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EDXRF and TXRF Analyses of Heavy Metal Pollution in Thika River Sediments, Water and Flora

Moywaywa Ben Asiago[1], Michael J. Mangala[1] and David Maina
[1]*Institute of Nuclear Science and Technology, University of Nairobi, Kenya*

Abstract
The levels of heavy metals, namely Mn, Cu, Zn, Ni, Pb in water, flora and sediments along the Thika River, Kenya were studied in September 2015, to investigate their distribution and to determine the extent of pollution. The levels of selected heavy metals were determined using total X-ray fluorescence for water samples and energy dispersive x-ray fluorescence for sediment and algae samples. In general, the concentration levels of heavy metals in water samples (μg l^{-1}) were; Mn (53.5 - 605), Cu (< 10 - 303), Zn (22 - 325), Ni (<15- 77), Pb (<10 - 84) while those in sediment samples (mg kg^{-1}) were; Mn (2230 - 8659), Cu (51 - 115), Zn (153 - 432), Ni (67 - 172), Pb (32 - 177). Similarly, the levels of heavy metals in Cladophora (mg kg^{-1}) were Mn (3719 - 21200), Cu (65 - 129), Zn (153 - 434), Ni (35 - 235), Pb (17-72). Statistical analyses also revealed that there was a significant difference in heavy metal concentrations between the three media for all elements studied. Based on enrichment factors, geoaccumulation indices, pollution load index and contamination factors, all sampled sediments were generally contaminated with Pb, Cu, Zn, Mn and Ni to a moderate degree, thus requires intervention to curb on the rising levels of pollutants. Statistically significant interrelationship was observed between sediments and Cladophora, which supports the idea that, Cladophora is an appropriate bio-indicator for heavy metal pollution.

Keywords: *heavy metal, Cladohphora, geoaccumulation index, heavymetal*

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I. Introduction

In general, recent rapid increases in population growth and industrialization have resulted in high demand for water, both for industrial and domestic uses across the world. However, in most developing countries, this population growth has not been accompanied by provision of sustainable quality water supplies and quality sanitation services (Rahman, 2011). Thika Town, Kenya, exemplifies a town that has undergone rapid industrial growth while its population has risen remarkably from 4,500 people reported in 1948 to 165, 342 people in 2009 (*Kenya Open Data Survey, 2014*).

The Thika River traverses Thika's industrial, residential and agricultural zones where these pollutants are introduced in the river waters along its profile with the possibility of heavy metal contamination- a potential threat to human health for the inhabitants. In some sections of the river, raw sewage, industrial effluents from nearby industries and municipal wastewater are directly released into the river (Gathua, 2015). Untreated effluents are released into the river without due consideration of their pollutants. The river water is further polluted by industrial and household wastes; human excreta and industrial effluents from industrial establishments such as textile factories, tanneries, garages and food processing factories (Odira, 1991).

Sediments act as a sink to such pollutants by accumulating them over time; consequently, they provide means through which toxicity is introduced to the food chain.

Some aquatic plants such as algae, found in sediments, absorb metals to their cellular structures (Kelly and Whitton, 1995). The amount of accumulated heavy metals depends largely on the degree of contamination of the sediments. Thus the level of heavy metals in such plants is an indicator of the level of contamination in the sediments. Few studies have been conducted on Thika river pollution. Mwangi (1988) investigated the effect of agricultural, domestic and industrial on the quality of the Thika-Chania River system and observed that the river was less polluted except for the isolated cases of chloride and iron pollution. Odira, (1991), investigated the pollution profile of Thika River and noted high pollution (3200 mg/l of suspended solids) in areas located close to the Thika Cotton Mills and Delmonte (K) Ltd. The study emphasized the need to ensure that the industries discharging their effluents directly into the river adhere to effluent standards. However, the study did not assess the extent of pollution.

This study investigated the levels of heavy metal contamination in Thika River water, sediments and algae, and their inter-relationships and determined the extent of contamination for evaluation of possible health hazards.

II. Methodology

Sample Collection

Sediment, water and *Cladophora* samples were collected from Thika River, which traverses Thika town (01 º 03'S 37 º 05E), Kenya. The study area is the river's profile that begins at (01.02023^{o}S, 037.06724^{o}E) under the bridge adjacent to the Blue Post Hotel and extends over a span of 13 Km to (01.04943^{o}S, 037.15179^{o}E) (Figure 1).

Selected plant species (*Cladophora*), water and surface river sediments samples were each collected at 32 selected sampling points. The samples were identified and labeled W01 - W32, A01 - A32 and S01 - S32 for the water, *Cladophora* and sediment samples, respectively. Each water sample was immediately acidified by spiking with a drop of concentrated hydrochloric acid. The elevation and geographical coordinates of each sampling point was determined using hand held global positioning system (GPS) of model Garmin Etrex 10. Sampling was done in September 2015 just before the onset of the short rains.

