Heavy Metal Distribution and Enrichment at Port-Reitz Creek, Mombasa

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Abstract—Port-Reitz Creek (04° 04' S, 39° 39' E) is one of the two main tidal mangrove fringed creeks found in Mombasa Island. It experiences semi-diurnal pattern of two low and two high tides every 24 hour cycle. Six stations were strategically positioned along the length of the creek and sampled for heavy metal (cadmium, copper, iron and zinc) content during July 1998. A peak of Cu and Zn (87 and 235 µg/g dry weight respectively) was observed at Station 2, which borders a steel factory and fish-processing firm. A correlation matrix showed close distribution pattern between Zn and Cu (r = 0.67) and between Fe and Cd (r = 0.62). A peak for Cd (6 µg/g dry wt) was observed at Station 3. Fluvial input in the creek was a source of Cd, Cu, Fe and Zn. Cd and Zn were of anthropogenic origin (Enrichment factor, EF > 1) while Cu seemed to be depleted (EF < 1). Lateral distribution of Cd, Cu, Fe and Zn on surface sediments showed a decline in concentration in a seaward direction.

INTRODUCTION

At present, the anthropogenic contribution of heavy metals into the environment far exceeds natural inputs (Nriagu & Pacyna, 1988). The impact of heavy metal pollution to coastal and estuarine ecologies could be substantial because of the variety of inputs to these areas. Potential land-based sources of heavy metals include river inputs, local runoff and atmospheric deposition (Galloway, 1979).

The estuarine environment is the last area for the removal of trace metals in their passage from the terrestrial to the marine environment (Scott et al., 1988). Bottom sediments are long-term integrators of geochemical processes, hence information from sediments can establish the long-term behaviour of trace metals in estuaries (Scott et al., 1988). Mangrove forests occur at the upper tidal levels on sheltered coastlines along the margins of tidal creeks and inlets. Inherent physical and chemical properties of mangrove muds confer an extraordinary capacity to accumulate materials discharged to the nearshore marine environment (Harbison, 1986).

This study presents baseline data on the lateral distribution and possible sources of cadmium, copper, iron and zinc along the Port-Reitz Creek, Mombasa.

Heavy metals in sediments at Port-Reitz Creek remain largely unexplored. Oteko's (1987) surveys of vertical sediment profiles at Makupa Creek (a peripheral creek joining the Port-Reitz Creek at the harbour) and Tudor Creek (adjacent to the study site) found enrichment factors for Zn, Cu and Cd to be 7.8, 3.3 and 6 respectively at Makupa and for Zn and Cu to be 2.3 and 0.5 respectively at Tudor. Heavy metal levels in surface sediments at Makupa Creek were 0.2, 84 and 311 µg/g dry wt, for Cd, Cu and Zn respectively (Oteko, 1987).

MATERIALS AND METHODS

Study area

Port-Reitz Creek (04º 04' S, & 39º 39' E) is one of the two main tidal mangrove-fringed creeks found in Mombasa Island. The creek was formed as a result of drowning of former river valleys due to sea level rise (Caswell, 1956), and is characterised by varying depth, with the upper zones being shallow, often less than 10 m deep. The channels fringing the mangroves have depths below 5 m. The lower sections forming the Kilindini channel where the main harbour is situated, have been extensively dredged to deepen the channel and therefore water depths vary from 30 to 40 m.

The creek experiences a semi-diurnal tidal pattern. Average tidal range is 1.0 m at neap tide and 2.5 m at spring tide. It receives freshwater from three seasonal river systems, namely Mwachi, Cha Shimba and Mambome. With a catchment area of 1480 km², Mwachi river is the largest (Kitheka et al., 1999).

