

Assessment of Heavy Metal Pollution in Sediment and Polychaete Worms from the Mzinga Creek and Ras Dege Mangrove Ecosystems, Dar es Salaam, Tanzania

A. Mtanga and J. Machiwa

University of Dar es Salaam, Department of Aquatic Environment and Conservation, P.O. Box 35064, Dar es Salaam, Tanzania

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Abstract— Metal pollution in the Mzinga creek mangrove stand was assessed and compared with a relatively pristine mangrove forest at Ras Dege in Dar es Salaam. The concentrations of cadmium, chromium, copper, lead and zinc in sediment and polychaete worms (*Capitella* sp.) were analyzed by ICP-AES and mercury was analyzed by a semi-automatic analyzer. Concentrations of most of the metals analyzed were higher in samples from Mzinga creek than from Ras Dege. Sediment samples from the Mzinga creek were enriched with Cu (EF = 7.4), Hg (EF = 5.3) and Cr (EF = 3.3) relative to sediment samples from Ras Dege, which were mostly at natural background levels. Polychaete worm samples from the Mzinga creek also accumulated high amounts of metals when compared to samples from Ras Dege. The data show perturbation of the Mzinga creek from human activities in the catchment.

INTRODUCTION

East African mangroves and the associated biota are decreasing in areal coverage because of over-exploitation for wood and tannin, clearance for agriculture, tourist resorts, salt pans and settlements (Wagner *et al.*, 1999; Semesi, 1991). Removal of mangrove forests has direct and indirect influences on aquatic organisms, as it deprives them of habitats as well as feeding and breeding grounds. Some mangrove areas in East Africa have been used as dumping sites for solid wastes and for sewage disposal. Such practices have resulted in the increase in levels of metals in the aquatic environment. Some studies have already indicated potential threat to mangrove ecosystems in Tanzania as a result of pollution from heavy metals (de Wolf *et al.*, 2001; Mremi & Machiwa,

2003). However, the extent of enrichment of heavy metals in mangrove ecosystems in relation to natural background levels in the region has not been adequately addressed.

Polychaete worms are one of the dominant infauna of soft bottom substrates and exhibit high stability and adaptability to different habitats (Sarkar *et al.*, 2005). Polychaete worms (*Capitella capitata*) are common in mangrove sediment and they serve as important descriptors of environmental conditions (Fisher *et al.*, 2000) and good indicators of sediment quality. In the present study sediment and polychaete worms have been used as proxies to assess the extent of metal pollution. The concentration of metals in the geochemically available sediment fraction (easily reducible and oxidisable phases) is analysed to assess the extent of vulnerability of infauna.

MATERIAL AND METHODS

Study area

The Mzinga creek mangrove stand is about 2.5 km south of Dar es Salaam harbour. The mangrove stand on Mzinga creek lies between latitude $06^{\circ} 52.330'$ to $06^{\circ} 53.059'$ S and longitude $039^{\circ} 17.556'$ to $039^{\circ} 18.599'$ E (Fig. 1). Activities in

the area include agriculture, fishing and mangrove harvesting, the site also receives runoff from residential and agricultural areas. The Ras Dege mangrove stand is located approximately 60 km south of Dar es Salaam, between latitude $06^{\circ} 52.389'$ to $06^{\circ} 53.071'$ S and longitude $039^{\circ} 27.689'$ to $039^{\circ} 27.620'$ E. It is remote from the city and less affected by human activity and was used as a reference site for assessing the extent of metal pollution in Mzinga creek.

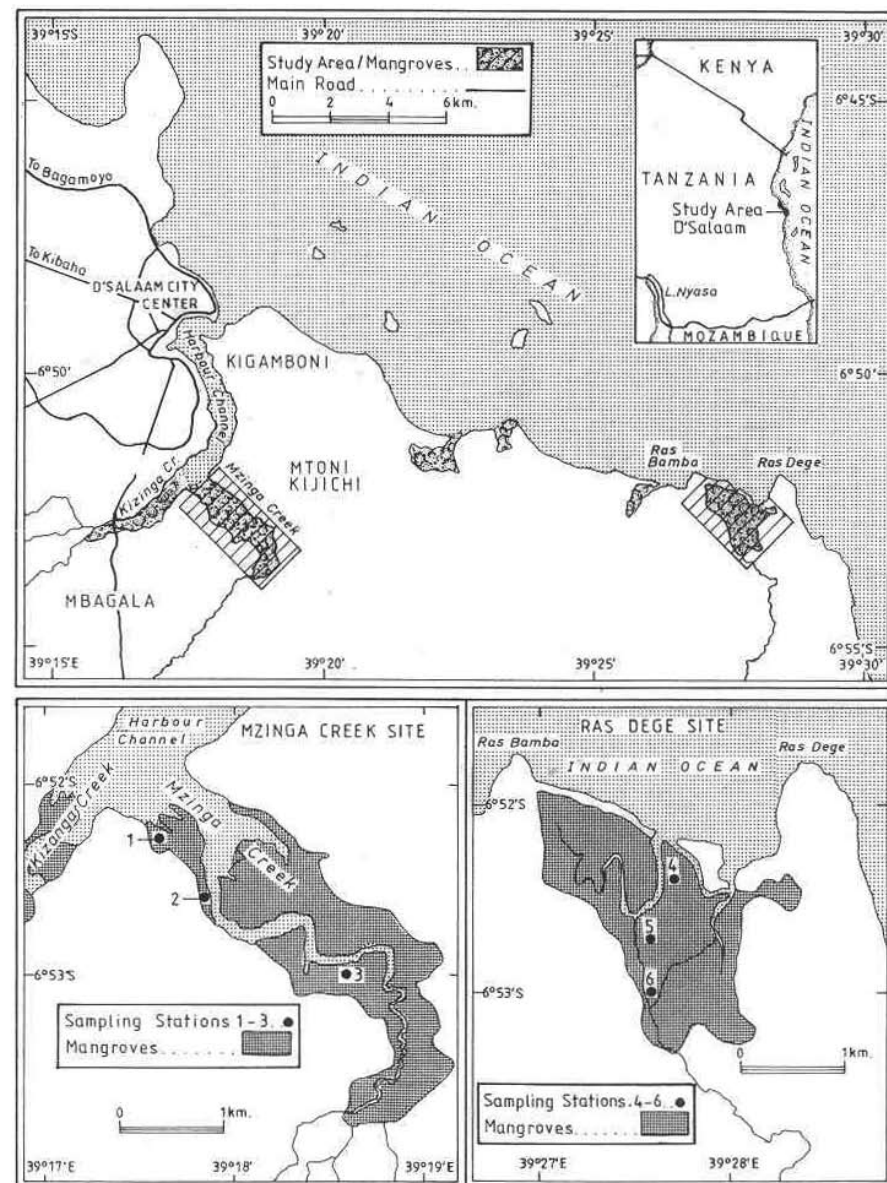


Fig. 1. Map of Dar es Salaam Coast showing the study sites, the potentially impacted Mzinga creek and relatively less impacted Ras Dege mangrove stands

