Environmental Health Risks Due to Anthropogenic Metals in Mtoni Estuary Ecosystem and its Environs, Tanzania

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Abstract: *Mangrove sediment samples from Kizinga and Mzinga creeks of Mtoni estuary were analysed for metals (Al, Fe, Mn, Cr Ni, Cu, Zn, As, Sr, Cd and Pb) to determine their current levels and their anthropogenic impact in a tropical estuarine environment. Standard sampling techniques were used. Samples were digested using a CEM Microwave Accelerated Reaction System (MARS) and analysis was carried out using a High Resolution Inductively Coupled Plasma Mass Spectrometer (HR-ICP-MS). Sandy particles were dominant, with < 6% of OM in estuary and < 9% in tributaries. Metal levels showed neither distinct depth gradient nor variation between seasons. A clear gradient from upstream of Kizinga and Mzinga rivers to estuarine mouth was observed. Pearson correlation matrix, Principal component analysis (PCA) and Enrichment factors (EF) indicated that most metals in Mtoni estuary probably originated from anthropogenic activities except Sr that was probably derived from natural origin. Levels of anthropogenic pollutants are indicative of human induced environmental change and have repercussions on environmental and human health as well as future status of estuary.*

Keywords: Metal levels, Mtoni estuary, Tanzania, Mangrove sediment, Enrichment factors

1 Introduction

Metal contaminants may enter the coastal environment via a number of pathways such as natural processes (including erosion of ore-bearing rocks, wind-blown dust, volcanic activity and forest fires) and processes derived from anthropogenic activities (Dell'Anno *et al.,* 2003; Chatterjee *et al.,* 2007; Tranchina *et al.,* 2008). Anthropogenic sources in mangrove ecosystems arise from industrial effluents and wastes, urban runoff, sewage treatment plants, runoff from agricultural field and domestic garbage dumps (MacFarlane and Bruchett, 1999, 2001; Dell'Anno *et al.,* 2003; Chatterjee *et al.,* 2007; Tranchina *et al.,* 2008). In addition, discarded automobiles and dumping metallic substances have been the common anthropogenic inputs of metals in the marine ecosystem (Kamau, 2002; Praveena *et al.,* 2010). As metals cannot be chemically degraded and are not subject to biological degradation, they are essentially a permanent addition to the aquaticenvironment. As a consequence, they get accumulated locally (MacFarlane and Bruchett, 2001; Defew *et al.,* 2005) and/or transported over long distances (Marchand *et al.,* 2006).

Mangrove sediments can act as sinks and later as sources of contaminants to marine environments (Chi, 2007; Guzzella, Roscioli, & Vigano, 2005; Müller et al., 1999; Pan et al., 2010). Hence, sediments can be used to evaluate pollutant sources, historical trends and fate processes, since the amounts of these compounds in sediments will reflect regional discharges(Lee et al., 2006; Moon et al., 2009; Müller et al., 1999). Contaminated sediments may therefore threaten the lives of organisms in the marine environment due to the toxicity, long time persistence, bioaccumulation and biomagnifications of (Kumar et al., 2008; Zhao et al., 2010). Mangrove environments in coastal areas have been increasingly impacted by increasing human population resulting in anthropogenic perturbations of estuarine and coastal environments adjacent to urban areas (Tam and Wong, 2000). In addition, industrialisation, urbanisation and their associated socio-economic activities have contributed to the input of significant amounts of pollutants into the marine environment, directly affecting the coastal systems. Many mangrove ecosystems are close to urban development areas and are obviously impacted by urban and industrial run-off, which contain the metals in the dissolved or particulate form (Defew *et al.,* 2005; Kamaruzzaman *et al.,* 2008).Direct and indirect disposal of waste products into rivers and estuaries has led to a significant increase in pollutant contamination (Alaoui *et al.,* 2010).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. 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). Therefore, this study was intended to gain knowledge of the current levels of metal contaminants in mangrove sediments in order to understand the extent of metal pollution, fate and bioavailability of the metals in mangrove ecosystems. The knowledge on the concentration and distribution of metals in the sediments will help to identify the source and risks of pollution in the marine systems of Tanzanian coast.

2 Methodology

2.1 Study area

The Mtoni estuary (Figure 1) is located at approximately 3 km south of Dar es Salaam (Tanzania) and is fed by 2 rivers: Kizinga and Mzinga. The creeks have mangrove trees such as *Avicennia marina, Bruguiera gymnorrhiza, Ceriops tagal, Rhizophora mucronata and Sonneratia alba* species growing on both sides (Mlay *et al., unpublished)*. The fresh water input from both rivers is low. An average base-line flow rate of 1 m^3/s is observed in Kizinga River with an increase up to $8m^3/s$ in the rainy season while the water-flow rate of the Mzinga River is unstable and lower than in Kizinga River (Van Camp *et al.,* 2013). Hence, the effect of the river discharges on the hydrodynamics of the Mtoni estuary is very limited. Seven sampling stations (E1 to E7; Figure 1) are located in the fresh water-marine mixing zone with salinities varying from almost fresh to brackish water and with somewhat higher salinities in the dry season (Mangion, 2011). Downstream this mixing zone (stations F5 to F8; Figure 1) the water becomes rapidly sea water while at the stations F1 to F4 more upstream are fresh water.

