Metal Contamination in Sediments of Coastal Rivers around Dar es Salaam, Tanzania

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ABSTRACT
Sediments from coastal rivers of Kizinga, Mbezi, Msimbazi, and Mzinga were used to determine contamination levels of Cd, Pb, Cr, Ni, Cu, Al, Mn, Fe, and Zn metals. Sampling and sample preparation were done as appropriate and analysis was done using high resolution inductively coupled plasma–mass spectrometry (HR ICP-MS). Higher levels of Cd, Pb, Cr, Al, Mn, Fe, and Zn were mainly observed in Msimbazi river. Whereas higher levels of Ni and Cu were observed in Kizinga river, higher levels of Mn were observed in Mbezi river. Mzinga river had lowest levels of most metals except Mn. Lowest levels of Mn were observed in Kizinga river. Despite of enrichment factor indicating varied contamination status of metals in rivers, geo-accumulation index, contamination factor, degree of contamination, modified degree of contamination, potential contamination index and environmental toxicity quotient have indicated that sediments from these rivers are polluted, with Msimbazi and Kizinga river sediments being more polluted. Pearson correlation and hierarchical cluster analyses have revealed that Cd, Cu, Pb, and Zn were strongly correlated to each other ($r^2 > 0.7$, $p < 0.05$), indicating that they similar anthropogenic origin, while Fe, Mn, Ni, Cr, and Al were strongly correlated to each other ($r^2 > 0.69$, $p < 0.05$), indicative of similar natural origin. This implies that there might be metal-related anthropogenic activities around or close to rivers that pose environmental and health risks. Urgent river management strategies are needed to minimise the continuous metal pollution of these rivers.

Keywords: *Metal Contamination, Environmental Toxicity Quotient, Mbezi, Msimbazi, Mzinga, Kizinga*

INTRODUCTION

Metals are contaminants because they are permanent additions to a given environment and are not subjected to any biological or chemical degradation (MacFarlane and Burchett 2001, Defew 2005).

In addition, they are persistent, toxic, can bioaccumulate as well as biomagnify in sediments and organisms. Sediments tend to act as a source as well as a depository (sink) of the metals (Chi et al. 2007). The presence of metals in sediments may pose a potential threat to marine and other organisms (Kumar et al. 2008, Zhao et al. 2010). As a result, levels of metals in sediments can be important indicators of toxicological risk, especially when they are substantially above natural levels.

Metals in sediments may originate from either natural or anthropogenic processes. Natural sources of metals may include natural weathering and erosion of parent rocks and dusts coming from the wind. Anthropogenic sources may include effluents, sewage, discarded automobiles, and metallic substances as well as wastes from industrial, municipal, and domestic sources (Chatterjee et al. 2007). Since the number of metals in sediments may also indicate local and regional discharges (Moon et al. 2009), sediments can be used to evaluate historical trends as well as fate processes.

The present anthropogenic contribution of the metals in the marine sediments in Tanzania and the impacts of metal contamination in the coastal ecosystems are alarming (Mihale 2017). Studies done on the marine component of Tanzania have revealed that metal pollution is a problem (Machiwa, 1992, Mremi and Machiwa 2003, Muzuka 2007, Mtanga and Machiwa 2007, Mrutu et al. 2013, Mihale 2017, Minu et al. 2018). Since there is a river-ocean continuum, there is a possibility of rivers being the source of the observed metals. Previous studies in Tanzania have identified the Msimbazi River as highly polluted due to metals (Ak'habuhaya and Lodenius, 1988, Machiwa, 1992; De Wolf et al. 2001). Such a situation may exist in other rivers as well. Due to rapid urbanisation and growth of settlements from the increased human population, the rivers are suspected to carry different wastes (agricultural, residential, municipal, etc) and discharges. Besides, industrialisation and the associated socio-economic activities taking place in the city could contribute to the significant input of pollutants in the rivers. For example, mushrooming of street garages, increase in small-scale industrial activities, and urban agriculture in valleys and near rivers could have a significant input of metals in these rivers. Furthermore, the disposal of wastes (direct or indirect) could lead to a significant increase in metal pollutants in the rivers. In view of this, the current situation regarding metal contamination in these rivers is not known with certainty. This

study was intended to assess the contemporary level of contamination of metals in the sediments of the selected coastal rivers of Kizinga, Mbezi, Msimbazi, and Mzinga.

METHODOLOGY

The Study Area

The study was conducted in four selected coastal rivers: Kizinga, Mbezi, Msimbazi, and Mzinga, which are among the twelve rivers that drain the city of Dar es Salaam. These rivers are presumed to be the major sources of contaminants from different areas of the city (Gaspare et al. 2009) because they receive metals from municipal wastes and discharges, farming (urban agriculture), residential as well as industrial (small and medium scale) sources. The Kizinga River drains the relatively urbanised areas of Keko, Chang'ombe, Kurasini, and Temeke (approximately 400,000 inhabitants; URT, 2013). Mbezi River that originates from the upper Mbezi drains the residential areas of Mbezi Msigani, Mbezi Mwisho, Mbezi Louis, Kimara B, Goba and Ukwamani. The Msimbazi River originates from the Pugu hills and its tributaries (Kinyerezi, Luhanga, Ubungo and Ng'ombe or Sinza) drain the Pugu, Gongo la Mboto, Vingunguti, Kinyerezi, Ubungo, Manzese, Tabata, Mabibo, Mburahati, Kigogo, Tandale, Buguruni, Mchikichini, Magomeni, Mwananyamala and Hananasif areas (Kironde, 2016, Ngassapa et al. 2018, Sawe et al. 2019). The Mzinga River drains the relatively rural areas of Vijibweni, Tuangoma, and Mji Mwema with a population of around 90,000 (URT, 2013). All these rivers flow into the Indian Ocean. Whereas the Kizinga and Mzinga rivers flow on the South of Dar es Salaam, Msimbazi flows onto the central, and Mbezi flows on the North of Dar es Salaam.