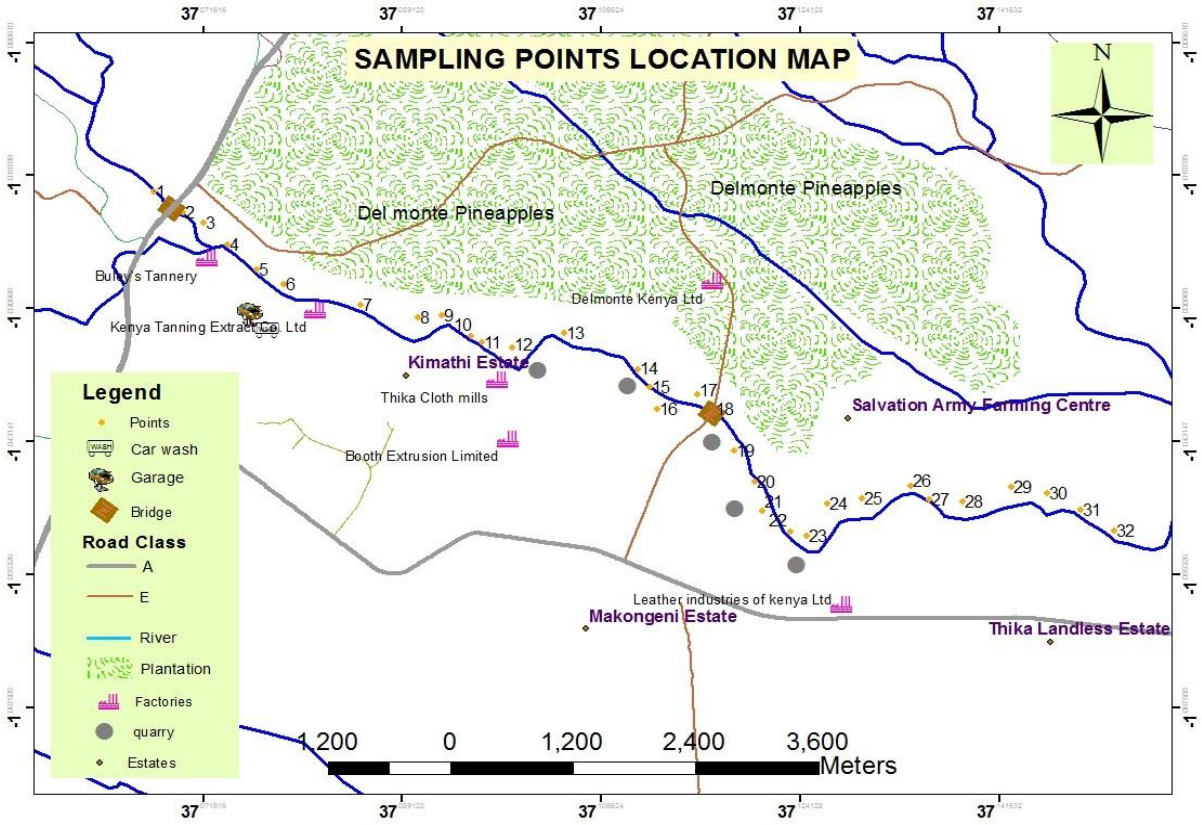

Figure 1: Sampling locations along the Thika River

Sample Preparation and Analysis

Approximately half litre of each water sample was filtered using WHATMAN number 42 filter papers to remove suspended solids. For each sample, three sub samples were prepared by pipetting aliquots of 20 ml of the sample into three separate vials and 10μl of Ga solution added as an internal standard solution (1000 ppm). The mixture was then shaken to achieve homogeneity and an aliquot of 10 μl of each standardized sub sample transferred to a clean carrier, dried at 50^{o} C, and analyzed with TXRF for heavy metal content.

Algae samples were dried to constant weight and crushed in a mortar and pestle to fine powder (~ 100μm) after sieving. Approximately 0.3 - 0.5 g of the homogenized mixture was then transferred to a die assembly, carefully positioned on a hydraulic press and pressure applied at between 5 - 8 tons for 3 - 5 minutes to ensure the powder was fully compressed into a pellet of 2.5 cm diameter. Pressure on the hydraulic press was then released slowly and the die assembly removed and subsequently disassembled to remove the pellet. The mass of the pellet was determined using an electronic balance and recorded. Triplicates of sample aliquots in form of pellets were prepared for EDXRF analyses for heavy metal content (International Atomic Energy Agency, 1997).

Sediment samples were dried to constant weight and crushed in a mortar and pestle to fine powder (~ 100μm) after sieving. Approximately 1.6 g of the fine sediment powder was mixed with approximately 0.4 g of starch binder and the mixture thoroughly mixed to achieve homogeneity. Approximately 0.3 - 0.5 g of the

homogenized mixture was then transferred to a die assembly, carefully positioned on a hydraulic press and pressure applied at between 5 - 8 tons for 3 - 5 minutes to ensure the powder was fully compressed into a pellet of 2.5 cm diameter. Pressure on the hydraulic press was then released slowly and the die assembly removed and subsequently disassembled to remove the pellet. The mass of the pellet was determined using an electronic balance and recorded. Triplicates of sample aliquots in form of pellets were prepared for EDXRF analyses for heavy metal content (International Atomic Energy Agency, 1997).

The enrichment factor was computed using the relation EF = $\left[{C_n}/{C_{ref}}\right] \Big/ \left[{B_n}/{B_{ref}}\right]$ where C_n is the content of the examined element in the examined environment; C_{ref} is the content of the examined element in the reference environment; B_n is the content of the reference element in the examined environment; B_{ref} is the content of the reference element in the reference environment (Ravichadran et al., 1995; Buat-Menard and Chesselet, 1979). In this study, the background level suggested by Taylor and McLennan (2001) for Fe (40000 $mg\ kg^{-1}$) was used.Table 1 shows five possible degree of contamination categories that can be obtained based on the use of enrichment factor.

Table 1: Five possible degrees of contamination categories that can be obtained based on the use of enrichment factor

Range of Enrichment Factor	Category of Contamination
EF < 2	Deficiency to minimal enrichment
2 < EF < 5	Moderate enrichment
5 < EF < 20	Significant enrichment
20 < EF < 40	Very high enrichment
EF > 40	Extremely high enrichment

The geoaccumulation index, according to Müller (1969) is given by $I_{geo}^{m} = \ln\left[C_m^{\mathrm{s}}/\left(1.5 \times C_m^{\mathrm{b}}\right)\right]$where C_m^{s} is the heavy metal concentration of each element, m, in the sample while the factor 1.5 minimizes the impact of possible changes in background values,C_m^{b}, which may arise from lithogenic changes in soils. The world rock averages as proposed by Taylor and McLennan (2001) were used as background concentrations. The geoaccumulation index consists of 7 categories as shown in Table 2;

Table 2: Categories of Geoaccumulation Indices and their Descriptions

Value	Category	Description
$I_{geo}^{m} > 5$	6	Extremely contaminated
$4 < I_{geo}^{m} > 5$	5	Strongly to extremely contaminated
$3 < I_{geo}^{m} > 4$	4	Strongly contaminated
$2 < I_{geo}^{m} > 3$	3	Moderately to strongly contaminated
$1 < I_{geo}^{m} > 2$	2	Moderately contaminated
$0 < I_{geo}^{m} > 1$	1	Uncontaminated to moderately contaminated
$I_{geo}^{m} = 0$	0	Uncontaminated

Contamination factor is obtained by the ratio $\mathrm{CF} = [C_{metal}]/\left[C_{background}\right]$ where C_{metal} is the heavy metal concentration of each element while $C_{background}$ is the background concentration of the heavy metal (Tomlinson et al., 1980). The world surface rock average as proposed by Taylor and McLennan (2001) were used as background concentrations.

The modified degree of heavy metal contamination in sediments is given by $mC_d = \frac{1}{N}\sum_{i=1}^{N} CF_i$where N represents the total number of elements analyzed. The degree of contamination, C_d, is the algebraic sum of all contamination factors $C_d = \sum_{i=1}^{N} CF_i$ (Tomlinson et al., 1980).

The contamination factor is determined to provide the magnitude of the degree of contamination in the sediment samples. The contamination factor and degree of contamination values are assessed on the basis of four descriptive categories as given in table 3 below:

Table 3: Categories of contamination factors and degree of contamination categories and their descriptions

CF	C_d	Description
CF < 1	$C_d < 6$	Low degree of contamination
1 < CF < 3	$6 < C_d < 12$	Moderate degree of contamination
3 < CF < 6	12 < CF < 24	Considerable degree of contamination
CF > 6	CF ≥ 24	Very high degree of contamination

The modified degree of contamination values are assessed based on seven descriptive categories as given in table 4 below:

Table 4: Categories of modified degree of contamination factors and their descriptions

mC_d categories	Description
$mC_d < 1.5$	Nil to very low degree of contamination
$1.5 \leq mC_d < 2$	Low degree of contamination
$2 \leq mC_d < 4$	Moderate degree of contamination
$4 \leq mC_d < 8$	High degree of contamination
$8 \leq mC_d < 16$	Very high degree of contamination
$16 \leq mC_d < 32$	Extremely high degree of contamination
$mC_d \geq 32$	Ultra high degree of contamination

The pollution load index (PLI) is given by; $PLI = (CF_1 \times CF_2 \times CF_3 \times ... \times CF_N)^{1/N}$ where N refers to the number of metals under study while CF is a contamination factors determined as shown above. When PLI < 1, the sediment is not polluted while PLI = 1 indicates presence of heavy metals at only their baseline levels. When PLI > 1, the sediment is polluted, hence the need for intervention to curb it (Tomlinson et al., 1980).

