

Research Article

Heavy metal concentrations in river riana waters in Kisii, Kenya

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Abstract

The purpose of the present research work was to assess the concentrations of heavy metals Lead (Pb), Nickel (Ni), Chromium (Cr), Manganese (Mn), Copper (Cu) and Zinc (Zn) in surface water samples from River Riana in Kisii County Kenya during dry and wet seasons. Water samples were collected from three sampling sites of the River Riana. The procedure required addition of 5.0ml concentrated HNO₃ to 50ml sample of water in 100ml beaker, heated on a hot plate to boil until the volume reduced to 20ml. A further addition of 5.0ml concentrated HNO₃, heated for 10 minutes, cooled and filtered using 0.42µm Whatman filter paper into a 50ml volumetric flask and topped up to the mark using distilled water. A blank solution was similarly prepared. Heavy metal analysis was done using Inductively Coupled Plasma Emission spectrometer (Shimadzu ICPE-9000). The results of the heavy metal mean concentration (ppm) for the water samples from the river were: Pb (.0626±.0399), Cr (0.005±0.003), Ni (0.0595±0.0884), Mn (0.2131±0.066), Cu (0.192±0.083) and Zn (0.2078±0.0725). The concentration of lead (Pb) in surface water were higher than the WHO, USEPA and KEBS recommended limits for drinking water while the concentrations of Nickel (Ni), Chromium (Cr), Manganese (Mn), Copper (Cu) and Zinc (Zn) were within the limits for drinking water standards. The independent t-test exposed significant differences (p<0.001) in heavy metal concentrations between the dry and wet seasons for metals Cr and Mn while there were no significant differences (p>0.001) between seasons for the metals Pb, Ni, Cu and Zn. It was concluded that the river was polluted with Pb and the possibility of food chain biomagnification and bioaccumulation with the potential of human toxic effects.

Keywords: Heavy metals oncentration; Toxic effects; WHO; USEPA; KEBS; Bioaccumulation; Recommended limits; River Riana.

Introduction

Heavy metals are broadly metals with density above 5g/cm³ that can be toxic to the environmental plants and organisms and accumulate in the environment because they are non-biodegradable, exhibit both toxicity and persistence and bioaccumulate in the food chains [1]. There are more than ten heavy metals such as Cobalt (Co), Lead (Pb), Mercury (Hg), Arsenic (As), Thallium (Ti), Nickel (Ni), Manganese (Mn), Zinc (Zn), Cadmium (Cd) and Chromium (Cr) that have a particular significance in ecotoxicology [2]. Heavy metals contamination is a great concern at global, regional and local level and their occurrence in waters and biota indicate the presence of natural and or anthropogenic sources [3, 4]. These heavy

metals Pb, Cu, Ni, Zn, Mn and Cr have the following [5] recommended limits: 0.01mg/l, 2.0mg/l, 0.07mg/l, 3.0mg/l, 0.40mg/l and 0.05mg/l respectively in drinking water. Toxicity may occur along the food chains when the contaminated species or substance is consumed, may accumulate to dangerous levels and be harmful to human health [6, 7].

Measurement of heavy metals in water is important because it is the route through which metals are flushed from a large area of land into oceans and inside the water these heavy metals get into the organism such as fish which is consumed by man. This gives an indication of pollution and can be done using water, sediment or some organism such as fish [8, 9]. The analyses of water or sediment samples, however,

are subject to a variety of shortcomings, in that the methods do not allow for the estimation of the quantity of the metal which is biologically available. Therefore, monitoring the concentrations in the environment and measure the bioavailability and resultant uptake by biota or people is often performed by means of biomonitoring [10,11] Levels of heavy metals have been found to increase from water, fish organs to sediments and vary during dry and wet seasons [12].

