International Journal of Advances in Scientific Research and Engineering (ijasre)

E-ISSN : 2454-8006

DOI: 10.31695/IJASRE.2024.8.9

Volume 10, Issue 8
August - 2024

Assessment of Heavy Metal Pollution in Water and Sediment of River Thiba, Kirinyaga County, Kenya

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ABSTRACT

Trace elements find their way into humans through ingestion, direct absorption or inhalation. All trace metals are toxic to animals and plants when present in excess amounts. The harmful effects of trace heavy metals in mammals may manifest as growth retardation, decrease in longevity, changes in reproductive cycles, chronic diseases and tumour formation. River Thiba catchment is Mt. Kenya forest and then flows through rocks, soil, farmlands, residential areas and town centres. Due to geological factors and human activities, trace heavy metals may be getting in river Thiba and since the water is used for domestic purposes and irrigation, it was necessary to determine the heavy metal concentration in the river. Sediment and water samples were collected along river Thiba during rainy and dry seasons. The samples were digested then concentrations of eight heavy metals determined using ICP-MS. The mean amounts of Cd, Cr, Ni, Pb, Zn, As, Mn and Se in sediment were 0.0908, 39.8969, 85.1085, 10.3918, 42.5555, 2.3679, 1678.3876 and 5.4907 mg/kg respectively during rainy season and 0.0628, 42.6319, 396.4692, 3.2669, 58.7585, 2.8139, 1766.4009 and 6.1059 mg/kg respectively during dry season. The mean concentration of the same metals in water was 0.0002, 0.0916, 1.0066, 0.0434, BDL, 0.0025, 1.8484 and 0.0038 ppm respectively during wet season and BDL, BDL, BDL, 0.0068, BDL, 0.00002, 0.0070 and BDL 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. During rainy season, the mean concentration of Cr, Ni, Pb and Mn in water were above WHO and KEBS/WASREB permissible limits but the concentrations of Cd, Zn, As and Se were below the limits. However, during dry season, all the eight heavy metal concentrations in water were below WHO, KEBS/WASREB permissible limits. As far as the eight heavy metals are concerned, water from river Thiba may not be potable during rainy season but is potable during dry season. However, further investigations should be carried out to determine other water parameters.

Key words: Heavy Metals, Sediment Pollution, Water Pollution, Potable Water, Carcinogenic, Teratogenic.

1.0 INTRODUCTION

Heavy metals find their way into human body by ingestion, direct absorption or by inhalation. An indispensable link in the food chain is the terrestrial or marine plant life from which humans receive trace elements directly or indirectly by feeding on herbivorous animals which depend on plants for their nutrition. Plants absorb trace elements either via the root system or by foliar absorption [1]. Some of the heavy metals in traces are considered to be essential for plants and animals and they serve some useful biological functions [2]. Some of the heavy metals that can get in soil and water as a result of natural or human activities include Cd, Cr, Ni, Pb, Zn, As, Mn and Se.

Cadmium and zinc are usually found together in nature due to their similarities in atomic structure and chemical properties. Whereas zinc is an essential element in human body, cadmium is considered as a toxic element [1]. It has deleterious effects on bone structure and kidneys [3] and acts as inhibitor of sulphydryl enzymes. The symptoms of cadmium toxicity include hypertension, respiratory disorders, damage to kidneys and liver, aminoaciduria (urinary excretion of aminoacids), hypecalciurea (urinary excretion of excessive calcium), glycosuria (excretion of blood sugar in the urine), proteinuria (urinary excretion of proteins), osteopororis (decalcification of the skeleton), formation of kidney stones and others [1, 4, 5, 6].

Chromium improves insulin sensitivity and also enhances carbohydrates, lipids and protein metabolism. Deficiency of chromium includes impaired glucose tolerance and less efficient control of cholesterol [7, 8]. Chromium toxicity depends on it's oxidation state with Cr (VI) being much more toxic than Cr (III). Actually, Cr (VI) is more easily absorbed than Cr (III) through oral or inhalation routes [9, 10]. Ingestion of Cr (VI) in high doses have resulted to acute effects on cardiovascular, respiratory, hepatic, haematological and even death [11, 12]. Chronic exposure to Cr (III) has been found to result in liver malfunction, renal failure, anaemia and weight loss [11, 12, 13].