Sampling and analysis of sediment and polychaete worm samples

Sampling of sediment was conducted during September 2005 in Mzinga creek and Ras Dege mangrove forests during low tide, using a hand corer (30 cm height, 6 cm internal diameter). Sediment core samples were collected in triplicate from stations 1 – 6 (Fig. 1). Surface sediment (0 – 2 cm) samples of the core were sliced and freeze dried, and then sieved through 1 mm nylon screen and thoroughly homogenized. A sub-sample of the bulk sediment was overnight extracted with hydrofluoric acid (40%, 60 ml), then 15 M nitric acid (15 ml) was added and the solution was evaporated to dryness on a hot plate. The residue was dissolved in 3 M nitric acid (10 ml), filtered through 0.45- μ m membrane filter and the final volume was adjusted with distilled deionized water (Thomson and Wash, 2003). Total Cu, Cd, Pb Cr, Zn Al, and Fe were analyzed with Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES). Fe values are not reported here, and Al values were used to calculate metal enrichment factors for use in the discussion. Another sub-sample of the bulk sediment was sequentially extracted in order to obtain metals from the reducible and oxidisable phases (the geochemically available fraction of metals). Samples of 2.0g finely powdered bulk sediment were placed in 100 ml polypropylene centrifuge tubes. The first leach, the reducible fraction, contains metals from hydrous oxides of iron and manganese as well as the aged poorly crystallized oxides of iron and carbonates in the sediment as well as exchangeable ions (Murray *et al.*, 2000). 20 ml of 0.04 M hydroxylammonium chloride (HA) in 25% acetic acid (HOAc) was added in the tubes. The samples were heated at 96° C in a water bath for 8 hours with intermittent agitation, and then centrifuged at 3000 rpm for 30 min. The supernatant solution was acidified with concentrated nitric acid and evaporated to dryness. The residues were dissolved in 1.0 M nitric acid (5 ml) in a volumetric flask and analyzed for metals (Ahlf *et al.*, 2002). For the second leach, nitric acid (0.02 M, 10 ml) was added to the sample that previously had been leached with HA/ HOAc (still in the centrifuge tubes). After heating for 2 hours at 85° C in a water bath, with occasional agitation

of the sample, 30% hydrogen peroxide (10 ml at pH 2) was added. The sample was reheated for 3 hours with intermittent shaking; 3.2 M ammonium acetate in 20% (v / v) nitric acid (10 ml) was added to the cooled sample. Finally, the sample was centrifuged for 30 minutes at 3000 rpm and the supernatant liquid was decanted into a beaker. The solution was evaporated to dryness and the residues were re-dissolved in 10 ml nitric acid (0.02M) and filtered through a 0.45 μ m membrane filter. The final volume was made with 1.0 M nitric acid, metals bound in labile organic complexes and insoluble sulfides were analyzed. Total mercury in the sediment samples was extracted according to Akagi & Nishimula (1991). A dry sediment sample (0.5 g) was accurately weighed into a beaker, distilled water (1 ml) was added and mixed with 2 ml of concentrated nitric acid/perchloric acid (1:1) and 5 ml of concentrated sulfuric acid. The solution was heated on a hot plate at $200 \pm 5^{\circ}$ for 30 min. Distilled water was added to make 50 ml, total mercury determined using a semiautomatic mercury analyzer (Sanso Seisakusho HG 201).

Polychaete worms were dug out of sediment at stations 1 – 6 (Fig. 1) using a shovel, with about 60 worms collected from each station. The sediment was sieved on a 2 mm mesh sieve in order to retain worms and larger particles. Polychaete worms (*Capitela* sp.) were collected, depurated and washed. Identification of worms was conducted using standard taxonomic literature (e.g. Richmond, 2002). The worms were oven dried at 50° C and crushed into fine powder. 1 g of a well homogenized powder was accurately weighed into 100 ml flask. Samples were digested with a mixture of 16 ml of concentrated HNO_3 and 4 ml of concentrated HClO_4 acid. The mixture was heated on a hot plate for 1 hour then cooled. The digest was transferred into a 50 ml volumetric flask and diluted to the mark with 2 M nitric acid. The solution was analyzed for Cd, Cr, Cu, Pb and Zn using ICP-AES. Total mercury was analysed by accurately weighing approximately 0.5 g (wet weight) of worm sample into a digestion flask. Distilled water (1 ml) was added in the flask and mixed with 2 ml of concentrated nitric acid/perchloric acid (1:1) and 5 ml of sulfuric acid. The solution was heated on a hot plate at $200 \pm 5^{\circ}$ C for 30 min. Distilled water was added to make 50 ml, total Hg was analyzed by Semiautomatic Hg analyzer.

Quality assurance/control included procedural blanks and analysis of Certified Reference Materials (CRMs): DORM-2 (dogfish muscle), DOLT-2 (dogfish liver) and PACS-2 (marine sediment). Variation between sample replicates was less than 5%, the accuracy of the results was good with respect to the certified values (Table 1).

Statistical analyses were based on the significance level at $P = 0.05$ and critical values of F at $\alpha = 0.05$. Single factor analysis of variance (ANOVA) was used for data analysis.

Differences in metal concentrations between Mzinga creek and Ras Dege mangrove stands were compared using student's t test (Zar, 1996).

$0.02 \pm 0.001 \mu\text{g g}^{-1} \text{ dw}$, $0.04 \pm 0.01 \mu\text{g g}^{-1} \text{ dw}$ in the oxidisable phase. The geochemically available Cd was only 6% of the total concentration. About 67% of the available Cd in the Ras Dege surface sediment was associated with organic matter and probably some sulfide minerals. The concentration of Cd in polychaete worms from Mzinga creek was $3.3 \pm 0.7 \mu\text{g g}^{-1} \text{ dw}$ and in samples from Ras Dege was $0.1 \pm 0.08 \mu\text{g g}^{-1} \text{ dw}$. A Student t test showed a significant difference in Cd concentration between worm samples from Mzinga creek and Ras Dege mangrove stands ($t(10) 10.979$, $P < 0.001$).

