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Multivariate Assessment of Metal Contamination in Mtoni Sedimentary Environment, Tanzania

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Abstract

Enrichment factor, geo-accumulation factor, contamination factor, degree of contamination, modified degree of contamination and potential contamination index were applied to assess the contamination of metals (Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd and Pb) in the Mtoni estuary sediments in Dar es Salaam, Tanzania. The sediment samples were sampled as appropriate, treated using established methods and analysed using inductively coupled plasma-high resonance mass spectrometry. The calculated enrichment factor values indicated contamination varying from minor (EF > 1) to severe contamination (EF > 50). The determined geo-accumulation index, contamination factor, degree of contamination, modified degree of contamination and potential contamination index values indicated severe contamination of all analysed metals in all the samples (Igeo > 5, CF > 6, DC > 48, mCd > 32 and PCI > 3). There is therefore, an urgent need to institute immediate mitigation measures to reduce the ecological, environmental and human risks taking into consideration that the anthropogenic activities, which are the main sources of these pollutants, are still going on in the area.

Keywords: Marine Sediments, Metal contamination, Pollution indices, Multivariate assessesment, Mtoni estuary

Introduction

Metal contaminants may enter the coastal environment via natural processes (e.g., erosion of rocks, and dusts emanating from wind) and other processes originating from anthropogenic activities (Dell'Anno et al. 2003, Chatterjee et al. 2007). In marine ecosystems, metals may anthropogenically come from wastes and effluents from sewage, industries, runoff from agricultural field as well as garbage dumps from domestic sources (Chatterjee et al. 2007). In addition, discarded automobiles and dumping metallic substances have been the common anthropogenic inputs of metals in the marine ecosystems (Kamau 2002, Praveena et al. 2010). As metals can neither be chemically degraded nor subjected to biological degradation, they become permanently added in a given marine environment. As a result, they accumulate locally (MacFarlane and Burchett 2001, Defew et al. 2005) and/or become transported over long distances (Marchand et al. 2006). Sediments have been both sinks and sources of metal contaminants in the marine environments (Guzzella et al. 2005, Chi et al. 2007). As a result, these sediments are used in the evaluation of pollutant fate processes, sources as well as their historical trends. This is because the amount of the pollutant is an indication of the regional discharges (Müller et al. 1999, Moon et al. 2009). Since metals are persistent, toxic and can bioaccumulate and biomagnify in organisms, their presence in sediments may pose potential threats to marine and other organisms (Kumar et al. 2008, Zhao et al. 2010).

Metal levels in marine sediments can be important indicators of toxicological risks, especially when they are substantially above natural levels. Assessment of contamination of sediments by metals can be done using various approaches, among others, enrichment factor (EF), geo-accumulation index (Igeo), contamination factor (CF), degree of contamination (DC), modified degree of contamination (mCd) and potential contamination index (PCI). The EF is commonly used in evaluating geochemical trends as well as a measure that indicates the degree and status of environmental contamination (Feng et al. 2004). EF is calculated as:

$$\mathrm{EF} = \frac{\left[X / M \right]_{\mathrm{Sample}}}{\left[X / M \right]_{\mathrm{Crust}}}$$

where X = concentration of a given metal and X/M = ratio of the concentration of metal *X* to a normalisation (reference) element.

The determination of EF values intends to minimise the variation of metals associated with variability in the mud/sand ratios (Abrahim and Parker 2008). EF can be a measure of changes or modification in the natural composition in the sediments as well as other environmental compartments (Pekey 2006). As observed, EF is reatively easy assessment tool where the values of each element are compared to a selected parameter for normalisation. As a result, EF only gives a rough estimation of the contamination level. For accurate assessment, other pollution assessment indices such as geo-accumulation index (Igeo), contamination factor (CF), degree of contamination (DC), modified degree of contamination (mCd) and potential contamination index (PCI) are used.

The geo-accumulation index (Igeo), can be used as a quantitative measure of metal pollution in marine sediments as a way to understand various lithogenic effects. The Igeo is given by:

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

where C_n is the concentration of a given metal, B_n is the background value of the corresponding metal in average crust (Nobi et al. 2010) and 1.5 is a factor that minimises the possible variations in the background values, which can originate from lithologic diferences in the sediments (Abrahim and Parker 2008). Igeo is used for evaluating temporal changes of metals based on geochemical background values (Li et al. 2016). Thus, Igeo can be used as an estimator of metal enrichment above a given baseline level.

