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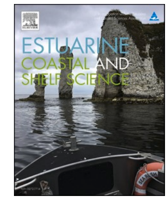

Tracing organic matter sources in the estuarine sediments of Vanga, Kenya, and provenance implications☆

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ABSTRACT

Mangrove ecosystems can potentially and indirectly modulate the effects of sea level rise due to their ability to trap and retain sediments. In order to gain a better understanding of the potential sediment sources and dynamics in the mangroves of Vanga, Kenya, inter-seasonal riverine, estuarine and coastal/marine sediments together with agricultural soil and mangrove tissues were studied. Elemental ratios (C/N) and carbon ($\delta^{13}C$) stable isotope composition, were analysed to disentangle sources of sediment organic matter (SOM) in the Vanga, Estuary. The organic carbon (C) content, C/N ratios and $\delta^{13}C$ values ranged between 0.1 and 2.4%, 9.9 to 35.5 and −24.8 to −19.9‰ respectively. These contents were also as expected relatively higher in mangrove tissues than in all the sediment samples. $\delta^{13}C$ values of mangrove sediments were higher than those of the mangrove tissues, which was attributed to rapid decomposition, dilution by freshwater and mineral organic matter (OM) discharged by the Umba River as well as outwashing by ebb tides. On average, C/N ratios were also observed to be greater than 10 in all samples collected during both the dry and wet season. This has been shown to reflect a pronounced contribution of allochthonous organic matter. Using a combination of $\delta^{13}C$ values and C/N ratio, the dominance of riverine POM was also evident from a Bayesian Stable Isotope Mixing Model in R-program (SIMMR) that indicated OM source mixing but with a dominant (~60%) contribution of riverine OM. The observed and modeled variability of SOM in the Vanga estuary points to the hypothesized influence of the Umba River on Vanga Estuary sediments but with evidence of potential material exchange and influence of tidal fluxes within the estuary.

1. Introduction

Fluvial systems are the vital link between the terrestrial biosphere and the oceans, delivering freshwater, nutrients, and sediments to the marine realm (Milliman et al., 2016; Tamooh et al., 2014). Tropical rivers transport approximately 60% of total riverine carbon and 35% of the total sediment fluxes to the global oceans (Milliman et al., 2016; Schlünz and Schneider, 2000). Organic matter (OM) pools in mangrove ecosystems comprise dissolved OM and particulates originating from fluvial inputs, combined with marine-derived local production, and lateral inputs (Rumolo et al., 2011; Bouillon et al., 2004). Source characterization is therefore crucial in understanding factors that affect rates of sediment transport, budgets and dynamics in the context of land use changes, geographic locations and climate variability, as well as biogeochemical cycles (Jennerjahn et al., 2009; Khan et al., 2015; Kennedy et al., 2004). Some of the OM sources in sediments include decayed plant biomass, *in-situ* production by phytoplankton, mangroves and submerged aquatic vegetation, as well as material derived from

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weathered organic-rich lithologies in the catchment (Blattmann et al., 2018; Petsch, 2013). Inevitably, the admixing of OM from the various sources occurs in mangrove habitats due to hydrodynamic effects of tidal loading and flushing (Rumolo et al., 2011; Jennerjahn et al., 2009). For example, adjacent coastal and marine OM and tidal influence dominate the source of sediment OM sources in mangroves with low organic carbon, while mangrove plants dominate the source of OM in mangroves with high sediment OM (Bouillon et al., 2008). Therefore, in a combined tidal-river dominated estuary, the influence of both river and tidal flush coupled with *in-situ* production complicates the elucidation of material exchange, sources and importance of OM (Kristensen et al., 2011; Jennerjahn and Ittekkot, 2002). Benthic consumers in mangrove ecosystems also play key role in the material production, consumption, conversion and export/exchange between ecosystems (Bouillon et al., 2008; Kristensen et al., 2011). Others have also shown that OM in large rivers carrying large loads have progressively older POC and low organic carbon (Marwick et al., 2015; Tamooh et al., 2014) compared to smaller rivers draining smaller catchments, carrying smaller loads and transporting sediments for short distances. Among other proxies, carbon (δ^{13}C) and nitrogen (δ^{15}N) stable isotopes signatures of estuarine OM reflect the signatures of the above-mentioned sources, the riverine δ^{13}C values being determined by the plant biomass and soil OM dominant within their catchment and source (Tamooh et al., 2014). Consequently, considerable research has utilized both carbon (C) and nitrogen (N) stable isotopes coupled with elemental carbon to nitrogen (C/N) ratios as tracers to identify and partition organic matter provenance in estuaries (Bouillon et al., 2008; Kusumaningtyas et al., 2019; Nasir et al., 2016; Tamooh et al., 2012; Thornton and McManus, 1994). This methodology makes use of the natural variation in OM derived from different sources reflecting the dominant primary producers in their locality of origin (Rumolo et al., 2011). The variation in the isotope composition of OM is a consequence of distinct photosynthetic pathways by different groups of plants; the C3, C4 and CAM plants (Fry, 2006; Rahayu et al., 2019) from where the OM is sourced. It is from these distinct pathways that the sediments/soils retain the isotopic signatures of the plant materials dominant in their source location. However, stable isotope signature overlap is inevitable in river-tide dominant estuary (Bouillon et al., 2008) and this overlap can confound the interpretation and source characterization of OM (Donato et al., 2011; Kennedy et al., 2004). The δ^{13}C vs. C/N values can be utilized to effectively distinguish between terrestrial and aquatic OM end-members (Rumolo et al., 2011; Kennedy et al., 2004), while δ^{13}C and δ^{15}N values can be effectively used to distinguish marine- and sewage-derived OM mainly because sewage effluent is characterized by low δ^{13}C and δ^{15}N values relative to marine-derived OM. δ^{13}C and δ^{15}N values of terrestrial-derived OM can overlap with sewage-derived signatures, making their use in highly polluted waters difficult (Nasir et al., 2016). Sediment organic matter with C/N ratios values greater than 10 are considered to indicate a terrestrial source because terrestrial OM is depleted in N compared to aquatic environments (Kennedy et al., 2004; Kristensen et al., 2008; Nasir et al., 2016). Similarly, δ^{13}C values have been used to distinguish plant-derived OM in catchments (von Fischer and Tieszen, 1995), with varying dominant vegetation e.g. terrestrial C3 and C4 plants has an average δ^{13}C of −30‰, mangrove leaves with average δ^{13}C values of −25 to −31‰ while marine derived OC has a typical δ^{13}C value of −20‰ (Bouillon et al., 2008) and bulk soil (Marin-Spiotta et al., 2009) with reported average δ^{13}C value of −27‰. On the other hand, the large δ^{15}N variability in marine OM can be attributed to the nitrogen fixing cyanobacteria that has much lower δ^{15}N values compared to the non-nitrogen fixing organisms (McKee et al., 2002). Based on this variability in OM signatures from various sources, end-member mixing models can be used to determine the proportions of the various contributing sources of OM, e.g., the open-source Bayesian isotope modeling packages like the Stable Isotope Mixing Model in R (SIMMR) (Kusumaningtyas et al., 2019; Parnell et al., 2013; Rahayu et al., 2019; Sasmito et al., 2020) or two-end mixing models (Bouillon et al., 2003; Kennedy et al., 2004; Thornton and McManus, 1994; Xiao and Liu, 2010). The aim of this study was therefore to determine the variation of sediment organic matter along Umba river by utilizing already developed and tested methodology of elemental and stable isotopes of carbon and nitrogen as natural tracers (Kusumaningtyas et al., 2019; Khan et al., 2015; Sasmito et al., 2020; Bouillon et al., 2003). Additionally, Bayesian modeling was utilized to constrain and characterize the potential sources of sediment OM (SOM) (Rahayu et al., 2019; Sasmito et al., 2020; Kusumaningtyas et al., 2019) within the Vanga, Estuary. In this study, a combination of δ^{13}C values and C/N ratios has been used to disentangle the sources contribution of different end members. Organic matter in estuarine systems with both riverine and tidal influences, are either produced autochthonous produced *in-situ*, allochthonous transported by rivers and tides or anthropogenic (Khan et al., 2015; Gonneea et al., 2004; Bouillon et al., 2008). Autochthonous OM plays key role in coastal ecosystem dynamics while terrigenous sediments have been shown to largely influence aquatic productivity with increased supply of terrigenous OM shifting systems from autotrophic to heterotrophic production (Deininger and Frigstad, 2019). Knowledge of sediment sources, consequently assist in understanding the sediment budgets and sedimentation within an ecosystem. This is crucial for mangrove ecosystems as sedimentation indirectly assist mangroves to build-up their elevations against local sea-level rise (Woodroffe et al., 2016). Therefore, it is vital to understand the localized sources of sediments in tropical estuaries and mangrove habitats. Source characterization also allows for planning and determination of site-specific sediment budgets and mangrove surface elevation changes vital in understanding the potential response of mangroves to the current and predicted sea level rise (Woodroffe et al., 2016) and consequently better mitigation measures. The holistic studies of sediment dynamics present an avenue for better understanding of carbon sequestration and climate change mitigation (Alongi, 2014; Woodroffe et al., 2016). In this study we hypothesize that the riverine OM sources are the dominant contributors to the total SOM in Vanga, Estuary. To test our hypothesis, we investigated the distribution of SOM in different sediment types from source to mouth and within the estuary. Based on the OM distribution we modeled the percentage contribution of each sediment type as an end-member source to the overall SOM in the Vanga Estuary.