The Mtoni estuary is highly impacted (PUMPSEA, 2007) by discharges of various origin: (1) the Kizinga and Mzinga rivers draining the mangrove forest (Kruitwagen *et al.,* 2008), (2) the wastewater drainage systems from industrial and residential areas (of a population of around 500,000 inhabitants; URT, 2013), (3) charcoal burning, (4) mangrove harvesting for residential places, (5) salt mining, (6) tourism and (7) urban agriculture (Taylor *et al.,* 2002).

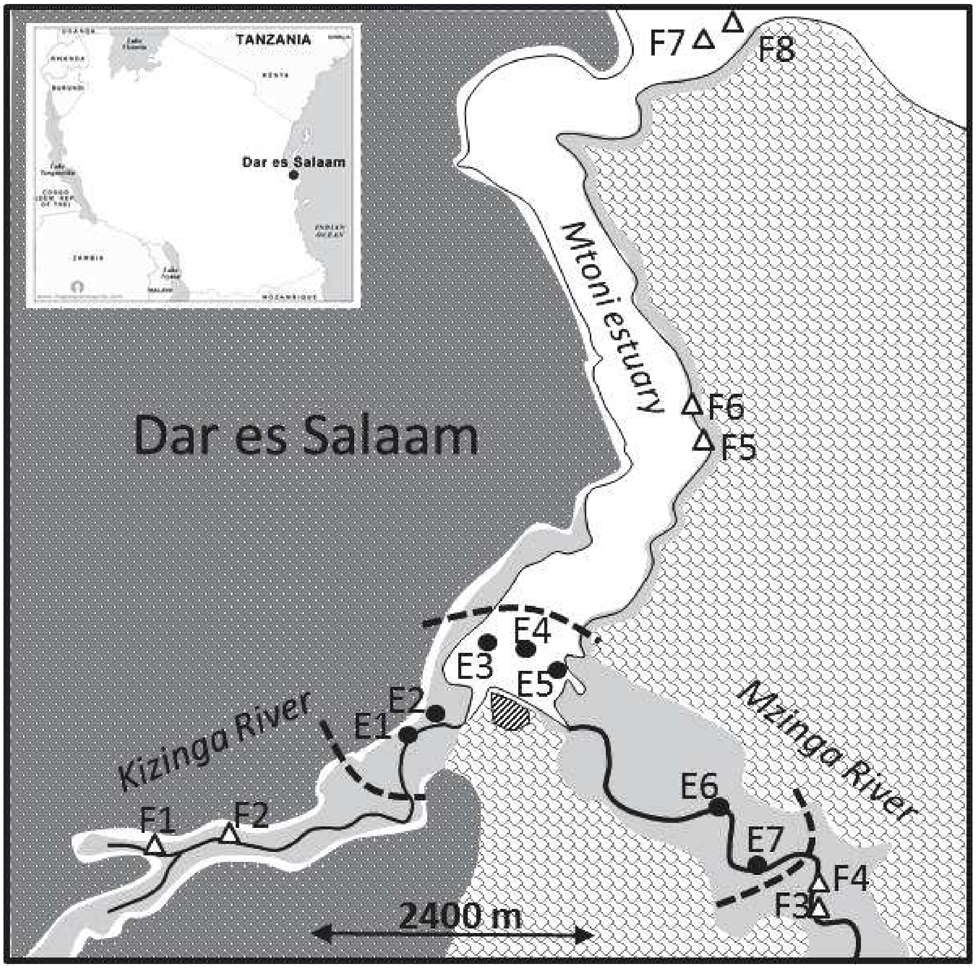

Figure 1: Sampling points in the Mtoni estuary (Dar es Salaam, Tanzania):E1 and E2 in the Kizinga River outlet, E6 and E7 in the Mzinga River outlet and E3-E5 at the confluence of both rivers. Stations F1-F2 in the freshwater Kizinga River, F3-F4 in the freshwater Mzinga River, F5-F6 at the Navy shore and F7-F8 at Kigamboni Seaway are additional sampling points. Dotted lines delimit the estuarine mixing zone. Dotted grey areas are urban zones, light grey areas around the river channel are mangrove forests, structured filled areas are predominantly agricultural zones, and black and white hatched zone is the Mtoni dumping site.

The Kizinga river that drains the urbanised areas of Keko, Chang'ombe, Kurasini and Temeke (approximately 700,000 inhabitants; URT, 2013) is suspected to carry a variety of wastes and discharges originating from agricultural (urban), industrial as well as residential sources (Taylor *et al.*, 2002). The Mzinga river, on the other hand, drains the rural areas of Vijibweni, Tuangoma and Mji Mwema with a population of around 110,000

(URT, 2013). Due to rapid growth of settlements along the Mzinga creek resulting from increased human population, the river is suspected to carry agricultural and residential wastes and discharges presumed to be emptied into the creek. The estuary further receives inputs from the Dar es Salaam harbour which is located near the mouth of the estuary during diurnal tides (up to 5 m amplitude) and from the Mtoni solid waste dumping site located in between the two rivers.