The contamination factor (CF) is a value obtained by dividing the observed value of the metal in samples to the reference value for the respective metal. The CF is given by:

$$\mathrm{CF} = \frac{C_s}{C_{ref}}$$

The commonly used reference values are average crustal abundance (Taylor 1964) and/or average shale values (Turekian and Wedepohl 1961). As can be seen, the CF considers contamination of individual element separately. It is possible to determine the overall contamination of all the analysed elements in the sample by calculating the degree of contamination (DC), which gives the summation of all the CFs for all the metals analysed (Håkanson 1980). The DC is given by:

$$\mathrm{DC} = \sum_{i=1}^{i=n} \mathrm{CF}_i \qquad \text{where}$$

$$\mathrm{CF} = \frac{C_{ave}}{C_{ref}}$$

where CF_i is a CF of an individual metal i, C_{ave} is average value of the analysed metal obtained from an area and C_{ref} is background value of individual metal.

To evaluate the magnitude of net contamination due to metals at a given area, modified degree of contamination, mCd, can be used. The mCd is given by:

$$\mathrm{mCd} = \frac{\sum_{i=i}^{i=n} \mathrm{CF}_i}{n}$$

where CF_i is the contamination factor of the metal i and n is the number of analysed metals.

In a marine ecosystem where metals exist as complex mixtures with variable changes in time and space, potential contamination index (PCI) of a metal can be used. PCI 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 average crust.

The increasing human population has resulted to anthropogenic perturbations of estuarine and coastal environments adjacent to urban areas (Tam and Wong 2000). Furthermore, industrialisation, urbanisation and their associated socio-economic activities have contributed to the significant inputs of pollutants into the environment, directly affecting the coastal ecosystems. Since most urban development areas and human activities are close to many marine ecosystems, the impacts of these activities to the environment cannot be neglected (Defew et al. 2005, Kamaruzzaman et al. 2008). For example, direct and indirect disposal of wastes have led to significant increase in pollutant contamination (Alaoui et al. 2010) into rivers and estuaries.

In Tanzania, significant amounts of wastes from agricultural, domestic and industrial sources are discharged into streams, rivers and estuaries with little or no treatment. At present, the anthropogenic contribution of the metals into the marine environment in Tanzania and the impacts of metal contamination in the coastal ecosystems are alarming (Mihale 2017). There has been an increase in industrial activities, street garages, dumping of metallic substances and urban agriculture in valleys and near rivers that drain their water into mangrove ecosystems (Ak'habuhaya and Lodenius 1988, Machiwa 1992, 2000, De Wolf et al. 2001, Taylor et al. 2002, Mremi and Machiwa 2003). With continuously high influx of anthropogenic products from increased urban population, industrial and agricultural activities, sewage input and burning of solid wastes, the magnitude of the problem cannot be underestimated. Studies by Machiwa (1992), Mremi and Machiwa (2003), Muzuka (2007), Mtanga and Machiwa (2007), Mrutu et al. (2013), Mihale (2017) and Minu et al. (2018) have revealed the levels and extent of the metal pollution in the Tanzanian marine sediments. However, little is known about the assessment of contamination using the pollution assessment indices. In fact, there is no study done in the area to assess the metal contamination by using different pollution assessment criteria. Therefore, this study was intended to evaluate the contamination of metals in the Mtoni estuary sediments using selected pollution assessment indices.

Materials and Methods

Study area

This study was conducted in Kizinga and Mzinga rivers of the Mtoni estuary, Dar es Salaam (Figure 1). The estuary is highly impacted (PUMPSEA 2007) by discharges from the mangrove forest (Kruitwagen et al. 2008), residential areas and industrial activities (URT 2013) as well as charcoal burning and urban agriculture (De Wolf et al. 2001). Whereas the Kizinga River drains the urbanised areas of the city, the Mzinga River drains the relatively rural areas (Mihale et al. 2013). The rapid development of settlements along the Mzinga creek has increased the waste discharges into the river, increasing the potential risks. There are also additional inputs from the Mtoni dumping site, located between the Kizinga and Mzinga Rivers, and the Dar es Salaam harbour, which is in close vicinity to the estuary (Sonda 2018).

