



## Assessment of the Quality and Quantity of Organic Matter in the Rufiji Mangrove Surface Sediments Using Biochemical Composition

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### Abstract

This study was carried out to investigate spatial changes in the quality and quantity of sedimentary organic matter in the Rufiji mangrove system, Tanzania. Sediment samples were collected from three sampling sites. Total organic matter in mangrove sediments ranged from  $7.28 \pm 2.02\%$  to  $10.58 \pm 1.34\%$ . Protein concentrations varied from  $1,145.33 \pm 20.33 \mu\text{g/g}$  to  $2,747.50 \pm 25.14 \mu\text{g/g}$  in the mangrove sediments. Total carbohydrates, lipids and biopolymeric carbon in mangrove sediments ranged between  $1,110.50 \pm 16.31 \mu\text{g/g}$  and  $1,914.17 \pm 27.79 \mu\text{g/g}$ ,  $1,436.50 \pm 24.13 \mu\text{g/g}$  and  $6,373.50 \pm 25.79 \mu\text{g/g}$ , and  $4,496 \mu\text{g C/g}$  and  $10,231.50 \mu\text{g C/g}$ , respectively. Tannins and lignins in mangrove sediments varied from  $817.67 \pm 12.97 \mu\text{g/g}$  to  $1786.50 \pm 30.74 \mu\text{g/g}$ , while stable carbon isotope ( $\delta^{13}\text{C}$ ) in Rufiji mangrove sediments ranged between  $-26.64 \pm 0.10 \text{‰}$  and  $-25.48 \pm 0.13 \text{‰}$ . Higher protein:carbohydrate (PRT:CHO) at station 3 indicated the presence of freshly deposited organic matter. The high lipid:carbohydrate (LPD:CHO) ratios observed in the Rufiji mangrove systems pointed towards the high quality of labile organic matter which supports benthic fauna. PCA revealed the association of variables and their distribution on trends across sites of the Rufiji mangrove system.

**Keywords:** Organic matter, biochemical composition, Rufiji, mangroves, sediments.

### Introduction

The overall geochemical processes prevailing in any aquatic system cannot be explained merely by the application of geochemical parameters such as general sedimentary characteristics, phosphorus fractionation or heavy metal distribution studies. Redox status of the sedimentary environments is directly linked with diagenesis, the process of organic matter demineralisation (Bouillon et al. 2003). Both autochthonous as well as allochthonous organic compounds resistant to degradation and those that survive diagenesis are stored in sedimentary environments depending on the redox state existing in the aquatic systems.

The assessment of the quantity and quality of organic matter, whether labile or refractory, is a prerequisite for explaining diagenetic processes. The biochemical composition of sedimentary organic matter has been used to gather information on the origin and parameters controlling the diagenetic fate of organic matter (Bouillon et al. 2004). It can be used for the evaluation of the quantity and quality of organic matter which can provide a clear insight into the biogeochemical characterization of the sedimentary environments.

Mangrove ecosystems display strong variability of major biogeochemical characteristics due to their dynamic ecotonal

locations (Dehairs et al. 2000). Several studies have been carried out in Rufiji estuary on the geochemical characteristics of water and surface sediments in a complex Rufiji mangrove ecosystem, but the quality and quantity of organic matter has been underreported (Shilla 2019, Minu et al. 2020, Shilla and Shilla 2020). This paper investigated the quality and quantity of organic matter in surface sediments of the Rufiji mangroves and adjacent estuarine stations in terms of the biochemical composition. The combinations of elemental and carbon isotopic composition can also be used to distinguish sources of organic matter in sediments and in settling particles (Shilla and Routh 2017). Therefore, along with biochemical composition,  $\delta^{13}\text{C}$  of the total organic matter was used to characterize the quality and quantity of organic matter in the study area.

## Materials and Methods

### Description of the study area

The study sites have been described in Shilla (2019). Briefly, the study sites are located in Rufiji estuary ( $39^{\circ} 07' \text{E}$ ,  $7^{\circ} 41' \text{S}$ ) to ( $39^{\circ} 45' \text{E}$ ,  $8^{\circ} 15' \text{S}$ ), 100 km south of Dar es Salaam City, in the Rufiji River delta (Figure 1). This river has a catchment area of 177,400  $\text{km}^2$  and is over 640 km long (UNEP 2001). About 30 km from the coast, the lower Rufiji River branches out into a series of channels forming an impressive delta, covering approximately 1200  $\text{km}^2$  with 530  $\text{km}^2$  covered by mangrove forests (Sørensen 1998). The four northern tributaries carry the bulk of the discharges into the Rufiji River. The southern part of the delta, which is sheltered, receives little fresh water, and the water in front of this part of the delta is clear, saline and features seagrass meadows and scattered patch reefs.

