

# Anthropogenic Sources of Heavy Metals in the Indian Ocean Coast of Kenya

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**Abstract** Water and surface sediment samples from Rivers Sabaki, Ramisi and Vevesi that flow into the Indian Ocean coast of Kenya were analysed for heavy metals. The sediment concentrations of exchangeable cations (in  $\mu\text{g/g}$ ) for Co, Cu, Mn, Ni, Pb, Sn and Zn ranged from 0.10 to 506.75 (for Mn at Sabaki), constituting between 2% and 20% of the total metal concentrations obtained by digestion with strong acid. Cu, Mn, Ni, Pb and Zn were more leachable with 0.1 N HCl. The total dissolved metal in water and the total sediment concentrations for Ag, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sn and Zn are given in the text. For dissolved metals, the metal/Mn ratios indicated higher concentrations of Ag in Sabaki River, Cd in Ramisi, Ni in Sabaki and Pb in Ramisi, respectively. In sediments, the metal/Mn ratios showed higher enrichment of Ag in Ramisi, Cd in Sabaki and Vevesi, and Zn in Sabaki, respectively. Enrichment factors showed elevated levels of Cd, Pb and Zn in sediment in River Sabaki and River Vevesi that were due to anthropogenic inputs through Athi River. The total dissolved metal concentration ranges for the three rivers were comparable with those ranges reported in rivers in South Africa but the sediment concentrations were below those of rivers in Europe and Asia where anthropogenic addition of some of the toxic elements such as Cu, Pb and Cd is evidently higher.

**Keywords** Water, surface sediment · Heavy metals · Rivers · Indian Ocean Coast of Kenya · Enrichment factors

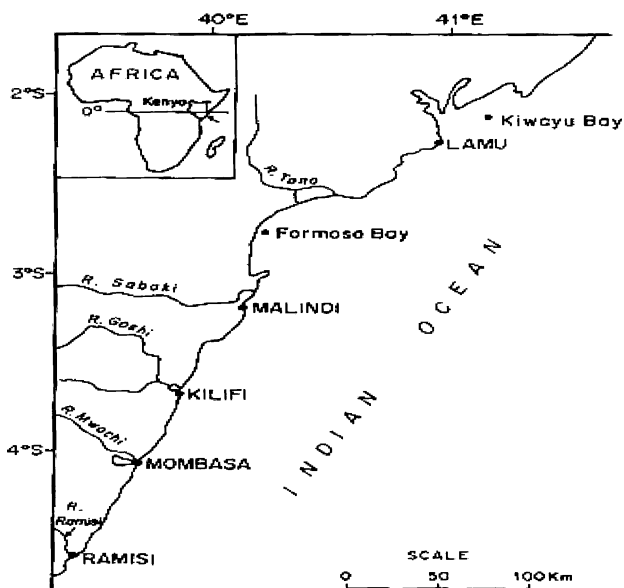
Studies on heavy metal pollution of river systems have recently attracted a lot of attention due to the need for acceptable drinking water quality and better understanding of environmental pollution of freshwater resources (Lee et al. 1998; Neal et al. 2000; Huang and Lin 2003; Powell and Alexander 2003; Reimann et al. 2003; Jain 2004; Adamo et al. 2005; Nyangababo et al. 2005; Okonkwo et al. 2005; Demirak et al. 2006; Deheyn and Latz 2006; Grosbois et al. 2006; Nicolau et al. 2006). Inland rivers and streams are also important sources of anthropogenic metal deposits into the seas and oceans (Everaarts and Nieuwenhuize 1995; Milward and Lin 2003; Adamo et al. 2005; Nicolau et al. 2006). Unlike organic contaminants, natural processes of decomposition do not remove heavy metals; instead heavy metals can be enriched by aquatic organisms and can therefore be converted to organic complexes that may even be more toxic (Jain 2004). Although fractionation is useful in determining the bio-availability and toxicity of heavy metals, the total content of heavy metals in water and sediment is useful in mapping out various hot spots as well as for identification of anthropogenic inputs (Lee et al. 1998; Huang and Lin 2003). Apart from human and industrial effluents, weathering of soil and rocks and volcanic eruptions are also other main sources of heavy metals discharging into the marine environment.

