Western Indian Ocean J. Mar. Sci. Vol. 9, No. 1, pp. 31 - 42, 2010
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Bioavailability of Sediment-bound Heavy Metals on the East African Coast

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Keywords: Metals, sediments, bioavailability, aqua regia extraction, sequential extraction.

Abstract—Currently, environmental risk assessment of metals is based on comparisons of toxicity thresholds against environmental exposure levels measured as total metals, despite the fact that not all heavy metals in the sediments are in bioavailable form to the biota. Analysis was undertaken for nine elements (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, and Zn) in sediment samples collected at eight sites along the Eastern African Coast following aqua regia extraction (to determine the total quantity of metals) and three-step BCR (Community Bureau of Reference) sequential extraction (to obtain the metal fractionation patterns in the sediments in this region). The results revealed that heavy metal levels at some locations were higher than at others. Cd, Mn and Co were more concentrated in labile fractions compared to the other elements. These metals are easily liberated into overlying water, making them available for biological uptake. More than 62% of the total concentrations of Fe and Zn were present in the residual fraction, being immobile and less bioavailable.

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INTRODUCTION

Human activities have been increasing more rapidly and widely in the recent past than ever before in human history. In developing countries, attempts to achieve long-term growth in the economy have resulted in consumption of enormous amounts of natural resources and the subsequent production of large amounts of waste. Contamination of aquatic ecosystems by heavy metals has been identified as one of the major concerns since the industrial revolution (Förstner & Wittmann, 1983; Vinogradov, 1953).

Most developing countries have, in the past, concentrated pollution research on inorganic contaminants other than heavy metals. Of the few studies carried out on heavy metals, a number have been focused on the total concentration of heavy metals in sediments (Kamau, 2001, 2002), despite the fact that this approach does not provide information on the mobility, bioavailability and toxicity of metals and, as such, is not of direct biological significance. The total metal concentration approach has recently been criticized as an inaccurate measure of potential risk (Harmsen *et al.*, 2005). This can be attributed to the fact that the proportion of contaminants that is bioavailable and liable to cause adverse biological effects is much smaller in magnitude due to sorption processes in sediments (Alexander, 2000). In order to accurately estimate the effects and potential risks associated with heavy metal contamination, the environmentally available fraction needs to be determined. Knowledge of this fraction would be more informative in setting environmental quality criteria and standards due to its direct relation to metal toxicity.

Estimates of the available fraction of metals in sediments can be obtained through tiered analytical methods, especially sequential extraction techniques (Tessier and Campbell, 1987). Sediments are usually subjected to sequential extraction using chemicals of decreasing pH and increasing oxidizing strength to remove various operationally-defined geochemical phases (Ngiam and Lim, 2001). The use of sequential extraction is effective in providing detailed information on the origin, species, biological and physiochemical availability, mobilization and transport of trace metals (Perin *et al.*, 1997; Tessier *et al.*, 1979). This study aimed at comparing the environmental availability of heavy metals in sediments samples collected from selected locations along the East African coast using three step-BCR sequential extraction. This technique was used to compare total metal concentrations with individual metal concentrations in the residual fractions, viz. the F1-Exchangeable F2-Reducible F3-Oxidizable, and F4-Residual fraction.

MATERIALS AND METHODS

Study area

Sediments samples were collected at eight sampling sites along the East African coast (Figure 1), selected on the basis of their proximity to urban areas or industrials activities. According to this criterion, sites close to urban or industrialized areas included Mikindani (K3) and Mtwapa (K4) in Kenya, the port of Massawa (E2) in Eritrea and Msimbazi (T2) in Tanzania. Sites relatively distant from sources of contamination were Chale (K1) and Gazi (K2) in Kenya, Gurgussum (E1) in Eritrea and Mbegani (T1) in Tanzania. The sites at Gazi and Chale were located within Gazi Bay, a shallow, tropical coastal system located on the southern coast of Kenya, approximately 50 km from Mombasa City. Mikindani and Mtwapa sites were both located in the Tudor Creeks. The site at Msimbazi was at the mouth of the Msimbazi River, an urban river that runs through the centre of the Dar es Salaam. Mbegani was in the town of Bagamoyo, 70 kilometres north of Dar es Salaam. Massawa is the main harbour of Eritrea and is located on the western side of the Red Sea. Gurgussum is located in the northern part of Massawa.

