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# Heavy Metal Contamination and Potential Ecological Risks in Surface Sediments along Dar es Salaam Harbour Channel

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**Abstract**

Investigation of heavy metal contamination along Dar es Salaam harbour channel was carried out in order to determine their current concentrations, sources and potential ecological risks to benthic biota. Sampling was carried out from January to May 2019 and samples analysed using ICP-OES and C-H-N-S analyser. Analysis of heavy metal relationships showed that, Cu, Zn, Cr, As, Ni, Co, Fe, Cd had strong relationships with each other, while Pb only related to Zn. Principal component analysis partitioned metals into two groups; PC1: Ni, Cr, Fe, Co, As, Cu, Cd, and Zn explaining 73.6% variance and PC2: Pb, Zn, and Cd with 13.7% variance. Similarly, Cd, Pb and Zn had severe to very high enrichments (Cd > Pb > Zn) showing serious anthropogenic contamination of these metals in sediments along Dar es Salaam harbour channel. Degree of contamination and potential ecological risks varied from low, moderate, to high; indicating that sediments were considerably contaminated with heavy metals. Levels of contamination varied in space and according to the type of heavy metal Higher contamination and ecological risks were revealed at the harbour area probably due to the observed high concentrations of Cd, Pb and Zn. Monitoring of metals should be emphasized in order to control contaminants release into this area from their sources.

**Keywords**: Dar es Salaam harbour channel, Heavy metals, Contamination, Sediments, Degree of contamination, Ecological risks.

## Introduction

Heavy metals contamination in sediments has been a growing challenge in Tanzania, mostly in the coastal marine waters which receive urban effluents. The main sources of heavy metals are from industrial, municipal and agricultural discharges. Heavy metals are among the most persistent pollutants in ecosystems due to their resistance to decomposition in natural conditions (Soliman et al. 2015, Mihale 2019). In sediments, metals accumulate up to concentrations above the background levels (Bai et al. 2011, Mahugija and Sheikh 2018), making sediments to be more toxic than the overlying water (Sivakumar et al. 2016, Mahugija and Sheikh 2018), and thus posing potential hazardous environment to benthic ecosystems. They either cause direct toxicity to benthic organisms or become a source of contaminants for bioaccumulation in the food chains (EPA 2002, den Besten and Munawar 2005). Some heavy metals (e.g., Fe, Zn, Cu, and Mn), however are essential, playing important roles in biological systems (Hogstand and Haux 1991), but become toxic at higher concentrations (Soliman et al. 2015, Custodio et al. 2019). Non-essential metals

such as Pb and Cd are usually potent toxins even at relatively low concentrations (Lee et al. 2019). Hence, accumulation of heavy metals in sediments threatens the survival and fitness of benthic ecosystems and increases stress and damage to aquatic systems.

Despite the alarming heavy metal contamination in coastal waters of Tanzania (Machiwa 2010, Mihale 2017), the information on heavy metal pollution status, extent of contamination and its ecological risks using pollution assessment indices are scarcely available. Pollution assessment indices are useful techniques for the comprehensive assessment of contamination in sediments and forecast the forthcoming negative impacts of contaminants to ecosystems (Kowalska et al. 2018), thus their applications in this study emphasized on the extent of heavy metal contamination along the harbour channel. The pioneer study for the assessment of the status of heavy metal contamination in sediments using pollution indices in Tanzania and the Western Indian Ocean was conducted by Mihale (2019) along Mtoni estuary, upstream of Dar es Salaam harbour channel. The observed heavy metals contamination in sediments along Mtoni estuary varied from moderate to considerable ecological risks.

This study aimed at assessing the metal contamination and potential ecological risks in surface sediments along Dar es Salaam harbour channel which is the main effluent receiving area along the coast. The established contamination status offers pre-requisite information for pollution control and formulation of monitoring guidelines in Tanzania and the Western Indian Ocean region.

## Materials and Methods

### Description of the study area

Dar es Salaam is located between latitudes 6°27′and 7°15′S and longitudes 39° and 39°33′E, extending about 100 km from Mpiji River in the north to Mzinga River in the south (Machiwa 2010). Dar es Salaam harbour channel is located in a sheltered inlet of a narrow bay protected from free seawater flushing (Figure 1). In this study harbour area is the area at the ship loading and off-loading area, while harbour channel includes the southern and northern parts of the harbour area.

The predominant water movements are tidal and seawater waves which influence the direction of localized inshore currents and fluvial flows from Mtoni and Msimbazi estuaries. These forces in turn govern the deposition and distribution of sediments in the harbour channel (Machiwa 2000). The study focused on Dar es Salaam harbour channel which is a recipient of the main rivers in Dar es Salaam City, including Mzinga, Kizinga and Msimbazi rivers, associated with port and shipping operation activities.

### Sample collection

Sampling campaigns were conducted from January to May, 2019 at Dar es Salaam harbour channel. Prior to sampling, a thorough survey was conducted to establish sampling stations using Global Positioning System based on the types of sediments and areal coverage of the harbour channel so as to acquire representative samples of the area. Sediment sampling was conducted according to the methods developed by EPA (2002) and Goh et al. (2014). Sediment sampling was conducted along the harbour channel from the southern part of the harbour near Mwalimu Nyerere bridge, at the harbour area and northern part of the harbour at the ship anchorage before offloading. A total of thirty-five (35) sampling stations were established, and at each station, three sediment samples were collected at 0–50 cm depth using a 50 cm piston gravity plastic corer. Samples were then kept in zip lock plastic bags, labelled, sealed and stored in a cool box containing ice blocks. Samples were then transported to the laboratory, kept in a refrigerator at 4 °C until analysis.