Nickel is essential in animals and has been shown to be present in RNA and DNA [14]. It is essential to some micro-organisms, animals (but not plants) and is associated with synthesis of vitamin B-12 although it is toxic at higher concentrations [1]. It is believed to inhibit various enzymes such as cytochrome oxidase, isocitrate dehydrogenase and maleic dehydrogenase. Nickel dust is also believed to be carcinogenic [1, 14].

Lead is a general protoplasmic poison which is cumulative, slow-acting, subtle and like other heavy metals, it has high affinity for sulphur. It exerts most of its activities through sulphydryl inhibition and also interacts with carboxyl and phosphoryl groups [1]. The major biochemical effects of lead is it's interference with heme synthesis leading to hematological damage and also inhibition of utilization of iron in the body [3]. Inorganic lead is able to replace calcium in bones and accumulate there as a reservoir for long-term release later to soft tissues [1, 15]. The most severe clinical form of lead poisoning is brain damage which produces clumsiness, subtle changes in mental attitude, sluggishness, poor memory, inability to concentrate, restlessness and hyper irritability [3]. Lead is quite toxic to young children because they cannot excrete much lead; consequently, they retain high percentage of ingested lead than adults. Exposure to lead can stunt a child's intellectual, behavioural and physical development [16].

Zinc is essential in human body and it's requirements increases during pregnancy, lactating period and growth age period [17, 18]. Moderate deficiency of zinc leads to retarded growth, delayed puberty, male hopogonadism, rough skin, poor appetite, slow wound healing, taste abnormalities and mental lethargy [19, 20]. Severe cases of zinc deficiency are diarrhoea, weight loss, pustular dermatitis, emotional disorder and intercurrent infections [19]. Zinc is required in protein synthesis, DNA synthesis, cell division, testicular size and functions and hormonal functions of various endocrine organs [21, 22]. Acute toxicity of zinc leads to nausea, gastric distress and disorientation [23]. Just like zinc deficiency, elevated zinc levels may compromise immunity [20, 21,24]. It has been found that if there is persistence of zinc intoxication, both copper and iron absorption are interfered with which may cause anaemia as a result of iron deficiency [25, 26].

Arsenic is a general protoplasmic poison and it affects all systems in the body. Major biochemical effects of arsenic are complexation with co-enzymes, uncoupling of phosphorylation and coagulation of proteins. Trivalent arsenicals combine with sulphydryl (-SH) groups in cells and thus inhibit the sulphydryl containing enzyme systems essential to cellular metabolism [27]. Low chronic doses of arsenic tend to accumulate in lipid rich tissues [28]. Arsenic is toxic to liver and it produces fatty infiltration and causes central necrosis and cirrhosis; affects bone marrow and cellular elements of blood [1]; is a carcinogen and greatly increases the risk of bladder cancer [5]. Arsenic also crosses placental membrane and is teratogenic [3, 6].

Manganese is found in bones, pancreas, kidneys and liver in little amounts [29, 30]. It helps in formation of connective tissues, clotting factors, bones, sex hormones and is necessary in brain and nerve functions. It is also an antioxidant enzyme superoxide dismutase (SOD) component [31, 32, 33]. Low quantities of manganese in the body may lead to bone malformation, infertility, weakness and seizures. However, large amounts of manganese in diet may lead to elevated manganese in body tissues [34, 35]. Manganese presents neurotoxicity that is unique because it begins with early psychiatric abnormalities and ends up with parkinsonian syndrome [30, 33]. It is an inducer of pro-inflammatory situation in glial cells through producing interleukins and Tumor Necrosis Factor-Alpha [36, 37]. Manganese triggers

DOI: 10.31695/IJASRE.2024.8.9

mitochondrial disruption by promoting influx of calcium leading to functional loss and terminal permeability of mitochondrial membrane [38].