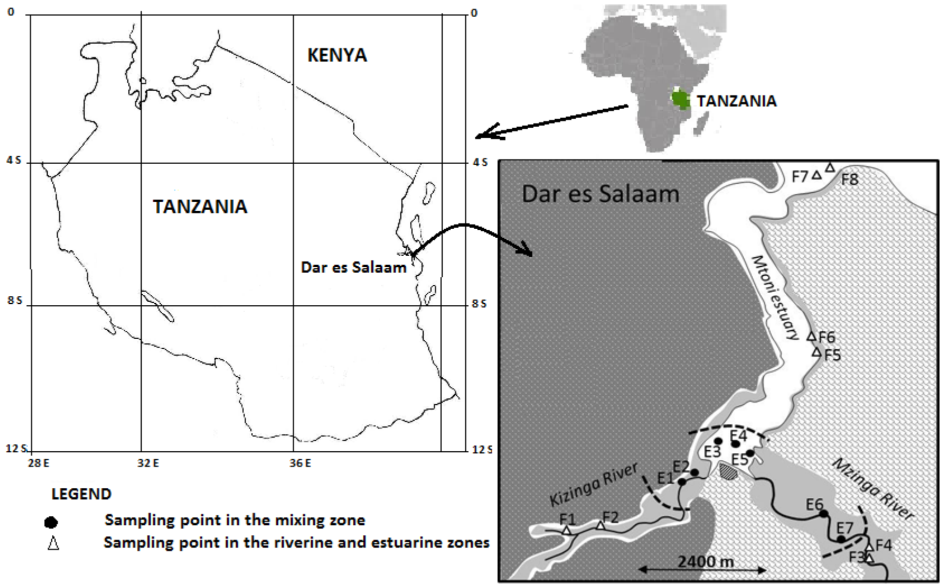

Figure 1: Map showing the sampling points in the Mtoni estuary, Tanzania: Dotted lines delimit the estuarine mixing zone, dotted grey areas are urban zones, light grey areas are mangrove forests, structured filled areas are predominantly agricultural zones and black and white hatched zone is the Mtoni dumping site. Adapted from Google maps and Mihale (2017).

Sampling

Fifteen sampling stations were selected as described by Mihale et al. (2013). The stations E1 to E7 (Figure 1) were within the fresh water-marine water mixing zone (estuary mixing zone). This zone has varying salinities (from fresh water to brackish water) that tend to increase during the dry season (Mangion 2011). The upstream stations (F1 – F4) were within the fresh water zone while the downstream stations (F5 – F8) were within the sea water zone. Sediment sampling was conducted during low tides in the mangrove forest creeks of both rivers and within the Mtoni estuary mouth (Figure 1). Two sampling campaigns were conducted in the estuarine sediments during wet (19th – 20th January 2011) and dry (15th – 16th August 2011) seasons.

Sediment samples were collected during the sampling campaigns as described by EPA (2001) and Mihale et al. (2013). The samples were packed appropriately as described by Mihale (2017) and transported to the laboratory of the Department of Analytical and Environmental Geochemistry, Vrije Universiteit Brussel (VUB), Belgium for further pre-treatment and analyses of the metals.

Determination of particle size

The determination of particle sizes in the sediments was done, as described by Mihale (2017), in three pre-selected stations having low (station E7), medium (station E2) and high (station E1) organic matter content to establish the relationship between metals and organic matter. The method used during the determination of particle size has been described in detail by Mihale (2017).

Determination of metal concentrations in marine sediments

Sample preparation for metal analyses

The lyophilised sediment samples in triplicate were pulverised (Fritsch Pulverisette) before chemical treatment. Then, the samples were digested using a CEM Microwave Accelerated Reaction

System (MARS 5®, Matthews, USA). Prior to digestion, the MARS® HP 500 digestion vessels were cleaned with 2% alkaline extran (Merck), rinsed with Milli-Q water and then cleaned with Emsure® nitric acid (65% w/w, Merck KGaA, Darmstadt, Germany). For each sample, an analytical amount (0.20 g) of Mtoni sediment was put into the digestion vessel together with Suprapur® hydrochloric acid (6 mL, 30% w/w, Merck KGaA, Darmstadt, Germany) and distilled Suprapur® nitric acid (2 mL, 65% w/w). The digestion 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 analysis. For each digestion session, blank samples as well as certified reference material (LGC 6139, River Clay sediment, Middlesex, UK) were included and treated in similar manner as the samples.

