DETERMINATION OF HEAVY METAL LEVELS IN SURFACE WATERS AND SEDIMENTS OF RIVER RIANA, KISII COUNTY, KENYA

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Abstract

In this paper, some trace metals were seasonally determined for six months between January -June 2021 (to cover both the wet and dry seasons) in surface water and sediments from River Riana in Kisii County. The river is an important source of drinking water and fisheries and receives an array of wastes from agricultural, industrial, commercial and sewage treatment. Consequently, this study evaluated the levels or concentrations of heavy metals (Pb, Cr. Ni, Mn, Cu and Zn) in surface water and surface sediments and the effect of seasonal variations on their concentrations. Samples were collected monthly from three sampling sites along the River and the results of heavy metal concentrations were compared with national and international guidelines including the Kenya Bureau of Standards, World Health Organization (KEBS/WHO) and WHO sediment quality guidelines (SQGs) respectively to establish pollution level. Metal concentrations in water and sediments were analyzed using inductively coupled plasma atomic emission spectroscopy (Shimadzu ICPE-9000) after nitric acid digestion. The results obtained showed that the mean range of heavy metals in water (ppm) were: Pb (0.031-0.196), Cr (<0.001-0.009), Ni (0.014-0.321), Mn (0.131-0.351). Cu (0.114-0.370) and Zn (0.132-0.326) while the mean range of metals in surface sediments (mg/kg) was; Pb (0.041-8.74), Cr (0.001-1.31), Mn (276-692), Cu (1.35-9.74) and Zn (6.37-15.67) respectively. The heavy metals Cr, Cu and Zn complied with the WHO and KEBS drinking water recommended safe limits while the Pb and Mn concentrations exceed the recommended safe limits but Ni concentrations exceeded KEBS recommend safe limit for drinking water. The mean monthly concentrations for the heavy metals in surface water and surface sediments for the River decreased in the order Mn>Zn>Cu>Pb>Ni.>Cr and Mn>Zn>Cu>Ni>Pb.>Cr respectively. The heavy metal concentrations were generally higher during the dry season than the wet season in both surface water and sediments however, there were no significant seasonal differences ($p>0.05$) except for Cr and Mn in water. All the heavy metals complied with WHO fresh water SQGs and exhibited no significant seasonal variations ($p \geq 0.05$) in water for surface sediments. The River Riana was contaminated by all the determined trace metals and this indicated potential toxicity risk, thus the need for regular monitoring. We recommended determination of other toxic metals in water, sediments and biota such as fish form this river

Keywords: *Heavy metals, concentrations, recommend safe limits, surface water and sediments*

Introduction

Heavy metal studies have been a major focus of research worldwide especially in the last two decades because the metals are highly toxic, persistence in the environment, exhibit accumulation hence biomagnification in food chains. Thus, heavy metals have gained significant attention by different scholars, environmental managers and policy makers and their presence has been reported in various aquatic ecosystems worldwide including lakes, coastlines, reservoirs, rivers and streams (Badr *et al.,* 2020, Õztûrk *et al*., 2020, Nzeve *et al.*, 2015). Some of these ecosystems include Wadi-Hanifah, Saudi Arabia (Abdel Baki *et al*., 2011), River Gadilam, Tamilnadu India (Ambedkar and Muniyan, 2012), River Nile (Osman and Klaos, 2010), Nzhelele River South Africa (Edokpayi *et al*. 2017), Mvudi River South Africa (Edokpayi *et al*. 2016), Lake Victoria Tanzania (Kisamo, 2003) and Tyme River in South Africa (Awofolu *et al.,* 2005). A few notable investigations on this subject in Kenya on heavy metals contamination of aquatic environments include heavy metal pollutants in sediments along the banks of Athi River in Machakos County (Kosgey *et al.,* 2016); heavy metals (Pb, Mn, Cu and Cd) in water from River Kuywa (Wasike *et al*.,2019); heavy metals in water and tilapia fish from Athi-Galana-Sabaki Tributaries (Muiruri *et al.,*2013); heavy metals in water surface sediments in five Rift Valley lakes (Ochieng *et al*., 2007) and concentrations of heavy metals in water, fish and sediments of Winam Gulf, Lake Victoria (Tole and Shitsama, 2013).Only a few authors have investigated the heavy metal levels in the study area (Rayori *et al*, 2022; Omoko *et al.* 2016) despite the huge collection of heavy metal pollution of the River which justifies this study because the river is an important source of drinking water, fisheries and irrigation. Presence of heavy metals in sediments and water is a severe threat to human health and livelihoods because rivers and streams are sources for fisheries, recreation, irrigation and drinking water as is the case for river Riana in Kenya.

The exponential growth in human population in the last few decades has been observed in many countries resulting in rapid industrialization to increase production of demand-driven industrial commodities hence increased release of toxic wastes containing heavy metals, In addition, this has caused over-exploitation of natural resources directly or indirectly including forests, water and minerals resulting in negative environmental impacts on the aquatic ecosystem causing degradation of both water and sediments quality (Tony *et al.* 2018; Ezemonye, 2019). Among the aquatic pollutants, heavy metals are known to adversely affect ecosystem structure and function because they are persistence, indestructible and toxic both in water and sediments and harmful to biota. Their presence indicate natural and or anthropogenic sources (Kanamarlapudi *et al.*, 2018; Qadir *et al.*, 2008; Huang et al 2020, Withanachchi *et al.* 2020). Elevated concentrations of heavy metals in water and sediments may be biomagnified along the aquatic food chains eventually affecting human health through the consumption of metal contaminated water or fish from such water (Nyingi *et al.,* 2016). Their presence in water even at low concentrations poses significant environmental concern and their analysis can be monitored by measuring metal levels in water; sediments and resident biota especially fish. However, heavy metals have acceptable recommended limits in water for example Pb (0.01mg/l), Ni (0.07mg/l), Cr (0.005mg/l), Mn (0.04mg/l), Zn (3.0mg/l) and Cu (2.0mg/l (Omoko *et al*., 2016. WHO, 2011). Toxicity is realized when the heavy metal levels exceed the recommended limits which are different for individual elements in drinking water (Muiruri, 2013). Toxic metals which pose hazardous effects include are copper (Cu), chromium (Cr), zinc (Zn), cadmium (Cd), arsenic (As), cobalt (Co), mercury (Hg) and lead (Pb) and are dangerous as the tend to bioaccumulate in food chains and can be harmful to humans and animals (Kanamarlapudi *et al.*, 2018; Bedassa *et al*., 2020). Thus heavy metals raise serious concerns over the potential health effects on humans due to cell function loss, cellular changes, carcinogenesis, and neurotoxicity (Muhammad *et al*., 2022)

