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Assessment of the Geochemical Characteristics of Water and Surface Sediments of Rufiji Mangrove Forest, Tanzania

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Abstract

This study was carried out to investigate the geochemical characteristics of the Rufiji mangrove systems using mineralogy and heavy metal analyses. Rufiji mangrove sediments showed predominance of fine grain size fractions with silt as the major component. Stoichiometric ratios of nutrients revealed phosphorus enrichment in Rufiji sediment. The overall order of heavy metal concentrations in sediments was: Fe > Mg > Mn > Zn > Cr > Ni > Pb > Cu > Co > Cd. There was no relationship between grain size and some of the heavy metal concentrations, except for Co, Cr, Fe, and Mg which negatively correlated with sand, and positively correlated with silt. The findings indicated minor enrichments for Pb and Zn, and no enrichment for all other metals. The estimated geo-accumulation index demonstrated very low values (Igeo < 0) in almost all metals, except Zn (Igeo > 1.0) at station 3, indicating that sediments of the Rufiji mangrove ecosystem are unpolluted to moderately polluted. Ongoing research on the transport of nutrients, distribution and behaviour of anthropogenic chemicals throughout the estuary, and over different seasons, may provide further insights on the processes and factors which modulate the spatial and temporal variability in geochemistry of this rich and diverse tropical estuarine system.

Keywords: Rufiji mangrove, Enrichment factor, Geoaccumulation index, heavy metal.

Introduction

The role played by mangrove ecosystems in the biogeochemistry of nutrients, organic matter and trace metals in the coastal environment cannot be overemphasized. Mangrove ecosystems are widely recognised as archives for anthropogenic contaminants (Machado et al. 2002, Alongi et al. 2004, Lewis et al. 2011, Bayen 2012, Bouchez et al. 2013). They have high ability of accumulating organic matter and are highly adapted to live in the extreme environmental conditions (Marchand et al. 2004). They perform imperative functions in nutrient cycling and energy flows in coastal environments (Dodds 2006, Lovelock et al. 2009, Donato et al. 2011). However, the knowledge of biogeochemical processes in the sediments of mangrove ecosystems to date is still limited (Pasco and Baltz 2011, Sousa and Dangremond 2011, Rigaud et al. 2013, Shilla et al. 2019). This is true for Rufiji estuary where, based on literature search, there are only a few studies that have investigated the geochemistry of heavy metals in surface sediments and water of the Rufiji mangrove forests (e.g., Minu et al. 2018, Shilla et al. 2019).

Heavy metals occur naturally in the soil and sediment environment from the pedogenetic processes of weathering of parent materials at levels that are regarded as trace (< 1000 mg/kg) and rarely toxic (Wuana and Okieimen 2011). Due to the human activities, most sediments may accumulate one or more heavy metals. The main sources of heavy metals into the mangrove systems include tidal activities, land runoff and rainfall. Other sources may be associated with miscellaneous kinds of anthropogenic activities such as shipping, dredging, and urban wastewater discharges. Due to its vicinity to the urban development areas, mangrove ecosystems are impacted by urban and industrial run-off containing trace and heavy metals in various forms (MacFarlane 2002). Consequently, concentrations of metals in the mangrove sediments tend to reflect the extent and sources of anthropogenic pollution (Guédron et al. 2012). Although at present the Rufiji estuary and its delta can be considered as one of the less polluted coastal areas in Tanzania, the presence of small-scale industries, agricultural activities, commercial fishing and other socioeconomic activities suggest that heavy metals from anthropogenic sources might also be released in significant amounts to this coastal environment.

Previous studies have indicated that sediments under reducing conditions, fine-grained, and rich in organic matters accumulate metals and make them unavailable for remobilization and biotic uptake (Abdallah 2011, Ahmed et al. 2011). Therefore, the increased degradation of mangrove forests can promote the remobilization of sediment-bound metals and accelerate its transport to adjacent ecosystems (Birch et al. 2013). The kinetics of heavy metals adsorption and desorption in the mangrove sediments depend, among other things, on sediment characteristics such as pH, redox potential (Eh), cationic exchange capacity, organic matter, clay content, salinity, iron and manganese oxides and the presence of other metals (Abdallah 2011, Ahmed et al. 2011).

Numerous geochemical assessment techniques, including enrichment factor (EF), geoaccumulation index (Igeo), sediment quality guidelines (SQGs), mean-effects range medium-quotient (m-ERM-Q) and potential ecological risk index (PER), have been used by several authors to determine the status of metal contamination in the sediments (Long et al. 1998, MacDonald et al. 2000, Long 2006, Zhang et al. 2014, Wang et al. 2015, Zhu et al. 2016, Huang et al. 2016, Christophoridis et al. 2019). Although each evaluation method has its own weakness assets and liabilities, the uses of these tools can provide valuable information to elucidate different aspects of pollution in relation to key geochemical parameters. Since the current study aims at providing the first overview of geochemical characteristics of water and surface sediments at the selected sites in the Rufiji estuary, two geochemical assessment techniques have been adopted. The adopted techniques, EF and Igeo, are capable of assessing the presence and intensity of anthropogenic contaminant depositions in surface sediments. Further information of these techniques is given in the methodology section.

