Seasonal Variation of Heavy Metal Concentration in Water of Rupingazi River, Kenya

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Abstract

Seasonal assessment of heavy metal concentration (Cu, Zn, Fe, Mn and Ni) in water of Rupingazi River was carried out during the wet season in May (2018) and dry times in January (2019). In this research water samples were collected from twenty sampling points along the river. The levels of the heavy metals in the water were measured with the Atomic Absorption spectrophotometer. Data that was obtained from the analysis of the water was analyzed using one-way analysis of variance. Mean heavy metal concentrations (mg/l) in water were Cu (0.01-0.31), Fe (0.00-1.82) and Zn (0.003-1.508) during the wet season and Cu (0.01-0.40), Fe (0.53-2.07) and Zn (0.02-1.81) during the dry season. The levels of zinc and copper were lower than the WHO limits for drinking water. Iron levels in most sampling stations either during the wet or dry season exceeded the limits. Analysis of the correlation coefficient showed a low, moderate or high correlation between the heavy metals in water during both seasons.

Key words: heavy metal, concentration, water, Rupingazi river, pollutants

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1. Introduction

One of the most important resource needed for sustainability of life on this planet is water (Dipak,2017). There are several sources of drinking water which include: rivers, lakes, and oceans. The most common source of water in the World are rivers whose quality is a great concern as it directly affects welfare of mankind (Sinha *et al*.,2003). Some of the dominant pollutants that have been discovered in river water are suspended solids, plant nutrients, biodegradable plant compounds, microbial pathogens and heavy metals (Bitton 1994, Paul &Sinha 2015). Human and aquatic life is many times endangered by the transportation and concentration levels of pollutants through rivers. Sumok (2001)and Amalo *et al*., (2019) observed that the fast growth in population, land expansion nearby the drainage basin, development of urban centers and industries have caused river water pollution and environmental degradation. In most developing countries, river contamination is a consequential and arising issue (Sinha *et al*., 2012). Therefore, from a water quality point of view, rivers have been studied widely over a long time than any other water bodies (Thomann &Muller 1987; Amalo *et al*., (2019)).

Heavy metals being one of the dominant pollutants in river water are of interest as they are found to accumulate through the food chain and cause environmental issues (Praveena *et al*.,2010 Paul &Sinha 2015). Heavy metals are elements that have high atomic weight and density (Raji *et al.,* 2016). Jarup,2003 defined them as the metals whose specific density is more than 5g/cm ^{3} which include zinc, copper, lead, manganese, arsenic, cadmium, chromium, iron and nickel that can either be found in soils, surface or underground water. It is worth noting that when heavy metals get into the environment they can remain there for a very long time without getting degraded and undergoing various chemical activity (Xu *et al*., 2015). When in the environment, the metals are transformed further into poisonous forms by microorganisms and changed into organic conformations, which can be detrimental to humans and aquatic ecosystems. (Hub *et al*., 2013, Zhao *et al*., 2016).

1.1 Sources of heavy metals and effects

Morais *et al*., 2012 explained that the metals found in the surroundings could be either natural such as erosion of soil and weathering of the earth's crust or anthropogenic activities like mining, effluents from industries, urban run-off, discharge of untreated sewage and agricultural sources through use of farm inputs such as fertilizers, herbicides and pesticides. The main sources of anthropogenic sources of heavy metals in the river are from agricultural activities, discharge of untreated wastes from industries and domestic sewage.

Some heavy metals such as zinc, copper, manganese, nickel and iron are beneficial within limits (WHO, UNICEF, 2008). They are used for cell division, growth, manganese and activation of enzymes in metabolisms.

These metals can become toxic if the limit is exceeded and cause liver and kidney failure, cancer, diabetes and damage the central nervous system. The limits of iron, copper, mercury, cadmium, arsenic, lead, zinc and chromium in drinking water are 0.1, 1.0 ,0.001, 0.005, 0.05, 0.05, 5.0 and 0.1 mg/l respectively. There are some metals such as lead and cadmium that are toxic irrespective of their concentration. The toxicity effects of heavy metals to humans will depend on their concentration, exposure path, period of exposure, age, hereditary and the nutritional status of the susceptible person (Tchounwou *et.al*, 2012). Pollution of freshwater and their sediments by heavy metals has become an international issue which has interested policy makers and researchers due to the toxicity linked with them and their bioaccumulation capability. (Li, 2014). Heavy metal pollution of river and water and sediments is associated with human activities that take place far and close to such as settlements, farms, game reserves, car wash, mining activities, storm water run-off (Chaves *et. al* 2016, de Melo *et al*.,2016).

