Original Article

Western Indian Ocean
JOURNAL OF
Marine Science

Metal pollution in mangrove ecosystems in Dar es Salaam, Tanzania

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Open access

Citation:
Mziraya P, Kimireia IA (2024) Metal pollution in mangrove ecosystems in Dar es Salaam, Tanzania. Western Indian Ocean Journal of Marine Science 23(2): 99-113 [doi: 10.4314/wiojms.v23i2.8]

Received:
December 21, 2023

Accepted:
October 24, 2024

Published:
December 13, 2024

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Abstract
Environmental pollution through accumulation of metals in estuarine, coastal, and marine waters is a worldwide issue. Most contaminants originate inland and pass through these environments before dispersing into the ocean. The objectives of this study were to determine metal concentration levels of Ag, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se and Zn in sediments, water, invertebrates and mangrove leaves collected from mangrove ecosystems along the coast of Dar es Salaam and Mbegani. Evidence of metal bioaccumulation of non-essential metals including Al, Cu, Fe, Mn and Zn was mostly found at sites located close to Dar es Salaam City centre, which decreased with increasing distance from the centre. *Avicennia marina* (mangrove leaves), *Uca spp*. and *Terebralia palustris* (invertebrates) were identified as suitable local species for monitoring metal concentrations in the region.

Keywords: Biomonitoring, invertebrates, mangrove leaves, sediments, water

Introduction
Environmental pollution due to metals in estuarine and coastal environments is a worldwide problem, since most contaminants from urban centres end up in these areas before dispersing into the ocean (Islam and Tanaka, 2004; Pan and Wang, 2012; Tam and Wong, 2000). Once introduced into these environments, the pollutants are distributed into different compartments that include sediment, water, plants, and animals, and eventually pose a risk to the ecosystem and humans. Concentrations of trace metals in water, sediments, and biota are usually the three measures used in marine habitats (Rainbow, 1995). Occurrence of metal pollution induced by anthropogenic inputs on coastal environments and estuaries is not uncommon, even in countries with low levels of industrialization in Africa (Biney *et al*., 1994; Otchere, 2019).

Species with the capacity of accumulating heavy metals in its tissues, which may be analyzed as a measure of metal bioavailability in the ambient habitat can be termed as a metal bio-monitor. Bio-monitors of metal pollution respond differently to different sources of bio-available metals (Rainbow, 1995). The levels of metal accumulation in marine organisms are not only attributed by water quality but also to different factors such as seasonality, temperature, salinity, diet, spawning and individual variation, among others. The levels of metals accumulated in some marine organisms may be higher than background concentrations and thus certain species and/or tissues of certain organisms can be suitable to use as bio-indicators of heavy metal pollution (Chan, 1989).

Mangrove ecosystems are intertidal estuarine wetlands thriving in relatively sheltered locations such as lagoons, bays and estuaries in tropical and subtropical regions and tend to face serious anthropogenic contamination due to their proximity to areas of dense human population, urban and industrial development and concentrated pressures from human activities (MacFarlane and Burchett, 2002; Sharma *et al*., 2021; Tam and Wong, 2000). Sediments in mangrove ecosystems are mostly anaerobic, reduced, and rich in sulphide and organic matter; thus have a high metal retaining capacity (Harbison, 1986; Lacerda *et al*., 1993; Machado *et al*., 2008; Silva *et al*., 1990; Tam and Wong, 1996). Mangrove wetlands along the coast of Tanzania are mostly located in sheltered bays, estuaries and river mouths and receive most of their freshwater inflow from rivers, streams and runoffs (Kruitwagen *et al*., 2008). Based on their location and ability to trap chemicals, the amount of contaminants in mangrove wetlands closely reflects the general level of pollution in coastal areas and the hinterlands (Kruitwagen *et al*., 2008). The most common pollution sources along the coast include sewage discharge, municipal, industrial and agricultural wastes, transportation activities, coastal area urbanization and erosion.

Tanzania is experiencing increasing pressure from urbanization and industrialization which has resulted in an increase in environmental degradation (De Wolf and Rashid, 2008; Machiwa, 1992; Semesi, 1992; Yhdego, 2021). This has eventually led to a severe decrease of water and sediment quality since most of the industrial, agricultural and residential wastes are disposed-off directly into natural drainage systems that end up in coastal ecosystems (Machiwa, 1992; Mremi and Machiwa, 2003). For example, Msimbazi River, which is located in Dar es Salam city was reported to receive average and peak untreated effluent rates of 256 m^3/h and 606 m^3/h of wastes from industrial and other anthropogenic sources (Ak'habuhaya and Lodenius, 1988; De Wolf *et al*., 2001).

Despite efforts undertaken to evaluate the potential environmental status of metal pollution along the coast of Dar es Salaam (De Wolf and Rashid, 2008; De Wolf *et al*., 2001; Kruitwagen *et al*., 2008; Machiwa, 1992; Mremi and Machiwa, 2003; Mtanga and Machiwa, 2008; Mtanga and Machiwa, 2007; Muzuka, 2008; Rumisha *et al*., 2012), there is paucity of information regarding contaminant accumulation and their respective effects on local marine flora and fauna in Tanzania. The objectives of the present study were: (i) to evaluate the extent of metal contamination in the local coastal environment (water and sediments) and in the resident organisms (invertebrates and mangroves) in mangrove ecosystems of Dar es Salaam and the Coastal Region of Tanzania; and (ii) to identify the most suitable metal pollution bio-indicators from the selected flora and fauna species (mangrove leaves and invertebrates).

Materials and methods

Study sites

The study was conducted in mangrove ecosystems in Dar es Salaam (Msimbazi, Mtoni Kijichi, Kunduchi, Mbweni and Mbutu) region and in Mbegani (Coastal region) in Tanzania (Fig. 1). Sites were selected based on distance from the Dar es Salaam city centre. Msimbazi mangrove ecosystem (39.273262 longitude and -6.79798 latitude) is in the city centre and receives wastewater discharges from the city. Mtoni Kijichi mangrove ecosystem (39.280047 longitude and -6.878884 latitude) is located along the Dar es Salaam harbour channel, approximately 2.5 km south of the city centre and receives waste from intensive traffic of fishing boats and ferries, municipal outflows, and adjacent residential and agricultural areas. These sites are considered to be highly polluted. Kunduchi mangrove ecosystem (39.211938 longitude and -6.657801 latitude) is located within a tourist hotel area and Kunduchi fishing village, approximately 20 km north of the Dar es Salaam city centre. Mbweni mangrove ecosystem (39.139344 longitude and -6.578716 latitude) is located at the Mpigi River mouth. The last two sites, Mbutu (39.479969 longitude and -6.880632 latitude) and Mbegani (38.87321 longitude and -6.394379 latitude) mangrove ecosystems, are situated south and north of the city centre, respectively, and are considered to be less polluted.

Sampling

Sampling was conducted in the months of August and September 2009, at low tide in the upper part of the intertidal. At each site, three replicate sediment samples (top 10 cm from the surface) and water samples were collected and transferred to clean zip lock polyethylene bags and into clean 50- mL polypropylene tubes, respectively. Leaves of the mangroves *Avicennia marina*, *Bruguiera gymnorrhiza*, *Ceriops tagal*, *Rhizophora mucronata*, and *Sonneratia alba*, and invertebrates (*Uca spp*., *Volema pyrum*, *Turbo* spp., *Terebralia palustris*, *Cerithidea decollata*, *Cerithium caeruleum*, *Diala lauta* and *Zeuxius olivaceus*) were also collected, washed with Milli-Q water to remove any adhering sediment particles and stored in clean polyethylene bags per species and site. Some species were not present at all the sites. The samples were transported on ice to the Laboratory of Ecophysiology, Biochemistry, and Toxicology, University of Antwerp, Belgium for analysis.