Materials and Methods

Description of the study area

The study sites are located in Rufiji estuary (39° 07´ E, 7° 41´S) to (39° 45´E, 8° 15´ S), about 100 km south of Dar es Salaam city, in the Rufiji River delta (Figure 1). This river has a catchment area of 177,400 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 km^2 with 530 km^2 covered by mangrove forests (Sorensen 1998). The four northern tributaries presently carry the bulk of the discharges into Rufiji River. The southern part of the delta, which is sheltered, receives little freshwater, and the water in front of this part of the delta are clear and saline and feature seagrass meadows and scattered patches of reefs. The detailed background information about the Rufiji estuary is given in Shilla et al. (2019).

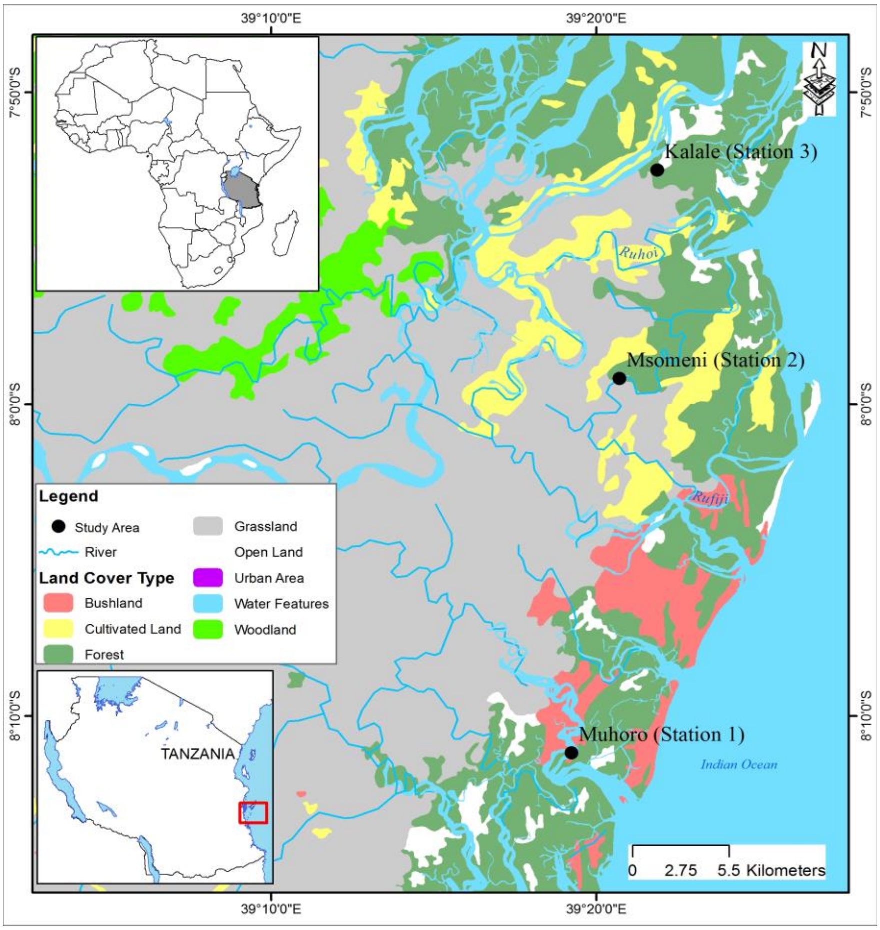

Figure 1: Map showing the Rufiji estuary, and the three sampling locations; Muhoro stream (station 1), Msomeni area (station 2), and Kalale stream (station 3) (Adapted from Shilla et al. 2019).

The present study was conducted at three locations (Muhoro – station 1, Msomeni – station 2, and Kalale – station 3), representing the south, middle and northern parts of the Rufiji estuary (Figure 1). These locations were chosen because they represent a variety of estuarine habitats (i.e., mangrove stands, mud flats, and adjacent seagrass meadows) with sufficient diversity and densities of consumer organisms.

Sample collection

Water and sediment samples were collected from three locations (Muhoro – station 1, Msomeni – station 2, and Kalale – station 3) during June and July 2014. Surface water samples were collected during high tide using a clean plastic 10 litres bucket and were transferred to new, sample-rinsed 5-L high-density polyethylene (HDPE) bottles and kept cold to prevent changes in the samples' chemical composition until analysis, which was conducted within 5 days of sampling. Surface sediment samples were collected during the low tide using a clean plastic spoon. In order to obtain a true representation of samples within the study area, water and sediment samples were collected from three different areas, spaced at 30 meters, within a study site and pooled together for analysis. Samples were kept in clean plastic bags and transported to the laboratory on ice and stored in a deep freezer at –20 ºC till further processing.