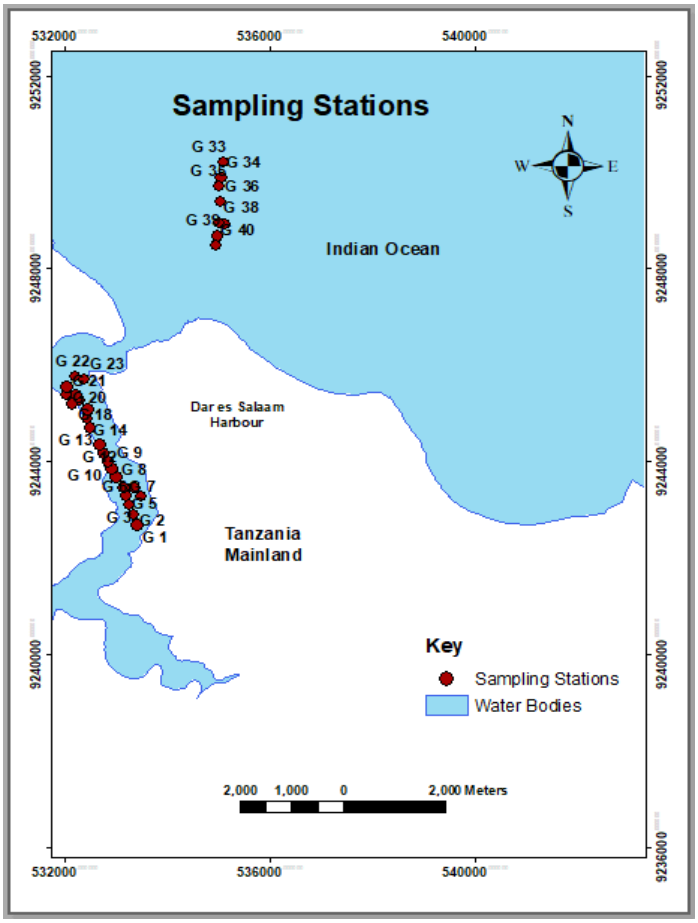


**Figure 1**: Map showing the sampling stations.

**Heavy metals analysis and determination of total nitrogen and total organic carbon in sediments**

Analysis of heavy metals followed EPA (2018), Hazardous Waste Test Methods/SW-846 Method 6010D for Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). Sediment samples were air dried for two days and grinded using mortar and pestle. About 1 g of the sediment sample was weighed and placed into Kjeldahl tubes, thereafter 10 ml of aqua-regia (HCl and $HNO_3$; 3:1 mixture) was added. The mixture was digested under Kjeldahl system (TR Gerhardt No.4021853) for two hours at 180 °C. Samples were allowed to cool to room temperature, and then filtered using Whatman filter paper no 41 into 100 ml volumetric flasks and filled up to the mark with deionized water. Heavy metals were analysed at the Government Chemist Laboratory Authority using ICP-OES (Thermo Scientific Icap 6000 series). Determination of total nitrogen and total organic carbon in sediments were carried out at the Nelson Mandela African Institution of Science and Technology. Samples were dried at 60 °C in an oven, a portion was grinded to fine powder using a porcelain mortar and pestle, homogenized and paced in an aluminium pan dried at 105 °C. After cooling, about 0.35 g of each sample was digested by addition of potassium dichromate and sulphuric acid, cooled and before addition of water to stop the reaction, phosphoric acid was added drop by drop until bubbling stopped in order to remove interferences from ferric ions and carbonates present in the sample. Wet samples were then oven dried at 40 °C for 24 hours and

then at 105 °C for 30 minutes for complete digestion of organic matter. Thereafter, the samples were placed in C-H-N-S analyser for analysis.

**Quality control**

Quality control included triplicate sampling of sediments and analysis, procedural blanks, and measurement of the Certified Reference Materials (IAEA-356) which were treated in the similar manner like the samples. Blank analysis was also used to monitor the precision of analysis in which results were blank corrected using respective mean blank concentrations before determination of the concentrations of each heavy metal and the reference. Precision of ICP-OES analysis was better than 5% relative standard deviation (RSD). The limits of detection of each heavy metal were set at three times of the standard deviation of the mean signal from the procedural blanks. The detection limits of each metal were as in Table 1.

The percentage recoveries of the measured metals based on the mean values compared to the certified reference materials ranged from 81.23% to 97.18% and RSD ranged from 4.11 to 10.36% (Table 2). The values were under the recommended limits of 80–120% for reference samples and ≤ 15% RSD (Addis and Abebaw 2017). The results indicated good agreement between the certified and the obtained values.

**Data Analysis**

***Data analysis using pollution indices***

Data were subjected to multivariate analysis using IBM SPSS Statistics ver. 25 software package through Pearson correlation matrix, principal component analysis through varimax rotation with eigenvalues >1 using Kaiser normalization to assess the relationships between metals and the distinction between groups of heavy metals. Pearson correlation and principal component analysis were considered significant when the correlation coefficients were greater than 0.05 ($\alpha = 0.05$) and eigenvalues greater than 1, respectively.

**Table 1**: Detection limits (µg/g) of the analyzed metals

| Metal | Detection limit | Metal | Detection limit |
|---|---|---|---|
| As | 0.004 | Cu | 0.002 |
| Cd | 0.0003 | Fe | 0.9 |
| Co | 0.0005 | Ni | 0.003 |
| Cr | 0.005 | Pb | 0.002 |
| | | Zn | 0.02 |

**Table 2**: Recovery and precision test results for the laboratory reference samples

| Metal | Reference value (mg/g) | Obtained value (mg/g) | Recovery (%) | RSD |
|---|---|---|---|---|
| Cu | 43 | 39.24 ± 1.57 | 91.26 ± 5.13 | 5.62 |
| Zn | 100 | 97.18 ± 2.11 | 97.18 ± 6.18 | 6.36 |
| Pb | 100 | 93.69 ± 1.16 | 93.69 ± 3.85 | 4.11 |
| Cr | 56 | 50.05 ± 1.22 | 90.16 ± 4.18 | 5.52 |
| Cd | 2 | 1.8 ± 0.68 | 94.43 ± 7.23 | 7.66 |
| As | 25 | 23.03± 0.65 | 92.12 ± 6.22 | 5.11 |
| Ni | 20 | 18.13 ± 2.14 | 90.66 ± 9.40 | 10.36 |
| Co | 5 | 4.06 ± 0.87 | 81.23 ± 7.10 | 7.87 |
| Fe | 400 | 366.16 ± 0.85 | 91.54 ± 4.22 | 4.61 |

Varimax values greater than 0.75 were considered strong significant correlations, 0.75–0.5 moderate and 0.50–0.30 low (Liu et al. 2003). Hierarchical cluster analysis (HCA) through squared Eucledian distances was used to establish the relationships between heavy

metals and their sources in sediments. Paired Student t-test was used to compare contaminants concentrations between sampling stations and the harbour area.