Analysis of variance, ANOVA, was used in this study to establish whether a difference exists in the mean heavy metal concentrations between the three media. The statistical relationship of heavy metal concentration between the three media was determined using Pearson correlation analysis.

III. Results And Discussion

The results for the validation of the accuracy and precision of the analytical methods used in this study are given in Table 5 and 6**.** The results of the levels of elements of interest in the three media as well as their interrelationships are also presented and the extent of heavy metal pollution in these media discussed.

Results of Analysis of Standard Reference Material (SRM) (IAEA09-PTXRF)

The accuracy of the EDXRF method used in this study was determined by analyzing PTXRF-IAEA09 river clay certified reference material from the International Atomic Energy Agency (IAEA) for the elements of interest. The results of analyses of the SRM using EDXRF spectroscopy are presented in Table 5. In general, there was no significant statistical difference between the experimental values and the certified values for all elements with estimated accuracy $\leq 10\%$.

Table 5: Results of PTXRF-IAEA09 river clay certified reference material analyses by EDXRF method (mg/Kg); n = 3, X $\pm$SD

Element	Experimental values	Certified values	Relative standard deviation (%)
Mn	1065 ± 80	940 - 1060	+9
Fe	29750 ± 1550	28700 - 30700	+3
Ni	30.6 ± 9.7	35.5 – 40.3	-10
Cu	17.8 ± 3.8	18.1 – 22.2	-1
Zn	76 ± 12.4	88.4 – 103.8	-10
Pb	36.6 ± 2.8	33.47 – 40.33	+7

Results of Analysis of Multi Element Standard

The KB multielement standard from Bernd Kraft GmbH was analyzed for Mn, Fe, Co, Ni, C and Zn to assess the accuracy of the TXRF procedure used for analyses of water samples in this study. The standard was a mixture of different metals having a concentration of 10 ppm each. Two metals, Cu and Co, were used interchangeably as internal standards. The results of the mean experimental values were compared with expected values to assess the accuracy of the method used in this study to analyses liquid samples. The $|t|$ values obtained in this test fell below the critical value (2.45) hence there was no evidence of occurrence of systematic errors. This implies that there were no significant differences in the results of measurements ($p < 0.05$) (Miller & Miller, 2010).

Table 6: Results of multi-element certified reference material (KB 10ppm) analysis by TXRF, X $\pm$SD

Element	Experimental values (*m*g/l)	
	Cu	Co
Mn	9.84 - 0.11	9.52 – 0.34
Fe	12.74 + 1.93	12.51 + 1.77
Co	10.34 + 0.24	10.00 + 0.00
Ni	10.16 + 0.11	9.83 – 0.12

Cu	10.00 + 0.00	9.67 – 0.23
Zn	11.50 + 1.06	11.12 + 0.79
Pb	10.55 + 0.39	10.55 + 0.39
$\|t\|$	1.83	1.14

Limits of Detection for solid form samples by EDXRF and water Samples by TXRF

The lower limits of detection of the elements under study were determined and a mean value obtained by averaging all the values obtained for all the sampled points. Table 7 shows the variation of lower limits of detection with increasing atomic number for both methods used in this study.

Table 7: Lower Limits of Detection for Heavy Metal Elements during EDXRF and TXRF Analysis

Element	Atomic Number	Lower Limits of Detection	
		EDXRF(mg/kg)	TXRF ($\mu g/l$)
Lead	82	10	10
Zinc	30	15	10
Copper	29	19	10
Nickel	28	24	15
Iron	26	67	25
Manganese	25	95	30

Heavy Metal Concentration Levels

Water Samples

The results of TXRF analyses of water samples are presented in Table 8.

Table 8: Results of TXRF analyses of water samples (µg l^{-1}), n=3, $\bar{X}$±SD

Element	Mn	Fe	Ni	Cu	Zn	Pb
W1	53.5 ± 8.0	630 ± 60	< 15	12.5 ± 2	35.0 ± 2.0	< 10
W2	76.0 ± 2.0	962 ± 31	< 15	< 10	27.0 ± 1.0	< 10
W3	87.0 ± 2.0	1378 ± 33	24.0 ± 4.0	16.0 ± 2.0	48.0 ± 6.0	< 10
W4	110 ± 12	1818 ± 59	< 15	28.0 ± 4.0	47.0 ± 4.0	15.0 ± 6.0
W5	221 ± 19	7919 ± 109	<15	24.0 ± 3.0	64.0 ± 3.0	62.0 ± 18
W6	203 ± 35	2534 ± 126	29.0 ± 4.0	< 10	69.0 ± 6.0	17.0 ± 5.0
W7	222 ± 4.0	2808 ± 323	< 15	12.5 ± 2.0	70.0 ± 2.0	13.0 ± 5.0
W8	160 ± 15	954 ± 46	21.0 ± 3.0	82.0 ± 7.0	56.0 ± 8.0	< 10
W9	605 ± 75	3309 ± 359	< 15	14.0 ± 2.0	157 ± 6.0	< 10
W10	201 ± 6.0	1547 ± 52	20.0 ± 2.0	23.0 ± 3.0	61.0 ± 9.0	< 10
W11	148 ± 18	2924 ± 464	21.0 ± 3.0	30.0 ± 5.0	45.0 ± 5.0	< 10
W12	213 ± 21	7290 ± 141	< 15	< 10	33.0 ± 3.0	< 10
W13	246 ± 17	1699 ± 289	< 15	44.0 ± 5.0	57.0 ± 6.0	< 10
W14	276 ± 12	1872 ± 63	< 15	29.0 ± 4.0	112 ± 6.0	55.0 ± 7.0
W15	226 ± 3	3668 ± 423	< 15	35.0 ± 1.0	163 ± 3.0	< 10
W16	429 ± 35	5430 ± 589	< 15	21.0 ± 3.0	75.0 ± 4.0	16.0 ± 5.0
W17	306 ± 35	2155 ± 43	< 15	17.0 ± 2.0	34.0 ± 1.0	13.0 ± 4.0
W18	244 ± 29	3171 ± 236	< 15	< 10	63.0 ± 4.0	12.0 ± 5.0
W19	297 ± 31	3152 ± 365	15.0 ± 2.0	115 ± 8.0	22.0 ± 1.0	< 10
W20	384 ± 9.0	9784 ± 1382	< 15	66.0 ± 7.0	38.0 ± 5.0	< 10
W21	450 ± 21	8072 ± 1079	22.0 ± 2.0	56.0 ± 6.0	46.0 ± 8.0	12.0 ± 4.0
W22	100 ± 16	2055 ± 118	< 15	303 ± 33	68.0 ± 20	< 10
W23	304 ± 40	4321 ± 134	< 15	12.0 ± 1.0	27.0 ± 3.0	< 10
W24	188 ± 18	5152 ± 750	< 15	32.0 ± 4.0	325 ± 30	14.0 ± 5.0
W25	309 ± 12	4119 ± 655	45.0 ± 5.0	153 ± 11	48.0 ± 3.0	20.0 ± 5.0

