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# Heavy metals in sediments from Makupa and Port–Reitz Creek systems: Kenyan Coast

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**Abstract**

Copper, zinc, lead and cadmium heavy metals were determined in sediments from the Kenyan Coast. Sediment samples were obtained from Makupa and Port Reitz Creek systems. The samples were digested using concentrated hydrochloric acid and the metal content determined using Atomic Absorption Spectrophotometer (AAS). The method of analysis was evaluated using Soil-7 certified reference material (International Atomic Energy Agency, IAEA). For comparison, sediment samples were also analysed using Energy Dispersive X-ray fluorescence technique and results obtained show good agreement. Higher metal concentrations were obtained in Makupa Creek sediments (Cu, $102 \pm 46.0$; Zn, $1017 \pm 840$; Pb, $103 \pm 35.8$; Cd, $51.0 \pm 14.3$) as compared to Port Reitz Creek system (Cu, $21.6 \pm 7.1$; Zn, $57.1 \pm 17.9$; Pb, $26.2 \pm 11.6$; Cd, $1.38 \pm 0.7$). There was significant ($p = 0.05$) variation in the elemental concentrations between and within sites. Industrial activities and a nearby municipal dumpsite were associated with the higher elemental concentrations particularly in Makupa Creek.


*Keywords:* Sediments; Heavy metals; Atomic Absorption Spectrophotometry; X-ray fluorescence; Certified reference material; Kenyan Coast

## 1. Introduction

Trace metals derived from natural inputs and anthropogenic emissions are ubiquitous in the global environment (Onyari, 1985; Nriagu, 1989, 1990; Blackmore, 1998; De Wolf et al., 2001). Sediments usually act as a sink for aquatic pollutants. Consequently, sediment-associated contaminants can influence the concentrations of trace metals in both the water column and biota if they are desorbed or become available to benthic organisms. One of the major problems that heavy metals cause with respect to their effects on aquatic organisms is their long biological half-life. Lead and cadmium in particular are recognised as toxic metals and incidences of environmental pollution are well known (Nriagu, 1990). Blackmore (1998) provided an overview of trace metal pollution (cadmium, copper, zinc, lead, etc.) in coastal environment in Hong Kong. Maximum lead concentrations in Hong Kong sediments (161 mg/kg) were greater than Darwin Harbour (91 mg/kg), but much less compared to the River Tees (990 mg/kg). The lead concentrations in typhoon shelter sediments (550 mg/kg) were comparable to those from North Sea (630 mg/kg). Okoye (1991) reported anthropogenic heavy metal enrichment of Cd, Co, Cu, Cr, Fe, Mn, Ni, Pb and Zn in the Lagos Lagoon, Nigeria, which was attributed to land-based urban and industrial wastes sources.

Whereas some heavy metals data have been reported along the Kenyan Coast (Norconsult, 1977; Wandiga and Onyari, 1987; Oteko, 1987; Everaarts and Nieuwenhuize, 1995; Williams et al., 1996), comprehensive information of trace metal content in the various abiotic and biotic compartments is insufficient. This study was therefore undertaken to document the trace element content and distribution of sea sediments derived from Makupa, and Port–Reitz Creeks, along the Kenyan Coast. The two creeks investigated receive varying loads of pollutants emanating from various anthropogenic inputs such as industrial, sewage and urban/domestic wastes. Of particular interest is the effect of the uncontrolled Kibarani dumpsite,

