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Spatial distribution of heavy metals in Msimbazi River mangrove sediments in Dar es Salaam coastal zone, Tanzania

Agnes MRUTU[1,2], Hudson H. NKOTAGU[1], Gebhard B. LUILO[3]

1- Department of Geology, University of Dar es Salaam, PO Box 35060, Dar es Salaam, Tanzania

2- Department of Chemistry, University of Missouri-Columbia, 125 Chemistry Building, 601 S. College Avenue, Columbia, MO 65211, USA

3- Department of Chemistry and Chemical Biology, University of New Mexico

1-University of New Mexico, Albuquerque, NM 87131, USA

agnesmrutu@gmail.com

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ABSTRACT

This paper reports on distribution of heavy metals in sediments of the Msimbazi River mangrove forest. The levels of heavy metal decreased with increasing depth as well as with increasing distance from mangrove to the Indian Ocean shoreline. The total metal levels of heavy metals ranged from 1000 to 27000 ppm (iron, Fe), 16 to 173 ppm (zinc, Zn), 3.1 to 76 ppm (lead, Pb), 13.2 to 71.2 ppm (chromium, Cr), 6.9 to 22.5 ppm (nickel. Ni), 4.1 to 17.4 ppm (cobalt, Co) and 0.03 to 3.90 ppm (cadmium, Cd). These observations indicate that Msimbazi River sediments have high metal retention. This is attributed, among other factors, to clay contents at 0 - 50 cm core that ranged from 15.78 to 85.04 % and its content decreased with increasing depth. Thus, the Msimbazi River sediments play a role in filtering heavy metals from the wastewater flowing through it prior to its discharge into Indian Ocean.

Keywords: Dar es Salaam, heavy metals, mangroves, Msimbazi River, sediments.

1. Introduction

Dar es Salaam is a fast growing city in Tanzania with inefficient industrial and domestic waste treatment infrastructures (DeWolf et al., 2001). As a result the untreated or partially treated industrial and municipal wastewaters are discharged in the environment and are drained to the ocean by the rivers flowing through the city (Mgana and Mahono, 1997; DCC 2004). The Msimbazi River is the river that passes through the city center and is reported to be receiving heavy loads of untreated or semi-treated wastewaters from the city (Bwathondi et al., 1991). A few studies conducted in sediments of the Msimbazi River reported high levels of heavy metal pollutants (A'khabuhaya and Lodenius, 1988) and pesticides (Mwevura et al., 2002). There are also other rivers in the city that drain pollutants into the Indian Ocean through Mtoni and Mbweni mangrove forests where sediment may act as a sink. The coastal sediment samples from the Dar es Salaam harbor (Machiwa 1992) and Msasani Bay (Muzuka, 2007) indicated high levels of heavy metals and so were sediments from mangrove forests in Mtoni (DeWolf et al., 2001), Msimbazi and Mbweni (Mremi and Machiwa, 2003).

Thus, in the absence of efficient wastewater treatment systems, mangrove sediments are the only important sink of heavy metals from wastewaters flowing through mangrove forests (UNEP, 1990). Unfortunately, accumulation of heavy metals and other pollutants in the sediments may affect the well-being of faunal community because mangroves are well-

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known for providing breeding sites and shelters to marine juvenile fish (Taylor et al., 2003). It is well-documented in the literature that heavy metals can be bio-accumulated in aquatic flora (Fargašová et al., 1997; Conti and Cecchetti, 2003) and in tissues of fish (Maheswari et al., 2006; Alibabić et al., 2007) and sediment texture may influence species abundances and distribution (Mlay et al., 2001). On the other hand human beings may be exposed and impacted by heavy metals through food chain. *Itaitai* disease (Nogawa, 1981; IPCS, 1992) and *minamata* disease (Harada 1972; Tsubaki and Irukayama 1977; Hirada 1995) are classic cases of heavy metal poisoning in humans reported in Japan. Although there are some studies that have investigated heavy metal pollution in sediments in Dar es Salaam coastal zone, these studies were limited to samples obtained from 0-25 cm depth in other mangrove systems in the outskirts of the city or in shoreline sediments. Apparently, no detailed study has reported heavy metal distribution in sediments of Msimbazi River mangrove forests which act as a natural filter of wastewaters draining from the Dar es Salaam city center and suburbs. Thus, we herein report the spatial distribution of cadmium (Cd), copper (Cu), chromium (Cr), iron (Fe), nickel (Ni), lead (Pb), zinc (Zn) in the Msimbazi River mangrove sediment located at the centre of the Dar es Salaam city. This study would shade light on the metal retention capacity of the mangrove system and its potential implication to benthic fauna.

2. Materials and methods

2.1 Study area and sampling sites descriptions

The study was carried out in the Msimbazi River mangrove forest located at the river mouth within the city of Dar es Salaam (DSM) at latitude 6^{o} 47' S and longitude 39^{o} 00' E (Figure 1). The Msimbazi River drains most of the waste from the city to the Msimbazi River which is covered by dense mangrove trees.