Since metal solubility is principally controlled by environmental pH, its concentration, its various types of species and oxidation states, the organic ligands and the redox environment of the aquatic system (Lee et al. 1998; Huang and Lin 2003; Davis and Leckie 1978; Jeon et al. 2003;

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**Fig. 1** The Indian Ocean coastal area showing R. Sabaki and R. Ramisi where samples were taken

Milward and Lin 2003; Warren et al. 2005; Grosbois et al. 2006), we expect heavy metal speciation in riverine systems to be unique and the total content to contribute significantly to the concentrations in the oceans or seas where the rivers discharge into (Berg et al. 1995; Cheevaporn et al. 1995; Everaarts and Nieuwenhuize 1995; Deheyn and Latz 2006; Nicolau et al. 2006). The determination of the physico-chemical parameters of natural waters such as pH, temperature, dissolved oxygen demand (DOD), turbidity, and alkalinity is also pertinent because they can modify heavy metal chemistry and toxicity on aquatic life and consequently act as indicators of water pollution (Everaarts and Nieuwenhuize 1995; Lim et al. 1995; Demirak et al. 2006; Deheyn and Latz 2006). Although, developing countries have been considered least polluted in the past, rapid industrial development and high population growth rates in these decades have gradually degraded quality of some of their natural waters and, subsequently, the coastal waters as the final recipients (Cheevaporn et al. 1995; Lee et al. 1998; Huang and Lin 2003). This paper reports on bioavailable heavy metal concentrations, total heavy metal content, and metal enrichment in surface estuarine sediment and water samples in three rivers, River Sabaki, River Ramisi and River Vevesi, as they discharge into the Indian Ocean Coast of Kenya (Fig. 1).

## Materials and Methods

The sampling sites were: at the shores/river mouths (Sabaki and Ramisi) into the Indian Ocean at the Indian Ocean Coast in Kenya. The river sediments were mixtures of

sand, silt and mud with varying proportions and degrees of compaction and characteristics and the samples were analysed for these physico-chemical characteristics. Generally the river mouths inside the entrance to the Ocean had coarse bottom sediments with considerable amounts of mud. Water and surface sediment samples were taken at about 1 km downstream from Ramisi Sugar Factory at Ramisi bridge (sample RMS2), at Daragube water pump (sample RMS1) upstream before the factory, in River Vevesi (a tributary of River Ramisi) at a point downstream from Daragube water pump (VVS) and from Sabaki River near the shore before getting into the Ocean (sample SB). Sampling sites were located at 4°36' S and 39°36' E (Ramisi samples) and at 3°10' S and 40°6' E (Sabaki bridge). Athi River flows from Ngong hills in central Kenya mainly through sand and rocks and mining industries for cement and other inorganic products at Athi River, through Yatta plateau, through major industries including tannery and food processing factories in Thika, through Ruiru and Limuru areas where agrochemicals and fertilizers are used in large scale coffee and tea farms and through municipal and domestic waste before joining into River Sabaki which discharges in to the Indian Ocean. River Ramisi flows through Shimba Hills in to the Indian Ocean at Ramisi and River Vevesi is a tributary of River Ramisi which has acidic pH because it passes through a bog downstream from Ramisi where sampling was done.

A sample of 500 mL of water was taken by immersing the bottles and lifting up and was mixed with 2 mL of concentrated HNO<sub>3</sub> to lower the pH of the water to <pH 2, filtered through 0.45 μm Millipore filters and stored in the fridge in the laboratory at 4°C before analysis. At each site additional samples of water were taken for analysis of electrical conductivity, pH, salinity and transparency. The temperature of the water was also determined in situ during sampling. Surface sediment (~0–2 cm layer) samples were taken from the same sites in triplicates using stainless steel Ekman grab, stored in polythene bottles and transported to the laboratory for storage at 4°C while awaiting analysis. The samples were taken during the rainy season in March. Before analysis, portions of sediment were mixed well and then a 20-g amount taken into a glass dish and dried at 105°C for 24 h in a Gallen Kamp oven, ground well in a Pestle and Mortar and sieved through 63 μm mesh sieve. The moisture content was determined by heating an aliquot at 105°C in the oven to obtain weight loss. The percent organic carbon content (OC) was also determined by heating in a furnace above 400°C. The rest of the sample was used for analysis of heavy metal.