Methods

Sampling

Sediment sampling was done during the wet and dry seasons of 2015 and 2019, as described previously (EPA, 2001), using a method described by Mihale et al. (2013). Five sampling stations were selected from each site and were located using a global positioning system (GPS, etrex 10, Garmin Ltd, USA). Sampling of sediments was done in the same locations in both seasons. A corer was used in areas with large sediment deposits while a plastic shovel was used to scoop the river sediments in areas with relatively low deposits like along the river banks. The use of a corer has been described by Mihale et al. (2013). A total of 80 samples

were collected from all the sites in both seasons. All sediment samples were packed in prior-labelled and zipped polyethylene bags, stored in iceboxes, and later frozen to −20 °C. Sediment samples were then air-transported while frozen to the laboratory of the Department of Analytical and Environmental Geochemistry, Vrije Universiteit Brussel (VUB), Belgium for analysis. Prior to metal analysis all samples were lyophilised (Leybold Heraus Lyophiliser).

Determination of Metals in Sediments

Sample Preparation

Sediment samples for the determination of metals were analysed using the method described by Mihale, (2017). Briefly, the lyophilised sediment samples in triplicate were pulverised (Fritsch Pulverisette) and digested using a CEM Microwave Accelerated Reaction System (MARS 5®, Matthews, USA). Prior to digestion, the MARS® HP 500 digestion vessels were cleaned appropriately (Mihale, 2017). For each sample, an analytical amount of sediment sample (≈ 0.20g) was put into the digestion vessel followed with Hydrochloric acid, (Suprapur®, 6 mL, 30% w/w, Merck KGaA, Darmstadt, Germany) and distilled nitric acid (suprapur®, 2 mL, 65% w/w). The MARS was programmed to operate at 150°C temperature, 1200 W (100%) maximum power, 15 min ramp time, 200 psi maximum pressure, and 15 min hold time. After cooling, Milli-Q water (40 mL) was added to each vessel and the contents were transferred into polyethylene bottles ready for metal analysis. Blank samples as well as certified reference material (LGC 6139, River Clay sediment, Middlesex, UK) were included in each digestion session and treated in a similar manner as the samples.

Metal Analysis

Nine metals: two major elements (Al, Fe), two minor elements (Mn, Cr), and five trace elements (Cd, Cu, Ni, Pb, Zn) were analysed in triplicate for each river sediment sample. The concentrations of the metals were determined using high resolution inductively coupled plasma–mass spectrometry, HR-ICP-MS (Thermo Finnigan Element II). Prior to ICP-MS analysis, the samples were diluted tenfold. The metal standards solutions were prepared by serial dilution of stock solutions made from ICM 224 (Radion), SM 70 (Radion), and XIII (Merck). Prepared working standards (1, 2, 5, 10, and 20 ppm) were run before and after every batch of 10 samples. Indium at a concentration of 1 µg/L was used as the

internal standard. A calibration curve drawn from the working standards of each metal was used to determine the concentration of metals in the sediments.

Assessment of Sediment Contamination

Assessment of contamination of metals in river sediments was done using six contamination indices: enrichment factor (EF), geo-accumulation index (Igeo), contamination factor, (CF), degree of contamination (DC), modified degree of contamination (mCd), potential contamination index (PCI) and environmental toxicity quotient (ETQ). Enrichment factor (EF), which is used in evaluating the status of contamination as well as geochemical trends (Feng et al. 2004, Pekey 2006) was determined using the formula:

$$EF = \frac{[X]_{sample}[Fe]_{crust}}{[X]_{crust}[Fe]_{sample}}$$

where *X* is the concentration of a given metal. Iron (Fe) was used as a normalisation (reference) element because its anthropogenic source is relatively not significant (Maftei et al. 2019).

The geoaccumulation index (Igeo), which is used in studying the lithogenic effects in sediments was determined by:

$$Igeo = \log_2\left(\frac{C_n}{1.5B_n}\right)$$

where *C* is the concentration of a given metal, *n*, *B* is the background value of the corresponding metal in the average crust (Nobi et al. 2010) and *1.5* is a factor that takes into account the variations in the background values originating from lithologic differences of the sediments (Abrahim and Parker 2008).

The contamination factor (CF) was determined by:

$$CF = \frac{C_{sample}}{C_{reference}}$$

where C_{sample} is the observed value of the metal in samples and $C_{reference}$is the reference value for the respective metal.