Possible sources of lead in water would be lead acid batteries, solder, alloys, cable sheathings, pigments, rust inhibitors and plastic stabilizers [13]. Lead enters the human body in many ways. It can be inhaled in dust from lead paints, or waste gases from leaded gasoline. It is found in trace amounts in many foods, notably fish, which are heavily subjected to industrial pollution. Pb can contaminate water and consequently enter the aquatic food chains [14]. Nickel is a naturally occurring element found in a number of mineral ores including Nickel sulphides, oxides and silicates. It is present in the enzyme urease and as such is considered to be essential to plants and some domestic animals. Exposure to Nickel to humans is through food and water [15]. The toxic effects of nickel include dry cough, bone nose and lung cancer, cyanosis, rapid respiration, shortness of breath, tightness of chest, chest pain and nausea [16]. Copper occurs in different states, chlorides, sulphates and carbonates. This metal is vital in cellular respiration, pigment formation and strengthening connective tissues. It is also a cofactor of various enzymes. Concentrations above 0.02mg/l may not be acceptable for consumption [17]. Copper can get into aquatic ecosystems from diverse sources for example from copper compounds used in fungicides, algicides, insecticides, wood preservatives, electroplating and azo dye manufacture [13]. Chromium Cr is used in metal alloys such as stainless steel, protective coating of metal (electroplating), magnetic tapes and pigment for paints, cement, paper, rubber and its soluble form is used in wood preservatives as well as additive in water to prevent corrosion in industrial and other cooling system [18].

Therefore, the potential source of chromium to drinking water contamination is industrial wastewater discharge to the

environment, sewage and fertilizers [19]. Manganese is among the metals in high abundance in the earth's crust and occurs with iron, Manganese does not exist in its elemental or pure form. In the body, manganese aids in the functioning of cellular enzymes, for example, pyruvate carboxylases, kinases and hydrolases. In general, Mn levels found in most drinking water do not raise health concerns. However, extended exposure to concentrations above 0.05mg/l in drinking water may cause some neurological disorders. Zinc is the second most abundant element in the human body after iron. In humans, it is essential for highly proliferating body cells, for instance the immune cells. No guideline value has been set for drinking water because the levels found in drinking water not of health concern. However, drinking water containing Zn levels above 3mg/l may not be accepted for consumption [17].

The current study was designed to determine the levels of heavy metals pollution in water obtained from the Riana River in Kisii County Kenya. The river is one of the major water sources in the study area and traverses both Kisii and Homabay Counties in Kenya. The river receives most of its water from streams that pass through Kisii town such as Nyakomisaro [20] and Nyanchwa. Although the water from the river is used for various activities including domestic, industrial and agricultural activities, the river receives large quantities of impurities from surface run-offs, agrochemicals, sewage discharges, domestic and industrial effluent. The water from the river serves a large population in both Kisii and Homabay Counties but there is little documentation on the levels of heavy metals in water. It was significant to identify the levels of heavy metals in the river to provide public awareness on the use and management of the water resources and prevent toxic impacts that may arise from pollution of the river. Heavy metal analysis important because this ecosystem provides drinking water as well as habitat for flora and fauna. Heavy metal contaminations can be monitored by using the metal levels in water [21].

Materials and methods

Description of the study area

The study was conducted on the upper part of the River Riana in Kisii County, Kenya. The river

tributaries including Nyanchwa and Nyakomisaro streams pass through Kisii Town and receive domestic, municipal, agricultural and industrial wastes. The river also receives water from sewage treatment works (STW) at Suneka which further contaminate the river downstream. The study area of the River Riana lies between latitude $S00^{\circ}39.622'$ and longitude $E34^{\circ}45.043'$ at an altitude of 1500m to 1800m above sea level. The locations of sampling sites S1 (Nyamataro Bridge), S2 (Nyagwekoa Bridge) and S3 (Riana Bridge) were S1 ($S00^{\circ}39.622'$, $E34^{\circ}45.043'$), S2 ($S00^{\circ}39.503'$, $E034^{\circ}43.101'$) S3 ($S00^{\circ}39.622'$, $E34^{\circ}45.043'$) respectively.

Sampling sites

Sampling sites (Figure 1) were selected based on location of the river and magnitude of human activities upstream and adjacent to the river and were approximately 5 to 6 km apart. Field investigations were carried out monthly during dry (January to March) and wet (April to June) seasons for the six months at the designated sites. Concentrations levels of heavy metals in water for the study period were recorded for each sampling site.