Rupingazi river is the most important river system in Embu County.It experiences commercial activities which involve large coffee and tea plantations. Other food crops and vegetables such as maize, beans, sweet potatoes, cabbages, kales, carrots and spinach are also grown for home use and trade purposes. As a result, farm inputs like fertilizers, herbicides and pesticides are used intensively. The quality of some of the inputs might have been enhanced with heavy metals for the reason that some are absolutely necessary for biological procedures in plants. These heavy metals are in the due course deposited into the river as a result of overflow during the rainy seasons. The river also accumulates pollutants from residential areas (areas of informal settlement). Recently there are concerns on the safety of plants and animals that use water from this river as the water could absorb and accumulate the heavy metals hence posing a risk to the consumers. In order to determine the appropriateness of the river in serving its objective and the harmlessness of its products, it is important to determine the levels of concentration of heavy metals in the water. There is no literature of heavy metals in Rupingazi river considering that water from this river is used for drinking and other domestic uses. In this study seasonal variations of concentration of heavy metals in water was determined

2.Materials and methods

2.1 Study area

River Rupingazi is a tributary of river Tana. It is found in Embu county. It flows from Manyatta region across Embu town to Mbeere constituencies then it joins river Tana basin at Masinga in Machakos county. Rupingazi river passes through three fundamental zones; upper, middle and lower catchment areas. The upper and middle areas are dominated by large scale agricultural activities like coffee and tea plantations and the main source of pollution in this area is from agrochemicals used in the farms. The lower section of the river receives pollutants from light industries (Jua kali industries).

2.2Sampling sites location

Twenty sampling points were identified from Kiungu to Embu town.The sampling points were established using GPS to ensure that the water and sediment samples were collected from the same points during the sampling period.in selection of the sampling points, some activities along the river were considered such as farming where there were coffee and tea plantations, settlements or residential activities, domestic and municipal waste disposal. In most of the sampling points cash crop and subsistence farming were the major activities along the river. In farming there is extensive use of fertilizers, pesticides and fungicides which are the likely contributors of the pollutants. Sampling points (15,16,17,18,19,20) were located near town and were likely to receive heavy metals from improper sewage disposal and Jua kali sector.