Tidal influence in the delta is considerable (REMP 2003). In the upstream part of the Rufiji catchment area, some small towns are located. Mangrove sections of the downstream part have partially been cleared for rice cultivation (Mshale et al. 2017). The mangroves provide the dominant habitat in the

estuary, but tidal marshes, seagrass meadows, and mud-flats are also present. Mangrove forests support an extensive food web through their large production of detritus, which is broken down by fungi and bacteria. Several omnivorous crustaceans of commercial importance spend part of their life cycles in mangroves feeding on the detritus, live benthic microalgae, occasional animal materials, and fine inorganic particles (Minu et al. 2018).

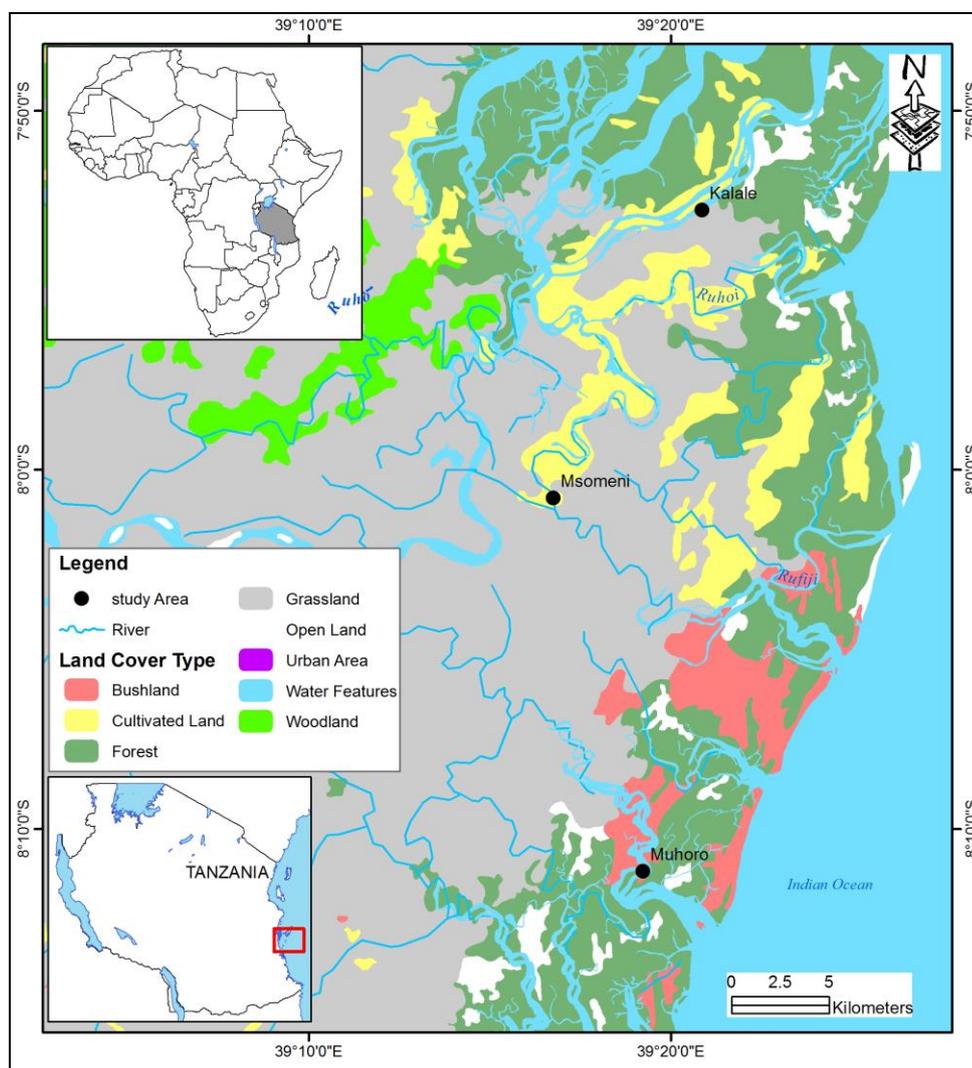
The present study was carried out in three locations (Muhoro–station 1, Msomeni–station 2, and Kalale–station 3), representing the south, middle and northern parts of the Rufiji delta (Figure 1). These locations were chosen because they are representative of the entire estuary and include a variety of adjacent habitats (i.e. mangrove stands, mud flats, and seagrass meadows) with sufficient diversity and densities of consumer organisms. The northern part (Kalale station) frequently develops flow restrictions due to converging tides entering from two adjacent inlets, whereas stations 1 and 2 experience tidal amplification. This well-known biodiverse mangrove wetland is under the threat of severe ecological degradation due to the ongoing activities including the construction of hydroelectric power station as well as agricultural activities. In this context, the surface sediment samples were collected from three locations (Figure 1).