Table 1. Comparison of certified values for the certified reference materials (CRMs) with analytical results of the concentration of metals ($\mu\text{g g}^{-1}$ except Hg, ng g^{-1}) in CRMs obtained by University of Dar es Salaam laboratory

CRMs		Cd	Cr	Cu	Hg	Pb	Zn
DOLT -2	Certified value	20.8	0.37	25.8	2.14	0.22	85.8
	Observed concentration	19.6	0.34	23.44	2.17	0.29	81.5
	% Recovery	94%	91%	90%	101%	131%	94%
DORM-2	Certified value	0.043	34.7	2.34	4.64	0.065	25.6
	Observed concentration	0.045	32	2.1	4.24	0.063	22.3
	% Recovery	104%	92%	89%	91%	96%	87%
PACS-2	Certified value	2.11	90.7	310	3.04	183	364
	Observed concentration	1.95	86.4	300.2	2.80	177	340
	% Recovery	92%	95%	96%	82%	96%	93%

RESULTS

Cadmium concentration in sediment and polychaete worms

Bulk sediment samples from Mzinga creek had total Cd concentration of $1.05 \pm 0.04 \mu\text{g g}^{-1} \text{ dw}$ and those from Ras Dege had $1.00 \pm 0.23 \mu\text{g g}^{-1} \text{ dw}$. A Student t test indicated no significant difference ($t(10) 0.461$, $P > 0.05$) between Cd concentration in bulk sediment samples from the two locations. The concentration of Cd in the reducible sediment phase of samples from Mzinga creek was $0.07 \pm 0.01 \mu\text{g g}^{-1} \text{ dw}$, in the oxidisable phase was $0.06 \pm 0.02 \mu\text{g g}^{-1} \text{ dw}$. The geochemically available Cd was 12% of the total concentration and 46% of the available Cd in the surface sediment was associated with labile organic matter and possibly to a lesser extent with sulfide minerals. For Ras Dege sediment samples, the concentration of Cd in the reducible phase was

Chromium concentration in sediment and polychaete worms

The concentration of total Cr in bulk sediment samples was $22.7 \pm 0.5 \mu\text{g g}^{-1} \text{ dw}$ in samples from Mzinga creek and $19.9 \pm 4.8 \mu\text{g g}^{-1} \text{ dw}$ in Ras Dege samples (Fig. 3). A Student t test showed no significant difference ($t(10) 0.461$, $P > 0.05$) between the concentration of Cr in bulk sediment samples from the two sites. The reducible phase of Mzinga creek mangrove sediment contained $6.1 \pm 1.8 \mu\text{g Cr g}^{-1} \text{ dw}$, Cr, the oxidisable phase had $1.5 \pm 0.6 \mu\text{g Cr g}^{-1} \text{ dw}$, forming 34% as the geochemically available Cr. Out of the available Cr in Mzinga creek surface sediment, only about 20% was associated with organic matter and sulfide minerals. The concentration of Cr in the reducible phase of sediment samples from Ras Dege was $1.1 \pm 0.9 \mu\text{g g}^{-1} \text{ dw}$ and in the oxidisable phase was $1.5 \pm 0.5 \mu\text{g g}^{-1} \text{ dw}$. The available Cr in the sediment was 13% of the total concentration,

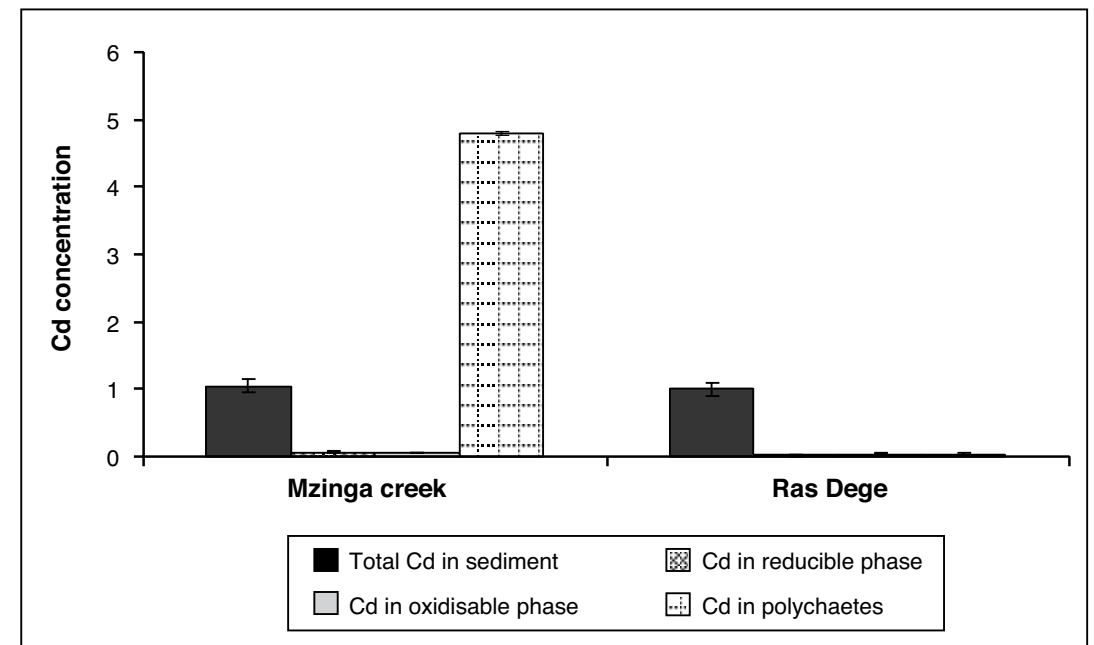


Fig. 2. Mean \pm SEM concentration of Cd ($\mu\text{g g}^{-1} \text{ dw}$) in sediment and polychaete worms from Mzinga creek and Ras Dege mangrove stands

