HEAVY METAL CONCENTRATION IN SEDIMENT AND WATER OF RIVER NYAMINDI, KIRINYAGA COUNTY, KENYA

Edward Njagi Silas, Ochieng Ombaka, Eric Chomba and Moses Muraya

Department of Physical Sciences, Chuka University.

DOI: https://doi.org/10.56293/IJASR.2024.6030

IJASR 2024
VOLUME 7
ISSUE 4 JULY – AUGUST **ISSN: 2581-7876**

Abstract: Toxic heavy metals get into humans through absorption, inhalation and ingestion. All heavy metals are toxic to animals and plants when present in excessive amounts. The adverse effects of heavy metals in mammals may manifest in disorders such as growth retardation, decrease in longevity, changes in reproductive cycles, chronic diseases and formation of tumours. River Nyamindi flows from Mt. Kenya Forest passing through rocks, soil, agricultural land, residential areas and urban centres. Geological factors and human activities may have made heavy metals get into the river water. Since the water is used for domestic purposes and irrigation, it was necessary to determine if heavy metal concentration in river Nyamindi has reached alarming levels. Water and sediment samples were collected along river Nyamindi during wet and dry season. The samples were digested appropriately and the concentration of eight heavy metals determined using ICP-MS. The mean amount of Cd, Cr, Ni, Pb, Zn, As, Mn and Se in sediment were 0.0882, 41.1219, 91.7718, 10.7445, 54.3880, 2.4561, 1753.5587 and 5.7648 mg/kg respectively during wet season and 0.0590, 39.1176, 559.0917, 0.3781,76.3715, 3.0114, 1714.4195 and 6.5488 mg/kg respectively during dry season. The mean concentration of the same metals in water was 0.00005, 0.0167, 0.1943, 0.0223, below detection limit (BDL), 0.0002, 0.1379 and BDL ppm respectively during wet season and 0.0009, 0.0005, 0.0148, 0.0184, BDL, 0.00003, 0.0080 and 0.00003 ppm respectively during dry season. The mean amount of Cr, Ni and Mn in sediment were found to be above WHO and US EPA permissible limits during both seasons. The mean concentration of Cr and Mn in water were above WHO and KEBS/WASREB permissible limits during wet season. However, during dry season, all the eight heavy metal concentrations in water were below WHO, KEBS/WASREB permissible limits. Therefore, as far as the eight heavy metals are concerned, water from river Nyamindi was not be potable during rainy season but was potable during dry season. However, further investigations should be carried out to determine other water parameters to confirm it's suitability as potable water.

Keywords: Sediment Pollution, Water Pollution, Heavy Metals, Potable Water

1. Introduction

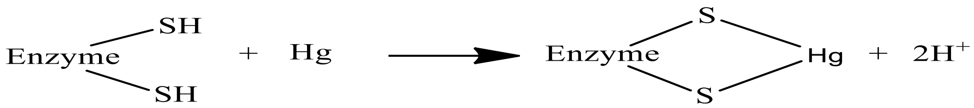
Trace elements find their way into humans either by direct absorption, inhalation or ingestion. Some heavy metals such as copper, cobalt, manganese, selenium and zinc are essential to both animals and plants in trace amounts (Tuorma, 2002). Minute traces of arsenic, chromium, nickel and tin have been found to be essential for animals but not for plants and whereas some physiological roles have been inferred for arsenic, cadmium and lead recently, mercury and silver have not yet been found to be essential for either plants or animals (Dara & Mishra, 2010). All heavy metals when present in excess quantities have been found to be toxic for animals and plants (Khan, 2014). In fact, the toxicity of all the essential trace elements follows the general trend; under supply leads to deficiency, optimum supply helps in healthy growth, and over-supply leads to toxicity and even death to the organisms (Dara & Mishra, 2010).

The adverse effects of heavy metal toxicity in biological systems may result from interaction of the metal with protein leading to denaturation, interaction with DNA leading to mutation, effects on cell membrane and effect on regulatory enzymes. These adverse effects on mammals may manifest in disorders such as retardation of growth, decrease longevity, detrimental changes in reproductive cycle leading to mortality of offspring, morbidity, pathological changes, symptoms of chronic disease and formation of tumors (Dara & Mishra, 2010). The toxicity due to the metals and their compounds is mainly determined by the delivery of the metal to the cell to attain a critical concentration level at the site of action and the cellular biochemical defense mechanism (Jarup, 2003).

Although the toxic action of the different metals may be different, most of them involve binding to the metabolically-active groups such as amino-, imino-, sulphurdry-, carboxyl-, phenolic- or phosphoryl groups (Dara and Mishra, 2010). Studies have shown that Cr, Ni, Cd and Be are potentially carcinogenic (Mulware, 2013). Elements like Be, Cr, Sr-90 and Pu -239 have been found to be potentially mutagenic. Furthermore, metals like Cd, Cu, Pb, Hg, Mo, Ni and Se in excessive amounts have been found to be potentially teratogenic (Tchounwou *et al.*, 2012). Some arsenic compounds have been found to be potentially carcinogenic, mutagenic as well as well as teratogenic (Dara & Mishra, 2010).

The heavy metal pollutants, like some other pollutants on acute or chronic exposure severely affect different body organs such as liver, kidneys, lungs, bones and brain (Balali-Mood *et al.,* 2021; Dara & Mishra, 2010). Although most heavy metals are known to exert biological effects through combination with sulphydryl groups, they can also combine with other groups especially in chelate configuration. For example, Hg and Ag can combine with amino-imidazole, phosphate and carboxylate groups; Pb can also combine with carboxylate and phosphate groups (Rubino, 2015; Dara & Mishra, 2010). Quite a good number of heavy metals apply toxic effects on tissues such as gastrointestinal mucosa, bone marrow, highly specialized cells such as neurons and renal tabular cells, and can also lead to excessive damage due to oxidative stress induced by formation of free radicals (Balali-Mood *et al.,* 2021; Jaishanker *et al.,* 2014, Dara & Mishra, 2010).