Potential ecological risks of heavy metal contamination were assessed using various pollution indices, including enrichment factor (EF) normalized by iron, since iron has a wide distribution in the Earth's crust (Saleh et al. 2018). EF was used to determine the anthropogenic influence on heavy metals contamination in sediments. Contamination factor (CF) was used to assess the degree of heavy metal contamination in sediments while classification of degree of contamination was conducted using geo-accumulation index (I*geo*) (Adeyemi et al. 2019, Krampah et al. 2019).

***Enrichment Factor (EF)***

The coefficients of enrichment were determined using average concentrations of metals in the Earth's crust established by Turekian and Wedepohl (1961) and expressed as:

$$EF = \frac{\left(\frac{Cm}{CFe}\right)sample}{\left(\frac{Cm}{CFe}\right)background} \qquad (1)$$

where, (Cm/CFe) sample is the ratio of concentration of heavy metal of interest and iron in the sample; (Cm/CFe) background is the ratio of heavy metal of interest and iron in the background rock (Adeyemi et al. 2019).

The contamination categories were recognized on the basis of the enrichment factor as follows: EF < 2 Deficiency to minimal enrichment, EF = 2–5 Moderate enrichment, EF = 5–20 Severe enrichment, EF = 20–40 Very high enrichment and EF > 40 extremely high enrichment.

***Contamination factor (CF)***

Contamination factor (CF) is the ratio between the concentration of heavy metal in the sample to that in the background, expressed as:

$$CF = \frac{(Cmetal)sample}{(Cmetal)background} \qquad (2)$$

where, (Cmetal)sample is the concentration of a metal in sample;

(Cmetal)background is the average concentration of a metal in a shale background in the Earth's crust (Adeyemi et al. 2019).

Contamination status is categorized into 6 categories; CF < 1 is low contamination; 1 ≤ CF ≤ 3 is moderate contamination; 3 ≤ CF ≤ 6 is considerable contamination; and CF ≤ 6 is very high contamination.

***Geo-Accumulation Index (Igeo)***

Igeo is expressed as:

$$Igeo = log2\left(\frac{Cn\ sample)}{1.5*Bn\ background)}\right) \qquad (3)$$

Where, Cn is the measured concentration of heavy metal in the sample, Bn is the average shale value, and 1.5 is the factor compensating the background data (correction factor) due to lithogenic effects (Sana'a 2015).

***Degree of contamination (CD)***

Is the sum of contamination factors for a given study area expressed as:

$$DC = \sum_{i=1}^{n} CF \qquad (4)$$

Measures the degree of overall contamination in surface layers in a particular sediment sample or sampling site (Sivakumar et al. 2016). It is classified as; CD < 6 low degree of contamination; 6 < CD < 12 moderate degree of contamination; 12 < CD < 24 considerable degree of contamination; and CD > 24 high degree of contamination.

***Potential Ecological Risk Coefficient (PERC)***

This is the multiplication of CF of each heavy metal and toxicological response factor (Tr) of individual heavy metals. According to Soliman et al (2015), it is calculated as;

$$PERC = CF_n\, xT_r \qquad (5)$$

Where, $CF_n$ and $T_r$ are the contamination factor and toxic response factor of individual heavy metals, respectively. According to Hakanson (1980), toxic response factor is established based on abundance principle by calculating potential biotoxicity from heavy metal abundances in a medium of interest like sediments, water etc and the sink factor which is the ratio of natural background concentrations of heavy metals and preindustrial reference values for sediments.

The toxic response factors for heavy metals Pb, Cd, Cr, Cu, Zn, Ni, As and Mn are 5, 30, 2, 5, 1, 5, 1 and 10, respectively (Darko et al. 2017) and the potential ecological risk coefficient categories are PERC ≤ 40 low ecological risk, 40 < PERC ≤ 80 moderate ecological risk; 80 < PERC ≤ 160 appreciable ecological risk; 160 < PERC ≤ 320 high ecological risk; and > 320 serious ecological risk (Soliman et al. 2015, Keshavarzi and Kumar 2020).

***Potential Ecological Risk Index (PERI)***

It is the sum of potential ecological risks coefficients of each metal (Er) expressed as:

$$PERI = \sum_{i=1}^{n} Er \qquad (6)$$

where Er = potential ecological risk coefficient.

The risks are categorized as PERI < 150 low ecological risk, 150 < PERI < 300 moderate ecological risk, 300 < PERI < 600 high ecological risk and PERI ≥ 600 significantly high ecological risk.

## Results and Discussion

### Heavy metals total concentrations in sediments

Heavy metal concentrations in the surface sediments (0–50 cm) at Dar es Salaam harbour channel varied significantly between metals and with sampling stations. Copper concentrations ranged from 2.32 to 76.60 mg/kg with an average of 18.24 mg/kg. Lead concentrations ranged from 0.20 to 208.47 mg/kg and the average was 27.51 mg/kg, with highest concentrations at the harbour area. Cadmium concentrations ranged from 0.15 to 5.79 mg/kg with average value of 1.75 mg/kg. High concentrations of Cd were observed in the southern part of the harbour with a gradual decrease to the north away from the harbour. Zinc concentrations ranged from 3.91 to 188.29 mg/kg and averaged at 54.51 mg/kg.

Chromium concentrations ranged from 6.66 to 72.45 mg/kg with an average value of 34.75 mg/kg. The harbour area had higher concentration of Cr relative to the channel area. Arsenic concentrations ranged from 0.93 to 15.8 mg/kg with an average value of 7.32 mg/kg, and showed high concentrations in the southern part of the harbour. The mean concentration of As was relatively higher in southern part of the harbour area than at the harbour. Nickel concentrations ranged from 0.20 to 20.36 mg/kg and the average was 8.80 mg/kg. However, concentrations of Ni were relatively low throughout the channel compared to other metals and the recommended targets

Mean concentrations of the heavy metals were compared in the harbour channel (sites GC1 - 9 and GC 31–40) and with those at the harbour area (sampling sites GC-10–30) as well as the established environmental quality targets. The mean concentrations of Cu, Pb, Cr and Zn at the harbour area were relatively higher than those in the channel, indicating additional inputs from anthropogenic activities at the harbour area. Cu, Zn, Cr and As concentrations were within the range of the concentrations reported in previous studies (Machiwa 2010, Mrutu et al. 2013, Kowalska et al. 2018). Mean concentrations of Pb and Cd were above the average shale concentrations in the Earth's crust (Turekian and Wedepohl 1961), threshold effect levels (Environment Canada 1994), Florida no effect level (MacDonald 1993) and WIO - Environmental quality targets (UNEP and CSIR 2009), indicating higher Pb and Cd contamination along Dar es Salaam harbour channel (Table 3).