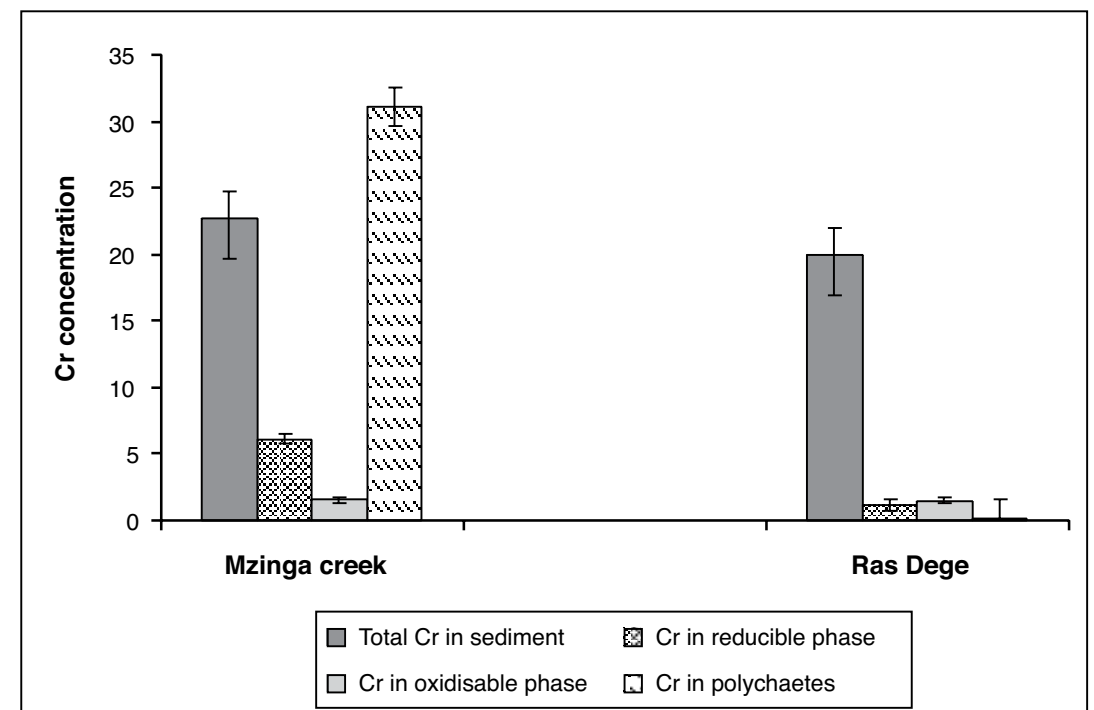


Fig. 3. Mean \pm SEM concentration of Cr ($\mu\text{g g}^{-1} \text{ dw}$) in sediment and polychaete worms from Mzinga creek and Ras Dege mangrove stands

of which about 58% was associated with organic matter and to a lesser extent with sulfide minerals. The concentration of Cr in worm samples from Mzinga creek was $31.1 \pm 15.1 \mu\text{g g}^{-1} \text{ dw}$ and in Ras Dege samples was $0.2 \pm 0.1 \mu\text{g g}^{-1} \text{ dw}$, the difference was significant ($t(10) 4.295, P=0.002$).

Copper concentration in sediment and polychaete worms

The concentration of total Cu in the bulk sediment samples from Mzinga creek was $9.5 \pm 2.1 \mu\text{g g}^{-1} \text{ dw}$ and from Ras Dege was $4.9 \pm 2.6 \mu\text{g g}^{-1} \text{ dw}$ (Fig. 4), the difference between the concentrations for the two sites was significant ($t(10) 3.047, P=0.012$). Copper in the reducible phase of sediment samples from Mzinga creek mangrove stand was $3.7 \pm 2.2 \mu\text{g g}^{-1} \text{ dw}$ and in the oxidisable phase was $0.8 \pm 0.4 \mu\text{g g}^{-1} \text{ dw}$. The available Cu in the sediment was 47% of the total concentration. Only a small proportion of the available Cu (about 18%) in the surface sediment in Mzinga creek was associated with organic matter and probably sulfide minerals. The concentrations of Cu in the reducible and oxidisable phases of sediment samples from Ras Dege were $0.03 \pm 0.01 \mu\text{g g}^{-1} \text{ dw}$ and $0.65 \pm 0.14 \mu\text{g g}^{-1} \text{ dw}$ respectively. The concentration of available Cu

was 14% of the total. In Ras Dege sediments, most of the available Cu (about 96%) was associated with organic matter and possibly sulfide minerals forming the oxidisable phases. The concentration of Cu in polychaete worm samples from Mzinga creek was $18.4 \pm 4.2 \mu\text{g g}^{-1} \text{ dw}$ and from Ras Dege was $0.3 \pm 0.2 \mu\text{g g}^{-1} \text{ dw}$, the difference was significant ($t(10) 10.589, P<0.001$).

Lead concentration in sediment and polychaete worms

The concentration of total Pb in the bulk sediment samples (Fig. 5) was higher ($14.6 \pm 2.3 \mu\text{g g}^{-1} \text{ dw}$) in samples from Mzinga creek than Ras Dege ($8.2 \pm 0.8 \mu\text{g g}^{-1} \text{ dw}$), and the difference was significant ($t(10) 6.595, P<0.001$). Lead concentration in the reducible fraction of sediment samples from Mzinga creek was $4.5 \pm 1.3 \mu\text{g g}^{-1} \text{ dw}$ and the oxidisable phase contained $1.5 \pm 0.6 \mu\text{g g}^{-1} \text{ dw}$. The concentration of available Pb in the sediment was 41% of the total, only 25% of the available Pb was associated with organic matter and sulfide minerals. For samples from Ras Dege, the concentration of Pb in the reducible phase was $1.3 \pm 0.4 \mu\text{g g}^{-1} \text{ dw}$ and in the oxidisable phase was $1.0 \pm 0.4 \mu\text{g g}^{-1} \text{ dw}$. The available Pb was 28% of the total concentration and