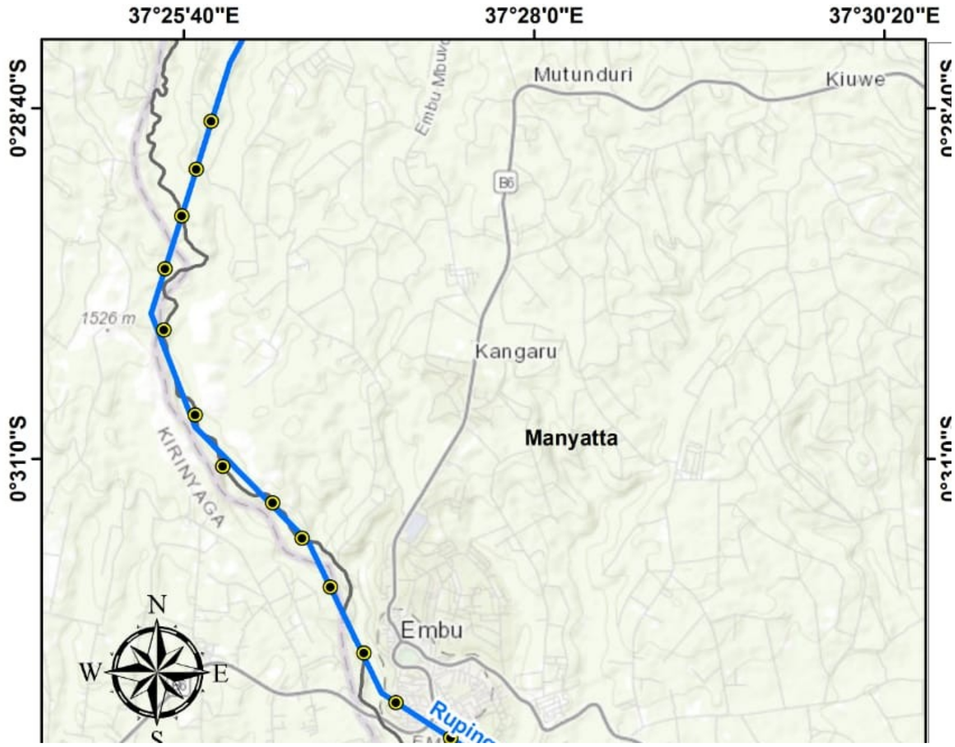

Figure 1: Map showing the section of Rupingazi river covered by the study

2.3 Water sampling and sample preparation

Sampling of the water was carried out in twenty sampling points over the rainy season in May (2017) and dry times in January (2018). During collection of the samples,Rupingazi river was separated into three regions; the uppermost, intermediary and lower regions. The upper and middle regions had six sampling points each and the lower part had seven sampling points. The distance between the sampling points was also be measured. Five samples were taken at each point across the river in both the dry and wet season. The bottle that was used for sample collection was dipped in the river. Mixing of the samples was done in order to get a uniform sample for each point. Before the samples were put in the bottles, they were cleaned and washed out using nitric acid at 10% in order to get rid of any metal on the bottle surfaces. Prior to collection of samples, the bottles were then rinsed using distilled water together with river water. Collection of water samples was done 30cm below the surface of water. The water samples were put in 500ml bottles. Whatman 0.45µm filter paper was used to filter the water in a flask to remove extraneous materials. After the samples were collected, they were acidified to a PH of less than 2 using analytical grade nitric acid.2ml nitric acid was put in the water. labeling of the samples was done and the date of sampling and sampling points were indicated. They were taken to a laboratory and stored awaiting digestion . Acidification was done to stop bacterial activities and accumulation of heavy metals on the container wall. The samples were stored for thirty days before analysis was done.

2.4 Digestion of water samples for metal analysis

Some drops of hydrogen peroxide will be added to this mixture and then heated at 100^0Cuntil the volume reduces to around 5ml.Whatman 0.45µm filter paper will be used to filter the mixture in a flask. The samples will be put into plastic bottles and labeled. They will then be stored awaiting analysis.

3 RESULTS AND DISCUSSIONS

Table 1 Heavy metals in water(mg/l) during the wet season

Site	Fe	Zn	Cu	Exceeding Limit
1	0.22±0.01^{c}	0.003±0.000^{a}	0.04±0.00^{bc}	
2	1.08±0.02^{i}	<LOD	<LOD	Fe
3	0.45±0.01^{e}	0.863±0.007^{c}	0.14±0.02^{e}	
4	0.94±0.05^{h}	1.061±0.013^{d}	0.04±0.00^{bc}	Fe
5	<LOD	<LOD	<LOD	
6	0.31±0.01^{d}	<LOD	0.01±0.00^{ab}	
7	0.00±0.00^{a}	<LOD	0.10±0.00^{d}	
8	0.01±0.00^{a}	<LOD	<LOD	
9	0.17±0.00^{bc}	0.004±0.000^{a}	0.12±0.01^{d}	
10	1.36±0.01^{j}	0.011±0.000^{a}	0.22±0.01^{f}	Fe
11	0.73±0.00^{g}	0.736±0.006^{b}	0.01±0.00^{a}	Fe
12	0.62±0.01^{f}	0.009±0.000^{a}	0.04±0.00^{c}	Fe
13	<LOD	<LOD	<LOD	
14	0.13±0.00^{b}	0.006±0.001^{a}	0.02±0.00^{abc}	
15	0.22±0.01^{c}	<LOD	<LOD	
16	1.55±0.02^{k}	1.286±0.045^{e}	0.16±0.01^{e}	Fe
17	1.72±0.01^{l}	1.419±0.004^{f}	0.31±0.01^{g}	Fe
18	1.74±0.00^{l}	1.508±0.007^{g}	0.29±0.00^{g}	Fe
19	1.73±0.01^{l}	1.508±0.007^{g}	0.29±0.00^{g}	Fe
20	1.82±0.01^{m}	1.449±0.019^{f}	0.31±0.01^{g}	Fe
Average	0.7400±0.04	0.4931±0.01	0.1050±0.003	
Limit	0.3	3	1	
%>Limit	146.67			
LOD	0.0025	0.002	0.003	

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Table 2 Heavy metals in water(mg/l) during dry seasons