Similarly, Machiwa (2010) and Mihale (2017) observed high concentrations of Cu and Cd in Mtoni creek upstream of the harbour channel, suggesting that they originate from anthropogenic activities in the City. High concentration of Pb in samples from the harbour area implied that its main sources were from anthropogenic activities at the harbour area. High As levels over the environmental quality targets in the southern part of the harbour was due to the presence of fine sediments in the area which coats with iron and manganese hydroxy-oxides forming complexes with As (Machiwa 2010). The concentrations of Ni were below all the recommended environmental quality targets, despite the fact that Ni and Pb are among the elements found in petroleum products,

lubricants and marine diesel oil (Mihale 2017, 2019). This indicated that low Ni was due to low carbon content in sediments to complex more Ni (Mrutu et al. 2013, Silva et al. 2019).However, the overall trend of heavy metal distribution was decreasing offshore, a trend similar to that observed by Mrutu et al. (2013), Mihale (2017), and Silva et al. (2019), associated with the changes in sediment grain size from clay-silt to sandy-pebble offshore (Mwakisunga et al. 2020).

**Sources of heavy metals in surface sediments along Dar es Salaam Harbour channel**

Pearson correlation (Table 4) and Principal component matrix (Table 5, Figure 2), partitioned heavy metals in two groups; PC1: Ni, Cr, Fe, Co, As, Cu, Cd and Zn explaining 73.6% of the variance, PC2: Pb, Zn and Cd explaining 13.7% of the variance. However, Cd had moderate significant correlation in both groups in varimax rotation. Hierarchical cluster analysis using agglomerative clustering and dendrogram method (Figure 3) grouped heavy metals into two groups, group I comprised of As, Co, Ni, Cu, Cr, Pb, Zn, Mn, and Cd, and group II contained Fe (Figure 3a). However, further clustering in absence of Fe, three groups were classified, group I: As, Co, Ni, and Cd, group II: Cu, Cr, and Pb, and group III was Zn.

Heavy metals in each group (i.e., PC1 and PC2) indicated close relationship to each other signifying similar sources. However, Zn and Cd had significant values in both PC1 and PC2 in rotated component matrix, while Pb only correlated with Zn (Table 2), thus indicating that heavy metals in the two groups had similar sources. Hierarchical Cluster Analysis (HCA) in presence of iron showed that group I (As, Co, Ni, Cu, Cr, Pb, Zn, Mn, and Cd) heavy metals were from anthropogenic sources, while group II (i.e. Fe) was from natural lithogenic processes. Furthermore, HCA in absence of Fe to investigate different sources of anthropogenic origins of heavy metals, showed three groups of similar sources (Figure 3b). Group I (As, Co, Ni, and Cd) metals were higher in the southern part of the harbour than at the harbour area and northern part of the harbour, indicating their fluvial origin from Mtoni estuary upstream, with the main sources from industrial, sewage and agricultural activities in the City (Silva et al. 2016, Mihale 2017). On the other hand, group II (Cu, Cr and Pb) corresponded with their high concentrations at the harbour area, thus indicating its predominant origin at the harbour area probably due to ship operations, maintenances, atmospheric deposition and local non-point sewage inputs from harbour surroundings. Likewise, group III (Zn) was largely from local non-point battery sources (Mihale 2017, Al-Edresy et al. 2019, Silva et al. 2019).

**Table 3**: Comparison of mean heavy metal levels (mg/dw) along Dar es Salaam harbour channel with the established environmental quality targets (n = 35)

| Metal | This study | Threshold effect level | Florida no Effect level | EQTs | Average shale concentration |
|---|---|---|---|---|---|
| Cu | 32.1 ± 13.8 | 18.7 | 28.0 | 18.7 | 45.0 |
| Zn | 105.6 ± 43.5 | 124 | 68.0 | 124 | 95 |
| Pb | 42.5 ± 20.9 | 30.2 | 21.0 | 30.2 | 20 |
| Cr | 57.2 ± 16.6 | 52.3 | 33.0 | 52.3 | 90 |
| Cd | 2.4 ± 0.8 | 0.68 | 1.0 | 0.68 | 0.3 |
| As | 10.8 ± 2.5 | 7.24 | 8.0 | 7.24 | 13 |
| Ni | 13.5 ± 5.1 | 15.9 | | 15.9 | 68 |

**Table 4**: Spearman correlation coefficients of heavy metals (n = 27, α = 0.05)

| | Cu | Zn | Pb | Cr | Cd | As | Ni | Co | Fe |
|---|---|---|---|---|---|---|---|---|---|
| Cu | 1 | 0.722 | 0.321 | 0.839 | 0.449 | 0.702 | 0.842 | 0.872 | 0.843 |
| Zn | | 1 | 0.796 | 0.701 | 0.513 | 0.643 | 0.677 | 0.679 | 0.710 |
| Pb | | | 1 | 0.280 | 0.465 | 0.457 | 0.274 | 0.214 | 0.310 |
| Cr | | | | 1 | 0.593 | 0.832 | 0.961 | 0.928 | 0.984 |
| Cd | | | | | 1 | 0.703 | 0.644 | 0.557 | 0.630 |
| As | | | | | | 1 | 0.856 | 0.769 | 0.875 |
| Ni | | | | | | | 1 | 0.965 | 0.974 |
| Co | | | | | | | | 1 | 0.949 |
| Fe | | | | | | | | | 1 |

**Table 5**: Principal components of heavy metals in sediments of Dar es Salaam Harbour channel total variance explained

| | **Component matrix** | | **Rotated component matrix** | |
|---|---|---|---|---|
| Variables | PC1 (73.584%) | PC2 (13.692%) | PC1 (73.584%) | PC2 (13.692%) |
| Fe | **0.971** | | **0.953** | |
| Ni | **0.962** | | **0.961** | |
| Cr | **0.953** | | **0.947** | |
| Co | **0.932** | | **0.959** | |
| As | **0.897** | | **0.789** | 0.427 |
| Cu | **0.878** | | **0.849** | |
| Zn | **0.818** | 0.454 | **0.531** | **0.77** |
| Cd | **0.708** | | **0.532** | **0.521** |
| Pb | 0.481 | **0.864** | | **0.988** |

Note: PC: Principal component; Percentages in brackets are explained contribution of principal component to the total eigenvalue's variance after varimax rotation.