Selenium is a component of amino acids found in active sites of enzymes in animals and is required in trace amounts [30]. At high amounts, selenium is toxic because it replaces sulphur in enzymes [39, 40]. In humans, selenium deficiency can lead to muscle necrosis, hypothyroidism, cardio-cerebrovascular, male infertility and also may increase risk of development of cancers of lung, skin, colon, esophagus and stomach [9, 41]. Selenium is associated with pathogenesis of type two diabetes melitus, liver damage, increased serum liver enzyme levels, higher hepatic insulin resistance, and high triglyceride levels [42, 43]. Chronic exposure to selenium compounds affects synthesis of thyroid hormone, impairment of natural killer cells activity, hepatotoxicity and also gastrointestinal disturbances [44, 45, 46]. Acute exposure selenium leads to dermatological effects which includes nail loss, hair loss and dermatitis [46]. Extreme cases of selenium poisoning can result to liver cirrhosis, pulmonary edema and death [47, 48].

River Thiba 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 Thiba.

2.0 MATERIALS AND METHODS

Water and sediment samples were collected in triplicates during dry and rainy season along rivers Thiba upstream from Kiumbu (about one kilometre downstream from Ngomano; the confluence of river Thiba and Nyamindi) to Ndiara (near Kianyaga town). The sampling points along the river were Kiumbu which was coded as C2, Ngomano (at the confluence of river Thiba and Nyamindi) and coded as C1, Kakawa (T1), Ndindiruku (T2), Kiamanyeki (T3), Kithogondo (T4), Kangai (T5), Karii (T6), Kutus (T7) and Ndiara (T8). The water samples were collected at a depth of about one foot below water surface (to avoid scum collection) using grab sampler then stored in plastic bottles. Important details such as collection date and code were noted. The samples were preserved by adding two drops of concentrated nitric acid to each of them before storing below 4^{o}C until they were digested [49, 50, 51].

Sediment samples were collected (at the same point and time with water samples) using auger sampler in triplicates. Stones and plant materials were removed by hands then 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 procedure and transported to laboratory where they were dried in an oven at 105^{o} C. To obtain analytical samples of sediment, coning and quartering technique was done [52]. Thereafter, the samples were ground to fine powder then stored at a temperature below 4^{o} C.

A mass of 0.5±0.025 g of each sediment sample 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 minute prior to sealing the vessels to allow 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 over 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 [53, 54, 55].

The water sample was shaken thoroughly in their plastic containers by use of hand. 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 extraction hood followed by 4±0.05 ml of perchloric acid. The vessels

DOI: 10.31695/IJASRE.2024.8.9

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 in chemistry laboratories using inductively coupled plasma-mass spectrometry (Agilent Technologies 7900 ICP-MS). The data was analyzed using statistical package for social sciences (SPSS) Version 26.

3.0 RESULTS AND DISCUSSION

3.1 Heavy Metals in Sediment of River Thiba from Kiumbu to Ndiara During Rainy Season

The amount of selected heavy metals in sediment from river Thiba during rainy season are presented in Table1.

Table 1: Amount of Selected Heavy Metals (mg/kg) in Sediment Along River Thiba during Rainy Season

