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Heavy Metal Distribution in Surface Sediments from Mtwapa and Shirazi Creeks, Kenyan Coast

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Coastal environments continue to attract heavy investment in various economic activities such as tourism, aquaculture, industrialization, agricultural, mining and urbanization. Coastal-zone pollution problems are becoming increasingly prevalent, with potentially adverse environmental and socio-economic effects. Consequently in global context, anthropogenic fluxes of contaminants such as heavy metals now exceed the natural flux in many areas. According to Novotny (1995) at least 13 trace metals are considered harmful to human health and to conservation of natural ecosystems. A survey of sediment core histories shows increasing inputs of lead and other metals into aquatic ecosystems from industrial discharges, mining operations, domestic and agricultural activities and from combustion of leaded automobile fuel (Onyari et al. 1989; Onyari et al. 1991; Nriagu 1996). Behrendt (1993) reported that diffuse loads of trace metals in the Rhine basin in Germany, increased from 18%, 42% and 40%, of the total load of Cd, Pb and Zn, in the 1970's to 58%, 66% and 56% respectively in the late 1980's. Copper contamination of Empress Augusta Bay and its mangrove forests, Papua New Guinea has been attributed to the fluvial transport of tailings from mining operations located 700 m above sea level in the central mountain range of the island, as far as 50 km inland (Jeffrey et al. 1988). Whereas some heavy metals studies in sediments have been done along the Kenyan coast (Everaarts and Nieuwenhuize 1995; Williams et al. 1996) no data has been published for Mtwapa and Shirazi Creeks. Our recent survey for Makupa and Port Reitz Creek system in Kenya's coastal zone revealed high levels of heavy metals at certain locations (Muohi 2002). Shirazi creek situated about 70 km south of Mombasa City is considered relatively pristine compared to the other creeks investigated. Since mining activities are envisaged in Kenya's southern coast region, it is important to document current levels of metals in the aquatic environment for effective monitoring and evaluation of anthropogenic sources. The aim of this study was therefore to investigate the heavy metals content of surface sediments from Funzi bay and Mtwapa creeks.

MATERIALS AND METHODS

Mtwapa Creek is located at about 20 km north of Mombasa City. It is connected to the Indian Ocean through a long narrow channel, characterized by reef linings

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at the entrance. Inward from the channel is a shallow, lagoon type bay. The creek receives raw sewage from nearby beach hotels, prison, underground seepage from septic tanks and urban wastes from Mtwapa municipality. River discharges into the creek include Lwandani (Mto Mkuu), Kwa Ndovu and Kidutani. Funzi bay is located at approximately 70 km south of Mombasa City. Funzi bay connects to Shirazi Creek and Ramisi estuary as illustrated in Figure 1. The sediment samples used in this study were collected from eight and seven stations within Mtwapa and Shirazi Creeks respectively using an Ekman grab. A total of 65 sea sediments were collected and they were labeled according to site, collection period (2001), station and sub-station as follows, T=Mtwapa Creek, S=Shirazi Creek, J=January, M=March, U=July. Stations were labeled in Arabic numbers and substations in lowercase alphabet letter (a, b, c). The samples were dried in an oven at 105^{o} C for 24 hrs to constant weight. They were crushed using a pestle and mortar and sieved to obtain 63 μm grain size. For analysis 1 to 2 g sediment sub-sample were digested in triplicate using hydrochloric acid as previously reported (Onyari et al.1989). The accuracy of the analysis was verified by analysis of IAEA's certified reference material, SL-1 and sea sediments using Atomic Absorption Spectrometry (AAS) and Energy dispersive x-ray fluorescence. The heavy metal concentrations were determined using a ChemTech Analytica 2000 Atomic Absorption Spectrophotometer. For XRF analysis the sediment sample was diluted with starch binder in 1:5 ratios and thoroughly mixed to ensure homogeneity. Subsequently five pellets weighing about 250 mg were prepared for each sample for XRF analysis as described by Maina (1984). Calculation of actual concentrations, regression analysis ANOVA, Tukey HSD significance test and Spearman rank correlation analysis was done using Excel and Statistica programs. The canonical correspondence analysis was done using CANOCO program.