Heavy metal ions such as Pb^{2+}, Hg^{2+} and Cd^{2+} acts as enzyme inhibitors. They attack ligands like –SH and $-SCH_3$ in cysteine and methionine amino acids in the enzyme structure as follows:



(Quyoom, 2014; Dara & Mishra, 2010). Heavy metal ion can also replace the right metal ion of similar charge and size from metalloenzymes and inhibit normal activity or induce toxicity for example, Cd^{2+}can displace Zn^{2+} and lead to cadmium toxicity (Jaishanker *et al.,* 2014). Cd^{2+} can inhibit activity of enzymes such as amylyse, carbonic anhydrase, adenosine, triphosphatase, alcohol dehydrogenase and carboxy peptidase. Pb^{2+} can inhibit activity of enzymes like carbonic anhydrase, cytochrome oxidase, alkaline phosphatase, adenosine triphosphatase and some important enzyme in the synthesis of "heme" (Dara & Mishra, 2010; Day & Cohen, 2013). River Nyamindi flows from Mount Kenya forest though rocks and soil. Flowing downstream, the water passes through agricultural lands, residential areas and urban centers. Weathering of rocks; surface runoffs from agricultural farms, residential areas and towns; and seepage of waste water to the river may be contributing to the water getting polluted with heavy metals as it flows downstream. The river water is consumed by people and animals as well as being used for irrigation. Therefore, the objective of this study was to determine the levels of heavy metals in water and sediment of river Nyamindi.

2. Materials and Methods

Water and sediment sampling were done during dry and wet season in triplicates along river Nyamindi. The sampling points upstream were Nyamindi village (N1), Riangeci (N2), Riandigiri (N3), Matandara (N4), Kathiriko (N5) and Kiamatero (N6). Water samples were collected using depth sampler and stored in plastic bottles. Details such as sample collection date, sample code and sampling site were noted. The sampling bottles were pre-soaked overnight (to avoid unpredictable changes in characteristic as per standard procedure) with 10% HCl, rinsed with distilled water and rinsed again using the waters from collecting points. The water samples were preserved by adding 2 drops of concentrated HNO_3 to each sample (in order to preserve metals and avoid precipitation) before storing them below 4^{o} C until analyzed (Kar *et al.,* 2008; Mwegoha & Kihampa, 2010; Reza & Sign, 2010).

Sediment samples were collected (at the same point and time with water samples) using auger sampler in triplicates. Stones and plant materials were removed then the samples were stored in plastic containers that had previously have been cleaned with 10% nitric acid and rinsed with distilled water. The samples were labelled appropriately as described in water sample collection, recorded and transported into laboratory where they were dried in an oven at 105^{o} C. To obtain analytical samples of sediment, coning and quartering technique was used (Nyakairu & Koeberl,

2000) thereafter, the samples were ground to fine powder using soil Deagglomerator Pulverisette 8 then stored at a temperature below 4º C.
Each sediment dry ground sample of 0.5±0.025 g was weighed out using Top pan Sartorius balance into an ultra-clean and dry inert polymeric microwave vessel. A volume of 9±0.5 ml of concentrated nitric acid was slowly added under fume extraction hood. After this, 4±0.05 ml of perchloric acid was added slowly followed by 1±0.05 ml of concentrated hydrochloric acid. The samples were left to react for 5±1 minutes prior to sealing the vessels to allow any gases to escape. The vessels were placed on the rotor then placed in the microwave digester (High performance microwave digestion system, ETHOS UP). The microwave digester was gradually heated to 150 º C in not less than 20 minutes then held at that temperature for another 20 minutes. After the last 20 minutes, the microwave automatically began cooling the samples and indicated when cooling was complete. After the cooling, the samples were quantitatively transferred into 250 ml volumetric flasks then filled to the mark using distilled de-ionized water (Fabjola *et al.,* 2015; Mangun, 2009; Kingston and Walter,1998). The water sample were hand shaken thoroughly in their plastic containers. A volume of 45 ml of the sample was measured into an ultra-clean and dry inert polymeric microwave vessel. A volume of 9±0.5 ml of concentrated nitric acid was then slowly added under fume hood followed by 4±0.05 ml of perchloric acid. The vessels were placed on the rotor then placed in the microwave digester (High performance microwave digestion system, ETHOS UP) then digestion and topping up to 250 ml was done in a similar way as was done for sediment.

Multi element standards of 10 ppm from Agilent Technologies was used as the stock solution. A calibrated micro pipette was used to transfer 0, 100, 200,300, 500 and 1000 µL of stock solution into well labelled 100 ml volumetric flasks to prepare 0,10, 20,30, 50 and 100 ppb standards, respectively. Each of these volumetric flasks was topped up to the marks using 5% nitric acid solution. These standards were used for preparing calibration curve. Heavy metal (Cd, Cr, Ni, Pb, Zn, As, Mn and Se) analysis was done using inductively coupled plasma-mass spectrometry (Agilent Technologies 7900 ICP-MS). The data obtained was analyzed using statistical package for social sciences (SPSS) Version 26 with confidence level of the study (α) = 0.05.

3. Results and Discussion

3.1 Cadmium in River Nyamindi

The amounts of Cd in sediment and water during wet and dry season along river Nyamindi are presented in Table 1.