Metal analysis using HR-ICP-MS

Metal analysis was carried out using a High Resolution Inductively Coupled Plasma Mass Spectrometer (HR-ICP-MS, Thermo Finnigan Element II). Samples were diluted tenfold prior to ICP-MS analysis. Metal standard solutions were prepared by serial dilution of stock standard solutions: ICM 224 (Radion), SM 70 (Radion) and XIII (Merck). Prepared working standards (1, 5, 10 and 20 ppm) were run before and after every batch of 10 samples. Eleven metals: two major elements (Al and Fe), two minor elements (Mn and Cr) and seven trace elements (As, Cd, Cu, Ni, Pb, Sr and Zn) were analysed in triplicate in each marine sediment sample. Indium at a concentration of 1 µg/L was used as the internal standard.

Data analysis

The analysed metal data were subjected to normal descriptive statistics (range, mean and standard deviation) and have been presented by Mihale (2017). These data were then used to determine the contamination status using the already established EF, Igeo, CF, DC, mCd and PCI formulae.

Quality control and quality assurance

The accuracy and precision of the analytical procedures were evaluated using the certified reference material (LGC 6139) and procedural blanks. The assessment of the analytical procedures involved the use of blanks that were treated and analysed in the similar manner as the samples. Procedural and analytical blanks were also used to monitor the precision of the analysis. All results were blank corrected using respective mean blank reading prior to determination of the concentrations. Precision of ICP-MS analysis was better than 5% relative standard deviation (RSD). The limits of detection (LOD) of each element was set to be 3 times the standard deviation (SD) of procedural blanks and are given in Table 1.

The percentage recoveries of the measured metals based on the mean values compared to the certified reference materials are given in Table 2. Metal recoveries ranged from 93.1% to 117.6% when the certified values for extractable metals were used, while the recoveries ranged from 72.1% to 129.9% when certified values for total metals were used. The obtained percentage recoveries were in good agreement with the certified values in the LGC 6139 reference material except for Cr when total metal values were used.

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

Metal	Detection limit	Metal	Detection limit
Al	3.849	Cu	0.129
Cr	0.058	Zn	1.412
Mn	0.048	As	0.058
Fe	4.526	Cd	0.004
Ni	0.194	Pb	0.020

Table 2: Certified and observed mean values (mg/kg) of metals and the percentage recovery (n = 7)

Metal	Extractable metals			Total metals		
	Certified value	Obtained value	Percentage recovery	Certified value	Obtained value	Percentage recovery
Al	-	43,300	-	57,000	43,300	76.0
Cr	80.0	94.1	117.6	126.0	94.1	74.7
Mn	-	1,170	-	1,100	1,170	106.4
Fe	-	41,600	-	32,000	41,600	129.9
Ni	38.0	42.1	110.8	44.0	42.1	95.7
Cu	92.0	93.7	101.8	96.0	93.7	97.6
Zn	513.0	580	113.1	530.0	580	109.4
As	27.0	30.7	113.7	-	30.7	-
Cd	2.3	2.4	102.6	-	2.4	-
Pb	160.0	149	93.1	176.0	149	84.7

Source: Mihale (2017)

Results

Assessment of metal contamination

Enrichment factors (EF) of the metals

The data used for calculation of EF values have been presented elsewhere (Mihale 2017). Generally, EF values are evaluated based on some agreed ranges. A value of one (unity) indicates neither depletion nor enrichment relative to values in the Earth's crust whereas EF >1 is an indication of magnification, more abundance than average. Specifically, EF < 1 indicates no enrichment, 1 < EF < 3 indicates minor enrichment, and 3 < EF < 5 is indicative of moderate enrichment. Furthermore, moderate severe enrichment is indicated by 5 < EF < 10, severe enrichment by 10 < EF < 25, very severe enrichment by 25 < EF < 50 and extreme severe enrichment by EF > 50 (Acevedo-Figueroa 2006, Chen et al. 2007, Essien et al. 2009).