2.2 Sampling

Sampling of sediments was conducted during low tides in the mangrove forest creeks of Kizinga and Mzinga and in the Mtoni estuary until the mouth (Figure 1). A first set of two sampling campaigns was conducted in the estuarine mixing zone (salinity between 20 and 35): one during the wet season and a second one during the dry season. Samples were collected from exactly the same locations (seven sampling stations) identified with a hand-held global positioning system (GPS). Two stations are located in the Kizinga River (E1 and E2), two in the Mzinga River (E6 and E7) and three in the confluence zone of the two rivers (E3, E4 and E5). In addition, in order to better understand the sedimentary characteristics in the studied estuarine mixing zone (samples E1-E7), a complementary sampling campaign was organised during a dry period at 4 representative locations: one in the freshwaters of Kizinga River (positions F1-F2), one in the freshwaters of Mzinga River (positions F3-F4) and two sites in the downstream marine waters close to (positions F5-F6) and at the mouth of the estuary (positions F7-F8) (Figure 1). Note that in the Kizinga River, sample F2 was taken at the junction of the river and a textile wastewater stream, while F1 was taken 400 m upstream of F2 very close to unauthorised human settlements.

Sediment sampling during the sampling campaigns was done as described by EPA, (2001) using a hand corer (30 cm height, 6 cm internal diameter). The corer was gently pushed in the mangrove sediments, closed at its upper end with a lid and smoothly removed by twisting and pulling. The sediments were then pushed out of the corer tube using a piston and sectioned into three segments corresponding to depth intervals of 0-3, 3-6 and 6-9 cm. Sampling of complimentary sediment samples, however, was done by scooping the top 5 cm sediment layer. 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 Chemistry, Vrije Universiteit Brussel (VUB) in Belgium and lyophilised (Leybold Heraus Lyophiliser) prior to the various geochemical analyses.

2.3 Determination of Particle Size

The grain size distribution was determined by an external laboratory at 3 stations with low, medium and high organic matter (OM) content in their sediments (stations E7, E2 and E1, respectively) to test the relation between both variables. Approximately 10 g lyophilised and homogenised sediment sample was prepared by removing salts, OM and carbonates using hydrogen peroxide and hydrochloric acid, respectively. A stable suspension was obtained after rinsing and adding 5 ml of a peptizing agent. The coarse fraction (> 75 µm) was separated by wet sieving on a 75 µm sieve, then dried at 105°C, and finally dry sieved. The grain-size distribution of the fine fractions 2-75 µm and <2 µm was obtained using the Sedigraph 5100 coupled to a Mastertech 51. The precision for 10 consecutive measurements on aliquots of the same sample was around 1% for each grain-size fraction.

2.5 Determination of Metal Concentrations in Marine Sediments

2.5.1 Sample preparation for metal analyses

The lyophilised sediment samples were pulverised (Fritsch Pulverisette) before chemical treatment. For metal analyses, the samples were then 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 the same manner as the samples.

2.5.2 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, Fe), two minor elements (Mn, Cr) and seven trace elements (Ni, Cu, Zn, As, Sr, Cd, Pb,) were analysed in each mangrove sediment sample. Indium at a concentration of 1 µg/L was used as the internal standard. The accuracy and precision of the analytical procedures were assessed using the certified reference material (LGC 6139) and procedural blanks.

2.6 Statistical Analysis

Statistical methods including Student's t-test, Pearson correlation and Principal Component Analysis (PCA) were used to evaluate differences and elucidate the relationships between various parameters. Student's t-test was performed using Microsoft spreadsheet for Windows 2007 whereas Pearson Correlation and Principal component analysis (PCA) were performed using IBM Statistical Package for Social Sciences SPSS (version 20.0) for Windows with the metals) values and the %TOC as variables, and using the concentrations of pollutants in both seasons. In all statistical analyses, a value of $p < 0.05$ was set as a criterion to indicate significant differences in the study.

2.7 Quality Control and Quality Assurance

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% RSD. The percentage recoveries of the measured metals based on the mean values compared to the certified reference materials are given in Table 1. 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 results indicated good agreement between the certified and the obtained values except for Cr and Pb when total metal values are used and for Sr because it lacks a certified value for extractable metals.

Table 1: Certified and observed mean concentrations (mg/kg) of metals in the certified reference material (LGC 6139) and the percentage recovery (n = 7)

	Extractable metals			Total metals		
Metal	**Certified value**	**Obtained value**	**Percent Recovery**	**Certified value**	**Obtained value**	**Percent Recovery**
Al	-	43,300	-	57,000	43,300	76.0
Cr	80.00	94.1	117.6	126.00	94.1	74.7
Mn	-	1,170	-	1,100	1,170	106.4
Fe	-	41,600	-	32,000	41,600	129.9
Ni	38.00	42.1	110.8	44.00	42.1	95.7
Cu	92.00	93.7	101.8	96.00	93.7	97.6
Zn	513.0	580	113.1	530.0	580	109.4
As	27.00	30.7	113.7	-	30.7	-
Sr	-	111	-	154.00	111	72.1
Cd	2.30	2.36	102.6	-	2.36	-
Pb	160.00	149	93.1	176.00	149	84.7

3 Results and Discussion

3.1 Grain Size Distribution

Sandy particles dominated the mangrove sediments in the study area, with sand (> 75 µm) contributing for more than 60% of the weight. The correlation between TOC and the fine grain size fraction (% < 2 µm) was good ($r^2 = 0.92$) this was still the case ($r^2 = 0.82$) between TOC and the mud + silt fraction (% < 75 µm). It is well-known that muddy sediments having a high TOC content but also a high amount of fine grain size fraction (< 2 µm), accumulate by far higher amounts of pollutants than sandy sediments (Baeyens et al., 1991). This means that TOC values can eventually be used to normalise the pollutant concentrations in the sediment versus the mud fraction (% < 2 µm).