RESULTS AND DISCUSSION

The accuracy of metal analyses were tested using IAEA Soil-7 certified reference material and the experimental values showed close agreement with certified values (Muohi 2002). Evaluation of the accuracy of the procedure was also done by analysis of sediments acid digested (AAS) and without digestion (XRF). The results presented in Table 1 demonstrate close agreement between the two independent analytical techniques. In XRF analysis, sample digestion was not necessary since the pellet method was used. Typical XRF spectrum of the sediments investigated is presented in Figure 2. Table 2 gives the metal content of copper, zinc, lead and cadmium in surface sediments. As shown, elevated levels of heavy metals were obtained in Mtwapa Creek sediments compared to the relatively pristine Shirazi Creek. According to a classification of elemental concentrations in sediments as low, medium and high (Donazzolo et al. 1984), Mtwapa creek sediments ranked in the medium and high concentration (Cu, Zn, Pb) except cadmium which had more than half the samples in the low concentration range. On the contrary, sediments from Shirazi creek mainly ranked in the low concentration range for all the elements investigated. On average, metal concentrations (mg kg^{-1}) in Mtwapa creek sediments, Cu (37.2± 16.3), Pb (58.4±

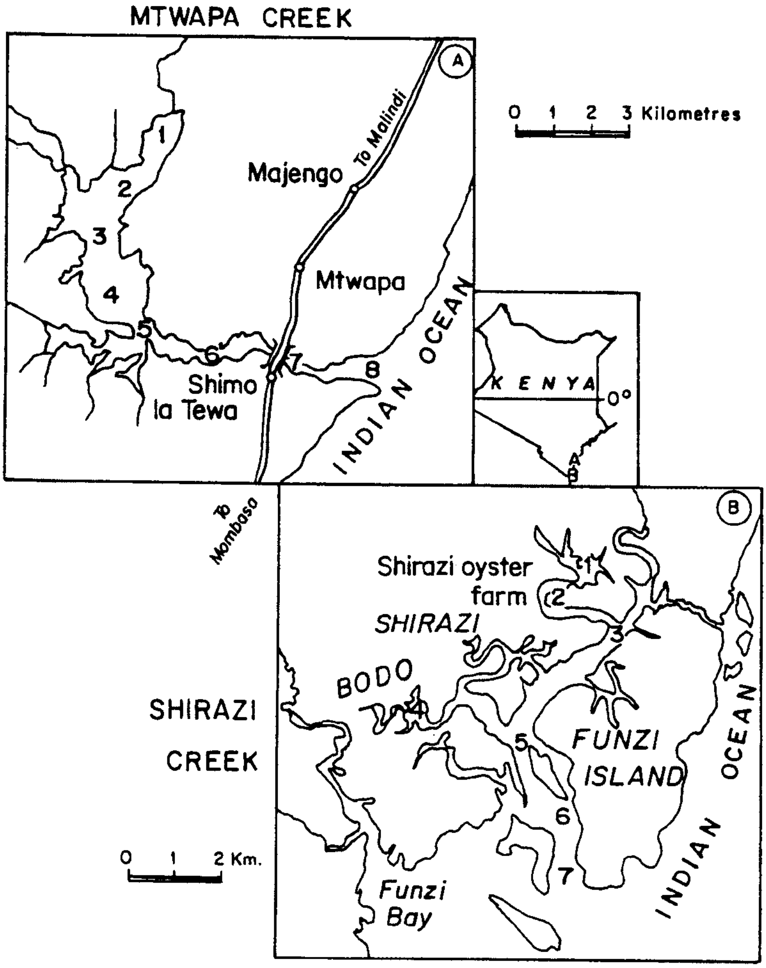

Figure 1. Location of sampling sites in Mtwapa and Shirazi Creeks, Kenya

17.6) and Cd (1.60± 1.20) exceeded the National Oceanic and Atmospheric Administration (NOAA) sediment quality guidelines, Cu =34, Pb = 46.7, Cd = 1.2 (Long et al.1995). However, the cadmium levels did not exceed the upper limit of the IMO/FAO/FAO/UNESCO/WMO/IAEA/UN/UNEP joint group of experts' guidelines on the scientific aspects of Marine pollution (GESAMP, 1985). The guidelines established for unpolluted sediment are lead (8-60) and cadmium (0.2-5 mg kg^{-1}). The heavy metals distribution profiles and landward-seaward trends in Mtwapa creek are presented in Figures 3 and 4 respectively. The regression trends (significant betas at 95% confidence level) indicate that metal concentrations in Mtwapa creek decreased seawards except for cadmium. Higher metal concentrations were obtained at a station located close to a hotel where several