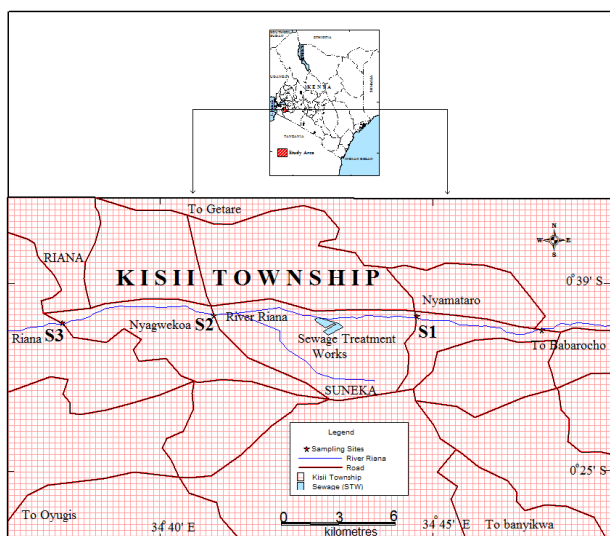


Figure 1. Map of River Riana showing the sampling sites

Quality assurance and control

All the chemicals used (hydrochloric Acid, HCL and, nitric acid (HNO_3) were analytical grade reagents (AGR). To prevent metal contamination, all glassware were washed and rinsed with 10% HCL followed by distilled water. Sample preparation and analysis was done using standard methods [22].

Collection of water

Water samples were collected for a period of six months from January to June 2021 during the dry and wet seasons respectively. Water samples were collected monthly from the selected sites S1, S2 and S3 of the River Riana. During each sampling session, water samples were collected three times a day: in the morning, at mid-day and in the evening. Water samples were collected according to the method described [23]. Water samples were collected using grab sampling method using 1L polyethylene bottles that were pre-conditioned with 5% nitric acid and rinsed thoroughly with distilled deionized water. At each sampling site, the polyethylene sampling bottles were rinsed at least three times before sampling. The pre-cleaned polyethylene sampling bottles were immersed about 10cm below the water surface. Triplicate samples from each site of the river were collected. The samples were acidified with concentrated nitric acid, placed in an ice-bath and transported to the laboratory for analysis. The samples were filtered through a $0.42\mu m$ micropore membrane filter and kept at $4^{\circ}C$ until analysis.

Digestion of water Samples for metal Analysis

Digestion was done in triplicates using concentrated nitric acid (AG) according to the method described by [24]. Concentrated nitric acid (5ml) was added to 50ml of water sample in 100ml beaker and then heated on a hot plate ($100^{\circ}C$) to boil until the volume reduced to 20ml. Another 5 ml of concentrated nitric acid was added, heated for 10 min and allowed to cool. About 5 ml of concentrated nitric acid was used to rinse the sides of the beaker and the solution was filtered using $0.42\mu m$ filter paper into a 50ml volumetric flask and topped up to the mark using distilled water. A blank solution was similarly prepared.

Elemental Analysis for heavy metals

Heavy metal analysis was done using ICP-AES spectrometer (Shimadzu ICPE-9000). The blanks were aspirated with analytical samples in order to obtain background adsorption. Instrument calibration was carried out with a range of standard solutions. The samples and blanks were aspirated into the ICP-AES and analyzed in triplicate and the mean values were used in data analysis. Each element had its own detection limit. Detection limit is the concentration

equivalent to the analyte signal which is equal to three times the standard deviation of a series of 10 replicate measurements of the calibration blank signal at the same wavelength [25]. The precision and accuracy of the analytical procedure was determined by spiking water samples with standards of known concentrations.

Data analysis

An SPSS version 26 program was used for statistical data analysis. Independent paired t-tests were used to test whether there were significant differences in the heavy metal concentration in water between the dry and wet seasons. One-way analysis of variance (ANOVA) was used to test if there were significant differences in heavy metal concentrations in water between different sampling sites at $p < 0.05$ significance level.

Results and discussion

Heavy metals in water

The mean levels of heavy metals Pb, Cr, Ni, Mn, Cu, and Zn during the study period were provided in Table 1. All the heavy metals studied were detected in river water samples.