In the Mtoni estuary, the high sand proportion implies that the capacity of the mangrove sediments to adsorb the metals, dioxins and dioxin like-polychlorinated biphenyls is medium to low. On the other hand, a high sand fraction favours abiotic processes such as enhanced diffusion of oxygen in the sediment making pollutants more bioavailable due to faster oxidation of organic matter and simultaneous release of associated persistent organic micro-pollutants such as dioxins (Davies & Tawari, 2010; Holmer, 2003).

3.2 Levels of Metals in the Mtoni estuary

3.2.1 Spatial Distribution of Metal Content in Sediments

The dominance of the sand fraction in the Mtoni estuarine sediments favours abiotic processes such as enhanced diffusion of oxygen in the sediment allowing faster oxidation of organic matter (Holmer, 2003; Davies & Tawari, 2010). As a result, there is simultaneous release of organic matter-associated pollutants such as metals, which may reduce the metal burden in the sediments.

Sediments from the Mtoni estuary showed varying spatial distributions in metal levels. Higher metal contents were observed in the upstream stations (F1 and F2 in the Kizinga River and F3 and F4 in the Mzinga River) than in the marine and mixing zone samples. This clearly indicates that the main contribution of metals in the estuary comes from the two rivers, which probably accumulate metal pollutants from various natural and human induced processes (see further sources of metals in the Mtoni estuary).

The depth profiles observed indicate that the estuarine sediments are rather fairly well-mixed and the gradient well smoothed out, making the profiles more or less uniform.The sediment mixing caused by tidal currents in the inter-tidal areas (up to 5m) ensures uniform vertical metal patterns and the high salinity (up to <35; Mangion, 2011) may facilitate metal diffusion in the sediments as previously observed by Li *et al.,* (2000). As a result, relatively low variation of metal levels with depth has been observed. Perhaps, a depth of 9-cm is not sufficient enough to observe any difference in the depth profiles. It will be interesting in the future to study the pollutant profiles in the deeper layers.

3.2.2Metal Contents in the Mtoni mixing zone

The spatial distributions of the metals in the estuarine mixing zone compared to literature data of metals in tropical estuarine or coastal seas sediments (Table 3.3) especially those related to Mtoni estuary or other Tanzanian coastal waters (Mtanga and Machiwa, 2007; Kruitwagen *et al.,* 2008; Rumisha *et al.,* 2012). Higher Al content was observed in Kizinga station E1, confluence stations E4 and Mzinga stations E6 and E7. Lowest Al content was observed at confluence station E5. The ranges of Al values observed in the mixing zone were within the range of the values observed by Kruitwagen *et al.,* (2008) and higher than those observed by Rumisha *et al.,* (2012).

The Cr content in the Kizinga station E1 was higher than in other stations in the mixing zone. A more or less similar Cr content was also observed in Mzinga stations E6 and E7 and in confluence stations E3 and E4. Lower Cr content was observed in Kizinga station E2 and confluence station E5. The Cr ranges in the Mtoni were within the range of values observed by Kruitwagen *et al.,* (2008), similar to values observed by Mtanga and Machiwa, (2007) and higher than those observed by Rumisha *et al.,* (2012) in a similar tropical environment (Table 3.3).

The contents of Fe and Mn showed a similar trend. Fe and Mn contents in the mixing zone were higher in the Kizinga station E1 than in both Mzinga stations E6 and E7. However, all were higher than the values in the Kizinga station E2 and in stations at the confluence region. Fe ranges observed in this study were within the range of values observed by Kruitwagen *et al.,* (2008) and higher than those observed by Rumisha *et al.,* (2012). On the other hand, Mn ranges in the Mtoni were higher than those observed by Rumisha *et al.,* (2012).

Ni, Cu and Pb contents in the sediments of the Mtoni mixing zone displayed a similar trend. Their levels were high in Kizinga station E1 and confluence stations E3 and E4. Whereas lower values of the metals were observed at confluence station E5, more or less similar values were observed in Kizinga station E2 and Mzinga stations E6 and E7. The ranges of Ni and Cu values observed in this estuary were within the range of values observed by Kruitwagen *et al.,* (2008), but higher than those observed by Rumisha *et al.,* (2012).

Table 2: Comparative Account of Metal Concentrations (µg/g dw) in Different Tropical Marine Sedimentary Environments