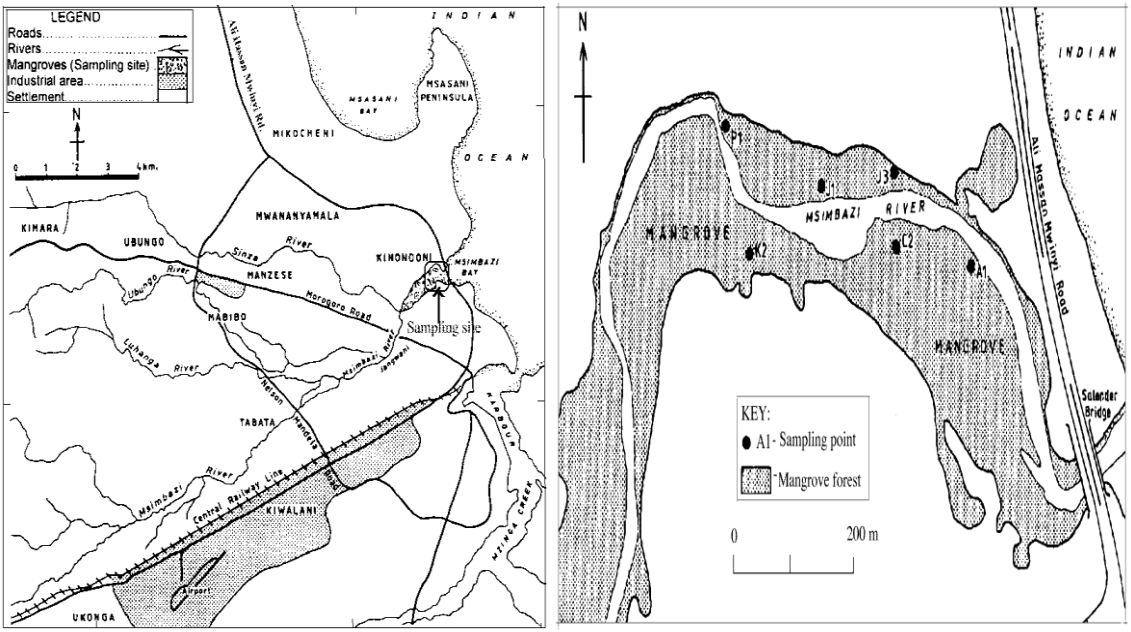


Figure 1: Sketches of study are (left) and sampling sites (right)

The sediments in these mangroves may be capable of restricting the influx of organic and inorganic pollutants into the ocean. Six sampling points were established with three points taken on each side of the river banks, i.e. points A1, C2 and K2 in the southern river bank and points J3, J1 and P1 on northern river bank (Figure 1). The sediment samples were collected

using a sediment corer from the study sites during low tide. Undisturbed sediment cores of 100 cm deep below sediment surface were collected and a total of six sediment cores were obtained.

Each sediment core was divided at intervals of 25 cm: 0 - 25 cm, 26 - 50 cm, 51 - 75 cm and 76 - 100 cm cores to produce four samples for each site. A total of 24 samples, each weighing 500 g, were collected and the samples were stored in clean polyethylene bags. The pH, electrical conductivity (EC) and redox potential were determined at the sampling site whereas cation exchange capacity (CEC), organic matter (O.M) content, sediment texture, were determined at the Department of Geology, University of Dar es Salaam. Sample preparation and heavy metal concentrations were analyzed at the Southern and Eastern Africa Mineral Center (SEAMIC) in Dar es Salaam, Tanzania

2.2. Determination of sediment pH and EC

The pH was measured *in situ* by using pH meter that was first calibrated using dilute standard buffers (pH 4 and pH 7). The pH values were taken in duplicate by immersing a well rinsed and dried electrode in sediment slurry and taken out when pH reading stabilized. The redox potential (mV) was measured by a high impedance voltmeter with calomel as a reference electrode. Redox electrodes were calibrated in pH adjusted 0.3 M phosphate buffers, saturated with chinhydron prior to taking any measurements in sediment samples. The EC meter was calibrated at room temperature. Sediment-distilled water, in a ratio of 1:1, was shaken well and EC (mSm/cm) was determined by dipping the electrode in the slurry.

2.3. Determination of sediment CEC and organic matter content

Determination of CEC of sediment samples was performed at the Department of Geology at the University of Dar es Salaam according to the method described in Allen (1989). An aliquot of 10 g of sediment sample that was oven dried at 100 ^{o}C was extracted with 250 mL ammonium acetate solution. The residues were repeatedly washed with portions of industrial alcohol solution and all washings were discarded. The residue were leached with approximately 30 mL portions of KCl solution to displace adsorbed NH_4^+-N and left for sometimes to allow filtering in between additions and continued until 250 mL was collected. The NH_4^+-N content was determined in the leachate by distillation of an aliquot with MgO followed by titration with M/140 HCl. The O.M content in oven-dried sediment samples was first extracted using the rapid dichromate oxidation technique in accordance with the Walkley-Black Method (Nielson and Sommers, 1982). The OM content in the digestate was quantified by back titration with 0.5 $FeSO_4$ solution with a few drops of ferroin indicator. A correction factor of 1.33 was used to adjust for organic carbon recovery in the samples at the digestion step and results were expressed as percent O.M (% O.M).

2.4. Determination of sediment texture

The particle size pipette method described in Gee and Bauder (1982). It involved a pre-treatment stage where 80 g of oven dried sediment samples were placed into a 200 mL flask and 100 mL of water was added followed by 10 mL of 1 M sodium acetate. The mixture was centrifuged for 10 minutes at 1500 rpm. The clear supernatant solution was poured off and the remaining sediment suspension was washed with 50 mL of distilled water. This mixture also was centrifuged and supernatant was decanted. This pre-treatment step was intended to

remove carbonates and soluble salts. Any organic matter in sediment suspension was oxidized by addition of 4 mL of H2O2 followed by heating until frothing ceased.

Separation of sand: The treated sediment mixture was filtered through a 270 mesh sieve placed on the powder funnel into a 1 L graduated cylinder. The sand was washed several times with distilled water. The filtrates were collected in the same cylinder and stored for analysis of silt and clay. The sand was placed in a pre-weighed evaporating dish (W_{dish}) and was oven-dried at 105 ^{o}C for an hour followed by cooling in a desiccator. The sand was transferred into a 300 mesh sieve using fine paint brush and was shaken for 15 minutes to remove traces of silt. The weight of silt (W_{silt}) in the dish was subtracted from total weight to obtain actual weight of sand (W_s).

$$Weight\ of\ sand, W_s = (W_{dish} + W_s) - W_{dish} - W_{silt} \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (1)$$