Laboratory analysis

Grain size distribution in sediments

Sediment samples from each site were mixed, oven dried at 60 °C for 72 hours, and ground to obtain a homogeneous sample. The particle size (0.05 µm to 900 µm diameter) distribution was then analyzed using a laser diffraction particle size analyzer (Master sizer S, Malvern Instrument Ltd, Worcestershire, UK). During analysis, 10 g aliquots of each sample were repeatedly analysed over five minutes to obtain an average size distribution profile.

homogeneous samples, from which a 0.3 g aliquot was placed in a Teflon digestion vessel. To each sample, 1 mL of concentrated nitric acid (HNO_3) (69 %) and 3 mL of hydrochloric acid HCl (37 %) were added. Samples were then extracted in closed vessels using a microwave (ETHOS 900, Milestone, Shelton, CT, USA). Samples were digested in four sequential steps

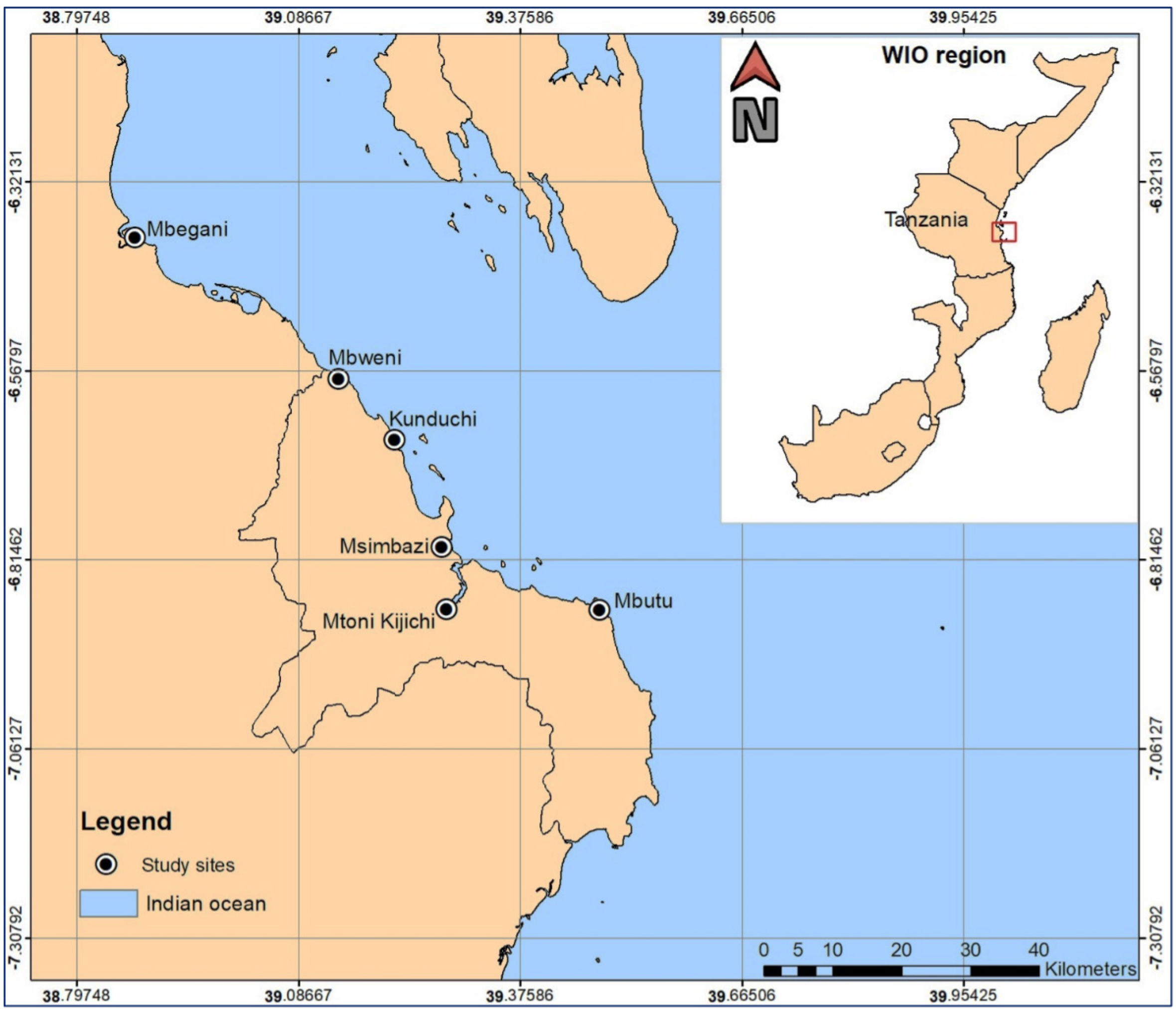

Figure 1. Map showing sampling sites.

Organic carbon content in sediments

Total Organic Carbon (TOC) in 1 g aliquots of dried sediment was determined using a Shimadzu TOC-VCPN analyzer equipped with a PC controller and a solid sample combustion unit (SSM-5000A).

Metal analysis of sediment

Sediment samples from each site were mixed, oven dried at 60 °C for 72 hours, and ground to obtain

(90, 200, 350, and 500 watts) for 5, 3, 5, and 5 min respectively. The Certified Reference Material (CRM) BCR 144R (sewage sludge of domestic origin) and laboratory blanks were analysed with batches of samples during the preparation stage and through the analytical measurements and data calculations for quality control (Table 1). After microwave digestion, samples were diluted with Milli-Q water to make the volume 50 mL and then stored at -20 °C until analysis. The

Table 1. The recovery rates (expressed as percentage of certified values) of the reference material BCR 144R (sewage sludge of domestic origin) used in this study.

			Measured and certified concentrations (µg/g) of metals in the reference material BCR 144R												
Reference material	**Type of samples used for**		**Ag**	**Al**	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Se**	**Zn**
		Measured value	8.68	22.25	151.4	1.82	14.34	97.39	291.1	4915	196.2	46.2	103.8	886	1038
BCR 144R	Sediments	RSD (%)	0.6	0.31	14.5	0.09	0.95	3.3	9.42	280.7	3	3.5	1.8	42	24
Sewage sludge of domestic origin		Certified value				1.82	15	104.3	308		207.9	47.7	106	932	
		Recovery (%)				**100.2**	**95.6**	**93.4**	**94.5**		**94.4**	**96.8**	**97.9**	**95.1**	

concentrations of metals (silver (Ag), arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), selenium (Se) and zinc (Zn)) were analysed using a High Resolution Inductively Coupled Plasma Mass Spectrometer (HR-ICP-MS; ELEMENT XR, Bremen Germany). Metal concentrations were corrected for recoveries in laboratory blanks.