Table 1. Mean Heavy metal concentration (ppm) during the study period (N=18)

Heavy metals	Minimum	Maximum	Mean	[15]
Pb	.018	.195	.0626±.0399	0.01
Cr	.001	.009	.0046±.003	0.05
Ni	.014	.330	.0595±0.088	0.07
Mn	.122	.351	.2131±0.066	0.40
Cu	.073	.374	.1922±0.083	2.0
Zn	.084	.320	.2078±.073	3.0

Lead (Pb) concentration in water during the study period

The mean Pb concentration (Table 1) in river water samples for the study period were higher than the recommended limit of 0.01mg/l [5], 0.05mg/l by both [26] and [27] on drinking water specification. The observed mean Pb concentration was significantly higher than the recommended limit 0.01mg/l [5] during the study period (95% CI, .03270 to .07241), $t(17) = 5.386$, $p = .000$ at $\alpha = .05$). ANOVA showed significant differences in the mean Pb concentration in water among the sites ($p = 0.034$, $\alpha = .05$). Tukey's HSD test exposed significant differences between sites S2 and S3. Similar studies have been done on Pb concentrations in

aquatic ecosystems in Kenya and other parts of the world. Comparable results to the current study were obtained [28] with recorded Pb levels in the range of 0.021 ± 0.004 to 0.035 ± 0.001 mg/l for water samples from River Tyume in South Africa. Related studies [29] recorded Pb levels in the water of Lake Victoria, Tanzania which were higher than the recommended limit of 0.01mg/l [5] but the values were slightly lower than the present study. Compared to the present study, other findings [30] recorded slightly higher Pb levels than the recommended limit [5] for water in the range of $ND - 0.011 \pm 0.001$ mg/l for the water samples obtained from Lake Hayq, Ethiopia

Closely related studies have been done on lead concentrations in water bodies in Kenya. Comparable results to the present study were obtained with mean Pb concentration range of $(0.57 \pm 0.09 - 3.36 \pm 1.15)$ mg/l for water from river Kuywa, Bungoma [31]. Slightly lower Pb concentrations than the present study were reported [32] for water samples from the Athi-Galana-Sabaki tributaries in the range 0.004 to 0.047mg/l. Higher mean Pb concentration of 0.1mg/l for water samples from Nairobi River [33] which was higher than the recommended limit of 0.01 mg/l [5]. Comparable higher results were reported in other studies with Pb level in the range (0.025-0.563 mg/l) for five Rift Valley lakes [34]. Pb concentrations (0.006-0.048 mg/l) for Lake Kanyaboli were recorded [35]. Similarly, mean Pb concentration of 0.2mg/l for water samples from Winam Gulf, River Nyando (0.19 mg/l) and River Sondu (0.015 mg/l) whose results closely compared with the present study. Closely related results were reported with mean Pb concentrations in the range of 0.26 to 0.99 mg/l for water samples from Lake Victoria [37]. Related studies reported Pb concentration ($< 10 - 84 \mu\text{g/l}$) in water in River Thika [38].

The independent sample t-test was conducted to compare the means of Pb in water during dry and wet season. The test exposed that the difference was not statistically significant for dry season ($M = .075$, $SD = .051$ and the wet season ($M = .172$, $SD = .245$); $t(16) = 1.160$, $p = .263$. The result suggested that the seasons did not have any effect on the concentration of Pb in water. Seasonal comparison of Pb in water was also presented in figure 2. In the current study, elevated Pb concentration in water samples from

the river were attributed to fossil fuel emissions due to closeness of the river to the main Kisii-Migori road, and motor washing activities along the river, agricultural farms where pesticides, fertilizers were used and sewage contamination, urban and industrial wastes [28]

Chromium (Cr) concentration in water during the study period

The mean Cr concentration (Table 1) in river water samples for the study period were lower than the recommended limit of 0.05mg/l [5, 26, 27]. ANOVA revealed that there were no significant differences in Cr mean concentration in water among the sites ($p=0.127$, $\alpha=.05$). The mean Cr concentration was found to be significantly lower than the recommended limit of 0.05mg/l [5]. Thus the river was not polluted by Cr during both dry and wet seasons. Similar studies reported lower mean Cr concentration of 0.02 mg/l in water from Nairobi River [12]. Similarly, lower Cr concentrations were reported in Masinga Dam with highest Cr mean concentration of $(0.006\pm 0.004$ mg/l) at Riakanau sampling site [39]. The present study compared closely with studies with Cr concentrations in the range of no detection to 0.068mg/l in water from Athi-Galana-Sabaki tributaries, Kenya was reported [32]. Compared to the present study higher Cr concentrations were reported Cr^{2+} in Aguobiri community surface water samples in the range of 0.002 to 0.42mg. The detected Cr in water samples in this study was attributed to anthropogenic activities including application of fertilizers and pesticides, industrial effluents wastewater contamination and motor washing along the river banks [40]. Comparable studies observed higher Cr mean concentration in water samples of 0.70 ± 0.026 ml/l for river Gadilam, Tamilnadu India [23].