### Sampling and analytical methodology

Surface sediment samples were collected from three locations during June and July 2014 by using a van Veen grab (0.042  $\text{m}^2$ ). In order to obtain a true representation of samples within the study area, sediment samples were collected in triplicates. Sediment samples were stored in clean glass containers and transported to the laboratory on ice and stored in a deep freezer at  $-20^{\circ}\text{C}$  till further processing. A portion of the wet sediment from each depth-interval was used for the texture analysis. Sediment texture was determined by pipette method after removing the inorganic carbonates using 10% HCl and organic matter using 15%  $\text{H}_2\text{O}_2$  (Martin et al. 2011). The

samples were freeze dried and were finely powdered using agate mortar and pestle for further analyses. Organic carbon in sediment samples was analysed using a C:N analyser (Carlo Erba Strumentazione NA 1500 nitrogen analyser, UK). To measure the organic carbon, sediment samples (about 10 mg) were spiked with a few drops of 5 M HCl and placed in an oven at 50 °C for at least 1 h to dry.

Decalcified samples were then analysed in the C:N analyser and the values recorded. The quality of this analysis was controlled by analyzing blanks (empty silver capsules) and a standard reference material (acetanilide). Sediment samples were analysed for grain sizes using a grain size analyser (Malvern Instruments Ltd, UK) and various size fractions were composed as recorded.



**Figure 1:** Map showing the study site at Rufiji Estuary, Tanzania. Three sampling locations are indicated in Muhoro stream (station 1), Msomeni (station 2), and Kalale stream (station 3).

Chlorophyll and phaeopigments (Phe) estimations were carried out according to standard procedures described by Lorenzen and Jeffrey (1980), Tolosa et al. (2004) and APHA (2005). Pigments were extracted with 90% acetone (24 hrs in the dark at 4 °C). After centrifugation, the supernatant was used to determine chlorophyll pigments (chl-a, chl-b and chl-c) and was acidified with 0.1 N HCl to estimate the concentrations of phaeopigments. Tannins and lignins in the sediments were extracted with 0.05 M NaOH solution for 90 min and filtered. To 5 ml aliquots of filtrates, 1 ml of citrate solution was added followed by 1 ml Folin reagent and 10 ml carbonate tartrate reagent and kept for 30 min and the absorbance was measured at 760 nm. The effects of Mg and Ca hydroxides and/or bicarbonates were suppressed by the addition of trisodium citrate solution (Nair et al. 1989). The biochemical constituents, tannins and lignins, and chlorophyll pigments were analysed spectrophotometrically (Double beam UV-visible spectrophotometer: SPECORD 200 PLUS, Analytikjena).

For the extraction of protein (PRT), 0.1 g of dried sediment was digested in 1 N NaOH by heating in a water bath for 5 min at 100 °C. The slurry was centrifuged, and an aliquot of clear supernatant, was used for estimation of protein using Folin phenol reagents (Lowry et al. 1951). Bovine serum albumin was employed as calibration standard. Carbohydrate (CHO) was analysed following phenol-sulphuric acid method (Dubois et al. 1956) using glucose as calibration standard. Total lipids (LPD) from sediment samples were extracted with chloroform and methanol (1:1 v/v, Bligh and Dyer 1959) and estimated using sulphophosphovanillin method (Barnes and Blackstock 1973) employing cholesterol as standard. Concentrations of proteins, carbohydrates and lipids were converted to carbon equivalents by multiplying with the following conversion factors: 0.49, 0.40 and 0.75 g of C/g, respectively (Fabiano and Danovaro 1994). The sum of protein, carbohydrate and lipid carbons is referred to as

biopolymeric carbon (BPC) (Fichez 1991, Fabiano et al. 1995), which is the amount of carbon available to benthic consumers.

All the analyses were carried out in triplicate and the average reported. For the analysis of sedimentary chlorophyll pigments, 0.5 g of freeze-dried sample was centrifuged with 90% acetone at 3000 rpm to separate the pigment from sediment and analysed spectrophotometrically.

Stable carbon isotope abundances are presented as  $\delta^{13}\text{C}$  values and are expressed relative to the PDB (Pee Dee Belemnite) standard:

$$\delta^{13}\text{C} = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000$$

where R = the ratio of the heavy isotope ( $^{13}\text{C}$ ) over the light isotope ( $^{12}\text{C}$ ).

#### Statistical analyses

Data were processed using the StatView® 5.0.1 (SAS Institute Inc. 1992–1998, Cary, NC), in order to obtain mean values, standard errors and confidence levels. Pearson's product-moment correlation test was used to check for significant relationships between grain size and organic matter content in the sediments. One way Analysis of Variance (ANOVA) was applied to check for differences across sampling stations. Statistical methods were performed with a 95% confidence interval and  $p < 0.05$  significance level.

### Results

#### Biochemical composition in the Rufiji mangrove sediments

The variations of total organic matter (TOM), total organic carbon (TOC), proteins (PRT), total carbohydrates (TCHO) and total lipids (TLP) in the surface sediments of Rufiji mangroves are presented in Table 1. The results of biopolymeric carbon (BPC), chlorophyll concentrations,  $\delta^{13}\text{C}$  as well as the spatial variations of PRT/CHO, TLP/CHO, Chl-a/Phaeo, tannins and lignins are also presented in Table 1.