Study site	Mtoni estuary, Tanzania[a]	Mtoni estuary, Tanzania[b]	Mzinga Creek, Tanzania	Mtoni estuary, Tanzania	Msimbazi, Tanzania	S. Buloh & S. Bongsu, Singapore	Hugli estuary, India	Cross River, Nigeria	San Jose lagoon, Puerto Rico	Andaman Islands, India
Al	18,200-48,000	3,300-31,900	-	5,430–61,900	461	-	-	-	-	2,938-4,384
Cr	14.2-35	5.4-460	22.7	14.4-6,240	1.0	16.6–32.1	12.1–84.4	19.2–37.9	-	12.7-20.4
Mn	56-133	32.3-680	-	-	23	-	228.3–716.9	-	-	29.2-134.4
Fe	9,500-25,200	1,600-23,510	-	8,070–59,100	461	-	-	598.2–993.2	1,600–4,600	2,638-4,888
Ni	4.6-14.7	1.8-80	-	7.9–156	0.35	7.44–11.7	6.86–52.5	14.2–35.0	-	7.04-12.0
Cu	6.3-14.8	1.5-400	9.50	3.70–4,050	0.3	7.06–32.0	4.30–45.3	23.0–36.2	29.0–211.0	80.9-87.9
Zn	24.8-77	6.9-260	35.1	43.9–2,450	4.0	51.2–120.2	22.96–205.0	126.4–212.3	266.0–530.0	12.2-23.0
As	1.8-7.3	2.6-8.1	-	-	0.2	-	-	-	4.50–24.0	-
Sr	18.9-34	na	-	-	-	-	-	-	-	-
Cd	0.05-0.10	0.03-0.37	1.05	0.9–28.1	0.01	0.18–0.27			0.20–4.70	0.8-1.52
Pb	6.9-13.2	2.0-32.8	14.6	47.2-385	0.8	12.3-31.0	n.d-44.5	7.2-26.6	16.0-548.0	3.90-5.40
Reference	This Study	This Study	Mtanga & Machiwa, (2007)	Kruitwagen *et al.*, (2008)	Rumisha *et al.*, (2012)	Cuong *et al.*, (2005)	Chatterjee *et al.*, (2007)	Essien *et al.*, (2009)	Acevedo-Figueroa *et al.*, (2006)	Nobi *et al.*, 2010

[a] Values from brackish sediment stations E1 to E7 in the mixing zone; [b] Values from stations F1 to F8 (freshwater to marine sediments); n.d = not detected

Cu ranges in this study were also similar to the values observed by Mtanga and Machiwa, (2007). Pb ranges in this study were lower than those observed by Kruitwagen *et al.,* (2008) and Mtanga and Machiwa, (2007), but higher than the values observed by Rumisha *et al.,* (2012).

Lower values of Zn were observed in the Mzinga stations E6 and E7 than in Kizinga stations E1 and E2 and confluence stations E3 and E4. Confluence station E5 had the lowest values of all. The Zn values in the sediments of the Mtoni mixing zone were higher than the values observed by Rumisha *et al.,* (2012), similar to those observed by Mtanga and Machiwa, (2007) and lower than those observed by Kruitwagen *et al.,* (2008) (Table 2).

A high As content was observed in Kizinga station E1 and Mzinga stations E6 and E7. While lower As values were observed in the confluence station E5, a more or less similar As content was observed in Kizinga station E2 as well as in confluence stations E3 and E4. The range of As observed in the Mtoni estuary was higher than the values observed by Rumisha et al., (2012).

Sr concentrations in the Mtoni mixing zone were all more or less similar. A slightly higher Sr content was observed in confluence station E4 and slightly lower Sr was observed in Kizinga station E2. No data for comparison were available in literature from similar tropical marine environments. The Cd content in the mixing zone was higher in Kizinga station E1 as well as in the confluence stations E3 and E4. In other stations, Cd content was more or less similar. The range of Cd values in the estuary was lower than that observed by Kruitwagen et al., (2008) and Mtanga and Machiwa, (2007), but higher than the values observed by Rumisha et al., (2012) in a similar marine environment.

3.2.3 Metal Contents in Additional Samples

Metal levels in the additional sampling stations (F1 – F8) are given in Table 3. Contents of Cr, Mn, Fe, Ni and Cu were the highest at the riverine station F2 while Zn, Cd and Pb were the highest at riverine station F1 of the Kizinga River. As levels were the highest at stations F3 and F4 in the Mzinga River. A clear gradient from the Kizinga upstream station F1 to the estuarine mouth (F8) is observed in the dry season for all metals except As (Table 3). This is also the case for most metals from the Mzinga station F3 to the estuarine mouth (F8) when omitting station F4.

The ranges of metal concentrations in the additional samples (end members) were, except for Al and Fe, all higher than those in the mixing zone samples. They are now more comparable to those of Kruitwagen *et al.,* (2008) except that the highest levels of Cr, Cu, Cd, Zn and Pb which were still about 10 times higher than our values. However, those high values were all related to one station close to our F2 station in the Kizinga River, which is also the most contaminated in our study. The observed values were all higher than the values reported by Rumisha *et al*. (2012), but the latter studied the coastal area of Tanzania which is a system that is still more diluted than most of the downstream sample stations in our study.

Table 3: Metal Concentrations (μg/g dw) in the additional samples from the Mtoni estuary

Metals	**Riverine**				**Marine**			
	Kizinga		**Mzinga**		**Navy shore**		**Kigamboni**	
	F1	**F2**	**F3**	**F4**	**F5**	**F6**	**F7**	**F8**
Al	31,900	7,900	13,900	4,800	17,600	12,700	3,300	4,120
Cr	27.8	460	16.4	6.20	15.5	11.6	5.38	6.46
Mn	384	680	375	163	80.4	80.4	32.3	35.4
Fe	12,400	23,510	9,200	3,600	7,400	5,600	1,600	2,000
Ni	12.1	80	7.23	2.70	5.78	4.33	1.84	2.10
Cu	16.4	400	9.35	4.91	9.12	7.20	1.52	1.94
Zn	260	149	56.4	24.6	38.2	31.4	6.9	8.5
As	3.34	2.61	7.70	8.13	3.39	3.78	4.96	5.10
Sr	na	na	na	Na	na	Na	na	Na
Cd	0.37	0.24	0.10	0.03	0.09	0.07	0.04	0.05
Pb	32.8	10.3	10.4	4.76	10.6	7.92	2.18	2.01

na= not analysed

3.2.4 Comparison with Sediment Quality Guidelines

To determine if the metals in the Mtoni estuary pose a threat to marine biota, the metal levels were compared to international sediment quality guidelines because such guidelines specific for the region are not available. Different sediment quality guidelines including the *National Oceanic and Atmospheric Administration* (NOAA), Canadian Council of the Ministers of the Environment (CCME), Ontario Ministry of Environment Screening level Guidelines and Probable effect levels (PEL) were used for comparison and the values for 7 metals (for Al, Mn, Fe and Sr no guideline values exist) are given in Table 4.