Variables (PC1and PC2: 87.276%) after Varimax rotation

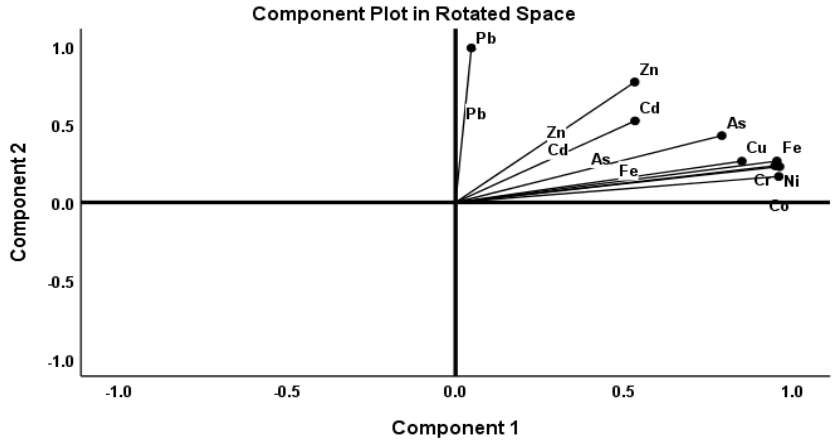


**Figure 2**: A two-dimensional component plot in rotated space of heavy metals.

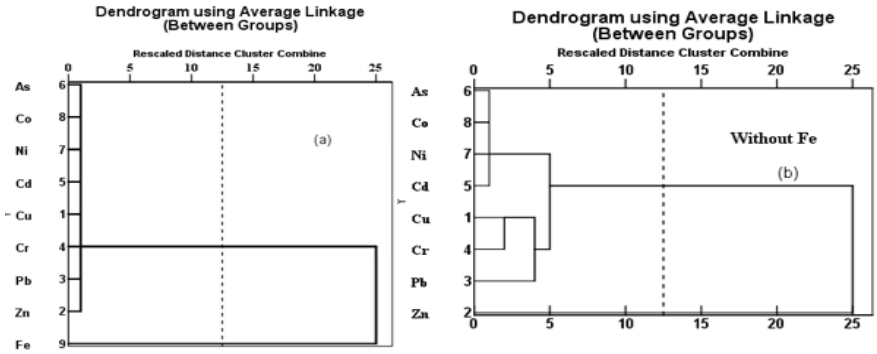


**Figure 3**: Hiererchical clustering dendrogram of heavy metals (a) with Fe and (b) without Fe metal.

**Heavy metals contamination levels along Dar es Salaam Harbour channel**

Pollution assessment indices were used to establish heavy metal contamination levels in sediments along Dar es Salaam harbour channel. Heavy metals had an overall enrichment order of Cd > Pb > Zn > As > Cu > Cr > Co > Ni, whereas Cu, Cr, Co and Ni had low enrichments. Arsenic showed moderate enrichments in the southern part of the harbour but low enrichment at the harbour area and offshore. Highest enrichments were for Cd, Pb and Zn (Figure 3a, b, c), respectively. Severe Cd enrichments (5 < EF < 20) were encountered in most of the sediments and very high enrichments (20 < EF < 40) in sediments from sampling stations G 2, 18, 33. Most of the sampling stations (50%) were moderately enriched with Pb (2 < EF < 5), while sampling stations G 15, 18, and 20 were severely enriched with Pb. Zinc was moderately enriched in 26% of the sampling stations (G-2, 3, 5, 8, 13, 14, 18, 21, and 22) and severely enriched in sampling station G-18 and 20.

The observed enrichment levels correspond to Mihale (2017, 2019) and Sawe et al. (2019), who observed moderate to severe enrichments for Zn, As, Cd and Pb at Mtoni Estuary upstream of the harbour channel and moderate enrichments of As, Cd and Pb at Msimbazi River, respectively. However, Cd showed severe to very high enrichments at the harbour channel as compared to Mtoni Estuary (Mihale 2019) indicating that Cd is largely transported by suspended particulate matter (Machiwa 2000), which settle in relatively calm water along Dar es Salaam harbour channel. Similarly, sediments from the harbour area had higher Pb enrichments (moderate to very high), contrary to Msimbazi estuary which had low to moderate Pb enrichments (Sawe et al. 2019), thus revealing that more Pb were coming from Mtoni estuary and at the harbour area.

Likewise, most of heavy metals showed low geo-accumulation indices, indicating natural to moderate contamination conditions, except for Cd which indicated moderate to heavily contaminated sediments along the channel. Pb indicated moderate to heavy contamination at the harbour area, affirming that much of Pb contamination was a result of anthropogenic activities at the harbour area. Manoj and Padhy (2014) classified geo-accumulation index (Igeo) as; Igeo < 0 uncontaminated; 0 < Igeo < 1 uncontaminated to moderately contaminated; 1 < Igeo < 2 moderately contaminated; 2 < Igeo < 3 moderate to heavily contaminated; 3 < Igeo < 4 heavily contaminated; 4 < Igeo < 5 heavily to extremely contaminated; and Igeo ≥ 5 extremely contaminated. However, the above contamination assessment relies on a single substance of interest, but assessment of combined contamination of heavy metals was developed by Hakanson (1980) as degree of contamination (Cd), and potential ecological risk index (PERI).