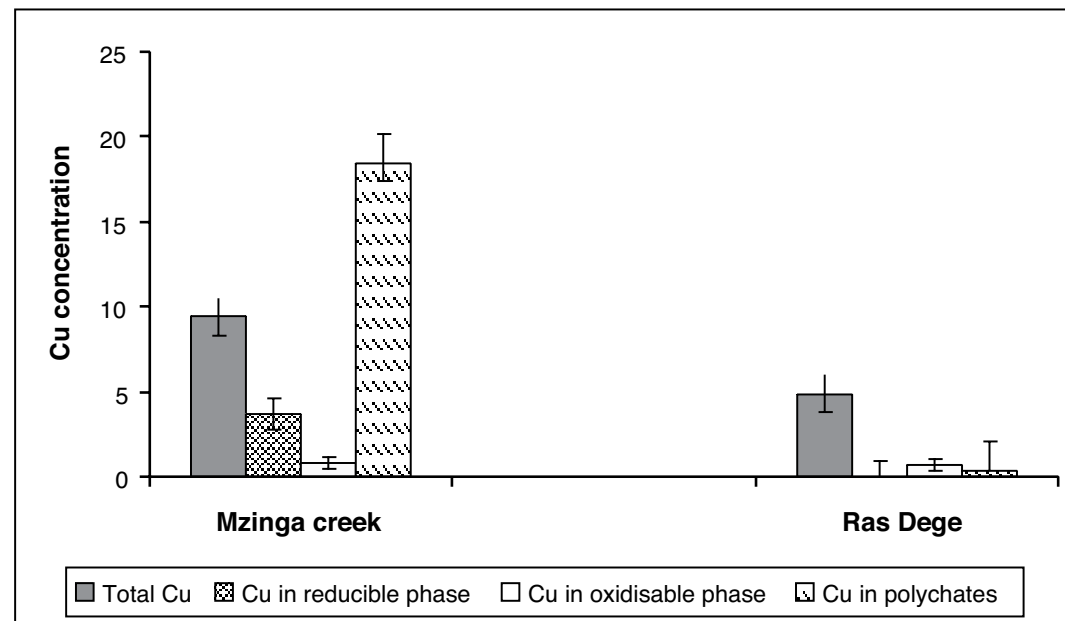


Fig. 4. Mean \pm SEM concentration of Cu ($\mu\text{g g}^{-1} \text{ dw}$) in sediment and polychaetes from Mzinga creek and Ras Dege mangrove stands

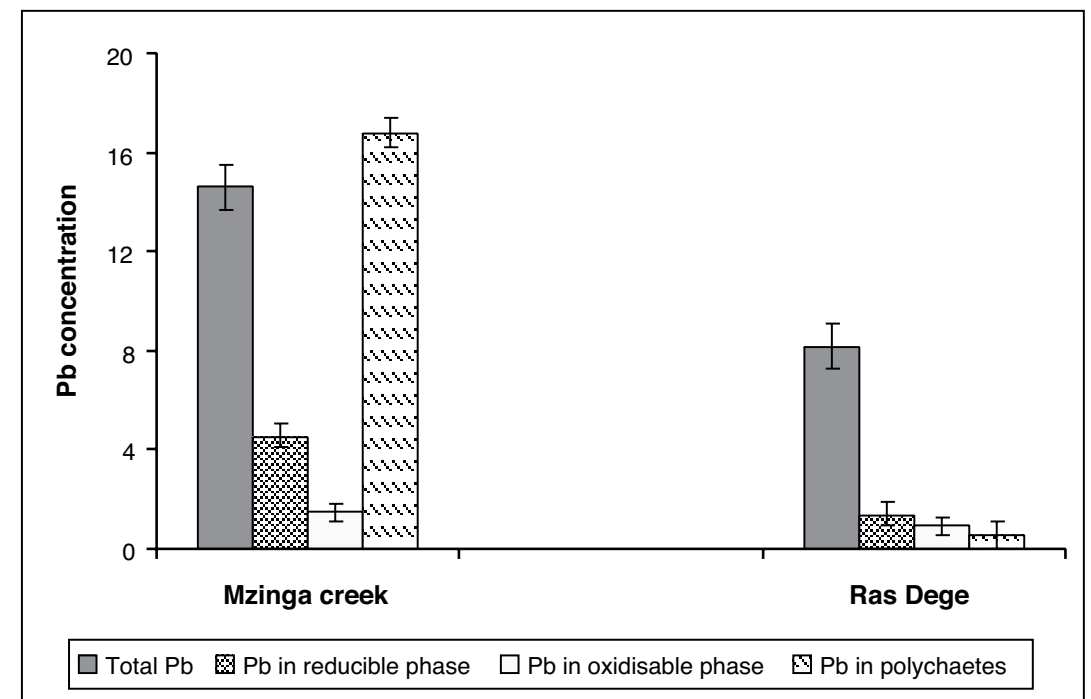


Fig. 5. Mean \pm SEM concentration of Pb ($\mu\text{g g}^{-1} \text{ dw}$) in sediment and polychaete worms from Mzinga creek and Ras Dege mangrove stands

43% of the available Pb was associated with organic matter and sulfide minerals. The concentration of Pb in polychaete worms was higher ($16.8 \pm 1.4 \mu\text{g g}^{-1} \text{ dw}$) in samples from Mzinga creek than samples from Ras Dege ($0.6 \pm 0.2 \mu\text{g g}^{-1} \text{ dw}$), the difference was significant ($t(10) 28.068, P<0.001$).

Zinc concentration in sediment and polychaete worms

The concentration of total Zn in bulk sediment samples was $35.1 \pm 7.1 \mu\text{g g}^{-1} \text{ dw}$ and $19.6 \pm 7.3 \mu\text{g g}^{-1} \text{ dw}$ for samples from Mzinga creek and for Ras Dege respectively (Fig. 6), and the difference was statistically significant ($t(10) 3.72, P=0.004$). The concentrations of Zn in the reducible and oxidisable phases of sediment samples from Mzinga creek were $10.2 \pm 4.4 \mu\text{g g}^{-1} \text{ dw}$ and $6.6 \pm 1.3 \mu\text{g g}^{-1} \text{ dw}$ respectively (Fig. 6). About 48% of total Zn was in the geochemically reactive phases. About 39% of the available Zn in the surface sediment of Mzinga creek was associated with organic matter and sulfide minerals. For sediment samples from Ras Dege, the

concentrations of Zn in sediment phases were $2.1 \pm 0.8 \mu\text{g g}^{-1} \text{ dw}$ in the reducible and $1.4 \pm 0.1 \mu\text{g g}^{-1} \text{ dw}$ in the oxidisable phases. The geochemically available Zn was 18% of the total concentration, 40% of the available zinc in the surface sediment was associated with organic matter and sulfides. Zinc concentration in polychaete worms was $58.7 \pm 2.0 \mu\text{g g}^{-1} \text{ dw}$ and $15.6 \pm 2.8 \mu\text{g g}^{-1} \text{ dw}$ in samples from Mzinga creek and Ras Dege respectively, and the difference was statistically significant ($t(10) 4.570, P=0.001$).