Heavy metals are highly hazardous contaminants due to their persistence, toxicity and bioaccumulation in water, sediment, air and biota and elements with densities of more than 5g/cm3, and atomic mass higher than 20 are considered heavy metals (Muhammad *et al*., 2019; Li *et al.* 2019, Duffus, 2002). Topmost heavy metals are Hg, Pb, As, Cd and Cr (Kim and Lee, 2017). Heavy metals are classified as essential and non-essential or toxic metals depending on their toxicity and nutritional value. Cu, Mn, Fe, Zn, Co are needed in minute quantities for the normal function and survival of living beings (Muhammad *et al*., 2019). Toxicity may occur along the food chain when the contaminated species or substance is consumed (Hang *et al.,* 2004,). These toxic metals including As, Pb and Cd are hazardous because they can cause severe health problems in minute quantiles. Health problems resulting from these metals include stomach disease, anorexia, heart disease, hypertension and cancer (Qian *et al*., 2020). Heavy metals cannot be broken down and are non-biodegradable, so when they enter the human body, they pose serious and hazardous impacts. They are considered toxic and dangerous when bioaccumulate into the human body and cause biological and physiological complications. There are various mechanisms of intoxication in the human body by heavy metals which can be acute or chronic since toxicity of metals depend on dosage and exposure time that is chronic or acute exposure (Muhammad *et al.* 2022).

The highest proportion of heavy metals are released into the environment from anthropogenic activities which include metal production, agricultural activities, transportation, mining and smelting operations, industrial and urban development among others and fertilizers have released specific quantities of heavy metals which have poisoned the land and the soil. (Moywaywa *et al.*, 2022, Ezemonye *et al*. 2019; Chaoua *et al.* 2019). Heavy metals such as, Cd, As, Cu, Ni and Zn are common pollutants and come from different anthropogenic source (Yahya *et al.*, 2018). They are also as a result of geochemical processes such as volcanic eruptions but continued steady growth in human population has as seen more release of heavy metals into water bodies as humans continue participating in activities that trigger more release of the concerned metals (Storelli *et al.* 2008). Therefore, measurement of heavy metals in water is very important because it is the route through which metals are flushed from a large area of land into oceans and gives an indication of degree of pollution because inside the water these heavy metals enter into the different environmental domains such as water and sediments (Beyhan *et al*., 2010). Sediments are a priority matrix in the monitoring the health of the aquatic ecosystems. The heavy metal sediment quality recommended safe guidelines for Pb, Ni, Cr, Cu and Zn are 35mg/kg, 0.4 mg/kg, 37.5 mg/kg, 30 mg/kg and 123 mg/kg respectively but the Mn sediment limit has not been documented (WHO, 20008). Sediments are an important sink of a variety of pollutants, particularly heavy metals and may serve as an enriched source for benthic organisms. Sediments have higher levels of heavy metals than the water which shows that sediments act as a sink for heavy metals (Storelli, 2008). Other authors have detected contamination of sediments with heavy metals in various aquatic ecosystems around the world and in Kenya (Õztûrk *et al,* 2009, Ambedkar and Muniyan, 2012; Wasike *et al*., 2019; Moywaywa *et al*., 2022).

The objective of the current study was to determine the concentrations of selected heavy metals in surface water and sediments during the dry and wet seasons in the River Riana of Kisii County, Kenya. This is because the river is located on a fragile ecosystem in Kenya and it is an important source of drinking water, animal watering, fisheries and irrigation. However, the quality of its water and sediments has been degrading to due agriculture and numerous human activities including sewage treatment and industrialization. Apparently, it was necessary to determine the level of some heavy metals present in water and sediments to ascertain the environmental impact of human activities including agriculture, sewage disposal, commercial and industrialization on the environment and the possible health consequences on humans. From the best of our knowledge and literature survey, no research has been carried out to determine the levels of heavy metals Pb, Cr, Ni, Mn, Cu and Zn in water and sediments in this river. Thus the results obtained from this analysis would provide background information on concentrations of heavy metals in water and sediments which will contribute to effective monitoring of ecosystem quality and health of inhabitant organisms in the river. This information would be useful to the public and the relevant government agencies including Nation Environmental Managements Authority (NEMA), Water Resource Management Authority (WARMA) and the Kisii County Government in proper management of the river ecosystem. In addition, this information may be used as a basis for literature for further research.