W26	205 ± 16	2852 ± 254	19.0 ± 5.0	15.0 ± 2.0	58.0 ± 4.0	< 10
W27	224 ± 29	2602 ± 296	20.0 ± 6.0	61.0 ± 2.0	79.0 ± 13	< 10
W28	144 ± 20	2261 ± 391	< 15	16.0 ± 1.0	73.0 ± 10	22.0 ± 7.0
W29	249 ± 23	2257 ± 234	22.0 ± 10	56.0 ± 11	76.0 ± 8.0	< 10
W30	239 ± 10	1426 ± 190	77.0 ± 13	13.0 ± 7.0	69.0 ± 11	84.0 ± 3.0
W31	140 ± 5	2097 ± 264	< 15	<10	64.0 ± 8.0	< 10
W32	210 ± 8	2369 ± 326	57.0 ± 4.0	100 ± 4.0	300 ± 5.0	49.0 ± 16
MIN	***53.5 ± 12***	***630 ± 21***	***< 15***	***< 10***	***22.0 ± 1.0***	***< 10***
MAX	***605 ± 26***	***9784 ± 198***	***77 ± 13***	***303 ± 33***	***325 ± 30***	***84.0 ± 3.0***
MEAN	**179**	**1499**	- - -	- - -	**94**	- - -

The concentration of Mn in water samples ranged from 53.5 ± 12μg l^{-1} to 605 ± 26 μg l^{-1}while the overall mean concentration was 179 μg l^{-1}. In general, Mn concentration levels in all water samples analyzed were above the EPA and WHO limits (50 μg l^{-1}) for drinking water. The high concentration levels observed at site 09 may be attributed to the close proximity of the Thika Cloth Mills Factory, whose waste waters may find its way into the river ecosystem.

The results of Cu concentrations in all water samples analyzed were below the WHO minimum levels (2000 μg l^{-1}). However, 13% of the samples exceeded the WHO limit (100 μg l^{-1}) and NEMA guidelines. The maximum Cu concentration (303 ± 33 μg l^{-1}) was recorded at site 22. The potential sources of contamination impacting this site include dust from mining activities in the quarry and wear of brake pads on vehicles plying the nearby road.

The Zn concentrations ranged from 22 ± 1.0 μg l^{-1} to 325 ± 35 μg l^{-1} with an overall mean concentration of 94 μg l^{-1}. The potential sources for a relatively high Zn concentration levels recorded at site 24 (325 ± 35 μg l^{-1}) include; the use of fertilizers and pesticides in the cultivation of pineapples by Delmonte (K) Ltd and combustion of fuel from the nearby road (Karageorgis, 2009).

The Ni concentrations ranged from < 15 μg l^{-1} to 77 ± 13 μg l^{-1}. The Ni concentrations in three water samples (W25, W30 and W32) tested exceeded the WHO limit (20 μg l^{-1}). The potential sources of high Ni levels at site 30 include; sewage from the nearby Thika Landless Estate, and combustion of diesel and fuel oil from vehicles plying along the nearby road (Clayton and Clayton, 1994; Clarkson, 1988).

The Pb concentrations ranged from < 10 μg l^{-1} to 84.0 ± 3.0 μg l^{-1} in 44% of the samples were above the WHO limits for drinking water (10 μg l^{-1}) and water supporting aquatic life (5.8 μg l^{-1}). The concentrations were notably high at points 05, 14 and 30 where values of (62 ± 18 μg l^{-1}), 55 ±7 μg l^{-1} and 84 ± 30 μg l^{-1}respectively were obtained. The potential sources of pollution at site 05 include; municipal waste , direct dumping of solid waste from neighbouring residential areas (Kiboko, Kimathi and Thika landless Estates) and release of industrial effluents from Booth Extrusion Limited, Thika Cloth Mills, Bulley's Tannery (Mahler et al., 2006).

The Fe concentrations in water ranged from 630 ± 21μg l^{-1} at site 01 to 9784 ± 198μg l^{-1} at site 20 with an overall mean concentration of 1499μg l^{-1}.

Algae Samples

Table 9 shows the levels of heavy metal concentration in algae samples. The heavy metal concentration levels generally occurred in the order Mn > Zn > Ni > Cu > Pb.

Table 9: Results of EDXRF analyses of *Cladophora* samples (*mg* kg^{-1}), n = 3, ± SD

Element	Mn	Fe	Ni	Cu	Zn	Pb
A01	11800 ± 849	112350 ± 5727	139 ± 6.0	123 ± 13	178 ± 11	38.0 ± 5.0
A02	21200 ± 781	149933 ± 5608	182 ± 30	104 ± 27	190 ± 2.0	41.0 ± 2.0
A03	16600 ± 707	144000 ± 6788	235 ± 35	72.0 ± 12.0	153 ± 13	48.0 ± 9.0
A04	10965 ± 687	120700 ± 7353	136 ± 15	86.0 ± 10	181 ± 22	42.0 ± 8.0
A05	9628 ± 517	122700 ± 5370	134 ± 35	73.0 ± 17	183 ± 2.0	40.0 ± 3.0
A06	10333 ± 961	131333 ± 7677	215 ± 14	89.0 ± 12	197 ± 14	46.0 ± 7.0
A07	8179 ± 251	111550 ± 7141	92.0 ± 7.0	71.0 ± 11	238 ± 27	46.0 ± 3.0
A08	5055 ± 144	116267 ± 2886	154 ± 25	110 ± 19	434 ± 17	72.0 ± 8.0

A09	5807 ± 104	124200 ± 3041	163 ± 11	80.0 ± 10	216 ± 5.0	41.0 ± 2.0
A10	3890 ± 77	114667 ± 3523	145 ± 35	65.0 ± 12	216 ± 14	46.0 ± 6.0
A11	3719 ± 32	107000 ± 8773	107 ± 37	88.0 ± 8.0	208 ± 7.0	41.0 ± 2.0
A12	4117 ± 186	112950 ± 9405	195 ± 28	79.0 ± 7.0	226 ± 18	51.0 ± 2.0
A13	4085 ± 239	117700 ± 4728	146 ± 32	82.0 ± 24	214 ± 14	47.0 ± 4.0
A14	4799 ± 225	138200 ± 4504	192 ± 18	111 ± 18	178 ± 5.0	49.0 ± 6.0
A15	5550 ± 389	153667 ± 12365	198 ± 7.0	129 ± 20	194 ± 8.0	52.0 ± 5.0
A16	9507 ± 404	50033 ± 2307	40.0 ± 3.0	80.0 ± 2.0	163 ± 8.0	17.0 ± 2.0
A17	5832 ± 370	80067 ± 2150	82.0 ± 10	75.0 ± 11	173 ± 13	42.0 ± 2.0
A18	7278 ± 467	74900 ± 4603	41.0 ± 7.0	78.0 ± 4.0	166 ± 5.0	33.0 ± 1.0
A19	4545 ± 101	26750 ± 1202	35.0 ± 2.0	92.0 ± 2.0	175 ± 1.0	19.0 ± 1.0
A20	5867 ± 261	159000 ± 4942	213 ± 6.0	109 ± 4.0	206 ± 14	59.0 ± 7.0
A21	6089 ± 315	106233 ± 3859	143 ± 41	94.0 ± 5.0	257 ± 10	39.0 ± 5.0
A22	11633 ± 379	109167 ± 3884	145 ± 6.0	74.0 ± 7.0	200 ± 3.0	34.0 ± 3.0
A23	9926 ± 385	137967 ± 2854	225 ± 36	119 ± 11	217 ± 10	52.0 ± 2.0
A24	7875 ± 549	143933 ± 11316	217 ± 38	129 ± 24	203 ± 4.0	50.0 ± 6.0
A25	11567 ± 231	138633 ± 987	227 ± 30	120 ± 7.0	226 ± 16	59.0 ± 3.0
A26	5990 ± 117	134200 ± 2443	179 ± 30	99.0 ± 7.0	200 ± 5.0	56.0 ± 2.0
A27	7875 ± 550	143933 ± 11316	216 ± 38	129 ± 24	203 ± 4.0	50.0 ± 4.0
A28	12400 ± 152	136133 ± 731	184 ± 28	88.0 ± 9.0	199 ± 9.0	45.0 ± 2.0
A29	12467 ± 301	133967 ± 3050	162 ± 3.0	87.0 ± 6.0	206 ± 9.0	50.0 ± 1.0
A30	10267 ± 102	134867 ± 5018	176 ± 9.0	97.0 ± 7.0	190 ± 9.0	51.0 ± 1.0
A31	7063 ± 564	127833 ± 8328	196 ± 14	89.0 ± 9.0	203 ± 18	47.0 ± 4.0
A32	9409 ± 255	130733 ± 5180	200 ± 5.0	105 ± 5.0	208 ± 10	47.0 ± 4.0
MIN	***3719 ± 243***	***26750 ± 763***	***35 ± 15***	***65.0 ± 21***	***153 ± 14***	***17.0 ± 3.0***
MAX	**21200 ± 781**	***159000 ± 5800***	***235 ± 34***	***129 ± 30***	***434 ± 22***	***72.0 ± 6.0***
MEAN	***8478***	***120174***	***155***	***95***	***206***	***45***