The degree of contamination (DC), which gives the overall contamination of all the analysed elements in the sample (Håkanson 1980), was determined by:

$$DC = \sum_{i=1}^{i=n} CF_i \qquad \text{where } CF = \frac{C_{average}}{C_{reference}}$$

where *CF* is a *CF* of individual metal *i, $C_{average}$* is the average value of the analysed metal obtained from an area and *$C_{reference}$*is background value of the individual metal.

The average crustal abundance (Taylor 1964) and/ or average shale values (Turekian and Wedepohl 1961) were used as reference values during the calculations of EF, Igeo, CF, and DC. The magnitude of the contamination due to metals in the study area was determined by the modified degree of contamination, mCd:

$$mCd = \frac{\sum_{i=i}^{i=n} CF_i}{n}$$

where *CF* is the contamination factor of the metal *i* and *n* is the total number of analysed metals.

The metals in the sedimentary environment exist as complex mixtures that change in space and time. So, contamination can also be determined using the potential contamination index (PCI), which is given by:

$$PCI = \frac{C_{maximum}}{C_{background}}$$

where *$C_{maximum}$* is the maximum level of the metal in the sediment and *$C_{background}$* is the baseline value of a corresponding metal in the average crust.

Furthermore, sediment contamination can be assessed using sediment quality based on toxicity. Here the environmental toxicity quotient (ETQ) is used. To get the elemental toxicity, each metal value multiplied to its total score (TS) was divided by the highest total score obtained from the United States Agency for Toxic Substances and Diseases Registry (ATSDR, 2019). The sum of the metal toxicities divided by the number of metal parameters analysed gives the ETQ as shown in the equation:

$$ETQ = \frac{\sum_{i=1}^{n} \left(C_i \times \frac{TS_i}{TS_x} \right)}{n}$$

where C is the observed concentration of the metal i, TS_i is the total score for each metal (Cd = 1318, Pb = 1531, Cr = 893, Ni = 993, Cu = 805, Al = 685, Mn = 797 and Zn = 913) and TS_x is the highest total score of the metal under consideration based on the ATSDR (ATSDR, 2019).

Quality Control and Quality Assurance

The certified reference material (LGC 6139) and procedural blanks were used to evaluate the accuracy and precision. Analytical procedures were assessed using blanks that were treated as real samples. Whereas instrumental precision was < 5% relative standard deviation (RSD), the limit of detection (LOD) was computed as 3 times the standard deviation of the average signal from the procedural blanks. The LODs of the analysed metals are given in Table 1.

Table 1: Detection limits (mg/kg, n = 3) of the analysed metals

Metal	Detection limit	Metal	Detection limit	Metal	Detection limit
Cd	4.0×10^{-3}	Ni	1.9×10^{-1}	Mn	5.0×10^{-2}
Pb	2.0×10^{-2}	Cu	1.3×10^{-1}	Fe	4.5
Cr	6.0×10^{-2}	Al	3.85	Zn	1.4

The mean recoveries of the measured metals were determined. Compared to the LGC 6139 certified reference material, the percentage recoveries of the analysed metals were 102.6% for Cd, 93.1% for Pb, 117.6% for Cr, 110.8% for Ni, 101.8% for Cu, 76.0% for Al, 106.4% for Mn, 129.9% for Fe and 109.4% for Zn. The ranges of percentage recoveries (93.1% - 129.9%) indicate that the obtained values are acceptable and so no correction was done to the observed levels of all metals.

Data Analysis

Descriptive (range, mean and standard deviation), Pearson correlation, and hierarchical cluster statistical analyses were computed using IBM SPSS version 23. Pearson correlation analysis was determined using the mean values of the metals from each river to assess the relationship of the metals in the rivers. Hierarchical cluster analysis (HCA) was used to group similar metals in the river sediments in the same classes and different metals in different classes. Prior to HCA, the data were normalised by Ward's linkage and the squared Euclidean distance was used as a similarity measure. Graphing was done using SigmaPlot (v.11).

FINDINGS AND DISCUSSION

Sediments Chemistry

Seasonal variation of the analysed metals was not significant ($p > 0.05$) for all metals, indicative of more or less constant input of the metals. The values of metals presented in this study are the average of the values between seasons. The mean values of the determined metals in the river sediments are presented in Figure 1. Levels of Cd levels in the Msimbazi river ranged from 160 mg/kg to 900 mg/kg (mean 359 ± 267 mg/kg) while the levels in the Mzinga river ranged from 30 mg/kg to 100 mg/kg (mean 67 ± 30 mg/kg). The Pb levels were observed to range from 3.2 x 10^4 mg/kg to 1.5 x 10^5 mg/kg (mean 6.5 x 10^4 ± 3.3 x10^4 mg/kg) in the Msimbazi and from 4.8 x10^3 mg/kg to 1.04 x10^4 mg/kg (mean 7.5 x10^3 ± 2.3 x10^3 mg/kg) in the Mzinga river (Figure 1).