Point	Cd	Cr	Ni	Pb	Zn	As	Mn	Se
C2	0.0761± 0.0006	33.5515± 0.0041	69.1258± 0.0330	10.5898± 0.0077	44.0068± 0.0072	2.1587± 0.0064	1217.8688± 0.7570	4.4417± 0.0097
C1	0.0381± 0.0006	42.8454± 0.0092	90.1803± 0.0660	10.1530± 0.0092	41.0483± 0.0064	3.1320± 0.0071	1746.8943± 2.2430	6.9934± 0.0086
T1	0.1202± 0.0033	34.2513± 0.0028	70.8137± 0.0650	11.4459± 0.0083	37.6893± 0.0049	2.1545± 0.0035	1538.3773± 2.7220	5.8593± 0.0032
T2	0.0541± 0.0009	44.5663± 0.0055	88.9061± 0.0710	7.4881± 0.0059	47.1434± 0.0044	2.2127± 0.0045	1431.7761± 0.4360	4.4417± 0.0025
T3	0.1823± 0.0046	35.8509± 0.0071	78.1208± 0.0760	10.9152± 0.0035	40.0047± 0.0062	2.2169± 0.0052	2193.8618± 6.5110	5.4813± 0.0033
T4	0.0561± 0.0007	43.2055± 0.0033	67.8782± 0.0550	7.5547± 0.0062	40.5509± 0.0085	1.9632± 0.0076	1604.0594± 3.1030	4.8198± 0.0072
T5	0.0240± 0.0004	33.1244± 0.0053	73.9169± 0.0870	11.9511± 0.0055	40.9388± 0.0075	2.3875± 0.0045	1645.1722± 1.8180	7.1824± 0.0046
T6	0.0481± 0.0008	50.3350± 0.0140	128.1840± 0.3980	8.9350± 0.0066	45.0140± 0.0077	2.2252± 0.0065	2122.8698± 7.2650	3.7801± 0.0025
T7	0.2705± 0.0076	43.0963± 0.0092	93.9105± 0.0760	12.9476± 0.0055	50.5437± 0.0340	2.5497± 0.0094	1672.4769± 2.8490	6.0483± 0.0092
T8	0.0381± 0.0005	38.1428± 0.0038	90.0485± 0.0650	11.9379± 0.0046	38.6149± 0.0025	2.6786± 0.0081	1610.5140± 1.8920	5.8593± 0.0075
Mean	0.0908± 0.0790	39.8969± 5.7550	85.1085± 18.0378	10.3918± 1.8690	42.5555± 4.0501	2.3679± 0.3390	1678.3876± 292.8288	5.4907± 1.1195
Limit	0.6	25	20	40	123	3	300	25

The amount of Cd in sediment from Kiumbu to Ndiara along river Thiba during rainy season ranged from 0.0240±0.0004 (T5) to 0.2705±0.0076 (T7) mg/kg with an average of 0.0908±0.0790 mg/kg. Cr values in the sediment ranged from 33.1244±0.0053 (T5) to 50.3350±0.0140 (T6) mg/kg and had a mean of 39.8969±5.7550 mg/kg. For Ni, values ranged from 67.8782±0.0550 (T4) to 128.1840±0.3980 (T6) mg/kg with a mean of 85.1085±18.0378 mg/kg. Pb values were ranging between 7.4881±0.0059 (T2) and 12.9476±0.0055 (T7) mg/kg with a mean of 10.3918±1.8690 mg/kg.

The amount of Zn in the sediment varied from 37.6893±0.0049 (T1) to 50.5437±0.0340 (T7) mg/kg and had an average of 42.5555±4.0501 mg/kg. The values of As were ranging from 1.9632±0.0076 (T4) to 3.1320±0.0071 (C1) mg/kg with a mean of 2.3679±0.3390 mg/kg. For Mn, the amount varied from 1217.8688±0.7570 (C2) to

DOI: 10.31695/IJASRE.2024.8.9

2193.8618±6.5110 (T3) mg/kg with a mean of 1678.3876±292.8288 mg/kg. Whereas Se values ranged from 3.7801±0.0025 (T6) to 7.1824±0.0046 (T5) mg/kg with an average of 5.4907±1.1195 mg/kg. The mean amounts of the heavy metals in sediment along river Thiba upstream from Kiumbu to Ndiara during wet season decreased in the order Mn>Ni>Zn>Cr>Pb>Se>As>Cd

These amounts of the heavy metals did not show any uniform general trend (increase or decrease) upstream from Kiumbu to Ndiara. It was noted that at T7 (Kutus), the values were highest for Cd, Pb and Zn and at T6 (Karii) which was the next sampling point after Kutus downstream had highest values of Cr and Ni. This could be due to T6 and T7 sampling points close proximity to Kutus town which points to a possibility of the heavy metals from this town finding their way to the river sediment through surface run-offs, seepage or both. During the rainy season, the mean amounts of Cd, Pb, Zn, As and Se in the sediment fell below the WHO and US EPA limit but the mean amounts of Cr, Ni and Mn were above the limits.