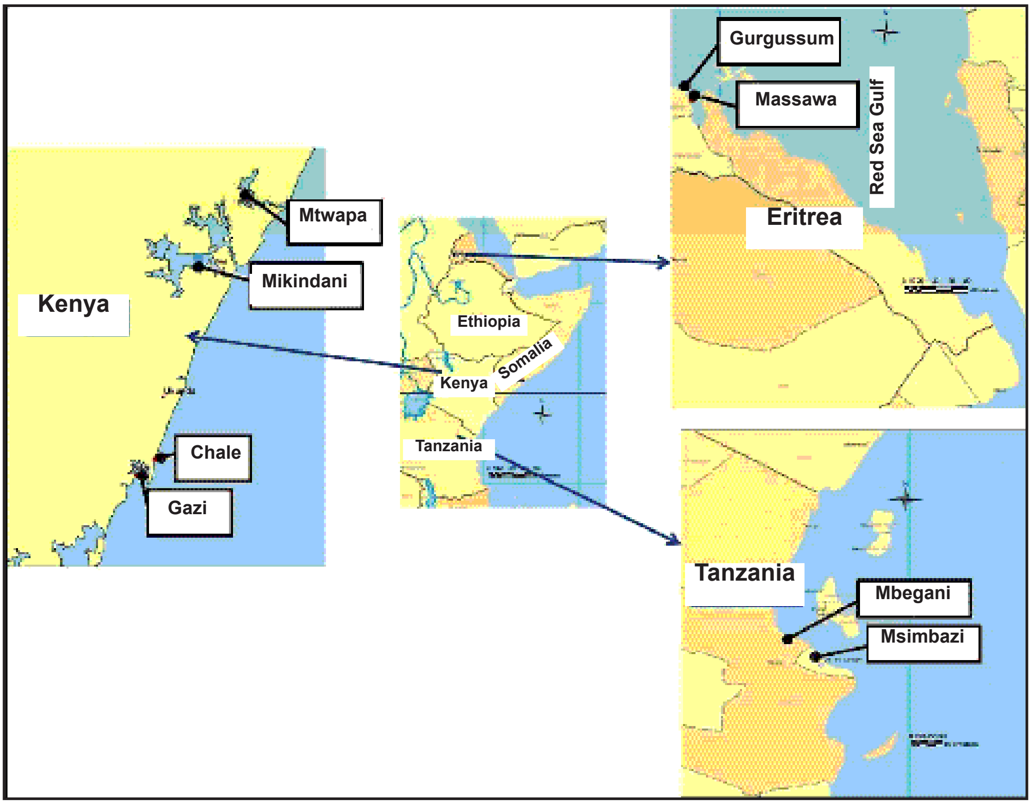

Figure 1. Map of the sampling sites at which coastal sediments were sampled for heavy metal analysis.

Sample collection and preparation

Sampling was conducted in August and September 2006. Three random sediment samples were collected to a depth of 10 cm at each site using plastic hand corers (Ø 8 cm), and extraneous material (such as debris and stones) removed. The samples were pooled at each location, mixed by hand, air-dried and placed in clean polythene bags for transport to the laboratory in Belgium. In the laboratory, about 1 kg of each sediment sample was freeze-dried. The samples were further mixed, ground in a mortar and sieved through a 500 µm sieve. Three replicate subsamples of approximately 1 g each were weighed for three-step sequential extraction, as well as three additional subsamples (approximately 0.5 g each) for aqua regia extraction.