2. Materials and methods

2.1. Study area

The Vanga estuary is located along the south coast of Kenya (4° 39' S and 39° 13' E). It receives freshwater and terrigenous sediments from the transboundary Umba River. The river is approximately 200 km long and drains its catchment from its source in the Usambara Mountains in northeast Tanzania, before crossing the Kenyan-Tanzanian border and flowing into the Indian Ocean through a ~3000 ha (Mungai et al., 2019) patch of mangroves at Vanga (Fig. 1). This site was chosen because Vanga Estuary is within a proposed transboundary conservation area (TBCA) between Tanzania and Kenya (Tuda et al., 2019). The proposed TBCA extends from Diani, Kenya in the north to Tanga, Tanzania in the south. (Fig. 1). This stretch of the coastal strip harbors rich, contiguous and connected marine and coastal biodiversity transcending the Kenya-Tanzania border. Due to the rich biodiversity and associated contribution to the socio-economics of the area, the TBCA has been recognized by international agencies including the World Wildlife Fund (WWF) and Convention for Biological Diversity (CBD) as a biodiversity hotspot that needs conservation attention. Fishing, smallholder crop and animal farming on the riverbanks of the Umba River are the main activities of inhabitants along the Umba River and coastal Vanga (Fortnam et al., 2020).

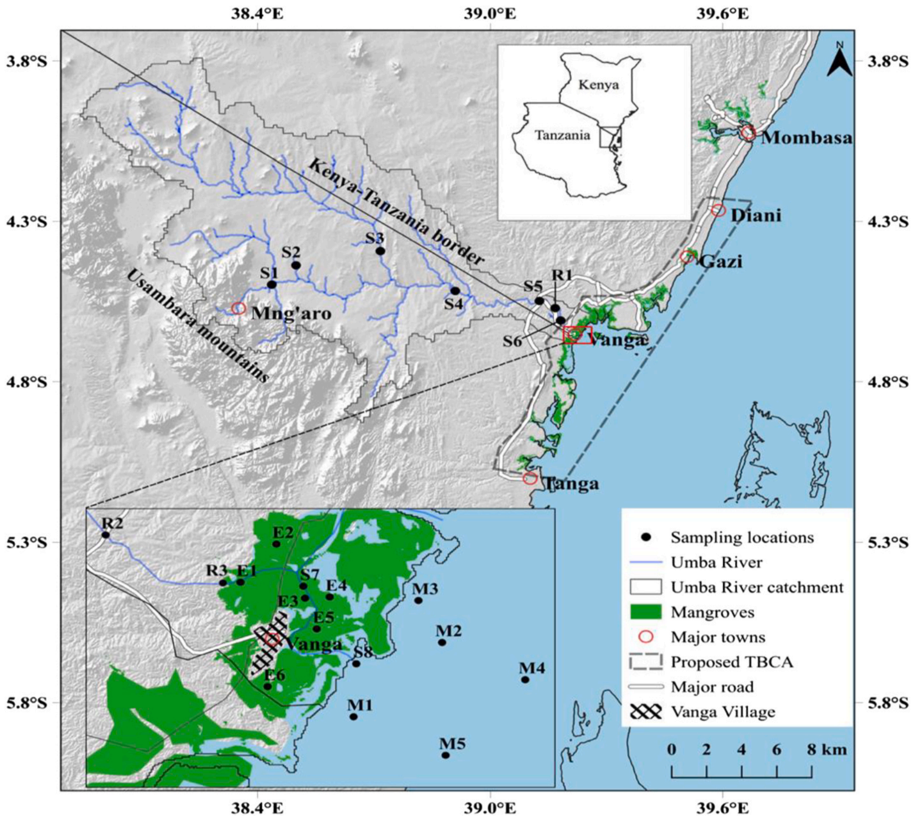

Fig. 1. Map of study area showing the course of the Umba River and sampling stations, from its source in the Usambara mountains in Tanzania to its mouth in Vanga Estuary, Kenya.

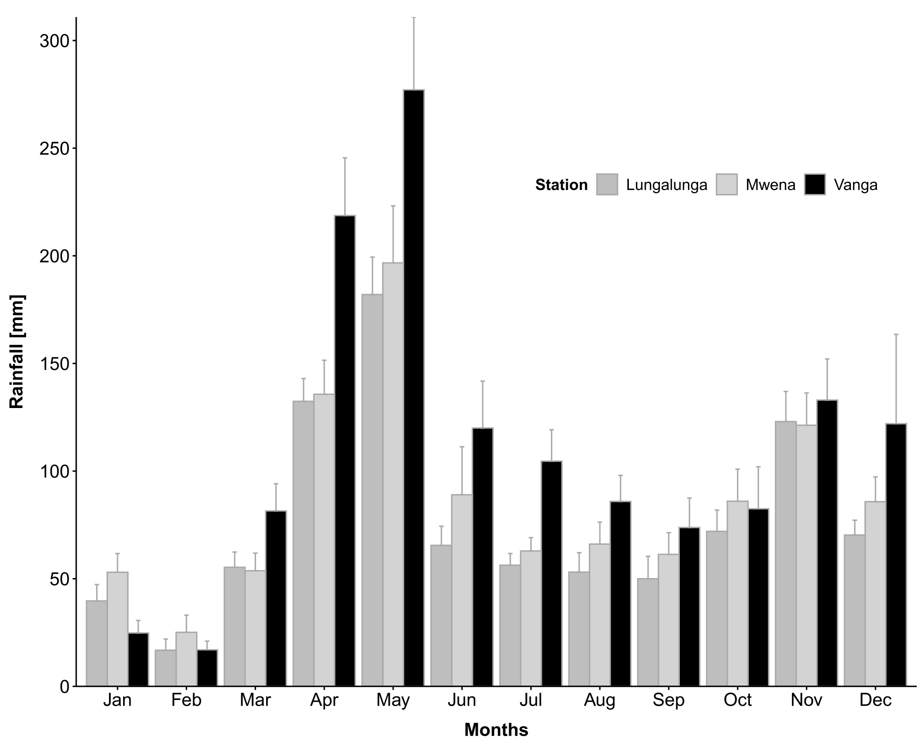

Fig. 2. 35-year (1960–1995) average precipitation in Mwena, 42-year average (1960–2002) precipitation in Lungalunga and 31-year (1960–1991) average precipitation in Vanga. All the stations are located in south coast of Kenya at a distance of 20 km and 10 km between Vanga-Lungalunga and Vanga-Mwena respectively. The error bars represent the standard errors of the historical mean monthly precipitation. Source: Kenya Meteorology Department (https://www.meteo.go.ke/).