Separation of silt and clays: The pipette method was used to separate silt and clay fractions. 10 mL of 5% sodium hexametaphosphate solution was added in the filtrate (silt and clay) in the 1 L graduated cylinder and was covered with stopper. The mixture was shaken end-over-end for one minute. After settling for 4.60 minutes at 22 ^{o}C, a 25 mL volume sub-sample was taken from the depth of 10 cm using a pipette. The solution was placed in a pre-weighed evaporating dish (W_{dish}) and was dried at 105 ^{o}C for an hour followed by cooling in a desiccator. The weight of this sample represented the silt and clay fraction (W_p). Another 25 mL taken at a depth of 10 cm after 7.60 hours was placed in an evaporating dish and was also dried at 105 ^{o}C for an hour followed by cooling in a desiccator. The weight of this sample represented the weight clay fraction (W_c). Finally, the weight of silt fraction was obtained by subtracting W_c from W_p and add weight of silt collected from sand fractionation.

$$Weight\ of\ silt\ and\ clay, W_p = [(W_{dish} + W_p) - W_{dish}] \times \frac{1000\ mL}{25\ mL} \ \ldots\ldots\ldots \ (2)$$

$$Weight\ of\ clay, W_{clay} = [(W_{dish} + W_c) - W_{dish}] \times \frac{1000\ mL}{25\ mL} \ \ldots\ldots\ldots\ldots\ldots\ldots \ (3)$$

$$Total\ weight\ of\ silt, W_{silt} = [W_p - W_c] + W_{silt\ (from\ sand\ fractionaion)} \ldots\ldots\ldots\ldots \ (4)$$

The weight of the remaining sediment samples was determined by adding 10 mL of 1 M $CaCl_2$ and 1 mL of 1 M HCl to the remaining suspension in the cylinder, to prevent the formation of calcium carbonate as well as promote flocculation. Once flocculation occurred the clear solution was removed using a siphon and discarded and the sediment flocculant was poured into the evaporation dish. The sample was oven-dried at 105 ^{o}C for an hour, cooled and weighed to obtain weight of remaining sample (W_r). Thus, the total weight of all fractions was calculated by adding all fractions. This weight is subtracted from the original weight of oven dried sample to account for any loss in weight in the procedure. The weight of each sediment fraction was expressed as percent of total weight of all components, W_t.

$$Weight\ of\ all\ components, W_t = W_{sand} + W_{silt} + W_{clay} + W_r \ \ldots\ldots\ldots\ldots\ldots\ldots \ (5)$$

2.5. Determination of heavy metals in sediments

The sediment sample preparation and determination of heavy metal concentrations of Cd, Cr, Co, Ni, Zn, Pb and Fe in sediments were performed according to procedures described in the analytical methods of atomic absorption spectrometry (Perkin-Elmer Corporation, 1994). For

each metal determined, the instrument was calibrated using working standards for different elements at different concentrations prepared in 5 % (v/v) HCl. The calibration curves were made for each element. Each heavy metal was determined using atomic absorption spectrophotometer model GBC 906AA (GBC Equipment Pvt Ltd, Victoria, Australia) with oxy-acetylene flame and hollow cathode lamps (HCL) of wavelengths 228.80 nm for Cd, 240.73 nm for Co, 324.75 nm for Cu, 357.87 nm for Cr, 248.33 nm for Fe, 232.00 nm for Ni, 217.00 nm for Pb and 213.86 nm for Zn.

3. Results and discussions

3.1 Physical chemical parameters

The results from pH and EC determinations indicated that pH ranged from 6.0 to 7.6 and EC ranged from 5.0 to 15.3 mSm/cm respectively. However, there was no significant variation of pH and EC of sediment with depth (Figure 2). The percent O.M content was generally lower at 0 - 25 cm core than at 26 - 50 cm cores and it then gradually decreased as depth increased from 26 - 50 cm to 76 - 100 cm (Figure 3). There was rapid decrease in redox potential with increasing depth in each sampling site and its values ranged from –400 to 150 mV. The highest redox potential was recorded in the 0 - 25 cm core and the lowest was recorded at the last 76 - 100 cm core (Figure 3).

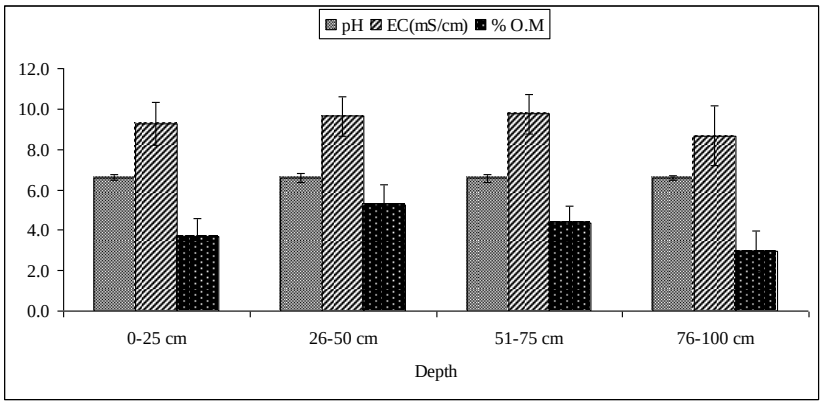


Figure 2: Variation in mean pH, EC and % O.M. in sediment samples with depth

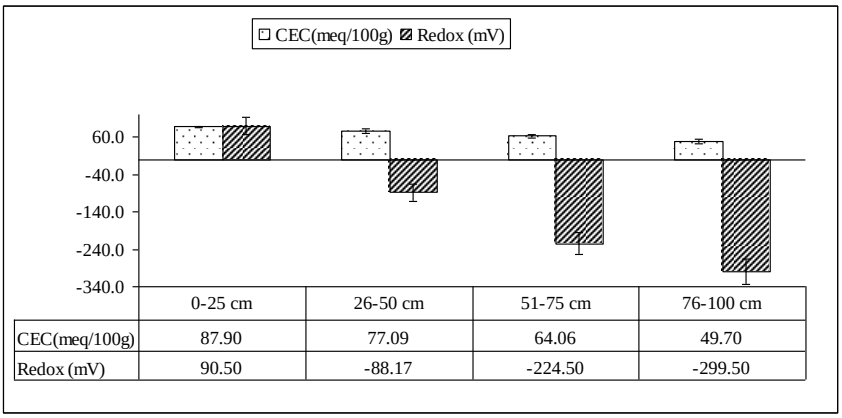


Figure 3: Variation in mean redox potential and CEC sediments at the Msimbazi River