A Perkin Elmer Atomic Absorption Spectrophotometer Model 2380 with an air/acetylene flame was used for analysis of the water and sediment samples after digestion with concentrated HNO<sub>3</sub>/HCl acid and preparation of

appropriate calibration standards using the method of Ochieng (1987). The accuracy of the method for sediment analysis was tested using a fortified IAEA reference soil sample according to the IAEA established method which involved taking 2.5 g of soil, subdividing into 0.5 g sub-samples, followed by digestion with the acid and a high mean recovery of 91% was obtained for this fortified sample.

## Results and Discussions

The OC was generally below 1% in all the estuarine sediment samples except for the silty-clay sediment at Sabaki site probably due to the greater primary productivity of the river mouth and high sediment load as a result of intense agricultural activities of Central Kenya highlands. River Sabaki is also known to experience a lot of siltation problems as well. Some of the sediment characteristics obtained were River Sabaki: pH 7.6, sand content (0.32%), silt content (42.5%), clay content (30.2%), Organic carbon (OC) content (4.7%), moisture content (MC; 20.3%), texture (silty clay), and River Ramisi: pH 7.4, sand content (45.2%), silt content (14.3%), clay content (6.8%), OC (0.73%), MC (19.7%), texture (sandy loam). The shores and river mouths attested to the complex sedimentation processes derived through hydrologic erosion, transport and deposition as described for other aquatic environments.

At River Sabaki sampling site, the organic carbon could accumulate as a result of precipitation. These three coastal rivers flow through relatively dry areas with low annual rainfall. However, they provide sources of drinking water and irrigation. Anthropogenic and geological disturbances such as torrents of tropical rainfall, floods, soil erosion, siltation and industrial effluents are expected to influence the organic and inorganic loads which would register significant footprints in the estuarine sediments. Increase in sediment moisture content can induce reduced conditions, for example  $\text{Cr}^{3+}$  formation can be favoured by reduction of  $\text{Cr}^{4+}$  as a result of enhanced solubility and lability of organic matter and at higher pH, higher concentration of Cd in sediment is found due to precipitation of dissolved

Cd. The coastal rivers had four-times the dissolved salt content compared with other inland rivers which discharge into Lake Victoria (Ochieng 1987). They also had higher electrical conductivities of 320–382  $\mu\text{S}/\text{cm}$ , higher temperatures as well as higher dissolved oxygen (DO) content.

The limnological data obtained for the sampling sites are shown in Table 1. From these data, the river water chemistry qualifies these rivers as suitable for aquatic life and for human use. The rivers Sabaki and Ramisi are slightly alkaline with mean pH values of 7.66 and 7.22–7.50, respectively, with DO contents of 8.0 and 5.7–7.0 mg/L (i.e. 95% and 72% saturation range), respectively, and low alkalinities in the sampling sites covered during the study. The temperatures (mean of  $26.4 \pm 1.60^\circ\text{C}$ ) were within maximum productivity range. River Vevesi (a tributary of River Ramisi) is different as it passes through a bog going downstream before the sampling site. Its water was acidic and had much lower alkalinity, lower DO and slightly higher electrical conductivity which are common for such water. The content of dissolved salts in freshwaters, as indicated by the electrical conductivity, has been used by some researchers as a general indication of their potential fertility. The electrical conductivities in freshwaters in Kenya, as has been found in the lakes, are influenced mainly by carbonate salts, which account for up to 80% of the conductivity in most cases. The remaining electrolytes are therefore present in low concentrations. Consequently the concentration of biologically valuable electrolytes such as phosphates and nitrates is therefore much lower in Kenyan freshwaters than expected (Ochieng et al. 2006; Ochieng et al. 2007). The water conductivity would be largely determined by  $\text{Ca}^{2+}$  and bicarbonate fluxes and would relate to these ions as does its pH. Table 2 shows the comparison of turbidity and DO content of the three rivers with those of international standards, considering different purposes for which their water is intended. According to these standards, these Kenyan rivers are not polluted and they fulfil the requirements except for the turbidity of R. Sabaki which was very high indicating that the water at the sampling point would not be suitable for direct drinking and industrial use as well as for fish and other animal habitat.

