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Sources of Heavy Metal Input Into Winam Gulf, Kenya

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Abstract Water and surface sediment from rivers Kisat, Nyamasaria, Nyando, Sondu-Miriu, Kuja, Awach, Yala, and Nzoia, which flow into Winam Gulf, were analyzed for heavy metals in order to assess the influence of the catchment activities on heavy metal input into the lake. Sampling was done both upstream and at river mouths where the rivers entered in to the lake. The mean sediment concentration of exchangeable cations (in μg/g) for Ag, Cd, Co, Cu, Mn, Ni, Pb, Sn, and Zn ranged from 0.01 to 263 (for Mn at Kuja). Ag, Cr, and Cd were poorly leachable with 0.1 MHCl but the other cations were found to be fairly exchangeable. Most exchangeable cations in sediment ranged between 2% and 20% of the total heavy metal content obtained by digestion with strong acid. The mean total dissolved metal (0.45 μm filter cut-off) and mean total sediment concentrations ranged from nd-16 (Ag), nd-8 (Cd), nd-23.3 (Co), nd-50 (Cr), 5–157.5 (Cu), 50–3276 (Mn), nd-54.1 (Ni), 7–93.6 (Pb), 25–219.5 (Zn) in μg/L and from nd-8.34 (Ag), 0.48–1.75 (Co), nd-1.78 (Cd), 2.92–5.36 (Cr), 3.90–150.2 (Cu), 133.5–7237 (Mn), 4.33–42.29 (Ni), 3.09–66.06 (Pb), 23.39–7.83 (Sn) and 23.39–350.8 (Zn) in μg/g dry weight, respectively. The rivers analyzed were found to be non-polluted in terms of sediment loads except river Kisat which was found to be polluted because of elevated levels of Pb, Mn, Cu, and Zn. Nyamasaria and Nyando were also found to have higher concentrations of Pb, Cu, and Zn than those reported previously in the lake sediment. The dissolved metal concentrations were acceptable by WHO maximum limits in drinking water except Mn which was above WHO limit in Kisat, Nyando, and Nyamasaria waters. Enrichment of Cd and Pb was found in all the river sediment samples with factors ranging from 2.12 at Kisat river mouth to 4.41 at Awach (for Cd) and from 1.49 (at Kisat river mouth) to 2.38 (at Nyando river mouth).

Keywords Water · Surface sediment · Heavy metals · Rivers · Winam Gulf · Kenya

Heavy metals are introduced into the aquatic environment as a result of weathering of soils and rocks, from volcanic eruptions and from various anthropogenic activities including mining and industrial processes. The use of metals or substances containing metal contaminants as is in the Jua Kali metal fabrication and scraping industries in almost all towns and cities in Kenya is a good example of the anthropogenic sources of heavy metals that discharge into the aquatic resources. The distribution processes of the metals entering natural waters are controlled by a dynamic set of physical–chemical interactions and equilibria and their solubilities are principally controlled by pH, concentration, type of metal species, organic ligands, the oxidation state of mineral components and the redox environment of the aquatic system (Lee et al.1998; Huang and Lin 2003; Davis and Leckie 1978; Jeon et al. 2003; Milward and Lin 2003; Warren et al. 2005; Grosbois et al. 2006). In the aquatic environment metals get enriched by aquatic organisms which convert them into complexes which may be even more toxic (Jain 2004). Metal speciation in rivers is unique because there are variations in loads

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and species with season and geology and the concentrations in the rivers contribute to the sediment deposition in lakes and oceans (Berg et al. 1995; Cheevaporn et al. 1995; Everaarts and Nieuwenhuize 1995; Wedepohl 1995; Deheyn and Latz 2006; Nicolau et al. 2006). Although rivers in developing countries were in the past considered to be least polluted, the scenario in these countries has changed rapidly due to rapid industrial development and degradation in freshwater quality and speciation studies of heavy metals in rivers is considered to be useful in understanding pollution regimes and catchment status (Cheevaporn et al. 1995; 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; Deheyn and Latz 2006; Demirak et al. 2006; Grosbois et al. 2006; Nicolau et al. 2006).