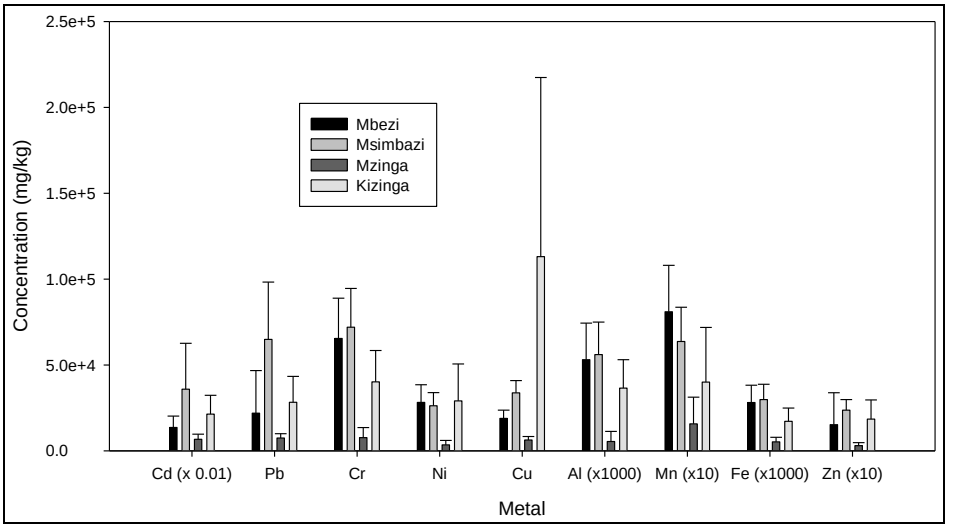

Figure 1: Variation of Metals in the coastal rivers

Similarly, Cr levels ranged from 3.1 x 10^4 mg/kg to 1.2 x 10^5 mg/kg (mean 7.2 x 10^4 ± 2.3 x10^4 mg/kg) in the Msimbazi river and from 3.8 x 10^3 mg/kg to 1.6 x 10^4 mg/kg (mean 7.7 x 10^3 ± 6.0 x10^3 mg/kg) in the Mzinga river. Levels of Al ranged from 1.9 x 10^7 mg/kg to 9.3 x 10^7 mg/kg (mean 5.6 x 10^7 ± 1.9 x10^7 mg/kg) in the Msimbazi river and from 1.3 x 10^6 mg/kg to 1.4 x 10^7 mg/kg (mean 5.4 x 10^6 ± 5.9 x10^6 mg/kg) in the Mzinga river (Figure 1).

Fe levels were observed to range from 1.3 x 10^7 mg/kg to 4.8 x 10^7 mg/kg (mean 3.0 x 10^7 ± 8.9 x10^6 mg/kg) in the Msimbazi river and from 3.6 x

10^6 mg/kg to 9.2 x 10^6 mg/kg (mean 5.2 x 10^6 ± 2.7 x10^6 mg/kg) in the Mzinga river. Levels of Zn were between 1.5 x 10^5 mg/kg and 3. x 10^5 mg/kg (mean 2.4 x 10^5 ± 6.1 x10^4 mg/kg) in the Msimbazi river and between 1.9 x 10^4 mg/kg and 5.6 x 10^4 mg/kg (mean 3.0 x 10^4 ± 1.76 x10^4 mg/kg) in the Mzinga river (Figure 1). The levels of Cd, Pb, Cr, Al, Fe and Zn in Mbezi and Kizinga rivers were between the values observed in the Msimbazi and Mzinga rivers.

Ni levels ranged from 1.2 x 10^4 mg/kg to 8.0 x 10^4 mg/kg (mean 2.9 x 10^4 ± 2.2 x10^4 mg/kg) in the Kizinga river and from 1.7 x 10^3 mg/kg to 7.2 x 10^3 mg/kg (mean 3.5 x 10^3 ± 2.5 x10^3 mg/kg) in the Mzinga river. Cu ranged from 5.5 x 10^3 mg/kg to 4.0 x 10^5 mg/kg (mean 1.1 x 10^5 ± 1.04 x10^5 mg/kg) in the Kizinga river and from 4.9 x 10^3 mg/kg to 9.4 x 10^3 mg/kg (mean 6.3 x 10^3 ± 2.0 x10^3 mg/kg) in the Mzinga river. Mbezi and Msimbazi rivers had Ni and Cu values that were between the values observed for Kizinga and Mzinga rivers (Figure 1). The Mn levels were between 4.4 x 10^5 mg/kg to 1.4 x 10^6 mg/kg (mean 8.1 x 10^5 ± 2.7 x10^5 mg/kg) in the Mbezi River and between 1.9 x 10^4 mg/kg to 9.2 x 10^5 mg/kg (mean 4.0 x 10^5 ± 3.18 x10^5 mg/kg) in the Mzinga River. The levels of Mn in the Msimbazi and Kizinga rivers were in between the values observed in Mbezi and Mzinga rivers.

High levels of Cd, Pb, Cr, Al, Mn, Fe, and Zn were observed in Msimbazi river. Whereas high levels of Ni and Cu were observed in the Kizinga river, high levels of Mn were observed in the Mbezi river. Low levels of most metals were observed in the Mzinga river except Mn where low levels were observed in the Kizinga river (Figure 1). The observed levels of all the metals in the Msimbazi River were higher than those observed by Rumisha et al. (2012) in the same river. This is indicative of the progressive pollution of the river. Similarly, the levels of the metals observed in sediments of all the rivers were higher than those observed in sediments of Cross River Nigeria (Essien et al. 2009) and Ghaghara river, India (Sigh et al. 2017). The levels of metals in the river sediments were higher than the average shale values (Turekian and Wedepohl 1961) as well as the values in the world river systems (Martin and Meybeck 1979).