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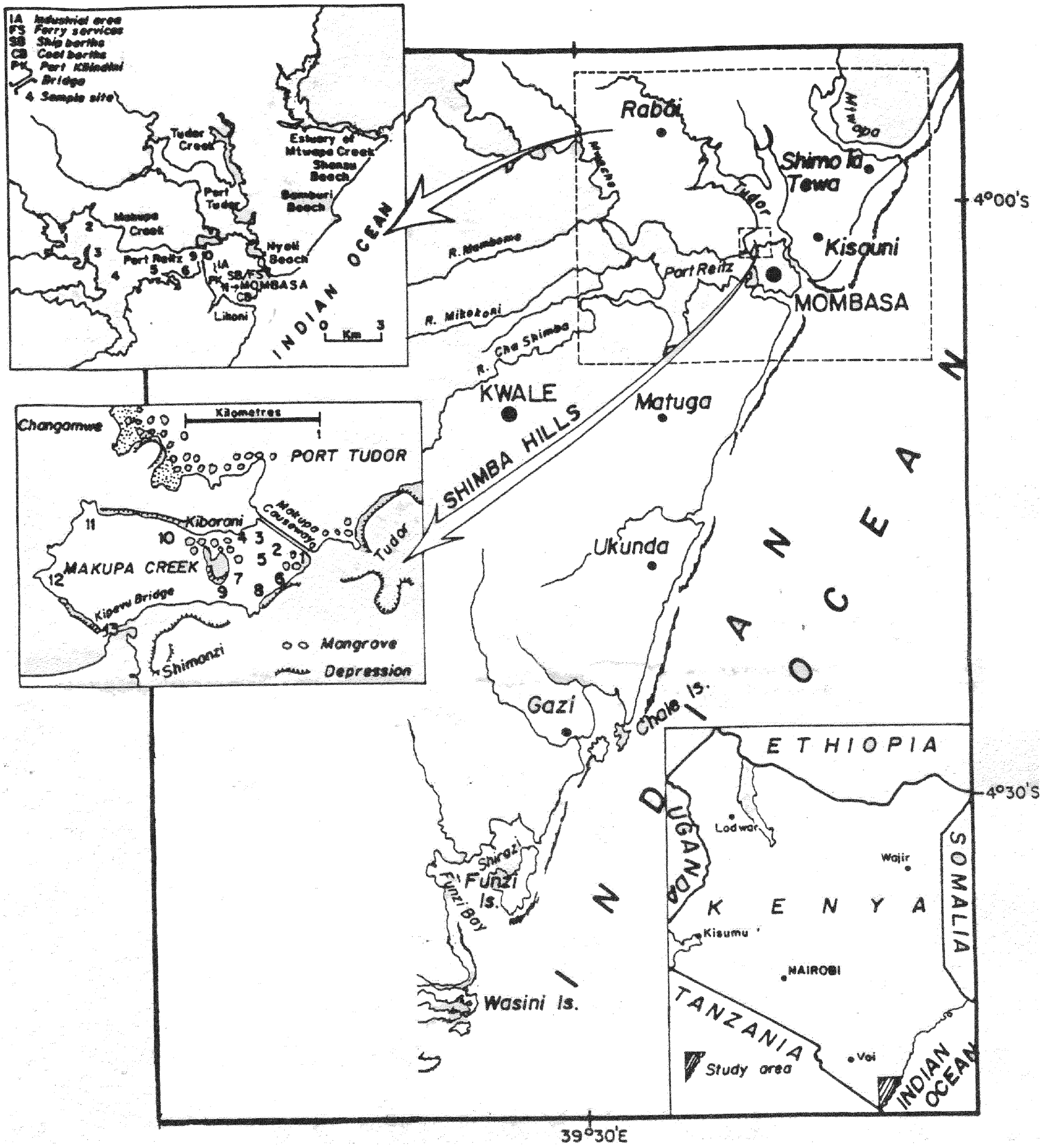


Fig. 1. Map showing the location of Makupa and Port Reitz Creek systems on the Kenyan Coast and the sampling stations in the specific sites.

located on the shores of Makupa Creek, where municipal refuse is currently dumped.

## 2. Materials and methods

### 2.1. Study area

Mombasa district has a coastline of about 32 km and covers an area of approximately 275 km$^2$, composed of the Island (13 km$^2$), mainland areas (197 km$^2$) and the Tudor, Kilindini/Port Reitz and Makupa Creeks (65 km$^2$) (Fig. 1). A causeway bridge (Makupa causeway) connects the Island to the west mainland, and in effect prevents mixing of the Makupa Creek with Tudor Creek waters. The Port–Reitz–Kilindini system supports a wide spectrum of associated industries, including oil refining,

Table 1
Observed and certified values (mg/kg) for IAEA Soil-7 CRM

| Technique | | Cu | Zn | Pb | Cd |
|---|---|---|---|---|---|
| AAS | observed | $9.4 \pm 0.09$ | $92.2 \pm 0.06$ | $65.6 \pm 0.04$ | $2.30 \pm 0.05$ |
| EDXRF | observed | $\leq 30.0$ | $99.0 \pm 5.28$ | $67.6 \pm 1.70$ | – |
| * | certified | 9–13 | 101–113 | 55–71 | 1.1–2.7 (NC) |

NC = Not certified. ≤ = Less than or equal to the detection limit. *Neutron activation analysis, AAS, Fluorimetry, Emission Spectroscopy, Colorimetry and Volumetry with or without sample pre-treatment and separation and preconcentration steps (Analytical Quality Control Service-IAEA, Austria).