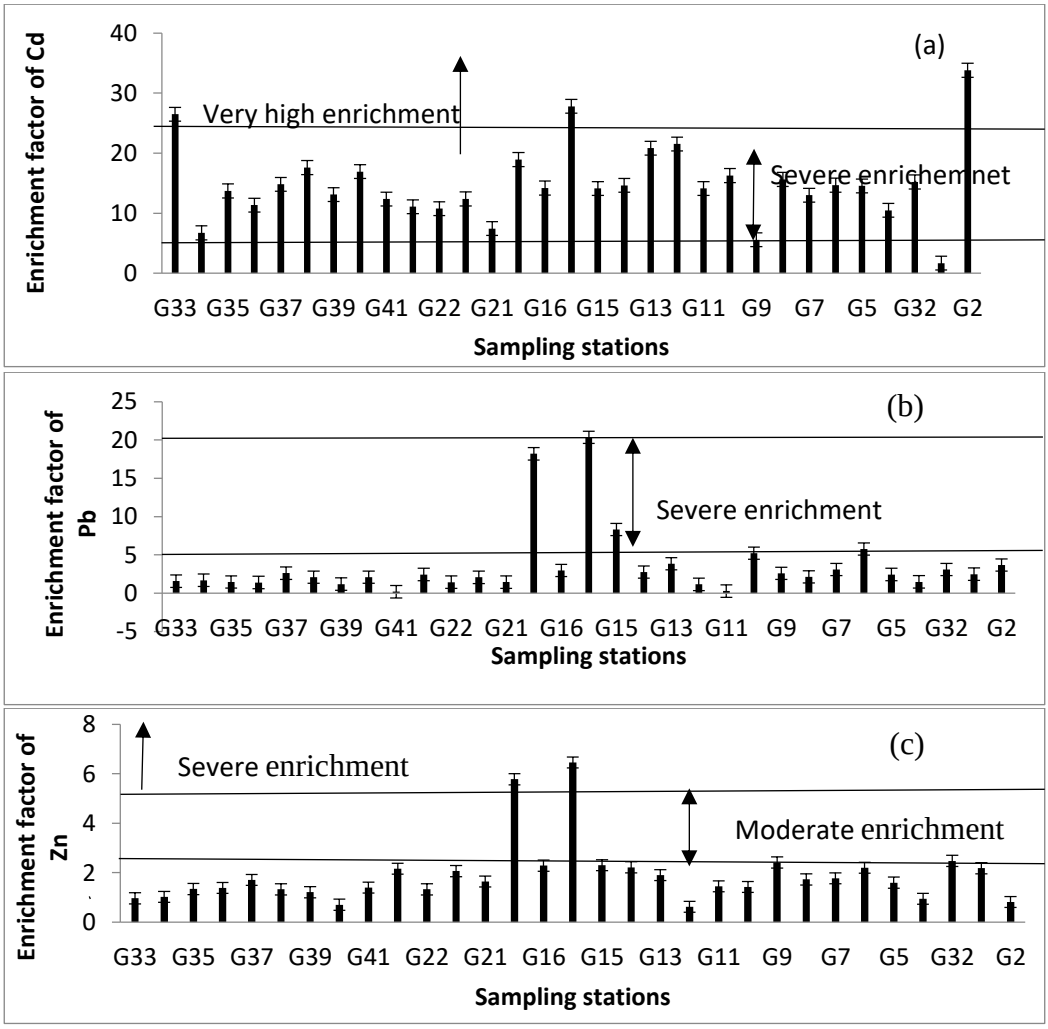


**Figure 3**: Three heavy metals of high enrichments in sediments along Dar es Salaam harbour channel.

The contamination factors and degree of contamination varied from low to very high contamination conditions. As, Ni, Co and Cr showed low contamination (CF < 1), Cu and Zn showed low ($0.06 \leq CF \leq 1.4$) to moderate ($0.06 \leq CF \leq 1.98$) contamination (Figure 4a, b). Pb had considerable to very high contamination ($0.01 \leq CF \leq 6.24$) at the harbour area (Figure 4d). Cadmium on the other hand showed a uniquely high contamination ($0.64 \leq CF \leq 11.27$) varying from considerable to very high contamination (Figure 4c).