2.2. Climate

East African tropical climate is controlled majorly by the large-scale pressure systems of the Western Indian Ocean and the two distinct monsoon periods (Ayugi et al., 2020). The pressure systems are attributed to a combination of mesoscale convective systems, globally propagating convection-triggering waves and the inertial instability in generating convection (Ayugi et al., 2020; Nicholson, 2018; Verschuren et al., 2009) with the effect of producing two rainy seasons between March and July and between October and November (Fig. 2). Long-term historical precipitation data from three stations (Vanga, Lungalunga, and Mwena) in south coast Kenya manifests two rainy seasons (Fig. 2). This pattern complements historical data from the Global Precipitation Climatology Centre (GPCC) online repository and shows a similar precipitation pattern (Fortnam et al., 2020).

2.3. Field sampling and pretreatment

Field sampling campaigns were conducted during i) the dry season in February–March 2019, ii) the wet season in June–July 2019, and iii) at the end of the wet season in July 2020 (Table 1). Surface sediment samples were collected in ten riverine stations along the Umba River (Fig. 1). Three of the sampling sites (S1, S2, S4) were on the Tanzanian side, while seven of the sampling sites (S5, S6, S7, S8, R1, R2, R3) were located on the Kenyan side. Estuarine intertidal surface sediments were collected in six stations close (10 m) to the main channel (E1, E3, E5) and farther (50 m) away from the main channel (E2, E4 and E6). Coastal/marine subtidal (<20 m depth) sediment samples were collected stations M1, M2, M3, M4 and M5 (Fig. 1). Surface (0–5 cm depth) sediment samples were collected using a hand-held corer and a mini Van Veen grab (Tamooh et al., 2012). Three replicate sediment samples were collected and placed in tight zip-lock plastic sample bags and placed in cooler boxes for further analysis in the laboratory. Sediment cores were taken in stations E1 to E5 using a 60 cm long *Hydrobios* sediment sampler. The extracted cores were subsampled every 5 cm in the top 20 cm and every 10 cm for the remainder of the core (Kusumaningtyas et al., 2019; Rahayu et al., 2019). Water sampling for suspended particulate organic matter (SPOM) was done using vacuum pump and Niskin bottle at depth 1–2 m below the river surface and 5 m below the sea surface. Subsequent extraction of SPOM from the water samples were done using the gravimetric method (Nasir et al., 2016). Environmental parameters were measured *in-situ* using Palin test and YSI multiparameter. Plant tissue samples comprising mature and freshly fallen yellow mangrove leaf samples and twig litter from *A. marina*, *R. mucronata*, *X. granatum*, *C. tagal* and *B. Gymnorrhiza* were collected by hand comprising of 2 leaves/sample. The leaves were washed and dried at 60 °C for 72 h (Bouillon et al., 2003).

2.4. Analytical methods

2.4.1. Laboratory analysis

Grain size analyses were made using the principle of diffraction and diffusion of monochromatic laser beam on suspended particles suing a Malvern© 2000 Mastersizer particle analyzer. Mean grain size (μm) was estimated according to (Folk and Ward, 1957). The principle is based on forward scattering of laser beam by suspended sediment particles. A range of 0.02 and 2000 μm can be measured. Sediment samples for OM analyses were dried at 60 °C for 48 h, grinded and homogenized using a Fritsch© Pulverisette 7 ball mill (Khan et al., 2015; Kusumaningtyas et al., 2019). Subsamples for organic carbon (C) and carbon stable isotope ($\delta^{13}C$) analyses were washed with diluted 1 N hydrochloric acid (HCl) first to remove potential carbonates and re-dried for 24 h at 40 °C. The sediment samples were then flash-combusted in a CN elemental analyzer (Eurovector EA3000 Elemental Analyzer) to obtain total carbon content (TC), total nitrogen (N) and organic carbon (C) content in. The samples were then measured for C and N stable isotope composition using a Thermo Finnigan Deltaplus Mass Spectrometer coupled to a Flash EA1112 Elemental Analyzer. Measured $\delta^{13}C$ and $\delta^{15}N$ values are denoted by the conventional delta (δ) notation and expressed in parts per million (‰) deviations from a VPDB and atmospheric nitrogen standards for $\delta^{13}C$ and $\delta^{15}N$ respectively. The isotopic ratios of $^{13}C/^{12}C$ and $^{15}N/^{14}N$ were defined by the equation below:

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

where $R = {}^{15}N/{}^{14}N$ or ${}^{13}C/{}^{12}C$. Data quality control throughout the analysis was ensured by running a reference standard (acetanilide) after every five runs. This was done mainly to permit corrections for machine drift and deviations to be incorporated prior to calculation of isotope abundances. The analytical precision of instruments was determined by replicate analysis of the standards which resulted in standard deviations of $C = \pm 0.09\%$, $N = \pm 0.02\%$ and $\delta^{13}C_{org} = \pm 0.07‰$.

2.4.2. Stable Isotope Mixing Model in R-program (SIMMR)

The Bayesian isotopic modeling package SIMMR was used to estimate the proportional contribution of potential sources to sedimentary OM in the mangroves of Vanga (Parnell et al., 2013; Sasmito et al., 2020; Kusumaningtyas et al., 2019; (Rahayu et al., 2019)). Various OM have distinct isotopic compositions borne of the different ways how different plants (the C3, C4 and CAM) fix carbon during photosynthesis (Rahayu et al., 2019; Kusumaningtyas et al., 2019). A combination of $\delta^{13}C$ and C/N was used as the input parameters in the model, because it solves the inherent challenge posed by the overlap of $\delta^{13}C$ values between C4 vegetation and marine-derived OM (Hemminga et al., 1994; Khan et al., 2015). Carbon to nitrogen (C/N) ratio can further distinguish aquatic and terrestrial OM due to relative high N content in marine-derived OM. SIMMR uses the Markov Chain Monte Carlo algorithm to disentangle the source and proportion of the contributing sources in an admixed sediment while incorporating uncertainties due to isotopic fractionation, concentration-dependencies and residual errors (Kusumaningtyas et al., 2019; Rahayu et al., 2019). The SIMMR model assumes that early degradation of organic matter in mangrove sediment does not significantly alter the stable isotope composition (Khan et al., 2015; Kusumaningtyas et al., 2019; Sasmito et al., 2020) and therefore the isotopic fractionation and concentration-dependencies are negligible. However, C/N ratios would expectedly vary with time as OM are degraded

Table 1
Showing grain size distributions of sediments along the Umba River.