Table 3: Sediment Quality Guidelines for different metals (µg/g dw)

	NOAA		CCME	PEL	ONTARIO
	ERL	ERM	(TEL)		(LEL)
Al	-	-	-	-	-
Cr	81	370	37.3	90	26
Mn	-	-	-	-	-
Fe	-	-	-	-	-
Ni	20.9	51.6	18	36	16
Cu	34	270	35.7	197	16
Zn	150	410	123	315	120
As	8.2	70	5.9	17	6
Sr	-	-	-	-	-
Cd	1.2	9.6	0.6	3.5	0.6
Pb	46.7	218	35	91.3	31

ERL = effect range low, ERM = effect range median, TEL = threshold effect level; PEL = probable effect level; LEL lowest effect level

Comparing the metal levels in the Mtoni estuary and the different sediment quality guidelines, it can be shown that Cr, Ni, Cu, Zn, As, Cd and Pb had lower values compared to CCME, PEL, TEL and NOAA guideline values. Ni, Cu, Zn, Cd and Pb had lower values than the lowest effect levels (LEL) described by the Ontario Ministry of Environment, whereas Cr and As levels were slightly higher that the LEL at the upper range. Using the US EPA toxicity classifications, As was moderately polluted (US EPA range for As is 3-8 ug/g), while other elements were not. This indicates that adverse biological effects related to these metals should be rather limited. However, Kruitwagen *et al.,* (2006) and De Wolf and Rashid (2008) observed some adverse effects on mudskippers and molluscs, respectively.

4 Sources of metals in the Mtoni sediments

4.1 Pearson Correlations and Principal Component Analysis (PCA)

In order to determine the relationship between metals and TOC, Pearson linear correlation matrix was generated and the coefficients are presented in Table 4. PCA was also employed and the results are presented in Table 5. A principal component (PC) is considered significant when its eigenvalue is greater than 1. The measured metal values and %TOC were used as variables (total 12), with the concentrations of the metals in the different sampling stations during wet and dry seasons as objects (total 42). The application of PCA indicated that the 12 variables can be represented by 3 new PCs that accounted for 88.82% of the total variance in the original data sets (Table 5). A two dimensional score plot is given in Figure 10.

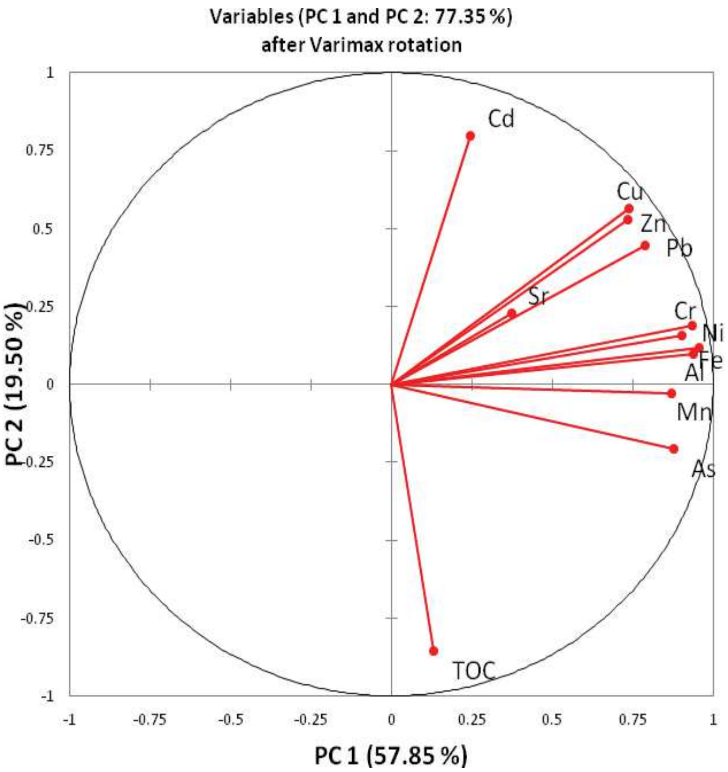

Figure 10: A two-dimensional score plot of metals in relation to %TOC in the Mtoni estuary

Combining the results of the Pearson correlation matrix (Table 6) and the PCA (Table 7), we can repartition the compounds in 3 groups: (1) Al, Cr, Mn, Fe, Cu, Ni, Zn, As and Pb form PC1, explaining 57.85% of the variance. Correlation coefficients between those elements range from 0.531 to 0.989; (2) Cd and TOC form PC2, explaining 19.5% of the variance. They are strongly anti-correlated with correlation coefficient equal to -0.51; and (3) Sr, which does not correlate with any element forms PC3 explaining 11.47% of the variance.