The concentration of Cr in river during the dry season (January to March) was compared with its concentration during the wet season (April to June) to establish if there were any seasonal differences in Cr levels during different seasons using the independent paired t-test comparison. The independent samples t-test was carried to compare the means of Cr in water during dry and wet season and the test revealed that the difference was statistically significant for dry season ($M= .007$, $SD= .001$); $t(16) = 4.522$, $p<.001$. Seasonal comparison of Cr in water was also presented in figure 2. The result

suggests that the seasons have an effect on the concentration of Cr in water from the river. The study results suggested that the mean concentration of Cr in water was higher during the dry season than during the wet season.

Nickel (Ni) Concentration in water during dry and wet seasons

The mean Ni concentration (Table 1) in river water samples for the study period were lower than the recommended limit of 0.07mg/l [5, 26, 27]. The Ni mean concentration in water samples during the study period for the River Riana was 0.0595 ± 0.0884 mg/l with a range of (0.014 to 0.330 mg/l). ANOVA revealed that there were no significant differences in Ni mean concentration in water among the sites ($p=.041$, $\alpha=.05$). The Ni mean concentration was not statistically significant. Comparable studies [40] recorded Ni in Aguobiri community Nigeria, surface water samples ranging from 0.001mg/l to 0.060mg/l which were lower than recommended limit of 0.07mg/l [5]. Studies in Lake Hayq, Ethiopia recorded Ni mean concentration of 0.018mg/l [30] which were lower than the permissible limit 0.07mg/l for Ni in drinking water [5]. Higher concentrations were determined where Ni concentrations (0.201-1.77mg/l) for River Tyume in South Africa were reported [28]. Related studies recorded dissolved Ni concentrations ($nd-54.1$ μ /l) in water for Winam Gulf, Kenya [41]. Comparable studies recorded Ni water concentrations (0.007-0.062mg/l) for Athi-Galana- Sabaki tributaries, Kenya[32], while similar studies reported Ni concentration ($<15-77$ μ g/l) in water in River Thika. Kenya [38].

The concentration of Ni in water during the dry season (January to March) was compared with its concentration during the wet season (April to June) to establish if there were any seasonal differences in Ni levels during different seasons using an independent paired t-tests comparison. An independent samples t-test was conducted to compare the means of Ni concentrations in water during dry and wet seasons. This exposed that the differences were not statistically significant for dry season ($M= .098$, $SD= .115$) and the wet season ($M= .021$, $SD=.009$); $t(16) = 1.977$, $p=.263$. The result suggests that the seasons did not have any effect on the concentration of Ni in water from the River Riana. Seasonal comparison of Ni in water

was also presented in figure 2. The presence of Ni in water samples indicated contamination with sewage, industrial and agricultural wastes.

Manganese (Mn) concentration in water during the study period

The Manganese (Mn) mean concentration (Table 1) in water samples during the study period for the River Riana was 0.213 ± 0.066 ppm with a range of 0.122 to 0.351 ppm. ANOVA showed no significant differences in Mn mean concentration in water among the sites at ($p=0.093$, $\alpha=0.05$). The mean Mn concentration for the river water was significantly lower than the recommended threshold of 0.4 mg/l for domestic water [5]. Therefore the Mn mean concentration of the water samples during the dry and wet seasons for the river were lower in all sites than the recommended limit of 0.40mg/l [27]. Thus water from the river was safe for drinking according the recommended standard [5]. Comparable studies by Ambedkar and Muniyan (2012) recorded maximum Mn mean level in water samples of 0.08 ± 0.006 ml/l for river Gadilam, Tamilnadu India. This was lower than the recommended limit of 0.40mg/l for Mn in drinking water [5]. Comparable higher Mn concentrations in water (0.533-1.087 mg/l) for Athi-Galana- Sabaki tributaries during dry season have been recorded [32]. Related studies to determine Mn concentration in water bodies include those done for Masinga Dam (0.006 ± 0.005 mg/l) [39]; Winam Gulf, Lake Victoria (0.05-3.276 mg/l) [41]; Lake Kanyaboli, Kenya (0.185-0.376 mg/l) [35]; in Rift Valley Lakes (0.50-0.282 mg/l) [34] and River Thika (53-653 μ g/l) [38]. The Mn concentrations in the present study were attributed to discharge of industrial effluents, fertilizers, leather, textile, solid waste dumping containing dry cell batteries along the river banks.