Sample preparation and analyses

Laboratory analyses for heavy metals and major elements were carried out at the Department of Thematic Studies, Environmental Change, Linköping University, Sweden. Dissolved nutrients were analysed at the Department of Aquatic Sciences and Fisheries, University of Dar es Salaam, Tanzania. All the analyses were carried out in triplicates and the average reported. The physico-chemical parameters of Rufiji estuary surface waters were analysed using standard methods (APHA 2005). Physical chemical parameters (pH, temperature, salinity and dissolved oxygen) in the water column were measured *in situ* using a multi-parameter water quality meter (Hanna Hi 9829). Samples for dissolved nutrients (nitrite, nitrate phosphate and silicate) were first filtered using GF/C filters (Whatman GF/F, 0.7 mm), thereafter absorbance and concentrations were determined spectrophotometrically using UV-VIS spectrophotometer (Genesis Thermospectronic). Briefly, nitrite was converted to an azo dye with sulphanilamide and N- (1-naphthyl) ethylene diamine dihydrochloride (Shilla et al. 2006). Nitrate was reduced to nitrite using copper-coated cadmium column and estimated as nitrite. Formation of phospho-molybdate complex using ascorbic acid as a reducing agent was used for phosphate determination (Shilla et al. 2006). Silicate was analysed by converting it into silicomolybdate complex, which is reduced, using ascorbic acid and oxalic acid to produce a blue solution.

Redox potential (Eh) of the fresh wet sediment was measured using Zobell's solution for the calibration of the electrodes (Findlay et al. 1995). The surface sediment samples were subjected to size analysis (Parkes and Taylor 1985) and grain size parameters were calculated (Meziane and Tsuchiya 2000). Sandy samples were repeatedly washed in distilled water for removal of salts and then dried. After drying, a sub-sample weighing about 40–50 g was treated with 15% H_2O_2 and 10% HCl to remove organic matter and shell materials in the sample and then dried. The sub-sample was subjected to sieving by ASTM test sieves of 8 inches diameter, with successive sieves spaced at 1/2φ intervals in order to obtain grain size data (Meziane and Tsuchiya 2000). Particle Size Analyzer (Model: Malvern Mastersizer 2000E, UK) was used to analyse silt and clay fractions of the sediment samples. Sediment samples were air dried and finely powdered using agate mortar and analysed for mineralogy using X-Ray Diffraction (XRD) (Moore and Reynolds 1997). Total carbon (TC), nitrogen (TN) and sulphur (TS) were determined using Vario EL III CHNS Analyser (Analysensysteme GmbH, Hanau, Germany). Sediment organic carbon (OC) was estimated by the procedure described in Shilla et al. (2008). The amount of total organic matter (TOM) was quantified by multiplying the organic carbon values with 1.724, a factor which is generally used to convert organic carbon (OC) to TOM.

Major elements from representative samples were analysed using X-Ray Fluorescence (XRF) method. Loss of ignition (LOI) was determined by using Thermo Gravimetric Analysis (TGA) method (Heiri et al. 2001). Heavy metals in the sediment samples were determined using Flame Atomic Absorption Spectrometer (AAS) (Perkin Elmer-3110) after digestion using di-acid mixture: ($HClO_4$:$HNO_{3,}$ 1:5) as described in Shilla et al. (2008). Intercalibration sediment (IAEA-433) sample (from the International Laboratory of Marine Radioactivity, IAEA) was used as a control for the analytical methods. Triplicate analysis of IAEA-433 showed good accuracy and the recovery rates ranged between 93.60 and 101.70% (Table 1). Reagent blanks were analysed in parallel with each batch of samples. Heavy metal concentrations in the blanks were < 1% of samples and the relative standard deviation in replicate samples was < 10%.

Table 1: Results of the analysis of standard reference material for heavy metals (IAEA-433)

Metal	Certified value (µg/g)	Obtained concentration (µg/g, n = 3)	Recovery (%)
Co	11.40 ± 2.10	10.67 ± 2.68	93.60
Cd	0.153 ± 0.26	0.148 ± 0.01	98.70
Cr	123.00 ± 1.40	112.00 ± 0.65	91.05
Cu	18.50 ± 2.70	18.20 ± 0.25	98.40
Fe	4.70 ± 0.14	4.64 ± 0.41	98.70
Mg	2.44 ± 0.23	2.32 ± 0.36	95.08
Mn	229.00 ± 15.00	223.47 ± 10.75	97.60
Ni	55.30 ± 3.60	54.16 ± 2.01	97.90
Pb	22.70 ± 3.40	24.90 ± 0.08	101.70
Zn	119.00 ± 12.00	120.64 ± 2.51	101.38

Computation of geochemical index

The computation of enrichment factor (EF) has been used in this study to evaluate the impact of anthropogenic activities related to the metal abundance in sediments. According to Ergin et al. (1991), EF is defined by the following equation:

$$EF = \frac{\left(\frac{C_X}{C_{Fe}}\right)_{Sample}}{\left(\frac{C_X}{C_{Fe}}\right)_{Crust}} \text{ ....(1)}$$

where:

Fe (iron) is chosen as a natural element of reference;

(C_X/C_{Fe}) Sample is the ratio between concentration of the element “X” and that of Fe in the sediment sample;

(C_X/C_{Fe}) Crust is the ratio between concentration of the element “X” and that of Fe in unpolluted reference baseline.

According to Birch et al. (2013), calculated EF values could be interpreted as follows: EF ≤ 1 = no enrichment; 1 < EF < 3 = minor enrichment; 3 < EF < 5 = moderate enrichment; 5 < EF < 10 = moderate-to-severe enrichment; 10 < EF < 25 = severe enrichment; 25 < EF < 50 = very severe enrichment; and EF > 50 = extremely severe enrichment.