In addition, it is believed that there is need for continuous monitoring of trace metals as part of studies aimed at identifying variables which play vital roles in the reproductive biology and biodiversity of lake Victoria (Mwamburi and Oloo 1995). Determining the total concentrations of heavy metals in rivers discharging into the lake can help in identifying sources of toxic metal inputs into the lake and the impact of catchment land use pattern on the lake. In this paper, we report on concentrations and enrichments of Ag, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sn, and Zn in water and surface sediments of seven rivers which discharge into Winam Gulf, lake Victoria, at various points.

Materials and Methods

The samples were taken from seven rivers which flow into Winam Gulf of Lake Victoria in Kenya, which lies within latitudes 0°11.2′N–1°12.6′S and longitudes 33°45.7′E–34°45.7′E, i.e., (i) from the Kisumu city zone: river Kisat [at Kisat bridge (KST1), at the delta and at the river mouth (KST2) before entry into the lake near car wash area and at the bridge], river Nyamasaria [at the delta, at Nyamasaria bridge approximately 2 km (NMS1) from the lake and at the river mouth (NMS2)], (ii) Southern zone: river Nyando [at the delta, at Ahero bridge approximately 50 km from the lake (NYD1) and at the river mouth (NYD2)], river Sondu-Miriu [at the delta (MRU1) and at the river mouth (MRU2) approximately 200 m from the lake], river Kuja [at the delta (KJ1) and at the river mouth (KJ2)], river Awach [at delta (AWC1) and at the river mouth (AWC2)] (iii) Northern zone, river Yala [at Yala bridge approximately 60 km from the lake(YL1)], river Nzoia [at Rwambwa bridge approximately 60 km from the lake (NZA1)].

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_3 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. This procedure was believed to be able to prevent microbial growth, flocculation and reduce any adsorption on container surfaces. 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 during sampling. Surface sediment (approximately 0–2 cm layer) samples were taken from the same sites in replicates of three using stainless steel Ekman grab and 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 2001. Before analysis, portions of sediment were mixed well and then a 20 g amount was 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 and determining the loss in weight. The percent carbon content was also determined by heating in a furnace above 400°C. The rest of the sample was used for analysis.

A Perkin Elmer Atomic Absorption Spectrophotometer Model 2380 with an air/acetylene flame was used for analysis of the samples after preparation of appropriate calibration standards. Due to expected low concentrations of the metals in the natural water samples and limited instrument sensitivity (limit of detection was 1 ppb), preconcentration of the water samples was done by evaporating 100 mL of the water to 4 mL on a hot plate. The digestion of the water samples was then achieved by adding 5 mL of 11.1 M HNO_3 (Analar grade obtained from Kobian, Nairobi, Kenya) and heating on the hot plate for 30 min. Some 10 mL of 16.3 M HCl (Analar grade from Kobian, Nairobi, Kenya) was added and digestion continued until the solution remained light brown or colourless. The volume was then adjusted to 25 mL with distilled water. For analysis of sediment, 0.70 g was weighed accurately to 0.1 mg accuracy and placed in a pre-cleaned digestion test tube and digested with 5 mL of 11.1 M HNO_3 at 95°C for 1 h. The solution was cooled and diluted with 13 mL distilled water, shaken well and then centrifuged at 5,000 g for 10 min. The supernatant was then analyzed for the metals. Calibration curve method was used to quantify heavy metal concentrations. 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 gram of soil, subdivided into 0.5 g sub-samples. The sub-samples, in five replicates, were placed in test tubes with 5 mL concentrated 11.1 M HNO_3 for digestion. A high recovery of 91% was obtained for this reference sample and was used to correct the AAS data obtained.