Table 2
Comparative analysis of sea sediments from Makupa and Port Reitz Creek systems using AAS and EDXRF

| Creek | Method | Sample | Cu | Zn | Pb | Cd |
|---|---|---|---|---|---|---|
| Makupa | AAS | KU1 | 116 ± 0.1 | 3200 ± 3 | 111 ± 0.2 | 46.9 ± 0.93 |
| | XRF | KU1 | 125 ± 9.3 | 3214 ± 21 | 109 ± 4.4 | – |
| | AAS | KU12 | 49.7 ± 0.82 | 336 ± 1.7 | 65.5 ± 1.03 | 64.2 ± 0.44 |
| | XRF | KU12 | 52.5 ± 5.42 | 352 ± 6.3 | 65.9 ± 2.13 | – |
| Port Reitz | AAS | PM10a | 31.7 ± 0.59 | 89.2 ± 1.24 | 46.8 ± 0.97 | 2.00 ± 1.27 |
| | XRF | PM10a | 40.7 ± 6.96 | 106.4 ± 11.3 | 53.8 ± 8.54 | – |
| | AAS | PM11c | 46.2 ± 0.08 | 90.1 ± 0.57 | 67.4 ± 2.32 | 1.89 ± 0.73 |
| | XRF | PM11c | 42.8 ± 3.38 | 121 ± 12 | 70.1 ± 8.60 | – |

Concentration values in mg/kg, dry weight.

manufacturing, and shipping activities as compared to the Tudor Creek. Cha Simba and Mwache rivers discharge approximately $40 \times 10^6$ and $50 \times 10^6$ $m^3$ freshwater into the Port Reitz Creek, respectively (Munga et al., 1993). The city authority in Mombasa operates a refuse collection service, which disposes approximately 60% of the domestic waste at an uncontrolled dumpsite known as Kibarani, on the shores of the Makupa Creek (Fig. 1, inset 2). Sludge from septic tanks/soak pits is also usually disposed of at the Kibarani dumpsite.

### 2.2. Sample collection

A total of 41 sea sediments were collected using an Ekman grab sampler. Sediment samples were collected from 11 and 13 stations in Port Reitz and Makupa Creeks, respectively. The samples were taken from at least three substations (middle of the creek channel and either side of the creek shoreline). The sediments were stored in polyethylene bags and labelled according to the site, month of collection, station and substation as follows, for Creeks; P = Port–Reitz and K = Makupa Creek. Sampling was done during January (J), March (M) and July (U) 2001. The stations were labelled in Arabic numbers, while substations were labelled in lowercase alphabet letters.

### 2.3. Sample preparation and analysis

Sediment samples were dried in an oven at 105 °C to constant weight (24 h), then ground and sieved. The fraction of the sediment material which passed through < 63 μm sieve was collected. For analysis, 1.0 ± 0.1 g duplicate subsamples were weighed into digestion tubes. After the addition of 20 ml conc. Hydrochloric acid, the samples were digested for 3 h at 100 °C in an aluminium heating block. The digestion mixture was cooled to room temperature and 1 ml hydrogen peroxide carefully added. The digestion tubes were heated for a further 30 min. The digests were allowed to cool and quantitatively transferred into 50 ml volumetric flasks and made up to mark using deionised water. The digestion mixture was transferred into 50 ml polypropylene bottles ready for analysis. Reagent blanks were prepared in a similar manner for every batch of samples to cater for matrix effects. For elemental analysis a Chem Tech Analytical 2000, Atomic Absorption Spectrophotometer (AAS) was used. All analyses were carried

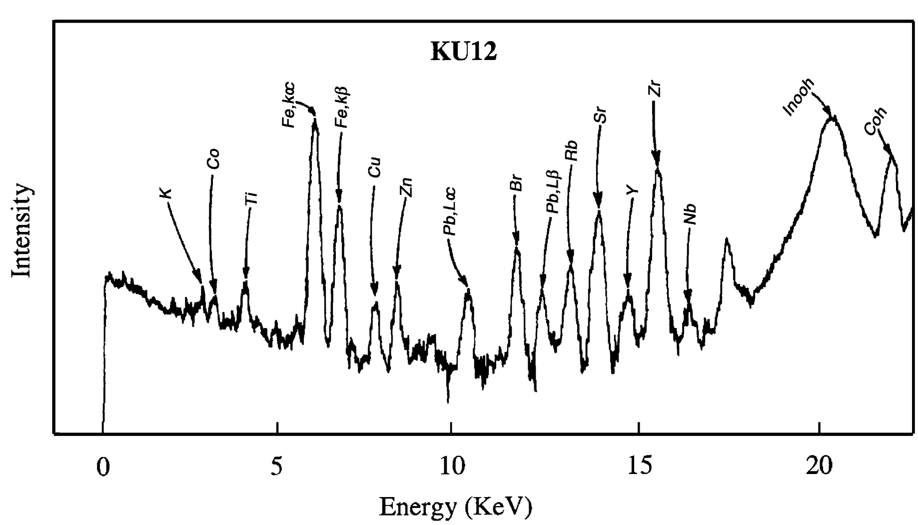


Fig. 2. XRF elemental spectrum of sediments from Makupa Creek, Kenyan Coast.