Table 1: Amount of Cd (ppm) in Sediment and Water Along River Nyamindi

Sampling point	Rainy season		Dry season	
	Sediment	Water	Sediment	Water
N1	0.0621±0.0008	BDL	0.0694±0.0005	BDL
N2	0.0721±0.0002	BDL	0.0602±0.0007	BDL
N3	0.0382±0.0006	BDL	0.0986±0.0007	BDL
N4	0.0481±0.0008	0.0002±0.00002	0.0310±0.0003	BDL
N5	0.2084±0.0045	BDL	0.0438±0.0001	BDL
N6	0.1002±0.0074	0.0001±0.00003	0.0511±0.0003	0.0055±0.00008
Mean	0.0882±0.0627	0.00005±0.00002	0.0590±0.0235	0.0009±0.0022
WHO limit	0.6	0.005	0.6	0.005

The average amount of Cd in sediment sampled from river Nyamindi from Nyamindi village (N1) to Kiamatero (N6) was 0.0882±0.0627 mg/kg during wet season and 0.0590±0.0235 mg/kg during dry season. The amount of Cd was a little higher during wet season compared to dry season. The average concentration of Cd in water along the same river course was 0.00005±0.00002 ppm during wet season and 0.0009±0.0022 during dry season. Just like for sediment, the concentration of Cd in water was higher during rainy season compared to dry season although during both seasons, the concentration was very low. The amount of Cd in sediment did not appear to affect it's concentration in water. For instance, sampling point N5 had the highest amount of Cd in sediment during wet season yet the concentration in water was BDL. It was also noted that the sampling points that had higher amount of Cd in sediment during rainy season did not necessarily have higher amount during dry season.

Independent-sample t-tests were conducted to establish whether there were differences in Cd amount in sediment and also in water from river Nyamindi during rainy and dry season. The results established that there was no statistically reliable difference between mean Cd amount in river Nyamindi sediment during rainy season (0.0882±0.0627 mg/kg) compared to dry season (0.0590±0.0235 mg/kg) t (10) = 1.066 at significance of t-test p = 0.311 and confidence level of the study (α) = 0.05. A similar t-test showed that there was no reliable difference between the mean Cd concentration in water of river Nyamindi during rainy season (0.00005±0.00002 ppm) and dry season (0.0009±0.0022 ppm), t (10) = -0.954, p = 0.362. A further t-test was run to determine whether there was a difference in the mean concentration of Cd in sediment and water from river Nyamindi. The t-test results revealed that during rainy season, there was significant difference in the mean concentration of Cd in sediment and water, t (10) = 3.443, p = 0.006. The t-test also indicated that during dry season, there was still significant difference in the mean concentration of Cd in sediment and in water, t (10) = -6.042, p = 0.001. These results revealed in river Nyamindi, that there was no effect of season on concentration of Cd in sediment or water; but there was discernible difference between the Cd amount in sediment and water during each season at the confidence level α = 0.05.

This study obtained values similar to those reported by Idiriah *et al.,* (2012), Tomno *et al.,* (2020), Muiruri *et al.,* (2013) and Budambula & Mwachiro (2006) on amount of Cd in river sediment and water. However, Wasike *et al.,* (2019), Javaid *et al.,* (2022) reported higher values than those reported in the present study showing that some rivers are more polluted with Cd than river Nyamindi. The amount of Cd in sediment of river Nyamindi falls below WHO permissible limit of 0.6 mg/kg and the concentration in water also falls below WHO and KEBS/WASREB permissible limit of 0.005 ppm (Ameh *et al.,* 2016; Omondi, 2017; Mahmud *et al.,* 2016; WASREB, 2008) implying that river Nyamindi is not polluted with Cd.

3.2 Chromium in River Nyamindi

The amounts of Cr in sediment and water during wet and dry season along river Nyamindi are presented in Table 2.

Table 2: Amount of Cr (ppm) in Sediment and Water Along River Nyamindi

Sampling point	Rainy season		Dry season	
	Sediment	Water	Sediment	Water
N1	34.3949±0.0081	BDL	32.2162±0.0022	BDL
N2	36.9219±0.0045	BDL	41.6762±0.0077	BDL
N3	30.1670±0.0063	BDL	38.6655±0.0049	BDL
N4	40.4863±0.0026	0.0630±0.00007	37.7108±0.0035	0.0017±0.00006
N5	50.9584±0.0250	0.0373±0.00004	39.7309±0.0057	BDL
N6	53.8026±0.0150	BDL	44.7058±0.0078	0.0010±0.00001
Mean	41.1219±9.3900	0.0167±0.0271	39.1176±4.1944	0.0005±0.0007
WHO limit	25	0.05	25	0.05

The mean amount of Cr in sediment from river Nyamindi was 41.1219±9.3900 mg/kg during wet season and 39.1176±4.1944 mg/kg during dry season. It was observed that the mean amount was slightly higher during wet season compared to dry season. It was also observed that the sampling points that had relatively high amount of Cr during wet season did not necessarily have high amount during dry season. On the same river, the mean concentration of Cr in water was 0.0167±0.0271 ppm during wet season and 0.0005±0.0007 ppm during dry season. The concentration of Cr in water was found to be higher during wet season than during dry season. It was observed that on most sampling points, the concentration of Cr in water was BDL. It was also noted that the sampling points that had higher amount of Cr in sediment did not necessarily have high amount of the same in water.

Independent-sample t-tests established that there was no statistically significant difference between mean Cr amount in river Nyamindi sediment during rainy season compared to during dry season, t (10) = 0.477, p = 0.311. A similar t-test found that there was no significant difference between the mean Cr concentration in water of river Nyamindi during rainy season and dry season, t (10) = 1.468, p = 0.173. However, results of t-test indicated that during rainy season, there was significant difference in the mean concentration of Cr in sediment and water, t (10) = 10.723, p =

0.001. The t-test also found that during dry season, there was still significant difference in the mean concentration of Cr in sediment and in water, t (10) = -22.844, p = 0.001.

The present study aligns with findings of Tomno *et al.,* (2020) who reported similar values of chromium in water of urban streams of Machakos municipality and Muiruri *et al.,* (2013) who reported chromium values close to those of this study in water from Athi-Galana-Sabaki tributaries. However, Mustafa (2019) reported higher chromium values in water from river Yobe of Nigeria and Javaid *et al.,* (2022) who reported much higher values of chromium in water from rice growing areas of Punjab in Pakistan. This may have been due to the longer period of rice farming in these areas coupled with excessive application of fertilizers and toxic agricultural chemicals which usually contain traces of heavy metals. The current study reported different values from those reported by Idriah *et al.,* (2012) who reported lower values (0.076-0.3071 mg/kg) of chromium in sediment along Abonnema shoreline in Nigeria and Omondi (2017) who reported much higher values (122 mg/kg) of chromium in sediment from river Nzoia in Kenya. The mean amount of Cr in sediment exceeded WHO and US EPA permissible limit of 25 mg/kg (Omondi, 2017; Ameh *et al.,* 2016) implying that sediment in river Nyamindi was Cr polluted according to WHO and US EPA standards. However, the concentration of Cr in water was below WHO set limit of 0.05 ppm.