Metal analysis of water

Water samples were acidified to 1 % with highly purified concentrated nitric acid and then diluted 5 and 20-fold for metal analysis. Arsenic (As), iron (Fe), and selenium (Se) were analyzed using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES; iCAP 4000, Thermo Scientific, Bremen Germany), while other metals (Ag, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn) were analyzed using HR-ICP-MS. Certified reference material SRM 1643e (reconstituted water) and laboratory blanks were analysed with batches of samples throughout the preparation stage, analytical measurements and data calculations (Table 2). Metal concentrations were corrected for recoveries in laboratory blanks.

Metal analysis of mangrove leaves

For each species and site, mangrove leaf samples were placed in pre-weighed 50 mL polypropylene tubes and dried at 60 °C to constant weight, to determine the moisture content. To each sample, 5 mL of highly purified nitric acid (HNO_3) (69 %) was added and allowed to digest at room temperature for 48 h. Samples were further digested on a hot block at 105 °C (±2 °C) for 30 min. An aliquot of 0.5 mL of hydrogen peroxide (27 % H_2O_2) was then added and the samples were left to digest for a further 25-30 min. The digested samples were allowed to cool to room temperature. 50 mL of Milli-Q water was then added to each sample. The samples were held at -20 °C until analysis. Concentrations of metals (Ag, Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, and Zn) were analysed using HR-ICP-MS. Analytical quality was evaluated

Table 2. The recovery rates (expressed as percentage of certified values) of the reference material SRM 1643e (reconstituted water) used in this study.

			Measured and certified concentrations (µg/g) of metals in the reference material SRM 1643e												
Reference material	**Type of samples used for**		**Ag**	**Al**	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Se**	**Zn**
		Measured value	1.09	141.87	60.32	6.51	26.61	21.15	23.03	97.06	39.54	62.92	20.11	11.69	76.26
SRM 1643e	Water samples	RSD (%)	0.02	0.92	1.33	0.21	0.87	0.84	0.84	0.18	1.04	1.27	0.43	0.13	1.02
Reconstituted water		Certified value	1.062	141.8	60.45	6.568	27.06	20.4	22.76	98.1	38.97	62.41	19.63	11.97	78.5
		Recovery (%)	**103**	**100.1**	**99.8**	**99.1**	**98.4**	**103.7**	**101.2**	**98.9**	**101.5**	**100.8**	**102.4**	**97.6**	**97.2**

Table 3. The recovery rates (expressed as percentage of certified values) of the reference material BCR 279 ((*Ulva lactuca*)) used in this study.

			Measured and certified concentrations (µg/g) of metals in the reference material BCR 279												
Reference material	**Type of samples used for**		**Ag**	**Al**	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Se**	**Zn**
		Measured value	0.07	586.85	2.92	0.26	2.1	10.51	13.06	2308	1989.34	12.76	12.82	0.61	48.77
BCR 279	**Mangrove leaves**	**RSD (%)**	0.01	22.42	0.12	0.02	0.08	0.8	0.84	83.18	52.87	0.45	0.68	0.1	5.8
Sea Lettuce (*Ulva lactuca*)		**Certified value**			3.09	0.274		10.7	13.14	2400	2090		13.5	0.593	51.3
		Recovery (%)			**94.6**	**96.6**		**98.2**	**99.4**	**96.2**	**95.2**		**94.9**	**103.3**	**95.1**

using certified reference material *Ulva lactuca* (BCR 279) and laboratory blanks (Table 3). Metal concentrations were corrected for recoveries in laboratory blanks.

Metal analysis of invertebrates

For each species and sampling site, the soft tissues of invertebrates were extracted from the shells and oven dried at 60°C to constant weight, and then cooled. Other laboratory procedures for metal analysis were the same as outlined for mangrove leaves. However, in this case, the certified reference material used was VMK 102 (mussel tissue) (Table 4). Blanks were also included to check for analytical quality. Metal concentrations were corrected for recoveries in laboratory blanks.

Statistical analysis

The data were first tested for normality and homogeneity of variance using Shapiro-Wilk and Levene's tests respectively. Most of the data were not normally distributed even after log transformation, and thus non-parametric equivalents were used. Metal concentrations in sediment and water from sampling sites were compared using a Kruskal-Wallis test (non-parametric one-way ANOVA). Comparisons of metal concentrations between sites and species of biota (mangrove leaves and invertebrates) were tested by the same approach for comparisons of more than two groups, and a Mann-Whitney U test for comparisons of two groups. Multiple comparisons between groups and/or species were performed using a Dunn's test. Correlation between metal concentrations in species of biota and sediments (environment) was done using a non-parametric Spearman rank correlation analysis. All the statistical tests were performed using GraphPad Prism 5 (GraphPad Software Inc., USA). The graphical presentation of data was done using GraphPad Software Inc., USA and R Core Team version 4.4.1 of 2024.

Table 4. The recovery rates (expressed as percentage of certified values) of the reference material VMK 102 (mussel tissue) used in this study.

			Measured and certified concentrations (µg/g) of metals in the reference material VMK 102												
Reference material	**Type of samples used for**		**Ag**	**Al**	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Se**	**Zn**
		Measured value	3.14	36.41	15	2.81	2.28	1.62	10	188.8	4.91	6.89	6.46	6.05	121
VMK 102		**RSD (%)**	0.19	1.91	0.6	0.22	0.24	0.18	0.39	13.12	0.33	0.51	0.11	0.65	2.28
Mussel tissue	**Invertebrates**	**Certified value**				2.9			10.1	192	4.7				114
(In-house reference material)		**Recovery (%)**				**96.8**			**98.7**	**98.3**	**104.4**				**106.2**

Results

Grain size distribution and total organic carbon content (TOC) in sediment

The grain size analysis indicates a wide range of grain sizes for most sampling sites (Fig. 2). The TOC content at the Mbegani site (3.74±0.12 %) was higher than at other sites (Fig. 3), followed by Msimbazi (2.53±0.13 %), Mbutu (2.33±0.08 %), Mbweni (1.92±0.03 %), Mtoni Kijichi (1.26±0.13 %), and Kunduchi (0.64±0.04 %).

Metal concentrations in sediments and water

Metal concentrations in sediments from all the studied sites ranged between 2.60-0.03 for Ag, 152.39-65.96 for As, 1.28-0.01 for Cd, 11.29-0.92 for Co, 50.19-7.35 for Cr, 57.77-1.81 for Cu, 5843.14-2243.21 for Fe, 344.24-21.49 for Mn, 17.64-2.67 for Ni, 60.90-1.56 for Pb, 102.19-42.59 for Se and 371.59-17.27 for Zn (µg/g) (Fig. 4). Metal concentrations in sediments were significantly different between sites (Kruskal-Wallis, $H \geq 11.16$, $p < 0.05$, Fig. 4) except for Fe ($H = 6.555$, $p = 0.256$). In general, high metal concentrations were recorded at Msimbazi and Mtoni Kijichi, while low concentrations were recorded at Mbutu and Mbegani (Figure 4). Metal concentrations observed in water samples depicted a different pattern where, for some of the studied metals (e.g. Zn, Pb, Mn, Cr, Cd, and Ag), there was a decrease in concentration from polluted (Msimbazi and Kijichi) to pristine (Mbutu and Mbegani) sites. For some other metals (Ni and Cu), the opposite pattern emerged (Fig. 5). Metal concentrations in water from all the studied sites ranged between 0.05-0.03 for Ag, 20.18-9.29 for As, 0.05-0.04 for Cd, 0.00-0.00 for Co, 0.38-0.14 for Cr, 1.38-1.03 for Cu, 7.32-3.93 for Fe, 0.80-0.50 for Mn, 2.72-1.28 for Ni, 0.05-0.05 for Pb, 69.22-31.57 for Se and 1.59-1.14 for Zn (µg/g) (Fig. 5).