Results and Discussion

The rivers sampled are very distinct as they flow through regions of similar geological characteristics in the lake basin which are relatively wet with moderate annual rainfall and the inhabitants practice small scale farming including maize and sugarcane farming and fishing. They provide an important source 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 sediments. Increase in sediment moisture content can induce reduced conditions, for example Cr^{3+} formation can be favored by reduction of Cr^{4+} as a result of enhanced solubility and lability of organic matter. The water pH, the nature and concentration of organic ligands, oxidation state and redox conditions within the environment would influence metal solubility. As an example, at higher pH, higher concentration of Cd in sediment is found due to precipitation of dissolved Cd. Some of the important limnological data were therefore recorded during the sampling period. The data collected are presented in Table 1. The river water at Kisat bridge and Kisat river mouth on river Kisat as well as at Nyamasaria bridge on Nyamasaria river was slightly alkaline. These two rivers receive industrial and municipal effluent in Kisumu city and are polluted. This is also shown by the low dissolved oxygen levels and high turbidities recorded at Kisat and Nyamasaria bridges, respectively. The mean temperatures recorded in all the rivers were within maximum productivity range. Industrial effluents also contribute to high salt contents in these Kisumu city rivers as shown by the high electrical conductivities in water at sampling points on river Kisat which passes through the main industrial area in the city before discharging into the lake. The water at Kuja and Awach river mouths was also alkaline. This could be due to mixing with lake water whose mean pH ranges from approximately 7.1 to 8.1. In Table 2, a comparison of the pH, turbidity, and dissolved oxygen content data obtained in this study with those of the international standard requirements for living environment for river is presented. Rivers Kisat and Nyamasaria are not suitable for fisheries habitat and recreation in view of their lower dissolved oxygen levels and higher turbidities as compared with the international requirements. Although the other rivers are not polluted, water samples from Yala (at Odhuro Bridge), Nzoia Bridge and Awach mouth indicated unsuitably higher turbidities than recommended for direct drinking water supply. However, this could only be a localized pollution problem as the samples were taken near town markets. The similarity in alkalinity of water from Yala and Nzoia rivers confirms the similarity in the catchments of the two rivers.

Since one major concern of metals in sediments is whether or not a sediment-ingesting organism can mobilize the metals or the lake and river waters can elutriate them, analyses to evaluate these two processes are preferred. As the pH of the gut of aquatic invertebrates usually ranges from slightly acidic to slightly alkaline, a 0.1 N HCl leach is recommended. Leachable heavy metal concentrations in sediments are shown in Table 3. The total exchangeable cations of the sediments are the protions 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. The table shows 0.1 N leachable (total exchangeable) trace metals. Some metals, such as Ag, Cd, and Cr were poorly

Table 1 Some limnological data taken in samples from Winam Gulf basin rivers

Site	pH	Temp (°C)	DO (mg/L)	Transp (cm)	Turb (FTU)	Alkalinity ($mgCaCO_3/L$)	Cond ($\mu S\ cm^{-1}$)
KST1	7.2	27.6	0.50	5.0	240.0	404.0	1,060
KST2	7.6	26.5	5.53	10.0	120.0	370.9	940
NMS	7.2	23.0	0.60	15.5	30.5	149.3	115.7
MRU1	7.45	24.0	5.30	40.0	13.5	31.0	160
KJ1	6.15	25.0	8.20	20.0	141.0	49.5	120
KJ2	7.85	26.0	5.53	120.0	11.1	43.1	100
AWC2	7.70	25.0	6.70	30.0	29.0	60.0	160.0
NZA1	6.75	25.5	7.1	10.0	27.0	252.0	88.0
NZA2	6.75	22.4	8.0	30.0	17.0	139.0	102.0
YL1	6.70	25.0	7.0	40.0	13.0	226.0	100
YL2	6.35	24.5	8.1	26.0	46.0	208.0	90.0

All data given are mean values; KST1: Kisat bridge; KST2: Kisat mouth; NMS: Nyamasaria bridge; KJ1: Kuja delta; KJ2: Kuja mouth; MRU1: Sondu-Miriu delta at Sondu; AWC2: Awach mouth; NZA1: Nzoia bridge; NZA2: Nzoia (Rwambwa bridge); YL1: Yala bridge; YL2: Yala (Odhuro bridge). nd: not detected, 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 living environment for rivers