Site	**Fe**	**Zn**	**Cu**	**Exceeding Limit**
1	2.07 ± 0.06^{h}	0.21 ± 0.01^{b}	<LOD	Fe
2	1.20 ± 0.13^{e}	0.33 ± 0.01^{c}	0.004 ± 0.000^{a}	Fe
3	0.96 ± 0.02^{cd}	0.74 ± 0.00^{h}	0.02 ± 0.00^{b}	Fe
4	0.77 ± 0.01^{b}	<LOD	0.01 ± 0.00^{b}	Fe
5	0.86 ± 0.01^{bc}	0.02 ± 0.00^{a}	<LOD	Fe
6	1.03 ± 0.01^{d}	0.48 ± 0.00^{e}	0.13 ± 0.01^{e}	Fe
7	0.99 ± 0.00^{cd}	0.04 ± 0.00^{a}	0.24 ± 0.00^{h}	Fe
8	1.99 ± 0.01^{h}	0.74 ± 0.02^{h}	<LOD	Fe
9	0.53 ± 0.00^{a}	<LOD	0.04 ± 0.00^{c}	Fe
10	2.04 ± 0.01^{h}	0.63 ± 0.00^{g}	0.11 ± 0.00^{d}	Fe
11	1.85 ± 0.02^{g}	0.52 ± 0.01^{f}	0.02 ± 0.00^{b}	Fe
12	0.43 ± 0.00^{a}	1.00 ± 0.00^{i}	<LOD	Fe
13	1.08 ± 0.04^{d}	0.76 ± 0.01^{h}	0.14 ± 0.00^{f}	Fe
14	0.98 ± 0.03^{c}	$0.430.00^{d}$	<LOD	Fe
15	0.94 ± 0.05^{c}	1.06 ± 0.01^{j}	0.04 ± 0.00^{c}	Fe
16	1.57 ± 0.03^{f}	1.36 ± 0.01^{k}	0.17 ± 0.00^{g}	Fe
17	1.72 ± 0.01^{g}	1.50 ± 0.01^{l}	0.29 ± 0.00^{i}	Fe
18	1.73 ± 0.00^{g}	1.64 ± 0.02^{m}	0.29 ± 0.00^{i}	Fe
19	1.75 ± 0.00^{g}	1.71 ± 0.01^{n}	0.31 ± 0.01^{j}	Fe
20	1.76 ± 0.00^{g}	1.81 ± 0.01^{o}	0.40 ± 0.00^{k}	Fe
Average	1.312 ± 0.004	0.7495 ± 0.022	0.0927 ± 0.0027	
Limits	0.3	3	1	
%>Limit	337.5			

3.1 Zinc (Zn) concentration (mg/l)

The mean concentration levels of Zinc in surface water for all sampling stations are represented in table 1 for the wet season and table 2 for the dry season.The range of the concentration of zinc was found to be 0.003-1.508 mg/l for the wet season and 0.02-1.81 mg/l for the dry season. Concentration of Zinc in the sampling stations was observed to vary significantly. Sampling stations 18,19 recorded significantly high levels during the wet season and 20 a high level of 1.81mg/l during the dry season. These high levels can be attributed to disposal of waste from light industries that manufacture furniture located near the river and corrosion of iron containing metals from Jua kali where motor vehicle repairs are done. There could also be leaching from farms adjacent to the river due to application of fertilizers. From the results there was no significant difference in the mean Zn concentration in sampling stations 5 and 7 during the wet season and 1,9,10 and 12during the dry season. The concentration of Zn in the surface water found in this research did not go beyond the recommended limit of 3mg/l for Zn levels in drinking water (WHO 2008).

3.2Copper (Cu) concentration (mg/l)

The mean concentration levels of Cu in surface water for all sampling stations are represented in table 1 for the wet season and table 2 for the dry season. The range of the concentration of Copper was found to be 0.01-0.31 mg/l for the wet season and 0.01-0.40 mg/l for the dry season. Concentration of Copper in the sampling stations was observed to vary significantly. Sampling stations 17,18,19 and 20 recorded significantly high levels during the wet season and the dry season. Copper is a natural deposit that is commonly found in Solids, rocks and rivers. It is discharged into water from weathering of rocks and effluents from industries and waste water treatment plants (Romo-Kroger et al 1994 and Hutchnison,2002). The copper that is found in the river water is as a result of enormous usage of pesticides and sprays that have copper compounds for farming use. (Al-Weher 2008). The concentration of copper in surface water found in this research did not go beyond the recommended limit of 1mg/l for copper levels in drinking water(WHO 2008).

3.3 Iron (Fe) concentration (mg/l)

The mean concentration levels of Iron in surface water for all sampling stations are represented in table 1for the wet season and table 2 for the dry season. The range of the concentration of Iron was found to be 0.01-1.82 mg/l for the wet season and 0.43-1.76 mg/l for the dry season. Concentration of Iron in the sampling stations was observed to vary significantly. Sampling stations16, 17,18,19 and 20 recorded significantly high levels during the wet season and the dry season. The increased levels of Iron could have been as a result of point sources of pollutants, anthropogenic sources that lead to pollution of river water and run offs. The concentration of Iron in surface water found in this research was beyond the recommended limit of 3mg/l for Iron levels in drinking water (WHO 2008).

The results of this research were compared with other studies that had been carried out in other rivers in the world.