**Table 1** Some of the limnological data obtained for the coastal rivers studied

River	pH	Temp ( $^\circ\text{C}$ )	DO (mg/L)	Transp (cm)	Turb (FTU)	Alkalinity mgCaCO <sub>3</sub> /L	Cond $\mu\text{S}/\text{cm}$
SB	7.66	25.2	8.0 (95%)	80	220	85.0	320
RMS1	7.22	28.7	5.7 (72%)	25	22.0	63.03	335
RMS2	7.50	27.3	7.0 (88%)	25	16.0	60.61	350
VVS	6.33	26.4	4.6 (58%)	75	3.5	19.8	382

SB Sabaki River, RMS1 Ramisi site 1, RMS2 Ramisi site 2, VVS Vevesi, DO dissolved oxygen, Transp transparency, Turb turbidity, Cond electrical conductivity

**Table 2** Comparing some of the limnological data of the rivers with international standard requirements for aquatic life in freshwaters

Purpose of utilization	pH	Turbidity SS (ppm)	DO (ppm)
Water supply conservation	6.5–8.5	≤25	≥7.5
Fisheries and recreation	6.5–8.5	≤50	≥5
Industrial/Agricultural and conservation of the environment	6.0–8.5	≤100 No observable floating matter	≥2
River Sabaki <sup>a</sup>	7.66	220 (FTU)	8.0 (95%)
River Ramisi <sup>a</sup>	7.36	19.0 (FTU)	6.4 (80%)
River Vevesi <sup>a</sup>	6.33	3.5	4.6 (58%)

<sup>a</sup> Data obtained in this study. Other data from Ochieng (1987)

The pH and DO values obtained for the three rivers were within international standard requirements for water supply for fisheries, recreation and industrial, agricultural and environmental conservation (Ochieng et al. 2006). The turbidity of the water from Sabaki was much higher (~10–60 times) than those of the other two rivers in the study. This river originates from Athi River which flows through agricultural region in central Kenya and is bound to carry more organic and sediment particles compared with the others in the study and therefore siltation could have occurred at the sampling points.

The concentrations of leachable heavy metals in sediment samples from three sampling sites are shown in Table 3. Some metals such as Ag, Cd and Cr were poorly extracted under the low acid strength employed or were extracted at concentrations below the detection limits. Generally most of the exchangeable cations in the estuarine sediments ranged between 2% and 20% of the total trace metal content obtained by digestion with concentrated acid. Co, Cu, Mn, Ni and Zn were fairly exchangeable and therefore represented the most mobile species in the sampling sites. Exchangeable cations seldom constitute the bulk of the total supply and often represent only a small

**Table 3** Total leachable concentration (μg/g dry weight) of heavy metals in sediment samples from the three sites

Metal species	Ramisi (RMS2)	Vevesi (VVS)	Sabaki (SB)
Ag	Bdl	Bdl	Bdl
Cd	Bdl	Bdl	Bdl
Co	0.53	0.17	0.10
Cr	Bdl	Bdl	Bdl
Cu	1.17	0.39	0.78
Mn	506.75	380.06	29.24
Ni	6.82	3.90	3.90
Pb	Bdl	Bdl	1.56
Sn	23.39	Bdl	Bdl
Zn	Bdl	7.18	35.08

Bdl below the detection limit

fraction of total which supports the results obtained in this study.

Weak acids digest only leachable and particle bound metals but strong acids dissolve constitutive metals from the mineral matrix, in addition. Spatial distribution of heavy metals in surface sediments is as a result of integrated changes occurring in the water column and concentrations of heavy metals in the sediment represent combination of chemical, biological and physical processes occurring in fluvial, estuarine and coastal environment. Solid surface chemistry influences cation exchange reactions and therefore controls adsorption and the proportion of leachable cations. Manganese oxides, for example, have high surface areas and high cation exchange capacities and act as strong scavengers for heavy metals such as Cr. In this case in sediments with high Mn in the matrix one would expect lower leachable concentration of Cr. The total exchangeable cations of the sediments are the proportions of the cations associated with the sediment solids that are subject to interchange with cations in solutions and aquatic biota, under conditions of little or no decomposition of the remainder of the sediments. They are chemically the most reactive part of the sediments. Cations in solution remain nearly at equilibrium with those in exchangeable form.