Metal concentrations in biota

Mangrove leaves

Metal concentrations in mangrove leaves from all the studied sites and species ranged between 0.13-0.00 for Ag, 511.01-6.07 for Al, 2.16-0.02 for As, 0.53-0.00 for Cd, 0.45-0.01 for Co, 1.17-0.02 for Cr, 14.73-0.55 for Cu, 541.27-15.83 for Fe, 187.48-10.86 for Mn, 2.61-0.02 for Ni, 5.05-0.01 for Pb, 3.23-0.06 for Se and 330.78-3.93 for Zn (µg/g). Metal concentrations in mangrove leaves differed significantly amongst sites and species (Kruskal-Wallis, $H \geq 22.65$, $p < 0.05$; Mann-Whitney, $U \geq 0.00$, $p < 0.05$) apart from Mtoni Kijichi and Mbweni, where there was no significant difference for some metals i.e. Al, As, Cd, Cr, Fe, Ni, and Pb for *B. gymnorrhiza* (Mann-Whitney, $U \geq 60.00$, $p > 0.05$). Metal concentrations were significantly different amongst all mangrove species (Kruskal-Wallis, $H \geq 10.84$, $p < 0.05$

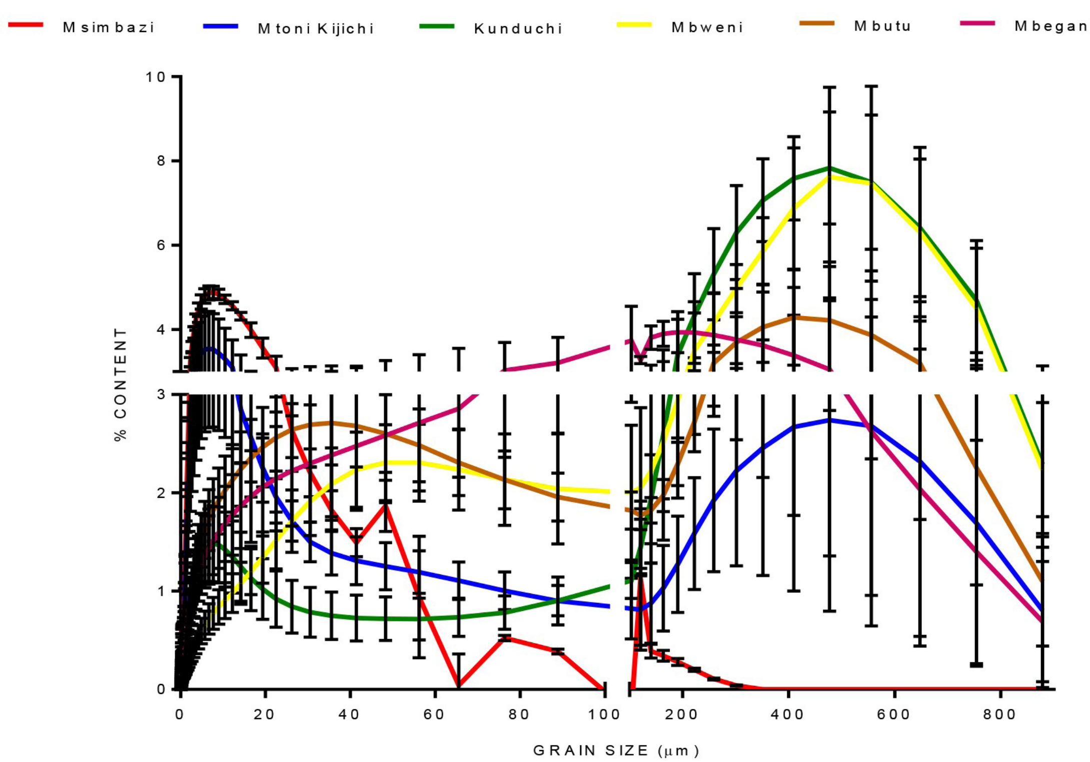

Figure 2. Particle size distribution of sediments (mean±SEM in µm) from the six sampling sites.

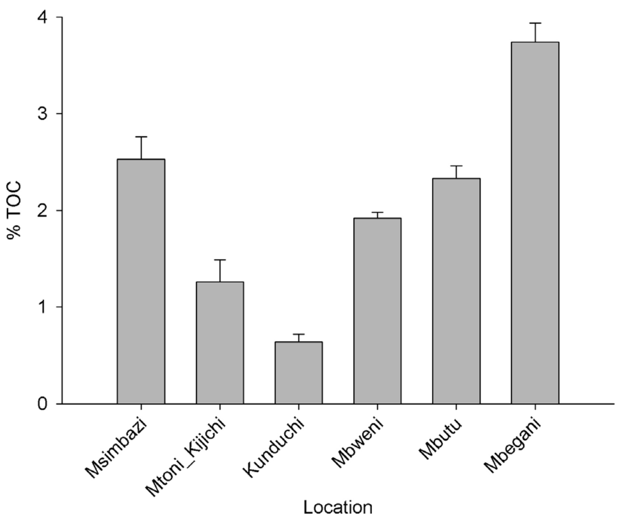

Figure 3. The total organic carbon (TOC) content in sediment.

or Mann-Whitney, $U \geq 0.00$, $p < 0.05$). Higher concentrations of metal were generally observed at Msimbazi and Mtoni Kijichi and mostly decreased with increasing distance from the city centre. Lower concentrations were mostly observed at Mbutu and Mbegani (Fig. 6).

Invertebrates

Metal concentrations in invertebrates from all the studied sites and species ranged between 7.68-0.18 for Ag, 1259.03-10.49 for Al, 85.99-3.64 for As, 7.19-0.10 for Cd, 29.94-1.67 for Co, 23.64-1.35 for Cr, 295.67-27.41 for Cu, 1803.45-178.49 for Fe, 1004.53-7.34 for Mn, 69.09-3.86 for Ni, 16.67-1.17 for Pb, 12.24-0.99 for Se and 710.68-28.60 for Zn (µg/g). Metal concentrations in invertebrates were significantly different amongst sites (Kruskal-Wallis, $H \geq 10.10$, $p < 0.05$; Mann-Whitney, $U \geq 0.00$, $p < 0.05$) apart from Kunduchi, Mbutu, and Mbegani, which showed no significant difference for a few metals (Al and Cd for *T. palustris*) (Kruskal-Wallis, $H \geq 3.89$, $p > 0.05$). The concentrations of metals showed a highly significant difference amongst invertebrate species (Kruskal-Wallis, $H \geq 8.83$, $p < 0.05$; Mann-Whitney, $U \geq 0.00$, $p < 0.05$) except for a few, which were not significantly different among species (Kruskal-Wallis, $H \geq 0.71$, $p > 0.05$; Mann-Whitney, $U \geq 23.00$, $p > 0.05$). Higher concentrations of metals were generally observed at Msimbazi and Mtoni Kijichi while lower metal concentrations were observed at Mbutu and Mbegani (Fig. 7).