The study of geoaccumulation index (Igeo) could be relevant in the examination of the contamination level of the sediment samples affected by metals. In Müller (1979) view, Igeo can be obtained by the following equation:

$$I_{geo} = Log_2\left(\frac{C_n}{1.5B_n}\right) \text{ ....(2)}$$

where C_n is the concentration of the metal (n) in sampled and analysed sediment and B_n is the background concentration of the same metal (n) and the factor 1.5 is the background matrix correction factor due to lithogenic effects which allows to analyse natural fluctuations in the content of a given substance in the environment and to detect very small anthropogenic influence. According to Barbieri (2016), the extent of metal pollution can be assessed based on the numerical values of Igeo grouped into seven enrichment classes as follows: Igeo < 0 (class 0, uncontaminated); Igeo of 0 – 1 (class 1, uncontaminated-to-moderately contaminated); Igeo of 1 – 2 (class 2, moderately contaminated); Igeo of 2 – 3 (class 3, moderately to strongly contaminated); Igeo of 3 – 4 (class 4, strongly contaminated); Igeo of 4 – 5 (class 5, strongly to extremely contaminated) and Igeo > 5 refers to class 6 or extremely contaminated.

Statistical analyses

Data were analysed using StatView® 5.0.1 Software (SAS Institute Inc. 1992–1998, Cary, NC). Statistical significance was determined at $p \leq 0.05$. Pearson’s product-moment correlation was used to test for significance of relationships between heavy metals, grain size and organic matter contents in the mangrove sediments. Normality of data was tested before analysis using Komolgorov-Smirnov test.

Results

Hydrographical parameters of Rufiji estuary

The hydrographical parameters measured in the Rufiji estuarine waters are presented in Table 2. Physical parameters did not vary significantly across stations. Inorganic phosphate was higher at station 1 (26.97 µmol/L) followed by station 2 (16.67 µmol/L) and 3 (12.95 µmol/L), while nitrite and nitrate concentrations varied from 1.01 to 1.80 µmol/L and from 2.43 to 6.25 µmol/L, respectively. Silicate concentrations ranged from 3.8 µmol/L at station 3 to 58.07 µmol/L at station 1. The variations in the hydrographical parameters at these stations could be attributed to the environmental settings. Station 3 was less alkaline and showed lower silicate and higher nitrate concentrations, which could be due to the limited water exchange with the estuary because of its almost closed nature. Stations 1 and 2 are much closer to the estuarine front when compared to station 3.

Table 2: The hydrographical parameters and sedimentary characteristics in the Rufiji mangrove system

Parameter	Station 1 (n = 3)	Station 2 (n = 3)	Station 3 (n = 3)
pH	6.35 ± 2.10	6.68 ± 2.33	4.42 ± 1.33
Salinity (psu)	21.37 ± 5.01	21.50 ± 9.22	23.85 ± 10.5
Alkalinity ($CaCO_3$ mg/L)	146.7 ± 22.1	160.0 ± 25.1	80.00 ± 22.6
DO (O_2 mg/L)	3.60 ± 1.12	5.77 ± 3.50	4.20 ± 2.32
Nitrite (µmol/L)	1.01 ± 0.20	1.27 ± 0.66	1.80 ± 0.11
Nitrate (µmol/L)	2.43 ± 1.31	2.47 ± 1.26	6.25 ± 2.03
Phosphate (µmol/L)	26.97 ± 8.14	16.67 ± 4.22	12.95 ± 7.09
Silicate (µmol/L)	58.07 ± 11.1	28.87 ± 10.4	3.80 ± 0.55
Sand (%)	17.4 ± 3.46	2.53 ± 2.30	11.35 ± 4.60
Silt (%)	53.07 ± 7.11	61.04 ± 8.21	42.01 ± 11.6
Clay (%)	29.51 ± 10.2	36.42 ± 13.9	13.35 ± 6.21
Total carbon (%)	5.07 ± 2.40	4.14 ± 1.77	4.39 ± 1.73
Organic carbon (%)	4.33 ± 2.54	3.20 ± 1.61	3.9 ± 0.26
Total nitrogen (%)	0.39 ± 0.12	0.03 ± 0.01	0.06 ± 0.01
Total sulphur (%)	0.4 ± 0.41	0.40 ± 0.02	1.03 ± 1.02
Eh	–41.33 ± 11.6	–27.3 ± 9.55	–245 ± 86.9

Results are presented as mean ± standard deviation.

Characteristics of Rufiji mangrove sediments

The characteristics of the Rufiji mangrove superficial sediments are presented in Table 2. Texture analysis revealed that silt comprised a major fraction of the sediments in the mangrove ecosystems. Sediment samples from station 1 were silty in nature, while sediment texture at station 2 was muddy in nature. Station 3 contained sediments which were characterised as sandy texture. The sediment pH values varied from 4.42 to 6.68 in the studied mangrove sediments. Eh values at station 3 were more reducing, while values from other stations showed a general anoxic condition.