Six sampling stations were strategically positioned in the creek to represent important features that could have a bearing on the distribution of heavy metals in the creek. Stations 1 and 6 marked the extremes of the creek, with Station 1 bordering the ocean and Station 6 lying at the river mouth. Stations 2, 3 and 4 were all located in stressed environments: Station 2 was in a small, peripheral lagoon within the creek next to a fish-processing factory, a dry dock and a steel factory; Station 3 was in the country's main harbour, while Station 4 was on a mad flat where the narrow (mangrove-fringed) section of the creek opens up to the port area depositing its suspended load (Fig. 1).

Sampling was conducted during July 1998. Six surface sediment samples were collected from each site, using a gravity corer with PVC core-liner. Four centimetres of the surface sediments were extracted from the core-liner and placed in labelled polythene bags. In the laboratory the sediments were air-dried (Ahmad et al., 1993) to a constant weight and homogenised with a pestle and mortar, in order to normalise for variation in grain size distribution.

Analytical methods

A portion of dried homogenised sample (0.2 g) was placed in a teflon-lined pressure container. One drop each of hydrochloric acid and nitric acid were
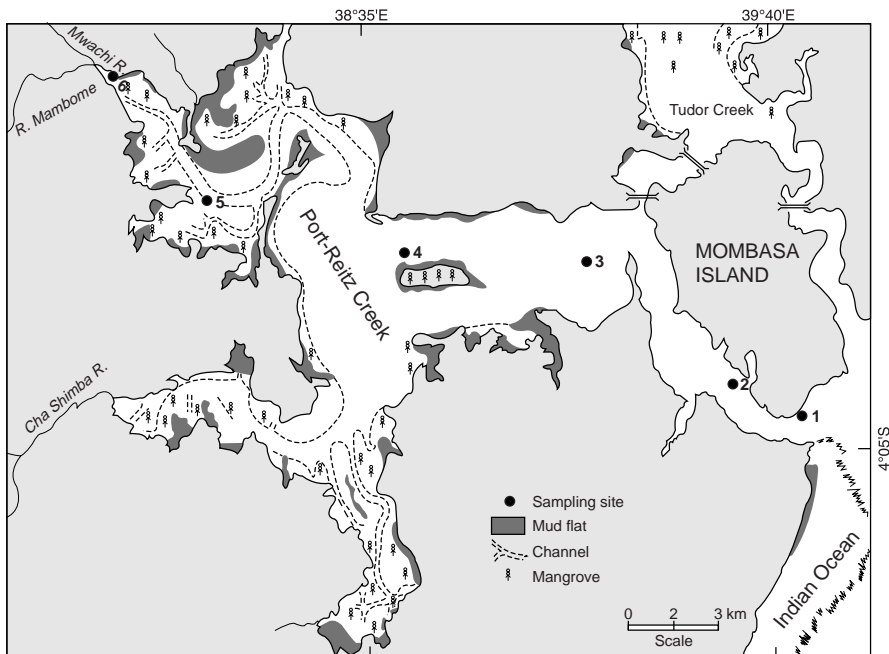

Fig 1: Map of Port-Reitz Creek showing sampling sites

added followed by 4 ml of hydrofluoric acid. The containers were sealed and placed in an oven at 125 ºC for 2 h (Varian, 1989). The containers were then removed from the oven, cooled and the contents transferred to teflon beakers. Five millilitres (5 ml) each of perchloric and hydrofloric acid were added and the mixture heated to produce white fumes of perchloric acid. The samples were cooled and 2 ml of hydrochloric acid added to dissolve the salts. The resultant mixture was made up to 50 ml with distilled water (Varian, 1989).

Heavy metal analysis was achieved by flame atomic absorption spectrometry (Varian Spectra AA10). Analytical and instrumental accuracy were tested using sea plant reference material IAEA 140. Differences between certified and measured results were always less than 10 %.