EF values can provide different values depending on the normalisation metal. Common normalisation metals (Al and Fe) are used for regional comparison as well as to differentiate anthropogenic sources from lithogenic ones (Zhou et al. 2007). Their co-variation with grain sizes and linear relationships with fine particle-size fractions (clay and silt) in most sediment (Liu et al. 2003) justify their use as normalisers. The normalisers compensate for both granulometric and mineralogical variability of metal concentrations in sediments (Aloupi and Angelidis 2001). However, intrinsic variations between the normalisation metals themselves can cause variations in the resulting EF values.

When the normalisation metal was Al, there was no enrichment in the mixing zone samples for all metals, after correction based on percentage recovery, except Zn, As, Cd and Pb. On the other hand, there were high enrichments in all riverine samples, F1 to F4 (Mihale 2017). However, when Fe was used as the normalisation metal, Cu, Zn, As, Cd and Pb were enriched in all the samples after correction using percentage recovery. As observed earlier, riverine samples (F1 – F4) were enriched as well. Using Fe as normalisation metal, mixing samples (E1 – E7) and downstream samples (F5 – F8) were also enriched (Table 3).

The EF results have indicated that there is minor contamination of Al, Cr, Mn and Ni in all the samples except riverine sample F2 close to a textile mill that had severe contamination of Cu. Moderate to severe contamination was observed for Zn, As, Cd and Pb in all analysed samples except F2 that had minor contamination of Pb.

Igeo values

Experimental data used for determination of Igeo values has been presented by Mihale (2017). The calculated Igeo values have indicated that there is contamination of all the analysed metals in all samples (Igeo > 2). In all metals riverine samples (F1 – F4) and marine samples (F5 – F8) were more contaminated compared to mixing zone samples (E1 – E7), indicative of extreme contamination of the analysed metals in the area (Table 4).

CF, DC and mCd values

The data obtained by Mihale (2017) were used for the determination of CF, DC and mCd. The CF values are grouped into four evaluation criteria according to Håkanson (1980) as follows: CF < 1 indicates low contamination; 1 < CF < 3 indicates moderate contamination; 3 < CF < 6 indicates high contamination; and CF> 6 indicates very high contamination (Håkanson 1980). The degree of contamination (DC) can be determined to provide information about the potential risks that can be posed by having such metals in a sedimentary environment (Cheng et al. 2013, Hou et al. 2013). There is no consensus on the categorization of contamination using the DC. Some researchers use DC values < 6 to indicate low contamination while others use DC values < 8. Similarly, other researchers show that moderate contamination is indicated by values 6 ≤ DC < 12 while others indicate using 8 ≤ DC < 24. Furthermore, high contamination is indicated by either 12 ≤ DC < 24 or 24 ≤ DC < 48. Very high contamination is either indicated by DC values greater than 24 or values greater than 48. When the values in a given area are extremely large like in the Mtoni sediments (Table 5), the choice of using either 6 or 8 as a categorization factor becomes immaterial.

The modified degree of contamination (mCd) can be evaluated using the following classifications as adopted from Maanan et al. (2015). The mCd < 1.5 indicates either no to very low contamination whereas low contamination is indicated by 1.5 ≤ mCd < 2. Furthermore, moderate contamination is indicated by 2 ≤ mCd< 4; high contamination by 4 ≤ mCd < 8; very high contamination by 8 ≤ mCd< 16; extremely high contamination by 16 ≤ mCd < 32 and ultra high degree of contamination by mCd ≥ 32 (Maanan et al. 2015). The results of CF, DC and mCd are given in Table 5.

The CF results have shown that all the analysed samples from the Mtoni estuary had very high contamination of the analysed metals (CF > 6). The riverine (F1 – F4) and some marine samples (F5 – F6) had higher CFs than the mixing zone samples and the remaining marine samples (F7 – F8). If the magnitude of the values determined is directly related to the extent of contamination, the Mtoni samples are therefore extremely contaminated. The determined DC values indicated that all the analysed samples in the estuary are severely contaminated (DC > 48). Similarly, the results of the mCd have shown that all samples in the study area are severely contaminated (mCd > 32) (Table 5).