Table 3 concentration of heavy metals in Rupingazi river in comparison to other rivers during the dry season

River	Fe	Zn	Cu	Reference
Rupingazi	1.3125	0.7495	0.0927	Present study
Migori	-	0.200	0.15	Olal,2015
Durgapur	23.39	-	0.281	Pobi *et al*.,2019
Tembi	0.26	0.20	0.30	Shanbehzadeh *et al*.,2014
Taipu	0.334	0.064	0.016	Yao *et al*.,2014
Iboe	7.36	0.03	0.02	Dan *et al*.,2014
Sokoto	29.29	0.38	0.31	Raji *et al*., 2016
Nile	0.4	-	0.01	Osman *et al*.,2012
Nzhelele	5.804	0.086	0.403	Edokpayi *et al*.,2017
Athi-Galana tributary	-	0.055	-	Muiruri *et al*.,2013
WHO drinking water guidelines	0.3	3	1	WHO, 2008
USEPA drinking water standards	0.3	5	1.3	USEPA, 2011
KEBS guidelines on drinking water	0.3	5	1	KEBS,2008

Table 4 concentration of heavy metals in Rupingazi river in comparison to other rivers during the wet season

Rivers	Fe	Zn	Cu	Reference
Rupingazi	0.74	0.4931	0.105	Present study
Migori	-	0.230	0.110	Olal, 2015
Durgapur	23.10	-	0.281	Pobi *et al*., 2019
Tembi	1.1	0.51	0.62	Shanbehzadeh *et al*., 2014
Taipu	0.423	0.19	0.043	Yao *et al*., 2014
Iboe	10.68	0.08	0.05	Dan *et al*., 2014
Sokoto	0.37	0.04	0.01	Raji *et al*., 2016
Nile	0.5	-	0.04	Osman *et al*., 2012
Nzhelele	2.304	0.065	0.385	Edokpayi *et al* ., 2017
Athi-Galana tributaries	-	0.065	-	Muiruri *et al*., 2013
WHO drinking water guidelines	0.3	3	1	WHO, 2008
USEPA drinking water standards	0.3	5	1.3	USEPA, 2011
KEBS guidelines on drinking water	0.3	5	1	KEBS, 2008

3.4 Correlation analysis

Correlation analysis was done to find out the relationship between the metals during the similar and different seasons

Table 5 Correlation matrix of the heavy metals during the wet season in water

	Cu	**Fe**	**Zn**
Cu	1	0.821	0.771
Fe		1	0.826
Zn			1

From the correlation matrix table in water during the wet season there was a high correlation between Fe versus Cu (0.821), Zn versus Cu (0.771) and Zn versus Fe (0.826).

Table 6 Correlation matrix of the heavy metals during the dry season in water

	Cu	**Fe**	**Zn**
Cu	1	0.3764	0.716
Fe		1	0.4302
Zn			1

The correlation matrix table showed that during the dry season in water, high correlation was between Zn versus Cu (0.716). Moderate correlation was between Zn versus Fe (0.4302) and low correlation between Cu versus Fe (0.3764). Moderate or high correlation between metals is an indicator that they could be having a similar source (human or natural), related dependence or similar behavior. High correlation also indicates similar levels of contamination or identical behavior as they are transported in the river system. Low or no correlation is an indicator that these metals are not related to each other. (Li *et al* .,2009; Chen *et al* .,2012;Suresh *et al* .,2012,;Jiang *et al* 2014). Correlation analysis was also done between similar metals during the different seasons.

Table 7 Correlation matrix of the heavy metals during the wet and dry season in water

dry				
wet		Cu	Fe	Zn
		0.83		
	Cu		0.4797	
	Fe			
	Zn			0.711
	Mn			
	Ni			

From table in water Cu and Zn had a strong correlation coefficient of (0.83) and (0.711) respectively. Fe had a moderate correlation of (0.4797). These correlations indicated that the metals could be having similar sources during both seasons (Jiang *et al.,* 2014)

4.0 Conclusion and recommendation

The results showed that zinc, copper and iron are present in the water of Rupingazi river. The levels of zinc and copper were lower than the WHO limits for drinking water. Iron levels in most sampling stations either during the wet or dry season exceeded the limits. Constant monitoring of heavy metal concentration in Rupingazi river is recommended considering that water from this river is used for drinking and other domestic uses. Significant correlation indicates similar levels of contamination or identical behavior as they are transported in the river system (Li *et al* .,2009; Chen *et al* .,2012;Suresh *et al* .,2012,;Jiang *et al* 2014). The metals could also be having a similar source (human or natural), related dependence or similar behavior.

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