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
Rivers in this study: range	6.15–7.85	10–240 (FTU)	0.5 (6%)–8.2 (97%)

Data obtained from Ochieng et al. (2006)

Table 3 Mean total exchangeable metal concentration (in μg/g dry weight) in sediment samples from three rivers in Winam Gulf basin

Metal species	AWC2	NZA2	KJ1	KJ2
Ag	nd	nd	0.01 ± 0.01	0.10 ± 0.02
Cd	0.049 ± 0.01	nd	0.01 ± 0.01	0.11 ± 0.04
Co	0.17 ± 0.10	0.02 ± 0.01	0.17 ± 0.12	0.10 ± 0.01
Cr	nd	nd	nd	nd
Cu	0.39 ± 0.04	1.38 ± 0.20	0.78 ± 0.33	nd
Mn	195 ± 11	172 ± 22	146 ± 24	263 ± 41
Ni	3.90 ± 0.44	4.57 ± 1.12	3.90 ± 0.44	3.90 ± .0.41
Pb	2.73 ± 0.42	nd	2.73 ± 0.34	1.56 ± 0.05
Sn	39.0 ± 10.1	nd	23.4 ± 1.22	nd
Zn	4.40 ± 1.22	7.34 ± 2.11	31.2 ± 9.22	nd

nd denotes 'below the detection limit', n = 3

extracted under the low acid strength employed or were extracted at concentrations below the detection limits.

Generally most of the exchangeable cations in the river sediments ranged between 2% and 20% of the total trace metal content obtained by digestion with concentrated acid. Cu, Mn, Ni, Pb, and Zn were fairly exchangeable. However, analysis of the sediments reveals that exchangeable cations seldom constitute the bulk of the total supply and often represent only a small fraction of the total. Weak acids digest only leachable and particle bound metals but strong acids also dissolves constitutive metals from the mineral matrix, in addition. Spatial distribution of heavy metals in surface sediments are as a result of integrated changes occurring in the water column and heavy metals in the sediment represent combination of chemical, biological and physical processes occurring in fluvial, estuarine, and coastal environment. Metal solubility is principally controlled by pH, concentration, type of ligands, oxidation state of species and redox conditions of the aquatic environment. At higher pH, higher concentration of Cd in sediment is found due to precipitation of dissolved Cd and vice versa. Increase in soil moisture content can induce reduced conditions within the sediment and this can influence the chemistry of certain species, for example Cr^{3+} formation by reduction of Cr^{4+} is favored because of enhanced solubility and lability of organic matter. Solid surface chemistry also influences cation exchange reactions and therefore controls adsorption and the proportion of leachable cations. For example, manganese oxides 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. This is also the case shown in the data presented in the table.

Table 4a, b show the total mean concentrations in sediment samples from the rivers. These values are compared with concentrations (in μg/g dry weight) obtained in rivers in Europe and Asia, which range from 0.073–9.5 (Cd), 5.1 (Co), 19.7–72.5 (Cr), 12–131 (Cu), 330–600 (Mn), 15–150 (Pb), 37–303 (Zn) (Lim et al. 1995; Huang and Lin 2003; Jain 2004; Adamo et al. 2005; Demirak et al. 2006). The values obtained for Pb, Cu, Zn, and Mn in Kisat river are higher in general than those obtained in river sediment in some other countries. However, compared with those of Keelung river in Taiwan near an industrial park which had sediment concentrations (in μg g^{-1} dry weight) of Zn (270), Cu (110), Pb (150), Cd (0.70), Mn (600), the anthropogenic influence is more heavily manifested in this Taiwan river (Huang and Lin 2003). But in general all these rivers in the lake basin in Kenya would be considered non-polluted in terms of sediment loads, based on shale standard and the background concentrations (Jain 2004; Adamo et al. 2005), included in the tables, except river Kisat which appeared to be significantly polluted because of high Pb, Mn, Cu, and Zn loads. The elevated levels are due to sewage and industrial effluent. Nyamasaria and Nyando also had higher concentrations of Pb, Cu, and Zn than the lake (Ochieng et al. 2006) influenced by surface runoff and geology of basin. The mean concentrations of Pb, Cu, and Zn were similar in two rivers Kisat and Nyamasaria in Kisumu city but these were higher than those reported recently in the Winam Gulf (Ochieng et al. 2006). A comparison of metal concentration in sediment with shale standard is generally taken as a quick practical method of tracing heavy metal enrichment (Jain 2004). The results of river Kisat show the effects of industrial and sewage effluent on the water system. Mean concentrations in river mouths and in deltas were generally lower than in