It is known that a large percentage of heavy metals in non-polluted lakes and rivers are generally incorporated in the crystal lattice of minerals that make up the bottom mud. This percentage would form part of the natural background level in the bottom mud in polluted waters on which the anthropogenic input would be based on. However, the concentration factors would be expected to change from time to time depending on the mixing patterns of the water, the water chemistry as well as on accumulation that in turn depends on nutrients and organic matter in the water column. The heavy metals that are not present in the crystal lattice are therefore distributed in organic matter, in hydrous Mn and Fe oxides, and in any discrete minerals formed by the metals.

The mean total concentrations in sediment samples from the four sampling sites are shown in Table 4. The three

**Table 4** Mean total trace metal concentration in sediment ( $\mu\text{g/g}$  dry weight) compared with background and shale concentrations

River	Ag	Cd	Co	Cr	Cu
SB	$0.27 \pm 0.21$	$0.12 \pm 0.21$	$0.39 \pm 0.12$	ND	$5.55 \pm 1.11$
RMS1	$18.52 \pm 1.34$	$0.21 \pm 0.13$	$0.96 \pm 0.24$	$3.63 \pm 0.24$	$23.47 \pm 4.11$
RMS2	$0.27 \pm 0.11$	$0.04 \pm 0.05$	$0.24 \pm 0.11$	ND	$1.46 \pm 0.35$
VVS	$0.27 \pm 0.22$	$0.39 \pm 0.20$	$1.00 \pm 0.33$	$2.92 \pm 1.10$	$19.49 \pm 4.44$
Back <sup>a</sup>	NL	$0.2 \pm 0.1$	$6.4 \pm 1.5$	$21.6 \pm 6.9$	$21 \pm 6.4$
Shale <sup>b</sup>	NL	0.3	NL	NL	45
River	Mn	Ni	Pb	Sn	Zn
SB	$97.45 \pm 11.5$	$9.55 \pm 1.55$	$6.24 \pm 1.44$	$38.98 \pm 7.56$	$277.4 \pm 110.2$
RMS1	$917.37 \pm 101.1$	$16.44 \pm 4.2$	$26.21 \pm 4.12$	$41.16 \pm 10.2$	$83.61 \pm 22.1$
RMS2	$204.65 \pm 40.4$	ND	$4.09 \pm 3.11$	$38.98 \pm 11.0$	$6.33 \pm 3.21$
VVS	$360.57 \pm 56.2$	$25.34 \pm 6.22$	$27.29 \pm 3.33$	$56.52 \pm 12.1$	$93.55 \pm 15.4$
Back <sup>a</sup>	$479 \pm 64$	NL	$23 \pm 3.7$	NL	$56 \pm 25$
Shale <sup>b</sup>	NL	NL	20.0	NL	95.0

SB Sabaki, RMS1 Ramisi site 1, RMS2 Ramisi site 2, VVS Vevesi, ND not detected, NL not in literature cited

<sup>a</sup> Background levels (Adamo et al. 2005)

<sup>b</sup> Average Shale concentrations (Jain 2004),  $n = 3$

rivers showed normal trend of trace metal contents in sediment except for elevated levels of Zn ( $277.4 \mu\text{g/g}$  dry weight) in Sabaki River. Sediment samples taken  $\sim 1$  km away downstream from Ramisi Sugar factory (i.e. at Ramisi Bridge) gave higher concentrations of metals than those sampled before the factory (i.e. at Daragube point), those taken even farther downstream from the factory at River Vevesi (a tributary of Ramisi) and those in Sabaki River. The factory effluents may either have contained traces of heavy metals that contributed to higher concentrations observed or the effluent may have enhanced deposition of heavy metals onto bottom sediments if it contained high organic load.

The three coastal rivers had relatively lower mean sediment total concentrations of heavy metals Cd, Cr, Cu and Pb than those reported in Dipsiz stream in Turkey and Naples Harbour in Italy (Adamo et al. 2005; Demirak et al. 2006). The range of mean total sediment concentrations (in  $\mu\text{g/g}$  dry weight) of Cd (from 0.04 to 0.39) was lower than those found in Yamuna River in India (mean of 9.5), Dipsiz stream in Turkey ( $0.80 \pm 0.60$ ) and Naples harbour in Italy (mean of 0.9; Jain 2004; Adamo et al. 2005; Demirak et al. 2006) but was comparable with that of Keelung river in Taiwan (range 0.073–0.70; Huang and Lin 2003). This tells us that the rivers investigated in our study were less exposed to anthropogenic inputs compared with the European waters. The level of Cd was also comparable to background levels as reported for Naples Harbour ( $0.2 \pm 0.1$ ) and shale concentrations (mean of 0.3; Jain 2004; Adamo et al. 2005). The ranges of the mean sediment concentrations of Co (0.24–1.0), Cr (ND–3.63) and