CEC decreased with increasing depth from the surface. This may be attributed to variation in sediment texture as defined by relative percentage of sand, silt and clay. The % clay and % silt decreased with depth whereas % sand increased with depth (Figure 4). The clay content

ranged from 23.0 to 85.0 % and silt ranged from 20.0 to 28.0 % whereas sand content ranged from 15 to 45 %. The % clay and % silt are relatively higher at the top two cores whereas % sand was higher at the bottom two sediment cores (Figure 4). This grain size distribution pattern would have significant influence on horizontal and vertical distributions of heavy metals in sediment.

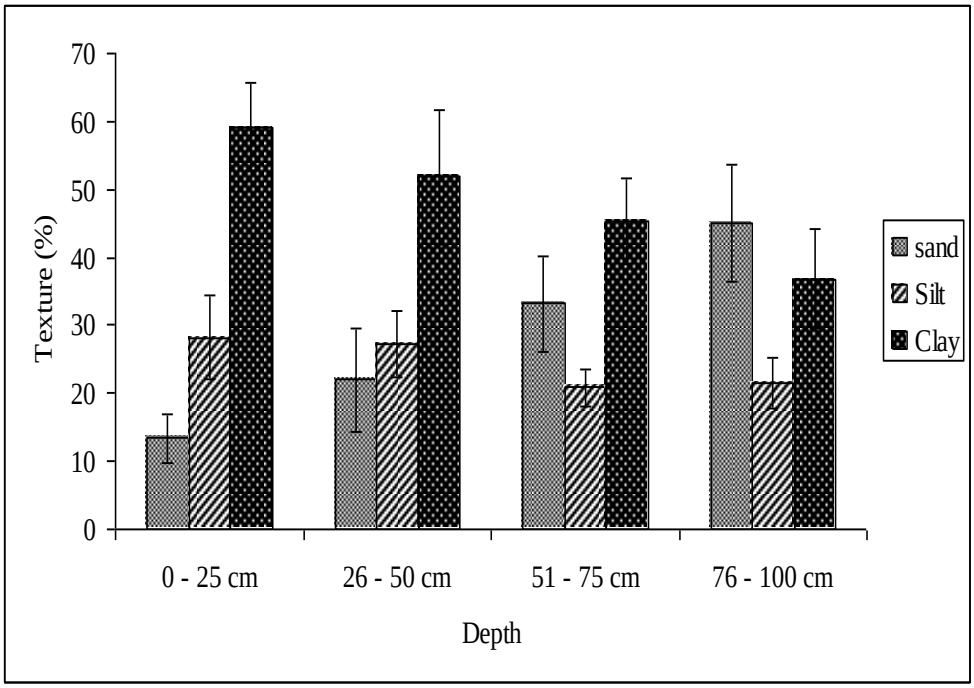


Figure 4: Variation in mean sand, silt and clay contents sediment cores

3.2 Horizontal distribution of heavy metals in the surface sediment

The results from the determination of Fe, Cd, Co, Cr, Ni, Zn, and Pb in sediment cores showed that heavy metal concentrations, in parts per million (ppm), at the surface (0 - 25 cm cores) decreased as one moves from upstream to downstream to the river mouth into the Indian Ocean (Table 1). Metals concentration in 0-25 cm sediment cores were in the order: Fe > Zn > Pb > Cr > Ni > Co > Cd (Table 1). The Fe levels decreased from 22000 ppm and 2700 ppm at upstream sites (P1 and K2) to 10000 ppm and 17000 ppm at downstream sites (J3 and A1) respectively. The average amount of Fe for all 0-25 cm cores was 19266.7 ± 2811.1 ppm. Cr, Co, Ni and Zn showed similar trend (Table 1).

The average values of Cr, Co, Ni and Zn in 0-25 cores were 50.5 ± 6.5 ppm, 12.4 ± 1.6 ppm, 16.2 ± 2.3 ppm and 120.0 ± 19.6 ppm respectively. On the other hand, Cd and Pb showed an opposite trend. The levels of metals, in upstream to downstream direction, increased from 1.62 ppm at P1 to 2.92 ppm at J3 for Cd and from 34.9 ppm at P1 to 38.0 ppm at J3 for Pb in the northern river bank. Whereas, in the southern river bank Cd levels increased from 1.87 ppm at K2 to 3.63 ppm at A1 but Pb levels decreased from 77.7 ppm at K2 to 62.0 ppm at C2 and then increased to 76.0 ppm at A1 (Table 1). The average values for Cd and Pb in 0-25 cm cores were 2.7 ± 0.4 ppm and 56.4 ± 7.3 ppm respectively. The surface sediments (0-25 cm cores) had higher Cd levels downstream than upstream which suggested that Cd was easily washed down the stream as water flowing through the mangrove stand. This observation may suggest that Cd seem to have weaker interactions with sediment particles or organic matter than Fe, Cr, Ni, Co, Pb and Zn (Table 1).