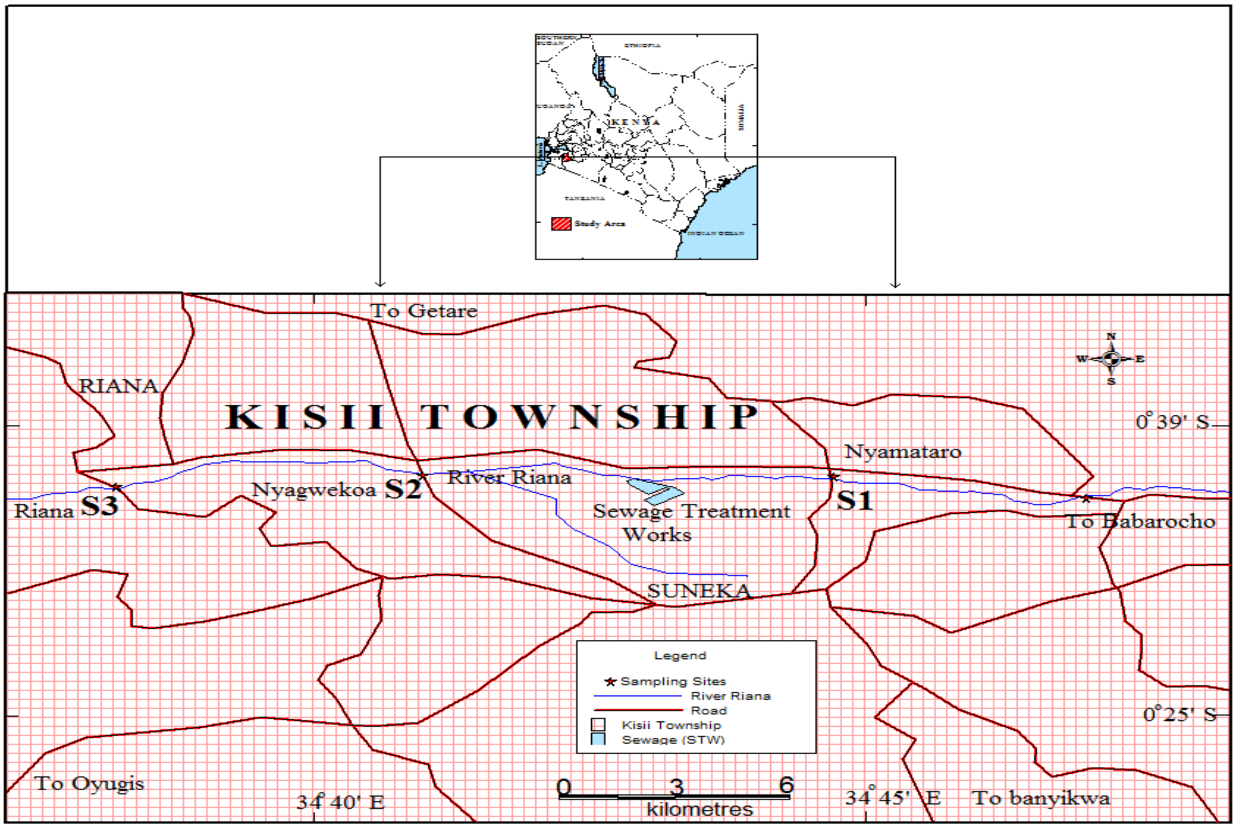
Materials and Methods

Study area

The study was carried out in the river Riana in Kisii County (Rayori *et al.*, 2022). Three sampling sites were selected based on the degree of human activities in the adjacent areas. The sampling sites were Nyamataro Bridge (S1), `Nyagwekoa Bridge (S2) and Riana Bridge (S3) whose geographical coordinates were S1 (S00°39.622', E34°45.043`), S2 (S00°39.503`, E034°43.101`), S3 (S00°39.496`, E34°40.097`) respectively as shown in Fig.1. The section of the river lies between 1500m to 1800m above sea level and became an area of interest in this research due to many anthropogenic activities in the adjacent areas.

Figure 1

Map of the study area site showing sampling sites.



Field Methods

The surface water and sediment samples were seasonally collected for a period of six months from January and June of 2021.The sampling sites were visited monthly for the study period. During each sampling session, water and sediment samples were collected very early in the morning, mid-day and in the evening to obtain triplicate samples from each site. The water samples for heavy metal analyses were collected in acid washed polyethylene bottles that were thoroughly rinsed with deionized water after washing with dilute nitric acid. At each sampling site, the polyethylene sampling bottles were rinsed several times with river water before sampling. The pre-cleaned polyethylene sampling bottles were immersed about 20cm below the water surface and 1L of water sample was collected. The samples were acidified with 2ml of concentrated nitric acid (AR grade) for preservation and placed in an ice-bath and transported to the laboratory for analysis. The acid pretreatment prevented heavy metal adsorption into the walls of the plastic containers. Sample bottles were labelled indicating the sampling date and site prior to transportation to the laboratory for analysis. The samples were filtered through a Whatman filter paper No 42 and kept at 4°C before analysis. Triplicate submerged sediment samples at least 30cm below the water level were collected using a grab sampler and stored in plastic bags. All the samples were stored in the cool box at 4^{0}C for transportation to the laboratory. Sediments were collected using a plastic spoon and placed into polyethylene bags where very fine materials accumulated with little or no water at all. Then samples were labelled for easy identification and stored below -20^{0}C before processing for heavy metal analysis (Ezemonye *et al*. 2019, Omoko *et al*., 2016, Okey-Wokeh and Wokeh, 2022)

Sample preparation and heavy metal analysis

Digestion of water samples for metal analysis was done in triplicates using concentrated nitric acid (Analytical Grade) and the mean results were summarized (Table 1). 5.0ml of concentrated nitric acid was added to 50ml of the water sample in 100ml beaker and then heated on a hot plate at 100 ^{o}C to boil until the volume reduced to 20ml. Another 5.0ml of concentrated nitric acid was added and then heated for 10 minutes and allowed to cool. About 5ml of concentrated nitric acid was used to rinse the sides of the beaker and the solution filtered using 0.42μm filter paper into a 50ml volumetric flask and topped up to the mark using distilled deionized water. The samples were analyzes directly (Okey-Wokeh and Wokeh, 2022; Zhuang *et al*. 2009, Õztûrk *et al.* 2009).The concentrations heavy metals in water were determined in triplicates using ICP-AES (ICPE Shimadzu-9000) and the average levels of heavy metals for the study period were summarized in Table 1