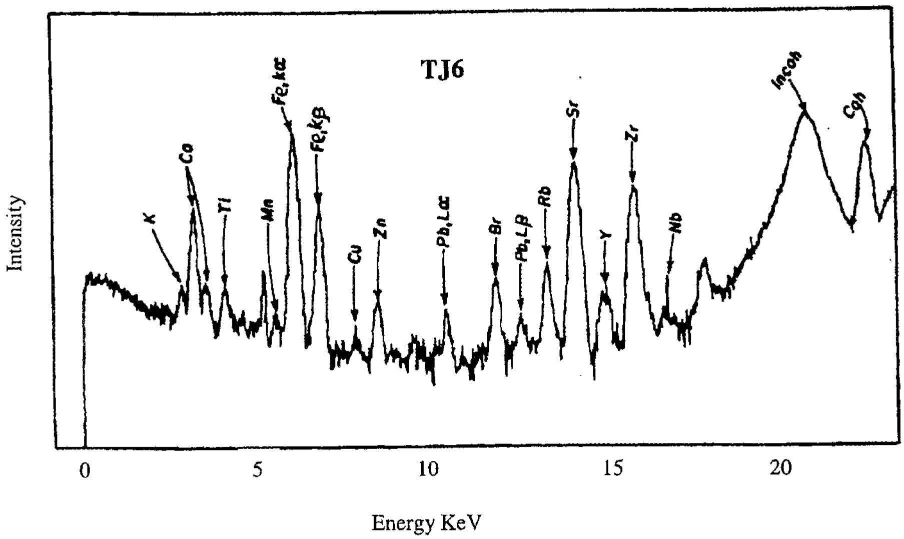

Figure 2. XRF spectrum of surface sediments from Mtwapa Creek.

boats and small ships are moored there. The results indicate anthropogenic inputs of lead, copper and cadmium from boating and urban activities. Generally in this creek, metal concentrations especially copper and zinc were higher in samples taken from sub-stations at the center of creek (suffix c) compared to those collected from shoreline substations (suffix a or b). The higher elemental concentrations obtained in sites at the center of Mtwapa creek channel suggests that there is transport of matter and pollutants along the creek. However, further sediment dynamics data in the creek is necessary to provide better understanding on the contribution of anthropogenic inputs versus natural inputs. In Shirazi creek, copper and zinc concentrations decreased from landward to seaward stations with

Table 1. Comparison of data on the concentrations of copper, zinc, lead and cadmium (mg kg^{-1} dry wt) in surface sediments analyzed using AAS and XRF.

Station	Method	Sample	Cu	Zn	Pb	Cd
Mtwapa						
	AAS	TJ4c	28.1± 0.25	49.5± 0.53	34.1± 0.70	0.90± 0.02
	XRF	TJ4c	30.0± 6.91	53.0± 12.2	46.9± 9.16	-
Shirazi						
	AAS	SU1b	9.90± 1.04	23.0± 0.46	13.3± 0.17	0.90± 0.09
	XRF	SU1b	≤ 25	27.9± 0.85	17.0± 2.28	-
	AAS	SM6c	7.10± 0.15	17.2± 0.92	38.0± 1.23	3.50± 0.69
	XRF	SM6c	≤ 25	20.5± 0.34	41.3± 4.19	-

Note: Detection limit of Cu using XRF pellet method is ≤ 25 mg kg^{-1} dry wt.