Contamination Status of River sediments

Metal Enrichment in River Sediments

The determined EF values of the selected metals in sediments of the four rivers are given in Figure 2. The EF values < 2 reflect no enrichment and

EF values > 2 indicate enrichment due to anthropogenic activities (Maftei et al. 2019). Using these criteria, the EF values of the metals ranged from 0.4 to 8.7, indicating minor enrichment to moderate severe enrichment.

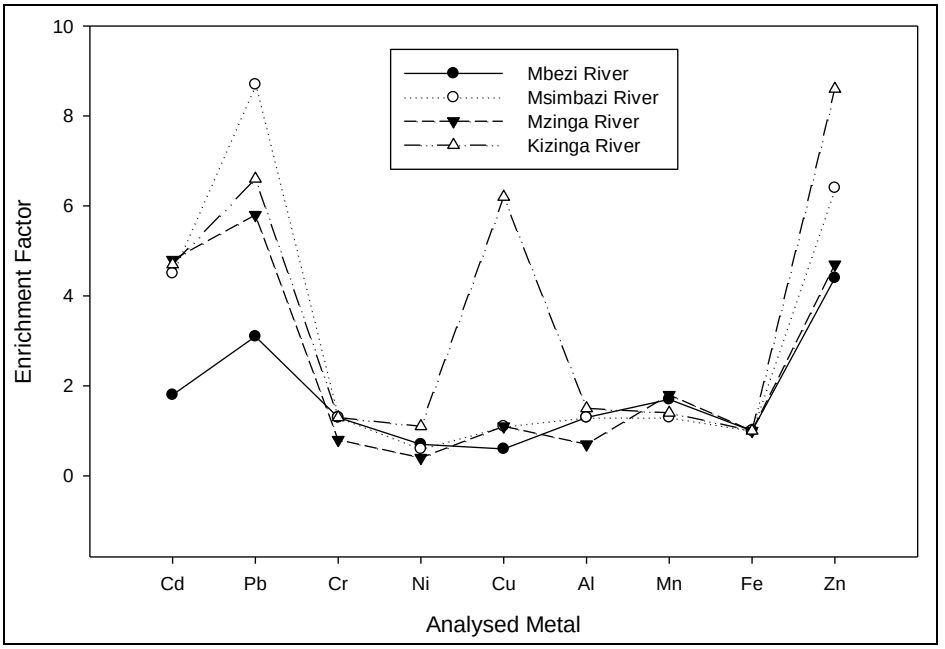

Figure 2: Enrichment Factors of Metals in the Selected Rivers

The findings have indicated that there is no or minor enrichment of Cr, Ni, Al, Mn, and Fe in all rivers (Figure 2). However, there is enrichment of Cr, Pb, and Zn in all rivers and minor enrichment of Cd in the Mbezi River, and moderate enrichment in other rivers. This is an indication that anthropogenic activities have no major consequences of the pollution of the river due to these metals. However, further deposition of the metals in the river sediments could cause enrichment of all the metals.

Geo-contamination Status of River Sediments

The geo-accumulation values of the analysed metals in river sediments are given in Figure 3. The Igeo value > 2 has been set as a criterion of assessment to indicate contamination. The determined Igeo values ranged from 4.8 to 11.6 (Figure 3). All the determined Igeo values in this study were > 2 indicating contamination of the respective metals in all the rivers. Based on this assessment criterion, all the rivers are contaminated with all nine metals.

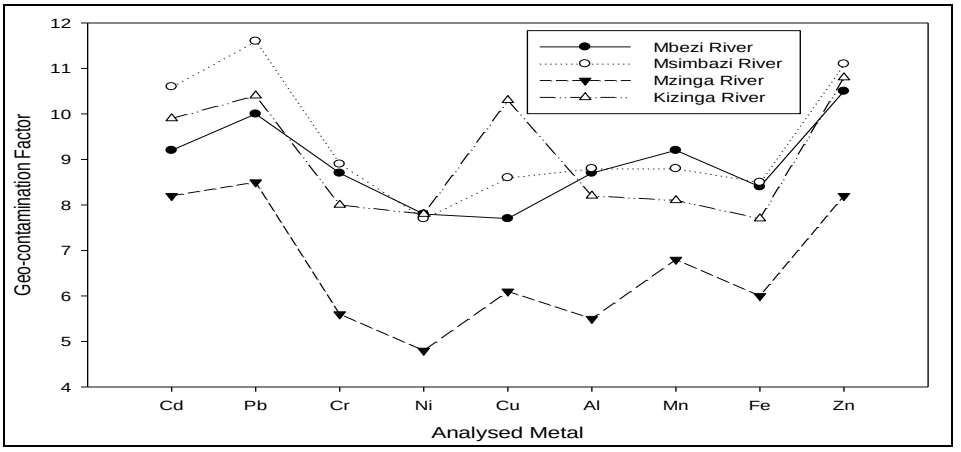

Figure3: Geo-contamination indices of Metals in the Selected Rivers

Contamination status using CF, DC, and mCD

The CF > 6 and DC >24 have been commonly used as evaluation criteria that indicate very high contamination (Håkanson 1980, Maftei et al. 2019), and mCD > 32 has been used to designate ultra-high contamination (Maanan et al. 2015). The determined values of CF, DC, and mCD for the selected metals in the coastal river sediments are given in Table 2. The calculated data for all metals have shown that the CF values are greater than 6, DC values are greater than 24, and mCD values are greater than 32. This is a clear indication that based on these criteria the sediments in the selected rivers are severely contaminated with all the metals.