Discussion

Sediments and water

In coastal areas, sediment characteristics, particularly the type and quantity of organic matter, grain size, cation exchange capacity, and mineral constituents, are known to have an important influence on metal binding and retention in sediments (Vertacnik *et al.*,

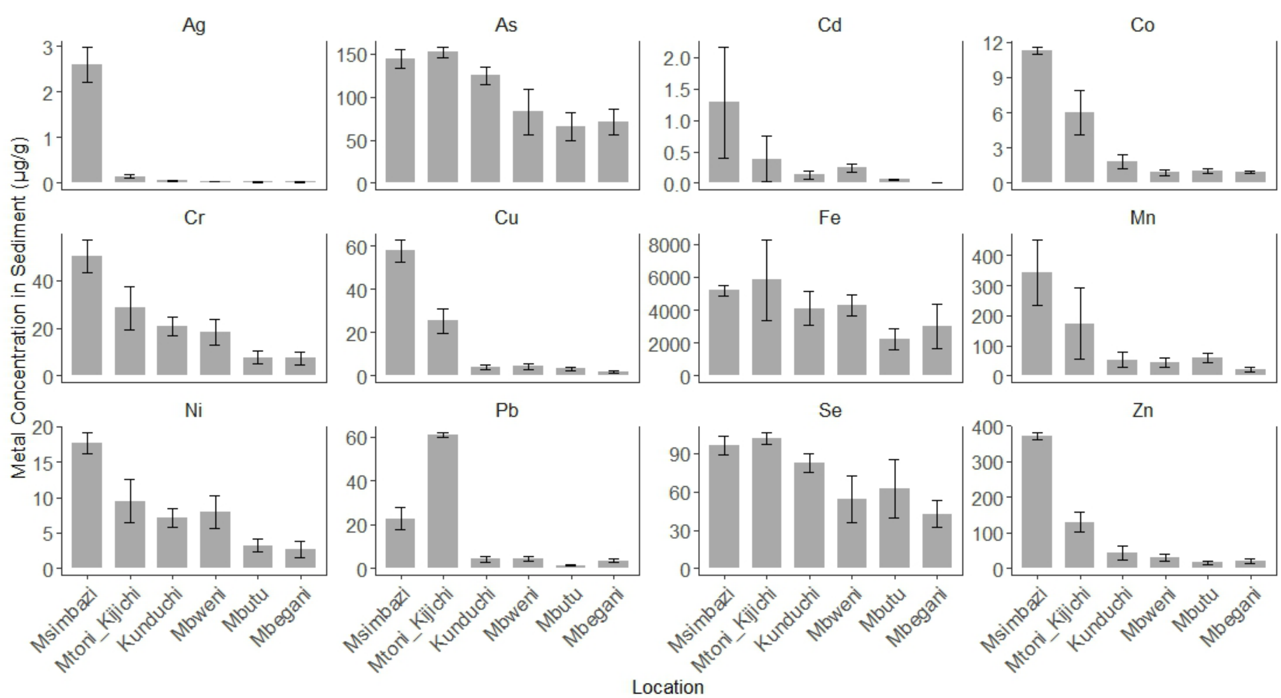

Figure 4. Metal concentration (mean ± SD) in sediments (µg/g dry weight).

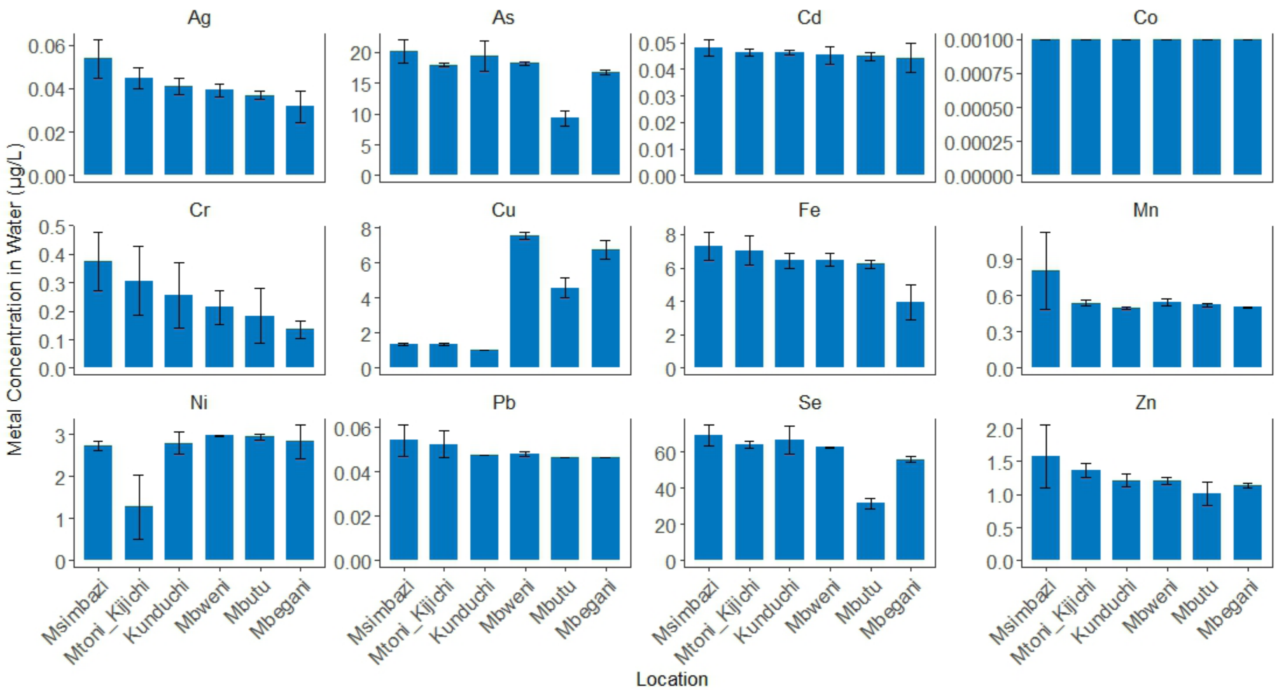

Figure 5. Metal concentration (mean ± SD) in water (μg/L).

1995). The fine-grained fraction (< 63 μm) of the sediment has a high surface area-to-volume ratio, and humic substances also provide a large surface area for metal adsorption (Cheriyan *et al*., 2015; Moore *et al*., 1989; Zhang *et al*., 2014). Sediments with high silt-clay and organic matter content have a high capacity to hold metals. In this study, Msimbazi and Mtoni Kijichi showed the highest silt-clay content, while Kunduchi, Mbweni, Mbutu, and Mbegani showed high sand contents (Fig. 2). This reveals that, metal concentrations observed in organisms in the more polluted sites may also have been in part due to enhanced bioavailability as a result of high silt-clay content and /or total organic carbon concentrations in sediments and vice versa for sites with sandy to coarse contents. The sediment from most sites, however, show a wide range of grain size. This may be due to the fact that sediment in especially vegetated locations like mangrove ecosystems, do not tend to be homogeneous. Non-homogeneity of sediments can be a result of various factors including the presence of decomposing organic matter. Another important point to note regarding sediment composition is that for some filter feeding and sediment-dwelling organisms, organic particles constitute an important direct source of metal intake. Therefore, locations with organically rich sediments will significantly increase metal bioavailability for these organisms.