Cu (1.46–23.47) were also lower than those of Naples harbour (means 5.1, 72.5, and 131, respectively). The Cr and levels were also lower than those of Dipsiz stream (mean of 19.70) and the background levels reported in Italy ( $21.6 \pm 6.9$ ). The mean Cu sediment concentration level was comparable to those reported for Yamuna River (mean of 22.2) and Keelung river (range 12–110) and Dipsiz stream ( $13 \pm 9.0$ ), but comparable to background ( $21.0 \pm 2.5$ ). Mean total Pb sediment concentration levels (range 4.09–27.27) also showed lower values compared with Naples harbour (mean 131), Yamuna river (mean of 60.3) and Dipsiz stream ( $83.60 \pm 56.2$ ) but the mean range for Zn (range 6.33–277.4) was comparable with Yamuna river (mean 59.2), Keelung (range 57–270), Dipsiz stream ( $37.00 \pm 26.0$ ) and Naples harbour (mean of 303). The values obtained for Mn were comparable with those of Keelung river (range 330–600) and Naples harbour (mean 389). All these show more anthropogenic influence contributing to higher concentrations of Co, Cd, Cu, Pb and Zn in some the European and Asian ecosystems. Ramisi sampling point after the former Ramisi Sugar Factory had higher levels of metals than Sabaki and Vevesi. This was mainly due to influence of the sugar factory. Sabaki River concentrations could be considered to be due to its geological origin as well as industrial effluent upstream such as the factories in Athi River and tannery factory in Thika. But in general all these three rivers would be considered non-polluted in terms of sediment loads, based on shale standard and the background concentrations. A comparison of metal concentration in sediment with shale standard is generally taken as a quick practical method of tracing



heavy metal enrichment (Wedepohl 1995; Jain 2004; Warren et al. 2005).

Everaarts and Nieuwenhuize (1995) obtained lower concentrations (in  $\mu\text{g/g}$  dry weight) of Cu (0.100), Zn (0.524), Cd (0.0117), Pb (0.137) and Mn (1.587) in estuarine sediment samples taken from Sabaki River mouth at the Indian Ocean Coast of Kenya (Everaarts and Nieuwenhuize 1995). This is expected because of mixing of the river water and the Indian Ocean water at the estuaries as his sampling points were more inside the ocean. In Lake Kariba in Zimbabwe the reported mean surface sediment concentrations (in  $\mu\text{g/kg}$ ) were comparable with R. Sabaki and ranged within 15.8–25.8 (Cr), 0.69–0.72 (Cd), 12.4–16.1 (Cu), 19.3–23.9 (Pb), 238.7–326.9 (Mn), 23.2–5.9 (Ni) and 68.2–71.1  $\mu\text{g/kg}$  (Zn), in Kassesse bay and in Cages (Berg et al. 1995). In the drainage basin of Lake Kariba metal (Cu, Mn, Pb and Zn) mining takes place and elevated levels above natural concentrations in the ecosystem are attributed mainly to these mining activities.

The dissolved metal concentrations of waters samples taken from the four sampling sites are presented in Table 5. The concentration levels of most of the heavy metals analysed are within acceptable range and, the waters would be considered suitable for drinking and for aquatic life forms such as fish (see Table 6). The concentration levels also pass the World Health standards for drinking water and the USEPA maximum concentration but do not conform to USEPA criteria of continuous concentration. However, the concentrations of Ag, Ni, Pb and Mn were above acceptable levels and more analysis should be done to confirm these high concentrations and to ascertain their sources. In Table 6, the concentrations of toxic metals in waters of rivers in Turkey, Italy and South Africa are included for comparison.