Enrichment factors (EF) for mean metal concentration in sediments at all the stations was calculated and used for comparison:

$$EF = \frac{X/Fe \text{ (sediment)}}{X/Fe \text{ (Earth's crust)}}$$

where X is the metal studied and X/Fe is the ratio of the concentration of element X to iron. Iron was chosen as the element of normalisation because natural sources (98 %) vastly dominate its input (Tippie, 1984). The crustal abundance data of Bowen (1979) were used for all EF values.

The enrichment factor (EF) is a convenient measure of geochemical trends and is used for making comparisons between areas (Sinex & Helz, 1981). A value of unity denotes neither enrichment nor depletion relative to the Earth's crust. Heavy metal data were subjected to correlation analysis and analysis of variance (ANOVA) to determine the association as well as the spatial variation (Yule & Kendall, 1993).

RESULTS

Iron concentrations were highest at Station 3, situated at the main harbour at 32,260 µg/g dry wt, but this was not significantly different (P > 0.05) from Stations 4 and 6, which had 28, 663 and 26, 167 µg/g dry wt respectively (Fig. 2). Copper and zinc were highest at Station 2 (87 and 235 µg/g dry wt respectively (Fig. 3). With the exception of Stations 2 and 3 located in areas of anthropogenic influence, spatial variation of zinc indicated a concentration gradient, with Station 6 (59µg/g dry wt) being the highest decreasing gradually towards Station 1, with 23 µg/g dry wt. Iron and Cadmium followed a different trend, with a positive correlation of r = 0.62. Station 3 also had the highest levels of Cd (6 µg/g dry wt). Enrichment factor (EF) values for both Cu and Zn were simultaneously lower than 1 only at Station 4 (Table 1).
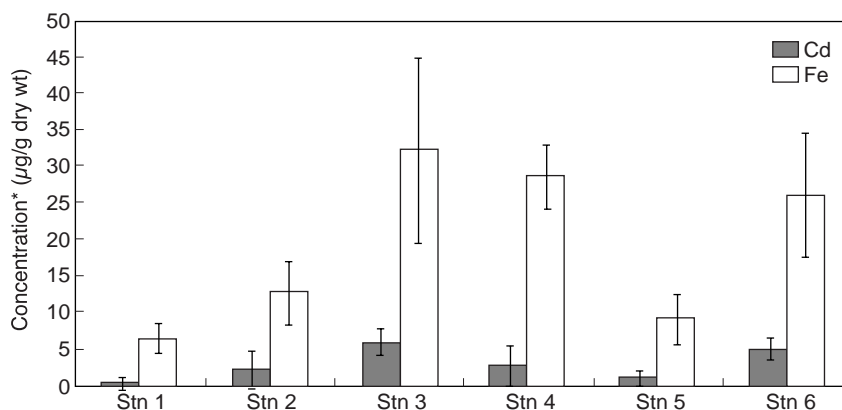

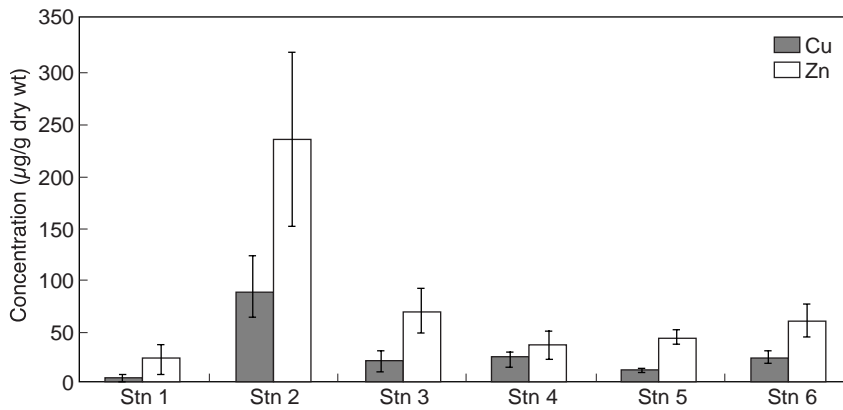**Fig. 2. Cadmium and Iron distribution in surface sediments at Port-Reitz creek, *Fe expressed as 10⁻³ µg/g (mg/g)**