Station	Environment	Sample size (n)	Dry season grain size				Wet season grain size			
			% Sand	% Silt	% Clay	Sediment classification after Folk and Ward (1957)	% Sand	% Silt	% Clay	Sediment classification after Folk and Ward (1957)
S1	Riverine	3	61.5	38.4	0.1	Silty sand	65.1	34.7	0.2	Silty sand
S2	Riverine	3	87.6	12.4	0.0	Silty sand	66.9	31.8	1.2	Silty sand
S4	Riverine	3	76.1	23.6	0.3	Silty sand	85.1	11.5	0.1	Silty sand
S5	Riverine	3	70.6	27.9	1.4	Silty sand	59.2	39.0	1.8	Silty sand
S6	Riverine	2	41.8	55.4	3.1	Sandy silt	46.7	50.7	2.7	Sandy silt
S7	Estuarine	11	43.4	54.1	2.4	Sandy silt	36.0	61.1	2.8	Sandy silt
S8	Marine	4	99.4	0.6	0.0	Sand	99.3	0.70	0.0	Sand

(Herbon and Nordhaus, 2013; Bouillon et al., 2003) and therefore, C/N ratios would potentially be underestimated in the model. To mitigate this, average of output proportions from a combination of different OM signatures has been utilized (Sasmito et al., 2020). In this study we have utilized a combination of i) $\delta^{13}C$ and C/N and ii) $\delta^{13}C$ and N/C which is a linear tracer for comparisons. Only the wet season was modeled because i) maximum riverine discharge and input (Tesfamariam et al., 2018 and ii) riverine and marine POM were collected only during the 2020 wet season and therefore provided a complete dataset (Table 1). Having defined *a priori* the model inputs, four major end-members (marine POM, riverine POM, mangrove leaf and litter and terrestrial C3 plants) that are incorporated in sediments were modeled. Mangrove leaf and litter were not separated because the OM variation between them has been shown to be either overlapping (Kusumaningtyas et al., 2019) or minimal (Bouillon et al., 2003). The mean and standard deviation of each end-member was calculated and input into the model. Then the dataset containing the values of mangrove sediments were also loaded into the model in order to resolve their source and proportions through several model iterations up-to 1000 times. The results were presented using a boxplot which depicts the 50% credibility interval (Rahayu et al., 2019).

2.4.3. Statistical analysis

Statistical analyses were performed using inbuilt packages in R-program (v. 1.1.463) (R Core Team, 2020). Differences of organic matter variables in sediments and plant tissues by stations, environment, species and sediment depths were analysed using analysis of variance (ANOVA). Data conformity to normal distribution was examined using the Shapiro-Wilk test of normality. The data that did not pass the normality test were transformed prior to ANOVA analysis (for detailed results see Supplementary Information 4).

3. Results

3.1. Grain size distribution

Grain size distribution of Umba River sediments fall within a narrow range between sand and silty sand for marine and riverine sediments, respectively. Estuarine sediments were classified as sandy silt due to the elevated silt content with minimal clay proportion compared to the riverine and marine sediments (Table 1).

3.2. Elemental and isotopic composition of sediment organic matter

The mean elemental and stable isotope data are presented in Table 2 and in Fig. 3. Significant inter-station variation ($p < 0.05$) was observed for OM properties during both seasons as well as by sediment type except ($p > 0.05$) for TC, C and C/N ratio during the dry season and only C/N ratio during the wet season. There was no significant ($p > 0.05$) variation in the sediment OM content between the two seasons except for C/N ratios and $\delta^{13}C$ values (Supplementary Information 4). $\delta^{13}C$ values were higher ($p < 0.05$) in marine sediments (−20‰) compared to both agricultural soil, riverine and estuarine sediments (−23‰) during both seasons (Table 2, Fig. 3a, b, 3d, 3e). A post hoc Tukey test further showed that the $\delta^{13}C$ values differed significantly ($p < 0.05$, $\alpha = 0.05$) between marine and estuarine sediment. Mean values of C/N, N/C, $\delta^{13}C$ and $\delta^{15}N$ intertidal and subtidal sediments differed significantly ($p < 0.05$) during both seasons except for $\delta^{13}C$ during the dry season (Supplementary Information 4) with further confirmation by a post hoc Tukey ($p = 0.033$, $\alpha = 0.05$). $\delta^{13}C$ values of intertidal sediments were lower than those of subtidal sediments during both seasons (See Supplementary information 3). Overall, majority of the estuarine sediments showed C/N ratios >10 during both seasons and by both intertidal and subtidal sediments (See Table 2 and Supplementary information 3).

Riverine sediments exhibited high $\delta^{15}N$ but relatively low $\delta^{13}C$ values (Fig. 3a and d) coinciding with high C/N ratios (>10) (Fig. 3b and c) during both seasons. On average, $\delta^{13}C$ values were highest (−19‰) in marine sediments during both the dry and wet season (Table 1). There was also a marked enrichment of ^{13}C in riverine (−21.9 ± 1.1‰) and agricultural soil (−21.9 ± 2.0‰) relative to estuarine sediments during the wet season (Table 1). High $\delta^{15}N$ values (>7‰) were observed in agricultural soils and riverine sediments (Table 1, Fig. 3c and f) compared to marine and estuarine sediments values (<6‰) during both seasons. Mangrove leaves and litter showed significant variation ($p < 0.05$) in C, TN, C/N ratio and $\delta^{13}C$ contents between both the species and plant tissues (Fig. 4 and Supplementary Information 4). On one hand, ^{13}C in *B. gymnorrhiza* leaves was relatively depleted (−30.4 ± 1.2‰) relative to *X. granatum* leaves (−27.9 ± 1.1‰) (Table 2). On the other hand, $\delta^{13}C$ values in mangrove litter was lowest in *A. marina* (−28.6 ± 1.3‰) compared to the marginally high values in C. tagal species (−27.9 ± 1.4‰). Generally, $\delta^{13}C$ values of leaves (−29.5 ± 0.4‰) and litter (−28.7 ± 1.0‰) in terrestrial C3 plants were lower compared to all the analysed mangrove species (Table 3, Fig. 4). There was a general non-variation of OM content between the measured mangrove tissues material ($p > 0.05$, see Supplementary Information 4) but relatively high $\delta^{13}C$ values and C/N ratios in mangrove litter than in mangrove leaves in all species (Table 3, Fig. 4). The C/N content in mangrove estuarine sediments showed high mean values (>13) during both seasons (Table 2, Fig. 3b, c, 3e, 3f) and were considerably lower than in the mangrove leaf and litter the primary producers (Table 3, Fig. 4). $\delta^{13}C$ values were higher in estuarine sediments including estuarine POM (−24‰) relative to mangrove leaves and litter (−28‰) (Tables 2 and 3). C/N ratios and $\delta^{13}C$ values of SPOM were relatively lower than those of the other sediments (Fig. 3e and f) but showed low and high $\delta^{15}N$ values in marine and estuarine POM respectively (Table 2).

Table 2
Mean values (±SD) of sediment elemental total carbon (TC), organic carbon (C) and total nitrogen (TN), C/N ratio (μg/μg dry weight), $\delta^{15}N$ and $\delta^{13}C$ stable isotopes from all sampled stations along the transboundary Umba River during both the dry and wet season.