Mean total organic matter (TOM) in mangrove sediments ranged from  $7.28 \pm 2.02\%$  to  $10.58 \pm 1.34\%$ . Station 3 exhibited higher mean TOM ( $10.58 \pm 1.34\%$ ) followed by station 1 ( $8.09 \pm 2.38\%$ ), while the mean TOM in sediments collected from station 2 was  $7.28 \pm 2.02\%$ . No significant difference in TOM was depicted across sites (Table 1; ANOVA,  $p = 0.203$ ). Mean protein concentrations in sediments of Rufiji mangroves varied from  $1,271.33 \pm 22.85$  in station 1 to  $2,747.5 \pm 25.14$  in station 3, with values at station 3 significantly higher ( $2,747.5 \pm 25.14$ ; Table 1;

ANOVA,  $p = 0.034$ ) than the values recorded in stations 1 and 2 ( $1,271.33 \pm 22.85$  and  $1,145.33 \pm 20.33$ , respectively). The quantity of protein nitrogen estimated by multiplying the protein contents with the factor 0.16 (Shilla 2019) for Rufiji mangrove and estuarine sediments varied from  $196.64 \pm 3.66$  in station 1,  $183.25 \pm 3.25$  in station 2 and  $439.6 \pm 4.02$  in station 3, making this station to have significantly higher protein contents than the rest of the stations (Table 1; ANOVA,  $p = 0.001$ ).

**Table 1:** Variations of biochemical components in sediments of the Rufiji mangrove system. Results of ANOVA are shown in the last column. Values are mean ( $\pm$  SD). TLP = Total lipids; TCHO = Total carbohydrates; PRT = Proteins; TOC = Total organic carbon; TOM = Total organic matter; BPC = Biopolymeric carbon; PRT-N = Protein nitrogen fraction.

	Site 1 (n = 9)	Site 2 (n = 9)	Site 3 (n = 9)	ANOVA p-value
Sand %	$42.12 \pm 16.40$	$32.01 \pm 12.00$	$46.82 \pm 20.24$	0.005
Clay %	$18.30 \pm 8.04$	$19.52 \pm 10.14$	$20.48 \pm 10.20$	0.001
Silt %	$36.72 \pm 16.56$	$28.90 \pm 11.38$	$40.74 \pm 18.34$	0.001
TLP ( $\mu\text{g/g}$ )	$2,464.33 \pm 28.09$	$1,436.50 \pm 24.13$	$6,373.5 \pm 25.79$	0.001
PRT ( $\mu\text{g/g}$ )	$1,271.33 \pm 22.85$	$1,145.33 \pm 20.33$	$2,747.50 \pm 25.14$	0.034
TCHO ( $\mu\text{g/g}$ )	$1,204.00 \pm 24.38$	$1,914.17 \pm 27.79$	$1,110.5 \pm 16.31$	0.454
BPC ( $\mu\text{g/g}$ )	$4,939.66 \pm 26.15$	$4,496.00 \pm 24.99$	$10,231.50 \pm 32.52$	0.014
TOC (%)	$4.70 \pm 1.39$	$4.23 \pm 1.17$	$6.15 \pm 0.78$	0.172
TOM (%)	$8.09 \pm 2.38$	$7.28 \pm 2.02$	$10.58 \pm 1.34$	0.203
PRT-N	$196.64 \pm 3.66$	$183.25 \pm 3.25$	$439.60 \pm 4.02$	0.001
Tannins and lignins ( $\mu\text{g/g}$ )	$1,600.33 \pm 24.46$	$817.67 \pm 12.97$	$1,786.5 \pm 30.74$	0.042
TOC/N	0.02	0.02	0.01	0.178
PRT/CHO	1.17	0.67	2.22	0.001
TLP/CHO	2.32	0.90	7.86	0.003
$\delta^{13}\text{C}$	$-26.38 \pm 0.09$	$-25.48 \pm 0.13$	$-26.64 \pm 0.10$	0.241
Chlorophyll-a ( $\mu\text{g/kg}$ )	$4.54 \pm 0.48$	$5.64 \pm 1.06$	$7.55 \pm 2.02$	0.005
Chlorophyll-b ( $\mu\text{g/kg}$ )	$1.24 \pm 0.06$	$2.01 \pm 0.01$	$3.84 \pm 0.87$	0.045
Chlorophyll-c ( $\mu\text{g/kg}$ )	$1.48 \pm 0.04$	$2.82 \pm 0.90$	$4.42 \pm 0.98$	0.010
Phaeophytin ( $\mu\text{g/kg}$ )	$6.42 \pm 2.74$	$8.96 \pm 2.84$	$13.10 \pm 3.64$	0.012
Chl-a/Phaeo	$0.71 \pm 0.13$	$0.63 \pm 0.05$	$0.58 \pm 0.02$	0.124

Total carbohydrates (TCHO) in Rufiji mangrove sediments were similar across stations (Table 1). At station 1, the recorded CHO value was  $1,204.00 \pm 24.38$ , while at station 2 and 3, the mean CHO content was  $1,914.17 \pm 27.79$  and  $1,110.5 \pm 16.31$ , respectively.