The concentration of Mn in water during the dry season (January to March) was compared with its concentration during the wet season (April to June) to establish if there were any seasonal differences in Mn levels in the river during the different seasons using an independent paired t-test comparison. The independent samples t-test exposed that there were statistically significant differences for the dry and wet seasons ($p < 0.001$). The results suggested that the mean concentration of Mn in water was higher during the dry season than

during the wet season. Seasonal comparison of Mn in water was also presented in figure 2. The result suggested that the seasons had an effect on the concentration of Manganese in water. In general, Mn levels found in most drinking water do not raise health concerns; however, extended exposure to concentrations above 0.05mg/l in drinking water may cause some neurological disorders [17]

Copper (Cu) concentration in water during the study period

The Cu mean concentration (Table 1) in water samples during the study period for the River Riana was 0.192 ± 0.083 ppm with a concentration range of 0.073 to 0.374 ppm. ANOVA exposed significant differences in Copper (Cu) mean concentration in water among the sites ($p=0.005$, $\alpha=0.05$). The Copper (Cu) mean concentration was found to be significantly lower than the recommended level of 2.0 mg/l [5] for drinking water. Similarly, Copper (Cu) concentration in water samples obtained from the river Riana in all the sampling sites during the dry and wet seasons were also lower than this acceptable limits of 1.5mg/l [26] but higher than the 0.1mg/l [27]; thus water from the River Riana was unsafe for drinking with regard to Cu concentration according the Kenyan recommended limits for drinking water.

Comparable studies recorded maximum Cu mean concentration in water samples of 0.50 ± 0.025 ml/l for river Gadilam, Tamilnadu India [23]. This was lower than the Cu acceptable limit of 2.0 mg/l [5] and 1.5 mg/l [26] for drinking water. Similar studies recorded Cu levels of 2.228 ppm in Nyakomisaro stream [20] which was higher than both the recommended limits [26, 27]. Similar studies recorded Cu levels in water from River Kuywa, Bungoma in the range of 1.10 ± 0.12 to 1.92 ± 0.14 mg/l [31] which were lower than the drinking water permissible limits of 2.0mg/l [5]. Comparable studies recorded lower Cu concentration (< 10 -343 μ g/l) in water in River Thika [38]. Comparable lower concentrations were reported in Masinga Dam at various sites: (0.003 ± 0.002 mg/l) at Riakanau, (0.006 ± 0.003 mg/l) at Kathini (0.018 ± 0.007 mg/l) at Tumutumu and (0.019 ± 0.003 mg/l) at Manyatta [39]. The observed Cu concentrations in water samples for the river Riana waters were attributed to surface runoffs which contained agrochemicals

including fertilizers and pesticides, sewage discharge, uncontrolled urban solid waste disposal near river banks at various points of the river.

The concentration Cu in water during the dry season (January to March) was compared with its concentration during the wet season (April to June) to establish if there were any seasonal differences in Cu levels during the different seasons using an independent paired t-test comparison. The test revealed that there were no statistically significant differences between the dry season ($M = .208$, $SD = .099$) and the wet season ($M = .177$, $SD = .076$); $t(16) = .774$, $p = .450$. Seasonal comparisons of Cu in water was also presented in figure 2. The result suggested that the seasons did not have any effect on the concentration of Cu in water.