	TN (%)	TC (%)	C (%)	C/N	$\delta^{15}N$ (‰)	$\delta^{13}C$ (‰)
Dry Season (2019)						
Riverine (n = 36)	0.1 ± 0.1	1.3 ± 1.2	1.1 ± 1.2	11.5 ± 2.3	7.4 ± 0.7	−23.8 ± 1.4
Estuarine (n = 19)	0.2 ± 0.1	2.1 ± 1.4	2.1 ± 1.3	15.5 ± 3.9	6.2 ± 0.9	−24.8 ± 0.8
Marine (n = 3)	0.01 ± 0.004	0.2 ± 0.1	0.1 ± 0.03	15.6 ± 8.3	3.8 ± 1.2	−19.9 ± 3.4
Soil (n = 3)	0.2 ± 0.01	2.7 ± 0.1	2.3 ± 0.1	9.9 ± 0.4	8.0 ± 0.1	−20.8 ± 0.2
Wet season (Jun–Jul 2019)						
Riverine (n = 34)	0.1 ± 0.1	0.8 ± 0.7	0.7 ± 0.7	22.3 ± 20.7	7.1 ± 1.5	−23.9 ± 1.1
Estuarine (n = 9)	0.2 ± 0.1	2.6 ± 1.4	2.6 ± 1.3	18.9 ± 16.7	5.1 ± 1.0	−24.9 ± 0.7
Marine (n = 3)	0.1 ± 0.1	1.9 ± 1.6	1.7 ± 1.6	21.0 ± 11.9	5.0 ± 0.9	−24.5 ± 1.1
Soil n = 6)	0.2 ± 0.1	2.4 ± 0.5	2.3 ± 0.5	11.2 ± 0.4	8.3 ± 0.9	−20.1 ± 0.5
Wet season (Jun–Jul 2020)						
Riverine (n = 10)	0.03 ± 0.03	0.4 ± 0.4	0.4 ± 0.4	12.7 ± 1.8	8.0 ± 0.8	−21.9 ± 1.1
Estuarine (n = 16)	0.1 ± 0.1	1.0 ± 1.2	0.9 ± 1.2	13.5 ± 3.9	5.9 ± 1.1	−23.8 ± 1.8
Marine (n = 6)	0.01 ± 0.01	0.3 ± 0.2	0.1 ± 0.1	13.1 ± 2.5	5.9 ± 0.6	−19.6 ± 1.8
Soil (n = 12)	0.2 ± 0.2	2.5 ± 1.9	2.5 ± 1.9	12.6 ± 0.9	8.0 ± 0.9	−21.9 ± 2.0
Riverine POM (n = 5)	0.3 ± 0.1	2.4 ± 0.6	2.2 ± 0.6	7.7 ± 1.9	8.5 ± 0.7	−24.4 ± 0.8
Estuarine POM (n = 4)	0.2 ± 0.1	1.2 ± 0.8	1.2 ± 0.8	6.0 ± 2.5	10.9 ± 2.7	−23.9 ± 1.2
Marine POM (n = 5)	0.6 ± 0.4	7.3 ± 4.0	4.9 ± 2.2	8.3 ± 1.1	6.6 ± 2.0	−20.9 ± 0.4

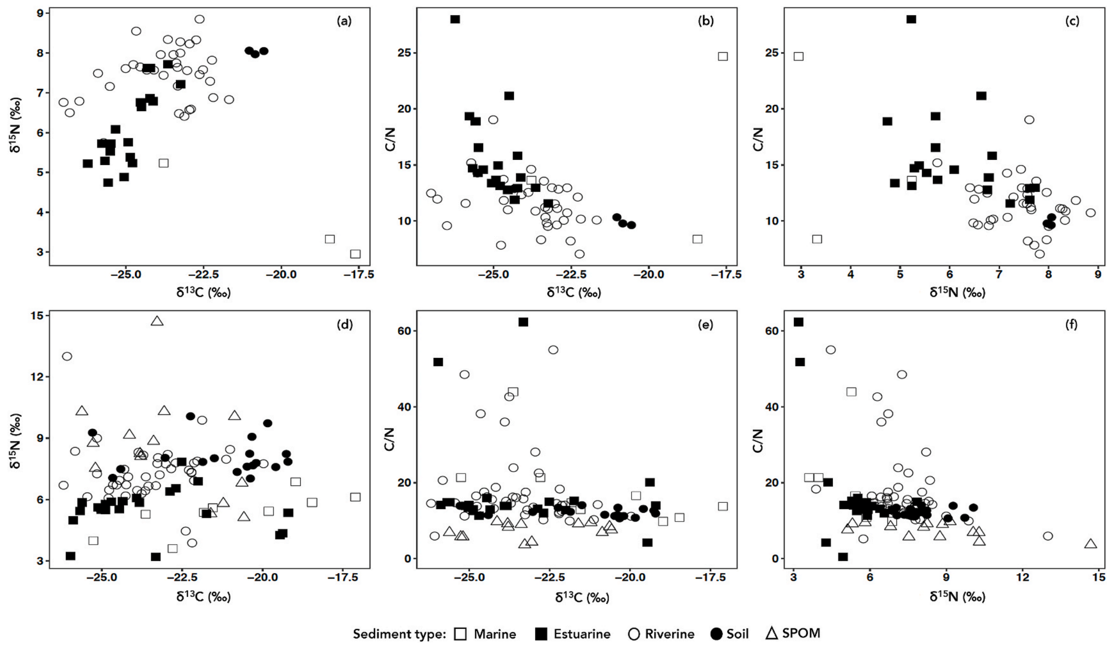

Fig. 3. Relationships between $\delta^{13}C$, $\delta^{15}N$ and C/N in different sediment samples, environments and during different seasons (top row (a to c) represent the dry season and bottom row (d to f) represent the wet season).

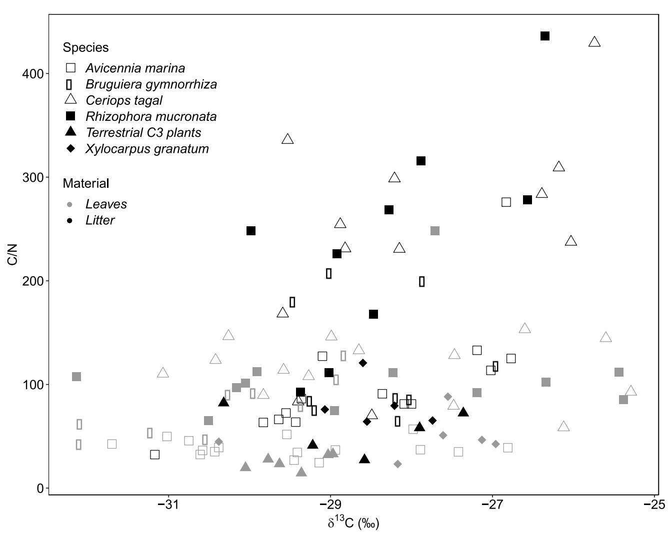

Fig. 4. Bi-plot of stable carbon isotope and elemental C/N ratios of mangrove leaf and litter of different species found in Vanga, estuary. The grey colored represents the leaves while the dark colored represents the litter.

3.3. Downcore profiles of organic matter composition

The bulk elemental and isotopic analyses of the estuarine sediments showed varied profiles, both, vertically within cores and spatially between different cores (Fig. 5). There was a significant variation ($p < 0.05$, see Supplementary Information 4) of sediment OM properties in different stations except for C/N ($p > 0.05$). On the contrary variation of sediment OM properties with depth was not significant ($p > 0.05$) except for dry bulk density (gcm^{-3}) and C/N ratio ($p < 0.05$).

Relative downcore decrease in C and TN was observed compared to an increase in C/N ratio and DBD (Fig. 5). Particularly the core E1 taken at station E1 (Fig. 1) showed a striking low C, TN, and relatively higher DBD values compared to the other cores. There was also a subtle decreases in TN in all the cores in the top 40 cm (Fig. 5b) and an increase at 50 cm.