Table 1: Heavy metal levels (ppm) at the 0-25 cm cores on the Msimbazi River banks

Site	Fe	Zn	Pb	Cr	Ni	Co	Cd
P1 (upstream)	22000	119	34.9	50.6	22.5	14.9	1.62
J1	18600	119	46.0	43.0	11.0	11.9	2.59
J3 (downstream)	10000	97	38.0	38.8	9.42	7.0	2.92
K2 (upstream)	27000	173	77.2	71.2	24.0	17.4	1.87
C2	21000	163	62.0	49.0	15.0	12.5	3.87
A1 (downstream)	17000	122	76.0	50.1	15.2	10.9	3.63

3.3 Vertical distribution of heavy metals in sediment cores

The vertical distribution of heavy metals is highly influenced variations in sediment texture and organic matter contents in sediment cores. In general, the average levels of heavy metals in the study site, expressed as mean ± SEM (standard error of the mean), decreased with increasing depth such that heavy metal levels in 0-25 cm cores were higher than in 76-100 cm cores (Figures 5 and 6). It is clear from that data that, Fe had very high concentration compared to the rest of the heavy metals in this study. Its levels ranged from 1000 ppm to 27000 ppm with an average of 14833.3 ± 1263.9 ppm. Zn ranked second and its levels ranged from 16 ppm to 173 ppm with a mean of 90.6 ± 9.4 ppm whereas Pb and Cr ranked third and their levels in sediment core showed similar pattern. The levels of Pb ranged from 3.1 ppm to 77.7 ppm with a mean of 44.4 ± 3.9 ppm whereas levels of Cr in sediment ranged from 13.2 ppm to 71.2 ppm with a mean of 43.2 ± 2.8 ppm. Ni and Co ranked fourth in terms of metal levels. The levels of Ni ranged from 6.9 to 24.0 ppm with a mean of 13.8 ± 1.0 ppm and the levels of Co ranged from 4.1 ppm to 17.4 ppm with a mean of 10.2 ± 0.7 ppm. Cd had the lowest levels of all metals and it amounts ranged from 0.03 to 3.90 ppm with a mean of 1.98 ± 0.20 ppm. Cd is normally found in trace amounts in natural environment and any amount above background levels is attributed to anthropogenic sources (IPCS 1992).

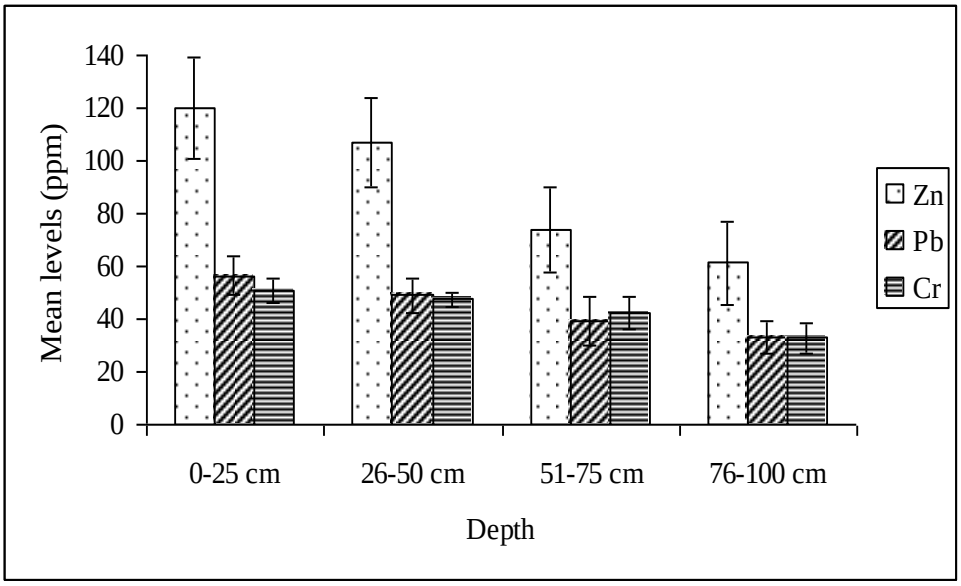


Figure 5: Mean levels (mean ± SEM) of Zn, Pb and Cr in the sediment at each depth (n = 6)

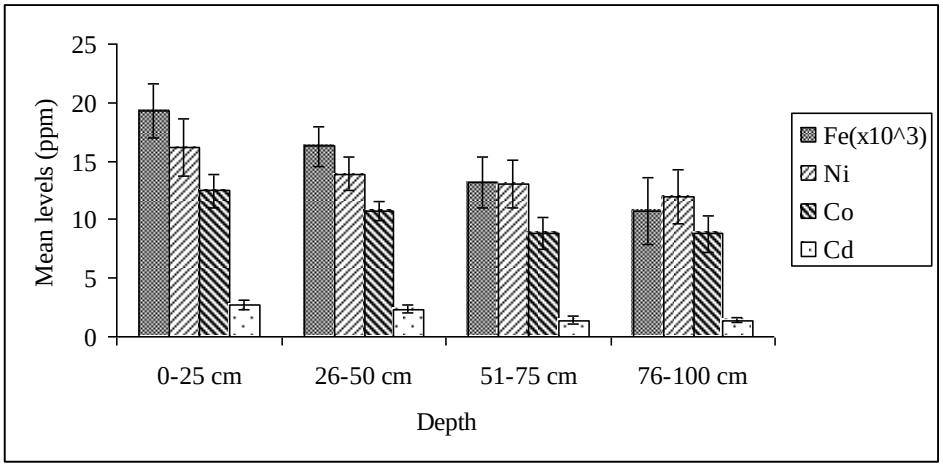


Figure 6: Mean levels (mean ± SEM) of Fe, Ni, Co and Cd in sediment at each depth (n = 6)

3.4 Physico-chemical parameter variation

Heavy metal pollution of sediments and its relationship to the physicochemical parameters were evaluated. The pH and EC of sediment cores remained more or less constant between 6 and 7 which may not significantly influence metal distribution. At low pH heavy metals are expected to be in solution as ions and EC would be higher where as at high pH, EC would be lower because most of the heavy metal ions form complexes with species such as hydroxyl groups (Christensen, 1989). Thus, neutral pH would favor weak complexation of some metals with organic matter and clay particles. CEC and redox potentials decreased significantly with increasing depth and these two factors are some what influenced by clay content in sediment that decreased with depth. This implies that as depth increases from the surface (0 - 25 cm) to the bottom (76 - 100 cm) the redox potential, CEC, clay content and heavy metals concentrations decreased whereas sand content increased. A simple correlation analysis of CEC with % clay showed positive correlation ($r = 0.72$) while EC showed negative correlation with % sand ($r = -0.80$). This indicates that CEC of the sediments was higher where clay content was also higher and vice versa. This is because clay has larger surface area to which metal ions can be adsorbed than sand.