Table 6: Pearson Correlation Coefficients for metals and sediment properties in the estuary (n = 42)*

	Al	**Cr**	**Mn**	**Fe**	**Ni**	**Cu**	**Zn**	**As**	**Sr**	**Cd**	**Pb**	**%TOC**
Al	1	0.98	0.82	0.98	0.91	0.76	0.74	0.85	0.58	0.37	0.85	-0.003
Cr		1	0.81	0.99	0.93	0.84	0.82	0.83	0.62	0.47	0.89	-0.05
Mn			1	0.82	0.73	0.65	0.64	0.78	0.47	0.19	0.66	0.06
Fe				1	0.93	0.81	0.79	0.88	0.57	0.42	0.86	0.01
Ni					1	0.79	0.78	0.80	0.55	0.47	0.85	0.02
Cu						1	0.89	0.53	0.57	0.73	0.88	-0.30
Zn							1	0.58	0.56	0.69	0.81	-0.26
As								1	0.49	0.15	0.62	0.20
Sr									1	0.59	0.59	-0.20
Cd										1	0.68	-0.51
Pb											1	-0.22
%TOC												1

- Significant values at α= 0.05 (two-tailed) are in bold

Table 7: Rotated Principal Component (PC) Matrix

	Principal Components (88.82%) [a]		
	PC1 (57.85%)	**PC2 (19.50%)**	**PC3 (11.47%)**
Al	**0.883**	0.009	0.051
Cr	**0.875**	0.035	0.067
Mn	**0.760**	0.001	0.012
Fe	**0.917**	0.014	0.047
Ni	**0.814**	0.025	0.051
Cu	**0.548**	0.320	0.038
Zn	**0.538**	0.280	0.036
As	**0.768**	0.043	0.056
Sr	0.139	0.052	**0.773**
Cd	0.060	**0.633**	0.183
Pb	**0.623**	0.198	0.064
TOC	0.017	**0.731**	0.000

[a] The percentage in brackets indicates the explained contribution of principal component to the total variance after varimax normalisation.

In aquatic sediments, the metal distribution is governed by many factors and processes: (1) the nature of the sediment (clay/sand/salt fractions, nature and amount of OM), (2) physical processes (mixing, advection, and diffusion), (3) redox processes, and (4) anthropogenic sources. However, it is not always necessary to have all that information to understand the metal distribution in the sediment. Based on the PCA loading and correlation coefficient results, metals in the estuary can be explained by some features as follows:

Principal Component 1: Cu, Ni, Cr, Mn, Zn, Al, Fe, As, Pb
These correlations suggest a contamination of both ferro and non-ferro metals associated with human activities in electronics and related works (Cu), paints and pigments (Cr), metallurgy and metal construction works (Cr, Mn, Cu, Ni, Al, Fe, Pb), anti corrosion and batteries (Zn), paints, pigments and as additive in petroleum fuel (Pb). Arsenic is extensively used in industry, farming and in agriculture while small amounts are used in, amongst others, the glass and ceramics industry. Arsenic derivates such as arsenates, arsenites as well as arsenic and arsenic acids are used as pesticides and herbicides (De Gieter and Baeyens, 2005). Due to the proximity of the Dar es Salaam harbour, it is likely that these metals are also transported from the harbour. Tides may facilitate the transport of metals upstream into the estuary.

Principal Component 2: Cd and TOC
Cd is a non-ferro metal linked with an anthropogenic source. This is clearly indicated by anthropogenic activities such as paints and pigments, metallurgy and metal constructions and wood preservative. Cd and TOC are negatively correlated. Despite having several anthropogenic activities in common, the source of Cd should be different from those for Cu, Ni, Cr, Mn, Zn, Al, Fe, As, Pb.

Principal Component 3: Sr
Sr is not correlated with any other metal or TOC. Though the abundance of Sr is lower (about 0.037%) in the earth's crust, it is one of the more abundant elements in sea water (0.0013%). The origin of the Sr levels in the Mtoni sediments should be clearly different from the sources of all other investigated elements.

4.2 Enrichment Factors (EF) of the Metals

Enrichment Factors for the metals in the Mtoni estuary were determined relative to the crustal abundance. EF values were normalised to Al (Figure 11) after correction of Al levels in the Mtoni sediments based on the percentage recovery. EF values were interpreted as follows: EF <1 = no enrichment, 1<EF<3 = minor enrichment, 3<EF<5 = moderate enrichment, 5<EF<10 = moderate severe enrichment, 10<EF<25 = severe enrichment, 25<EF<50 = very severe enrichment and EF<50 = extremely severe enrichment (Acevedo-Figueroa, 2006; Chen *et al.*, 2007; Essien *et al.*, 2009).

The EF values in the mixing zone samples indicated no enrichment for all metals except Zn, As, Cd and Pb. Whereas minor enrichment (EF <3) was observed for Zn, Cd and Pb, As was enriched in all mixing zone samples (EF values 3-6). Exceptionally high enrichments were observed in additional samples in the riverine stations (F1 and F2 in the Kizinga River and F3 and F4 in the Mzinga River). Kizinga station F2, for example, situated close to where wastewaters from the textile mill enters the Kizinga River, was highly enriched with all metals (EF >4) except Sr. Arsenic (As) was also exceptionally enriched in all the riverine as well as the marine samples (up to EF = 59 in Mzinga station F4, Figure 3.2). Similar As enrichment in all samples was observed in the intertidal sediments of Mbweni, Kunduchi, Msasani, Msimbazi, Mji Mwema and Geza Ulole in the Dar es Salaam coast (Rumisha *et al.,* 2012).