Table 3: Enrichment factors after normalisation using Fe

Zone	Location	Code	Al	Cr	Mn	Ni	Cu	Zn	As	Cd	Pb
Riverine	Kizinga	F1	1.8	1.2	1.8	0.7	1.2	16.9	8.4	11.2	10.6
		F2	0.2	1.1	1.7	2.3	16.0	5.1	3.5	3.8	1.8
	Mzinga	F3	1.0	1.0	2.4	0.5	1.0	4.9	26.2	4.1	4.5
		F4	0.9	1.0	2.7	0.5	1.3	5.5	70.6	3.1	5.3
Mixing zone	Confluence	E1	0.2	0.7	0.6	0.3	1.8	6.7	23.1	9.3	8.4
		E2	0.3	0.8	0.5	0.4	2.3	8.7	18.5	11.3	10.3
		E3	0.4	1.0	0.6	0.4	2.8	10.6	16.8	13.4	13.0
		E4	0.4	0.9	0.6	0.4	2.6	8.8	17.0	14.2	11.7
		E5	0.4	0.9	0.6	0.4	2.5	8.0	20.7	14.0	12.6
		E6	0.3	0.6	0.7	0.4	1.3	4.2	39.2	7.1	8.3
		E7	0.2	0.5	0.7	0.3	1.3	3.8	23.9	5.7	6.4
Marine	Navy	F5	1.6	1.2	0.6	0.5	1.2	4.2	14.3	4.6	5.8
		F6	1.6	1.1	0.9	0.5	1.2	4.5	21.1	4.7	5.7
	Kigamboni	F7	1.4	1.9	1.2	0.8	0.9	3.5	97.0	9.4	5.5
		F8	1.4	1.8	1.0	0.7	0.9	3.4	79.8	9.4	4.0

Table 4: Geo-accumulation indices of metals in the Mtoni

Zone	Location	Code	Geo-accumulation index									
			Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb
Riverine	Kizinga	F1	8.0	7.5	8.1	7.2	6.6	7.5	11.3	10.3	10.7	10.6
		F2	6.0	8.2	8.9	8.1	9.3	12.1	10.5	9.9	10.1	8.9
	Mzinga	F3	6.8	6.7	8.0	6.8	5.8	6.7	9.1	11.5	8.8	9.0
		F4	5.3	5.3	6.8	5.4	4.4	5.8	7.9	11.6	7.1	7.8
Mixing Zone	Confluence	E1	3.7	5.2	5.1	5.8	4.2	6.7	8.6	10.4	9.0	8.9
		E2	2.9	4.4	3.7	4.7	3.3	5.9	7.8	8.9	8.2	8.1
		E3	3.7	5.2	4.4	5.2	4.0	6.7	8.6	9.2	8.9	8.9
		E4	4.0	5.3	4.7	5.5	4.2	6.8	8.6	9.6	9.3	9.0
		E5	2.9	4.1	3.7	4.3	3.1	5.7	7.3	8.7	8.1	8.0
		E6	3.7	4.8	5.0	5.6	4.2	5.9	7.7	10.9	8.4	8.7
		E7	3.4	4.7	5.0	5.6	3.8	5.9	7.5	10.1	8.1	8.2
Marine	Navy	F5	7.2	6.7	5.8	6.5	5.5	6.7	8.5	10.3	8.6	9.0
		F6	6.7	6.2	5.8	6.1	5.1	6.3	8.2	10.5	8.3	8.6
	Kigamboni	F7	4.7	5.1	4.5	4.2	3.9	4.1	6.0	10.8	7.5	6.7
		F8	5.1	5.4	4.6	4.6	4.1	4.4	6.3	10.9	7.8	6.6

