the flow of phytoplankton through tidal dynamics. However, the true phytoplankton value is hard to determine in semi-closed bays and estuaries like sampling areas. Thus, we applied an average value of the suspended organic matter (POM) as a potential carbon source of sediment in the present study.

The value of $\delta^{13}C$ in organic matter can be used to distinguish organic matter in sediments and different organic matter derived from different plants. The difference in the value of $\delta^{13}C$ between terrestrial and phytoplankton is because terrestrial plants take CO_2 directly from the air during photosynthesis, and phytoplankton takes dissolved CO_2 or HCO_3^- in water. Through photosynthesis, taking CO_2 directly from the air, terrestrial C3 plants, including higher plants, create organic matter with $\delta^{13}C$ value ranging from –29.4% to –27‰ [21–22]. According to the United States Environmental Protection Agency, the organic carbon source contribution was estimated by an iso_error calculation file provided in excel format [23]. In the study area, the primary sources of organic matter include mangrove materials and suspended organic matter in the sedimentary environment. The seagrass materials (SG) were not considered potential carbon sources in sediment due to low biomass and rare abundance. For statistical analysis, the analysis of variance (ANOVA) was performed in Sigma Plot 12.0 software to determine the spatial differences in sediment characteristics.

3. Results and Discussion

3.1. Sediment characteristics

The sediment samples are sticky mud with dark gray color. The sediment composition varied spatially from mangrove to seagrass bed (Figure 2). The sand content in SG2 was highest while in RNM was highest. In contrast, the silt content was highest (Figure 2). In sampling transects, it was caused by the tidal dynamics in transporting sediments. The decreasing tidal energy from Ba Che River watershed to mangrove forests causes large sediment particles to be deposited at the edge of the forest, and the smaller particles size of sediments are transported and accumulated inside the forest during high tide [24–25]. Furthermore, mangrove roots and trunks play important roles in reducing wave and tidal current velocity, providing a stable environment for sediment deposition.

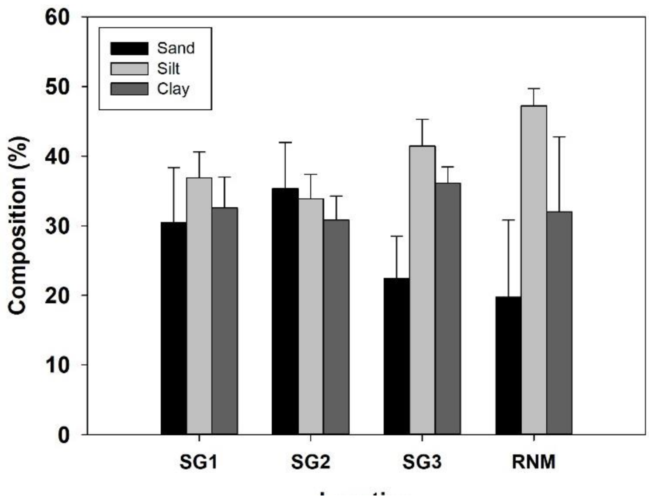
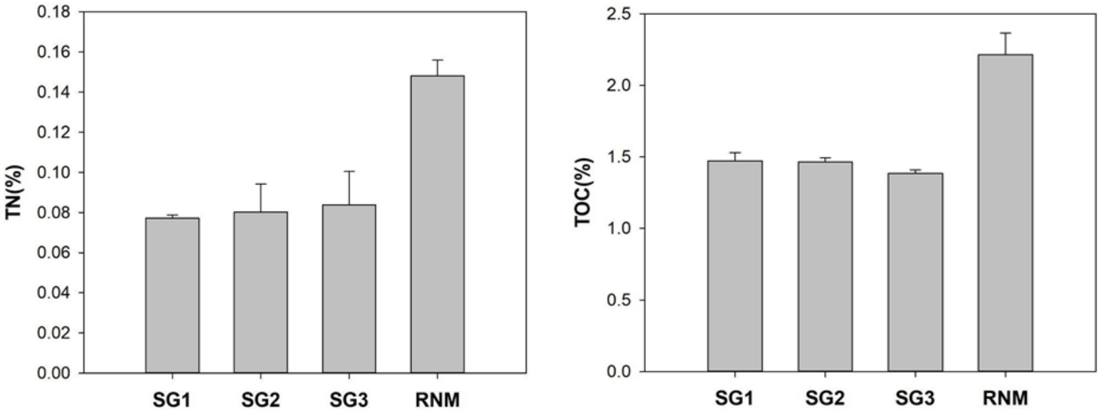


Figure 2. The grain size composition in sediment in the study area.

The bulk density of sediments at the mangrove forest was 1,431 ± 0.15 (g/cm^3), which was smaller than that of seagrass areas with average values of 1,501 ± 0.06; 1,495 ± 0.06 and 1,546 ± 0.03 g/cm^3 for SG1, SG2, and SG3 zone, respectively. This difference may be related to the increase in fine-grained sediment and organic matter content in the mangrove forests. However, the density value of sediments in this area is relatively high compared to other mangrove forests in Vietnam and Asia–Pacific regions [14, 15, 19].