Mercury concentration in sediment and polychaete worms

The concentration of total Hg in mangrove sediment (Fig. 7) was significantly higher ($t(10) 5.472, P<0.001$) in samples from Mzinga creek ($93.38 \pm 33.40 \text{ ng g}^{-1} \text{ dw}$) than Ras Dege ($17.45 \pm 5.79 \text{ ng g}^{-1} \text{ dw}$). Total Hg concentration was also significantly higher ($t(10) 2.910, P=0.016$) in polychaete worms from Mzinga creek ($511.19 \pm 4.30 \text{ ng g}^{-1} \text{ ww}$) than in samples from Ras Dege ($23.10 \pm 6.20 \text{ ng g}^{-1} \text{ ww}$).

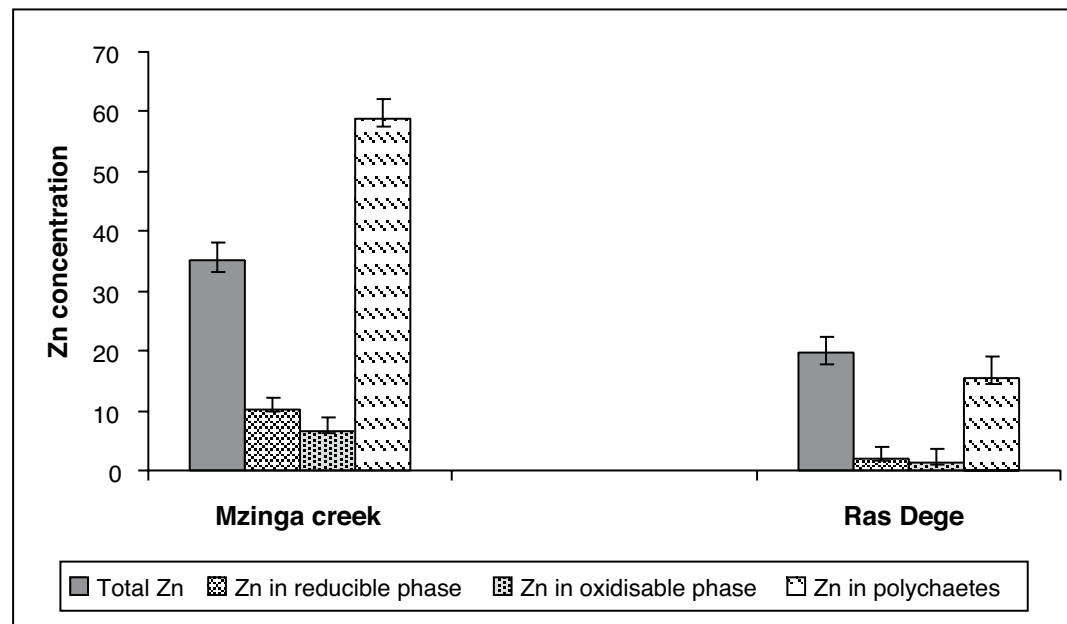


Fig. 6. Mean \pm SEM concentration of Zn ($\mu\text{g g}^{-1}$ dw) in sediment and polychaete worms from Mzinga creek and Ras Dege mangrove stands

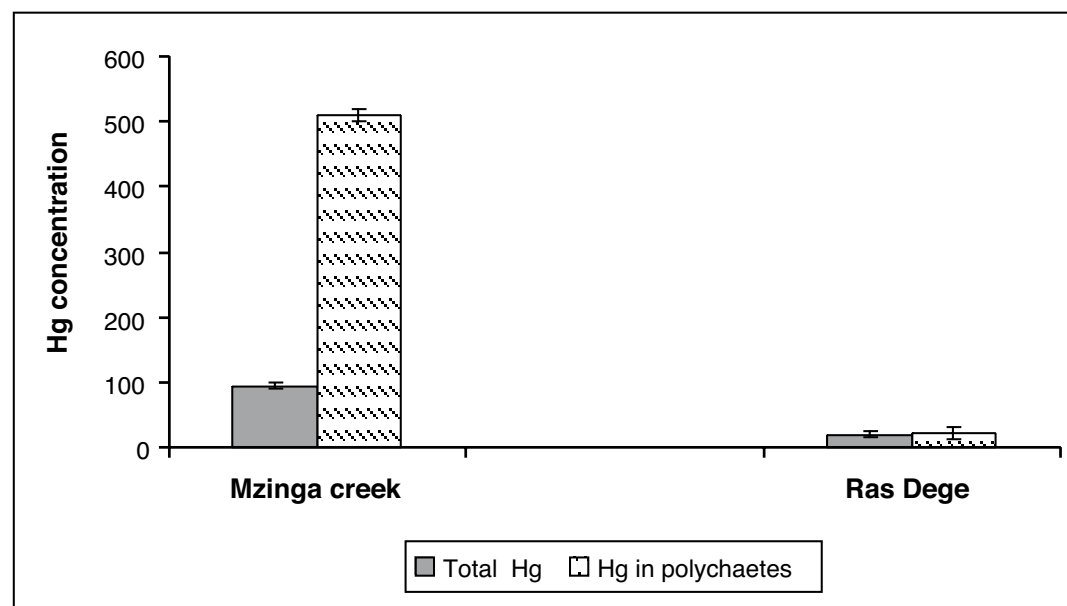


Fig. 7. Mean \pm SEM concentration of Hg (ng g^{-1}) sediment (dry weight) and polychaete worms (wet weight) from Mzinga creek and Ras Dege mangrove stands

DISCUSSION

Enrichment of metals in the mangrove sediments

The enrichment factors (EF) for metals in the sediments of the Mzinga creek and Ras Dege mangrove stands were calculated with respect to crustal values of respective elements (Camusso *et al.* 2002; Martin & Whitfield, 1983) normalized to Al concentration.

$$EF = \frac{\left(\frac{Me}{Al}\right)_s}{\left(\frac{Me}{Al}\right)_c}$$

Where: $\left(\frac{Me}{Al}\right)_s$ is the ratio of the concentration of the element of interest to aluminium in the sediment and $\left(\frac{Me}{Al}\right)_c$ is the ratio of the element to Al in the crust.