Major elements

Analyses of the Rufiji mangrove sediments by CHN-S (Table 2) revealed high levels of total carbon with values between 4.14 and 5.07%. Organic carbon ranged between 77 and 85.4% of the total carbon, while total nitrogen and total sulphur contents ranged between 0.03 to 0.39% and 0.4 to 1.03%, respectively across the sampled sites. All these values were higher at station 1 compared to the other two stations. Sediment texture, carbon and nitrogen varied across sites in Rufiji mangrove sediments, while sulphur contents were higher at station 3 relative to the levels recorded in stations 1 and 2.

Sediment samples from the three sampled sites were analysed for major elements in order to ascertain their background concentrations. Results from XRF analyses indicated that silicon was the main element across all the three stations, followed by aluminium and iron (Table 3). Calcium and phosphorus levels at station 3 were higher compared to stations 1 and 2. The sulphur content in samples from station 3 was the highest of all the stations. TGA analysis revealed that the moisture content in the sediment samples was about 8.6% while the weight loss at 900 °C was about 27%.

Table 3: Major elemental composition and TGA results (weight %) of Rufiji mangrove sediments

Compound	Station 1 (n = 3)	Station 2 (n = 3)	Station 3 (n = 3)
SiO_3	30.4 ± 3.61	26.5 ± 6.90	25.60 ± 6.72
TiO_2	0.70 ± 0.11	0.80 ± 0.04	0.50 ± 0.02
Al_2O_3	14.3 ± 2.34	15.4 ± 4.35	11.42 ± 4.28
MnO	0.04 ± 0.21	0.05 ± 0.04	0.04 ± 0.01
Fe_2O_3	8.90 ± 2.48	9.60 ± 0.40	5.80 ± 1.83
CaO	1.80 ± 1.02	0.86 ± 0.24	8.80 ± 4.30
MgO	2.60 ± 1.14	2.50 ± 0.32	1.60 ± 1.10
Na_2O	4.50 ± 1.58	3.30 ± 1.18	3.40 ± 0.66
K_2O	2.50 ± 0.26	2.30 ± 2.08	1.80 ± 0.82
P_2O_5	0.60 ± 0.21	0.60 ± 0.52	7.06 ± 0.94
SO_3	0.10 ± 0.11	0.12 ± 0.10	1.24 ± 0.20
Cr_2O_3	0.04 ± 0.04	0.04 ± 0.01	0.03 ± 0.02
CuO	0.02 ± 0.02	0.02 ± 0.02	0.02 ± 0.02
NiO	0.01 ± 0.04	0.01 ± 0.02	0.01 ± 0.04
Rb_2O	0.01 ± 0.02	0.01 ± 0.02	0.01 ± 0.02
SrO	0.03 ± 0.10	0.05 ± 0.12	0.06 ± 0.04
ZnO	0.01 ± 0.06	0.02 ± 0.01	0.06 ± 0.06
ZrO_2	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.02
LI -1	8.60 ± 6.18	8.70 ±1.87	8.40 ± 3.28
LI -2	26.4 ± 10.5	26.6 ± 13.4	28.80 ± 6.92

LI-1 = Loss on Ignition at 110 °C, LI-2 Loss on Ignition at 900 °C; Results are presented as mean ± standard deviation.

Concentrations of heavy metal in sediments

The concentrations of heavy metals in the surface sediments from the study sites are presented in Table 4. The concentrations of metals in sediments were in the order: Fe > Mg > Mn > Zn > Cr > Ni > Pb > Cu > Co > Cd. Cadmium and zinc were higher at station 3, while cobalt, nickel and chromium were lower at station 3. Copper, lead, iron, magnesium and manganese exhibited similar values. The mean concentrations of cadmium ranged between 0.07 and 0.15 µg g^{-1} and was the highest at station 3, while cobalt ranged between 9.51 and 22.70 µg g^{-1} and exhibited lower values at station 3 compared to the other stations. Chromium was the lowest at station 3, with the range between 38.86 and 88.04 µg g^{-1}. Copper and iron varied from 22.77 to 30.24 and 37869.43 to 57366.67 µg g^{-1}, respectively, and showed no significant spatial variations ($p > 0.05$) across sites. Magnesium showed lowest concentration at station 3, with a range between 8,357.37 and 16,988.00 µg g^{-1}, while manganese did not show any spatial trend, and its concentrations ranged between 162.30 and 267.00 µg g^{-1}. The concentrations of nickel were the highest at station 2 with a range between 23.62 and

67.89 µg g^{-1}. Lead depicted a similar pattern in its distribution with its concentrations ranging between 14.92 and 35.08 µg g^{-1}. Zinc represented highest concentrations at station 3 when compared to other stations with a range between 113.80 and 256.91 µg g^{-1}.

Geochemical index

The analysis of the enrichment factors of the various heavy metals in the study area (Figure 2) indicates a minor enrichment for Pb and Zn and no enrichment for other metals.

The geoaccumulation index estimated for the heavy metals from the sediments of the study area (Figure 3) exhibited very low values (1geo < 0) in the case of almost all metals except Zn (1geo > 1.0 in station 3), which indicated the sediments of the mangrove ecosystem are unpolluted to moderately polluted with heavy metals.