In general, the Mn concentration levels in *Cladophora* ranged from 3719 ± 243*m*g kg^{-1} at site 11 to 21200 ± 781 *m*g kg^{-1} at site 02, while the overall mean concentration was 8478 *m*g kg^{-1}. Other sampling sites with similarly high Mn concentrations include 03, 28 and 29 with 16600 ± 350 *m*g kg^{-1}, 12400 ± 467 *m*g kg^{-1} and 12467 ± 633 *m*g kg^{-1}, respectively. The high Mn levels recorded at site 02 and 03 may be attributed to atmospheric deposition of exhaust fumes from automobile using the busy Thika-Meru highway. The use of agrochemicals in the cultivation of crops may be potential causes of the relatively high Mn concentration levels in sites 28 and 29 (Agency for Toxic Substances and Disease Registry, 2012).

The Cu concentrations (*m*g kg^{-1}) in *Cladophora* ranged from 65 ± 21 at site 10 to 129 ± 30 at sites 24 and 27. The concentration (*m*g kg^{-1}) is also high in samples A15 (129 ± 28), A01 (123 ± 24), A25 (120 ± 28) and A23 (119 ± 26). The overall mean concentration for Cu in these samples was 95*m*g kg^{-1}. The potential pollutants at site 24 and 27 include automobile brakes. At site 23, the potential sources of pollution include raw sewerage and effluent from leather industries. Mining activities at the quarries located approximately 50 metres inland is also a potential source of pollutants at this site (Agency for Toxic Substances and Disease Registry, 2004).

The Zn concentrations (*m*g kg^{-1}) in algae ranged from 153 ± 14 at point 03 to 434 ± 22 at sampling point 08 with the overall mean concentration being 206 *m*g kg^{-1}. The potential sources of high Zn concentration level in algae at this site include mining activities from a nearby quarry, and industrial waste from the Thika Cloth Mills (Agency for Toxic Substances and Disease Registry, 2005).

The Ni concentration levels in algae ranged from 35 ± 15 *m*g kg^{-1} at site 19 to 235 ± 34 *m*g kg^{-1} at site 03 with an overall mean concentration of 155 *m*g kg^{-1}. Other high concentration levels of 215 ± 38 *m*g kg^{-1}, 213 ± 31 *m*g kg^{-1}, 225 ± 32 *m*g kg^{-1}, 217 ± 32 *m*g kg^{-1} and 227 ± 43 mg kg^{-1}were recorded at sites 06, 20, 23 and 24 and 25 respectively. Point 06 was characterized by nearby anthropogenic activities; such as farming (bananas

and pineapples) and open garage situated approximately 300 m from the river. Human waste, garage waste and agrochemicals from farming activities were possible causes for high Ni concentration levels in these samples (Mbuvi *et al.*, 2013). Besides, there were active mining activities in a nearby quarry; as potential point sources of heavy metal river pollution. Industrial waste (point 23) and agrochemicals from cultivation of bananas, kales as and pineapples (point 25 and 27) are possible causes of high Nickel levels.

The Pb concentration levels in *Cladophora* ranged from 17 ± 3 *m*g kg^{-1} at point 16 to 72 ± 6 *m*g kg^{-1} at sampling point 08 with an overall mean concentration of 45 *m*g kg^{-1}. The potential contributors of higher Pb concentration levels include direct dumping of Pb containing wastes from nearby residential areas.

Sediment Samples

Table 10 shows the results of heavy metal concentrations in sediment samples. The heavy metal concentration levels generally occurred in the order Mn > Zn > Ni > Cu > Pb.

Table 10: Results of EDXRF analyses of sediment samples (*m*g kg^{-1}), n = 3, $\bar{X}$± SD