The present study obtained mean amount of Pb of 10.3918±1.8690 mg/kg during wet season which is lower than 22.95±15.11 mg/kg that was reported by Gathumbi and collaborators [56]. This may be due to phasing out of leaded petrol which was earlier used in petrol powered water pumps that are used in Mwea region. Moywaywa reported higher mean amounts of Mn, Ni, Zn and Pb in sediment from Thika river [57] showing that Thika river may be more polluted with heavy metals than river Thiba. Omondi reported lower Mn concentration but higher Ni, Cr, Zn, Pb and As concentration in sediment from river Nzoia [58] which shows that river Thiba may be less polluted than river Nzoia. Idiriah and collaborators reported far much lower concentrations of Zn, Pb and Cr in sediment collected along Abonnema shoreline in Nigeria [59].

3.2 Heavy Metals in Sediment of River Thiba from Kiumbu to Ndiara During Dry Season

The amount of selected heavy metals in sediment sampled along river Thiba during dry season are given in Table 2.

Table 2: Amount of Selected Heavy Metals (mg/kg) in Sediment Along River Thiba during Dry Season

Point	Cd	Cr	Ni	Pb	Zn	As	Mn	Se
C2	0.0292± 0.0008	34.8881± 0.0084	445.3931± 0.4580	0.4845± 0.0039	53.9087± 0.0670	2.8721± 0.0094	1856.6108± 3.9050	4.8996± 0.0018
C1	0.0475± 0.0006	34.2762± 0.0049	467.8451± 0.6910	0.2615± 0.0047	56.7001± 0.0330	2.5988± 0.0073	1682.6449± 4.3420	6.6289± 0.0083
T1	0.0701 ±0.0008	47.9639± 0.0049	95.3359± 0.0850	10.1497± 0.0067	44.5538± 0.0076	3.0697± 0.0084	1844.6100± 2.5180	4.7253± 0.0077
T2	0.1242± 0.0027	34.6627± 0.0035	64.2392± 0.0280	10.2168± 0.0044	32.8121± 0.0079	2.3750± 0.0085	1597.5113± 2.6710	5.3868± 0.0039
T3	0.0541± 0.0009	26.1350± 0.0076	63.2156± 0.0570	9.8610± 0.0035	41.0933± 0.0093	2.2627± 0.0063	1851.5847± 6.2820	4.0637± 0.0066
T4	0.0821± 0.0004	44.4167± 0.0088	520.5808± 0.7870	0.4760± 0.0048	72.0498± 0.0940	3.0223± 0.0055	1791.4658± 2.3060	8.0700± 0.0066
T5	0.0456± 0.0005	42.4511± 0.0074	538.0829± 0.1980	0.2753± 0.0015	76.6965± 0.0410	2.8875± 0.0044	1862.6627± 4.5260	6.1489± 0.0054
T6	0.0785± 0.0009	57.6709± 0.0390	741.2449± 0.6250	0.0523± 0.0004	80.5621± 0.0280	3.4536± 0.0064	1758.8775± 4.4860	8.4542± 0.0085
T7	0.0602± 0.0003	64.0501± 0.0490	591.6598± 0.4610	0.2682± 0.0017	88.9347± 0.0260	3.0955± 0.0081	1745.5984± 3.6280	7.0130± 0.0055
T8	0.0365± 0.0007	39.8045± 0.0027	437.0949± 0.5110	0.6233± 0.0049	40.2741± 0.0940	2.5025± 0.0093	1672.4425± 1.8070	5.6681± 0.0037
Mean	0.0628± 0.0276	42.6319± 11.4988	396.4692± 238.9054	3.2669± 4.7021	58.7585± 19.5531	2.8139± 0.3721	1766.4009± 92.0517	6.1059± 1.4419
Limit	0.6	25	20	40	123	3	300	25