Sample digestion

Total metal extraction (Aqua regia extraction)

Extractions of total metal content of the sediments were performed in aqua regia. The three replicate subsamples (approximately 0.5g each) were carefully weighed and placed in digestion vessels to which 1.5 ml analytical grade HNO_3 (69%) and 4.5 ml HCl (37%) were added and digested in a digestion microwave oven (model ETHOS 900, Milestone, Shelton, CT, USA). The samples were digested at 90, 200, 350 and 500 watts for 5, 3, 5 and 5 minutes respectively. Three replicate standard and procedural blank samples were included with each batch of samples that were digested in the microwave oven. Products of digestion were transferred to polypropylene vials and diluted to 50 ml with Milli-Q water and stored at -20°C for metal analysis. Certified sediment reference material (CRM 141R) was used for quality control.

Three-step sequential extraction

The three-step sequential extraction procedure used in this study was based on the protocol recommended by The

Table 1: Analytical procedure for European Community Bureau of Reference (BCR) three-step sequential extraction of metals from sediments.

Phase definition	Chemical reagents and experimental protocol
Exchangeable and carbonate	Step 1: 1g subsample with 40 ml of 0.11M CH3COOH, shaken for 16 hours at a speed of 400 rpm and 20°C.
Reducible	Step 2: 40 ml 0.5M $NH_2OH.HCl$ (pH 2 adjusted with HNO_3) added to residue, shaken for 16 h (at 20°C and speed of 3000 rpm).
Oxidizable	Step 3: 10 ml of 8.8M H_2O_2 (pH 2-3) added to residue, digested for 1 h at 20°C, heated to 85°C, digested for 1 h, 10 ml H_2O_2 added, digested at 85°C for 1 h, 50 ml 1M CH_3COONH_4 (pH 2) added and shaken for 16 h.

European Institute for Reference Material and Measurements (Geel, Belgium, http://www.irmm.jrc.be), also described by (Ure *et al*., 1993). Analyses were performed on three replicate sediment samples from each site, following the procedure summarized in Table 1. Concentrations of metals in the residual fractions were calculated as the difference between the total metal concentration in the sediments and the sum of concentrations of specific metals in the extracted fractions. Samples of Freshwater Sediments Reference Material (BCR 701) were included with each batch of samples (through the three steps) for verification of the measurements.

Metal determination

Metal concentrations in the solutions were analysed with an Inductively Coupled Plasma Mass Spectrometer (ICP-MS, Varian, Australia). Yttrium was used as an internal standard to correct for signal interference due to differences between calibration solutions and the samples.

RESULTS AND DISCUSSION

Total metal concentrations

Recovery of metals in the reference materials used to check the accuracy of the analytical procedures were between 95-107% of the certified values in the aqua regia extractions and between 97-105%, 81-92% and 83-97% in the F1, F2 and F3 fractions respectively.

The mean heavy metal concentrations in the sediments samples are presented in Figure 2. Fe occurred at the highest concentrations and Cd at the lowest concentrations at all the sampling sites. The order of abundance of the various metals at all the sampling sites was Fe>Al>Mn>Zn>Cr>Ni>Cu>Co>Cd.

The Kenyan site 3 (Mikindani) and Eritrean sites 1 and 2 (Gurgussum and the port area) were found to be the most polluted in terms of total heavy metals. On the other hand, Kenyan sites K1 and K2 (Chale and Gazi) were found to be the least polluted (Figure 2). There were significant differences between the urbanized and non-urbanized sites in Kenya ($p<0.01$, $t=7.452$) and Tanzania ($p<0.05$, $t=2.415$). This confirms the results of a previous study (e.g. Biney *et al*., 1994) in which it was demonstrated that, in most parts of Africa, the effects of pollution were mostly evident around urban areas; more remote areas manifested relatively low background levels of metal contamination. A lack of significant differences ($p>0.05$, $t=0.2039$) between Eritrean sites 1 and 2 may be due to the fact that they are subjected to the same anthropogenic influences or have similar elemental composition in the surrounding bedrock.