Table 3
Heavy metal content (mg/kg, dry weight) in sediments from Makupa and Port Reitz Creeks and other regions

| Creek | Copper | Zinc | Lead | Cadmium | Reference |
|---|---|---|---|---|---|
| Makupa | 50.9–229 (102 ± 46.0) | 276–3193 (1017 ± 840) | 54.6–165 (103 ± 35.8) | 31.0–81.9 (51.0 ± 14.3) | Present study |
| Port Reitz | 11.3–45.1 (21.6 ± 7.1) | 30.7–92.9 (57.1 ± 17.9) | 15.7–71.2 (26.2 ± 11.6) | 0.55–3.24 (1.38 ± 0.7) | Present study |
| Port Kilindini and Port Tudor | 32 ± 20 | 110 ± 76 | 55 ± 47 | 2.5 ± 1.8 | Nyatebe (1990) |
| Port Tudor, Reitz and Kilindini | – | – | 34–427 | 1.5–3.0 | Williams et al. (1996) |
| Severn Estuary, UK | 38 | 280 | 119 | – | Chester and Stoner (1975) |
| Tolo Harbour, Hong Kong | 6.80–231 | 38.9 | 20.2–187 | 5.9–6.8 | Wong et al. (1980) |

out using an air–acetylene flame at optimum instrument operating conditions recommended by the manufacturer. The calibration standards were prepared from 1000 ppm stock solutions to obtain calibration standards of 0.02–2, 0.4–25, 0.3–30 and 0.02–2.0 ppm for zinc, copper, lead and cadmium, respectively. Evaluation of the accuracy of the analytical method was done using SOIL-7 Certified Reference Material obtained from International Atomic Energy Agency (IAEA). Two techniques were used for comparison, Atomic Absorption Spectrophotometer and Energy Dispersive X-ray Fluorescence (EDXRF). Evaluation of precision, reproducibility and repeatability was performed by replicate analyses of selected samples. EDXRF analyses (Canberra detector Model SL80175) were

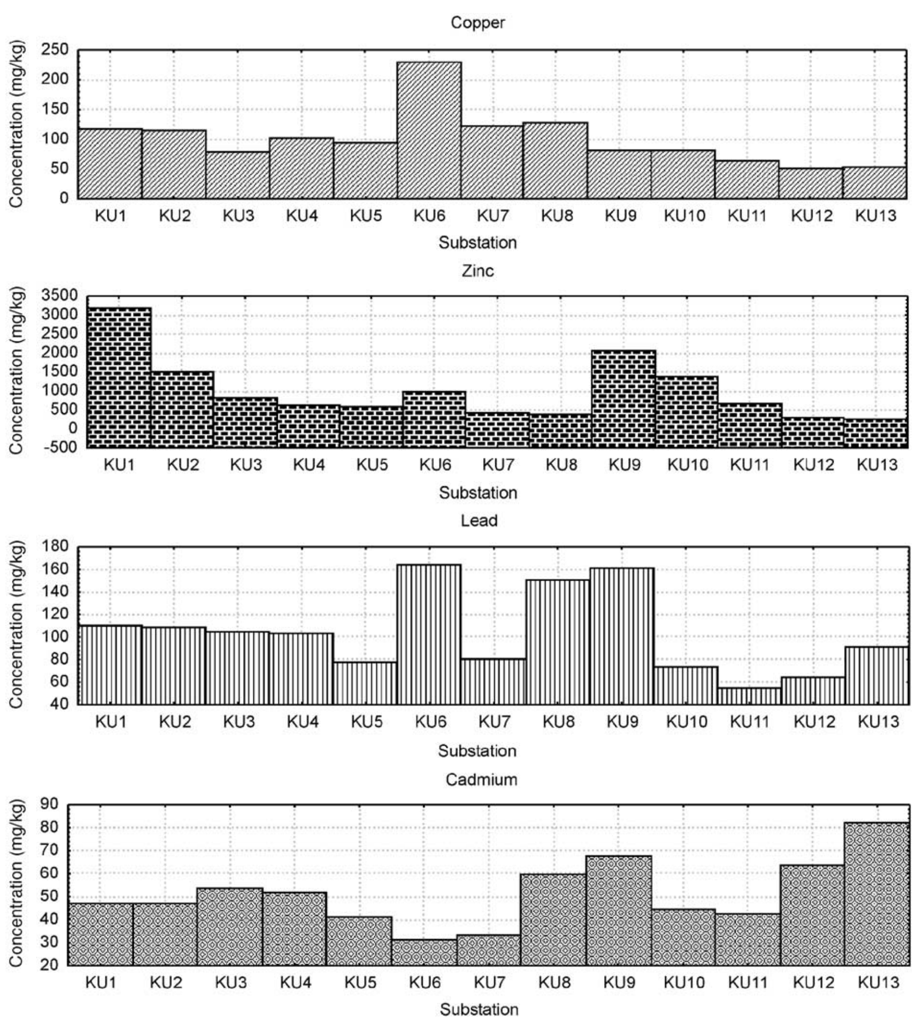


Fig. 3. Distribution of copper, zinc, lead and cadmium in the Makupa Creek sediments.