Thus, heavy metals distribution would essentially be affected by clay content which in turn contributes significantly to the accumulation of heavy metals in the sediments. The observed rapid decrease in redox potential with depth (Figure 3) implies that anoxic condition increased as the depth increased from the surface that reduces oxidation processes. The top sediment cores are somewhat constantly aerated with water flowing through. This facilitates the oxidation process to occur more easily than in deep sediment cores. Previous sediment studies performed in the mangrove sediments or seashore sediments along the Dar es Salaam coastal area did not report any pH, EC, CEC, redox potential measurements.The most important sources of organic matter in mangrove sediments are organic materials from surface runoffs and decomposing leaf litters from mangrove trees. The observed low % O.M at 0 – 25 cm cores may be attributed to the fact that the top core is constantly washed with flowing water and hence expected to have higher microbial activities than the core beneath it. This is why % O.M increased first from 0-25 cm core to 26-50 cm core and then decreased gradually with depth (Figure 2). The percentage O.M showed insignificant correlation with the levels of heavy metals in the sediments ($-0.01 \leq r \leq 0.41$).

3.5 Comparison of heavy metal levels in sampling sites to other sites

The amount of Fe in the southern river bank averaged at 18041.7 ± 1394.1 ppm and 11625.0 ± 1692.6 ppm in the northern river bank. In terms of concentration, Fe showed positive correlations with other six metals ($0.49 \leq r \leq 0.96$) and similar relationships were also reported in surficial sediments of Dar es Salaam coastline (Muzuka, 2007). Previous studies in other mangrove systems in Dar es Salaam city showed that benthic biota, polychaetes, also had high levels of Fe (Mremi and Machiwa, 2003; Mtanga and Machiwa, 2007). The benthic biota in our study site might be exposed to high Fe level because the average Fe level in 0-25 cores was 19266.7 ppm which is higher than those reported in the sediments of Dar es Salaam port (Machiwa, 1992; Muzuka, 2007). A study conducted by Muzuka (2007) also noted that amounts of Fe in sediments outside the port were higher at river mouths of Msimbazi River, Tegeta and Manyema Creeks. This indicates that mangroves forests are not 100 % efficient in removing Fe from the wastewaters. Our study has also found that Fe decreased slightly from 27000 ppm (at K3) and 22000 ppm (at P1) at upstream sites to 17000 ppm (at A1) and 10000 ppm (J3) to the downstream sites (Table 1). However, the average amount of Fe at each sampling site in southern river bank was higher at K2 than at A1 whereas in northern river bank Fe levels were higher at J1 than at P1 or J3 (Figure 7). Elevated levels of Fe at J1 is associated with higher clay content as the average % clay at J1 site was 52.9 % which was higher than 36.15 % at P1 and 37.3 % at J3. Noteworthy, the average % clay in the southern river bank decreased from 57.93 % at K2 to 54.09 % at A1 and so was the trend in average Fe levels.The average amount of Zn in the southern river bank was 119.5 ± 11.1 ppm which was relatively higher than in northern river bank where metal levels was 61.6 ± 9.7 ppm and Zn levels at 0-25 cm cores averaged at 120.0 ppm. The average amount of Zn in sites C2 was lower than at sites K2 upstream and A1 downstream (Figure 7) which is attributed to lower % clay at C2 (53.49 %) than at K2 (57.9 %) and A1 (54.1 %). The average levels of Zn at J1 were higher than at P1 and J3 because the site had higher % clay at J1 (52.9 %) than P1 (37.3 %) and J3 (36.2 %). Thus, the metal could easily be washed away down the stream by the flowing water. The average levels of Zn reported in this study are higher than those reported for Msimbazi and Mtoni sediments (Mremi and Machiwa, 2003), Mzinga Creek and Ras Dege sediments (Mtanga and Machiwa, 2007) and Dar es Salaam port (Muzuka, 2007). This clearly indicates that there is a substantial Zn pollution in sediments of the Msimbazi River mangrove forest. The levels of Zn also showed positive correlation with Pb, Fe, Co, Cr and Ni ($0.43 \leq r \leq 0.85$) which suggest these metals have common origin or source.

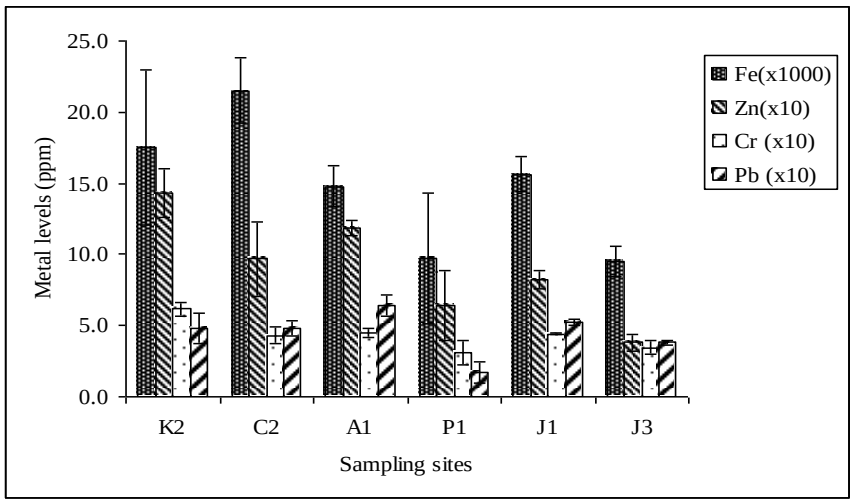


Figure 7: The average levels of Fe, Zn, Cr and Pb (mean ± SEM) at each sampling site