Three-step sequential extractions: Exchangeable and associated carbonate phases (F1)

The most abundant metals in Fraction 1 were Cd, Mn and Co,

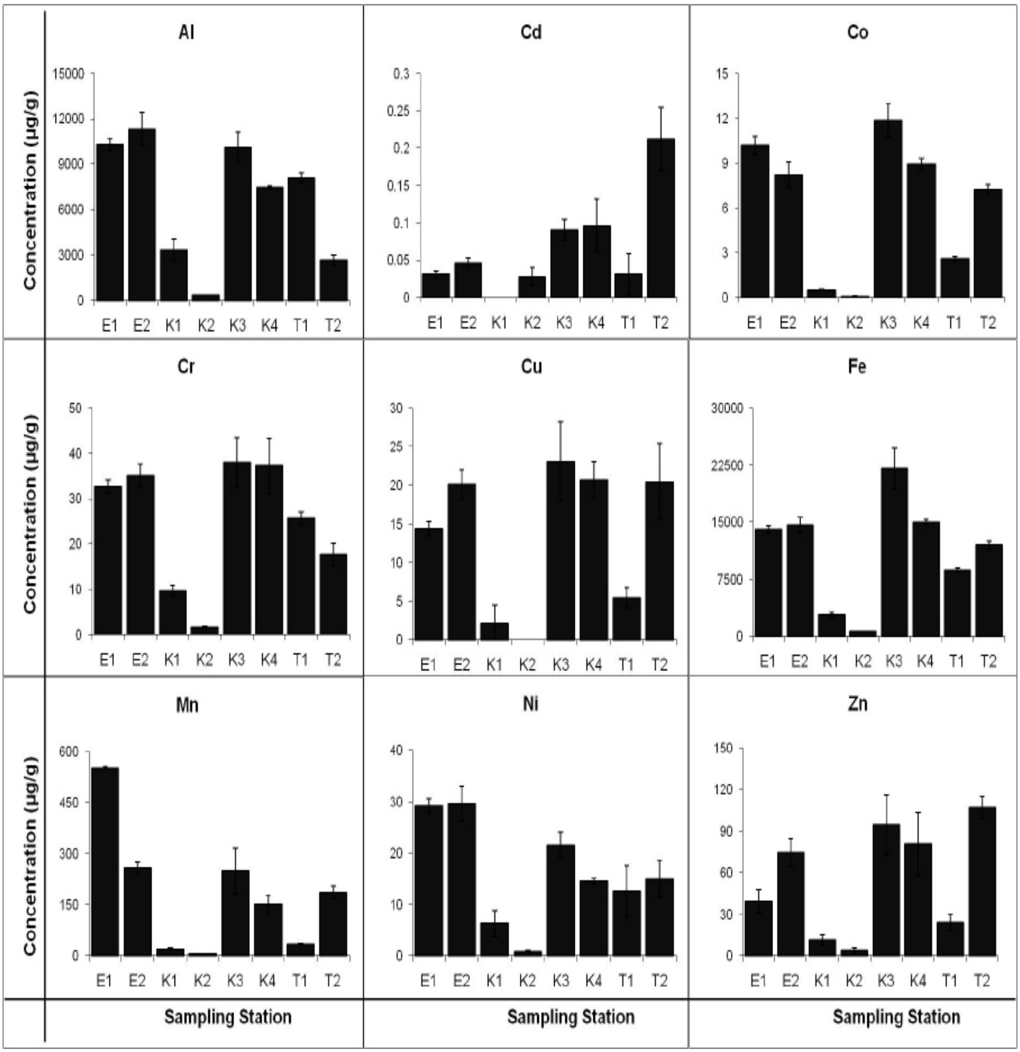

Figure 2. Total heavy metal concentrations (mean ± S.D. in µg g^{-1}) measured in East African coastal sediments following microwave assisted acid digestion.

comprising 19.3-49.7%, 8.1-28.2% and 2.1-22.4% of the total metals respectively at most of the sites (Figure 3). The order of abundance of the metals in this fraction was: Cd>Mn>Co=Zn>Ni>Al>Fe>Cu>Cr. Low concentrations of most metals in the exchangeable fraction indicated that anthropogenic sources contributed less to the sedimentary metal pool at all sampling sites. The higher abundance of metals such as Cd, Mn, Ni and Co in this fraction may be attributable to the ability of these metals to adsorb on sediments or to their presence in clays, Fe and Mn hydrated oxides. Changes in water ionic strength and pH could result in release of these elements into the overlying water (Tessier *et al*., 1979). This makes metals in this fraction the most mobile (Table 2) and readily-available metal for biological uptake in the environment.