Table 3
Mean (±s.d.) elemental C/N ratios and carbon stable isotope ($\delta^{13}C$) of mangrove leaves and litter from the Vanga Estuary, Kenya. n = number of samples.

Species (no. of samples)	Material	$\delta^{13}C$ (‰)	C/N
C. tagal (n = 14)	Leaf	−28.3 ± 1.8	116.2 ± 27.4
C. tagal (n = 12)	Litter	−27.9 ± 1.4	244.4 ± 97.4
B. gymnorrhiza (n = 9)	Leaf	−30.4 ± 1.2	77.9 ± 27.2
B. gymnorrhiza (n = 9)	Litter	−28.5 ± 0.8	122.7 ± 53.9
R. mucronata (n = 12)	Leaf	−28.5 ± 2.1	109.0 ± 44.3
R. mucronata (n = 9)	Litter	−28.3 ± 1.2	238.3 ± 100.1
A. marina (n = 16)	Leaf	−29.5 ± 1.4	38.9 ± 8.36
A. marina (n = 14)	Litter	−28.6 ± 1.3	100.9 ± 55.9
X. granatum (n = 6)	Leaf	−27.9 ± 1.1	49.4 ± 19.5
X. granatum (n = 5)	Litter	−28.4 ± 0.4	81.1 ± 20.7
Terrestrial C3 plants (n = 6)	Leaf	−29.5 ± 0.4	25.1 ± 6.6
Terrestrial C3 plants (n = 5)	Litter	−28.7 ± 1.0	56.2 ± 20.0

3.4. Determination of proportional OM sources using SIMMR model

Model input parameters are presented in Supplementary Information 1. The model revealed that the sediment OM in the Vanga estuary, had varied sources with discernible mixing as seen in the bi-plots of $\delta^{13}C$ and C/N ratio (Fig. 6, see Supplementary Information 1 for details). Riverine POM was the dominant OM source in the sediments that accumulated in the Vanga estuary (Fig. 7). The riverine POM which would expectedly include both agricultural soil from surface runoff from the hinterland, contributed over 50% (median = 60%) of total sediment OM (Fig. 7). Marine POM was the second largest contributor of OM to the estuarine sediments of Vanga with close to 20% (median = 18%). However, when N/C ratio was utilized (Supplementary Information 1), marine POM contributed slightly more up to 50% (median = ~40%) compared to riverine POM which contributed up to 40% (median = ~27%) (Fig. 7, Supplementary Information 1). OM derived from mangroves and terrestrial C3 plants both contributed less than 20% to the overall sedimentary OM (Fig. 7) but the contribution of terrestrial C3 plants was marginally high compared contribution of mangroves leaves and litter (Fig. 7, Supplementary Information 1). Based on the average from the two combinations, $\delta^{13}C$ and C/N and $\delta^{13}C$ and N/C, the overall contribution from each end member was 45%, 32%, 13% and 8% for riverine

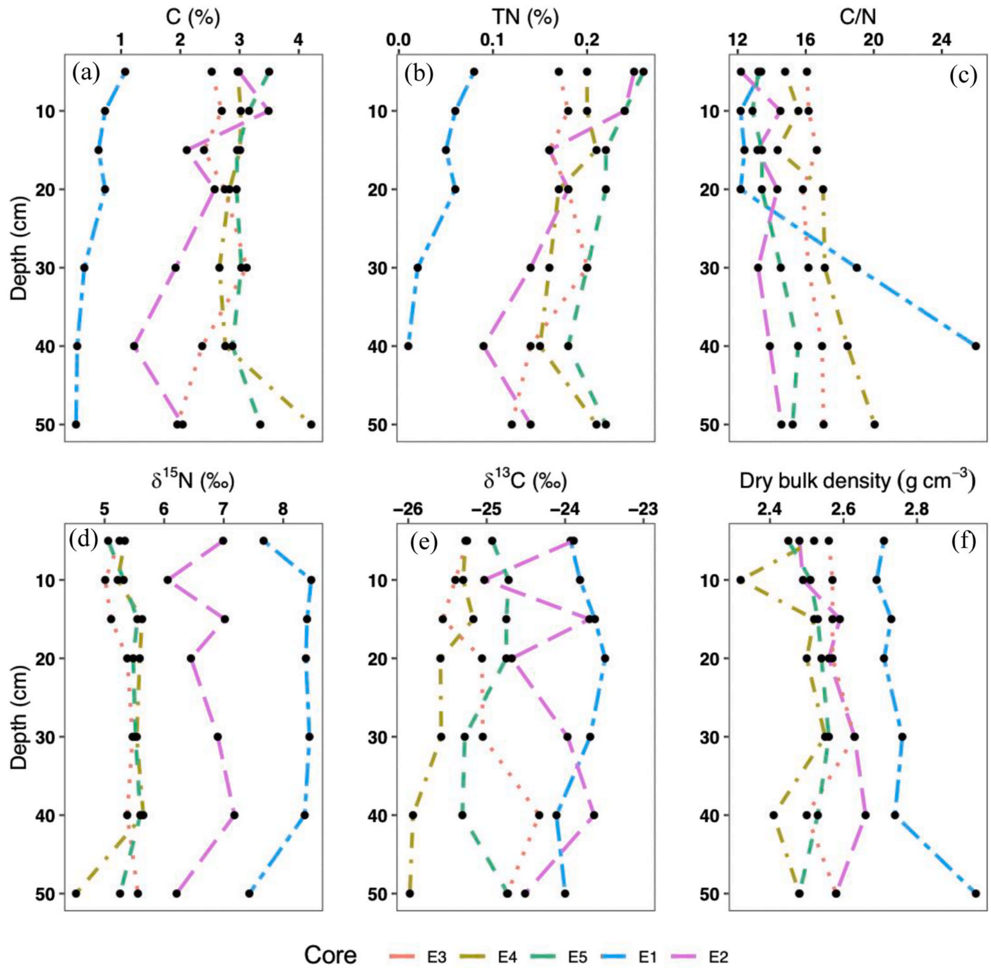

Fig. 5. Downcore variation of (a) organic carbon, (b) total nitrogen, (c) C/N ratio, (d) δ^{13}C (e) δ^{15}N and (f) dry bulk density with soil depth of up to 50 cm in the Vanga Estuary.

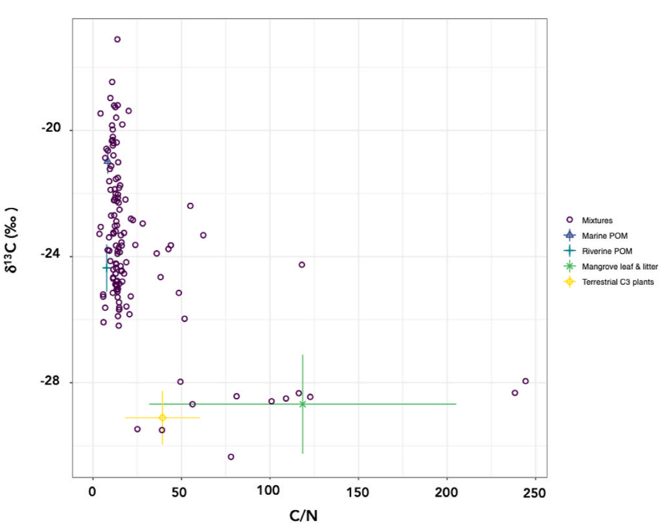

Fig. 6. Bi-plot of δ^{13}C and C/N ratio of sediments from the study area along the Umba River and potential end-member mixing. The average values of the selected end members are shown.