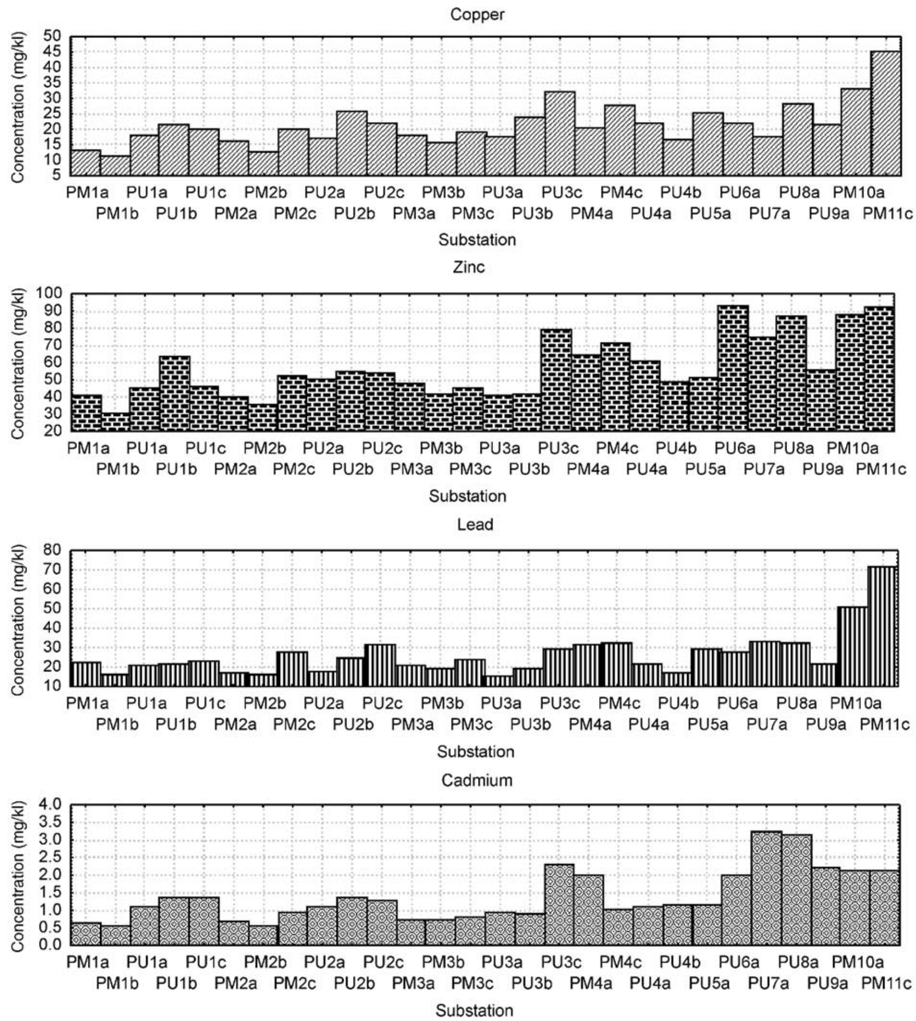


Fig. 4. Distribution of copper, zinc, lead and cadmium in the Port Reitz Creeks system.

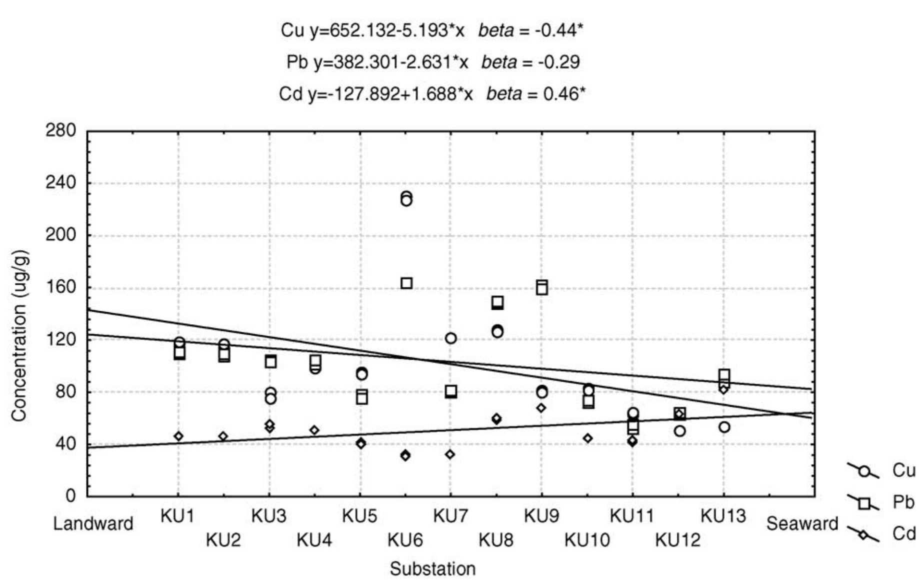


Fig. 5. Landward–seaward elemental (Cu, Pb and Cd) concentration trends in Makupa Creek sediments.