Table 5: The CFs, DC and mCd values from the Mtoni estuary

Zone	Location	Contamination Factors (CFs)											DC	mCd
		Code	Al	Cr	Mn	Fe	Ni	Cu	Zn	As	Cd	Pb		
Riverine	Kizinga	F1	387.6	272.5	404.2	220.2	144.0	273.3	3714	1856	2467	2343	12081	1208.1
		F2	96.0	451.0	715.8	417.6	952.4	6667	2129	1450.0	1600	736	15212	1521
	Mzinga	F3	168.9	160.8	394.7	163.4	86.1	155.8	805.7	4277.8	666.7	742.9	7622.7	762.3
		F4	58.3	60.8	171.6	63.9	32.1	81.8	351.4	4516.7	200.0	340.0	5876.7	587.7
Mixing Zone	Confluence	E1	19.0	55.5	51.7	84.8	27.8	152.0	568.5	1958.9	784.9	710.8	4413.9	441.4
		E2	11.2	31.2	19.5	39.3	14.7	91.2	339.9	728.2	444.1	406.6	2125.8	212.6
		E3	19.1	55.7	30.7	53.8	23.6	151.1	572.4	903.0	720.1	699.3	3228.8	322.9
		E4	24.2	59.3	38.4	67.1	26.6	171.5	589.1	1139.4	952.3	785.2	3853.2	385.3
		E5	11.5	26.2	19.6	30.2	13.0	75.8	243.0	625.6	423.8	379.9	1848.4	184.8
		E6	19.5	41.1	47.9	73.1	27.6	92.7	304.4	2867.7	522.5	606.0	4602.4	460.2
		E7	16.1	37.7	48.5	70.8	20.8	91.6	269.3	1695.3	404.2	453.9	3108.4	310.8
Marine	Navy	F5	213.9	152.0	84.6	131.4	68.8	152.0	545.7	1883.3	600.0	757.1	4588.9	458.9
		F6	154.3	113.7	84.6	99.5	51.5	120.0	448.6	2100.0	466.7	565.7	4204.6	420.5
	Kigamboni	F7	40.1	52.7	34.0	28.4	21.9	25.3	98.6	2755.6	266.7	155.7	3479.0	347.9
		F8	50.1	63.3	37.3	35.5	25.0	32.3	121.4	2833.3	333.3	143.6	3675.2	367.5

PCI values

The data used for determining PCI have been presented elsewhere (Mihale 2017). The PCI values for the Mtoni sediments were also determined. Based on the prescribed classification, low contamination was indicated by PCI < 1; moderate contamination by 1 < PCI < 3 and severe contamination by PCI > 3 (Davaulter and Rognerud 2001). The PCI results in the Mtoni sediments ranged from 387.6 for Al to 6667 for Cu. In fact, the lowest PCI value observed in Mtoni was almost 130 times the PCI value for severe contamination. These values are higher than the PCI category value of > 3 that indicates severe contamination. The PCI data have shown that the study area is severely contaminated with all metals, indicating the level of contamination of the estuary. These findings are in agreement with findings observed in other four contamination indices: Igeo, CF, DC, and mCd.

Discussion

Assessment of contamination in the Mtoni estuary

Assessment of contamination using the six assessment criteria has shown that the Mtoni estuary sediments are contaminated. All the assessment criteria have shown that all the samples from the area are contaminated, indicating that the whole area is contaminated. As observed the level of contamination varies from one contamination assessment criterion to another. The EF calculations have shown variations of the contamination of selected metals from minor enrichment to extremely severe contamination. The EF values for Pb and Ni observed in the Mtoni estuary were slightly higher than those observed in Hara Biosphere Reserve, Iran (Nowrouzi and Pourkhabbaz 2014). Similarly, EF values of Cd observed in the Mtoni estuary were lower than those observed in Hara Biosphere Reserve (Nowrouzi and Pourkhabbaz 2014). On the other hand, EF values from the Mtoni were higher than those observed in Izmir Bay, Turkey for Cr, Mn, Fe, Cu, Zn, Cd and Pb (Özkan 2012).

Geo-accumulation indices have indicated that the contamination of the metals ranged from contamination to extreme contamination. The determined Igeo levels in the Mtoni were higher than those observed in Izmir Bay, Turkey for Cr, Mn, Fe, Cu, Zn, Cd and Pb (Özkan 2012). The geo-accumulation values observed indicated that all samples from the Mtoni sediments were highly contaminated. The determined CF values in the Mtoni estuary were very high compared to those reported by Özkan (2012) for Cr, Mn, Fe, Cu, Zn, Cd and Pb and in a similar study done in India by Sivakumar et al. (2016) for Cr, Mn, Fe, Cu, Ni and Zn. Similarly, the determined degree of contamination, modified degree of contamination and potential contamination index have indicated that the area is extremely contaminated with these metals. The determined DC values in the Mtoni estuary were very high compared to those observed in Izmir Bay (Özkan 2012) for Cr, Mn, Fe, Cu, Zn, Cd and Pb and in Tamilnadu, India (Sivakumar et al. 2016) for Cr, Mn, Fe, Cu, Ni and Zn. Similarly, the mCd and PCI values observed in the Mtoni estuary were very high compared to those observed by Sivakumar et al. (2016) for Cr, Mn, Fe, Cu, Ni and Zn.