Samples	Mn	Fe	Ni	Cu	Zn	Pb
S01	8659 ± 215	131966 ± 3000	154 ± 32	107 ± 30	160 ± 11	46.0 ± 4.0
S02	5341 ± 141	127800 ± 4600	145 ± 32	68.0 ± 15	161 ± 16	42.0 ± 6.0
S03	6417 ± 356	106533 ± 2887	121 ± 36	62.0 ± 10	154 ± 14	43.0 ± 1.0
S04	7001 ± 326	126733 ± 7830	137 ± 5.0	81.0 ± 17	175 ± 15	43.0 ± 3.0
S05	4399 ± 403	107667 ± 7815	156 ± 45	70.0 ± 23	171 ± 17	49.0 ± 7.0
S06	5155 ± 284	107200 ± 4828	114 ± 27	65.0 ± 19	176 ± 13	42.0 ± 2.0
S07	4136 ± 341	118267 ± 6120	116 ± 23	82.0 ± 18	330 ± 20	90.0 ± 5.0
S08	3665 ± 99	115967 ± 1501	118 ± 18	107 ± 22	432 ± 17	110 ± 7.0
S09	4380 ± 202	117667 ± 1504	144 ± 40	66.0 ± 25	167 ± 2.0	51.0 ± 5.0
S10	4815 ± 158	97367 ± 2532	84.0 ± 22	63.0 ± 16	155 ± 12	38.0 ± 4.0
S11	5119 ± 186	104767 ± 5052	149 ± 40	82.0 ± 26	182 ± 22	44.0 ± 2.0
S12	2795 ± 207	100100 ± 6483	85.0 ± 29	62.0 ± 27	153 ± 15	36.0 ± 3.0
S13	3097 ± 295	126800 ± 4279	156 ± 18	78.0 ± 24	156 ± 5.0	37.0 ± 3.0
S14	4686 ± 206	121967 ± 6390	155 ± 21	84.0 ± 6.0	174 ± 13	78.0 ± 6.0
S15	2901 ± 67	103200 ± 3061	110 ± 13	63.0 ± 31	167 ± 10	32.0 ± 1.0
S16	4433 ± 215	77635 ± 1955	101 ± 16	75.0 ± 15	225 ± 8.0	47.0 ± 3.0
S17	4025 ± 200	99100 ± 2645	81.0 ± 17	70.0 ± 6.0	155 ± 12	49.0 ± 5.0
S18	6902 ± 202	96267 ± 1150	72.0 ± 20	70.0 ± 15	161 ± 7.0	42.0 ± 3.0
S19	4977 ± 155	108500 ± 3439	107 ± 34	85.0 ± 12	162 ± 3.0	45.0 ± 1.0
S20	4263 ± 84	105800 ± 12225	93.0 ± 17	90.0 ± 21	166 ± 18	44.0 ± 3.0
S21	4540 ± 33	101167 ± 2182	123 ± 43	92.0 ± 10	155 ± 16	44.0 ± 5.0
S22	5602 ± 318	114700 ± 6601	118 ± 54	51.0 ± 40	168 ± 16	54.0 ± 5.0
S23	6403 ± 260	99700 ± 819	107 ± 18	80.0 ± 6.0	176 ± 9.0	39.0 ± 2.0
S24	3036 ± 144	110333 ± 8254	112 ± 36	100 ± 25	337 ± 10	90.0 ± 5.0
S25	4221 ± 116	109300 ± 3439	121 ± 27	115 ± 14	396 ± 31	177 ± 10
S26	4775 ± 329	113350 ± 4850	166 ± 20	81.0 ± 25	184 ± 7.0	54.0 ± 2.0
S27	2230 ± 28	130733 ± 4105	134 ± 43	64.0 ± 39	161 ± 13	52.0 ± 2.0
S28	6604 ± 234	97967 ± 4285	122 ± 22	80.0 ± 37	172 ± 6.0	53.0 ± 4.0
S29	6567 ± 400	103500 ± 5345	100 ± 29	66.0 ± 15	182 ± 14	49.0 ± 4.0
S30	4626 ± 91	107400 ± 3843	67.0 ± 20	87.0 ± 20	163 ± 4.0	47.0 ± 5.0
S31	4532 ± 90	112700 ± 1414	118 ± 21	85.0 ± 35	188 ± 13	36.0 ± 4.0
S32	5211 ± 357	130733 ± 9335	172 ± 11	75.0 ± 24	172 ± 13	53.0 ± 4.0
MIN	***2230 ± 154***	***77635 ± 6900***	***67 ± 26***	***51.0 ± 40***	***153 ± 15***	***32.0 ± 6.0***
MAX	***8659 ± 436***	***131966 ± 6100***	***172 ± 34***	***115 ± 22***	***432 ± 21***	***177 ± 11***
MEAN	***4817***	***109198***	***119***	***78***	***198***	***56***

The Mn concentration levels in sediment samples ranged from 2230 ± 154 *m*g kg^{-1} at site 27 to 8659 ± 436 *m*g kg^{-1} at site 01 while the overall mean concentration was 4817 *m*g kg^{-1}. Point 01 is located under a bridge nearby the Blue Post hotel along the busy Thika - Meru highway and is susceptible to atmospheric deposition of exhaust fumes from automobile using the nearby road as the potential source of high Mn concentration levels (Agency for Toxic Substances and Disease Registry, 2012).

The lowest Cu concentration was 51 ± 26 *m*g kg^{-1} at point 22 while the highest concentration was 115 ± 22*m*g kg^{-1}at sampling point 25. Point 25 was characterized by intensive pineapple farming a few metres inland and therefore susceptible to agrochemicals carried by surface runoffs as the potential pollutants (Agency for Toxic Substances and Disease Registry, 2004).

The Zn concentration levels ranged from 153 ± 16 *m*g kg^{-1} at site 12 to 432 ± 21 *m*g kg^{-1} at point 08. The high Zn levels at site 08 indicates the possible source of pollutants from nearby Thika Cloth Mills (TCM)

and mining activities from nearby quarry (Agency for Toxic Substances and Disease Registry, 2005). Heavy metal accumulation at this site is exacerbated by presence of stagnant water.

The Ni concentration levels in sediments ranged from 67 ± 26 *m*g kg^{-1} at site 30 to 172 ± 34 *m*g kg^{-1}at site 32 while the overall mean concentration was 119 *m*g kg^{-1}. Nickel is a common pollutant from the repeated usage of phosphate fertilizers in soil (Mortvedt, 1995). The high Nickel concentration levels noted in this study may be attributed to the use of commercial phosphate fertilizers in the nearby Delmonte pineapple farm and raw sewage from the nearby residential units in the adjoining land.

The Pb levels ranged from 39 ± 5 *m*g kg^{-1}, at point 23, to 177 ± 11 *m*g kg^{-1}, at point 02, while the overall mean concentration was 56 *m*g kg^{-1}. Major potential contributors to high Pb concentrations include mining activities at the nearby quarry and dumping of solid waste (Agency for Toxic Substances and Disease Registry, 2007).

In general, the concentrations of Mn, Cu, Zn, Ni and were highest in *Cladophora* in all sampling locations except a few isolated cases.

Relationship of Heavy Metal Distributions in Water, Algae and Sediments

Table 11 summarizes the results of analysis of variance (ANOVA) of heavy metal concentration levels in the three media. The mean elemental concentrations relationships between the three media significantly differ from one another; Zn (F (175) > F_{crt} (3.09)), Cu (F (156) > F_{crt} (3.09)), Mn (F (100) > F_{crt} (3.09)), Ni (F (57) > F_{crt} (3.11)), Pb (F (50) > F_{crt} (3.11)).

Table 11: Summary of Results of Analysis of Variance of Heavy Metal Concentrations in Water, *Cladophora* and Sediments

Element	Source of variation	SS	df	MS	F	P-Value	F Critical
Zinc	Between Groups	871235	2	435618	175	3.23E-32	3.09
	Within Groups	231963	93	2494	-	-	-
	Total	1103198	95	-	-	-	-
Copper	Between Groups	407444	2	203722	156	1.78E-30	3.09
	Within Groups	121165	93	1303	-	-	-
	Total	528609	95	-	-	-	-
Manganese	Between Groups	1.16E+09	2	5.78E+08	100	7.65E-24	3.09
	Within Groups	5.4E+08	93	5809583	-	-	-
	Total	1.7E+09	95	-	-	-	-
Nickel	Between Groups	3095384	2	1547692	57	4E-16	3.11
	Within Groups	2170263	93	27128	-	-	-
	Total	5265648	95	-	-	-	-
Lead	Between Groups	37964	2	18982	50	1.3E-14	3.11
	Within Groups	29885	78	383	-	-	-
	Total	67849	-	-	-	-	-

Table 12 shows the results of Pearson Correlation Analysis of heavy metal concentration among the three media. Generally, strong correlation in heavy metal concentration was found between sediments and algae for most elements; Mn (r = 0.4679), Pb (r = 0.3684), Cu (r = 0.7542), and Zn (r = 0.6142). This supports the assertion that algae grow on sediments and are appropriate bio-indicators for heavy metal pollution.