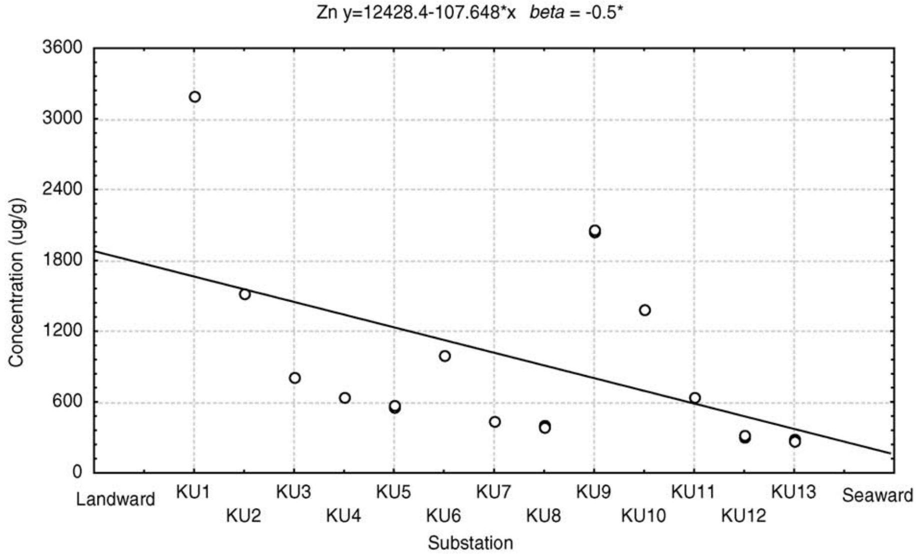


Fig. 6. Landward–seaward zinc concentration trend in the Makupa Creek sediments.

done using the pellet preparation method as described by Kinyua (1982). Calculation of actual concentrations, Regression analysis, ANOVA, Turkey HSD test and Spearman rank correlation analysis was done using Excel and Statistica programs.

## 3. Results

Table 1 gives the AAS and EDXRF analytical results obtained for IAEA Soil-7 Certified Reference Material (CRM). Accuracy is the degree of conformity of a given measurement to a standard or a true value. The results shown in Table 1 indicate good agreement between experimental and certified values.

Table 2 gives the results of trace metals analysis obtained using AAS and EDXRF techniques. The data show good agreement between the two independent techniques employed, attesting to the good accuracy of the procedure used for analysis of the sediments. Cadmium could not be analysed using XRF since the primary X-ray excitation source used was radioactive $^{109}$Cd.

Fig. 2 gives the typical EDXRF elemental spectrum obtained for Makupa Creek sediments. As shown, the elements present in Kenya's marine sediments include potassium, calcium, titanium, iron, copper, zinc, lead, bromine, rubidium, strontium, yttrium, zirconium and niobium.

The mean elemental content in sediments and concentration ranges obtained for the creeks investigated are summarised in Table 3. A global comparison is also pro-

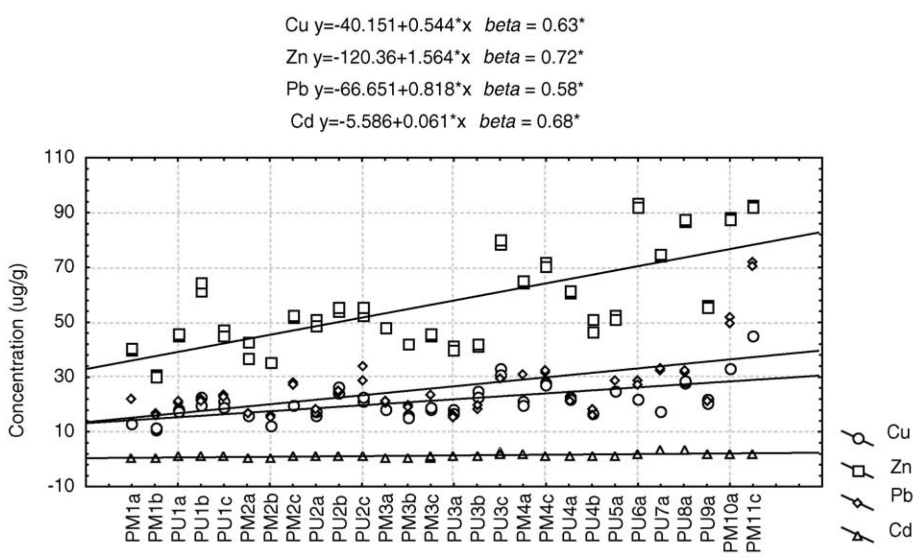


Fig. 7. Landward–seaward elemental concentration trends in Port Reitz Creek sediments.

vided. Figs. 3 and 4 shows the histograms of the concentration means and distribution profiles obtained for copper, zinc, lead and cadmium in Makupa and Port Reitz Creeks' sediments.