Reducible fraction or fraction associated with Fe and Mn oxides (F2)

Cu, Zn, Fe were the most abundant metals in Fraction 2, comprising between 3.6-32.3%, 4.1-29.1% and 9.0-17.4% of the total metals respectively (Figure 3). The order in abundance of metals in this fraction at most sites was Cu>Zn>Fe>Cd>Co>Al>Mn>Cr>Ni. Cu, Zn and Fe were found to be important in the reducible fraction compared to the other labile fractions. This could be due to the fact that Fe and Mn oxides constitute a significant sink for heavy metals in aquatic system under oxidizing conditions as explained by Gibbs *et al*., (1997). The higher concentration of elements such as Cu, Zn, and Fe associated with this fraction are adsorbed to the Fe-Mn colloids (Jenne, 1968), illustrating the ability of Fe-Mn oxides to scavenge trace metals from solution through processes such as adsorption and co-precipitation (Lim and Kiu, 1995). Site-to-site variations in the concentration of metals in this fraction may be attributable to the fact that the mechanisms of their adsorption and co-precipitation are sensitive to changes in redox potential, rendering them moderately mobile and affecting their relative concentration (Table 2). This fraction thus carries a significant burden of metals, making substantial quantities potentially available to biota with changes in environmental conditions.

Oxidizable fraction or bound to organic matter (F3)

Al, Co, Cr and Ni were the most abundant metals in this fraction, comprising 2.0-27.8%, 4.7-33.4%, 2.3-51.5% and 3.1-32.4% of the total metals respectively (Figure 3). The order in abundance of metals in this fraction at most sites was Cr>Co>Ni>Al>Cd>Mn>Cu>Fe>Zn. The oxidizable fraction of some metals was relatively important at some stations, especially Al (K1, K4, T1 and T2), Cr (K2, K4, Ti and T2), Co (K2, K1), Ni (K1, K2, K3, K4 and T2) and Cd (K2) as shown in Figure 3. This is in agreement with the findings of Perin *et al*., (1997) which indicated that organic matter is important in regulating the amount of free or bioavailable metals in sediment. Metals in this fraction are not considered mobile or freely available (Table 2) as they are thought to be associated with stable, high molecular weight humic substances that slowly release only small amounts of metals.

Residual fraction (F4)

Most metals were more abundant in the residual fraction than in the labile fraction at a number of the sites (Figure 3). Fe was the most abundant element in the residual fraction in terms of relative abundance (in comparison to the other fractions), constituting 62.0-91.2% of the total metal concentration

Table 2: Relative mobility and availability of trace metals in sediments (modified from Salomons, 1995).

Metals and association	Mobility
Exchangeable and associated with carbonated phases	High; changes in major cationic composition (e.g. in estuarine environments) may cause their release.
Metals associated with Fe-Mn oxides	Medium; changes in redox conditions may cause mobilization.
Metals associated with organic matter	Medium/low; follows trends in decomposition/ oxidation of organic matter.
Metals fixed in crystalline phase (residual fraction)	Low; only available with weathering.

in the sediments. The relative abundance of the other elements in the residual fraction varied between 62.4-95.1% for Zn to 18.8-68.4% for Cd (Figure 3). The order in abundance of metals in the residual fraction was: Fe>Zn>Al>Ni>Cu>Cr>Co>Mn>Cd.