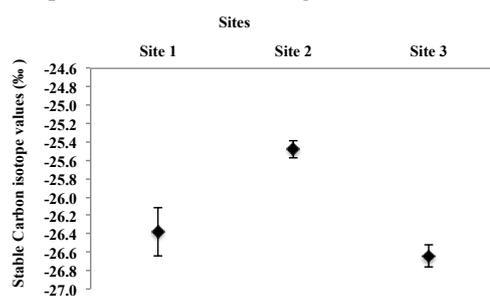
Total lipid (TLP) contents in Rufiji mangrove sediments exhibited variations from  $1,436.50 \pm 24.13$  at station 2 to  $6,373.5 \pm 25.79$  at station 3. The concentration of TLP at station 3 was significantly higher compared to values recorded in both stations 1 and 2 (Table 1; ANOVA,  $p = 0.001$ ).

The biopolymeric carbon fraction of the

sedimentary organic carbon in mangrove sediments ranged between  $4,496.00 \pm 24.99 \mu\text{g C/g}$  and  $10,231.50 \pm 32.52 \mu\text{g C/g}$ . BPC fraction was significantly higher at station 3 than at other stations, and was least at station 2 (Table 1; ANOVA,  $p = 0.014$ ). Tannin and lignin contents in mangrove sediments varied from  $817.67 \pm 12.97 \mu\text{g/g}$  to  $1,786.50 \pm 30.74 \mu\text{g/g}$  with values higher at station 3 compared to other sites (Table 1; ANOVA,  $p = 0.042$ ).

Estimated chlorophyll pigments exhibited significant spatial variations and were in the range: chl-a:  $4.54 \pm 0.48$ – $7.55 \pm 2.02 \mu\text{g/kg}$  (ANOVA,  $p = 0.005$ ), chl-b:  $1.24 \pm 0.06$ – $3.84 \pm 0.87 \mu\text{g/kg}$  (ANOVA,  $p = 0.012$ ), chl-c:  $1.48 \pm 0.04$ – $4.42 \pm 0.98 \mu\text{g/kg}$  (ANOVA,  $p = 0.010$ ). Concentrations of chlorophyll pigments in the sediments followed the trend: chl-a > chl-c > chl-b (Table 1). Generally, station 3 exhibited significantly higher pigment concentrations compared to stations 1 and 2 (Table 1). The ratio of chl-a to phaeopigments revealed no significant difference across the sites ( $p = 0.124$ ).

The stable carbon isotope ( $\delta^{13}\text{C}$ ) of total organic matter in Rufiji mangrove sediments ranged between  $-26.64 \pm 0.10 \text{‰}$  and  $-25.48 \pm 0.13 \text{‰}$ , with station 3 exhibiting more depleted with  $^{13}\text{C}$ , whereas station 2 recorded comparative enrichment (Figure 2).



**Figure 2:** Variation of carbon stable isotopes across three sites in sediments of the Rufiji mangroves system.

### Discussion

The biochemical composition of the Rufiji sedimentary organic matter showed a dominance of lipids followed by proteins and

carbohydrates. The biochemical composition of the sedimentary organic matter seems to be quite different from other coastal systems, which is usually characterized by the dominance of proteins and carbohydrates over lipids (Pusceddu et al. 2004). The high concentrations of sedimentary lipids, proteins and carbohydrates recorded in Rufiji mangrove sediments could be related to the morphodynamic, hydrological and physico-chemical characteristics of mangrove systems. The shallow water depth and high sedimentation rates of mangrove ecosystems support the settling of organic matter without significant degradation. Significantly higher values of total lipids in the study region especially at station 3 might be due to its preservation under highly anoxic conditions (Manju et al. 2012).

Biopolymeric carbon, which is regarded as the sum of three biochemical compounds (lipids, proteins and carbohydrates) (Manju et al. 2012, Salas et al. 2015), varied from 4,496 to 10,231  $\mu\text{g/g}$  in the mangrove sediments with lipids being the dominant class among labile organic compounds, followed by protein and carbohydrates. LPD contributions to the labile organic matter pool in these sediments at stations 1, 2 and 3 were 49.89%, 31.95% and 62.29%, respectively. PRT contributions to the labile organic matter pool at stations 1, 2 and 3 were 25.74%, 25.47% and 26.85%, respectively. CHO contributions to the total organic matter pool at stations 1, 2 and 3 were 24.37%, 42.58% and 10.85%, respectively. Minu et al. (2020) suggested that about 5–15% of sedimentary detritus, depending on the environmental characteristics are available at any time for benthic consumers. In this study, BPC exhibited its highest concentration at station 3 in the sediments of Rufiji mangroves accounting for 11 to 62% of total organic carbon.