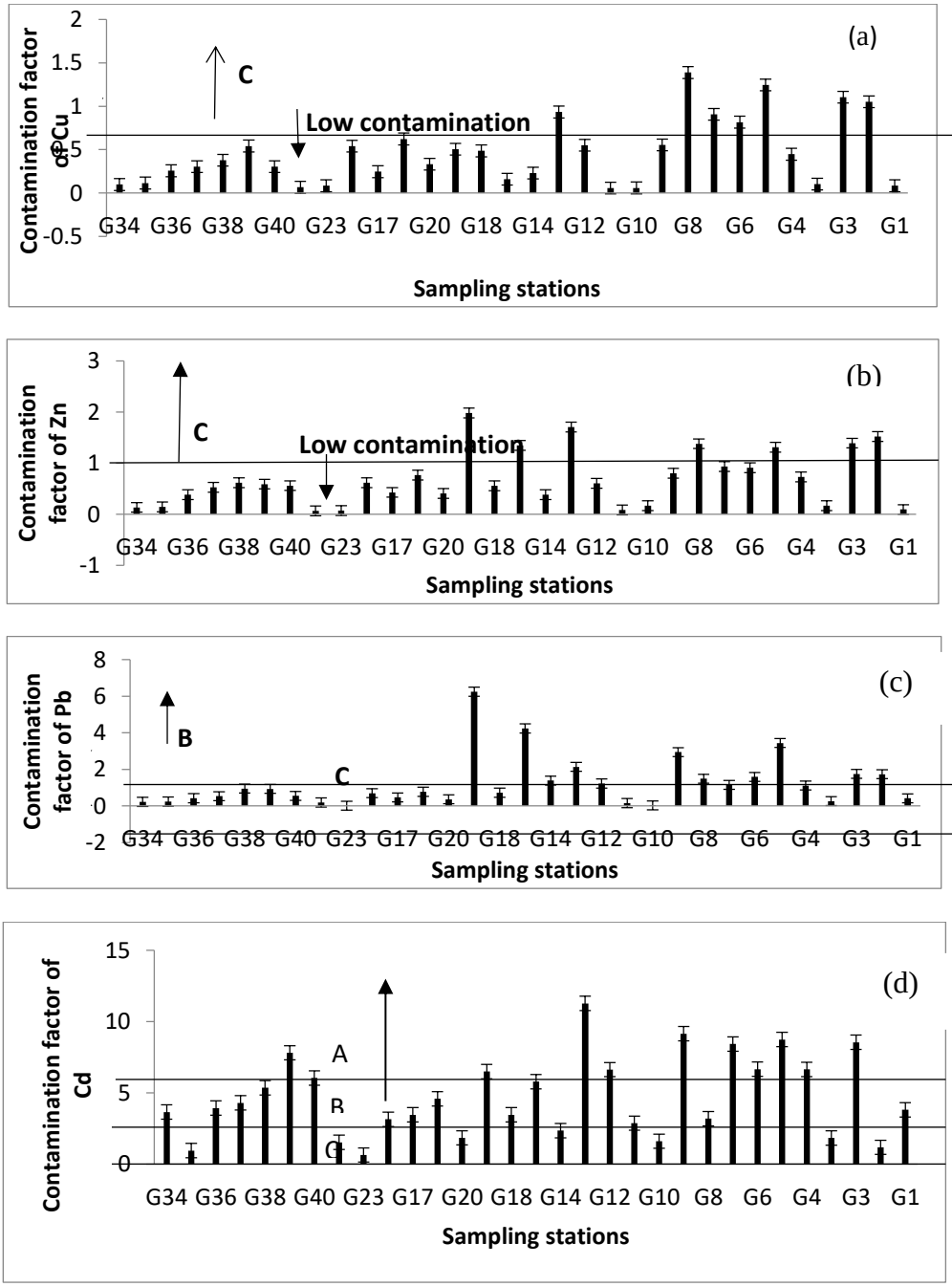


**Figure 4**: Heavy metals with relatively high contamination factors along Dar es Salaam harbour channel. **Note:** A = Very high contamination; B = Considerable contamination; C = Moderate contamination.

An overall degree of contamination order was Cd > Pb > Zn > As > Cu > Cr > Co > Ni, indicating that heavy metals contamination in sediments was largely contributed by Cd, Pb and Zn. Degree of contamination varied from low to considerable contamination, 32% of the sampling stations had low degree of contamination in the northern part of the

harbour, 39% had moderate degree of contamination in the southern part of the harbour, while 26% had a considerable degree of contamination at the harbour area (Figure 5). Contamination factors of almost all metals had strong positive correlation ($R^2 > 0.5$) with the overall degree of contamination except for Cu (Figure 6).

Severe to very high contamination of Cd throughout the harbour channel was similarly observed by Manoj and Padhy (2014), Saleh et al. (2018) and Al-Edresy (2019) in estuaries at tropical river of Chottanagpur plateau and Aden coast, Southern Yemen, in which the main sources were from urban anthropogenic activities. Moderate to severe contamination of Pb at the harbour area ascribed anthropogenic source at the harbour. Moderate to severe contamination of Zn was observed in the southern part of the harbour channel, however the values were lower than those observed at Mtoni estuary (Mihale 2019). Thus, higher levels of heavy metals in Mtoni estuary influenced the levels of heavy metals downstream at the harbour channel transported by suspended particles (Mrutu et al. 2013, Mihale 2017, Silva et al. 2019).

**Ecological risks of heavy metals contamination in surface sediments**

The potential ecological risks index (PERI) was established to ascertain the potential ecological risks of heavy metals in sediments along the harbour channel. The values of PERI varied with sampling stations (Figure 7) and the ecological risk classification ranged from low to high of which 54.8% of the sampling stations had low ecological risk (< 150), 35.5% had moderate ecological risk (150 < PERI < 300) and 6.5% high ecological risk (300 < PERI < 600) at the harbour area.

Moderate to high potential ecological risks were revealed mainly at the harbour area and the southern part, which were similar areas with high heavy metal contamination factors and degree of contamination. This suggests that most of heavy metals along the harbour channel were from urban anthropogenic activities. However, the overall contamination and potential ecological risks were mainly influenced by the high concentrations of Cd, Pb and Zn indicating high inputs of Cd, Pb and Zn in the area. High ecological risks of Cd and Pb were similar to that observed by Mihale (2017) at Mtoni estuary showing the potential contribution of Mtoni estuary to contaminate the harbour channel. Moderate to high potential ecological risks of heavy metals in sediments along Dar es Salaam harbour channel threaten the survival of benthic ecosystems and the transfer of heavy metals through bioaccumulation in the food chain to human beings.

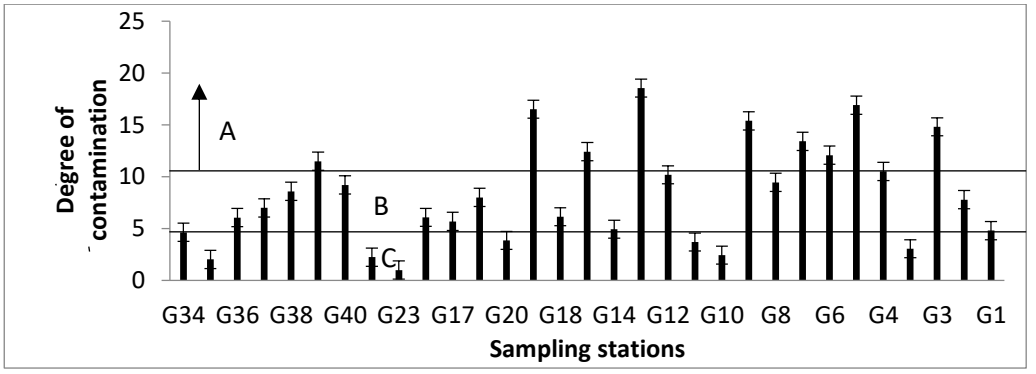


**Figure 5**: Degree of contamination of heavy metals in the sediments of Dar es Salaam harbour channel. **Note**: A = Considerable degree of contamination; B = Moderate degree of contamination; C = Low degree of contamination.