The metals in the residual fraction are usually retained within the crystal lattice of minerals and in well-crystallized oxides, and are thus considered to be immobile (Tessier *et al*., 1979). As reported elsewhere (Gibbs, 1977), absolute concentrations of metals in this fraction are not affected by anthropogenic inputs. The results of this work therefore indicate that sediment-bound metals along the East African coast are mostly of natural geochemical origin.

Labile fraction

When considering the labile fraction (the sum of F1, F2 and F3), the most mobile elements at most sites were found to be Cd, Mn and Co. The order of abundance of labile metals was: Cd>Mn>Co>Cr>Cu>Zn>Ni>Al>Fe. Despite the fact that the total level of metals at Gazi was low (compared to the other sites), a substantial amount (41.9-65% of the total) of most metals (Al, Cd, Co and Mn) at this site were in the mobile fraction. A relatively high bioavailability of extractible metals was notable at Gazi and may be attributable to naturally-occurring processes such as weathering of the parent rock, the grain size of the sediment, or the prevailing environmental conditions which could be enhancing dissolution of the metals. Sites K2 (Co, Cr), T1 (Cd, Co, Cr, Ni) and T2 (Cu) had substantial quantities (>40%) of these metals in the labile fraction. As stated by Fernandes (1997), the occurrence of metals in more easily-leached phases would characterize samples collected at polluted sites. This could be true of T1 and T2, since the likelihood of these sites being polluted is evident from the amount of metals extracted using aqua regia.