Certainly, high TOC values alone do not imply high metal bioaccumulation. For example, in this study, Mbegani and Mbutu showed high TOC content, but other factors such as grain size distribution and distance from sources of pollution have contributed to low levels of metal contamination at these sites.

Differences in metal concentrations in sediments can be partly attributed to differences in site distance from the city of Dar es Salaam, which is considered a major pollution source. In general, sites in Dar es Salaam (Msimbazi and Mtoni Kijichi) recorded higher levels of metal concentration, while sites located far away from the city centre (Mbutu and Mbegani) had comparatively low metal pollution which indicates a decrease in metal pollution with increasing distance from the city centre. Studies by Kruitwagen *et al*. (2008), Mremi and Machiwa (2003), and Mtanga and Machiwa (2007) have reported similar results showing decreasing metal pollution with distance from Dar es Salaam city. The Msimbazi River was reported by Ak'habuhaya and Lodenius (1988), De Wolf *et al*. (2001), Mihale (2013), and Mihale (2021) as being heavily polluted. Kruitwagen *et al*. (2008), Machiwa (1992), and Mwevura *et al*. (2002) reported that the harbour of Dar es Salaam, which is located within the Mtoni Estuary, contains high levels of pollutants. Higher levels of metal concentration recorded at

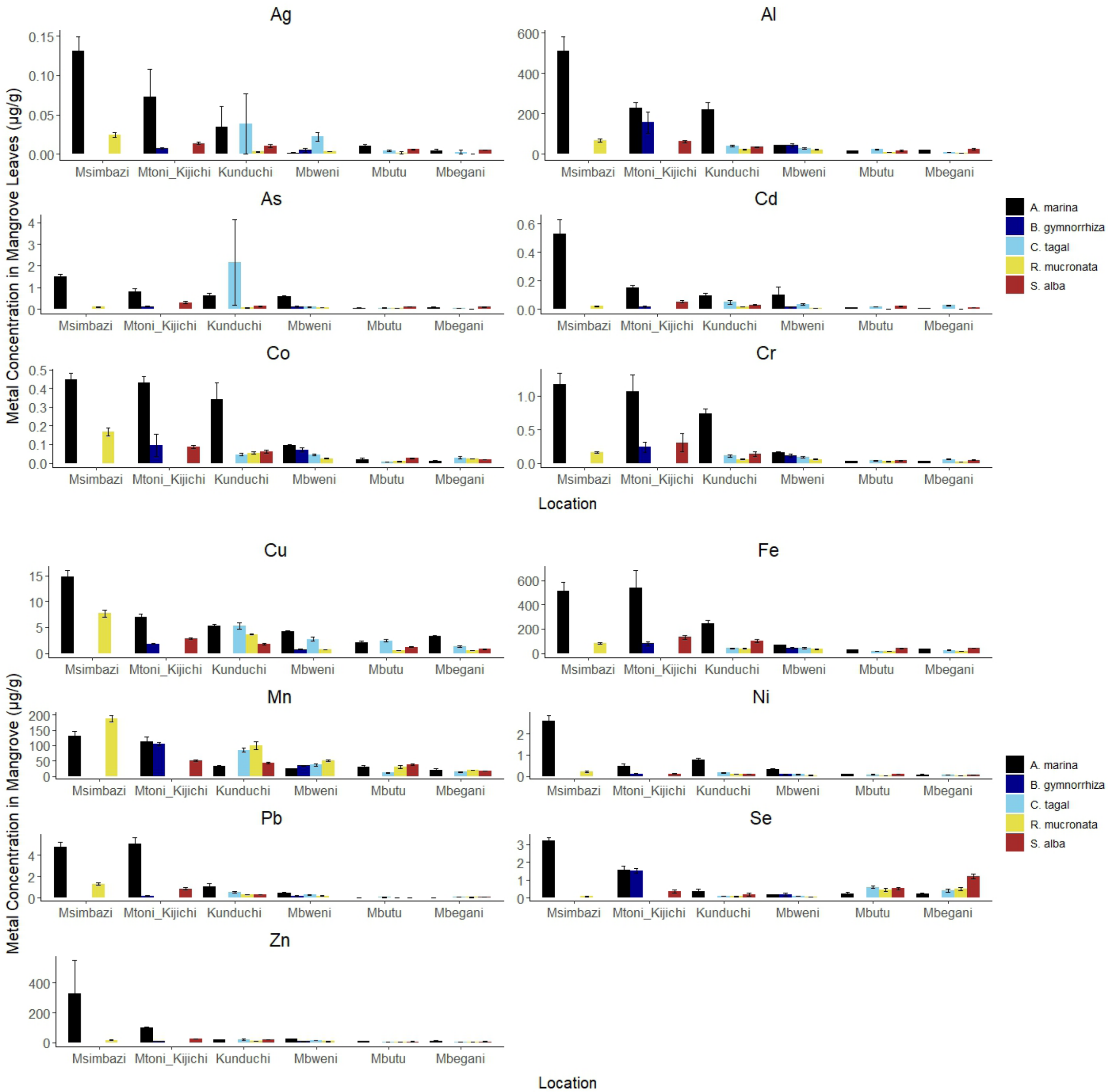

Figure 6. Measured values of different metal concentrations (mean±SD in µg/g dry weight) in mangrove leaves.

Msimbazi and Mtoni Kijichi may also be attributed to sediment grain size characteristics (high silt-clay and organic matter content) which have an influence on sediments capacity to hold metals.

Some metal concentrations in water did not conform to a general pollution decrease at sampling sites away from the city centre. Factors such as the presence of some localized sources (besides Dar es Salaam) at some distant sites may have contributed to higher than expected concentrations of these metals at these sites. Overall, water metal concentrations alone may generally not be a very good indicator of pollution unless at a much larger spatial scale.

Mangrove leaves

One of the main challenges studying (especially for monitoring purposes) chemical concentrations in large plants (trees) is to find suitable parts that represent the whole tree and that are easy to work with, preferably non-destructively, and thus allow repeated sampling. Leaves seem to be good candidates, but some challenges remain, mainly on how to standardize the age of the leaves. However, this is often overcome by