In Makupa Creek, copper concentrations were higher in stations near the Makupa causeway and Kibarani dumping site (Zone A = station KU1-9) as opposed to those towards Kipevu Bridge (Zone B = station KU10-13) with a statistically significant regression gradient as illustrated in Fig. 5. Zinc concentrations generally decreased towards the Kipevu Bridge as shown in Fig. 6. However, the trend was interrupted at stations KU9 and KU 10 where zinc concentrations relatively increased. The former is located near some industrial effluent outfall, whereas the latter is in close proximity to the Kibarani dumping site, as illustrated in Fig. 1. Lead concentrations were generally higher in section A stations, but the decreasing trend towards Kipevu Bridge was not statistically significant as shown in Fig. 5. However, cadmium concentrations increased towards the Kipevu Bridge, with a statistically significant gradient.

In Port Reitz Creek, elemental profiles of the four elements analysed increased from the landward stations to those towards Kilindini harbour. The regression trends were statistically significant as demonstrated in Fig. 7. A Turkey honest significant difference test revealed that on average, there was significant variation ($p = 0.00012$ for all) in the notably higher copper, zinc, lead and cadmium elemental concentrations between Makupa Creek and the rest of the Port Reitz Creek systems collectively, at 95% confidence level. Significant elemental concentrations calculated from the concentrations per substation showed that copper correlated positively with lead and negatively with cadmium in the Makupa Creek. However, all elements investigated correlated positively in Port Reitz Creek.

According to a classification of elemental concentrations in sediments as low, medium or high as proposed by Donazzolo et al. (1984), the values obtained in our study were classified as shown in Table 4. All the sediment samples from Makupa Creek ranked in the high concentration range for copper, zinc and cadmium, while 92% of the samples ranked in the high concentration range for lead. Conversely, none of the samples from Port Reitz Creek ranked in the high concentration range for zinc and cadmium, while only 4% samples ranked in the high concentration range for both copper and lead.

Table 4
Classification of elemental concentrations in Makupa and Port Reitz Creeks sediments

| Element | Guideline (mg/kg) (Donazzolo et al., 1984) | Makupa sediments (%) | Port Reitz sediments (%) |
|---|---|---|---|
| Copper | Low (< 15) | 0.00 | 10.7 |
| | Medium (15–50) | 0.00 | 85.7 |
| | High (> 50) | 100 | 3.57 |
| Zinc | Low (< 40) | 0.00 | 7.14 |
| | Medium (40–200) | 0.00 | 92.9 |
| | High (> 200) | 100 | 0.00 |
| Lead | Low (< 40) | 0.00 | 92.9 |
| | Medium (40–60) | 7.26 | 3.57 |
| | High (> 60) | 92.3 | 3.57 |
| Cadmium | Low (< 1.5) | 0.00 | 67.9 |
| | Medium (1.5–6) | 0.00 | 32.1 |
| | High (> 6) | 100 | 0.00 |

## 4. Discussion

The Makupa causeway separates Makupa Creek from Tudor Creek. Consequently, a localised build up of organic, inorganic matter and heavy metals is anticipated in Makupa Creek as a result of the inefficient flushing and the multiple sources of pollution. The effluent outfalls near stations KU 9 and KU 10, probably from some of the industries along this creek, contribute to the elevated zinc levels observed. The higher lead concentrations obtained at some stations in this creek are attributable to the heavy motor vehicle traffic along both Makupa causeway and Kipevu Bridge, as well as the petrol depots along the creek. This is consistent with published data (Onyari et al., 1991; Nyatebe, 1990), which demonstrate high lead levels in roadside soils. Effluent outfalls were observed near station KU 9 and KU 12. At the time of sampling, the shoreline was covered by a layer of black oily substance, indicating presence of oil in the effluents discharged into the creek. Cadmium concentration was highest at stations KU 13 near Kipevu Bridge. Inputs of cadmium to the environment are derived from various diffuse sources. According to Boehm and Schaefers (1994), primary materials containing cadmium and their concentrations (mg/kg) are zinc ore concentrates (1000–12,000), lead ore concentrates (3–500), copper ore concentrates (30–1200), iron ore (0.12–0.30), hard coal (0.50–10.0), heavy oil (0.01–0.10), phosphate ore (0.25–80) and soils, global average (0.01–0.7). Cadmium and zinc pollutions are linked to at least two zinc containing products, automobile tyres and galvanised metals, which are significant sources in urban areas. The deposited metals accumulate in street dust and may be transported as aqueous emissions during storm runoff or dispersed as wind-blown dust (Robert and Udo, 1994).