3.3 Nickel in River Nyamindi

The amounts of Ni (ppm) in sediment and water during wet and dry season along river Nyamindi are given in Table 3.

Table 1: Amount of Ni (ppm) in Sediment and Water Along River Nyamindi

Sampling point	Rainy season		Dry season	
	Sediment	Water	Sediment	Water
N1	74.9157±0.0650	BDL	479.3399±0.6990	BDL
N2	76.9449±0.0880	BDL	617.6797±0.4990	BDL
N3	63.7684±0.0390	BDL	580.0957±0.2950	BDL
N4	92.3219±0.0760	0.6792±0.00035	518.3989±0.6980	BDL
N5	129.7994±0.2760	0.4863±0.00027	559.2734±0.1330	0.0890±0.00008
N6	112.8805±0.0370	BDL	599.7628±0.6550	BDL
Mean	91.7718±25.2196	0.1943±0.3071	559.0917±52.0464	0.0148±0.0363
WHO limit	20	0.1	20	0.1

The average amount of Ni in sediment from river Nyamindi was 91.7718±25.2196 mg/kg during wet season and 559.0917±52.0464 mg/kg during dry season. On the same course of the river, the average concentration of Ni in water was 0.1943±0.3071 ppm during wet season and 0.0148±0.0363 during dry season. The concentration of Ni in river water was found to be higher during wet season than during dry season. Independent-sample t-tests results revealed that there was statistically reliable difference between mean Ni amount in river Nyamindi sediment during rainy season and during dry season, t (10) = -19.793, p < 0.001. On the other hand, t-test results indicated that there was no reliable difference between the mean Ni concentration in water during rainy season and dry season, t (10) = 1.421, p = 0.186. Results of t-test also indicated that during rainy season, there was significant difference in the mean concentration of Ni in sediment and water, t (10) = 8.894, p = 0.001. The t-test also indicated that during dry season, there was still significant difference in the mean concentration of Ni in sediment and water, t (10) = -26.312, p = 0.001. This study reported Ni values that closely agree with Omondi (2017) who reported a mean nickel value of 0.01574 ppm in water from lower river Nzoia and Muiruri *et al.,* (2013) who reported Ni concentration ranging from BDL to 0.062 ppm.

It was found that during both seasons, the amount of Ni in sediment exceeded WHO and US EPA permissible limits which are set at 20 mg/kg and 16 mg/kg respectively (Ameh *et al.,* 2016; Omondi, 2017; Samlafo, 2006). The average concentration of Ni in water of river Nyamindi during wet season was above WHO permissible limit of 0.1 ppm (Mahmud *et al.,* 2016; WASREB, 2008) but during dry season, the concentration of nickel was BDL from all sampling points except N5 that recorded a concentration of 0.0890±0.00008 ppm which was below permissible limit set by WHO.

3.4 Lead in River Nyamindi

The amounts of Pb in sediment and water during wet and dry season along river Nyamindi are presented in Table 4.

Table 4: Amount of Lead (ppm) in Sediment and Water Along River Nyamindi

Sampling point	Rainy season		Dry season	
	Sediment	Water	Sediment	Water
N1	12.4343±0.0035	0.0097±0.00007	0.1765±0.0018	0.0724±0.00003
N2	11.7891±0.0085	0.0090±0.00004	0.5943±0.0046	0.0044±0.00004
N3	10.8809±0.0027	0.0050±0.00004	0.2351±0.0022	0.0079±0.00007
N4	10.7975±0.0047	0.0339±0.00008	0.4103±0.0056	0.0106±0.00003
N5	9.2169±0.0085	0.0539±0.00006	0.4811±0.0024	0.0112±0.00001
N6	9.3480±0.0075	0.0225±0.00087	0.3712±0.0065	0.0037±0.00002
Mean	10.7445±1.2847	0.0223±0.0210	0.3781±0.1546	0.0184±0.0266
US EPA limit	40	0.015	40	0.015

The average amount of Pb in sediment from river Nyamindi was 10.7445±1.2847 mg/kg during rainy season and 0.3781±0.1546 mg/kg during dry season. The average amount of Pb in sediment during rainy season was about twenty-eight times higher than during dry season. It was noted that all the sampling points had lower amount of Pb during dry season than rainy season. On the same course of river, the average concentration of Pb in water was 0.0223±0.0210 ppm during rainy season and 0.0184±0.0266 ppm during dry season. The average concentration of lead in river water was found to be slightly higher during rainy season than during dry season. It was also observed that the sampling points that had higher amount of Pb in sediment did not necessarily have a corresponding higher concentration of the same metal in water.

Independent-sample t-tests established that there was statistically significant difference between mean amount if Pb in river Nyamindi sediment during rainy season compared to during dry season, $t (10) = 19.624$, $p < 0.001$. Unlike in sediment, t-test found that there was no significant difference between the mean concentration of Pb in water of the river during rainy season and dry season, $t (10) = 1.004$, $p = 0.339$. The results of t-test also showed that during rainy season, there was significant difference in the mean concentration of Pb in sediment and water, $t (10) = 8.239$, $p = 0.001$. The t-test also showed that during dry season, there was still significant difference in the mean concentration of Pb in sediment and in water, $t (10) = -5.616$, $p = 0.001$.