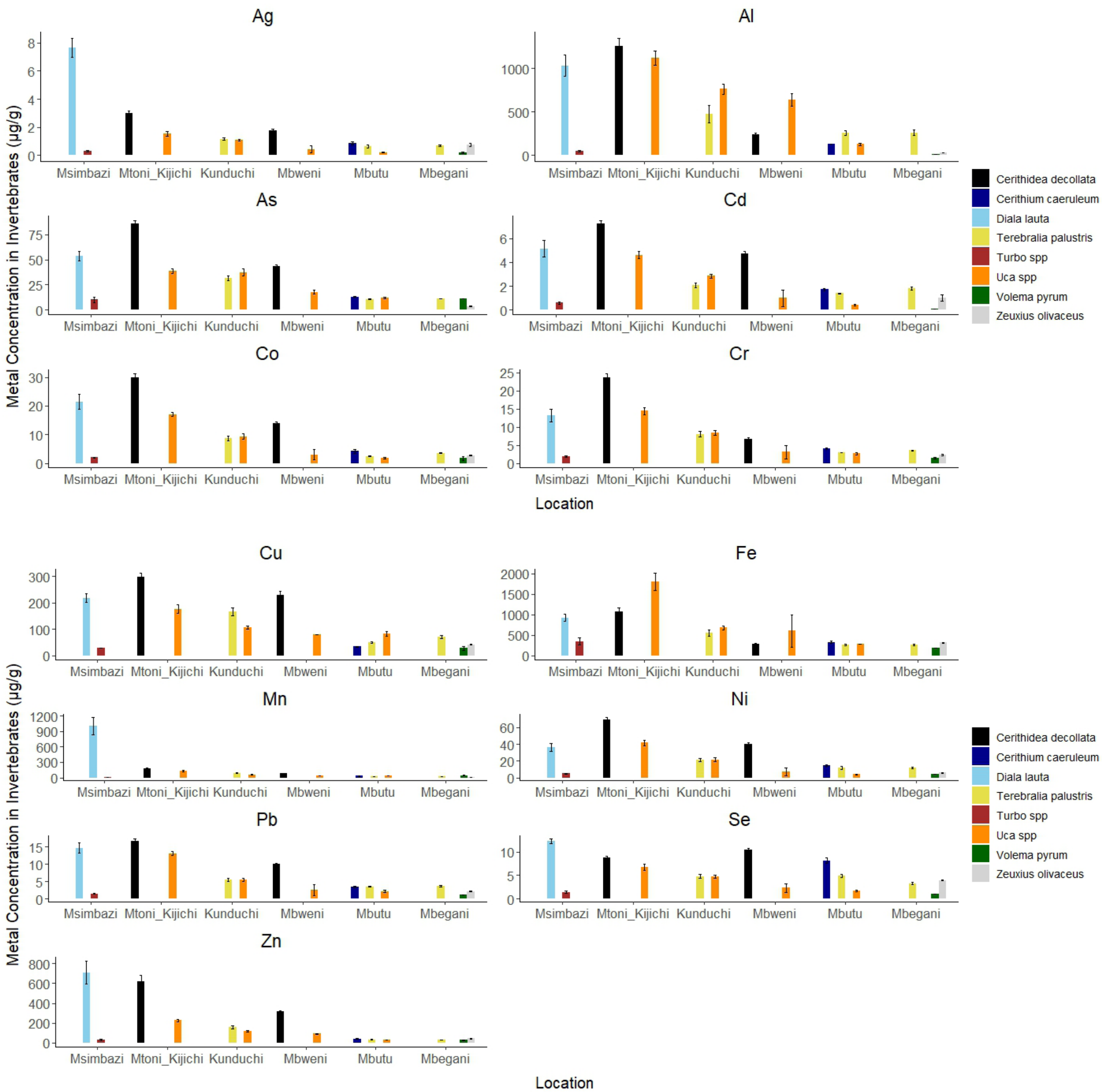

Figure 7. Metal concentrations (mean±SD in µg/g dry weight) in invertebrates.

always sampling either fresh leaves or those that have just fallen. Furthermore, leaves are easy to collect, store and transport. Metal determination procedures are fairly easy in leaves compared to other plant materials. Mangrove leaves have been used in several studies and revealed reasonable levels of metal concentrations (Al Hagibi *et al*., 2018; Almahasheer *et al*., 2018; Caregnato *et al*., 2008; Defew *et al*., 2005; MacFarlane, 2002; MacFarlane and Burchett, 2001; MacFarlane *et al*., 2007; Mremi and Machiwa, 2003; Parvaresh *et al*., 2011).

The differences in metal concentrations among mangrove species, and among sites, may be attributed fundamentally to differences in the levels of metal pollution among the study sites. The closest sites to Dar es Salaam city, such as Msimbazi and Mtoni Kijichi, are generally more polluted than those far away sites (Mbutu and Mbegani). Although there are only a few published studies on the status of metal pollution and their accumulation in mangrove trees, a study by Mremi and Machiwa (2003) showed similar results where metal concentrations in leaves of *A. marina* at Msimbazi were higher than those at Mbweni, which is located far from Dar es Salaam city. Mangroves are highly tolerant of metals despite their potential exposure to metal contaminated sediments (Yan *et al*., 2017). Their tolerance is partly attributed by their ability to exclude metals or regulate the uptake of metals at the root level and limit translocation to the shoot (MacFarlane and Burchett, 2002; Rahman *et al*., 2024). It was suggested by a number of laboratory-based toxicity trials that metal concentrations required to cause a significant negative effect in mangroves may be higher than in comparable aquatic and terrestrial plants (MacFarlane *et al*., 2007). For example, MacFarlane and Burchett (2002) found Pb (0–800 µg g^{-1}) to have little negative effect in the seedlings of *Avicennia marina*. In *A. marina*, Cu and Zn showed low relative toxicities in terms of emergence and biomass, with LC_{50}'s of 566 µg g^{-1} for emergence for Cu and 580 µg g^{-1} for Zn. The reduction in growth/biomass parameters had LOEC values of 400 µg g^{-1} for Cu and 500 µg g^{-1} for Zn. An inhibition of leaf and root development in *Kandelia candel* (L.) Druce seedlings was observed only at the highest applied metal concentrations (400 µg g^{-1} Cu and Zn) (Chiu *et al*., 1995). Based on the above studies, it is clear that the levels of metal contamination in mangrove plants reported in this study do not seem to pose a serious impact on these ecosystems along the coast of Tanzania. However, continuous input of metal contaminants in the studied area may lead to harmful effects in the future.

A. marina showed generally higher metal concentrations overall. These differences may be attributed to differences in metal uptake, tolerance, and metal accumulation capacities amongst mangrove species. The differences may be brought by their distinct morphological specializations for dealing with periodic inundation, anoxic sediments and maintenance of osmotic balance in (hyper) saline environments. For example, members of the families Avicennaceae and Sonneratiaceae possess aerial roots termed 'pneumatophores', while Rhizophoraceae possess aerial stilts to enable gaseous exchange and oxygenation for respiration (MacFarlane *et al*., 2007). Their nutritive root anatomy varies widely among taxa and even within families. Most mangrove species possess roots with two barriers to transport Na+ and other ions to the vasculature, with layers of epidermis and endodermis. The mechanism to deal with the regulation and /or exclusion of ion transport differs depending on whether a species is a salt secretor or a non-secretor. A greater ion mobility and translocation is generally shown by secretors (Lawton *et al*., 1981).

In some mangrove genera, for example *Avicennia* and *Aegiceras*, excessive Na+ and K+ are excreted through specialized glands or glandular trichomes on adaxial and abaxial leaf surfaces, a mechanism which is absent in non-secretors such as *Rhizophora* and *Sonneratia* (MacFarlane and Burchett, 1999). Mangroves with glandular tissues tend to excrete heavy metals concurrently with other solutes (MacFarlane and Burchett, 2000). Variations in mangroves glandular tissue to deal with the challenges of excess cations in saline environments and morphology/function of nutritive root tissue may thus have significant implications for metal accumulation, transport, partitioning and excretion amongst mangrove species (MacFarlane *et al*., 2007).