The sediment samples were air dried in the laboratory, ground and sieved with a 2mm mesh and preserved in brown polyethylene papers to prevent them from contamination and any adverse environmental conditions until analysis. Digestion pf sediments involved weighing 0.50g of sediment sample into acid washed glass beaker followed by addition of 20ml of aqua raga (a mixture of HCL and HNO_3 in the ratio 3:1 and 10% of (30% hydrogen peroxide) H_2O_2 in which the H_2O_2 was added in small amounts to avoid overflow while covering the beaker with a watch glass. The beaker was heated in a hot plate at 90^{0}C for 2hours before washing the walls of the beaker and watch glass with distilled deionized water while the mixture was filtered into 100ml volumetric flask. The volume was made to 100mlmark with distilled deionized water. Blank solutions were treated in the same way as the samples (Okey-Wokeh and Wokeh, 2022. Õztûrk *et al.* 2009

Determination of heavy metals in all the samples was carried out using ICP-AES (ICPE Shimadzu-9000). The accuracy of the analytical procedure was checked by using standard reference materials (water: SPS SW2 Reference material for measurement of elements in surface water and sediments: BCR- 646 Fresh water sediments: IRMM-Institute for Reference Material and Measurements. The samples were analyzed simultaneously using a multielement ICPE Shimadzu-9000. Mean levels of heavy metals for the study period in water and sediments were summarized in Table1 and 2 respectively

Instrument calibration

The calibration standards were prepared from 100ppm ICP multielement standards and were acid marched to the digested samples for both surface water and sediments respectively. The multielement ICPE Shimadzu-9000 has an automatic wavelength selection system which completely automates the worrying task of wavelength selection. After measurement, the best wavelengths were selected for the measurement of sample frequency from all of the wavelengths registered in its memory and the measured results were displayed in its monitor.

Results and Discussion

Heavy metals in water

The results of the heavy metal concentrations in River Riana is as shown in Table1 and included the heavy metal monthly means and ranges.

Table 1

Descriptive summary of heavy metal monthly concentration (ppm) in River Riana water.

	Sampling months					
Heavy metals concentrations (ppm)	January	February	March	April	May	June
Pb	0.073±0.026	0.063±0.000	0.067±0.016	0.070±0.017	0.043±0.055	0.035±0.013
Range	(0.035-0.106)	(0.041-0.195)	(0.068-0.089)	(0.048-0.089)	(0.031-052)	(0.018-0.050)
Cr	0.008±0.001	0.007±0.002	0.006±0.001	0.004±0.002	0.003±0.002	0.003±0.002
Range	(0.007-0.008)	(0.004-0.009)	(0.004-0.007)	(<0.001-0.008)	(<0.001-0.006)	(0.001-0.003)
Ni	0.050±0.006	0.128±0.135	0.102±0.019	0.014±0.000	0.025±0.006	0.022±0.006
Range	(0.031-0.112)	(0.026-0.320)	(0.024-0.254)	(0.014-0.041)	(0.017-0.056)	(0.014-0.018)
Mn	0.238±0.041	0.251±0.040	0.287±0.055	0.163±0.024	0.161±0.013	0.158±0.025
Range	(0.176-0.277)	(0.211-0.300)	(0.210-0.351)	(0.131-0.190)	(0.156-0.184)	(0.122-0.189)
Cu	0.198±0.078	0.252±0.089	0.217±0.078	0.188±0.051	0.159±0.002	0.186±0.070
Range	(0.114-0.315)	(0.205-0.370)	(0.119-0.321)	(0.125-0.251)	(0.073-0.288)	(0.130-0.226)
Zn	0.242±0.082	0.258±0.050	0.257±0.030	0.199±0.066	0.168±0.080	0.166±0.050
Range	(0.132-0.326)	(0.147-0.262)	(0.179-0.309)	0.084-0.226	0.104-0.212	0.084-0.236

Data Analysis

Data obtained was analyzed using computer program IBM Statistical Package for Social Scientists (SPSS version 26) to obtain descriptive statistics and t-tests. The t-tests were used to compare levels of significance for the dry and wet seasons for samples at 95% confidence intervals.

Table 1 shows that Pb concentration was in range (0.018-0.195ppm) its mean monthly concentrations for all the months was higher the recommended limit of 0.01mg/l (WHO, 2011; KEBS, 2015). The determined Pb concentration equally exceeded 0.05mg/l recommended limit (USEPA; 2006) except during the month of June 2021 when the Pb concentration was in the range (0.018-0.050ppm). The presence of Pb in the river water was attributed to surface runoff from garages and motor washing points, application of agrochemicals including pesticides, insecticides and fertilizers, sewage contamination, urban and industrial wastes (Awofolu, 2005). The water from the River Riana was therefore unsuitable for domestic uses and human consumption. Other studies have reported Pb concentration (0.0003-0.019 mg/l) in water from Avsar Dam Lake in Turkey (Ozturk et al., 2009). Higher Pb concentrations than the current study in water have been reported with mean Pb concentration range (0.57±0.09-3.36±1.15 mg/l for water from river Kuywa Bungoma (Wasike et al., 2019). However, other authors have reported lower Pb concentrations than the present study water for water samples from the Athi-Galana-Sabaki tributaries in the range 0.004mg/l to 0.047mg/lm (Muiruri et al. 2013). Other related studies have reported Pb mean concentration of 0.1mg/l for water samples from Nairobi River (Mbui et al., 2016) which was higher than the recommended limits of 0.01mg (WHO, 2011; KEBS. 2015). In parallel studies, Pb amounts that exceeded the current study were reported (0.025-0.563 mg/l) for five Rift Valley lakes Ochieng et al., 2007).