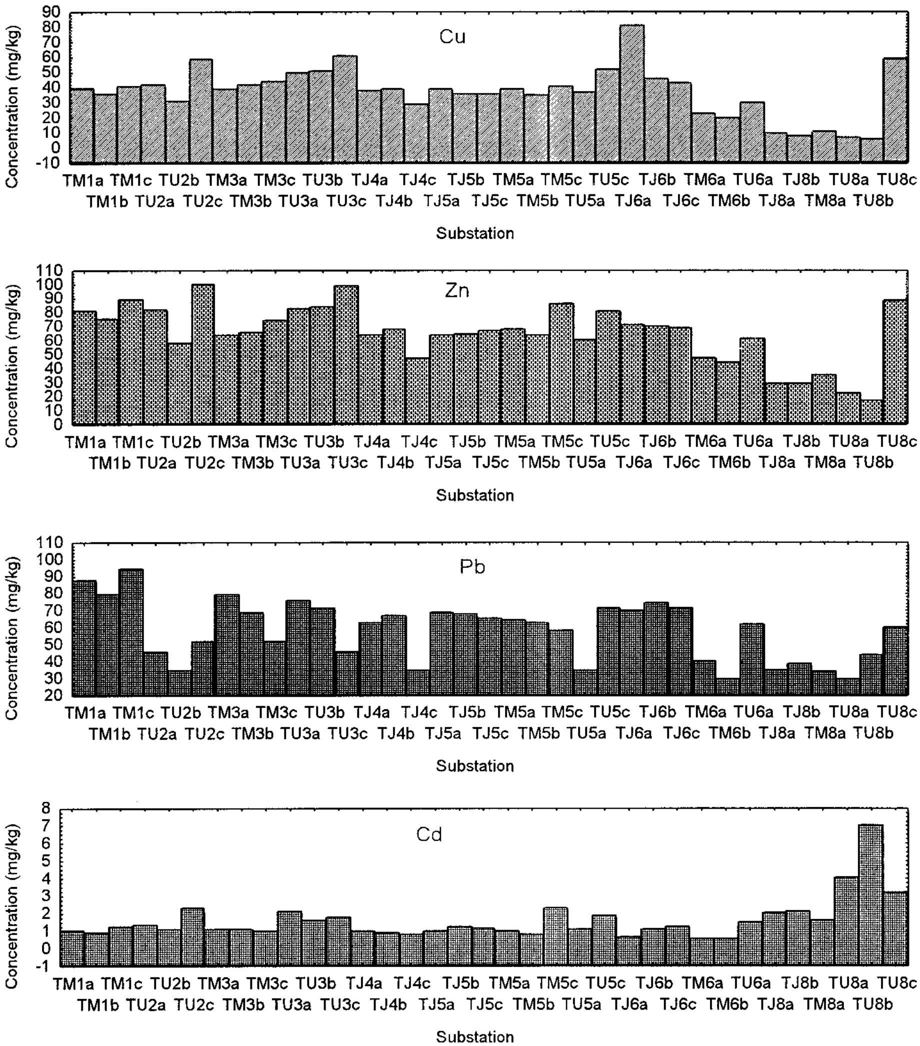

Figure 3. The distribution of heavy metals at sites within Mtwapa Creek

statistically significant regression gradient as illustrated in Figure 5. However lead concentrations in sediments increased towards seaward stations, which is attributable to use of leaded gasoline in boats around Funzi bay. Turkey honest significant test demonstrated significant variation in copper, zinc and lead (p=0.00011 for all) concentrations between Mtwapa and Shirazi creeks at 95% confidence level. Cadmium levels did not however, show significant variation (p=0.16034) between the two creeks. This suggests that cadmium levels are close to natural levels for the majority of sediments investigated except for some locations. In Mtwapa creek, copper correlated positively with zinc and lead, while zinc correlated positively with copper, lead and cadmium.