In order to explain the link between the observed levels of metals in mangroves and those found in the surrounding environment (particularly sediments), correlation analysis was performed between metal concentrations in mangrove species and those observed in sediments. As expected, the results showed in many cases a clear positive relationship between metal concentrations in mangrove leaves and those in the sediments (Table 5). However, in principle, this relationship is not always expected to be perfect. As shown in this study, some cases (metals and/or species) showed relatively weak or no significant correlations. This is because accumulation of metals in any organism is not only dependent on the total concentration of the metal in the environment or distance from a pollution source, but it also depend on other factors such as sediment characteristics (organic matter content, grain size, etc.). In this study, the sites showed differences in both grain size profiles and organic carbon content of sediment. Such differences play a big part in the observed differences in metal accumulation in mangrove trees.

According to results presented on Figure 6, *A. marina* generally accumulated higher concentrations than other mangrove species for most metals, especially at sites located closest to Dar es Salaam city. This elucidates its wider tolerance and accumulation capacity of metals. This species is also widely distributed throughout the study sites and many other mangrove sites along the coast of Tanzania. A. *marina* can thus be used as a bio-monitor of metals along the coast of Tanzania since it fits more of the criteria for metal bio-monitoring than other mangrove species. *A. marina* was also used in a number of previous studies of metal contamination as far as mangrove ecosystems are concerned (Alhassan and Aljahdali, 2021; Aljahdali and Alhassan, 2020; Caregnato *et al*., 2008; MacFarlane, 2002; MacFarlane and Burchett, 1999,

Table 5. Correlation of sediment metal concentrations (μg/g dry weight) and mangroves metal concentrations (μg/g dry weight). *p* values in bold indicate significance level at ≤0.05.

Metal	*A. marina*		*C. tagal*		*R. mucronata*		*S. alba*	
	r	*p*	r	*p*	r	*p*	r	*p*
Ag	0.61	<0.001	0.26	**0.047**	0.88	<**0.001**	0.70	<**0.001**
As	0.71	<**0.001**	0.72	**0.000**	0.54	<**0.001**	0.63	<**0.001**
Cd	0.85	<**0.001**	0.41	**0.001**	0.77	<**0.001**	0.80	<**0.001**
Co	0.70	<**0.001**	-0.11	0.418	0.62	<**0.001**	0.87	<**0.001**
Cr	0.86	<**0.001**	0.47	<**0.001**	0.85	<**0.001**	0.69	<**0.001**
Cu	0.82	<**0.001**	0.44	<**0.001**	0.75	<**0.001**	0.84	<**0.001**
Fe	0.76	<**0.001**	0.73	<**0.001**	0.88	<**0.001**	0.80	<**0.001**
Mn	0.79	<**0.001**	-0.06	0.638	0.56	<**0.001**	0.66	<0.001
Ni	0.75	<**0.001**	0.36	**0.006**	0.80	<**0.001**	0.52	<**0.001**
Pb	0.86	<**0.001**	0.77	**0.000**	0.90	<**0.001**	0.95	<**0.001**
Se	0.55	<**0.001**	-0.21	0.118	-0.36	<**0.001**	-0.57	<**0.001**
Zn	0.81	<**0.001**	0.75	**0.000**	0.84	<**0.001**	0.83	<0.001

2000, 2001, 2002; MacFarlane *et al*., 2003; MacFarlane *et al*., 2007; Maurya and Kumari, 2021; Usman *et al*., 2013).

Invertebrates

Sites closest to Dar es Salaam city (Msimbazi and Mtoni Kijichi) were more contaminated with metals than more distant sites (Mbutu and Mbegani). This was also reported by other studies (Kruitwagen *et al*., 2008; Machiwa, 1992; Kazimoto *et al*., 2018; Mtanga and Machiwa, 2007. It is important to note here that besides the level of pollution and bioavailability, many other factors can result in differences in metal concentrations observed in marine organisms. Biological differences and tolerance levels among species, is one of the main secondary factors that can influence metal concentrations in organisms. Mubiana *et al*. (2006) showed the importance of other biological factors, like body size and physiological condition, as well as some environmental variables such as tidal effect.

Invertebrate species (*Uca spp*. and *T. palustris*) found at more than two sites were correlated with sediment metal concentrations (Table 6). This was performed to get a general picture of the relationship between the environment and organisms. The results generally show a clear significant correlation between what is in the environment to what these species of invertebrates

Table 6. Correlation of sediment metal concentrations (μg/g dry weight) and invertebrate metal concentrations (*Uca spp*. and *Terebralia palustris*, μg/g dry weight). *p* values in bold indicate significance level at ≤0.05.

Metal	*Uca* spp.		*Terebralia palustris*	
	r	*p*	r	*p*
Ag	0.88	<**0.001**	0.62	**0.001**
As	0.84	<**0.001**	0.80	<**0.001**
Cd	0.83	<**0.001**	0.22	0.285
Co	0.87	<**0.001**	0.52	**0.006**
Cr	0.89	<**0.001**	0.63	**0.001**
Cu	0.62	<**0.001**	0.54	**0.004**
Fe	0.86	<**0.001**	0.64	**0.001**
Mn	0.32	**0.039**	0.67	<**0.001**
Ni	0.83	<**0.001**	0.63	**0.001**
Pb	0.75	<**0.001**	0.64	**0.001**
Se	0.84	<**0.001**	0.56	**0.002**
Zn	0.94	<**0.001**	0.71	<**0.001**

have accumulated. *Uca spp.* and *T. palustris* are widely distributed among study sites. *Uca spp.* and *T. palustris* are both good bio-indicators of metal contamination and can be used as a bio-monitor in a metal- and species-specific bio-monitoring programme.

With respect to previous studies, Mtanga and Machiwa (2007) observed higher metal concentrations in the oyster *Saccostrea cucullata* collected from Mzinga creek (Mtoni Kijichi) compared to Ras Dege (which is close to Mbutu). In their study, higher concentrations were found for some metals such as Zn and Cu. Generally, Mtanga and Machiwa (2007) observed a decreasing level of metal concentrations in organisms away from the centre of Dar es Salaam. Mremi and Machiwa (2003) also observed the same trend of metal contamination in the crab *Neosarmatium meinerti* except for Co, Ni and Zn, for which crabs at Mbweni had higher and or equal concentrations compered to Msimbazi and Mtoni Kijichi.

Conclusions

The study provides evidence of metal accumulation in the environment (sediments and water) and biota (mangrove leaves and invertebrates) for especially Al, Fe, Mn, Zn, Cu, Se and As, which can be linked to (or explain) metal contamination prevailing at each site. For the purpose of choosing a suitable local mangrove species to be used as a bio-monitor or bio-indicator, *Avicennia marina* is recommended. Among the invertebrates studied, *Uca spp.* and *Terebralia palustris* have the best qualities as bio-monitors or bio-indicators of metal contamination in the region. Metal concentrations in the environment and biota were generally high at sites located close to Dar es Salaam city centre and decreased with increasing distance from the centre, indicating a need for establishment of a multi-species (representing both plants and animals) monitoring program for assessing metal pollution along the coast of Tanzania. According to the observed differences in environmental variables (TOC, grain size distribution) amongst sites, it is recommended that future studies include assessing the relative bioavailability of metals to explain cases where the expected relationship between metal concentrations in the environment and those found in the organisms are either weak or masked.

Acknowledgments

The authors are highly grateful to VLIR-OUS who funded the first author's MSc studies and made this work possible. We are extending our sincere gratitude to the University of Antwerp, Laboratory of Ecophysiology, Biochemistry and Toxicology for allowing us to use their laboratory facilities during sample preparation and analysis.

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