The current study found lower levels of Pb compared to Gathumbi *et al.,* (2013) which could be attributed to presence of petrol-powered pumps next to water courses which were initially using leaded petrol (which was being used before that time) that was possibly leaking into river. The amount of Pb reported by Moywaywa (2018) in sediment from Thika river was much higher than what was found in sediments of river Nyamindi showing that human activities in the current study area has not resulted to much Pb pollution in the sediment. This study closely agrees Omondi (2017) who reported a mean of 13 mg/kg of Pb in sediment from lower river Nzoia and Jepkoech *et al.,* (2013) who reported a range of 0.63-1.27 mg/kg of Pb during dry season and 0.75-1.31 mg/kg Pb during wet season in sediment from Sosiani river showing that agricultural activities in Kenya so far may not have contributed to Pb pollution of river sediment. The sediment of river Nyamindi are not polluted with Pb metal since the mean amounts of Pb were below US EPA permissible limit of 40 mg/kg (Omondi, 2017; Ameh *et al.,* 2016). The concentration of Pb in water of this river was above permissible limit by WHO (0.01 ppm) and US EPA (0.015 ppm) but was below WASREB permissible limit of 0.05 ppm (Wasike *et al.,* 2019; Mahmud *et al.,* 2016; WASREB, 2008). This implies that using Kenyan standards, the water of river Nyamindi was not polluted with Pb.

3.5 Zinc in Rive Nyamindi

The amounts of Zn in sediment and water during wet and dry season along river Nyamindi are presented in Table 5.

Table 5: Amount of Zn (ppm) in Sediment and Water Along River Nyamindi

Sampling point	Rainy season		Dry season	
	Sediment	Water	Sediment	Water
N1	39.1437±0.0043	BDL	76.4621±0.0410	BDL
N2	36.1477±0.0061	BDL	73.5968±0.0780	BDL
N3	32.7516±0.0058	BDL	57.2619±0.0440	BDL
N4	38.4861±0.0092	BDL	54.0231±0.0450	BDL
N5	50.0610±0.0280	BDL	116.5999±0.3850	BDL
N6	54.3880±0.0470	BDL	76.3715±0.0190	BDL
Mean	41.8297±8.4683	BDL	75.7192±20.3638	BDL
WHO limit	123	5.0	123	5.0

The average amount of Zn in sediment from river Nyamindi was 41.8297±8.4683 mg/kg during wet season and 75.7192±20.3638 mg/kg during dry season. This average amount was about one and a half times higher during dry season than during wet season. It was observed that the sampling points that had relatively higher amount of Zn during wet season did not necessarily have relatively higher amount during dry season. On the same river course, the concentration of Zn in water was BDL for all sampling points during both wet and dry season. Independent-sample t-tests results established that there was significant difference between mean amount of Zn in river Nyamindi sediment during rainy season compared to during dry season, $t\ (10) = -3.479$, $p = 0.006$. There was no difference in concentration of Zn in water of river Nyamindi since all sampling points had concentration BDL. The t-test results also showed that during rainy season, there was significant difference in the mean concentration of Zn in sediment and water, $t\ (10) = 12.099$, $p = 0.001$. The t-test further revealed that during dry season, there was still significant difference in the mean concentration of Zn in sediment and in water, $t\ (10) = -8.314$, $p = 0.001$.

It was noted that the amount of Zn in sediment from Nyamindi and during wet and dry seasons was below the permissible limit by WHO and US EPA which is set at 123 mg/kg and 110 mg/kg, respectively (Ameh *et al.,* 2016; Samlafo, 2006). It was conspicuously noted that the concentration of Zn in river water from all sampling points along river Nyamindi during wet and dry season was BDL. This shows that sediment in this river may have been acting as sink for Zn ions that may have been getting into the river. This study therefore found that river Nyamindi is not polluted with Zn. This study obtained values similar to those obtained by Omondi (2017) who reported Zn values ranging from 40-100 mg/kg in sediment from lower river Nzoia. However, Moywaywa (2018) reported higher mean amount of Zn (198 mg/kg) in sediment from Thika river implying that Thika river may be more polluted than river Nyamindi and Jepkoech *et al.,* (2013) reported much lower values of Zn in sediment (between 2.79-6.73 mg/kg) but obtained higher values in dry season compared to wet season which agrees with the current study. This study is coherent with Ebah *et al.,* 2016 who reported higher amounts of Zn in sediment during dry season than during wet season. However, this study does not concur with Idiriah *et al.,* (2012), Omondi (2017), Mustafa (2019) and Tomno *et al.,* (2020) who reported higher concentration of Zn in river water from their study areas. Possibly, their study areas were more Zn polluted or the sediments were not very efficient in acting as Zn ions sinks.

3.6 Arsenic in River Nyamindi

The amounts of arsenic in sediment and water during wet and dry season along river Nyamindi are given in Table 6.

Table 62: Amount of As (ppm) in Sediment and Water Along River Nyamindi

Sampling point	Rainy season		Dry season	
	Sediment	Water	Sediment	Water
N1	2.3084±0.0073	0.0000	3.8040±0.0071	0.0000
N2	2.3708±0.0063	0.0001±0.00006	2.8914±0.0033	0.0001±0.00002
N3	2.2918±0.0092	0.0001±0.00007	2.7489±0.0058	0.0000
N4	2.4706±0.0033	0.0009±0.00007	2.6180±0.0045	0.0001±0.00001
N5	2.5455±0.0023	0.0000	2.8336±0.0044	0.0000

N6	2.7494±0.0051	0.0001±0.00004	3.1725±0.0068	0.0000
Mean	2.4561±0.1734	0.0002±0.0003	3.0114±0.4298	0.00003±0.00005
US EPA limit	3	0.01	3	0.01

The mean amount of As in sediment from river Nyamindi was 2.4561±0.1734 mg/kg during wet season and 3.0114±0.4298 mg/kg during dry season. The mean amount of As was slightly higher during dry season compared to wet season. The sampling points that had relatively higher amount of As in sediment during wet season did not necessarily have higher amount during dry season. On the same course of the river, the average concentration of As in water was 0.0002±0.0003 ppm during wet season and 0.00003±0.00005 ppm during dry season. The concentration of As in the river water was found to be over six times higher during wet season than during dry season. It was also observed that the sampling points that had higher amount of As in sediment did not necessarily have higher concentration of the same in water.