DOI: 10.31695/IJASRE.2024.8.9

The amount of Cd in sediment during dry season varied from 0.0292±0.0008 (C2) to 0.1242±0.0027 (T2) mg/kg with an average of 0.0628±0.0276 mg/kg. Cr values ranged from 26.1350±0.0076 (T3) to 64.0501±0.0490 (T7) mg/kg with a mean of 42.6319±11.4988 mg/kg. Ni amount varied from 63.2156±0.0570 (T3) to 741.2449±0.6250 (T6) mg/kg with a mean of 396.4692±238.9054 mg/kg. Amount of Pb varied from 0.0523±0.0004 (T6) to 10.2168±0.0044 (T2) mg/kg with a mean of 3.2669±4.7021 mg/kg. Zn amounts ranged from 32.8121±0.0079 (T2) to 88.9347±0.0260 (T7) and had an average of 58.7585±19.5531 mg/kg. For As, the amount varied from 2.2627±0.0063 (T3) 3.4536±0.0064 (T6) mg/kg with an average of 2.8139±0.3721 mg/kg. Mn had amounts varying from 1597.5113±2.6710 (T2) 1862.6627±4.5260 (T5) mg/kg with a mean of 1766.4009±92.0517 mg/kg. Whereas Se values ranged from 4.0637±0.0066 (T3) 8.4542±0.0085 (T6) mg/kg with a mean of 6.1059±1.4419 mg/kg. The mean amounts of the heavy metals in the sediment during dry season decreased in the order Mn>Ni>Zn>Cr>Se>Pb>As>Cd. Just as during rainy season, it was noted that during dry season, sampling point T7 (Kutus) had highest amounts of Cr and Zn; T6 (Karii) which is the next sampling point after Kutus downstream had highest values of Ni, As and Se suggesting that there may be activities in and/or around Kutus town that contributeing to higher amounts of these heavy metals in the sediment. During dry season, the average content of Cd, Pb, Zn, As and Se in sediment were below the limit set by WHO and US EPA but the average contents of Cr, Ni and Mn were above the limits.

The current study obtained mean amount of Pb of 3.2669±4.7021 mg/kg during dry season which is much lower than 22.95±15.11 mg/kg that was reported by Gathumbi and collaborators on a study carried out in the same area [56]. This may be an indication that lower quantities of Pb may be finding their way in river Thiba since petrol powered water pumps that are usually placed next to the river use unleaded petrol. Moywaywa reported higher mean amounts of Mn, Zn and Pb in sediment from Thika river [57] implying that Thika river could have been more polluted with these heavy metals than Thiba river. Omondi [58] reported lower amount of Mn, close amount of Ni and higher amounts of Cr, Zn, Pb and As in sediment from river Nzoia showing that river Thiba sediment was less polluted than river Nzoia.

3.3 Heavy Metals in Water of River Thiba from Kiumbu to Ndiara During Rainy Season

The amounts of selected heavy metals in water sampled along river Thiba during rainy season are given in Table 3.

Table 3: Amount of Selected Heavy Metals (ppm) in Water Along River Thiba during Rainy Season

Point	Cd	Cr	Ni	Pb	Zn	As	Mn	Se
C2	0.0003± 0.00004	0.1536± 0.00015	1.9008± 0.00073	0.0038± 0.00006	BDL	0.0074± 0.00003	6.8320± 0.00052	0.0092± 0.00004
C1	0.0004± 0.00003	0.1768± 0.00071	0.8468± 0.00031	0.0135± 0.00004	BDL	0.0014± 0.00008	1.3190± 0.00028	BDL
T1	BDL	BDL	BDL	BDL	BDL	0.0001± 0.00001	0.0177± 0.00002	BDL
T2	0.0004± 0.00002	0.1214± 0.00033	3.2534± 0.00062	0.0085± 0.00002	BDL	0.0060± 0.00003	3.2295± 0.00043	0.0138± 0.00003
T3	0.0003± 0.00006	0.1927± 0.00024	2.0554± 0.00035	0.0141± 0.00005	BDL	0.0048± 0.00004	3.4972± 0.00035	0.0092± 0.00002
T4	0.0001± 0.00005	0.0960± 0.00004	1.1054± 0.00039	0.0163± 0.00007	BDL	0.0025± 0.00005	1.5181± 0.00022	BDL
T5	BDL	BDL	0.0701± 0.00006	0.0024± 0.00001	BDL	0.0003± 0.00006	0.2879± 0.00014	0.0004± 0.00008
T6	0.0002± 0.00001	0.0561± 0.00007	0.4881± 0.00053	0.0244± 0.00002	BDL	0.0020± 0.00005	1.4682± 0.00044	0.0058± 0.00007
T7	0.0001± 0.00001	0.1196± 0.00067	0.3455± 0.00044	0.0999± 0.00005	BDL	0.0004± 0.00003	0.2959± 0.00048	BDL
T8	BDL	BDL	BDL	0.1243± 0.00007	BDL	0.0001± 0.00008	0.0183± 0.00003	BDL
Mean	0.0002± 0.0002	0.0916± 0.0741	1.0066± 1.0849	0.0434± 0.0554	BDL	0.0025± 0.0027	1.8484± 2.1484	0.0038± 0.0052
Limit	0.005	0.05	0.1	0.015	5.0	0.01	0,1	0.01