Table 2: CF, DC, and mCD of Metals in the Selected Rivers

Assessment index		Mbezi River	Msimbazi River	Mzinga River	Kizinga River
	Cd	9.07	23.93	4.48	14.25
	Pb	15.65	46.34	5.36	20.20
	Cr	6.42	7.06	0.75	3.94
	Ni	3.36	3.13	0.42	3.46
	Cu	3.15	5.62	1.06	18.84
	Al	6.45	6.81	0.66	4.43
	Mn	8.52	6.70	1.66	4.22
	Fe	5.00	5.30	0.93	3.05
CF ($\times 10^2$)	Zn	21.76	33.83	4.33	26.38
DC ($\times 10^2$)		79.37	138.73	19.63	98.77
mCD ($\times 10^2$)		7.94	13.87	1.96	9.88
ETQ ($\times 10^5$)		30.42	32.12	3.17	20.97

Environmental Toxicity Quotient

Sediment quality based on toxicity were classified based on the toxicity range (pollution level) such that ETQ < 10 indicates low toxicity, 10 <

ETQ < 50 indicates moderate toxicity, 50 < ETQ < 100 indicates high toxicity, 100 < ETQ < 300 indicates very high toxicity, and ETQ > 300 indicates extremely high toxicity (ATSDR, 2019). Table 2 has indicated that the ETQs of all rivers were in the extremely high toxicity range. The average contribution of the analysed metals to the ETQ varied between rivers. The contribution of Al to the ETQ was more than 95%, which implies that Al metal is the major contributor to metal pollution in all rivers. This could be supported by the fact the metal has gained use in the building industry. The contribution of other metals to ETQ followed the trend Mn > Zn > Cr > Pb > Ni > Cu > Cd in the Mbezi river and Mn > Zn > Pb > Cr > Cu > Ni > Cd in the remaining rivers.

Potential Contamination Indices

The potential contamination indices of the analysed metals in sediments of the coastal rivers are given in Table 3. The determined PCI values in the study area were all greater than the set value of greater than 3. This is indicative of the severe contamination of all the metals in the four coastal river sediments.

The sediment contamination indices used in this study have all presented various contamination levels. While the EF has displayed a slightly different contamination status, other contamination indices have similar status for all the metals in the river sediments. This variation can be explained by the fact that EF uses a terrestrially derived element as a normaliser (Fe in this study), which is not the case with other indices. Mihale (2019) observed that EF values for the same metal may vary even by varying the normalization metal.

Table 3: Potential Contamination Indices of Metals in the Selected Rivers

Metal	Mbezi River	Msimbazi River	Mzinga River	Kizinga River
Al	1154.4	1123.7	168.9	1069.1
Cr	1066.0	1147.4	160.8	875.0
Mn	1473.3	1011.6	394.7	972.6
Fe	837.4	857.6	163.4	605.1
Ni	562.4	485.7	86.1	952.4
Cu	422.2	787.3	155.8	6666.7
Zn	9642.9	5206.0	805.7	6239.9
Cd	1466.7	6000.0	666.7	3000.0
Pb	6457.1	10652.1	742.9	5193.6

Correlation of Metals in River Sediments

In order to assess the relationship of the metals in the coastal river sediments, Pearson correlation coefficients were determined. The metals in coastal river sediments indicated varying levels of correlation at $p < 0.05$ (Table 4). A significant correlation is an indication that the correlated metals have similar behaviour and common source. Suresh et al. (2011) indicated that metals that have good correlations have characteristic similar transport behaviours as well as common sources and vice versa. Table 4 has shown that Cd, Cu, and Pb were strongly correlated to each other by $r^2 > 0.78$, with Cd correlating with Pb at $r^2 = 0.82$ and Cd correlating with Cu at $r^2 = 0.83$. In addition, Cu had strong correlation with Zn ($r^2 > 0.7$, $p < 0.05$). A strong correlation between Cd, Cu, and Pb with each other is indicative of a common source. Similarly, Fe, Mn, Ni, Cr, and Al were strongly correlated to each other by $r^2 > 0.69$, with Cr correlating with Al, Fe, Ni, and Mn at $r^2 > 0.76$. The highest correlations were shown between Cr and Ni as well as between Cr and Al ($r^2 = 0.96$), followed by Ni and Fe ($r^2 = 0.92$). Strong correlations between Fe, Mn, Ni, Cr, and Al with each other clearly indicate a characteristic common source or behaviour.