EF¹ relative to earth's crust for metals in sediment samples from Mzinga creek were >1 (Table 2), with Cd having the highest EF of 15.8 followed by Hg (3.5). Sediment samples from Ras Dege had EF¹ \leq 1 relative to average crust values. Hence, the concentrations of metals in Ras Dege sediments were assumed as a good representative of natural background values. The EF values for metals in

Mzinga creek sediment were recalculated based on the respective concentrations of metals in Ras Dege sediments. The recalculated EF² for metals in Mzinga creek sediment are presented in Table 2. In this case, Cd had lower EF suggesting that Cd has a relatively higher natural background concentration in the mangrove sediments relative to the average crust value. Higher EF² > 5 were observed for Cu and Hg suggesting contamination of sediments. In any case, comparison of metal levels with natural background concentrations where they exist, rather than average crust values gives reasonable EFs. Despite the observed enrichment, the concentrations of metals in Mzinga creek mangrove sediments were within the recommended sediment quality criteria (Table 2).

Heavy metal pollution

The concentration of total Cd analyzed in sediment samples from Mzinga creek ($1.05 \pm 0.04 \mu\text{g g}^{-1}$) was three times higher than its concentrations in sediment samples from Ras Dege. The calculated EF of Cd in Mzinga creek sediment relative to Ras Dege sediment was 2. The EF for Cd in Mzinga creek was lower compared to the EF > 26 reported by Kamau (2002) in Port Reitz creek, Kenya. The concentration of geochemically available Cd in the reducible and oxidisable sediment phases in

Table 2. Heavy metal concentration ($\mu\text{g g}^{-1}$) in sediment from Mzinga Creek and Ras Dege compared with sediment quality guidelines (ANZECC and ARMCANZ, 2000). Also shown are Enrichment Factors of metals in Mzinga Creek and Ras Dege sediments relative to crust values (EF¹) as well Enrichment Factors of metals in Mzinga Creek relative to Ras Dege levels (EF²)

	CONCENTRATION		ANZECC		EF ¹ Mzinga C.	EF ¹ Ras Dege	EF ² Mzinga C.
	Mzinga C.	Ras Dege	*Low	*High			
Cd	1.05 \pm 0.04	1.20 \pm 0.20	1.5	10	15.8	1.0	2.0
Cr	22.7 \pm 0.5	19.9 \pm 4.8	80	370	3.2	1.0	3.3
Cu	9.5 \pm 2.7	4.9 \pm 2.6	65	270	1.0	0.3	7.4
Hg	0.09 \pm 0.01	0.02 \pm 0.01	0.15	1	3.5	1.1	5.3
Pb	14.6 \pm 2.3	8.2 \pm 0.8	50	220	1.2	0.6	2.1
Zn	35.1 \pm 7.1	19.6 \pm 7.3	200	410	1.9	1.5	2.9

ANZECC and ARMCANZ, 2000 – Australian and New Zealand Guidelines for Fresh and Marine Water Quality (Australian and New Zealand Environment and Conservation Council, and Agriculture and Resource Management Council of Australia and New Zealand) cited in Cox and Preda, 2005.

*Low sediment quality guideline – Trigger value above which further ecosystem specific investigation is recommended

*High sediment quality guideline – Highly contaminated sediments which are likely to have a biological impact, further investigation is required.

Mzinga creek mangrove sediments was higher (12.4 % of the total Cd in the sediment) than in Ras Dege sediments (6 % of the total Cd in sediment) indicating high bio-availability and potential bio-accumulation. Indeed, polychaete worms from Mzinga creek had 33 times higher Cd concentration than in samples from Ras Dege. The available Cd was equally distributed in the oxide/carbonate minerals and organic matter in the sediment.

The concentration of Cr in sediment samples from Mzinga creek was higher than in samples from Ras Dege suggesting input of the metal from the catchment. Mremi and Machiwa (2003) reported similar values of Cr in Msimbazi, Mtoni and Mbweni mangrove forests along the Dar es Salaam coast. The concentration of geochemically available Cr was higher in Mzinga creek mangrove sediments (34 % of total Cr in sediment) than in Ras Dege (13 % of the total Cr in sediment). The high proportion of bio-available Cr in Mzinga creek sediments was reflected by the higher concentration of Cr in the polychaete worm samples. The concentration of Cr in polychaete worms from Mzinga creek was approximately 155 times higher than in samples from Ras Dege. Higher levels of Cr ($22 \pm 4 - 164 \pm 14 \mu\text{g g}^{-1}$) in worms have been reported by Sarkar *et al.* (2005) in Sundarban mangrove forest in India where the source of Cr was discharge from a nearby tannery.

The concentration of Cu in sediment from Mzinga creek was about twice higher than in samples from Ras Dege. The concentration of geochemically available Cu was higher in Mzinga creek sediment (48 % of total Cu) compared with Ras Dege (14% of total Cu), suggesting a large amount of bio-available Cu as reflected in the worms. Polychaete worms from Mzinga creek had about fifty seven-fold higher concentration of Cu than in samples from Ras Dege, indicating accumulation of the metal by infauna. Most of the bio-available Cu was associated with oxide/carbonate minerals in Mzinga creek sediments, whereas in Ras Dege, 96% was associated with organic matter/sulfide minerals suggesting *in situ* natural sources.

Total Pb in Mzinga creek sediment was about double the concentration in sediment samples from Ras Dege. The concentration of geochemically available Pb was higher (41% of total Pb) in

sediment samples from Mzinga creek compared with Ras Dege sediments (27% of total Pb). The high concentration of geochemically available Pb in Mzinga creek sediment indicates mobility in the environment (Muniz *et al.*, 2004; Amusan and Adeniyi, 2005) as confirmed in the worms sampled. The concentration of Pb in polychaete samples from Mzinga creek was 32 times higher than in samples from Ras Dege.

The total concentration of Zn in sediment was 1.6 times higher in Mzinga creek than Ras Dege and the EF was 2.9 relative to Ras Dege sediments. The concentration of Zn in Mzinga creek sediments was lower compared to $68.2 \mu\text{g g}^{-1}$ dw reported by Ong *et al.* (2006) in Kerteh mangrove sediment in Malaysia. The concentration of Zn in the geochemically available phases of sediment samples from Mzinga creek was higher (48 % of total Zn) than in samples from Ras Dege (18 % of total Zn), suggesting higher bio-availability in Mzinga creek sediments. Nevertheless, the concentration of Zn in polychaete worms from Mzinga creek was only about fourfold higher than in samples from Ras Dege, suggesting involvement of physiological/metabolic effects by the organism. However, Sarkar *et al.* (2005) reported higher concentrations of Zn ($78 - 126 \mu\text{g g}^{-1}$ dw) in polychaete worms in mangrove sediments in India.