Table 4 Mean total trace metal concentration in sediment (μg/g dry weight) compared with those reported (a) in other areas (b) in other areas in the world

River	Ag	Cd	Co	Cr	Cu
(a)					
KST1	1.30 ± 0.22	0.92 ± 0.33	1.12 ± 0.22	3.25 ± 0.33	26.54 ± 6.44
KST2	2.50 ± 0.31	1.78 ± 1.11	0.58 ± 0.21	3.90 ± 0.36	150.22 ± 15.3
NMS	nd	nd	1.00 ± 0.11	4.87 ± 1.13	7.02 ± 1.22
NYD1	0.10 ± 0.11	0.88 ± 0.42	1.46 ± 0.23	5.36 ± 1.33	43.85 ± 10.1
NYD2	nd	0.16 ± 0.12	1.00 ± 0.20	2.92 ± 1.02	27.29 ± 4.76
MRU1	nd	0.20 ± 0.10	0.54 ± 0.06	3.90 ± 1.12	3.90 ± 1.24
MRU2	8.34 ± 1.22	0.64 ± 0.22	1.10 ± 0.11	4.71 ± 0.46	15.92 ± 3.22
KJ1	0.10 ± 0.10	1.35 ± 0.32	1.31 ± 0.22	3.90 ± 0.62	35.57 ± 10.1
KJ2	0.91 ± 0.23	0.11 ± 0.02	0.53 ± 0.15	3.25 ± 0.55	4.33 ± 0.43
AWC1	0.10 ± 0.11	0.68 ± 0.21	1.75 ± 0.21	4.87 ± 2.01	43.66 ± 8.44
AWC2	0.49 ± 0.21	1.71 ± 0.22	0.48 ± 0.14	2.92 ± 0.42	3.90 ± 0.42
NZA1	0.27 ± 0.20	0.27 ± 0.21	0.96 ± 0.34	3.90 ± 0.44	17.54 ± 5.41
Back[a]	nl	0.2 ± 0.1	6.4 ± 1.5	21.6 ± 6.9	21 ± 6.4
Shale[b]	nl	0.3	nl	nl	45
River	Mn	Ni	Pb	Sn	Zn
(b)					
KST1	7237 ± 140	24.92 ± 4.46	38.13 ± 10.2	75.83 ± 22.3	350.8 ± 44.4
KST2	3014 ± 122	36.06 ± 4.56	66.06 ± 23.1	47.75 ± 23.4	217.9 ± 36.4
NMS	5282 ± 346	22.44 ± 5.22	16.57 ± 4.45	nd	40.54 ± 14.6
NYD1	2635 ± 222	37.32 ± 7.64	29.92 ± 9.56	38.98 ± 34.6	204.6 ± 56.4
NYD2	623.7 ± 102	31.18 ± 8.11	21.83 ± 9.42	23.39 ± 12.6	159.4 ± 66.3
MRU1	1101 ± 116	9.55 ± 4.32	10.14 ± 2.33	38.90 ± 15.4	73.67 ± 23.4
MRU2	1825 ± 241	28.88 ± 10.2	3.09 ± 0.44	43.11 ± 12.4	250.6 ± 101.1
KJ1	133.5 ± 64.4	36.47 ± 4.44	50.09 ± 12.4	38.92 ± 11.6	198.8 ± 78.2
KJ2	227.5 ± 66.2	4.33 ± 1.22	6.93 ± 2.33	62.83 ± 22.3	26.00 ± 6.44
AWC1	1316 ± 120	42.29 ± 10.3	32.55 ± 6.77	38.96 ± 16.4	168.0 ± 19.4
AWC2	438.5 ± 72.4	9.55 ± 4.33	9.75 ± 2.45	38.93 ± 12.4	23.39 ± 4.44
NZA1	838.1 ± 100.4	25.34 ± 5.44	15.59 ± 2.11	23.39 ± 11.1	76.01 ± 18.4
Back[a]	479 ± 64	nl	23 ± 3.7	nl	56 ± 25
Shale[b]	nl	nl	20.0	nl	95.0