Table 4: Correlation matrix of the analysed metals in the selected rivers

	Cd	Pb	Cr	Ni	Cu	Al	Mn	Fe	Zn
Cd	1								
Pb	**0.817**	1							
Cr	0.368	0.418	1						
Ni	0.444	0.429	**0.960**	1					
Cu	**0.832**	**0.784**	0.529	**0.599**	1				
Al	0.247	0.310	**0.956**	**0.876**	0.406	1			
Mn	0.503	0.453	**0.757**	**0.841**	**0.711**	**0.691**	1		
Fe	**0.665**	**0.592**	**0.841**	**0.917**	**0.815**	**0.709**	**0.824**	1	
Zn	0.571	0.567	0.482	0.459	**0.699**	0.485	**0.681**	0.505	1

Bold values indicate significant correlations at the $\alpha = 0.01$ (2-tailed).

Principal Component Analysis

Principal component analysis (PCA) after varimax rotation with Kaiser normalisation, as a multivariate analysis, was used to check for similarities and differences between metals in the coastal river sediments. A varifactor or principal component (PC) was considered significant when its eigenvalue was > 1.5 (Shrestha and Kazama, 2007). Prior to PCA, the suitability of the data was checked by performing Kaiser–Meyer–Olkin (KMO) and Bartlett's sphericity tests. The KMO value

obtained was 0.774 and Bartlett's test of sphericity was 0.000, (χ = 216.775, df = 36), indicating the usefulness of such a statistic (Varol, 2011; Li et al. 2013). The measured metals were used as variables (total 9), with the concentrations of the metals in the different sampling sites of each river as objects (total 180).

The PCA computations have indicated that the 9 variables from different stations of the rivers can be represented by 2 new varifactors that accounted for 85.53% of the total variance in the original data sets (Table 5).

Table 5 Rotated Principal Component Matrix

Parameter	1st PC	2nd PC
Cr	**0.953**	0.228
Al	**0.944**	0.107
Ni	**0.934**	0.297
Mn	**0.760**	0.472
Fe	**0.758**	0.560
Cd	0.149	**0.924**
Pb	0.168	**0.884**
Cu	0.366	**0.881**
Zn	0.376	**0.670**
Eigenvalue	6.107	1.590
Contribution Rate (%)	46.104	39.422
Accumulated contribution rate (%)	46.104	85.526

The PCA loading distribution of metals has indicated that Cr, Al, Ni, Mn, and Fe have strong loadings in the first PC, which accounted for 46.1% of the total variance. Furthermore, Cd, Pb, Cu, and Zn have strong loadings in the second PC that accounted for 39.4% of the total variance (Table 5). This coincides with the computed correlation coefficients (Table 4) and a two-dimensional scatter plot (Figure 4).