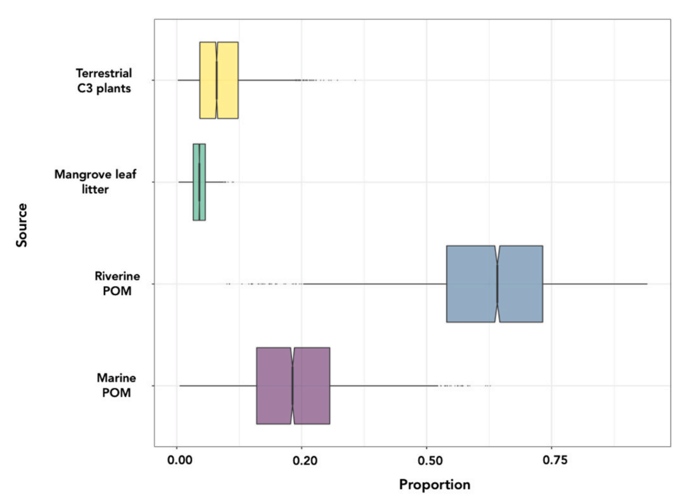

Fig. 7. SIMMR model outputs of proportional contribution of end-members to total sediment organic matter during wet season (boxes represent the 50% credibility interval of individual end-member proportional contribution; lines within boxes represent median values).

POM, marine POM, terrestrial C3 plants and mangrove leaf and litter, respectively (see Supplementary Information 1). There was a positive and relatively high correlation between marine POM and terrestrial C3 plants in both δ^{13}C and C/N (0.67) and δ^{13}C and N/C (0.55) combinations (Supplementary Information 1). However, there was an observed low positive and high negative correlation between marine POM, riverine POM and mangroves leaf and litter.

4. Discussion

4.1. Spatio-temporal variability of sediment organic matter

Organic carbon (C) content in estuarine sediments were higher than marine sediments during both seasons (Table 2) attributable to proximity to mangroves the primary producer (Bouillon et al., 2003). Agricultural fertilizer input in the catchment farms could explain the high C values recorded in riverine sediments during the rainy seasons (Kiteresi et al., 2012; Ray et al., 2018). Further, the high C/N ratios between 13 and 19 during both seasons (Table 2) indicates the influence of the Umba River as it has been postulated that C/N ratios >10 are indicative of a terrestrial origin of detritus (Bouillon et al., 2003; Tamooh et al., 2012). Additionally, high C/N values in estuarine sediments (Fig. 3b) during the dry season, reflect reduction in river discharge and dominance of tidal fluxes and the additional contribution of organic matter from the sea (Kusumaningtyas et al., 2019; Rahayu et al., 2019; Rumolo et al., 2011). The relatively high C/N ratios in estuarine sediments (Table 2) also suggests the variable contribution of both terrestrial (river-derived) and *in-situ* produced material (Bouillon et al., 2003) but the inverse proportionality of C and δ^{13}C values in estuarine sediments have been shown to reflect the contribution of terrestrial material (Middelburg et al., 1996). However, in this study there was no clear correlation between C and δ^{13}C values in estuarine sediments, which could mean multiplicity of sources of OM and mixing within the Vanga, Estuary. The grain size distribution of Umba River sediments is classified within a narrow range between sand, silty sand and sandy silt (Kimeli et al., 2021). The average sediment grain sizes in the Vanga Estuary (S7) classified under sandy silt (see Table 1), indicates that the influence of grain size on the OM distribution is minimal. We therefore conclude that the dynamics, variation and distribution of OM in the Vanga estuary is attributable to the different sources of OM and transportation, deposition and post-deposition processes. This processes include mixing, decomposition and dilution (Bouillon et al., 2003; Kristensen et al., 2008). The δ^{15}N and δ^{13}C signatures and the C and TN values obtained in this study are comparable to those reported from other studies in similar settings (Hemminga et al., 1994; Jennerjahn and Ittekkot, 2002; Tamooh et al., 2014). Others have postulated that C/N ratio of SOM increases towards the range of proximal mangroves vegetation (Kennedy et al., 2004) but was not the case in this study. Estuarine sediments exhibited markedly low C/N (between 13 and 19 during both seasons) compared to the dominant primary producers, the mangroves with an average 118.7 (Table 2). δ^{13}C values were also higher in estuarine sediments (−24‰) relative to mangrove leaves and litter (−28‰) which we attributed to rapid decomposition and degradation of mangrove plant tissue as well as possibility of contribution by other low C/N primary producers (Kennedy et al., 2004). However, in river dominated estuaries, terrigenous OM is predominant due to freshwater runoff. This predominance of terrigenous OM diminishes seawards in sediment organic matter as it is replaced by POC as the freshwater flux is weakened by the increasing tidal push (Yu et al., 2010). δ^{13}C values were relatively higher (−21.9 ± 1.1‰) in riverine sediments during the wet season. These values also match the δ^{13}C values of agricultural soil (−21.9 ± 2.0‰) during the same season. The increased contribution of highly enriched modern C4 plants could explain the high δ^{13}C values. Indeed, this is supported by field observation of small-scale maize cultivation along the Umba River especially in the middle section (Station S4) and most parts of the catchment on the Kenyan side. The δ^{15}N enrichment in agricultural soil and riverine sediments (Table 1, Fig. 3a and c) can be attributed to possible input of organic fertilizer from animal waste (Garg and Bhatnagar, 1999) in the cultivated land in the upper catchment that end up in the river through erosion and surface runoff. The relatively low δ^{13}C values (~-24‰) in the estuarine samples can be attributed to the introduction of ^{13}C-depleted OM from proximal mangroves (Kristensen et al., 2008) however, dilution due to river inflow and the potential input of low δ^{13}C values from excessive mineralization within the water column or in the intertidal sediments could also explain the low δ^{13}C values (Bouillon et al., 2008; Kristensen et al., 2008). ^{13}C-enrichment in marine POM relative estuarine POM sediments during both seasons (Table 2), agrees with the findings of others (Hemminga et al., 1994; Kazungu et al., 1996) in similar environments. They attributed this gradient and variation to inwelling of marine-derived OM including relatively ^{13}C-enriched seagrass materials. This could also explain the observed and relatively high δ^{13}C values in subtidal sediments than in intertidal sediments (See Supplementary Information 3) where the lighter ^{12}C have been preferentially utilized during decomposition by benthic organisms (Middelburg et al., 1996). SOM in intertidal and subtidal sediments represent different OM degradation states due to water depths variation, residence times and bed-load transportation (Dauwe et al., 2001; Dauwe and Middelburg, 1998). Therefore, fresh organic matter in mangrove-dominated intertidal areas are dominated by primary production from plant material mainly mangrove tissues (roots and leaves). Mixing, typical for a combined river-tide dominated systems, can cause a large range of values due to admixing of outwelled carbon with organic matter from other sources (Middelburg et al., 1996; Middelburg and Nieuwenhuize, 1998). Additionally, δ^{13}C values in suspension/settling particles and surficial sediments are identical in mangrove settings (Hemminga et al., 1994) and therefore, with no localized elevation in sediment C content e.g. close to point discharges, it is proposed that the dynamic processes in the mangroves of Vanga result in relatively efficient mixing and redistribution of sediment as postulated by Andreetta et al. (2014). The mixing and entangling of potential sources (Fig. 6) could be attributed to bioturbation, burrowing and overturning the sediments. The overturning of sediments by the crabs could promote a reduction in C partly due to increased oxidation of organic matter due to increased gaseous exchange facilitated by sesarmid crab channels (Andreetta et al., 2014; Bouillon et al., 2008). Considering the inevitable mixing and reworking of sediments by microbial communities coupled with degradation of some tracers including C/N and δ^{15}N, the main advantage of stable isotopes is the capability to define "upper and lower limits" of proportional contributions to the sediment OM by different sources (Bouillon et al., 2008; Kristensen et al., 2008).