Table 4: Concentrations (µg/g) of heavy metals in the surface sediments of the Rufiji mangrove system

Metal	Station 1 (n = 3)	Station 2 (n = 3)	Station 3 (n = 3)
Cd	0.07 ± 0.01	0.08 ± 0.01	0.15 ± 0.01
Co	20.49 ± 3.24	22.70 ± 2.48	9.51 ± 0.08
Cr	79.83 ± 8.64	88.04 ± 6.82	38.86 ± 2.86
Cu	26.57 ± 4.68	30.24 ± 4.66	22.77 ± 3.98
Fe	48,825.00 ± 42.82	57,366.67 ± 50.42	37,869.43 ± 28.68
Mg	15,167.33 ± 38.54	16,988.00 ± 42.68	8357.37 ±18.46
Mn	267.00 ± 26.86	245.59 ± 12.64	162.30 ± 6.86
Ni	55.23 ± 6.24	67.89 ± 8.64	23.62 ± 3.64
Pb	31.33 ± 3.48	35.08 ± 3.04	14.92 ± 2.88
Zn	113.80 ± 4.12	120.47 ± 4.92	256.91 ± 10.86

Concentrations are presented as average ± standard deviation.

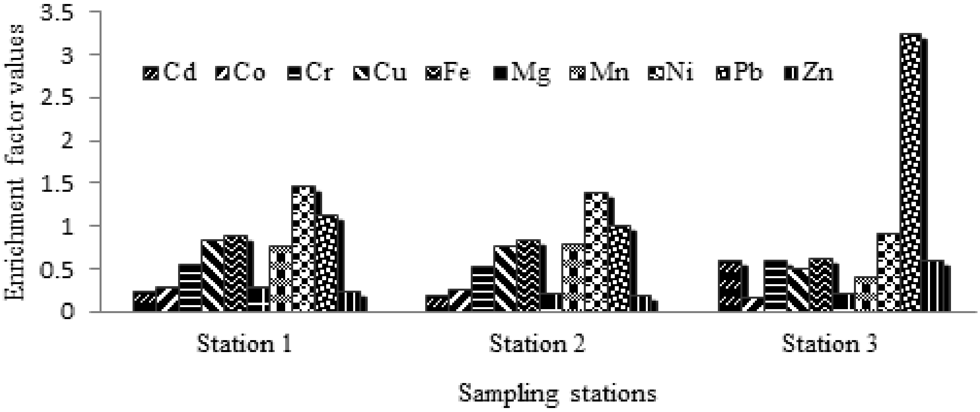

Figure 2: Enrichment of heavy metals in Rufiji mangrove sediments.

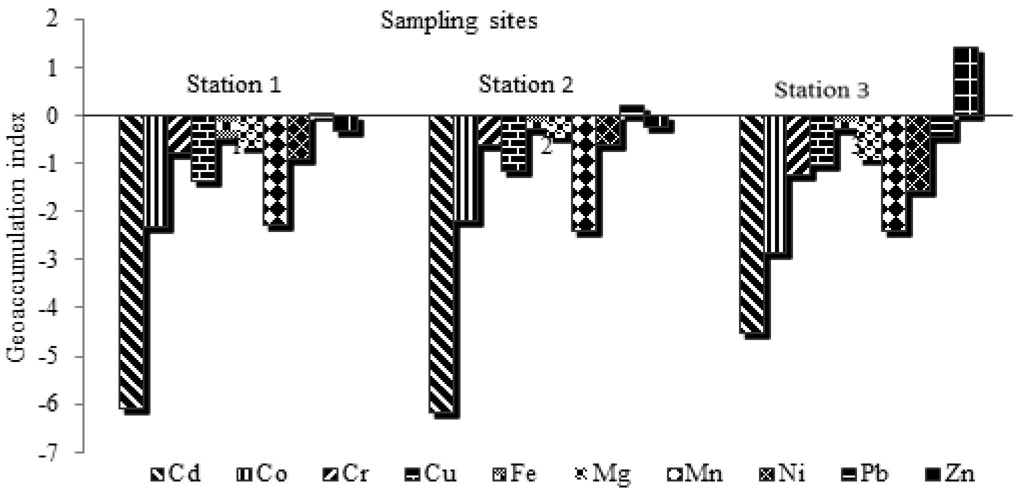

Figure 3: Geoaccumulation index for heavy metals in Rufiji mangrove sediments.

Discussion

The texture of the sediments is known to have significant roles on the physico-chemical processes as well as on the species diversity (Shilla et al. 2008). Fine particles have greater surface areas and amounts of organic carbon, clay, iron, or aluminium with ability to concentrate metals (Santschi et al. 2001, Myers and Thorbjomsen 2004). In this study, sedimentary analyses showed predominance of fine grain size with silt as the major component in all sediment samples from the mangrove sediments. Organic carbon, nitrogen, and sulphur did not show any spatial distribution trend. No correlation ($p > 0.05$) was observed between organic carbon, nitrogen, sulphur composition and texture (Table 5), indicating the absence of any granulometric dependence. Existence of positive correlation between sediment organic carbon (OC) and total nitrogen (TN) indicates a common source of organic matter (OM) to these elements. It has been reported that organic matter is better preserved under anoxic conditions (Lehmann et al. 2002). A significant negative correlation between organic matter and the redox potential (Eh) found in this study suggests their preservation in the anoxic condition. The Rufiji mangrove sediments were slightly acidic with high negative redox potential indicating that the sediments were anoxic in nature, particularly station 3 which was highly in reducing conditions. Analyses of major elements revealed high mass percentages of calcium and phosphorous at station 3, which were about 10 times higher than the other two stations, suggesting that these elements are likely to be preserved in highly reducing or anoxic environments as observed in other studies (Lehmann et al. 2002).