The mean Cr concentration in the River was in the range (<0.001-0.008ppm) while the Cr monthly average concentrations for all the months of the study period were lower than the recommended limit of 0.05mg/l (WHO, 2011; KEBS, 2015). Since the Cr level complied with the drinking water quality standards, the water from the River Riana was thus suitable for domestic uses and human consumption with regard to Cr level in the water. The contamination of the river with Cr was attributed to sewage pollution, contamination with fossil fuels, pesticides, fertilizers and discharges from untreated urban and industrial wastes (Awofolu et al., 2005). The observed Cr concentration closely compared with the Cr concentration (0.001- 0.012 mg/l) observed in water from Avsar Dam Lake in Turkey (Õztûrk et al. 2009). The current study was in agreement with other studies which reported lower mean Cr concentration of 0.02 mg/l in water from Nairobi River (Mbui et al., 2016) and Masinga Dam with mean Cr concentration (0.006±0.004 mg/l) at Riakanau sampling site (Nzeve et al., 2015). The present study compared closely with other studies which recorded Cr concentrations in the range of no detection to 0.068mg/l in water from Athi-Galana-Sabaki tributaries, Kenya (Muiruri et al. 2013). The low Cr levels detected in the river was an indication that the river was not polluted with Cr due to fewer human activities such wood preservation and treatment that contribute to Cr contamination.

The Ni concentration in the River was reported (Table 1) in the range (0.014-0.254ppm) and its monthly average concentrations in the river for all the months of the study period exceeded the recommended limit of 0.07mg/l except for February 2021 (WHO, 2011). However, the Ni monthly means for all the months never exceed the KEBS recommended limit of 0.2mg/l (KEBS, 2015). Thus, the water from the River Riana was safe from domestic uses and human consumption according to the KEBS standards. Related studies in Lake Hayq, Ethiopia recorded Ni mean concentration of 0.018mg/l (Tibebe et al., 2019) which were lower than the WHO safe limit of 0.07mg/l for Ni in drinking water The observed Ni concentration exceeded the Ni concentration (0.0004- 0.014mg/l) determined in water from Avsar Dam Lake, Turkey (Õztûrk et al. 2009). Comparable results with higher Ni values than the current study were determined by other studies with Ni concentrations (0.201-1.77mg/l) in River Tyume in South Africa (Awofolu, 2005). Other authors recorded dissolved Ni water concentrations (nd-54.1 μ/l) for Winam Gulf in Kenya (Lalah et al., 2008). Very closely related results to the current study recorded Ni water concentrations (0.007-0.062mg/l) for Athi-Galana- Sabaki tributaries, Kenya (Muiruri et al. 2013) and for Ni concentration (<15-77μg/l) in water for River Thika in Kenya (Moywaywa et al. 2022). Ni is a major alloy used in production of stainless steel and discharge of this metal into the water in elevated concentrations can be dangerous since it is carcinogenic (Bazrafshan et aL. 2015). The presence of Ni was attributed to wastes containing agrochemicals such as fertilizers, solid wastes containing battery wastes adjacent to the river, fossil fuel from motor vehicles and contamination with industrial effluents.

The mean Mn concentration (Table 1) in the river water in range (0.014-0.277ppm) and the Mn average monthly concentrations for all the months of the study period were lower than the recommended limit of 0.4mg/l (WHO, 2011). However, the determined Mn levels exceeded the KEBS recommended limit of 0.10 mg/l (KEBS, 2015). Since the Mn concentration exceeded the Kenyan water quality standards the water from the River Riana was thus unsuitable for domestic uses and human consumption. The contamination of the river with Mn was attributed to sewage pollution, contamination with fossil fuels, pesticides, fertilizers and discharges from untreated urban and industrial wastes (Awofolu et al., 2005). Other related studies also recorded maximum Mn mean level (0.08±0.006ml/l) in water samples for river Gudillam, Tamilnadu India (Ambedkar et al. 2012) which were equally lower than the WHO permissible limit of 0.40mg/l for Mn in drinking water. Comparable studies to the current research, higher Mn concentrations in water (0.533-1.087mg/l) were reported for Athi-Galana- Sabaki tributaries during dry season (Muiruri et al. 2013). Some authors in Kenya have reported Mn concentration in various water bodies including Masinga Dam (0.006±0.005mg/l) by (Nzeve et al., 2015). Winam Gulf, Lake Victoria (0.05 mg/l-3.276mg/l) by (Lalah et al, .2008) Lake Kanyaboli (0.185-0.376mg/l) by (Ochieng et al, 2008); Rift Valley Lakes0.50mg/l to 0.282mg/l) by (Nyingi et al., 2016) and River Thika (53-653μg/l) by (Moywaywa et al., 2022).

The mean range of Cu concentration (Table1) in the river water (0.073- 0.370 ppm) during study period were lower than the recommended safe limits of 2.0mg/l and 1.0 respectively (WHO, 2011; KEBS. 2015). Since the Cu concentration was lower than international and national recommended safe limits, water from the River was suitable for drinking and domestic uses. This low Cu concentration closely compared with results from other studies including 0.50± 0.025ml/l in Gadilam River, Tamilnadu India (Ambedkar et al. 2012) and Cu concentration in the range (<10-343μg/l) in water from River Thika (Moywaywa et al., 2022). However, other authors recorded slightly higher Cu levels than the current study in the range (1.10±0.12-1.92±0.14mg/l) for water from River Kuywa, Bungoma (Wasike et al, 2020) and Cu concentration of 2.228 ppm in Nyakomisaro stream in Kisii County (Omoko et al., 2013). Similar closely related Cu concentrations were reported in Masinga Dam at various sites including Riakanau (0.003±0.002 mg/l), Kathini (0.006±0.003 mg/l), Tumutumu (0.018±0.007 mg/l) and Manyatta (0.019±0.003 mg/l) which were lower than the recommended safe limits in drinking water (Nzeve et al., 2015). The determined Cu levels in present study were attributed to surface runoffs with agrochemicals including fertilizers and pesticides, sewage discharge, uncontrolled urban solid waste disposal near river banks at various points of the river (Ambedkar et al. 2012). Cu is an essential element needed for metabolic processes in the human body but consumption of water or food with elevated Cu above the recommended limit causes negative impacts on both the nervous and circulatory systems (Hussain, 2021). Therefore, we recommended regular and sustainable assessment and monitoring of the River Riana ecosystem to ensure environmental safety and health of biota.