Natural environment has background level of various toxic metals and a level above it is usually associated with anthropogenic sources. In this study the average all metal levels in the southern river bank was 52.9 ± 5.0 ppm higher than 35.9 ± 5.0 ppm in the northern river bank. Similarly, the average Pb in 0-100 cm cores increased from K2 to A2 but it increased from P1 to J1 and then decreased to J3 (Figure 7). This could be attributed to increase in clay from K2 (49.9 %), C2 (71.12 %) to A1 (77.2 %) at 0-25 cm cores but it increased from P1 (45.3 %) to J1 (70.0 %) and then decreased to J3 (39.55 %). The average levels of Pb in 0-25 cm cores, where most biological processes occur, was 56.4 ppm. These levels are exceedingly higher than those reported in sediments at Mtoni, Mzinga Creek and Msimbazi River (Mremi and Machiwa, 2003; Mtanga and Machiwa, 2007). The Pb levels in the 24 samples showed positive correlation with other metals ($0.36 \leq r \leq 0.67$) and all metals showed positive correlation with % clay ($0.39 \leq r \leq 0.60$) which implies that clay content plays a role in their retention of Pb and other metals studied.

The average level of Cr in the southern river bank had 49.9 ± 3.5 ppm which was observed to be higher than 36.4 ± 3.3 ppm recorded in the northern river bank. The average Cr levels in 0-25 cm cores were 50.5 ppm which was higher than the levels reported in samples from coastal sediments or sediments from other mangrove forests in Dar es Salaam (Mremi and Machiwa, 2003; Mtanga and Machiwa, 2007; Muzuka, 2007). The Ni levels in the sediment were comparatively higher than that of Co. The average Ni level in the southern river bank averaged at 16.7 ± 1.2 ppm which was higher than 10.9 ± 1.2 ppm in the northern river bank. The average amounts of Ni decreased gradually from K2 to A1 and from P1 to J3 (Figure 8). The surface sediment cores (0-25 cm) had an average of 16.2 ppm but all these levels were lower than those reported by Mtanga and Machiwa (2007) and comparable to those reported by Muzuka (2007).

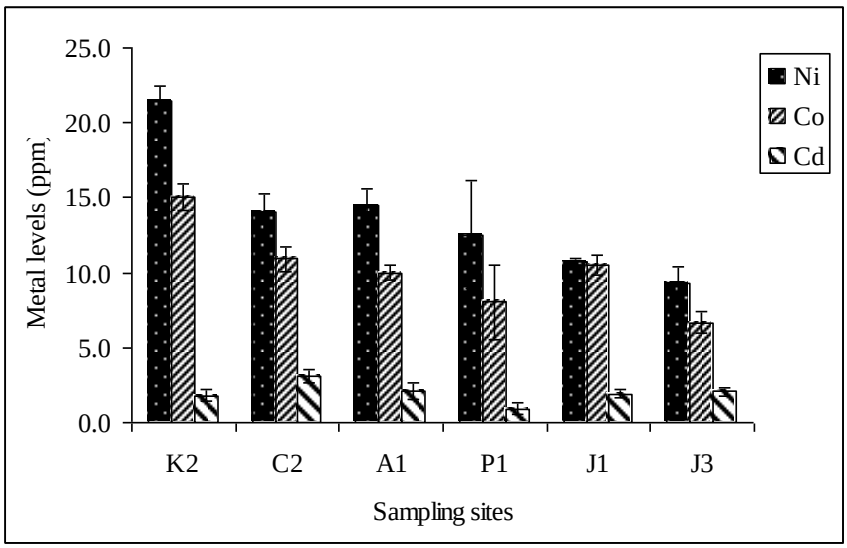


Figure 8: The average levels of Ni, Co and Cd (mean ± SEM) at each sampling site

On the other hand the average level of Co in the southern river bank had 12.0 ± 0.8 ppm which was higher than 8.4 ± 0.9 ppm in the northern river bank and the levels decreased from upstream sites to downstream sites (Figure 8). The average Co levels in 0-25 cm cores was 12.4 ppm which was higher than those reported in coastal sediments (Mremi and Machiwa, 2003; Muzuka, 2007). While the average levels of Ni in 0-100 cm cores decreased from K2

to A1in the southern bank, the levels increased from P1 to J1 and then decreased to J3 (Figure 8). The Ni and Co levels showed positive correlation with Fe, Cr, Pb, and Zn levels ($0.36 < r < 0.89$) which may suggest that these metals have common origin or source. The average level of Cd in the sediment in the southern river bank was 2.6 ± 3.5 ppm higher than 1.6 ± 3.5 ppm in northern river bank. The pattern in Cd levels in 0-25 cm cores showed the levels increase from upstream to downstream sites an average of 2.7 ppm. However, the average Cd levels at each sampling sites generally increased from K2 to C2 and from P1 to J3 (Figure 8). This indicates that Cd is poorly interacting with sediment grains and it may easily be washed down the stream. All levels Cd were higher than those reported by Mtanga and Machiwa (2007) but lower than those reported by Muzuka (2007). Since Muzuka (2007) sampled surface sediments along the coastline which might accumulated Cd damped in by flowing streams and that is in agreement with Cd trend observed in our study.

3.6 Potential ecological impacts of heavy metal levels in sediments to aquatic life

Heavy metals are potentially toxic to marine and freshwater invertebrates when they are present in very high concentrations. Studies on heavy metal levels in sediments of Mtoni, Msimbazi River, Mzinga Creek and Ras Dege have showed that biota can bioaccummulate more heavy metals than those in sediments (De Wolf et al., 2001; Mremi and Machiwa, 2003; Mtanga and Machiwa, 2007). It is also known that mangroves are breeding and nursery sites for some marine fish. The juvenile fish may feed on flora and fauna in the sediment and through food chain the amount of metals in fish may be exceedingly higher than that in the environment. In this study we found that the average amounts of the seven heavy metals in the 0-100 cm cores or 0-25 cm cores were higher than the mean background levels (Buchmann, 1993). Table 2 shows that sediments of Msimbazi River in Dar es Salaam (DSM) were contaminated with the heavy metals investigated in the study. However, it is worth looking at those heavy metals that were present above the lowest effects levels set by OME (1999). The levels of Fe in 0-25 cm cores at sampling sites P1 (22000 ppm), K2 (27000 ppm) and C2 (21000 ppm) were above the lowest effect levels whereas the levels of Cd in sediment cores exceeded the lowest effect level (Table 2). The average values of Cr and Co in the sediments cores were generally below the lowest effects values of 26 ppm and 50 ppm respectively (Buchmann, 1993). The average values of Ni in 0-25 cm cores and 0-100 cm were 16.2 ppm and 13.8 ppm respectively but they were within the acceptable level of 16.0 ppm (Table 2).

