

Levels of Heavy Metals in Water, Fish (*Oreochromis niloticus*) and Sediment from the Afram River, Ghana

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Original Research Article

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Article History

Received: 10.03.2018

Accepted: 20.03.2018

Published: 30.03.2018

DOI:

10.21276/haya.2018.3.3.7



Abstract: In aquatic ecosystems, metal concentrations are monitored by measuring the levels in fish, water and sediments. Contribution of heavy metals in the water bodies include industrial effluents, fossil fuels burning, agricultural runoffs, geological weathering domestic waste and human and animal excretions. Water, sediment and fish samples from the river were used to assess the levels of heavy metals concentration in the river. The objective of this study was to measure the concentration of levels of the heavy metals (Cd, Co, Cr, Zn, Pb, Cu, Fe, Mn and Ni) in samples of water, fish (*Oreochromis niloticus*) and sediments from Afram River. Heavy metal concentration and selected physicochemical parameters (Electrical conductivity, Temperature, TDS and pH) of the water samples were determined. Levels of the heavy metals (Cd, Co, Cr, Zn, Pb, Cu, Fe, Mn and Ni) in water, fish (*Oreochromis niloticus*) and sediments from Afram River were determined using VARIAN AA 240FS-Atomic Absorption Spectrometer in an acetylene- air flame. In the fish (*Oreochromis niloticus*) samples, the highest concentrations of 50.46 mg/kg, 34.18 mg/kg, and 15.60 mg/kg were recorded for the metal Fe in the fish gills, bones and muscles respectively whereas the lowest concentration of < 0.08 mg/kg was recorded for the metal Cd in the gills, bones and muscle. The concentration of 0.455 mg/L was highest for the Pb metal in the water sample and a lowest of <0.002 mg/L for Co. In the sediment, Fe recorded the highest concentration of 167.03 mg/kg and a lowest concentration of < 0.027 mg/kg in Cd. The concentration of Mn and Pb in fish samples exceeded the WHO acceptable limit. The concentrations of the metals Pb and Ni in the water were also higher than the WHO permissible limit. The physicochemical parameters pH, conductivity, temperature and TDS which were measured for the water were also within the limit. In the sediments, Fe recorded the highest whilst Cd recorded the least concentration.

Keywords: Heavy metals, Afram River, Cadmium, lead, Manganese, Nickel, Chromium, Iron, Cobalt, Copper, Zinc, Sediment, water and Fish.

INTRODUCTION

In recent times, environmental issue such as pollution of water bodies with heavy metal has become a great concern. In river water, the existence of toxic metals affects the local people's lives based on the daily requirements [1]. Almost all surface waters play a major role in the economy of some inhabitants and are used in artisanal fisheries [2]. Surface waters in Ghana serve a valuable means such as absorbing floodwaters and protecting biodiversity [3]. Throughout the world, marine resources, rivers, estuaries, lakes, coastal systems are at risk by the issues of water pollution which include siltation, heavy metals, acidification, eutrophication and toxins (pesticides, POPs). They bring about contamination of downstream and marine ecosystems, ecosystem dysfunction, and loss of biological diversity and alteration of aquatic habitats [4].

In many developing countries, contamination of a river with heavy metals is a serious water quality issue due to the fact that population growth and urbanization has not kept pace with improvement in water and sanitation [5].

According to Burger *et al.*, [6], fish in aquatic systems have been established to be good bioindicators of heavy metal contamination due to the fact that they are at distinct trophic levels and are unlike in sizes and ages.

Afram River is a major source of water for people living in southern Ghana. The rapid population growth along the Afram River has necessitated proper conservation and efficient utilization of freshwater body, Afram River for sustainable development. This is necessary because of the increase in road construction, charcoal burning, municipal waste disposal and farming

activities found within the Afram catchment area has the potential to deteriorate the water quality. The ecosystem could be polluted by toxic metals from these activities. In Ghana, surface waters are deteriorating due to heavy metals pollution [7]. As a result of these anthropogenic influences on the Afram River, it has become necessary to investigate the levels of heavy metals in the fish, sediment and water from Afram River.

REVIEW OF LITERATURE

Water pollution

Olaniran [8] defined water pollution as water that it is not fit for drinking, cooking, bathing or other uses as a result of excessive amounts of pollutants. The quality of water sources is decreasing worldwide due to the pollution of water resources associated with resource depletion, increasing populations, industrialization, and urbanization [9].