nd: not detected, nl: not in literature cited, 1, 2: sampling sites, [a]Background levels (Adamo et al. 2005), [b]Average Shale concentrations (Jain 2004)

the river upstream indicating dilution effects (e.g., in Kisat, Awach, and Sondu Miriu).

The dissolved metal concentrations in the waters analyzed are presented in Table 5a, b. The concentration levels of heavy metals in all rivers are within accepted range, and in terms of heavy metal concentration, the waters would be suitable for drinking and for aquatic life forms, such as fish (see Table 6). They qualify by the World Health standards for drinking water but, in general, do not conform to USEPA standards. Kisat, Nyando, and Nyamasaria had higher levels of Mn than the WHO maximum limit in drinking water. Some of the concentrations of toxic metals in waters of rivers in Turkey, Italy, and South Africa are included and are quite comparable (Okonkwo et al. 2005; Demirak et al. 2006). The surface run-off and geochemical nature of drainage basin strongly influence composition of waters of small streams and therefore variability in data in small streams with variation in rainfall is expected although this was not addressed in this study. Therefore, we may expect significant differences between seasons for heavy metal concentrations in these rivers, as was demonstrated in Pb, Cu, Zn, and Cd in rivers in South Africa (Okonkwo et al. 2005).

Practically all the naturally occurring elements of the earths crust can be found in natural waters. It is assumed that the variations caused by rainfall, anthropogenic inputs, channel morphology, chemical and biological reactions in

Table 5 Dissolved metal concentration in river water (μg/L)

River	Ag	Cd	Co	Cr	Cu
(a)					
Kisat 1	4.0 ± 1.01	8.0 ± 2.11	19.0 ± 3.22	25.1 ± 2.44	157.5 ± 23.4
2	nd	5.1 ± 1.33	nd	50.0 ± 10.2	40.0 ± 5.40
Nyando 1	75.1 ± 14.2	2.4 ± .32	23.2 ± 4.11	25.0 ± 2.33	57.9 ± 11.6
Miriu 1	nd	8.0 ± 1.36	nd	nd	5.0 ± 1.22
Kuja 1	nd	2.0 ± 0.31	19.0 ± 2.45	nd	50.0 ± 13.2
Awach 2	nd	2.0 ± 0.44	nd	nd	10.1 ± 0.76
Nyamasaria 1	1.0 ± 0.21	2.2 ± 0.26	6.1 ± 1.33	25.5 ± 6.54	16.5 ± 2.78
Nzoia 1	3.0 ± 0.32	nd	10.0 ± 2.22	nd	30.0 ± 6.71
	16.1 ± 2.11	nd	nd	nd	20.0 ± 1.99
Yala 1	3.1 ± 1.11	nd	6.0 ± 0.43	nd	10.1 ± 0.66
2	nd	nd	6.0 ± 0.64	nd	10.0 ± 0.74
River	Mn	Ni	Pb	Sn	Zn
(b)					
Kisat 1	693 ± 104	52.5 ± 11.2	60 ± 14	500 ± 140	135 ± 15
2	738 ± 210	nd	7.0 ± 2.11	500 ± 122	219.5 ± 22.6
Nyando 1	3276 ± 421	54.1 ± 12.4	93.6 ± 36.8	300 ± 76.4	124.8 ± 24.6
Miriu 1	nd	13.0 ± 3.21	51 ± 11	nd	44 ± 14
Kuja 1	94 ± 22	nd	50 ± 16	nd	55 ± 21
Awach 2	138 ± 44	19.1 ± 2.22	nd	nd	55 ± 12
Nyamasaria 1	624 ± 142	32.3 ± 11.6	61.8 ± 21.0	nd	64.8 ± 8.1
Nzoia 1	50 ± 10	13.0 ± 2.34	29.5 ± 4.44	nd	89.1 ± 23
2	600 ± 256	13.0 ± 3.21	15.0 ± 1.44	nd	33.0 ± 11
Yala 1	94 ± 33	nd	42.0 ± 4.56	300 ± 60.4	26.0 ± 8.22
2	138 ± 56	31.0 ± 7.84	34.0 ± 5.23	nd	25.0 ± 3.68