Table 12: Results of Pearson Correlation Analysis

Element	Media	*Water*	*Algae*	*Sediments*
Mn	Water	1		
	Algae	-0.2840	1	
	Sediments	-0.1579	0.4679	1
Ni	Water	1		
	Algae	-0.3902	1	
	Sediments	-0.0658	-0.0618	1
Pb	Water	1		
	Algae	-0.0482	1	
	Sediments	0.0138	0.3684	1
Cu	Water	1		
	Algae	0.07663	1	
	Sediments	-0.0431	0.7542	1
Zn	Water	1		
	Algae	-0.0189	1	

	Sediments	0.3372	0.6142	1

Extent of Heavy Metal Pollution in Sediments

The extent of heavy metal contamination of sediments collected along the Thika River was determined using pollution indices namely; enrichment factors (EF), geo-accumulation factors (I_{geo}), pollution loading indices (PLI) and modified contamination factors.

Enrichment Factors

Figure 2 summarizes the percentage frequency of occurrence of each category of.

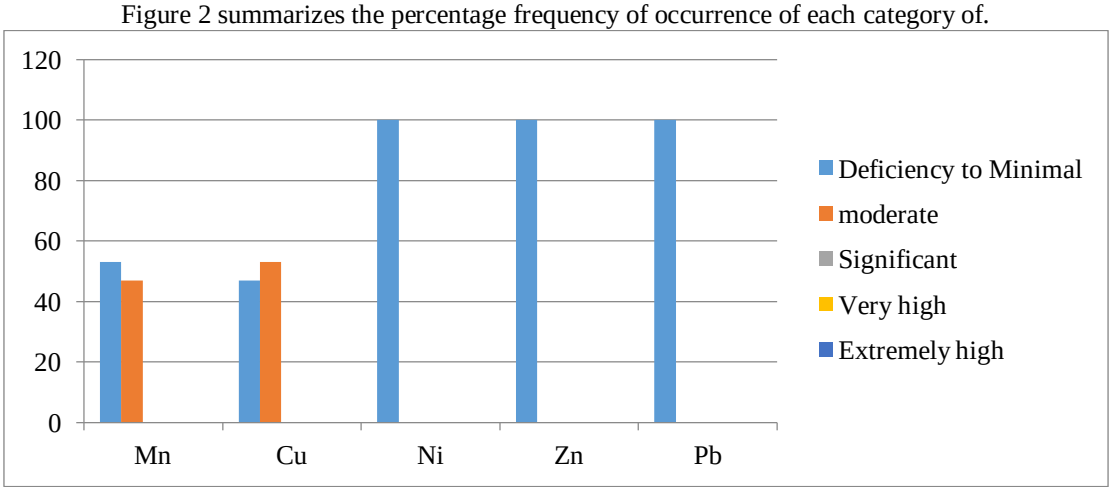

Figure 2: Summary of percentage frequency of currency of each category of enrichment for each heavy metal of interest

In general, sediment samples are equally enriched (minimal (EF < 2) – moderate ($2 \leq EF \leq 5$)) with Mn and Cu, but minimally enriched with Ni, Zn and Pb.

Geo-accumulation Indices ($\mathbf{I^m_{geo}}$)

Figure 3 summarizes the percentage frequency of occurrence of each category of geoaccumulation indices. Most sediment samples (97%) are moderately contaminated ($1 \leq I^m_{geo} > 2$) in Mn while 3% are moderately contaminated. Most sampling locations were unpolluted to moderately polluted with Ni ($0 \leq I^m_{geo} > 1$) while 3% of the samples were unpolluted. All sampling locations were unpolluted to moderately polluted with Cu ($0 \leq I^m_{geo} > 1$). Most locations (88%), were unpolluted to moderately polluted ($0 \leq I_{geo} > 1$) with Zn while 12% were moderately polluted with Zn. Most locations (87%) were unpolluted to moderately polluted with Pb ($0 \leq I^m_{geo} > 1$) while locations 13% were moderately polluted ($1 \leq I^m_{geo} > 2$).

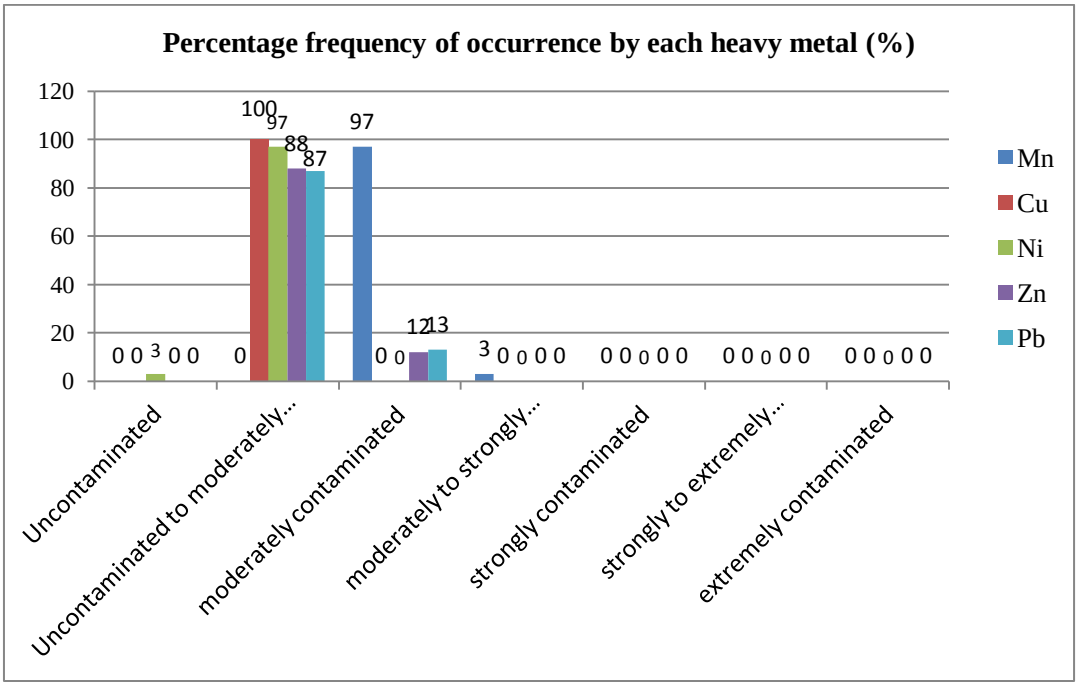

Figure 3: Summary of percentage frequency of currency of each category of Geoaccumulation indices.

Contamination Factors (CF), Modified Degree of Contamination (mC_d) and Pollution Load Indices (PLI).
Based on contamination factors and PLI, all sampling locations are polluted. Appendix C summarizes the results of contamination factors (CF), modified degree of contamination (mC_d) and pollution load indices (PLI) of sediment samples analyzed in this study.

Table 14: Summary of the percentage frequency of occurrence of each category Pollution load Index and modified degree of contamination

Pollution Load Index		**Modified Degree of Contamination**					
Polluted	Unpolluted	Low	Moderate	High	Very high	Extremely high	Ultra high
100	0	9	88	3	0	0	0

Based on results of enrichment factors, geoaccumulation indices, pollution load index (PLI), contamination factors and modified degree of contamination, all sampled sediments were generally contaminated with Pb, Cu, Zn, Mn and Ni to a moderate degree.

IV. Conclusion And Recommendations

The variation of heavy metal levels in water samples ($\mu g\ l^{-1}$) were as follows: Mn (53.5 - 605), Cu (< 10 - 303), Zn (22 - 325), Ni (< 15- 77), Pb (< 10 - 84) with mean concentrations ($\mu g\ l^{-1}$) of 179 and 94, for Mn and Zn, respectively. Heavy metal contamination levels in water samples, in this study, is variously impacted by; nearby industries, dust from the nearby mining activities and the chemical fertilizers used in the nearby commercial pineapple farms and combustion of fuel from the vehicles plying the nearby roads and therefore unsuitable for drinking.