Almost all surface waters play a major role in the economy of some inhabitants and are used in artisanal fisheries [2]. Surface waters in Ghana serve a valuable means such as absorbing floodwaters and protecting biodiversity [3].

Impact of water pollution on ecosystems

Throughout the world, marine resources, rivers, estuaries, lakes, coastal systems are at risk by the issues of water pollution which include siltation, heavy metals, acidification, eutrophication and toxics (pesticides, POPs). They bring about contamination of downstream and marine ecosystems, ecosystem dysfunction, loss of biological diversity and alteration of aquatic habitats [4].

Heavy metals

Duffus [10] defines heavy metals as group of metalloids and metals with an atomic density greater than 4 g/cm^3 . Heavy metals are persistent environmental contaminants and are natural constituents of the earth crust [11, 12].

Metals such as zinc, copper are classified as essential metals due to the fact that they play a role in biological systems. On the other hand, metals such as lead, cadmium become toxic in small quantities and are therefore non-essential metals [13]. Human activities that release heavy metals into the environment according to Alloway [14] include fossil fuel combustion, metallurgical industries, pesticides and fertilizers, mining and smelting.

MATERIALS AND METHODS

By maintaining a distance of about 30 cm, from the river bank twelve sediment samples were collected from twelve points in the river. At about 15 cm, the Eckman bottom grab sampler was dropped to the bottom of the river and the sediment samples were collected, at each sampling points. The top of the sediments was sampled and loaded in pre-cleaned labelled, airtight polyethylene bags. In a thermo-insulated box, the sediment samples were stored on ice, and transferred to the laboratory for preparation and analysis. No preservatives were added to the samples.

Twelve (12) fresh fish (*Oreochromis niloticus*) samples were bought from the fishermen directly along the Afram River (Table-1). The fish (*Oreochromis niloticus*) samples were conveyed to the laboratory after arranging them in polyethylene bags and loaded on ice blocks in a thermo insulator box. Prior to preparation, the fish samples were washed with deionized water, labelled and frozen.

Table-1: The weights, width and lengths of the fish (*Oreochromis niloticus*) samples

Fish sample	Weight (g)	Width (cm)	Length (cm)
F1	132.4	8	15
F2	240.6	10	18
F3	235.6	10	18
F4	131.7	9	16
F5	202.5	9	18
F6	155.1	8	16
F7	165.1	8	16
F8	201	9	18
F9	130.5	7.5	16
F10	140.5	8	16
F11	150.2	8	16
F12	129.6	7	15

For the water samples, pre-conditioning of the sampling bottles was done with 5 % nitric acid and rinsed with distilled de-ionized water. With hand gloves, sampling was done facing the direction of the flow of the river. At about 10 cm below the water

surface, the pre-cleaned polyethylene sampling bottles were immersed. At each sampling point of about 40 cm apart, 500 ml of the water samples were taken. Temperature and pH were measured on site. At each of the twelve sampling points, two sets of water samples

were collected; one was for the physicochemical parameters and the other for trace element analysis. To discourage the formation of precipitates and keep the metal ions in the dissolved state, the water samples for trace metal analysis was acidified with 1 % nitric acid. The samples were kept over ice in an ice chest and transported to the laboratory.

Sample preparation

The fish, sediment and the water samples were digested according to the procedure described by Hoenig and de Kersabiec [15]. 0.50g of fish sample (gills, bones and muscle) was weighed into a previously acid washed labelled 100 ml polytetrafluoroethylene (PTFE) Teflon bombs. 6 ml of 30 % concentrated nitric acid (HNO_3), and 1ml of 30 % hydrogen peroxide (H_2O_2), was added to each sample in a fume chamber. The samples were then loaded on the microwave carousel. The vessel caps were secured tightly using a wrench. The complete assembly was microwave irradiated for 22 minutes using milestone microwave lab station ETHOS 900. The completely digested samples were allowed to cool to room temperature and the volume made up to 20 ml.