Zinc (Zn) concentration in water during dry and wet season

The Zinc (Zn) mean concentration (Table 1) in water samples during the study period for the River Riana was 0.208 ± 0.073 mg/l with a range of 0.084 to 0.320 mg/l. ANOVA exposed significant differences in Zinc (Zn) mean concentration in water among the sites ($p = .000$, $\alpha = .05$). Tukey's HSD test for separation of means showed that there were significant differences between sites S1 and S2, S2 and S3. The mean concentration of Zn was significantly below the recommended limit of 3.0 mg/l [5]. Zinc (Zn) concentration in water samples from all the sampling sites were also lower than the recommended limits of 5.0mg/l and 0.5mg/l respectively [26, 27] during both seasons. This was an indication that water from the River Riana was safe for drinking with regard to Zn. Comparable lower Zn concentrations were determined and recorded mean Zn level in water samples of 0.10 ± 0.002 ml/l for river Gadilam, Tamilnadu India [23]. Compared to this study, higher Zn concentrations have been reported in various studies including: Athi-Galana-Sabaki Tributaries ($0.002 - 0.695$ mg/l) [32]; Lake Kanyaboli, Kenya ($0.185 - 0.376$ mg/l) [35]; Rift Valley Lakes ($0.50 - 0.282$ mg/l) [34] and Winam Gulf, Lake Victoria ($0.025 - 0.2195$ mg/l) [41]. Also, lower Zn concentrations have also been reported in Nyakomisaro stream 0.141 ppm [20] which was also lower than the recommended limits of 3.0 mg/l and 0.5mg/l respectively [5, 26]. Lower Zn levels in water of Lake Baringo

($0.01 - 0.31$ μ /ml) from all sampling points were reported [42] which were also below the recommended limit of 3.0mg/l [5]. Comparable lower concentrations were reported ($<22 - 325$ μ g/l) in water in river Thika [38]. Similar lower Zn concentrations were reported in Masinga Dam sites: (0.108 ± 0.018 mg/l) at Riakanau (0.092 ± 0.013 mg/l) at Kathini, (0.132 ± 0.019 mg/l) at Tumutumu and (0.111 ± 0.018 mg/l) at Mathauta sites [39]. It has been noted that water contaminated with Zn could be toxic to other aquatic fauna and poisonous to human consumers [29].

The concentration of Zn in water during the dry season (January to March) was compared with its concentration during the wet season (April to June) to establish if there were any seasonal differences in Zn levels during the different seasons using an independent paired t-test comparison. The test showed that there was no statistically significant difference for dry season ($M = .238$, $SD = .069$) and the wet season ($M = .177$, $SD = .065$); $t(16) = 1.908$, $p = .075$. The result suggested that the seasons do not have any effect on the concentration of Zinc in water. Seasonal comparisons of Zn in water was also presented in figure 2. The Zinc concentration observed in the river Riana water was attributed to urban effluents, motor body panel beating, solid waste dumpsites near the river banks and sewage discharge into the river at various points.

Comparison of heavy metals concentrations in water during different seasons

Heavy metal concentrations comparison between the dry and wets seasons were presented in Figure 2.

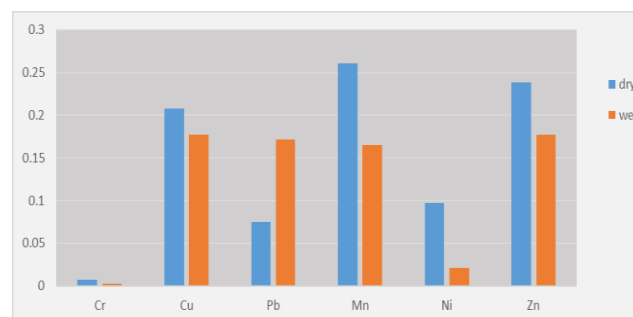


Figure 2. Seasonal comparisons of heavy metals in water during dry and wet seasons

All metals were higher in water during dry season except for Pb; this was attributed to evaporation of the water leading to an increase in concentration of the metals in water. The

elevated Pb concentrations during wet season were attributed to surface runoffs from farms and roads into the river during the rains increasing its concentration. The comparison of heavy metals in water at different seasons are shown in the figure 2.

Conclusion

The study revealed contamination of the River Riana waters with all the heavy metals studied. This was attributed to increased human activities in the catchment area of the river including agricultural, industrial and commercial activities which generate wastes including heavy metals. Concentration levels of all the heavy metals investigated in the river water were within the recommended limits for drinking water except Pb whose concentration was higher than both the limits provided [5, 6]. Thus water from River Riana was not suitable for drinking and other domestic uses with regard to Pb concentrations as this presented direct fears of lead toxicity to humans. There were very high possibilities of heavy metal bioaccumulation in the river because living organisms' in higher trophic levels absorb the heavy metals from the water and other organisms in lower trophic levels and concentrate them in their tissues and this may lead to a rise in concentrations of the heavy metals in the food chains presenting fears of increased toxicity levels.

Conflict of interest

Authors declare there are no conflicts of interest.

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