The results of the t-test indicated that there was statistically significant difference between mean amount of As in the sediment during rainy season and dry season, $t(10) = -2.935$, $p = 0.015$. However, results of a similar t-test established that there was no statistically significant difference between the mean As concentration in river water during rainy season and dry season, $t(10) = 1.129$, $p = 0.285$. The results of the t-test also indicated that during rainy season, there was significant difference in the mean concentration of As in sediment and water, $t(10) = 34.698$, $p = 0.001$. The t-test further revealed that during dry season, there was still significant difference in the mean concentration of As in sediment and in water ppm), $t(10) = -17.161$, $p = 0.001$.

The mean amount of As in sediment from river Nyamindi during wet season was below US EPA permissible limit that is set at 3 mg/kg (Ameh *et al.,* 2016). However, during dry season, amount of As was slightly above the US EPA limit implying that river Nyamindi sediment may be slightly polluted with As during dry season. It was observed that the concentration of As in river Nyamindi water was quite low in the study area and was below the US EPA and WHO/WASREB permissible limit of 0.01 and 0.05 ppm respectively. This implies that the water of river Nyamindi is not polluted with As. This present study does not align with Omondi (2017) who reported a mean of 10 mg/kg As in sediment from lower river Nzoia which implies that river Nyamindi may be less polluted with As compared to lower river Nzoia. This study results differs with findings of Mustafa (2019) who reported mean values of 1.88 and 3.96 ppm of As in irrigation water in Lahore and Gujranwala rice growing areas respectively in Punjab, Pakistan. This shows that water from these areas of Pakistan may be highly polluted with As unlike river Nyamindi water.

3.7 Manganese in River Nyamindi

The amounts of Mn in sediment and water during wet and dry season along river Nyamindi are presented in Table 7.

Table 7: Amount of Mn (ppm) in Sediment and Water Along River Nyamindi

Sampling point	Rainy season		Dry season	
	Sediment	Water	Sediment	Water
N1	1466.3647±0.8170	0.0327±0.00005	2208.4804±7.2440	0.0095±0.00007
N2	1529.8162±1.8480	0.0286±0.00005	1586.2441±1.0960	0.0074±0.00009
N3	1385.3230±0.7770	0.0673±0.00002	1609.8181±2.7210	0.0074±0.00003
N4	1184.3248±0.7970	0.5268±0.00047	1556.9655±4.2840	0.0114±0.00002
N5	3130.7051±9.2440	0.1245±0.00003	1603.2709±3.8040	0.0050±0.00008
N6	1823.1723±2.5860	0.0473±0.00006	1721.7379±5.7410	0.0073±0.00002
Mean	1753.5587±706.1931	0.1379±0.1937	1714.4195±248.4616	0.0080±0.0022
Limit	300	0.1	300	0.1

The average amount of Mn in sediment from river Nyamindi was 1753.5587±706.1931 mg/kg during wet season and 1714.4195±248.4116 mg/kg during dry season. The average amount of Mn in sediment was almost equal during both seasons although it was slightly higher during wet season. On the same river course, the average concentration of Mn in water was 0.1379±0.1937 ppm during wet season which was much higher than the concentration during dry season which was 0.0080±0.0022 ppm. It was noted that the sampling points that had higher amount of Mn in sediment did not necessarily have higher concentration of the same metal in water.

Independent-sample t-tests results indicated that there was no reliable difference between mean Mn amount in river Nyamindi sediment during rainy season and dry season, t (10) = 0.127, p = 0.901. Similarly, results of t-test established that there was no reliable difference between the mean Mn concentration in river water during rainy season and dry season, t (10) = 1.642, p = 0.162. Further t-test results revealed that during rainy season, there was significant difference in the mean concentration of Mn in sediment and water, t (10) = 6.081, p = 0.001. The t-test also indicated that during dry season, there was still significant difference in the mean concentration of Mn in sediment and in water, t (10) = -16.902, p = 0.001.

This study closely agrees with Omondi (2017) who reported a slightly lower manganese mean of 1163 mg/kg in sediment from lower river Nzoia and Moywaywa (2018) who reported a higher mean of 4817 mg/kg. The results of the current study align with Moywaywa (2018) who reported manganese mean concentration of 0.179 ppm in water from Thika river and Omondi (2017) who reported a mean concentration of 0.078 ppm in water from lower river Nzoia. This present study is also in line with Wasike *et al.,* (2019) who reported manganese concentration of 0.13-0.20 ppm in water during wet season and 0.12-0.14 ppm during dry season which showed that the concentration was lower during dry season just as in the current study. In the current study and those of Moywaywa (2018) and Omondi (2017), the amount of Mn in sediment was very high yet the concentration of the same in water was comparatively very low which shows that the river sediment may be an effective sink for Mn. The amounts of Mn in sediment from river Nyamindi highly exceeded US EPA permissible limit that is set at 300 mg/kg (Ameh *et al.,* 2016) implying that sediment from this river has high amount of Mn which could be due to high amount that is naturally found in the surrounding soils. During rainy season, the mean concentration of Mn in water from river Nyamindi was above WASREB permissible limit of 0.1 ppm but during dry season, the concentration was below the WASREB limit (Ameh *et al.,* 2016).

3.8 Selenium in River Nyamindi

The amounts of Se in sediment and water during wet and dry season along river Nyamindi are given Table 8.