The study has revealed that most measured parameters exhibited significant variations across the sites ( $p < 0.05$ ) with higher values at station 3, with exception of CHO, TOC, TOM, TOC/N, Chl-a/Phaeo and  $\delta^{13}\text{C}$ , ( $p > 0.05$ , Table

1). Sedimentary protein concentrations in the Rufiji mangrove system reflected the productivity of marine ecosystems and it appears to be a good descriptor of the trophic status of the benthic systems at different spatial scales (Pusceddu et al. 2004). Carbohydrates which include polyhydroxylated compounds ranging in size from 5–6 carbon sugars to large biopolymers (starch and cellulose) are much higher in vascular plants than in algae. In mangroves, litter is primarily composed of non-nutritive complex carbohydrates that are difficult or impossible for detritivores to digest. Lipids in sediments are derived not only from aquatic biota, but also from higher plant wax. Lipids in surface sediments are abundant in eutrophic systems than in oligotrophic systems. Like proteins, this also indicates the productivity of the system. The dominance of lipids and protein over carbohydrates indicated the nutritive value as the freshness of the labile organic matter in the sediments of the Rufiji mangrove system.

Protein to carbohydrate ratio (PRT:CHO) is used as an index for determining the origins of materials present in sediments and to distinguish between the presence of fresh materials and the age of sedimentary organic matter (Cividanes et al. 2002). The dominance of carbohydrates and lower PRT:CHO ratio (<1) are typical features of detrital heterotrophic environments (Manju et al. 2012). Since proteins are more readily used by bacteria than carbohydrates, high PRT:CHO ratios indicate recently produced organic matter, while low PRT:CHO ratios suggest the presence of aged organic matter (Manju et al. 2012) and the role of proteins as potentially limiting factor for the benthic consumers (Salas et al. 2015). PRT:CHO ratio varies depending on the depth and the trophic status of the system (Pusceddu et al. 2004). Values of the protein to carbohydrate ratio greater than 1 are typically reported immediately after a microphytobenthic bloom (Salas et al. 2015) or after the deposition of freshly produced phytoplankton (Pusceddu et al. 2004).

PRT:CHO ratio can also be used for

classifying benthic trophic status which in turn reflects patterns of nutrient enrichment (Pusceddu et al. 2004). PRT:CHO ratio in the Rufiji mangrove sediments ranged between 0.67 and 2.22. Higher PRT:CHO at stations 1 and 3 (> 1) indicated the presence of fresh organic matter, while a lower ratio (station 2) indicated the presence of aged or less degradable organic matter.

The lipid content and lipid to carbohydrate ratio (LPD:CHO) have been used as good indices for describing the energetic (food) quality of the organic contents in the sediments (Gremare et al. 2002). Lipid concentrations have also been associated with the most labile fraction of sedimentary organics and it is considered as the best descriptor for meiofauna abundance and biomass over enzymatically hydrolysable amino acids or protein contents (Gremare et al. 2002). LPD:CHO ratio in Rufiji mangrove sediments ranged from 0.90 to 7.86. The high LPD:CHO ratio, which is an index of energy character, support the fact that mangroves are generally considered as promoters of estuarine production. The estimated LPD:CHO ratio was significantly higher at station 3 compared to other stations (Table 1). The high LPD:CHO ratios observed in the Rufiji mangrove systems indicated the high quality of labile organic matter which supports benthic fauna in the delta.

Tannins and lignins form a significant fraction of refractory OM and its estimation provides valuable information on the input of terrestrially-derived organic detritus in marine systems (Lin et al. 2006). Tannin and lignin contents in this study displayed significant spatial variations ( $p = 0.042$ ) with a range of 817 to 1,787  $\mu\text{g/g}$ . The tannin and lignin contents recorded in the study area (Table 1) might be originating from terrestrial vascular plant debris. The abundance of phenolic compounds in mangrove systems has been reported by other researchers (Hernes and Hedges 2000, Hernandez et al. 2001, Kraus et al. 2003, Renjith et al. 2013, Akhil et al. 2013). Spatial variation of chlorophyll pigments in the surface sediments can be attributed to light

availability and dissolved oxygen (DO) contents in the water column (Moreno and Niell 2004). Trend-wise, these pigment concentrations were very comparable with results from other estuaries (Sujatha et al. 2015). A highly significant positive correlation (Table 2) of chlorophyll pigments with a fine-grained fraction (silt and clay) implied the effects of grain size on the pigment distribution in sediments (Moreno and Niell 2004). Autochthonous water column input contributes chlorophyll to sediments (Szymczak-Zyla and

Kowalewska 2007). In all stations, the estimated ratios of chl-a to phaeopigments and chl-a/(chl-a + phaeopigments) were low (< 1) signifying that phaeopigments, the early breakdown product of chl-a degrade more slowly. This ratio could also be used to suggest the relative rate and time frame of phytoplankton deposition in the estuarine environment. The combined use of these ratios in this study suggested rapid and recent deposition of phytoplankton in Rufiji mangrove sediments (Hagy et al. 2005).