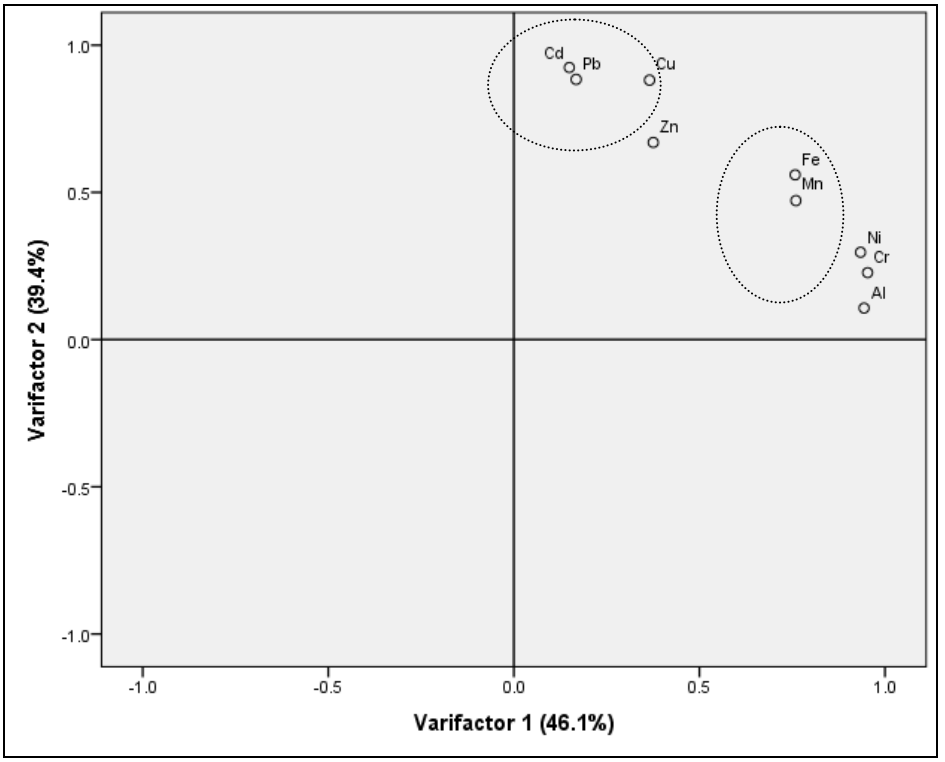

Figure 4: Two-dimensional score plot of metals in the selected rivers

The PCA loading distribution of metals has indicated that Cr, Al, Ni, Mn, and Fe have strong loadings in the first PC, which accounted for 46.1% of the total variance. Furthermore, Cd, Pb, Cu, and Zn have strong loadings in the second PC that accounted for 39.4% of the total variance (Table 5). This corresponds with the computed correlation coefficients (Table 4) and a two-dimensional scatter plot (Figure 4). The findings indicate that probably Cd, Cu, Pb, and Zn have a common source or origin in all river sediments, which is different from that of Mn, Al, Fe, Cr, and Ni. The Cd, Cu, Pb, and Zn could have an anthropogenic related source while Mn, Al, Fe, Cr, and Ni could have a natural related source. This is an indication that there might be metal-related anthropogenic activities around or close to these rivers. As a consequence, the anthropogenic metals could be stored in the sediments and then transferred to other environmental matrices (e.g., water) through physical, chemical, or biological means such as sedimentation, hydrodynamic, and mineralisation processes. Table 4 has also shown that Cu is strongly correlated with Fe and Zn by r^2

> 0.70, indicating that Cu metal could have both anthropogenic and natural origins.

Hierarchical Cluster Analysis

Hierarchical cluster analysis was applied to classify more related metals within the same class and less related metals into different classes. The HCA has further illustrated the interconnectivity of the metal contaminants in the selected rivers. A dendrogram of the metals (Figure 5) has shown that two clusters are evident. One cluster constitutes metals from the natural source (Al and Fe) and another cluster constitutes the metals from the anthropogenic source.

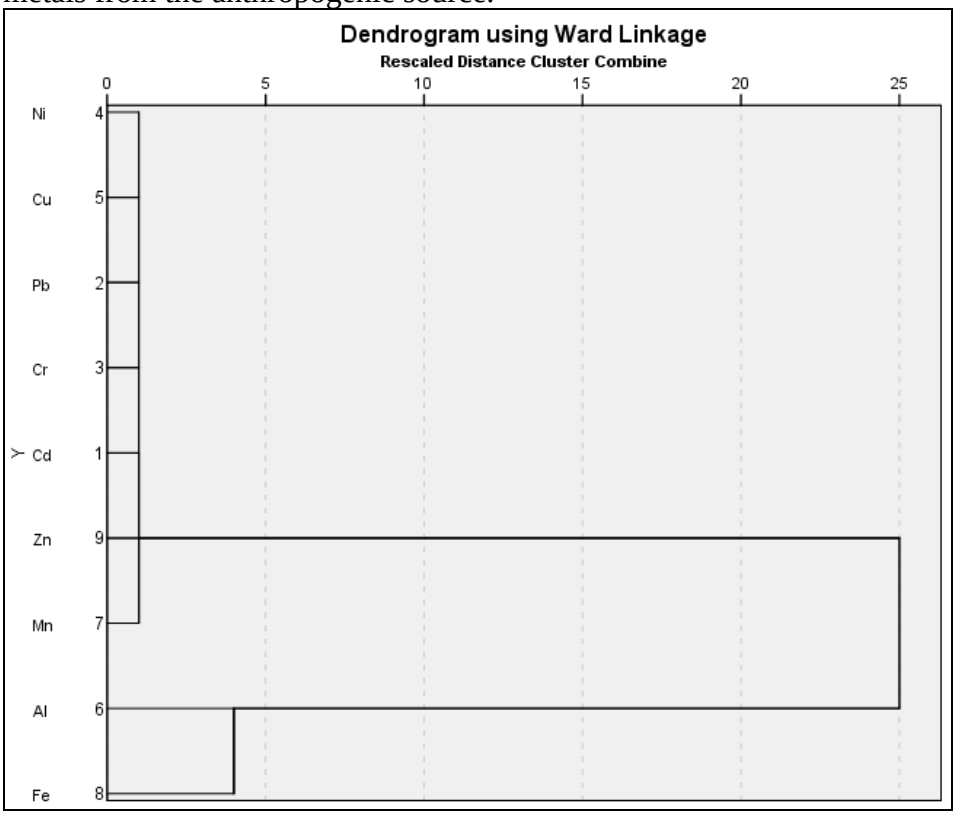

Figure 5: Dendrogram showing Clusters of Analysed Metals based on Selected Rivers

CONCLUSION

The pollution status of the selected metals in sediments of coastal rivers has been established. While high levels of most metals were observed in the Msimbazi river, low levels were observed in the Mzinga river.

Pearson correlation coefficients, PCA, and HCA have indicated significant associations of Mn, Al, Fe, Cr, and Ni on one hand and Cd, Zn, Cu, and Pb on the other, indicating the natural and anthropogenic origin, respectively. The anthropogenic source could be due to the metal-related activities around the rivers. Continuous deposition of such metals could pose environmental and health risks. Though the EF contamination index has indicated varied contamination status of the metals in the rivers, Igeo, CF, DC, mCD, and PCI contamination indices, as well as ETQ, have indicated that sediments from these coastal rivers are more polluted, with the Msimbazi and Kizinga River sediments being the most polluted of all the rivers. There is an urgent need to instituting river management strategies along the coast in order to minimise the continuous release of metals from their sources.

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