Fig. 3. Copper and Zinc distribution in surface sediments at Port-Reitz creek

Table 1. The mean sediment heavy metal concentrations in μg/g dry wt, enrichment factors (EF), and the minimum and maximum values for each station at Port-Reitz creek, Mombasa

Metal	Station	Min	Max	Mean ± SD			EF
Fe	1	4,268	17,401	6,562	±	2,106	
	2	5,893	9,596	12,751	±	4,366	
	3	16,060	42,660	32,260	±	12,684	
	4	23,388	35,052	28,663	±	4,401	
	5	4,969	12,668	9,223	±	3,493	
	6	15,607	37,964	26,167	±	8,490	
Cd	1	N.D.	2.2	0.5	±	0.9	26.4
	2	N.D.	5.3	2.5	±	2.5	71.7
	3	4.5	9.3	6.0	±	1.7	69.3
	4	N.D.	6.8	2.8	±	2.8	36.8
	5	0.5	3.3	1.3	±	1.0	52.2
	6	3.3	7	5.2	±	1.5	74.2
Cu	1	2.3	7	5.5	±	2.1	0.7
	2	73.3	156	87.2	±	35.4	5.6
	3	13	32.3	20.5	±	10.6	0.5
	4	21.5	29.3	25.5	±	3.4	0.7
	5	10.3	13.3	12	±	1.2	1.1
	6	14.5	32.8	24	±	6.9	0.8
Zn	1	8.8	42.8	23.3	±	15.2	1.9
	2	98.5	340	234.9	±	84.7	10.1
	3	36.0	97.5	69.5	±	21.6	1.2
	4	25.5	55.5	36.5	±	14.2	0.7
	5	37.3	46.3	44.0	±	6.9	2.6
	6	37.8	80.5	59.2	±	15.8	1.2

*N.D.= not detectable.

DISCUSSION

As it is widely accepted that heavy metals are immobilised in sediments, one would expect Station 4, which is a sediment sink, to reflect this in its EF values. This Station had comparatively the lowest EF value for Zn and also EF < 1 for Cu. There is therefore a possibility that heavy metals are released from the sediments at this Station.

Copper and Zn concentrations correlated well (r = 0.67), corroborating the results of Rees et al. (1996), who found a correlation coefficient of 0.69 for Cu and Zn at the Port-Reitz harbour area. These two elements had peaks at Station 2, where levels reached 87.2 and 234.9 μg/g dry wt respectively. Enrichment factors were also high for both metals in this station, an indication that the station was a point of anthropogenic input. The station was highly enriched in Cd, Cu and Zn. Its high EF values for Cu and Zn to an order of magnitude of 4 to 10 times higher than the rest of the stations could be due to its geographic positioning, giving it pollutant sinking properties.

Areas such as peripheral lagoons that are sheltered from strong tidal currents are subject to less erosion, and tend to act as sinks for contaminated sediments (Rees et al., 1996). While we expected Fe values to be highest at Station 2 due to its proximity to a steel factory, the observed reading suggests otherwise. The level of iron in this station was significantly higher than Station 1 (P < 0.05), similar to Station 5, and significantly

lower than all the other stations. This observation suggests preferential induced depletion of Fe in the sediments at this station. This station was observed to contain the black sediments associated with anoxia and these emitted a characteristic hydrogen sulphide smell, an indication that the sediments were oxygen-deficient. A fish-processing factory discharges all its untreated high-oxygen-demand effluents at the site. Increasing nutrients levels causes a change in the redox conditions of the sediments, leading to oxygen deficiency which leads to an initial dissolution of hydrated manganese oxide, followed by that of iron compounds (Förstner & Patchineelam, 1976).