**Table 2:** Correlation between sedimentary parameters in Rufiji mangrove sediments (n = 14)

	Sand	Silt	Clay	TOC	TOM	TLP	PRT	CHO	T&L	PBC	Chl-a	Chl-b	Chl-c	Phe
Sand	1													
Silt	<b>-0.86</b>	1												
Clay	<b>-0.90</b>	-0.32	1											
TOC	-0.33	-0.40	-0.39	1										
TOM	-0.18	-0.46	-0.33	<b>0.95</b>	1									
TLP	-0.43	0.28	-0.47	<b>0.70</b>	<b>0.94</b>	1								
PRT	-0.07	0.36	0.20	<b>0.79</b>	<b>0.84</b>	0.40	1							
CHO	-0.19	0.16	-0.34	0.17	0.26	0.35	0.21	1						
T&L	-0.41	-0.06	-0.25	<b>0.69</b>	0.14	0.29	-0.09	0.16	1					
PBC	-0.41	0.20	0.02	<b>0.76</b>	<b>0.80</b>	<b>0.84</b>	<b>0.70</b>	0.25	0.24	1				
Chl-a	-0.25	0.95	<b>0.90</b>	0.34	0.41	0.44	0.07	0.34	0.12	0.34	1			
Chl-b	-0.13	<b>0.81</b>	<b>0.85</b>	0.20	0.41	0.45	0.04	0.35	0.17	0.28	<b>0.83</b>	1		
Chl-c	-0.40	<b>0.75</b>	<b>0.72</b>	0.01	0.38	0.43	0.07	0.27	0.23	0.25	<b>0.66</b>	<b>0.95</b>	1	
Phe	-0.05	<b>0.90</b>	<b>0.88</b>	0.33	0.34	0.37	0.06	0.24	0.05	0.40	<b>0.94</b>	<b>0.72</b>	<b>0.52</b>	1

Stable carbon isotope signatures ( $\delta^{13}\text{C}$ ) of the various carbon inputs are often different, and therefore can be used as powerful tracers of carbon sources in various ecosystems (Hu et al. 2006). Enzymatic and diffusional fractionation processes lead to discrimination against  $^{13}\text{C}$  during photosynthesis that varies between C3, C4 and Crassulacean Acid Metabolism (CAM) plants (Brugnoli and Farquhar 2000). In C3 plants (woody plants),  $\text{CO}_2$  is fixed within the Calvin cycle yielding C3 compounds as first products and an isotopic signature that varies between  $-21\text{‰}$  and  $-35\text{‰}$ . In C4 plants,  $\text{CO}_2$  is first fixed in C4 organic acids that transport the carbon to separate tissues where sugar synthesis within the Calvin cycle takes place. The isotopic composition in C4 plants ranges between  $-9\text{‰}$  and  $-20\text{‰}$  (Badeck et al. 2005).

CAM plants have an intermediate isotopic signature between C3 and C4 with variation

depending on the proportion of carbon fixed in the dark into C4 organic acids in the light via the Calvin cycle. Marine organic matter consequently typically has  $\delta^{13}\text{C}$  values between  $-20$  and  $-22\text{‰}$ . The  $\sim 7\text{‰}$  difference between organic matter produced by C3 land plants and marine algae has successfully been used to trace the sources and distribution of organic matter in coastal ocean sediments (Brugnoli and Farquhar 2000). In the present study, the observed  $\delta^{13}\text{C}$  values for mangrove sediments pointed towards the vascular plant input (mangroves- C3 woody plants). Comparatively more enriched value for  $\delta^{13}\text{C}$  was recorded at station 2 and more depleted values at stations 1 and 3. Generally, more enriched values were observed in the low organic carbon site, and more depleted values in organic-rich sediment sites. From the observed relationships, it can be assumed that due to the almost closed nature of station 3, much of the mangrove area is rarely

inundated because of the low tidal flushing and act as retention sites where mangrove carbon is a significant contributor to the sediment organic carbon pool.

The sediments from station 2 reflect a balance between inputs (possibly including microphytobenthos) and carbon imported from the water column during high tide. The more depleted  $\delta^{13}\text{C}$  values reported for the mangrove sediments indicate a major contribution of organic matter from the vascular plants. Various studies using the bulk parameter approach have shown that organic matter in the mangrove systems exhibit higher  $\delta^{13}\text{C}$  values of plant origin (Manju et al. 2012, Manju et al 2016).

Correlation analysis of mangrove sediments (Table 2) showed that BPC had highly significant positive relations with total organic carbon, total lipids and proteins. Total lipids showed highly significant positive correlations with total organic carbon. Proteins also showed significant positive correlations with total organic carbon and total organic matter. Significant correlations for tannins and lignins with total organic carbon were observed in mangrove systems. The relationships exhibited by the variables pointed towards the adsorption and diagenetic process controlling the distribution of the biochemical components in the Rufiji mangrove sediments.