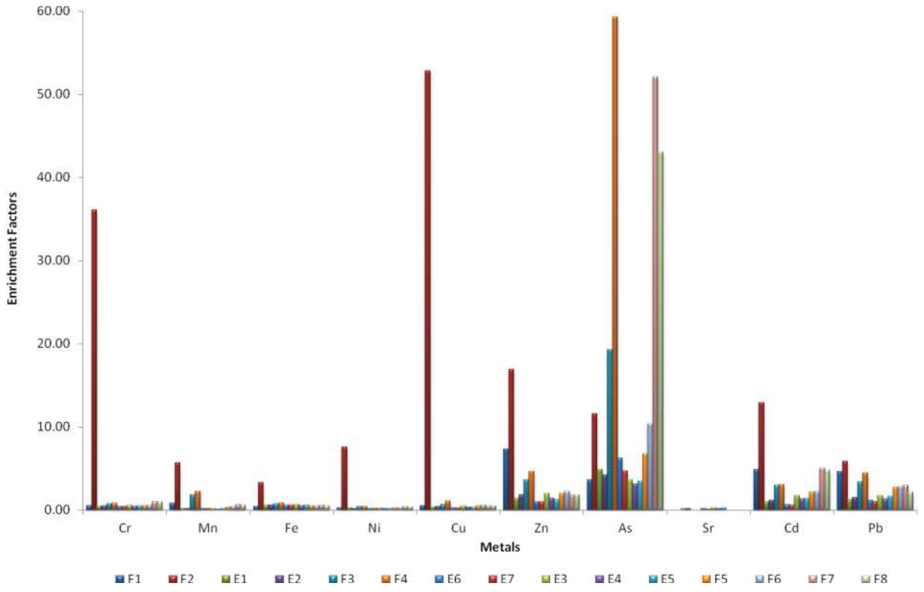

Figure 11: Metal Enrichment Factors in samples from the Kizinga River (E1, E2, F1 and F2), Mzinga River (E6, E7, F3 and F4), confluence stations (E3, E4, E5) and downstream area (F5, F6, F7 and F8) of the Mtoni estuary.

Concentrations of metals in sediments can be important indicators of toxicological risk, especially when they are substantially above natural levels. To be able to appreciate such increased levels, EF values were calculated. Higher EF values in the Mtoni estuary for several metals at various sites clearly indicate the effect of anthropogenic activities. A similar trend for Cu, Cr, Zn and Pb in the Mtoni estuary (Kruitwagen *et al*., 2008) and for Cr, Zn, As, Cd and Pb in the coastal area of Dar es Salaam (Rumisha *et al*., 2012) was observed. Highly enriched values in the riverine zone as compared to marine and mixing zones could be due to anthropogenic activities in and around the river banks. Agricultural, industrial as well as domestic activities could be the main sources of the metals particularly in this area where (i) very few residents are connected to proper sewage systems, (ii) most industries discharge effluents without proper treatment and (iii) most discharges are directed into the valleys, rivers and ocean implicitly or explicitly (Rumisha *et al*., 2012). For example, stations F1 and F2 in the Kizinga River are close to unauthorised human settlements. In addition, station F2 receives effluents from the nearby households and it is close to a textile factory, which may supply industrial effluents containing various amounts of metals. In the case of Mzinga stations F3 and F4 and estuarine stations F5 and F6, the enrichment could be due to unauthorised human settlements where solid wastes from urban agriculture, households and small industries are trashed away. What is observed in the marine samples (F5-F8) could be due to cumulative effect of pollution from human and industrial sources and the transport of metals from the two rivers. As Figure 3.2 indicates, Al and Fe have background enrichments with no anthropogenic effects. Other analysed metals, however, exceeded the expected natural background levels and therefore have an anthropogenic origin. Metals exceeding background levels must be carefully monitored because they are a potential threat to the ecosystem and humans.

5.0 Conclusion

Trace metal levels in the Mtoni estuarine sediments do not show a gradient with neither depth nor seasonal variation between the wet and the dry season. A clear decreasing concentration gradient in downstream direction from Kizinga and Mzinga rivers towards the mouth of the estuary is observed for almost all elements except As.All the metals showed high enrichment factors. The highly enriched areas in the riverine zones as compared to marine and mixing zones could be due to local anthropogenic activities. Agricultural, industrial as well as domestic activities could be the main sources of the metals particularly in this area where (i) very few residents are connected to proper sewage systems, (ii) most industries discharge effluents without proper treatment and (iii) most discharges are directed into the valleys, rivers and ocean implicitly or explicitly (Rumisha *et al*., 2012). For example, stations F1 and F2 in the Kizinga River are close to unauthorised human settlements. In addition, station F2 receives effluents from the nearby households and is close to a textile factory, which could supply industrial effluents containing variable amounts of metals.

Between the stations F1 and F2 there is a small metal industry for making local cooking utensils. In the case of Mzinga stations F3 and F4 and estuarine stations F5 and F6, the enrichment could be due to unauthorised human settlements where solid wastes from urban agriculture, households and small industries are trashed away. Since highly enriched enrichment factors are observed for several toxic metals they should be carefully monitored because they are a potential threat to the ecosystem and humans. The pollutant levels observed in sediments of the Dar es Salaam region indicate possible ecological and human risks that may emanate from these contaminants.

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