4.2. Downcore variation of sediment OM composition

Downcore variations of OM composition was observed in the different stations and were attributed to the varied sources of sedimentary OM in the estuarine sediments. However, the near-uniform profiles indicate the expected mixing typical for estuarine habitats like our study area. The non-varying content of δ^{13}C and δ^{15}N downcore ($p > 0.05$) has been attributed to reduced and limited microbial decomposition due to anoxia (Rumolo et al., 2011; Kusumaningtyas et al., 2019; Sasmito et al., 2020) and reduced microbial activity due to overturning of sediments. The striking variation of OM properties in core E1 (Fig. 5) is probably attributed to its location within the study. This particular station is close to the river mouth (Fig. 1) and relatively elevated and therefore only flooded during spring tide and extreme river discharge during peak wet season. Consequently, being starved of fresh OM, leading to the observed low C and TN and corresponding enrichment of the heavier δ^{13}C and δ^{15}N (Fig. 5). Additionally, the increased dry bulk density (DBD) downcore is also associated with loss of moisture and dryness that causes more sediment sub-surface compaction. Downcore variations in the contents of TC content, C/N ratio and δ^{13}C values could also reflect temporal (tidal and seasonal) variability in the OM proportions from the different sources.

4.3. Modeled sources of sediment organic matter

The sediment OM that accumulates in the Vanga estuary showed a mixed source (Fig. 6) with riverine POM contributing more 55–73% (median = 60%) of total SOM (Fig. 7). This can be attributed to the influence and Umba River terrigenous input and the increased discharge during the wet season (Tesfamariam et al., 2018). Marine POM was the second largest contributor of OM to the Vanga Estuary at 15–30% (median = 22%) (Fig. 7, Supplementary Information 1). This confirms the influence of the tidal fluxes and the material exchange within the estuary as espoused in Bouillon et al. (2003). Strikingly, the contribution of autochthonous sources of OM (<10%) predominantly mangrove tissue analysed in this study was the lowest (Fig. 7). This is attributed to rapid degradation and possible dilution from the Umba River freshwater discharge and rapid outwashing by tidal ebbs (Kristensen et al., 2008; Sasmito et al., 2020) and further supported by the observed lower C content in estuarine sediments in Vanga during both the dry (2.1 ± 1.3%) and the wet (1.9 ± 1.5%) seasons (Table 2). It could also be explained by the observed contribution of marine POM from adjacent habitats introduced ^{13}C-enriched seagrass OM (Rahayu et al., 2019). Dilution due to mineral OM derived from erosion in the wider Umba River catchment and delivered by the Umba River could have further reduced the influence of the mangrove tissue-derived OM to the overall sediment OM. Dittmar et al. (2001), also postulated that autochthonous aquatic primary production contribute subordinately to the total mangrove SOM. Evidently when N/C ratio was utilized in the model (See Supplementary Information 1) with the dominance of marine POM to the total SOM marginally surpassed riverine POM. As mentioned earlier N/C is a linear tracer compared to C/N ratio which is bound to temporally and spatially vary markedly especially in plant tissues (Gonneea et al., 2004; Dittmar et al., 2001). Vanga has been identified as a mangrove loss hotspot (Mungai et al., 2019) mainly due to anthropogenic impacts and therefore this could exacerbate mangrove OM export to adjacent coastal habitats by tidal flush and reduces the retention of OM in the Vanga estuary sediments reducing their contribution to the overall SOM. However, this rather unusual minimal influence of mangrove-derived OM in the mangrove sediment in Vanga is not an isolated case as it has been shown that local plant production contribution to the overall sediment OM can be variable (Bouillon et al., 2003; Bosire et al., 2005; Middelburg and Nieuwenhuize, 1998). The low δ^{13}C values (more negative) exhibited in estuarine sediments during both during the dry (−24.9 ± 0.8‰) and the wet (−23.6 ± 2.1‰) seasons (Fig. 3, Table 2) coupled with low C content could be attributed to increased resuspension due to hydrodynamics (Jennerjahn et al., 2009; Kusumaningtyas et al., 2019) that subsequently promote enhanced decomposition. This relatively low δ^{13}C values are close to riverine δ^{13}C values support the observed pronounced contribution of riverine organic carbon sources to the cumulative sediment OM in the Vanga estuary. Large negative correlation between end-members (Supplementary Information 1Sa) indicates the source contribution could not be resolved by the model. In this study, the high negative correlations between marine POM and river POM (−0.97) could further indicate the potential mixing of sediments and material exchange (Bouillon et al., 2003; Kristensen et al., 2011) within the Vanga Estuary. The non-distinction of marine POM from river POM could also indicate the influences of tidal fluxes and dilution by mineral OM delivered by Umba River. However, the positive but low correlation between marine POM and both terrestrial C3 plants (0.55) and mangrove tissues (0.37) indicate that these end-members are distinguishable however their contribution to the total SOM is not substantive (Sasmito et al., 2020). In this regard, more site-specific end-members, monthly and seasonal data need to be incorporated into the model for better source resolution and characterization.

4.4. Implications to sediment provenance

The comparison of δ^{13}C and C/N ratio values from different potential sources of OM to the mangrove estuary of Vanga coupled with analyses of bulk sediment samples allowed for the possible identification of dominant sources of OM to the estuary. In this study the C/N ratio recorded in estuarine sediments were >10 indicating a predominant terrestrial source of OM to the mangroves of Vanga, which confirms the hypothesized connectivity of Umba River catchment and the downstream sediment dynamics in the Vanga Estuary. The lack of damming along the Umba River means that sediment retention would occur mostly further downstream, especially in the mangrove forests where conditions for sediment deposition and retention are favorable. This study also showed that marine-derived OM contributes substantially to the total sediment OM and brings to fore the material exchange between the estuary and adjacent coastal and marine habitats. With this realization, and coupled with the geochemical composition of Umba River bank and bottom sediments (Kimeli et al., 2021) which showed the influence of the geology of the Umba River catchment, further targeted research is merited. Umba River therefore would be a good case study for further long-term monitoring to further understand inter- and intra-seasonal quantitative sediment and OM fluxes and budgets. This further information would assist managers in having a holistic approach to a catchment-wide management, conservation and mitigation in regard to the response of the mangroves to sea-level rise.

5. Conclusions

This study gives insights into the contribution of different sources of OM deposited in the estuarine mangroves of Vanga. Seasonality influence is minimal in the OM distribution along the gradient of Umba River. Riverine OM has been shown to be the dominant contributor to the mangrove sediment OM and there is strong case for material exchange in the Vanga Estuary influenced mainly by physical mixing (hydrodynamics, freshwater input) both horizontally within the estuary and vertically in the sediments. This is supported mainly by the minimal contribution of from mangrove-derived OM to the sedimentary organic matter of Vanga. The relatively enhanced contribution of riverine POM compared to marine POM and *in-situ* production indicates the connectivity between the wider Umba River catchment and implications and concerns for better land use and catchment-wide management, especially, in the context of the proposed TBCA between Tanzania and Kenya. To further understand and resolve sources and the influences of the same, more site-specific and representative end-member samples and the hydrodynamic regime, river discharge and sediment budgets merit further in-depth study.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ecss.2021.107636.

Data availability statement

The datasets generated during and/or analysed during and for the current study are available from the corresponding author on reasonable request.

CRediT author statement

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