One method of showing metal enrichment in sediment is by comparison of metal concentration ratios, where species concentrations are expressed as ratios of conservative

metals which occur in much higher concentrations such as Al, Mn and Fe (Jain 2004). The ratios of trace elements can reveal geochemical imbalances shown in elevated trace levels, where high metal concentration ratios (e.g.  $M/\text{Mn}$ ) are normally attributed to anthropogenic activities. The metal/Mn ratios for dissolved metal species ranged from  $6.56 \times 10^{-3}$  (Cd) to  $2.205 \times 10^{-1}$  (Zn) in River Sabaki water, from  $3.448 \times 10^{-2}$  (Ag) to 2.86 (Sn) in River Ramisi site 1, and from  $2.17 \times 10^{-3}$  (Ni) to  $6.5 \times 10^{-1}$  (Zn) in River Ramisi site 2. No concentrations of Mn were determined in Vevesi water consequently no values of metal/Mn ratios for this river were calculated. The metal/Mn ratios for sediments ranged from  $1.23 \times 10^{-3}$  (Cd) to 2.846 (Zn) in Sabaki,  $2.29 \times 10^{-4}$  (Cd)– $9.11 \times 10^{-2}$  (Zn) for Ramisi 1,  $1.95 \times 10^{-4}$  (Cd)– $1.90 \times 10^{-1}$  (Sn) for Ramisi 2 and from  $7.48 \times 10^{-4}$  (Ag) to  $2.59 \times 10^{-1}$  (Zn) in Vevesi. For dissolved metals, the data indicate higher concentration/enrichment of Ag in Sabaki River, Cd in Ramisi and Ni in Sabaki and Pb in Ramisi, respectively attributable to recent discharge from factory effluent. In sediments, the metal/Mn ratios showed higher concentration/enrichment of Ag in Ramisi, Cd in Sabaki and Vevesi, and Zn in Sabaki. Some of these metal/Mn ratios can be supported by EF (Enrichment Factor) values in Table 7 showing enrichment of Cd, Pb and Zn in R. Sabaki and R. Vevesi. The high EF indicate contamination in Sabaki River as it flows through Thika and Athi River industrial regions and contamination of River Vevesi by the former Ramisi Sugar factory. The metal/Mn ratios show discharge from Factory effluent at Ramisi River in the water at site 2, and the sediment EF ratios also confirm enrichment of Cd and Pb in both sites in Ramisi.

In conclusion, the sampling points considered in this study provided a suitable indication of anthropogenic inputs and sediment enrichment of toxic heavy metals including Cd, Pb, and Zn in Rivers Sabaki, Vevesi and Ramisi which discharge in to the Indian Ocean coast of

**Table 5** Dissolved metal concentration in river water ( $\mu\text{g/L}$ )

River	Ag	Cd	Co	Cr	Cu
SB	100 $\pm$ 12.4	5.0 $\pm$ 2.22	36 $\pm$ 4.12	25 $\pm$ 2.44	22.5 $\pm$ 6.22
RMS1	4.0 $\pm$ 2.11	5.0 $\pm$ 1.68	6.0 $\pm$ 2.30	7.6 $\pm$ 1.34	10 $\pm$ 2.10
RMS2	3.0 $\pm$ 1.44	8.0 $\pm$ 2.11	6.0 $\pm$ 3.10	4.3 $\pm$ 2.10	45 $\pm$ 10.4
VVS	ND	ND	ND	25 $\pm$ 5.40	7.5 $\pm$ 2.22
River	Mn	Ni	Pb	Sn	Zn
SB	762 $\pm$ 101.2	81 $\pm$ 6.21	68 $\pm$ 4.40	ND	168 $\pm$ 46.2
RMS1	116 $\pm$ 12.54	13 $\pm$ 2.11	7.0 $\pm$ 2.30	300 $\pm$ 16.4	75.5 $\pm$ 13.6
RMS2	138 $\pm$ 13.40	0.3 $\pm$ 0.02	34 $\pm$ 5.44	ND	91 $\pm$ 15.7
VVS	ND	13 $\pm$ 3.12	25 $\pm$ 3.40	ND	33 $\pm$ 10.4

Note: SB Sabaki, RMS1 Ramisi site 1, RMS2 Ramisi site 2, VVS Vevesi, ND not detected, n = 3

**Table 6** Mean concentrations (in µg/L) of some toxic metals determined in the three coastal river waters compared with those of WHO (1998) and USEPA (1999) acceptable standard limits, background and other levels determined in other rivers