3.2. TOC, TN and organic matter contents in sediments

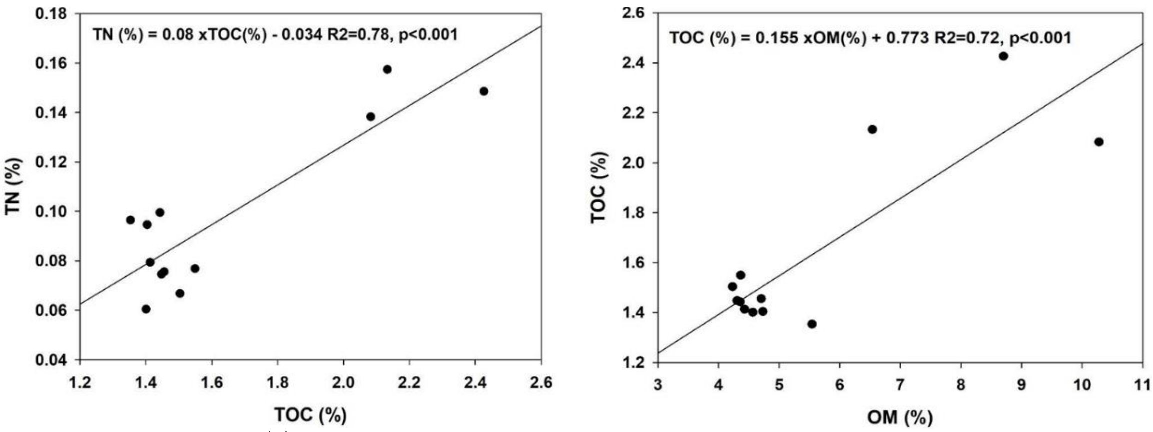
The average TN (± SD) concentration in sediment ranged from 0.077 ± 0.002% to 0.148 ± 0.008% and tended to increase gradually from the estuary to the mangrove forest (Figure 3a). The ANOVA results showed a clear difference between the TN content in mangroves and the seagrass sediments (ANOVA, $p < 0.05$). This difference may be related to the high abundance of decomposing organic matter in mangrove forests compared to the seagrass area, which provides an important nitrogen source in sediments [26–27]. Additionally, the seagrass beds are often flooded by tides, and nitrogen in the sediment can be exchanged with the water column, leading to a decreasing trend in the TN content in the sediment. However, the TN content in sediments from Tien Yen Bay is not too high compared to the mangrove and coastal tidal flat areas in Vietnam [22, 28].



(**a**) (**b**)

Figure 3. The TN (a) and TOC (b) content in sediments.

The OM content varied spatially with sampling location. The OM in mangrove sediment is higher than in seagrass areas, ranging from 4.3 ± 0.05% to 8.51 ± 1.53% for SG2 and RNM zone, respectively. Similarly, the TOC content in the sediment showed an increasing trend from the seagrass beds into the mangrove forests (Figure 3b). ANOVA analysis showed a statistical difference in TOC content among mangrove and seagrass sediments (ANOVA, $p < 0.05$). However, the spatial difference of TOC between the sampling locations in the seagrass bed was not observed in this area. The average TOC content in the mangrove sediment was 2.21 ± 0.15% which was lower than other sites in the Asia–Pacific region [13, 14, 20]. The increasing TOC in mangrove sediment is related directly to abundant organic matter sources from mangrove litters such as fallen branches and leaves [15, 18, 29].



(**a**) (**b**)

Figure 4. The relationships between TN and TOC (a) and TOC and OM (b) in sediments.

In addition, the TOC content can be affected by the sediment deposition rate and the maturity level of mangroves. When the sediment deposition rate is high, organic matter can escape the decomposition of microorganisms faster, so it is better preserved. Therefore, the sediment deposition rate is important in conserving and retaining OM in coastal areas. The maturity level of mangroves also has a positive relationship with TOC in sediments. The TOC and TN in sediment have a close relationship (Figure 4a), which indicates that the nitrogen content in mangrove sediments comes mainly from organic matter. The correlation between TOC and OM (Figure 4b) is similar to previous research in Tien Yen Bay, Red River Delta, Thanh Hoa, and Can Gio mangrove forests [14, 19, 20, 28].

3.3. Sources of sedimentary organic carbon in sediments

In the present study, the organic matter sources of sediments include mangrove (Man), seagrass (SG), and suspended organic matter (POM). The values of $\delta^{13}C$ (‰) was showed in

Table 1. The organic matter sources in the area have a clear difference in values of δ^{13}C (‰) and can be used to determine organic carbon sources in sediments. However, the δ^{13}C (‰) value of SG is significantly higher than those of sediments, mangroves, and POM, indicating that seagrass is not a significant source of OC in sediment. Thus, a stable isotope mixing model was applied for estimating OC sources in sediments.

Table 1. The δ^{13}C (‰) value of potential organic carbon sources in sediments.