The concentrations of the heavy metals in sediments were in this order: Fe > Mg > Mn > Zn > Cr > Ni > Pb > Cu > Co > Cd. Surprisingly, Pearson correlation analyses of the chemical parameters of the mangrove sediments (Table 5) revealed that a number of heavy metals under this investigation did not correlate with grain size, except for Co, Cr, Fe, and Mg which negatively correlated with sand, and positively correlated with silt. This may suggest that other physicochemical parameters such as amount of dissolved oxygen and redox potential in the sediment may be influencing the behaviour and distribution of heavy metals as explained in ensuing paragraphs. Mg and Pb showed highly significant negative correlations with organic carbon, while Zn showed significant positive correlation with total nitrogen. Co, Cr and Ni recorded positive correlations with redox potential and negative correlations with sulphur. Cd and Zn revealed significant inverse correlations with Eh and positive correlations with sulphur.

During early diagenesis, the changing redox conditions in aquatic sediments can transform metals into different chemical forms. The major changes that take place in oxic waters and anoxic sediments had significant effects on the speciation and bioavailability of many heavy metals (Dong et al. 2000). Sulphate is the main electron acceptor which drive organic matter oxidation in anaerobic marine sediments, after oxygen utilization in the top few millimetres of sediment (Gaillard et al. 1989). Under oxic conditions, Pb, Ni and Co can be easily adsorbed on oxide fractions (Dong et al. 2000). On the contrary, in anaerobic conditions, active co-precipitation of metal sulphide rapidly removes Co, Cu, Ni, Pb and Zn from the dissolved phases (Schlieker et al. 2001). These specific behaviours of the heavy metals under varying redox conditions can be used as tracers of geochemical characteristics in mangrove sediments. Pyrite is a significant sink for heavy metals due to its ability to incorporate them during its formation. The sulphate-reduction process tends to decrease the dissolved Fe concentrations, reflecting the precipitation of Fe and S in the form of pyrite (Marehand et al. 2003). Active sulphide co-precipitation during anaerobic conditions results in preferential rapid removal of metals from the dissolved phase making them unavailable (Schlieker et al. 2001). This seems to be the plausible mechanism for concentrations of heavy metals recorded in the Rufiji mangrove sediments. The presence of rich organic matter and the reducing environment in this substratum creates a selective affinity for heavy metals. For example, Cd showed highly significant negative correlation with Eh and positive correlation with sulphur. Adsorption and desorption of Cd is highly variable depending on the types of colloids and prevailing pH-Eh conditions. Cd can be adsorbed in larger quantities by organic matter or Fe oxyhydroxides, but the presence of other metals, especially Zn, can inhibit the adsorption of Cd (Alloway 1990). Zinc is a very mobile element under oxidizing and acidic conditions; however, in reducing environments, Zn substantially decreases in mobility due to its affinity for sulphur and the tendency to form sulphide phases (Alloway 1990). Its significant negative correlation with Eh and positive correlation with sulphur supports the retention under anoxic conditions.

Under oxic conditions, Pb, Ni and Co can be easily adsorbed on Mn oxides (Dong et al. 2000). Chromium (Cr) is of low geochemical mobility in any conditions of pH-Eh, although at low pH the presence of Mn oxides can promote Cr oxidation to more mobile phases (McGrath and Smith 1990). This particular heavy metal which does not form sulphide minerals is immobilized as refractory Cr-organic compounds in mangrove sediments (Lacerda et al. 1991). In the present study, the poor association of Mn with other metals suggests that Mn-oxide may be the only minor host phase for these elements in this reducing mangrove environment. Lead is the only chalcophile element that is immobile under any pH-Eh conditions, although acidic conditions can trigger Pb desorption to a greater degree than alkaline environments.

Stoichiometric ratios of nutrients are used to determine the origin and transformation of organic matter and their implications to geochemical signatures (Hecky et al. 1993). Hecky et al. (1993) predicts a range of C:P ratios of 28 to 56 by mass and a range of N:P ratio of 4 to 9 by mass for algal materials. The C:P ratios varied widely in the study region (1.8 to 28.3) and were very low at station 3. N:P ratios also showed considerable variations among stations and ranged between 0.17 and 2.25. N:P ratios were also very low at station 3, indicating high enrichment of phosphorus at station 3. Both these ratios were far below the predicted range signifying existence of phosphorus enrichment in the mangrove sediments of the Rufiji mangrove. The lower N:P ratios are also indicative of excessive benthic nitrogen recycling (Alongi et al. 2004). It is worth noting that, based on these ratios; denitrification and benthic release of nitrogen in Rufiji mangroves could be playing significant roles in sustaining the productivity of the system. Clay minerals such as kaolinite which is abundant in tropical sediments is very efficient in phosphate adsorption (Alongi et al. 2004). This indicates that silty and claydominated sediments of Rufiji estuary tend to favour the higher retention of phosphorus, further justifying its high concentrations in station 3 compared to other stations.