The preferentially depleted Fe level at Station 2, reflected positively on the EF values for the rest of the metals since Fe was taken as the element of normalisation. This effect was more pronounced with Cd.

Although Station 2 acted as a sink, its effect did not spill over to Station 1. Studies on trace metals in natural waters have established a strong enrichment of metals in suspended matter, and the importance of this material as a transport medium (Wollast, 1982). Consequently, if metals are discharged to the nearshore zone, sheltered environments are more likely to accumulate this particle-borne load.

There seemed to be three sources of Zn input into the creek, around Stations 2, 3 and 6. Station 6 was a source of fluvial input whose effect seems to filter though the system as it was gradually diluted along the creek. Station 3 was located in a harbour, and due to the diversity of activities involved, it was not easy to speculate on the mode of pollution. The major source of Cu input into the creek was at Station 2, but there was also some fluvial input through Station 6, which was mainly terrigeneous.

There seems to be two main sources of Fe and Cd input, located at Stations 3 and 6. The standard deviation of Fe at Station 3 was however quite high, indicating point introduction. Some ships undergo painting while docked, and this involves chipping corroded parts before fresh paint can be applied. The lateral distribution of Cd, Cu, Fe and Zn on surface sediments at Station 5 and 6, whose predominant metal source was fluvial, and Station 1 which was at the ocean mouth, showed a decline in concentration in a seaward direction, in the classical pattern of conservative behaviour. Apart from the river input, Stations 2, 3 and 4 also experience other anthropogenic inputs. A significant gradient in the spatial distribution of suspended particulate matter (SPM) existed at Port-Reitz (Kitheka et al., 1999). Stations located in the upper zones experience high SPM concentrations while the lower zones fronting the Indian Ocean were characterised by clear water and low SPM concentrations (Kitheka et al., 1999). According to Turekian (1977) estuarine sediments are metal repositories and only a minor fraction of material escapes to coastal waters. The above trend reflects the declining influence of the Mwachi River in the seaward direction; there was a sharp decline in all the heavy metal concentrations between Station 6 bordering the river and Station 1 at the Ocean mouth.

CONCLUSION

The enrichment factors found for Cu and Zn compare favourably with studies done elsewhere in the world. Rule (1986) reported EF values for Cu and Zn in an offshore site 27 km of the Chesapeake Bay mouth, of 0.2 and 2 respectively while Bopp & Biggs (1973) reported EF values for Cu and Zn at Delaware Bay of 2 and 10 respectively. With respect to these two elements the Port-Reitz system is relatively healthy, with no signs of sink action except at Station 2. Cadmium, however, is highly enriched, indicating sinking.

Areas with EF < 1 should be viewed with caution as they imply preferential release of these elements, making them bioavailable. Physico-chemical variation might cause the release of heavy metals bound in sediments. Heavy metals can be readily mobilised into solution under reduced redox potential and pH conditions (Chester & Hughes, 1967). Exposure of sulphide minerals in sediments to atmospheric oxygen results in a lowering of pH-values, and a new distribution and transformation of heavy metals bound to the sediments takes place. Increased salinity can also cause dissolution due to the competition of active sites (Mance, 1987). Station 4 is of concern as both Cu and Zn are depleted, the station is a mud flat and part of it is exposed during low tide with

possible effects on the salinity of the sediment. Exposure will encourage evaporation and thus elevate salinity.

Although high Cd levels were observed, they compared well with some sites elsewhere. The Southern East coast of India, between Madras and Kanniyakumari has been reported to have Cd levels on surface sediments of up to 6.05 µg/g dry wt, Cu levels of 105 µg/g dry wt and Zn 144 µg/g dry wt (Subramanian et al., 1990). Xavier (1986) reported Cd levels of 4.66 µg/g dry wt for samples collected at the coast of Catalonia. The results of our study indicate that Stations 6 and 3 should be monitored more closely in longer-term samplings, as their Cd concentrations were quite high.

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