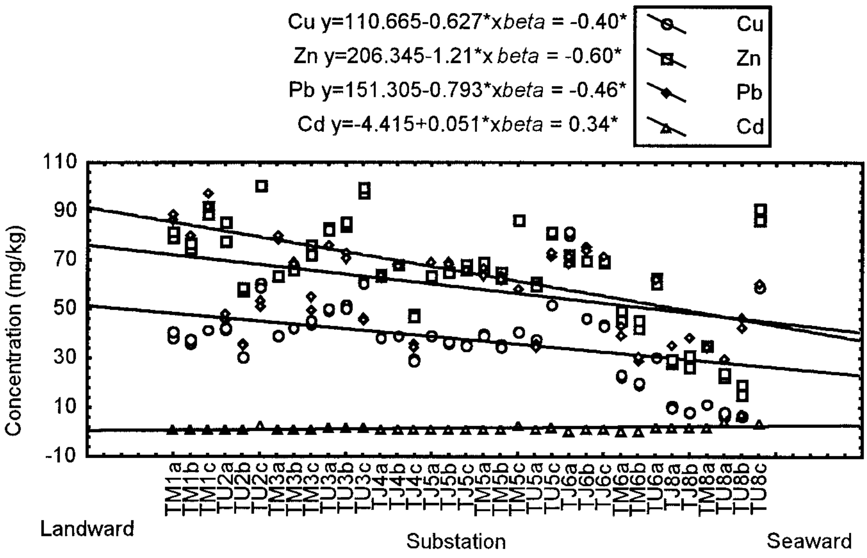

Figure 4. Landward-seaward metal content trends in Mtwapa Creek sediment

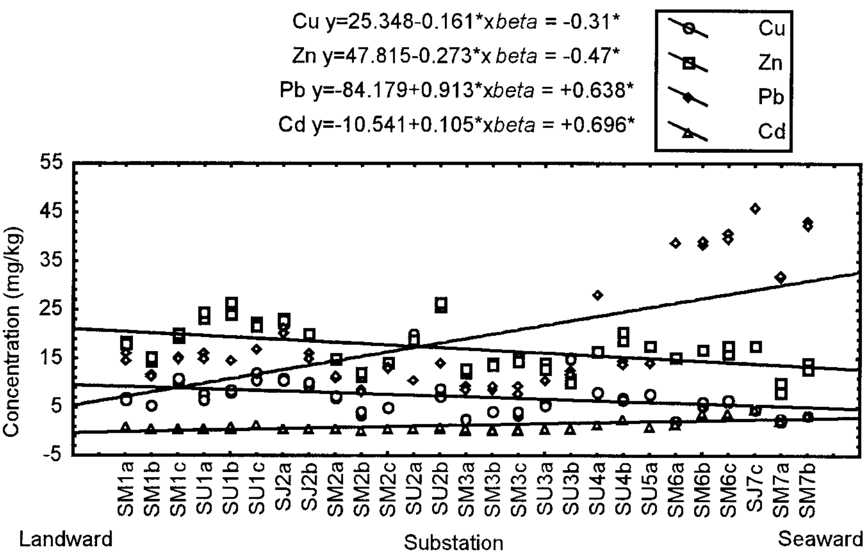

Figure 5. Landward-seaward metal content trends in Shirazi Creek sediments

In Shirazi creek, copper correlated positively with zinc, while lead correlated positively with cadmium. The results of correspondence analysis isolated the Makupa creek stations on one side of the vertical axis together with the elemental arrows. Evidently, the lowest metal concentrations were obtained in Shirazi creek sediments, which were clustered directly opposite the Makupa creek sediments as shown in Figure 6. On the basis of our results the creeks under investigation

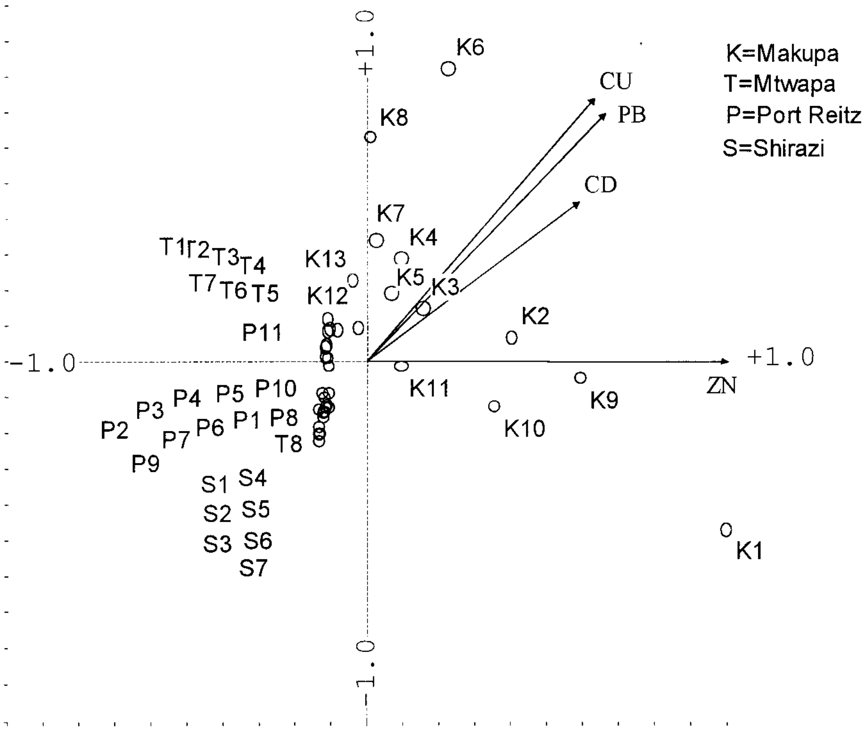

Figure 6. Graphical representation of canonical correspondence analysis

Table 2. Heavy metal concentrations (mg kg^{-1} dry wt) in sediment samples.

Site	Cu	Zn	Pb	Cd
Mtwapa				
Range	6.50-80.7	17.2-100	29.5-94.6	0.57-7.02
Mean±δ	37.2± 16.3	65.0± 20.6	58.4± 17.6	1.61± 1.20
Shirazi				
Range	2.20-19.9	9.10-26.2	8.50-45.9	0.32-4.73
Mean±δ	7.10± 4.00	17.1± 4.40	19.4± 11.9	1.31± 1.20
New York harbor (Carmody et al.1973)	-	-	25-370	0.5-4.0
San Francisco Bay (Bradford & Luoma,1980)	-	-	9-174	0.5-3.3
Port Reitz (Muohi 2002)	11.3-45.1	30.7-92.9	15.7-71.2	0.55-3.24
Makupa (Muohi 2002)	50.9-229	276-3196	54.6-150	31.0-81.9

may be ranked in order of most to least influenced as follows, Makupa > Mtwapa > Port-Reitz > Shirazi. The heavy metal content in Shirazi Creek (pristine setting) is several order of magnitudes lower than other Creeks investigated.

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