DOI: 10.31695/IJASRE.2024.8.9

The concentration of Cd in river Thiba water from Kiumbu (C2) to Ndiara (T8) during rainy season varied between BDL and 0.0004±0.00003 (C1) ppm and had a mean of 0.0002±0.0002 ppm. Cr concentration ranged from BDL to 0.1927±0.00024 (T3) ppm with a mean of 0.0916±0.0741 ppm. Nickel concentration varied from BDL to 3.2534±0.00062 (T2) ppm with an average of 1.0066±1.0849 ppm. Concentration of Pb ranged between BDL and 0.1243±0.00007 (T8) ppm and had an average of 0.0434±0.0554 ppm. The concentration of Zn in all the sampling points along river Thiba course was BDL. As concentration was ranging from 0.0001±0.00008 (T8) ppm to 0.0074±0.00003 (C2) ppm and had a mean of 0.0025±0.0027 ppm. Mn had concentration varying from 0.0177±0.00002 (T1) ppm to 6.8320±0.00052 (C2) ppm and a mean of 1.8484±2.1484 ppm. Whereas the concentration of Se ranged between BDL and 0.0138±0.00003 (T2) ppm with a mean of 0.0038±0.0052 ppm. The mean concentrations of the heavy metals in water along river Thiba upstream from Kiumbu to Ndiara during wet season decreased in the order Mn>Ni>Cr>Pb>Se>As>Cd>Zn. It was observed that there was no trend in increase or decrease in concentrations of the heavy metals in water sampled from river Thiba water either downstream or upstream between Kiumbu and Ndiara during the rainy season.

The sampling point T2 (Ndindiruku) had the highest concentration of Ni and Se whereas sampling point C2 (Kiumbu) had the highest concentrations of As and Mn. It was noted that at sampling point T1 (Kakawa), the concentration of Cd, Cr, Ni, Pb, Zn and Se were BDL. Similarly, it was noted that the concentration of Zn in water from all the sampling points along river Thiba was BDL. During the rainy season, the mean concentrations of Cr, Ni, Pb and Mn in the river water were above WHO and KEBS/WASREB permissible limit but the mean concentrations of Cd, Zn, As and Se fell below the limits. This study obtained lower concentrations levels of Pb and Cd than the ones reported by Wasike and collaborators [60] on water of Kuywa river during wet season. [60] also reported lower level of Mn than what is reported in this study. Muiruri and collaborators [61] reported very close concentration levels of Pb and Cd, lower levels of Ni, Cr and Mn and higher level of Zn in river water from Athi-Galana-Sabaki tributaries during wet season compared to what is reported in the current study.

3.4 Heavy Metals in Water of River Thiba from Kiumbu to Ndiara During Dry Season

The concentration of selected heavy metals in water sampled along river Thiba during dry season are given in Table 4.