Enrichment factors and geo-accumulation indices corroborated the absence of heavy metal pollution in Rufiji mangrove sediments. The mobility of Zn decreases substantially due to its affinity for sulphur under reducing sediment conditions (Alloway 1990). The lack of significant enrichments of other metals in mangrove sediments may be caused by their ability to form strong soluble complexes with reduced sulphur causing enhanced migration of these elements from sediments to the water column (Huerta-Diaz and Morse 1992). This could imply that these soluble complexes are toxic to the benthic fauna; therefore, further investigations using ecotoxicity tests need to be carried out to confirm migration of these elements and their possible toxicity to benthic organisms.

Table 5: Pearson's correlation coefficients between sedimentary parameter and heavy metals in Rufiji mangroves. Bolded number indicate significant correlation, p < 0.05

	Sand	Silt	Clay	pH	Eh	TC	OC	TN	TP	TS	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Zn
Sand	1																			
Silt	**-0.86**	1																		
Clay	-0.16	-0.32	1																	
pH	**-0.59**	0.39	0.17	1																
Eh	-0.18	-0.13	**0.81**	-0.1	1															
TC	0.48	-0.32	-0.22	0.06	**-0.55**	1														
OC	0.41	-0.43	-0.25	-0.05	**-0.56**	**0.99**	1													
TN	0.43	-0.17	-0.43	-0.03	**-0.74**	**0.95**	**0.94**	1												
TP	0.25	0.04	-0.43	0.14	**-0.97**	**0.53**	**0.56**	**0.71**	1											
TS	0.26	-0.10	-0.37	0.35	**-0.83**	0.42	0.45	**0.51**	**0.89**	1										
Cd	0.23	0.06	-0.43	0.16	**-0.93**	0.45	0.49	**0.62**	**0.95**	**0.89**	1									
Co	**-0.69**	0.42	0.48	0.16	**0.81**	**-0.60**	**-0.68**	**-0.69**	**-0.87**	**-0.82**	**-0.86**	1								
Cr	**-0.62**	0.39	0.46	-0.01	**0.77**	**-0.58**	**-0.67**	**-0.64**	**-0.86**	**-0.86**	**-0.87**	**0.97**	1							
Cu	-0.36	**0.60**	-0.46	0.14	**-0.69**	0.35	0.28	**0.57**	**0.58**	0.28	0.49	-0.20	-0.12	1						
Fe	**-0.66**	**0.71**	-0.30	0.24	-0.36	-0.30	-0.37	-0.06	0.29	0.21	0.26	0.12	0.20	**0.69**	1					
Mg	**-0.80**	**0.59**	0.37	0.19	**0.61**	**-0.76**	**-0.85**	**-0.75**	**-0.69**	**-0.61**	**-0.66**	**0.91**	**0.91**	-0.06	0.45	1				
Mn	-0.23	0.25	-0.14	0.26	0.03	-0.02	-0.10	-0.07	-0.16	0.07	-0.18	0.23	0.25	-0.03	0.21	0.37	1			
Ni	-0.22	0.18	0.49	0.00	**0.86**	**-0.55**	**-0.61**	**-0.65**	**-0.87**	**-0.87**	**-0.87**	0.25	**0.92**	-0.24	0.04	**0.78**	-0.07	1		
Pb	-0.37	0.41	0.42	0.33	**0.67**	**-0.85**	**-0.89**	**-0.91**	**-0.66**	-0.45	**-0.56**	**0.92**	**0.69**	-0.41	0.20	**0.87**	0.28	**0.65**	1	
Zn	0.12	0.21	-0.44	0.15	**-0.97**	**0.59**	**0.59**	**0.78**	**0.96**	**0.76**	**0.93**	**0.79**	**-0.74**	**0.74**	0.33	**-0.74**	-0.16	**-0.78**	**-0.71**	1

Eh = Redox potential; TC = Total Carbon; OC = Organic Carbon; TN = Total Nitrogen; TP = Total Phosphorus; TS = Total Sulphur

Conclusions

Generally, sedimentary analyses showed the predominance of fine-grained substratum, and silt was the major fraction in Rufiji mangrove sediments. Stoichiometric ratios of nutrients (C:P and N:P) showed possibilities of phosphorus enrichment in the mangrove sediments of the Rufiji mangrove. The lower N:P ratios indicated excessive benthic nitrogen recycling. The overall order of heavy metal concentrations in the sediments was: Fe > Mg > Mn > Zn > Cr > Ni > Pb > Cu > Co > Cd. The enrichment factor calculated using iron as normalizing element, indicated minor enrichments for Pb and Zn and no enrichments for all other metals. The geo-accumulation index estimated for the present study exhibited very low values (1geo < 0) in almost all metals, except Zn (1geo > 1.0 at station 3) showing that the mangrove sediments in Rufiji delta are generally unpolluted to moderately polluted. Further study on geochemical signatures throughout the estuary and in different seasons is expected to provide more insights on the processes and factors which modulate spatial and temporal variability in geochemistry of this rich and diverse tropical estuarine system.

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Declaration of Conflict of Interest

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

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