Limit	Ag	Cd	Cr	Cu	Mn	Ni	Pb	Zn
HDL <sup>a</sup>	NL	NL	NL	50	50	NL	NL	$5 \times 10^3$
MPL <sup>a</sup>	50	10	50	$1 \times 10^3$	500	NL	100	$1.5 \times 10^4$
USEPA CMC <sup>b</sup>	NL	4.3	16	13	NL	NL	65	120
USEPA CCC <sup>b</sup>	NL	2.2	11	9	NL	NL	2.5	120
TC <sup>c</sup>	10	10	50	$2 \times 10^4$	NL	50	100	100
Sabaki <sup>d</sup>	100	5.0	25	22.5	762	81	68	168
Ramisi 1 <sup>d</sup>	4.0	5.0	7.6	10	116	13	7.0	76
Ramisi 2 <sup>d</sup>	3.0	8.0	4.3	45	138	0.3	34	91
Vevesi <sup>d</sup>	ND	ND	2.5	7.5	ND	13	25	33
Gediz <sup>e</sup>	NL	2–8	1–17	4–84	NL	NL	10–110	3–46
Lambro <sup>f</sup>	NL	0.1–4.8	2–66	1.1–134	NL	NL	2.2–139	NL
Dipsiz <sup>g</sup>	NL	0.17	0.09	0.37	NL	NL	0.41	1.05
Dzindi <sup>h</sup>	NL	1.6–3.3	NL	2.1–2.6	NL	NL	10.5–12.3	2.1
Back <sup>i</sup>	NL	0.02	NL	1.00	NL	NL	0.20	10

NL not in literature cited, ND not determined, HDL highest desirable level in drinking water, MPL maximum permissible level in drinking water

<sup>a</sup> WHO (1981)

<sup>b</sup> CMC criteria maximum concentration, CCC criteria continuous concentration

<sup>c</sup> TC threshold concentration for aquatic life (fishes) tolerance

<sup>d</sup> Levels obtained in this study

<sup>e</sup> Gediz river

<sup>f</sup> Lambro River in Italy (Adamo et al. 2005)

<sup>g</sup> Dipsiz stream in Turkey

<sup>h</sup> Background concentration (Demirak et al. 2006)

<sup>i</sup> Dzindi River in S.Africa (Okonkwo et al. 2005)

Kenya which can influence their deposition and accumulation in the coastal environment. These enrichments were influenced by inputs upstream from the central regions of Kenya and by the Ramisi Sugar factory effluent. The total exchangeable sediment cations results showed that Cu, Mn, Ni, Pb and Zn were fairly exchangeable and their leachability could have been influenced by organic carbon loads, recent anthropogenic discharge and redox conditions in the rivers. In general, exchangeable cations in sediment ranged

**Table 7** Enrichment factors (EF) based on Mn and given mean crust concentrations

Metal species	Mean crust concentration (µg/g) <sup>a</sup>	Sabaki	Ramisi 1	Ramisi 2	Vevesi
Mn	950				
Cd	0.11	7.798	1.977	1.688	9.340
Cu	50	1.082	0.486	0.136	1.027
Pb	14	4.345	1.938	1.356	5.136
Zn	75	36.057	1.161	0.392	3.286

<sup>a</sup> Huang and Lin (2003),  $EF = (X/Mn)_{\text{sample}} / (X/Mn)_{\text{crust}}$ , where X concentration of metal species, Mn concentration of Mn

from 0.10 to 506.75 µg/g for Co, Cu, Mn, Ni, Pb, Sn and Zn constituting between 2% and 20% of total metal concentrations obtained by digestion with strong acid. The leachable Cu, Mn, Ni, Pb and Zn therefore represent the most mobile species in the sampling sites. For dissolved metals, the metal/Mn ratios indicate higher concentrations of Ag in Sabaki River, Cd in Ramisi, Ni in Sabaki and Pb in Ramisi, respectively. In sediments, the metal/Mn ratios show higher enrichment of Ag in Ramisi, Cd in Sabaki and Vevesi, and Zn in Sabaki, respectively. Enrichment factors (EF) also confirm elevated levels of Cd, Pb and Zn in sediment in River Sabaki and River Vevesi which were due to anthropogenic inputs through Athi River. The mean total dissolved metal concentration ranges for the three rivers were comparable with those ranges reported in rivers in South Africa (Okonkwo et al. 2005) but the sediment concentrations were below those of rivers in Europe and Asia where anthropogenic addition of some of the toxic elements such as Cu, Pb and Cd is evidently higher.

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