Table 4: Amount of Selected Heavy Metals (ppm) in Water Along River Thiba during Dry Season

Point	Cd	Cr	Ni	Pb	Zn	As	Mn	Se
C2	BDL	BDL	BDL	0.0186± 0.00005	BDL	0.0000	0.0067± 0.00001	BDL
C1	BDL	BDL	BDL	0.0022± 0.00003	BDL	BDL	0.0061± 0.00003	BDL
T1	BDL	BDL	BDL	0.0011± 0.00003	BDL	0.0001± 0.00002	0.0096± 0.00001	BDL
T2	BDL	BDL	BDL	0.0130± 0.00005	BDL	BDL	0.0040± 0.00003	BDL
T3	BDL	BDL	BDL	0.0038± 0.00007	BDL	BDL	0.0093± 0.00004	BDL
T4	BDL	BDL	BDL	0.0032± 0.00008	BDL	0.0000	0.0037± 0.00006	BDL
T5	BDL	BDL	BDL	0.0077± 0.00006	BDL	0.0000	0.0066± 0.00006	BDL
T7	BDL	BDL	BDL	0.0048± 0.00004	BDL	0.0001± 0.00008	0.0083± 0.00005	0.0000
T8	0.0073± 0.00005	BDL	BDL	0.0069± 0.00008	BDL	0.0000	0.0085± 0.00008	BDL
Mean	BDL	BDL	BDL	0.0068± 0.0057	BDL	0.00002± 0.00004	0.0070± 0.0021	BDL
Limit	0.005	0.05	0.1	0.015	5.0	0.01	0.1	0.01

DOI: 10.31695/IJASRE.2024.8.9

During the dry season, the concentration of cadmium in river Thiba water from Kiumbu to Ndiara was BDL for the all sampling points except T8 (Ndiara) where the concentration was 0.0073±0.00005 ppm. The concentrations of chromium, nickel, zinc and selenium was also BDL for all the sampling points except selenium at T7 whose concentration was 0.0000 ppm. The concentration of lead was ranging between 0.0011±0.00003 (T1) ppm and 0.0186±0.00005 (C2) ppm and had an average of 0.0068±0.0057 ppm. The concentration of arsenic was varying from BDL to 0.0001±0.00002 (T1) ppm with a mean of 0.0068±0.0057 ppm while the concentrations of manganese was ranging from 0.0037±0.00006 (T4) ppm to 0.0096±0.00001 (T1) ppm with a mean of 0.0070±0.0021 ppm. The mean concentrations of the heavy metals in water along river Thiba upstream from Kiumbu to Ndiara during dry season decreased in the order Mn>Pb>Cd>As>Cr/Ni/Zn/Se. It was observed that most sampling points in the river had the heavy metal concentrations BDL apart from lead, manganese and arsenic (at some sampling points) which recorded low concentrations.

During the dry season, the mean concentrations of all eight heavy metals fell below WHO and KEBS/WASREB limit [16, 62] implying that the river water was not polluted with these metals. The study obtained lower concentrations levels of Pb, Cd and Mn than those reported on water of Kuywa river during dry season [60]. Muiruri and collaborators reported higher concentration levels of Ni, Mn, Zn, Cd and Cr in water from Athi-Galana-Sabaki tributaries during dry season [61] compared to findings of this study indication that river Thiba is less polluted compared to these rivers. The study [61] reported concentration of lead in the tributaries water that was close to what is reported in this study.

4.0 CONCLUSION AND RECOMMENDATIONS

Sediment from rivers Thiba contained all the eight heavy metals at varying levels. During both rainy and dry seasons, the mean amounts of Cd, Pb, Zn, As and Se were found to be below the permissible limit of WHO and US EPA for unpolluted sediment but the mean amounts of Cr, Ni and Mn were above the limits. During rainy season, the mean concentrations of Cd, Zn, As and Se in water were below the permissible limit set by WHO and KEBS/WASREB but Cr, Ni, Pb and Mn mean amounts were above the limits. However, during dry season, all the eight heavy metal mean amounts in water from the river 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). It is recommended that people should avoid drinking water from river Thiba during rainy season and further studies require to be conducted to determine other water parameters (physical, biological and chemical) to confirm whether water from this river is potable.

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