Table 8: Amount of Se (ppm) in Sediment and Water Along River Nyamindi

Sampling point	Rainy season		Dry season	
	Sediment	Water	Sediment	Water
N1	6.6153±0.0045	BDL	5.6681±0.0071	BDL
N2	6.8043±0.0066	BDL	7.8777±0.0034	0.0002±0.00001
N3	5.2923±0.0057	BDL	7.5895±0.0051	BDL
N4	4.6308±0.0028	0.0000	6.0524±0.0092	BDL
N5	4.4418±0.0043	BDL	6.3406±0.0056	BDL
N6	6.8043±0.0044	BDL	5.7642±0.0085	BDL
Mean	5.7648±1.1085	BDL	6.5488±0.9518	0.00003±0.00008
Limit	2.5	0.01	2.5	0.01

The average amount of Se in sediment from river Nyamindi was 5.7648±1.1085 mg/kg during wet season and 6.5488±0.9518 mg/kg during dry season. The average amount of Se in sediment was slightly higher during dry season compared to wet season. It was noted that the sampling points that had relatively higher amount of Se during wet season did not necessarily have higher amount during dry season. On the same course of river, the concentration of Se in river water from all sampling points was BDL during both wet and dry season except point N2 during dry season which had a very low concentration of 0.0002±0.00001 ppm. The concentration of Se in river Nyamindi water may generally be said to be very low.

Independent-sample t-tests results indicated that there was no statistically significant difference between mean amount of Se in river Nyamindi sediment during rainy season compared to during dry season, t (10) = -1.314, p = 0.218. A similar t-test established that there was still no statistically significant difference between the mean concentration of Se in the river water during rainy season and dry season, t (10) = -1.000, p = 0.363. However, independent sample t-test results revealed that during rainy season, there was significant difference in the mean concentration of Se in sediment and water, t (10) = 12.738, p = 0.001. The t-test also found that during dry season, there was still significant difference in the mean concentration of Se in sediment and in water, t (10) = -16.852, p = 0.001. During both seasons, the amount of Se in sediment was above 2.5 mg/kg threshold limit proposed by Van Derveer & Canton (2009) but the concentration of Se in water was below WASREB, WHO and US EPA permissible limits of 0.01, 0.04 and 0.05 ppm respectively (Wasike *et al.,* 2019; Mahmud *et al.,* 2016; WASREB, 2008) implying that the river water was not Se polluted. The present study is in line with Njuguna *et al.,* (2021) who reported Se concentration BDL from all sampled sites on Ewaso Nyiro river surface water. The present study also aligns with Minuye *et al.,* (2020) who reported Se values ranging from 0.0031- 0.007 ppm in selected waters of Ethiopian rivers.

4. Conclusion and Recommendations

Sediment from river Nyamindi was found to contain the eight heavy metals at varying levels. The mean amount of Cd, Pb and Zn were found to be below the permissible limit of WHO and US EPA for unpolluted sediment but Cr, Ni and Mn amounts were above the limits. During rainy season, the mean concentration of Cd, Pb, Zn, As and Se in water from the river were below the permissible limit set by WHO and KEBS/WASREB but Cr and Mn mean concentrations were above the limits. However, during dry season, all the eight heavy metal mean concentrations in water from river Nyamindi were below WHO and KEBS/WASREB permissible limit which shows that water from this river may not be polluted with these heavy metals and so may be used as potable water (as far as the 8 heavy metals are concerned). Therefore, water from river Nyamindi may not be potable during rainy season since the amounts of Cr and Mn were found to be above WHO and KEBS/WASREB limits. Further studies require to be conducted to determine other water parameters (physical, biological and chemical) to confirm whether water from river Nyamindi is potable.

References

1. Ameh, O. S., Anna, K. N. & Halahala, T. S. (2016). Heavy Metal Seasonal Distribution in Shore Sediment Samples Along the Coastline of Erongo Region, Western Namibia. *European Journal of Scientific Research*, 139(1),49-63.
2. Balali-Mood, M., Naseri, K., Tahergorabi, Z., Khazdair, M. R. & Sadeghi, M. (2021). Toxic Mechanisms of Five Heavy Metals: Mercury, Lead, Chromium, Cadmium and Arsenic. *Frontiers in Pharmacology*, 12,643972
3. Budambula, N. L. M. & Mwachiro, E. C. (2006). Metal Status of Nairobi River Water and their Bioaccumulation in *Labeo cylindricus*. *Water, Air and Soil Pollution*, 169,275-291
4. Dara S. S., & Mishra D. D. (2010). Environmental Chemistry and Pollution Control. S. Chand & company Ltd, New Delhi. Pp. 116-119, 159-184.
5. Day, J. A., & Cohen, S. M. (2013). Investigating the Selectivity of Metalloenzyme Inhibitors. *Journal of Medicinal Chemistry*, 56(20), 1021.
6. Ebah, E., Tersagh, I. & Okpokwasili, G. C. (2016). Studies on Seasonal Variation and Effect of Heavy Metal Pollution on Microbial Load of Marine Sediment. *American Journal of Marine Science*, 4(1),4-10.
7. Fabjola, B., Marco, L., Laura, B., Alberto, B., Laura, E. D., & Elza, B. (2015). Evaluation of Heavy Metals Contamination from Environment to Food Matrix by TXRF: The Case of Rice and Rice Husk. *Journal of Chemistry*, 2015, 1-12.
8. Gathumbi, J. K., Kanja, L. W., Maitho, T. E., Mbaria, J. M., Nduhiu J. G., Gitau, F. K., Nderitu, J. G., Lucy, M. W. & Maloba, K. (2013). Assessment of Lead and Copper in Fish and Soil Sediments in Kirinyaga South District, Kenya. *Journal of Applied Sciences in Environmental Sanitation*, 8(3),145-150
9. Idiriah, T. J. K., David-Omiema, S. & Ogbonna, D. N. (2012). Distribution of Heavy Metals in Water and Sediment Along Abonnema Shoreline, Nigeria. *Resources and Environment*, 2(1),33-40.
10. Jaishanker, M., Tseten, T., Abalagam, N., Mathew, B. B., & Beeregowda, K. N. (2014). Toxicity, Mechanism and Health Effects of Some Heavy Metals. *Interdisciplinary Toxicology*, 7(2), 60-72.
11. Jarup, L. H. (2003). Hazards of Heavy Metals Contamination. *British Medical Bulletin*, 68(1), 167-182.
12. Javaid, S., Ashraf, K., Sultan, K., Siddiqui, M. H., Ali, H. M., Chen, Y. & Zaman Q. (2022). Risk Assessment of Potentially Toxic Metals and Metalloids in Soil, Water and Plant Continuum of Fragrant Rice. *Agronomy*, 12(10), 2480