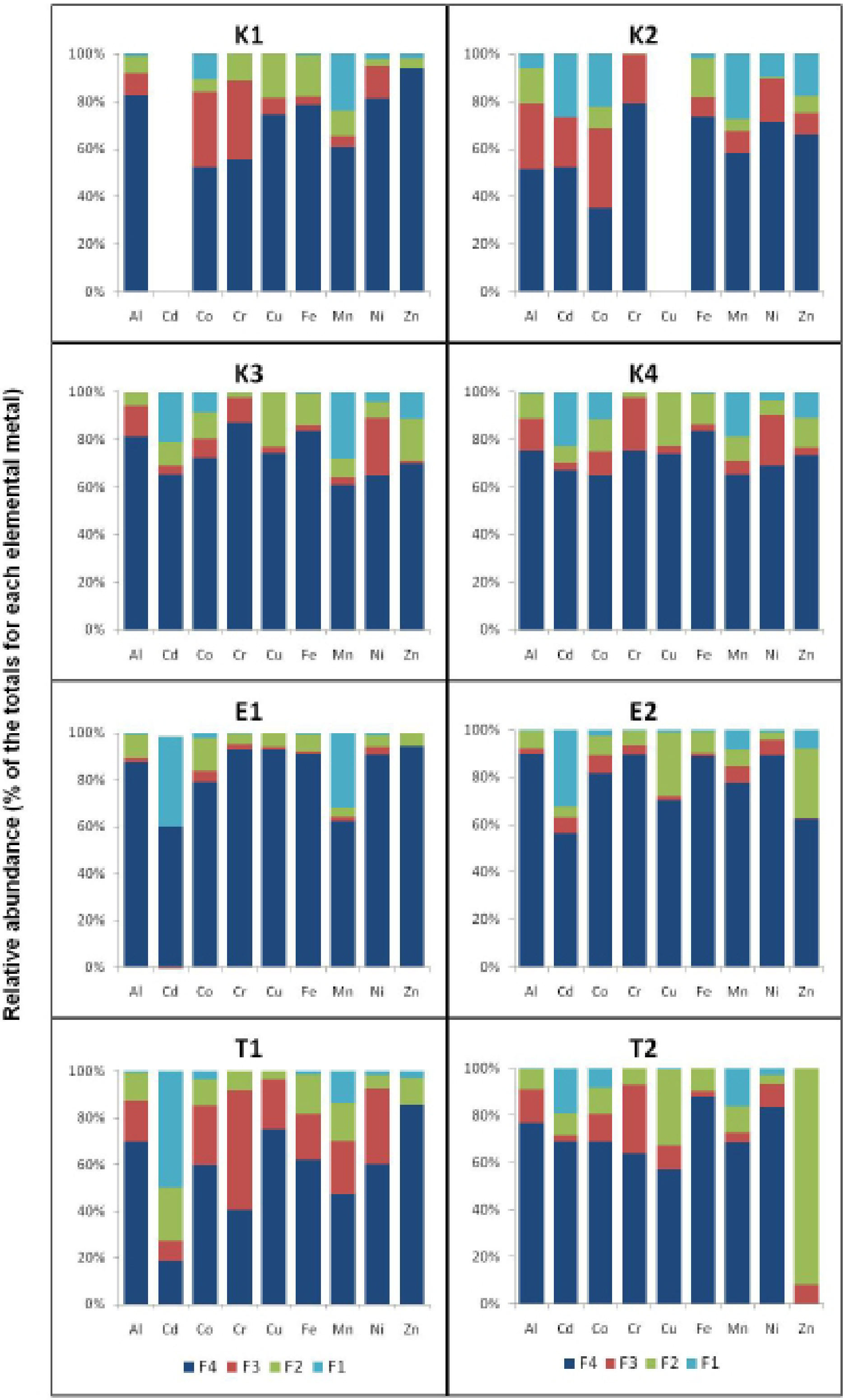

Figure 3. Exchangeable (F1), reducible (F2), oxidizable (F3) and residual (F4) metal fractions in East African coastal sediments.

Metals of interest

Heavy metals manifested differing concentrations in the various sediment fractions. Fe and Cu in the sedimentary fractions followed the order, F4>F2>F3>F1; Mn and Cd, F4>F1>F2>F3; Cr, Ni, Al and Co, F4>F3>F2>F1; and Zn, F4>F2>F1>F3. A high proportion of most of the metals was found in the residual fraction (F4), making them relatively less bioavailable. This has been reported elsewhere by Usero *et al*., (1998), Chester *et al*., (1988) and Belzunce-Segarra *et al*., (1997). Substantial amounts of Mn (16.4-31.9%), Cd (31.3-81.2%), Cr (3.84-51.5%), Co (18.2-65%) were also found in the non-residual fraction, as variously reported by Ngiam and Lim (2001), Usero *et al*., (1998), Lin and Chen (1996), Tessier *et al*., (1979) and Olazabal *et al*., (1997). This suggests that considerable quantitites of Mn and Cd may be released into the environment if the environmental conditions change, favouring their desorption and making them potentially bioavailable for uptake by organisms.

Concentration of metals such as Co (K1, T1, K2 and K4), Al (Gazi), Zn (Msimbazi) and Cr (T1) were exceptionally high in the non-residual fraction at the sites indicated, suggesting that these metals could be anthropogenic in origin and easily mobilized into the water compartment, making them more bioavailable depending on the environment conditions.

CONCLUSIONS

In this study, the extraction of metals from sediments using aqua regia yielded differences between the concentration of metal at sites in the proximity of urban areas and those less influenced by anthropogenic activities. However, the results of sequential extraction revealed that most of the metals were present in the residual fraction. The results of sequential extraction thus indicate that the metals in East African coastal sediments are natural in origin. This therefore has implications in Environmental risk Assessments (ERAs), as the consideration of total metal concentrations will obviously lead to an overestimation of environmental pollution. Future exposure assessments (especially if the results are to be used for ERAs) should focus on bioavailable metals.

Some sites, in particular Gazi, had relatively high levels of bioavailable metals, despite the fact that they were relatively unpolluted in terms of total metal concentrations. Future studies should strive toward determining local factors that affect the bioavailability of metals in such unpolluted systems.

Acknowledgments**:** This work was part of East African metal contamination pilot study organized by Antwerp University with partial funding from Vlamse Interuniversitaire Raad (VLIR)-Belgium. We appreciate the assistance accorded to this study by these two Institutions. We are also indebted to all the technical staff in the Tanzania Fisheries Research Institute, Ministry of Fisheries Eritrea and Kenya Marine and Fisheries Research Institute that helped with sampling in the field.

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