Source of OM	δ ^{13}C (‰)	n	Reference
POM	–25.0 ± 0,9	4	[30]
SG	–14.8 ± 1,7	8	[30]
Mangrove (Man)	–28.8 ± 1,2	39	[3]

The value of δ^{13}C (‰) at all sampling sites is showed in Figure 5. The lowest δ^{13}C was found in the mangrove forest, with an average of –27.36 ± 0.28‰. The δ^{13}C values of sediment increased gradually from SG3, SG2 to SG1, with average values of –26.71 ± 0.24, –26.34 ± 0.20 and –26.28 ± 0.05‰, respectively. Research results observed a statistically significant difference among sampling locations of the δ^{13}C value in sediment (ANOVA, $p < 0.05$). The δ ^{13}C values decreased gradually from the estuary to mangrove forests, which reflected the possibility of changing the origin of OC in sediments [20, 21, 28]. The value of δ^{13}C (‰) in mangrove sediments ranged from –26.01 to –27.06, within the range of POM and Man. The stable mixing model showed that the mangrove materials contributed 64.6 ± 14.9%, 38.4 ± 14.9%, 39.8 ± 15 %, and 48.8 ± 14.9% for the RNM, SG1, SG2, and SG3 areas, respectively (Figure 5).

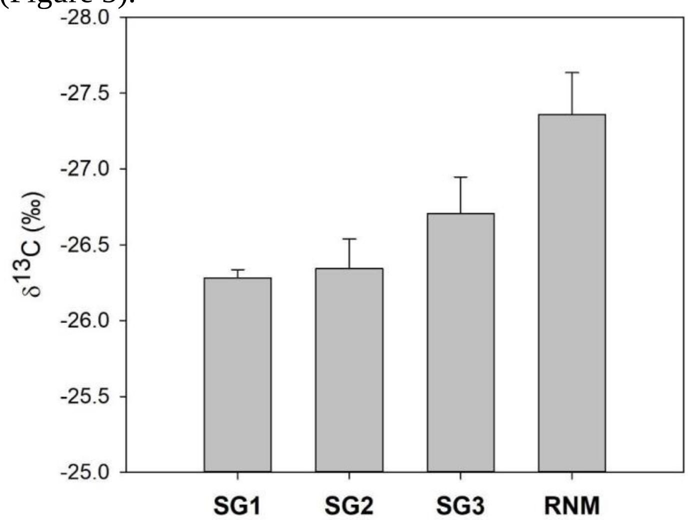


Figure 5. The value of δ^{13}C (‰) in coastal sediment.

3.4. Roles of mangrove forest in organic carbon accumulation

Research results showed that mangrove materials significantly contribute to OC sources of mangrove sediment and adjacent habitats (Figure 6). The mangrove forest biomass is significantly higher than seagrass, which provides a vital source of OC for coastal waters. The POM in coastal water and estuaries in sampling areas was higher than the previous research in Thanh Hoa, Red River Delta [4,22]. This pattern may be related to the geomorphological settings of Tien Yen Bay, causing the mangrove materials to not be accessible and exported to open water, leds to low values of δ^{13}C in POM samples [21]. The second reason may be that seagrass grows only seasonally, so it will not be a significant source of sediments [31]. Overall, mangrove materials play important roles in carbon accumulation in sediment. The mangrove materials contribute significantly to sedimentary OC accumulation in the forest and adjacent habitats. Thus, the conservation and development of mangrove forests will play important roles in carbon sequestration and climate change mitigation.

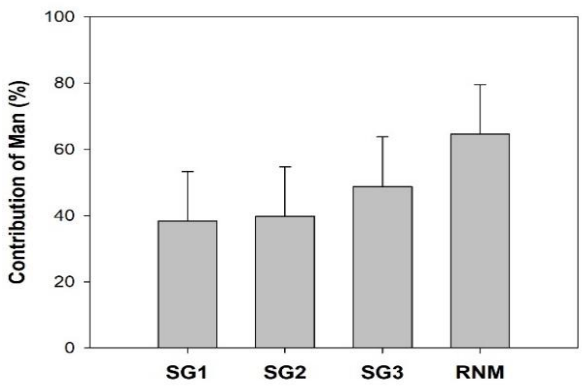


Figure 6. Contribution of mangrove materials for organic carbon buried in sediments.

4. Conclusions

The present results showed that mangroves might accumulate large amounts of organic carbon and fine–grained sediments in coastal areas. The fine–grained sediment content tends to increase from estuaries towards mangrove forests, indicating the roles of mangroves in enhancing sediment deposition and lower tidal dynamics. The values of OM, TOC, TN, and $\delta^{13}C$ in sediments varied spatially with sampling sites along mangroves and seagrass beds transect. The stable isotope mixing model results indicated that mangrove materials contribute significantly to organic carbon sources of sediment in both mangrove and seagrass beds areas. Therefore, conserving mangrove forests and adjacent ecosystems will enhance carbon storage and reduce greenhouse gas emissions from coastal areas.

Supplementary Materials: None

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Conflicts of Interest: The authors declare no conflict of interest.

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