The variation of heavy metal concentration levels in sediment samples ($mg\ kg^{-1}$) were as follows: Mn (2230 - 8659), Cu (51 - 115), Zn (153 - 432), Ni (67 - 172), Pb (32 - 177) with mean concentrations of 4817, 119, 78, 198 and 56 for Mn, Ni, Cu, Zn and Pb respectively.

The heavy metal variations in *Cladophora* samples ($mg\ kg^{-1}$) were as follows: Mn (3719 - 21200), Cu (65 - 129), Zn (153 - 434), Ni (35 - 235), Pb (17 - 72). The mean concentrations ($mg\ kg^{-1}$) of Mn, Zn, Ni, Cu, and Pb were 8478, 206, 155, 95 and 45 respectively.

There is a significant difference in heavy metal concentration among the three media, following the ANOVA analyses. The levels of heavy metal concentration in sediments and algae generally occurred in the order Mn > Zn > Ni > Cu > Pb but slightly higher in algae in comparison. However, water samples showed a slightly different order in concentration levels (Mn > Zn > Cu > Ni > Pb).

There is strong correlation between sediments and algae for most elements; Mn (r = 0.4679), Pb (r = 0.3684), Cu (r = 0.7542), and Zn (r = 0.6142). This supports the assertion that algae grow on sediments and are appropriate bio-indicators for heavy metal pollution monitoring.
Based on results of enrichment factors, geoaccumulation indices, pollution load index (PLI), contamination factors and modified degree of contamination, all sampled sediments were generally contaminated with Pb, Cu, Zn, Mn and Ni to a moderate degree, hence requires intervention to curb on the rising levels of pollutants.

Recommendations
In summary, the study recommends the following measures for mitigation of pollutants in these environmental media:
a) There is need to create public awareness to the residents using the river water for domestic purposes on the status of pollution levels;
b) There is need for environmental protection agencies such as NEMA to establish necessary intervention measures to curb the rising levels of pollutants in the river; For instance, introduce bamboo plants along the banks of this river to help in its detoxification;
c) There is need to critically evaluate the actual components of industrial and municipal waste discharges into the Thika River;
d) Further studies should be carried out to determine the other sources; organic and inorganic, that contribute to the pollution of the river ecosystem.

References

[1]. Rahman, (2011).Assessment of Heavy Metal Contamination of Sediments of Some Polluted Rivers. *A Thesis submitted in partial Fulfillment of the Requirements for the degree of Master of Science in Civil and Environmental Engineering*, pg. 7-119
[2]. Kenya Open Data Survey 2014. *2009 Census Volume 1Table 3 Rural and Urban Population*. <https://www.opendata.go.ke/Population/2009-Census-Vol-1-Table-3-Rural-and-UrbanPopulati/e7c7-w67t/1>. Accessed 22/08/2016
[3]. Gathua, N. (2015). "Gatuaganya residents decry pollution of Chania River." <http://www.hivisasa.com/kiambu/environment/79222>.
[4]. Odira, P.M.A. (1991). 'Pollution Profile of Thika River.' *17th WEDC Conference: Infrastructure, Environment, water and People*, pg. 285-288
[5]. Kelly, M.G. & Whitton, B.A. (1995). The trophic diatom index: a new index for monitoring eutrophication in the rivers. *Journal of Applied Phycology*. 7: 433-44
[6]. Mwangi, G. K. (1988). The Effect of Industrial, Domestic and Agricultural Effluents on the Quality of the Waters of Thika-Chania River Systems
[7]. International Atomic Energy Agency TECH-DOC-950. (1997). Sampling, Storage and Sample Preparation Procedure for X-ray Fluoreascence Analysis of Environmental Materials. IAEA.Austria, Vienna. pg. 15-36
[8]. Ravichadran, M., Baskaran, M., Santschi, P. H. & Bianchi, T. (1995). History of trace metal pollution in Sabine-Neches Estuary, Beaumont, Texas.*Environmental Science and Technology*. 29:1495 1503
[9]. [9] Buat-Menard, P. &Chesselet, R. (1979).Variable influence of atmospheric flux on the trace metal chemistry of oceanic suspended matter.*Earth and Planetary Science Letters.* (42) 398-411
[10]. Taylor, S. R. and McLennan, S. M. (2001). Chemical composition and Element Distribution in the Earth's Crust. Pg. 698-719 <https://mafiadoc.com/chemical-composition-and-element-distribution-in-59c9a5e61723dde180db8e7d.html>. Accessed 22/08/2016
[11]. Tomlinson, D. L., Wilson, J. G. Harris, C. R. and Jeffrey D. W. (1980). Problem in the assessment of Heavy metals levels in estuaries and the formation of a pollution index, *HelgolanderMeeresuntersuchungen*, 33(1): 566-575
[12]. Miller, J. N. & Miller, J. C. (2010). *Statistics and Chemometrics of Analytical Chemistry*. Harlow: Pearson education Limited
[13]. Karageorgis, A. P., Katsanevakis, S. &Kaberi, H. (2009).Use of Enrichment Factors for the assessment of heavy Metal Contamination in the Sediments of Koumoundourou Lake, Greece.*Water air soil pollut.*Springer, (204), p243-258.
[14]. Clayton & Clayton. (1994). *Patty's Industrial hygiene Toxicology, 4th Ed*. A Wiley-Interscience Publication. New York. pg. 2157-2173 Ed
[15]. Clarkson, T. W. (1988). *Biological Monitoring of Toxic Metals*. Plenum Press, New York, pg. 265-282
[16]. Mahler, B. J. (2006). Van Metre, P. C. & Callender, E. (2006).Trends in metals in urban and reference lake sediments across the United States, 1970 to 2001.*Environmental Toxicology and Chemistry*, 25(7), 1698-1709
[17]. [17] Agency for Toxic Substances and Disease Registry (ATSDR). (2012). Toxicological Profile for Manganese: potential for Human Exposure, Atlanta, GS: U.S. Department of Health and Human Services. https://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=102&tid=23
[18]. Agency for Toxic Substances and Disease Registry (ATSDR). (2004). Toxicological profile for Copper. Atlanta, GS: U.S. Department of Health and Human Services. https://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=206&tid=37
[19]. Agency for Toxic Substances and Disease Registry (ATSDR). (2005). Toxicological Profile for Zinc. Atlanta, GS: U.S. Department of Health and Human Services. <https://www.atsdr.cdc.gov/toxprofiles/TP.asp?id=302&tid=54>
[20]. Mbuvi, H. M., Murungi, J., & Chengo, K. (2013). Speciation of Chromium and Nickel in Open-Air Automobile mechanic Workshop Soils in Ngara, Nairobi, Kenya
[21]. Mortvedt, (1995).Heavy metal Contaminants in inorganic and organic fertilizers.*Fertilizer Research.* Kluwer Academic Publishers. 43(3): 55-61
[22]. Agency for Toxic Substances and Disease Registry (ATSDR). (2007). Toxicological Profile for Lead: Public health Statement. Atlanta, GS: U.S. Department of Health and Human Services. <https://www.atsdr.cdc.gov/PHS/PHS.asp?id=92&tid=22>