0.2g of sediment sample was weighed into a labelled 100 ml polytetrafluoroethylene (PTFE) Teflon bombs which was earlier washed with acid. 4 ml of 96 %, sulphuric acid (H_2SO_4), 2 ml of 40 % hydrofluoric acid (HF), were added in a fume chamber to each sample. Afterward, the samples were packed on the microwave carousel. Using a wrench, the vessel caps were fastened. Using milestone microwave lab station

ETHOS 900, the complete assembly was microwave irradiated for 21 minutes. The completely digested samples were allowed to cool to room temperature and the volume made up to 20 ml.

5.0g of water sample were weighed into 100 ml polytetrafluoroethylene (PTFE) Teflon bombs which was earlier washed with acid and labelled. In a fume chamber, 6 ml of 65 % concentrated nitric acid (HNO_3), 3 ml of 35 % concentrated hydrochloric acid (HCl) and 0.25 ml of 30 % hydrogen peroxide (H_2O_2) were added to each individual sample. Unto the microwave carousel, the samples were then loaded. Using a wrench, the vessel caps were fastened. For 26 minutes, using milestone microwave lab station ETHOS 900, the entire assembly was microwave irradiated.

METAL ANALYSIS

With double distilled water, the digesterate was top to 20 ml mark and assayed for the presence of Zinc (Zn), Lead (Pb), Copper (Cu), Cobalt (Co), Chromium (Cr), Cadmium (Cd), Iron (Fe), Manganese (Mn) and Nickel (Ni) using VARIAN AA 240FS- Atomic Absorption Spectrometer in an acetylene-air flame. With the same conditions as the samples, reference standards used for the elements of interest, blanks and duplicates of samples were digested. Digestion of the reference standards and blanks were done under the same conditions as the samples.

Duplicates: To check the reproducibility of the method used. Working conditions for the analysis of heavy metals by AAS is presented in table-2.

Table-2: Working conditions for the analysis of trace elements by atomic absorption spectrophotometer

ELEMENT	WAVELENGTH nm	LAMP CURRENT nA	SLIT WIDTH nm	FUEL	SUPPORT
Zn	213.9	5	1.0	ACETYLENE	AIR
Pb	217.0	5	1.0	ACETYLENE	AIR
Cu	324.7	4	0.5	ACETYLENE	AIR
Fe	248.3	5	0.2	ACETYLENE	AIR
Mn	279.5	5	0.2	ACETYLENE	AIR
Cr	357.9	7	0.2	ACETYLENE	AIR
Ni	341.5	4	0.2	ACETYLENE	AIR
Cd	326.1	4	0.5	ACETYLENE	AIR
Co	345.4	7	0.2	ACETYLENE	AIR

Determination of physicochemical parameters

The pH and temperature were determined on site. The pH of the samples was measured using a WAG-WE30200 pH meter and temperature with a digital thermometer. The Electrical conductivity and

Total Dissolved Solids of water samples was measured using the WAG-WE30210 Bench conductivity/TDS meter.

RESULTS

Table-3: Data for Physicochemical parameters of the water sample

PARAMETER	MINIMUM	MAXIMUM	MEAN±SD
pH	6.01	6.51	6.33±0.15
TEMPERATURE(°C)	25.0	25.5	25.3±0.17
TDS(mg/L)	54.4	56.9	55.2±0.91
CONDUCTIVITY(μS/cm)	108.9	112.1	110.4±1.61

The temperature ranged from $25.0^{\circ}\text{C} \pm 0.17$ to $25.5^{\circ}\text{C} \pm 0.17$ (Table-3) with the lowest of 25.0 ± 0.17 and highest of 25.5 ± 0.17 . The pH values obtained were acidic. It varied between 6.01 – 6.51. pH value of 6.01 was the least while the highest pH of 6.51 was obtained (table-3).

The lowest Electrical conductivity, EC was $108.9 \mu\text{S}/\text{cm}$ whereas the highest EC of $112.1 \mu\text{S}/\text{cm}$ was obtained. The EC varied between $108.9 \mu\text{S}/\text{cm}$ to $112.1 \mu\text{S}/\text{cm}$ with a mean of $110.4 \pm 1.61 \mu\text{S}/\text{cm}$ (table 3). The mean total dissolved solid, TDS of the Afram

River was below $1000 \text{ mg}/\text{L}$. The highest TDS was $56.9 \text{ mg}/\text{L}$ and the lowest was $54.4 \text{ mg}/\text{L}$ (table 3).