Table 2: Comparison of mean heavy metal levels in sediments and sediment screening guidelines

	This study	MtM*	MrM	M	Bkg	LEL	SEL
Fe	14833.3 (0-100 cm)			7454.6 (IH)	18000	20000	40000
	19266.7 (0-25 cm)			1975 (OH)			
Cd	1.98 (0-100 cm)	1.05 (3.3) Mz		3.6 (IH)	~0.2	0.6	10
	2.7 (0-25 cm)	1.00 (0.1) Rd		6.8 (OH)			
Co	10.20 (0-100 cm)		5.0 (Ms)	4.7 (IH)	6.7	50	-
	12.4 (0-25 cm)		5.0 (Mt)	Bdl (OH)			
Cr	43.17 (0-100 cm)	22.7 (31.1)	35.7	21.6 (IH)	37	26	110

		Mz	(Ms)				
	50.5 (0-25 cm)	19.9 (0.2) Rd	36.8 (Mt)	9.7 (OH)			
Ni	13.76 (0-100 cm)		22.3 (Ms)	15.5 (IH)	13	16	75
	16.2 (0-25 cm)		21.4 (Mt)	16.8 (OH)			
Zn	90.55 (0-100 cm)	35.5 (58.7) Mz	31.6 (Ms)	58.4 (IH)	48	120	820
	120.0 (0-25 cm)	19.6 (15.6) Rd	17.9 (Mt)	7.2 (OH)			
Pb	44.44 (0-100 cm)	14.6 (16.8) Mz	31.7 (Ms)	35.4 (IH)	16	31	250
	56.4 (0-25 cm)	8.2 (0.6) Rd	27.1 (Mt)	29.7 (OH)			

*Amounts in bracket indicate heavy metal levels in polychaetes
MtM = Mtanga and Machiwa (2007); **MrM** = Mremi and Machiwa (2003)
M = Muzuka (2007); **Mz** = Mzinga Creek; **Rd** = Ras Dege mangroves
Ms = Msimbazi and Mtoni mangroves; **IDH**= inside the DSM harbor; **ODH** = outside the DSM harbor
LEL = Lowest effect level, is level of pollution that can be tolerated by most benthic organisms (OME, 1999)
SEL = Severe effect level, is the level of pollution that can be detrimental to benthic communities (OME, 1999)
Bkg =Background levels of metals in sediments (Buchmann, 1993)
Bdl = below detection limit

However, the situation was different when individual sampling sites were considered. The levels of nickel in 0-25 cm cores at upstream sampling sites P1 (22.5 ppm) and K2 (24.0 ppm) were above the lowest effect level. While the average values of Zn in the 0-100 cm cores and 0-25 cores were below 120 ppm set for lowest effect level, Zn levels in 0-25 cm sediment cores in the southern river bank were higher than 120 ppm. The lowest effect level for Pb is set at 31 ppm and therefore the average Pb levels for 0-100 cm cores (44.4 ppm) and 0-25 cm cores (56.4 ppm) were higher than the reference value. When the northern river bank was considered, it was found that 0-25 cm core at sampling site P1 (34.9 ppm) had lead levels above the lowest effect level for Pb (Table 2) whereas in sampling sites J1 and J3 all cores had Pb levels ranging from 34.6 ppm to 57.0 ppm which is higher than reference value (OME 1999). However, in the southern river bank all samples at sampling sites K2, C2 and A1 had levels ranging from 34.4 ppm to 77.7 ppm with an exception of 76-100 cm core at K2 which had 27.9 ppm. Therefore, Pb levels in southern river bank were generally higher than the lowest effect level for Pb. Further comparison of the heavy metal levels to reference guidelines for severe effect levels (OME, 1999) revealed that none of the seven heavy metals exceeded the reference value (Table 2).

4. Conclusions and recommendations

This study demonstrated that mangrove sediments of the Msimbazi River were contaminated with Cd, Co, Cr, Ni, Zn, Pb and Fe. Most of these heavy metals exceeded the lowest effect level particularly at the first two sediment cores (0-50 cm) where most bioforms inhabit. The

fact that heavy metal levels in sediment decreased with increasing depth to 100 cm indicates that heavy metals determined in our study are mostly of anthropogenic origin and were mostly drained to the area by the wastewater flowing through from the urban center. The sediment texture, clay particles in particular, were responsible for the heavy metal retention from wastewaters because our study revealed high levels of the metals where there was high clay content as well. Although Msimbazi River mangrove sediments showed high heavy metal retention, the study found that the metal retention is not 100% efficient. This is because the heavy metal levels in surface sediment decreased with increasing distance towards the Indian Ocean. Thus, benthic fauna in beaches and coastal sediments are prone to heavy metal contamination. Three other studies have shown that benthos and sediments in beaches and sediments in Dar es Salaam coastal zone are indeed contaminated with heavy metals (Mremi and Machiwa, 2003; Mtanga and Machiwa, 2007; Muzuka, 2007). Since the total heavy metal levels and clay content decreased with increasing depth, we recommend a study speciation of heavy metals in order to determine what percent is bioavailable to benthic flora and fauna that in turn may serve as food sources for juvenile fishes. We also recommend isotopic tracing study so as to determine the contribution of anthropogenic sources from natural sources of heavy metal pollutants in sediments.

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