The mean monthly Zn concentrations were in the range (0.084- 0.370 ppm) and were lower than the recommended guidelines 3.0mg/l and 5.0mg/l respectively (WHO, 2011; KEBS, 2015). Since the Zn concentration was lower than the recommended water quality standards, the water from the River was therefore suitable for drinking and other domestic uses. This study agreed with other authors who recorded lower mean Zn concentrations in water samples (0.10± 0.002ml/l) for river Gadilam, Tamilnadu India (Ambedkar et al. 2012). Lake Kanyaboli (0.185-0.376mg/l) in Kenya (Ochieng et al., 2008) and Winam Gulf (0.025-0.2195mg/l) in Lake Victoria (Lalah et al., 2008) and Nyakomisaro stream through Kisii town (0.141ppm) in Kenya (Omoko et al., 2013). The work further agreed with other investigations including studies in Lake Baringo (0.01-0.31μ/ml) in Kenya (Nyingi et al., 2016); River Thika (<22-325μg/l) in Kenya (Moywaywa et al., 2022); Masinga Dam: (0.108±0.018 mg/l) at Riakamau (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 (Nzeve et al., 2015). Zn has many important biological functions in living organisms and plays a number of physiological roles in cells, but has also adverse effects on humans and other organisms when it exceeds the recommended limits (Edokpayi et al. 2017). Water contaminated with Zn may be toxic to other aquatic fauna and poisonous to human consumers (Kisamo, 2003). The Zinc levels observed were attributed to fertilizers, galvanized iron sheets, batteries, urban effluents, motor garages and motor washing adjacent to the River.

Heavy metals in sediments

The heavy metal sediment quality guidelines (SQGs) for: Pb (35mg/kg), Ni (65mg/kg), Cr (37.5 mg/kg), Cu (30 mg/kg) and Zn (123 mg/kg) were used to evaluate the level of surface sediment contamination in the river Riana (WHO, 2008). The results for these heavy metals levels (Table 2) in surface sediment indicated that mean range of Pb concentration in sediments (0.041- 9.74 mg/kg) during the study period did not exceed the WHO recommended sediment guideline of 35mg/kg (WHO, 2008). This results closely compared with earlier authors who recorded Pb concentrations (1.775-4.157mg/kg) in sediments for Mvudi River in South Africa (Edokpayi et al., 2016) and Pb concentration (0.64- 6.35 mg/l) in sediments for Avsar Dam Lake in Turkey (Õztûrk et al., 2009). In related studies Pb concentration (11.14-14.47 mg/kg) in sediments concentration exceeded Pb concentration from the current study but lower than the WHO recommended safe limit in Masinga Dam, Kenya (Nzeve et al., 2014).

Table 2

Descriptive summary of heavy metal levels in sediments (mg/kg) during the study period

	Sampling months					
Heavy metals concentrations (ppm)	January	February	March	April	May	June
Pb	1.69±3.27	1.08±1.23	5.74±3.02	1.48±0.319	1.342±0.509	1.334±1.02
Range	(1.45-3.27)	(0.041-2.63)	(1.26-8.74)	(1.00-1.76)	(0.973-206)	(0.662-2.500)
Cr	0.005±0.002	0.46±0.055	0.006±0.078	0.065±0.078	0.606±0.852	0.084±0.118
Range	(0.002-0.007)	(0.007-0.129)	(0.003-0.177)	(0.001-0.176)	(0.004-1.81)	(0.003-0.242)
Ni	3.94±0.943	4.47±1.74	3.45±1.157	3.51±0.978	6.19±1.78	8.918±1.455
Range	(2.45-4.59)	(1.48-5.48)	(1.45-4.36)	(2.13-4.33)	(3.78-6.44)	(1.780-9.740)
Mn	413±141.41	405.3±160.61	368.32±153.68	478.00±166.36	467±105.85	452.0±140.04
Range	(383-610)	(268-630)	(245—585)	(206-693)	(329-586)	(256-574)
Cu	466±1.25	4.98±1.10	5.44±2.711	13.75±1.89	5.117±2.289	6.173±3.950
Range	(4.33-6.34)	(4.77-5.94)	(2.46-9.02)	(1.35-5.45)	(3.34-8.30)	(3.330-9.740)

Recent studies in other aquatic ecosystems have reported lower Pb sediment concentration (32-177μg/l) in River Thika (Moywaywa *et al.*, 2022) than the current study. Higher Pb concentrations in sediments than the current study were reported for the Rift Valley Lakes of Kenya (10.92-38.98 mg/kg); Lake Kanyaboli (11.42-153.90 mg/kg) and of Winam Gulf in Lake Victoria (3.09-66.05 mg/kg) (Ochieng *et al*., 2007; Ochieng *et al*., 2008; Tole and Shitsama, 2013). The Pb concentration obtained in this study was due to fewer anthropogenic activities in the area and the observed variations in concentrations of Pb level in sediments was attributed to various factors such as atmospheric deposition, solid wastes containing battery wastes, agro- chemicals containing pesticides and insecticides, industrial effluents, fossil fuels from transportation vehicles, leaded petrol from transportation vehicles, lead paints and car-wash activities adjacent to the River Riana. The recorded Pb sediment level was higher in sediments than water because sediments act as heavy metal sinks in aquatic ecosystems (Storelli et al. 2008)