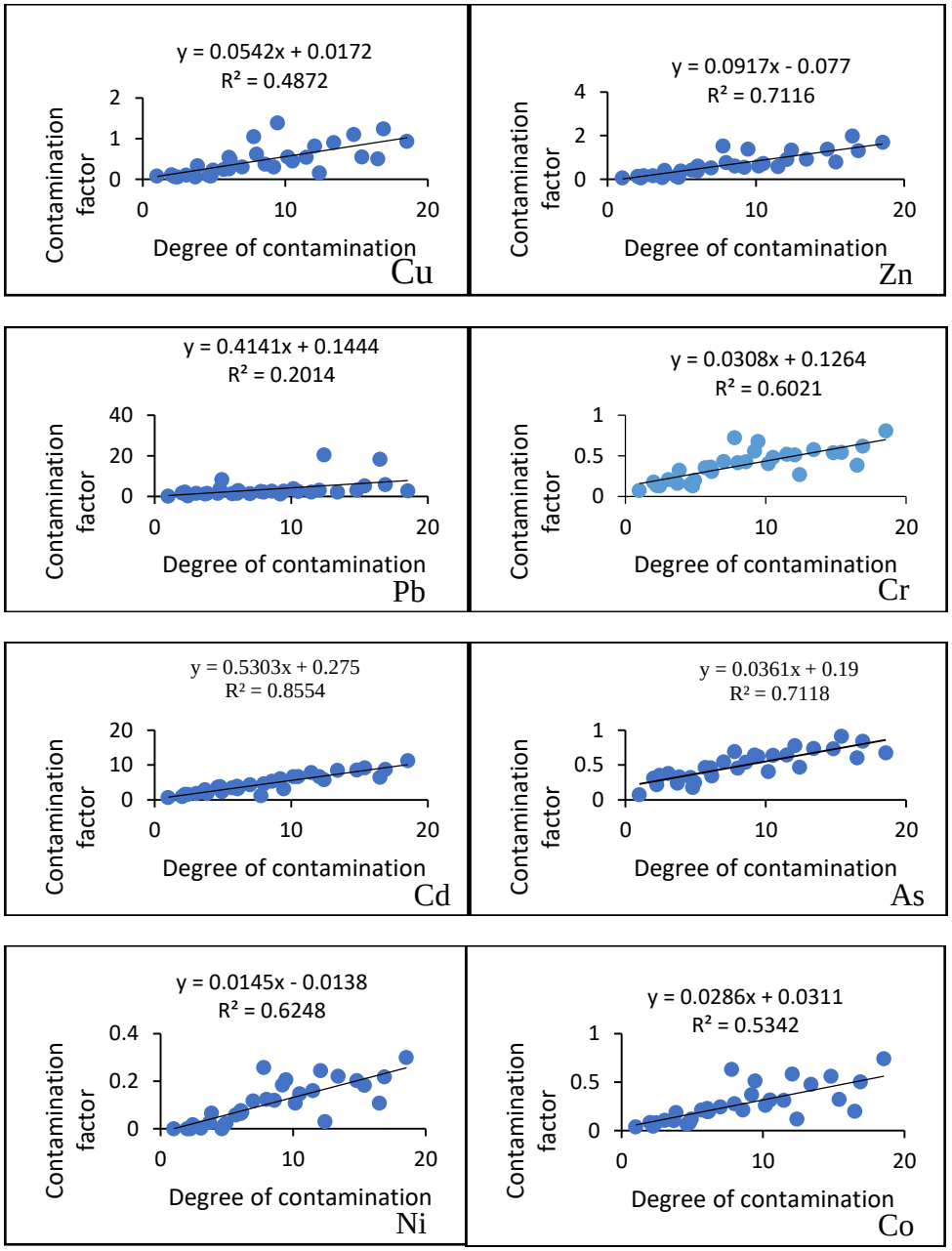


**Figure 6:** Relationship between contamination factors and degree of contamination.

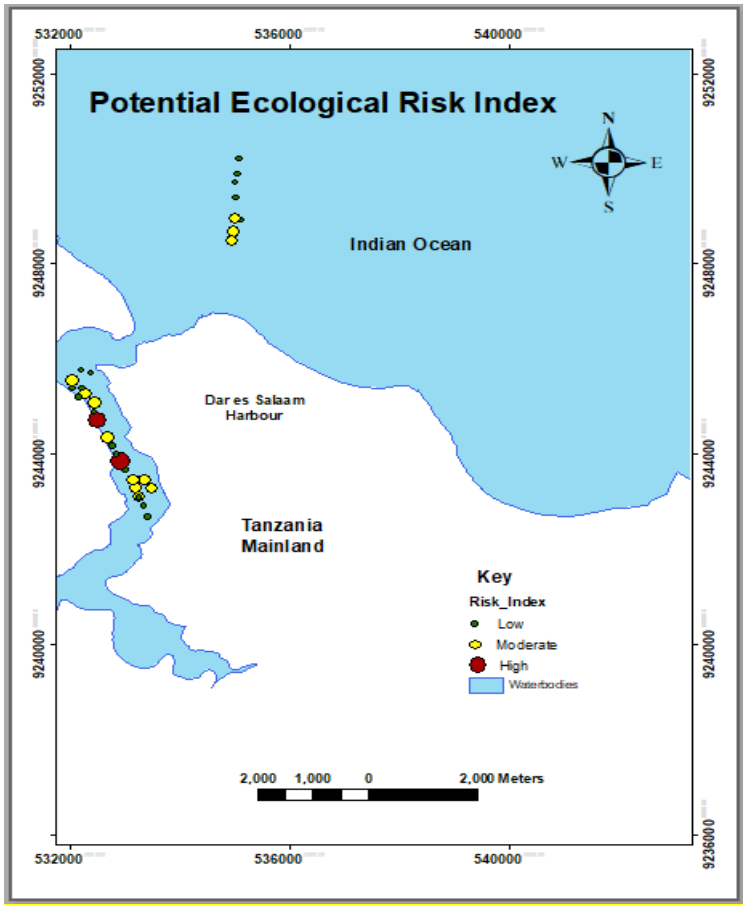


**Figure 7**: Potential ecological risk status of heavy metals at Dar es Salaam harbour channel.

## Conclusion

Spatial and typological variations of heavy metal contamination in sediments along Dar es Salaam harbour channel provides a contamination status and control criteria in heavy metal point sources. Variations in the degree of contamination and ecological risks of heavy metals give clues of contamination sources which offer pre-requisite contamination information to deal with for heavy metal pollution control. Moderate to considerable degrees of contamination with moderate to high potential ecological risks of heavy metals (Cd, Pb and Zn) pose threats to the survival of benthic biota and the ecological sustainability in coastal marine waters of Dar es Salaam coast. These effects may propagate through the food chain to affect human health. This necessitates for a need of anthropogenic contamination control over sediment quality deterioration and the study of toxicity effects of heavy metals to the benthic biota along coastal marine waters in the Western Indian Ocean.

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## Conflicts of Interest

Authors declare no conflicts of interest regarding the publication of this paper.

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