13. Jepkoech, J. K., Simiyu, G. M. & Arusei, M. (2013). Selected Heavy Metals in Water and Sediment and their Bioaconcentrations in Plant (*Polygonum pulcrum*) in Sosiani River, Uasin Gishu County, Kenya. *Journal of Environmental Protection*. 4,796-802.
14. Kar, D., Sur, P., Mandal, S., Saha, T., & Kole, R. (2008). Assessment of Heavy Metal Pollution in Surface Water. *International Journal of Science and Technology*. 5, 119-124.
15. Khan, S. R.., Sharma, B., Chawla, P. A. & Bhatia, R. (2021). Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES): A Powerful Analytical Technique for Elemental Analysis. *Food Analytical Methods*, 15, 666-688
16. Kingston, H. M. & Walter, P.J. (1998). The Art and Science of Microwave Sample Preparations for Trace and Ultratrace Elemental Analysis in Inductively Coupled Mass Spectrometry, A. Montaser, Wiley-VCH, New York. Pp 33-81.
17. Mahmud, H. N. M., Huq, A. K. O. & Yahya, R. (2016). Removal of Heavy Metal Ions from Waste Water/Aqueous Solution by Polypyrrole-based Adsorbent. A Review. *RSC Advances*, 6, 14778
18. Mangun, S. J. (2009). Microwave Digestion – EPA Method 3052 on the Multiwave 3000. Field Application Report, PerkinElmer Inc, Shelton, CT 06484. USA.
19. Minuye, A., Zenge, F. & Chandravanshi, B. S. (2020). Levels of Selenium in Selected River, Well and Bottled Waters in Ethiopia by Microwave Plasma-Atomic Emission Spectroscopy. *Bulletin of the Chemical Society of Ethiopia*, 34(2),215-226.
20. Moywaywa, B. A. (2018). Heavy Metal Pollution Sediment, Water and Flora Along Thika River. Master of Science Thesis, University of Nairobi, Kenya. Pp 44-48
21. Muiruri, J. M., Nyambaka, J. M. & Nawiri, M. P. (2013). Heavy Metal in Water and Tilapia Fish from Athi-Galana-Sabaki Tributaries, Kenya. *International Food Research Journal*, 20(2), 891-896.
22. Mulware, S. J. (2013). Trace Elements and Carcinogenicity: A Subject in Review. *Biotechnology*, 8(2), 55-64.
23. Mustafa, U. N. (2019). Assessment of Heavy Metal Pollution in Water, Soil & Rice Grown Around River Yobe, Nigeria. Master of Science Thesis, Kampala International University, Kampala, Uganda. Pp 37-42.
24. Mwegoha, W. J. S., & Kihampa, C. (2010). Heavy Metal Contamination in Agricultural Soils and Water in Dar es Salaam City, Tanzania. *African Journal Environmental Science and Technology*, 4(11)**,** 763-769.
25. Njuguna, S. M., Gitonga, K. B., Onyango, J. A., Gituru, R. W. & Yan, X. (2021). Ecological and Health Risk Assessment of Potentially Toxic Elements in Ewaso Nyiro River Surface Water, Kenya. *SN Applied Sciences*, 3,148
26. Nyakairu, W. A. G., & Christian, K. (2000). Mineralogical and Chemical Composition and Distribution of Rare Earth Elements in Clay-Rich Sediments from Central Uganda. Institute of Geochemistry, University of Vienna, Althanastrasse 14, A-1090 Vienna, Austria.
27. Omondi, C. (2017). Distribution of Heavy Metals in Water and Sediments of Lower River Nzoia, Master of Science Thesis, University of Nairobi, Kenya. Pp 30-36.
28. Quyoom, S. (2014). An Overview of Inhibition of Enzymatic Activities by Heavy Metal Ions. *Chemical Science Review and Letters*,3(11), 381-387
29. Reza, R., & Singh, G. (2010). Heavy Metal Contamination and it's Indexing Approach for River Water. *International Journal of Environmental Science and Technology*, 7(4)**,** 785-792.
30. Rubino, F. M. (2015). Toxicity of Glutathione-Binding Metals: A Review of Targets and Mechanisms. *Toxics*, 3, 20-62.
31. Samlafo, B. V. (2006). Levels of Cadmium in Soil, Sediment and Water Samples from Tarkwa and it's Environs. *African Journal of Educational Studies in Mathematics and Sciences*, 4,53-59
32. Tchounwou, P. B., Yedjou, C. G., Patlolla, A. & Sutton, D. J. (2012). Heavy Metal Toxicity and the Environment. *PubMed Central*, 101, 133-164.
33. Tomno, R. M., Nzeve, J. K., Mailu, S. N., Shitanda, D. & Waswa, F. (2020). Heavy Metal Contamination of Water, Soil and Vegetables in Urban Streams in Machakos Municipality, Kenya. *Scientific African*, 9,1-9
34. Tuorma, T. E. (2002). Chromium, Selenium, Copper and other Trace Minerals in Health and Reproduction. *The Journal of Orthomolecular Medicine*, 15, 145.
35. Van Derveer, W. D. & Canton, S. P. (2009). Selenium Sediment Toxicity Thresholds and Derivation of Water Quality Criteria for Fresh Water Biota of Western Streams. *Environmental Toxicology and Chemistry*, 16(6), 1260-1268.
36. Wasike, P. W., Nawiri, M. P. & Wanyonyi, A. A. (2019). LEVELS of Heavy Metals (Pb, Mn, Cu & Cd) in Water in River Kuywa and Adjacent Wells. *Environment and Ecology Research*, 7(3), 135-138.

37. Water Services Regulatory Board (WASREB) (2008). Guidelines on Water Quality and Effluent Monitoring, Nairobi, Kenya. Pp 25-27.