1: site 1, 2: site 2

Table 6 Comparing mean concentration ranges (in μg/L) of some heavy metals determined in the river waters with those of WHO and USEPA (1999) standard limits, background and other levels in other rivers

Limit	Cd	Cr	Cu	Mn	Pb	Zn
HDL[1]	nl	nl	50	50	nl	5×10^3
MPL[1]	10	50	1×10^3	500	100	1.5×10^4
CMC[2]	4.3	16	13	nl	65	120
CCC[2]	2.2	11	9	nl	2.5	120
TC[3]	10	50	2×10^4	nl	100	100
Range in this study	nd-8	nd-50	5–157.5	50–3276	nd-93.6	25–219.5
Gediz[a]	2–8	1–17	4–84	nl	10–110	3–46
Lambro[b]	0.1–4.8	2–66	1.1–134	nl	2.2–138.8	nl
Dipsiz[c]	0.171	0.092	0.365	nl	0.405	1.051
Dzindi[d]	1.6–3.3	nl	2.1–2.6	nl	10.5–12.3	2.1
Back[e]	0.02	nl	1.00	nl	0.20	10

nl: not in literature cited, nd: not detected, HDL: highest desirable level in drinking water, MPL: maximum permissible level in drinking water, [3] TC: threshold concentration for aquatic life tolerance (safe for most fishes), [1] WHO drinking water standards,1981; [2] CMC: EPA criteria maximum concentration, [2] CCC: EPA criteria continuous concentration, [a] Gediz river in Turkey, [b] Lambro river in Italy, [c] Dipsiz stream in Turkey (Demirak et al. 2006), [d] Dzindi River in South Africa (Okonkwo et al. 2005), [e] Background concentration world average (Demirak et al. 2006)

the water environment and by inflow and outflow balance will affect all the metal species equally, given the nature in similarity in properties of these transition metals. One method of showing metal enrichment in sediment caused by these factors is by comparison of metal (M) 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). This is because in natural river environments, inorganic elements as well as metals exist together in relative proportions to each other. These ratios are dependent on a larger number of processes in geochemical cycle including weathering transport and deposition. Therefore ratios of trace elements can reveal geochemical imbalances due to elevated trace, where high metal concentration ratios (e.g., M/Mn) are normally attributed to anthropogenic activities. We worked out the metal/Mn ratios for sediment concentrations and dissolved metal concentrations for the seven rivers and compared the ratios obtained. The metal/Mn ratios for dissolved metal species did not show any obvious imbalances among the rivers except a 10-fold increase in Cr in Kuja river water. River Kuja had higher amounts of other heavy metals in its sediment compared with other lake basin rivers as it drains through gold rich region although its water had very low concentration of detectable amounts compared with its bottom sediments. Similarly there were no obvious imbalances among river sediment although enrichment in Zn was found in Nzoia river sediment. Enrichment factors [$EF = (M/Mn)_{sample}$ /$M/Mn)_{crust}$] were also calculated for Cd, Cu, Pb, and Zn according to the method of Huang and Lin (2003). The results showed enrichment factors of Cd in all the rivers (ranging from 2.12 at KST1 site to 4.41 in AWC1), Pb enrichment factor of 1.49 KST2, 2.38 at NYD2 and 2.07 at KJ2 and Zn enrichment factor of 1.74 at KJ1.

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