The concentration of total Hg was five times higher in mangrove sediment samples from Mzinga creek than in samples from Ras Dege, the EF relative to Ras Dege sediment was 3.5 indicating contamination. Mirlaen *et al.* (2003) reported higher concentrations of Hg (20 - 17,840 ng g^{-1} dw) in estuarine sediments in south Brazil, the hotspot areas corresponded with anthropogenic discharges of wastes directly in the estuary. Polychaete worm samples from Mzinga creek had 22 times higher Hg than in samples from Ras Dege suggesting Hg contamination.

Generally, it is obvious that Mzinga creek mangrove stand is threatened with metal pollution. The level of metals in the sediments is alarming if compared with the Ras Dege mangrove stand which is far from Dar es Salaam city. Even though the levels of metals are within the recommended sediment quality criteria, necessary management steps have to be taken. There is an urgent need to minimize input of domestic and industrial wastes in

Mzinga creek catchment and in the Dar es Salaam harbour.

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REFERENCES

- Akagi, H. & Nishimura, B. 1991. Mercury speciation in the environment. In: Suzuki, T., Imura, N and Clarkson, T.W (eds). *Advances in Mercury Toxicology* Plenum Press, New York pp 53-76.
- Ahlf, W., Hollert, H., Neumann-Hensel, H. & Ricking, M. 2002. A guidance for the Assessment and evaluation of sediment quality. *J. Soils and Sediments* **13**: 351-356.
- Amusan, A.A & Adeniyi I.F. 2005. Genesis, classification and heavy metal retention Potential of soils in mangrove forest, Niger Delta, Nigeria. *J. Human Ecol.* **17**: 255 - 261.
- Camusso, M., Galassi, S. & Vignati, D. 2002. Assessment of river Po sediment quality by micropollutant analysis. *Water Res.* **36**: 2491 - 2504.
- Cox, M.E. & Preda, M. 2005. Trace Metal Distribution within Marine and Estuarine Sediments of Western Moreton Bay, Queensland, Australia: Relation to land use and setting. *Geographical Res.* **42**: 173 - 193.
- De Wolf, H., Ulomi, S.A., Backeljau, T., Pratap, H.B. & Blust, R. 2001. Heavy metal levels in the sediments of four Dar es Salaam mangroves: Accumulation in, and effect on the morphology of the periwinkle, *Littoraria scabra* (Mollusca: Gastropoda). *Environ. Int.* **26**: 243 - 249.
- Fisher, W.S., Oliver, L. M., Winstead J.T & Long, E. R. 2000. A survey of oyster *Crassostrea virginica* from Tampa Bay, Florida: Associations of internal defense measurements with contaminant burdens. *Aquat. Toxicol.* **15**: 115 - 138.
- Kamau, J.N. 2002. Heavy metal distribution and enrichment at Port - Reitz creek Mombasa. *Western Indian Ocean J. Mar. Sci.* **1**: 65 - 70.
- Martin, J.M. & Whitfield, M. 1983. The significance of River inputs to the ocean. In C. S. Wong, E. Bayle, K. W. Bruland, J. D. Bruton & E.D. Goldberg (eds). *Trace metals in Seawater*. Plenum Press, New York.
- Mirlaen, N., Andrus, V.E. & Baisch, P. 2003. Mercury pollution sources in sediments of Patos Lagoon estuary, Southern Brazil. *Mar. Pollut. Bull.* **46**: 331 - 334.
- Mremi, S.D. & Machiwa, J.F. 2003. Heavy metal contamination of mangrove sediments and the associated biota in Dar es Salaam, Tanzania. *Tanzania J. Sci.* **29**: 62 - 75.
- Muniz, P., Danulat E., Yannicelli B., Garcial-Alonso, J., Medina, G. and Becego, M.C. 2004. Assessment of contamination by heavy metal and petroleum hydrocarbons in sediments of Montevideo harbour (Uruguay). *Environ. Int.* **29**: 1019 - 1028.
- Murray, R.W., Miller, D. J. & Kryc, K.A. 2000. *Analysis of major and trace elements in rock, sediments and interstitial waters by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)*. Ocean Drilling Program, Texas A and M University, USA.
- Ong, M. C., Kamaruzzaman, B. Y., Shazeli, N. A. M. & Rosnan, Y. 2006. Distribution and Normalization of lead, copper and zinc in Terengganu mangrove surface sediment, Malaysia. *J. Sustainability Sci. & Manag.* **1**: 74 - 84.
- Richmond, M.D. (ed) 2002. A field guide to the seashores of Eastern Africa and the Western Indian Ocean Islands. Sida/SAREC - UDSM. 461 pp. ISBN 91-586-8783-1.
- Sarkar, S.K., Bhattacharya, A., Giri, S., Bhattacharya, B., Sarkar, D., Nayak, D.C. & Chattopadhyaya, A.K. 2005. Spatiotemporal variation in benthic polychaetes (Annelida) and relationship with environmental variables in a tropical estuary. *Wetlands Ecol. & Manag.* **13**: 55 - 67.
- Semesi, A.K. 1991. Management plan for the mangrove ecosystem of the mainland Tanzania. Vol. 4. Mangrove Management plan of Dar es Salaam. Ministry of Tourism, natural Resources and Environment Forest and Beekeeping division. Dar es Salaam 292 p.
- Thompson, M. & Walsh, J.N. 2003. *The handbook of Inductively Coupled Plasma Spectrometry*. Viridian Publishing, Surrey. 316 pp.
- Wagner, G.M., Malya, U., Juma, S., Mgaya, Y.D., Wahule, O. & Mahika, G. 1999. A preliminary investigation for an integrated Community based Approach to Conservation and Restoration of Marine Ecosystems along the Dar es salaam Coast. African Development Foundation, Dar es salaam 124p.
- Zar, J. H. 1996. *Biostatistical analysis*. Second Edition. Prentice-Hall, Englewood Cliffs, New Jersey. 718pp.