Total carbohydrates did not correlate with any sedimentary parameters. The higher concentrations of carbohydrates in mangrove sediments pointed towards the possibility of inputs of vascular plant materials, especially mangrove litter. The absence of any significant correlations among some sedimentary parameters suggests different origins and diagenetic pathways of the respective parameters.

The biogeochemical processes taking place in the aquatic system mainly control the quality and quantity of sedimentary organic matter. A Principal Component Analysis (PCA) was employed to deduce the geochemical processes in the Rufiji mangrove system. The main aim of PCA was to reduce the number of variables

that needed to be considered into a smaller number of indices, principal components, which can be more easily interpreted (Spencer 2002).

PCA analysis of Rufiji mangrove sediments revealed three components without significant differences accounting for a total of 92.84 % variance (Table. 3). The first component accounted for 35.77 % of the total variance and showed very high positive loadings on total organic carbon, total organic matter, carbohydrates, proteins and BPC. But this component had no significant loadings on sediment texture, one of the major redox indicator, signifying autochthonous input including the mangrove litter as the main source of organic matter in Rufiji mangrove sediments.

**Table 3:** Factor loadings for various biochemical components in Rufiji mangrove sediments

Sedimentary variable	Principal components		
	PC 1	PC 2	PC 3
Sand	0.224	0.179	<b>0.937</b>
Silt	-0.165	0.238	<b>-0.943</b>
Clay	0.011	<b>-0.948</b>	0.064
Total organic carbon	<b>0.934</b>	0.237	<b>0.611</b>
Total organic matter	<b>0.879</b>	0.280	0.379
Lipids	0.408	<b>0.901</b>	0.098
Proteins	<b>0.693</b>	<b>0.740</b>	-0.146
Carbohydrates	<b>0.664</b>	<b>-0.507</b>	0.246
BPC	<b>0.607</b>	<b>0.784</b>	-0.081
Contribution rate (%)	35.77	34.84	22.23
Accumulated contribution rate (%)	35.77	70.61	92.84

Component 2 exhibited high negative loadings on clay and positive loadings on lipids, proteins and BPC accounting for 34.84 % of the total variance. It also revealed a statistically significant negative loading on carbohydrates, pointing towards the diagenetic pathway. The low negative loading pattern of carbohydrates might be due to the preferential remineralisation of lipids and proteins,

signifying that anaerobic diagenetic processes account for the second major biogeochemical process in these ecosystems. It is customary that carbohydrates are diagenetically weaker than proteins under anoxic conditions, but the reverse is true under oxic conditions (Badeck et al. 2005). Component 3 accounted for 22.23 % of the total variance and exhibited high positive loadings on the sand and negative loadings on silt and total organic carbon. Due to the positive loadings on organic carbon and low loading on clay, it seems that the third component was attributed to geochemical processes which include siltation and sorption/desorption rather than diagenesis.

### Conclusions

Sedimentary organic matter was high in sediments of the Rufiji mangroves. The percentage ratio of the labile to the total organic matter indicated that most of the deposited organic matter was refractory in nature. The discrepancy between the high amounts of organic matter and its low nutritional value suggests that these ecosystems behave as a detrital trap and organic matter tends to accumulate. Texture analysis implied the predominance of silt and clay in the Rufiji mangrove sediments. The high lipid content and LPD/CHO ratio reflected the quality of organic matter to support benthic fauna, and is indicative of a better preservation of lipid compounds in the sedimentary environment. Lower PRT/CHO ratio suggested a detrital heterotrophic environment in the Rufiji mangrove environment. This ratio is also indicative of the low hydrodynamic conditions in Rufiji mangroves favouring the accumulation of sedimentary organic matter. From the bulk parameter approach, it could be seen that organic matter in sediments of the Rufiji mangrove systems is of higher plants origins. Biopolymeric carbon and the algal contributions to BPC provided important information on the better understanding of the trophic status of the area. Estimated TOC/N ratios implied the combined inputs of both terrestrial and autochthonous organic matter to

sediments of Rufiji mangrove system. The more depleted  $\delta^{13}\text{C}$  value of bulk sedimentary organic matter implied terrestrial inputs of vascular plant debris, which was supported by higher concentrations of tannins and lignins. Chl-a/phaeopigment ratio and chl-a/(chl-a + phaeopigment) ratio, revealed rapid and recent deposition of phytoplankton detritus to sediments. Grain size and total organic carbon contents had substantial influence on the distribution of the biochemical composition of the Rufiji mangrove sediments. Principal component analysis revealed the association of variables and their distribution trends across the studied sites. A biomarker approach (molecular level characterization) is recommended to achieve more specific information on the degradation status of organic matter in the complex Rufiji ecosystem.

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