The determined mean range for the study period for Cr concentration (0.001- 1.81 mg/kg) in sediments and its monthly Cr average concentrations for all the months were lower than the SQG (37.5mg/kg) for Cr (WHO, 2008), however, sediments have the capacity to accumulate heavy metals with time and mobilize them back to water and food chain (WHO, 2011). Thus we suggested the need for constant monitoring and assessment of sediment quality in this river to ensure ecosystem safety and to reduce heavy metal bioaccumulation in food chains so as to protect ecosystem health as well as human health The results obtained were exceed by very high Cr mean sediment concentration of 9500 ppm reported in the Wadi Hanifah, Saudi Arabia (Abdel-Baki *et al.*, 2011); higher Cr concentration (9.41-19.9 mg/l) for Avsar Dam Lake in Turkey (Ozturk *et al*., 2009) and Cr concentrations (44.23-149.52mg/kg) in sediments for Mvudi River in South Africa (Edokpayi *et al.,* 2016). In Kenya, some authors have also reported Cr concentrations exceeding the current study in various aquatic ecosystems including Cr concentrations (44.23-49.62mg/kg) in Masinga Dam (Nzeve *et al.*, 2014); Cr sediment concentrations (0-25.89mg/kg) for rivers in Lake Victoria Basin have been reported (Ondiere *et al*., 2017). Lower Cr sediment concentration (2.92-5.36μg/g) than the currents study was recorded for heavy metal inputs into Winam Gulf, Kenya (Lalah *et al*., 2008). The observed concentration in sediments in this study was attributed to agricultural discharges containing pesticides and fungicides, fossil fuels, industrial and sewage discharge into the river, solid waste dumping on the river banks and surface runoff containing Cr based wood preservatives. The mean Cr concentration at Riana Bridge (site S3) was attributed to sewage contamination from Suneka Sewage Treatment works. However, the low Cr levels in sediments of this river indicated that the river was not Cr polluted due to low anthropogenic activities in the area but we recommended regular assessment and monitoring of the river ecosystem for heavy metals to prevent potential toxic effects.

The determined Ni sediment mean range for the study period (Table 2) for Ni concentration (1.45-9.74 mg/kg) and the monthly Ni mean concentrations for all the months were lower than the Ni SQG of 65mg/kg (WHO, 2008) but caution should be taken since sediments have the capacity to Although the determined Ni sediment concentration was lower than the recommended limit, sediments have the capacity to accumulate heavy metals gradually and mobilize them in the water and food chains (WHO, 2011), Therefore, we recommended continuous assessment the river sediments for heavy metals to ensure sustainable ecosystem health and health of biota including fish since water from this river is used for fisheries and some irrigation. The results obtained exceed Ni concentrations in sediments of Athi River 0.01912 ppm (Kosgey *et al*., 2015) but were lower than Ni sediments concentration (10.8- 39.4 mg/l) for Avsar Dam Lake, Turkey (Õztûrk *et al*., 2009). A number of authors have recorded relatively lower Ni concentration in sediments including Winam Gulf (4.33-42.99 μg/g) by (Lalah *et al*., 2008) and River Thika (68-172μg/l) by (Moywaywa *et al.*, 2022). The presence of Ni in sediments in the study was attributed to industrial wastes, runoffs containing pesticides and insecticides, fossil fuels from transportation vehicles and battery wastes into the river.

The determined mean range of Mn concentration (206-693 mg/kg) for the study period in sediments (Table 2) revealed that Mn had the highest sediment concentration that all the investigated heavy metals, however, manganese sediment limit is not documented in larger amounts (WHO, 2011). The results obtained in the current study were lower than the Mn sediments concentration in range (279- 1638 mg/kg) for Mvudi River in South Africa (Edokpayi *et al*., 2016); Masinga Dam in the range (259.12 -642.34 mg/kg) by Nzeve *et al.*, 2014 and lower than Mn concentrations in Winam Gulf, Lake Victoria in the range 133 to723.7mg/kg (Lalah *et al*., 2008). The high concentrations of Mn in sediments in the study area was attributed to washing of topsoil, cans and leaching of dry batteries which are emptied into the river as runoffs (Nwankwoala and Ekpewerechi, 2016). Therefore, we suggested periodic assessment and monitoring of the river ecosystem including pollution of sediments with heavy metal because sediments have the capacity to as sinks for heavy metals hence accumulate heavy metals and gradually mobilize them in the water and food chains (WHO, 2011).

The determined sediment heavy metal mean range for the study period (Table 2) for Cu (1.35-9.74 mg/kg) and the monthly Cu mean concentrations for all the months were lower than the Cu SQG of 30 mg/kg (WHO, 2008). Although the determined Ni sediment concentration was lower than the recommended limit, sediments have the capacity to accumulate heavy metals gradually and mobilize them in the water and food chains (WHO, 2011). We recommended the need for continuous assessment the river sediments for heavy metals to ensure sustainable ecosystem health and health of biota. The results determined were exceed by very high Cu mean sediment concentration (13.22-1027mg/kg) in sediments for Mvudi River in South Africa (Edokpayi *et al*., 2016) and Cu sediments concentrations (18.8- 38.4 mg/l) in Avsar Dam Lake, Turkey (Õztûrk *et al*., 2009). Comparable results to the present study with mean Cu sediment concentrations (1.46-20.85 mg/kg) in surface sediments have been reported for the five Rift Valley Lakes in Kenya (Ochieng *et al*., 2007). Winam Gulf of Lake Victoria, Kenya (3.90-150.2 mg/kg) has been reported (Lalah *et al*., 2008). Similarly, in River Thika the Cu concentration (51-115μg/l) was recorded (Moywaywa *et al.*, 2022); equally in Lake Elmentaita in Kenya Cu concentration (2.93$\pm$0.66-134.07$\pm$27.05mg/kg) was reported (Ondiere *et al*., 2017); also in Masinga Dam Cu concentration (11.38$\pm$2.77-23.38$\pm$6.54 mg/kg) was determined (Nzeve *et al*. 2014). Whereas the Cu sediment concentration was lower than the recommended sediments limit, sediments have the capacity to accumulate heavy metals and mobilize them in the water and food chains (WHO, 2011). In the current study, Cu concentration in sediments was attributed to surface run-offs, agrochemicals including fertilizes and copper containing pesticides and sewage contamination.