It is clearly observed that using the six environmental contamination assessment criteria the sediments in the selected areas of the Mtoni estuary are highly contaminated with the selected metals. It is only EF that has shown that some metals in the selected locations are not highly contaminated. The variation of EF values to other assessment criteria can be acceptable due the fact that EF values are calculated based on a normalisation substance (Al, Fe or total organic carbon). Once there is change in the normalisation substance, there is a possibility for EF values to change. For example, when EF values were calculated using Al as a normalisation metal, there was no contamination to some metals. However, when Fe was used as a normalisation metal many metals indicated contamination (from minor to extreme contamination). The variation of EF values in this area can be supported by the fact that the area has more than 60% by weight sandy particles (> 75 µm) (Mihale 2017). Despite the fact that the correlation between total organic carbon (TOC) and grain size fraction (> 2 µm) was good (r^2 = 0.92), the correlation between TOC and either Al or Fe was poor (r^2 < 0.01). As a result, variations of the EFs using these normalisation metals are expected. In fact, there was poor correlation between TOC and all the analysed metals in the area (Mihale 2017). This can be evidenced by Figure 2, which indicated very little association between the analysed metals and TOC.

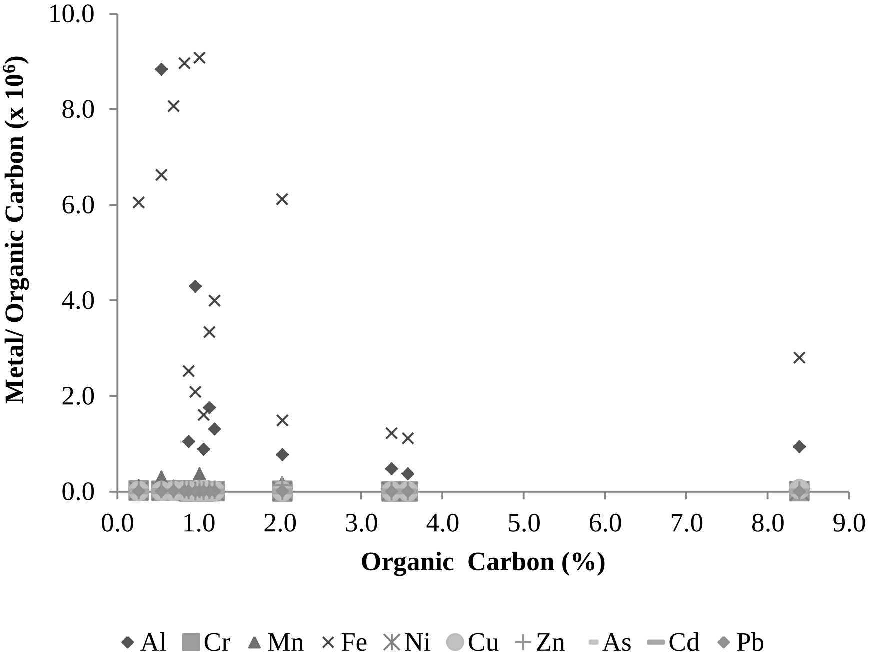

Figure 2: Relationship between metal/organic carbon and TOC in Mtoni sediments.

The findings imply that the whole area of Mtoni is severely contaminated with the selected metals. As observed by Mihale (2017), the magnitude of contamination in this area is indicative of anthropogenic activities. While the riverine zone is characterised by various industrial, domestic and agricultural activities, the marine area are characterised by harbour and fishing activites. The situation is worsened when there are discharges of untreated effluents into the streams and rivers to the estuary.

Conclusion

Multivariate assessment of metal contamination in the Mtoni estuary sediments using enrichment factor, geo-accumulation factor, contamination factor, degree of contamination, modifies degree of contamination and potential contamination index has been applied. The findings have revealed that though EF showed a large variability of contamination, the Mtoni estuary is severely contaminated by all the analysed metals based on the other assessment critria used in this study. Since the magnitude of contamination in this area is alarming, there is an urgent need to institute mitigation measures immediately to reduce the ecological, environmental and human risks taking into consideration that the anthropogenic activities, which are the main sources of these metal pollutants, are going on. Furthermore, a comprehensive study on rivers and streams passing through industrial and residential areas in major cities in Tanzania is recommended to unveil the contamination status of water bodies and the surrounding environs.

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