The increase of elemental levels from landward stations (Port Reitz Creek) to stations towards the Kilindini port may be attributed to the fact that the inland stations were basically within Mwache Creek. Mwache Creek is the most landward part of the Port Reitz–Kilindini complex. It is located about 15 km away from Mombasa City and therefore is not so much influenced by the effects of human activities. The little human settlements and its riparian catchments do not yet have pronounced influence on the creek. The increased elemental concentrations in Kilindini are partially attributable to port activities such as loading and offloading of industrial goods, cleaning, ballasting, maintenance practices such as painting, antifouling applications, fuelling activities and oil refinery operations. For instance, copper is used in electrical equipment, alloys, antifouling paint for ships' hull, as an algaecide and wood preservative (WHO, 1998). Zinc is ubiquitous in nature and is used in form of zinc oxide in paint formulations among other applications (WHO, 2001). Lead in its metallic form is generally used in battery casings and plates (WHO, 1989). Tetraethyl lead is still currently used as a petrol additive in Kenya and the East African region. Consequently, the use of leaded gasoline in ships and boats as well as spillage during shipment and other operations will inevitably result in higher lead levels in the environment. Referring to cadmium, its compounds are also used in areas such as electroplating of metals, as pigments or stabilisers in plastics, in alkaline batteries and in alloys with other metals such as copper. Such anthropogenic inputs will contribute to increased levels of cadmium in the environment.

Dead mangrove trunks observed in the Makupa Creek especially near Makupa causeway suggest mangrove ecosystem destruction. Most of mangrove sediment metabolism is through sulphate reduction, which releases high quantities of hydrogen sulphide and bicarbonate to pore waters and even to waters overlying the sediments. Under such physico-chemical conditions, the formation of sulphide minerals is favoured, precipitating dissolved trace metals, in particular the "soft" B type metals such as Zn, Hg, Ni, Cu and Cd (Berner, 1984; Harris et al., 1993). Although mangroves act as a sink of many trace metals, studies done in Australia demonstrate that changing physical-chemical conditions can turn the ecosystem into a net source of these pollutants, conveying them into local food chains (Harbinson, 1981, 1984, 1986). Lacerda and Vannucci (1998) also observed that the immobilisation of pollutants in mangroves is tightly linked to the ecosystem health and once the typical conditions of mangroves are changed (e.g. through deforestation, erosion, fish farming), they shift from long-term sinks into sources of the accumulated pollutants. This phenomenon is being investigated further in the Makupa Creek ecosystem.

Considering the sediments analysed from Port Reitz Creek system, very few ranked in the high concentration range. This is because most samples were collected from Mwache Creek, due to sampling limitations in the approximately 30-m-deep Kilindini harbour. As a result of dredging in the port channel, it was not possible to collect sediments from many sites using the Ekman grab sampler. The sediments obtained from Kilindini harbour shoreline were sandy and the 63-μm grain-size sediments were rarely obtained through sieving. Donazzolo et al. (1984) working on heavy metal content and lithological properties of sediments in the North Adriatic reported that all metals investigated accumulated in the fine fraction (< 63 μm) with the following percentages: Hg, 95%; Zn, 68%; Pb, 82%; Cu, 79%; Cd, 74%; Ni, 70%; Cr, 65%; Co, 65%, and Fe, 64%. This phenomenon is attributable to the greater surface area for adsorption of matter on the finer grains. Considering the vast nature of the Kilindini Port plus the relatively efficient mixing of the water in the harbour and main Indian Ocean basin, there is certainly much greater dilution effect on potential pollutants, unlike the situation prevailing in the Makupa Creek, where inefficient mixing of the water is apparent.

## 5. Conclusion

Results of our study indicate that Makupa Creek is relatively polluted in comparison to Port Reitz Creek. This is as a result of the various anthropogenic inputs highlighted. The inefficient mixing of Makupa Creek with the Indian Ocean waters compounds the problem. There is a need therefore for the critical evaluation of the actual components of the discharges from the various industries, municipal sewage outfalls and waste disposal practice at the Kibarani landfill site, located on the shores of the Makupa Creek. Cleanup and remediation measures in and around the Makupa Creek are necessary. Whereas the economic, political and social benefits associated with the construction of the Makupa causeway cannot be underestimated, inclusion of culverts in the construction would certainly improve tidal mixing and flushing of the Creek.

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