The recorded results for Zn concentration for the study period (Table 2) with a mean Zn range (3.56-16.67 mg/kg) in sediments during the study period. The monthly average Zn concentrations for all the months of the study period were also lower than the WHO SQG sediment safe limit of 123mg/kg (WHO, 2008). The results obtained in the current study were lower than the Zn sediments concentrations (4.481- 39.58mg/kg) in sediments for Mvudi River in South Africa (Edokpayi *et al*., 2016). Similarly, he results obtained were exceed by very high sediment Zn concentrations in the range (60.04$\pm$25.633-75.84$\pm$ 27.684mg/kg) reported for Masinga reservoir (Nzeve *et al*., 2014) and sediment Zn concentration in the range (23.39-350.80 mg/kg) for Winam Gulf in Lake Victoria, Kenya (Tole and Shitsama, 2013). However, this exceeded Zn sediment concentration (153-

432μg/l) from River Thika (Moywaywa *et al.*, 2022). The Zn concentration in the sediments was attributed to alloys such as brass and bronze, batteries, fungicides and pigments (Akan *et al.*, 2010). While the Zn sediment concentration was lower than the recommended limit in this study, sediments acts as heavy metal sinks and have the capacity to accumulate heavy metals gradually and mobilize them in the water and food chains (WHO, 2011). Thus the need for sustainable assessment and monitoring of the river to maintain ecosystem and human health was suggested. The presence of Zn in sediments in the current study was attributed to the *jua kali* artisans using zinc in galvanizing steel and iron, agricultural waste from farms using Zn based pesticides in the catchment area of the river.

Effect of seasons on heavy metal concentrations in water and sediments at River Riana

Concentrations of heavy metals in water bodies may be influenced by changes in weather conditions of the river catchment and water chemistry because during the wet season heavy metal concentrations may increase due surface runoffs as a result of various land use activities in the catchment including mining, settlements, dumpsites, agriculture and dilutions from high amounts of rainfall. The major factor contributing to increase heavy metal concentration during the dry season is evaporation because dilution factor is removed (Edokpayi *et al,* 2016). In general, a slightly higher average heavy metal concentrations was observed during the dry season than average concentrations during the wet season (except Cu) for all the investigated heavy metals in the river Riana (Table 3).

Table 3

Descriptive summary of seasonal heavy metals concentration (ppm) in water at River Riana during the dry and wet season.

Sampling Season	Pb	Cr	Ni	Mn	Cu	Zn
Dry	0.0753	0.0067	0.0976	0.2612	0.2076	0.2381
Wet	0.0498	0.0023	0.0214	0.1649	0.177	0.1774
Mean	.0626±.040	.0046±.003	.059±0.088	213±0.066	.192±0.083	.208±.073
P value	>0.05	<0.05	>0.05	<0.05	>0.05	>0.05
WHO (2011)	0.01	0.05	0.07	0.40	2.0	2.0

Statistical analysis using the independent samples t-test was conducted to compare the means of heavy metal concentrations in sediments in the river during dry and wet season. The test exposed significant seasonal differences ($p<0.05$) for Cr and Mn in water while no significant differences between the seasons ($p>0.05$) were observed in water for Pb, Ni, Cu and Zn implying that seasons had an effect on the concentrations of heavy metals Cr and Mn in water in the river

Table 4

Descriptive summary of heavy metals concentration in sediments (mg/kg) at River Riana during the dry and wet season.

Sampling Season	Pb	Cr	Ni	Mn	Cu	Zn
Dry	1.793	0.038	3.642	395.67	5.042	11.24
Wet	1.484	0.069	4.057	466.56	4.826	9.758
Mean	1.639±0.890	.05378±.083	3.849±1.485	431.11±155.67	4.934±2.346	10.501±3.513
P value	>0.05	>0.05	>0.05	>0.05	>0.05	>0.05
WHO (2008)	35	37.5	65	-	30	123

Effect of seasons on heavy metal concentrations in sediments at River Riana

Generally the heavy metal concentrations were higher in both water and sediments during the dry season than the wet season due to concentration factor and evaporation (Okey-Wokeh and Wokeh, 2022). However, when data analysis using the independent samples t-test was conducted to compare the means of heavy metal concentrations in sediments in the river during dry and wet season, there were no statistically significant differences ($p > 0.05$) between the dry and the wet seasons for all the metals investigated Pb, Cr, Ni, Mn, Cu and Zn. Thus we suggested that the seasons do not have any effect on the concentration of heavy metals in sediments and the presence of these heavy metals in the sediments in this ecosystem was attributed industrial wastes, agricultural discharge, fossil fuel wastes, lead paints, lead pipes and sewage treatment activities adjacent to River Riana in Kisii County in Kenya. (Okey-Wokeh and Wokeh, 2022; Akan *et al.,* 2010).

Conclusions and Recommendations

Conclusions

The determined concentrations of heavy metals Cu and Zn were within the WHO and KEBS drinking water recommended safe limits. The monthly mean Mn values were within the WHO guidelines for drinking water for all the months of the study period for the water samples obtained from the River Riana. Similarly, the average monthly concentrations in water for heavy metals Cr, Ni were within the KEBS recommended limits for all the months of the study period. The mean monthly concentrations for the heavy metals in the River Riana water decreased in the order: Mn>Zn>Cu>Pb>Ni.>Cr while their concentration in sediments deceased in the order: Mn>Zn>Cu>Ni>Pb>Cr. The concentrations of all the investigated heavy metals were within the WHO sediment recommended guidelines.in water and sediments. The heavy metal concentration was generally higher during the dry season than the wet season in both water and sediments and no significant differences ($p > 0.05$) were detected in concentrations between the season in both water and sediments except for Cr and Mn in water ($p < 0.05$). The presence of all the heavy metals in water and sediment samples portrays the potential toxic effects in this aquatic ecosystem, thus precautions should be taken to safeguard the river against anthropogenic activities that increase levels of heavy metal contamination in the river.

Recommendations

There is need for regular and sustainable monitoring of heavy metal levels in surface water and surface sediments of the river Riana by Nation Environmental Managements Authority (NEMA), Water Resource Management Authority (WARMA) and the Kisii County Government to avoid heavy metal toxic effects because the river ecosystem. There is need for the National Government through Government agencies such as NEMA, WARMA to develop a multidisciplinary public education and participation on environmental issues affecting rivers like Riana

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Competing interests

Authors have no other conflicting interests

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