Metal concentration in sediment

The mean levels of 0.77 ± 0.31 , 1.87 ± 0.30 , $<0.03 \pm 0$, 0.89 ± 1.66 , 9.39 ± 5.81 , 2.29 ± 0.56 , 1.42 ± 0.69 , 167.03 ± 3.42 , $0.39 \pm 0.27 \text{ mg}/\text{kg}$ were recorded for the heavy metals Co, Cr, Cd, Cu, Mn, Pb, Zn, Fe and Ni in the sediment respectively.

The highest value of $167.03 \pm 3.42 \text{ mg}/\text{kg}$ was recorded for the metal, Fe and the metal Ni recorded the least concentration of $0.39 \pm 0.2739 \text{ mg}/\text{kg}$ (table-4).

Table-4: Mean metal concentrations in sediment (mg/kg)

METALS	Range	Mean \pm SD	IAEA Standard
Fe	163.2-171.98	167.03 ± 3.42	25700
Mn	3.11 – 16.36	9.39 ± 5.81	631
Cu	$<0.04 - 4.96$	0.89 ± 1.66	11
Pb	1.40 – 2.99	2.29 ± 0.56	60
Cd	<0.027	$<0.03 \pm 0$	1.3
Cr	1.45 – 2.36	1.87 ± 0.30	60
Co	0.17 – 1.07	0.77 ± 0.31	8.9
Zn	0.29 – 3.73	1.42 ± 0.69	104
Ni	$<0.01 - 0.76$	0.39 ± 0.27	26

Metal concentration in the water

The average concentration was 0.455 ± 0.16 , 0.008 ± 0.1 , $<0.008 \pm 0$, 0.132 ± 0 , 23 , $<0.004 \pm 0$, 0.148 ± 0.53 , $<0.012 \pm 0$, 0.032 ± 0.05 , $<0.002 \pm 0 \text{ mg}/\text{L}$ for the metals Pb, Cr, Cd, Fe, Zn, Ni, Cu, Mn and Co

respectively. All the metals analysed were present in the water. The highest concentration of $0.455 \pm 0.16 \text{ mg}/\text{L}$ was recorded for the metal Lead. The metal Cobalt recorded the least concentration of $<0.002 \pm 0 \text{ mg}/\text{L}$ (table-5).

Table-5: Mean metal concentrations in water (mg/l)

METALS	Range	Mean \pm SD	WHO Standard
Fe	$<0.024 - 0.748$	0.132 ± 0.23	1.0
Mn	$<0.008 - 0.200$	0.032 ± 0.05	0.1
Cu	<0.012	$<0.012 \pm 0$	2
Pb	0.200– 0.616	0.455 ± 0.16	0.01
Cd	<0.008	$<0.008 \pm 0$	0.003
Cr	$<0.004 - 0.020$	0.008 ± 0.01	0.05
Co	<0.002	$<0.002 \pm 0$	-
Zn	<0.004	$<0.004 \pm 0$	3
Ni	0.04– 0.208	0.148 ± 0.53	0.07

Metal concentration in fish

The mean concentration of heavy metals in the fish samples (gills, muscle and bones) are presented in table 6. With the gills, the highest concentration of $50.46 \pm 24.99 \text{ mg}/\text{kg}$ was recorded for metal Fe and the lowest concentration of $<0.08 \pm 0 \text{ mg}/\text{kg}$ was recorded for metal Cd.

With the Bones, metal Fe recorded the highest concentration of $34.18 \pm 13.27 \text{ mg}/\text{kg}$ whereas Cd was lowest concentration at $<0.08 \pm 0 \text{ mg}/\text{kg}$. The muscles

recorded highest concentration of $15.60 \pm 1.91 \text{ mg}/\text{kg}$ for the metal Fe and lowest concentration of $<0.08 \pm 0 \text{ mg}/\text{kg}$ for Cd. The concentrations of the metals Fe, Mn, Cu, Pb, Cd, Cr, Co, Zn, Ni were 50.46 ± 24.99 , 12.61 ± 4.82 , 0.35 ± 0.18 , 2.91 ± 1.47 , $<0.08 \pm 0$, 3.20 ± 0.08 , 1.25 ± 0.82 , 2.97 ± 0.76 , $2.77 \pm 1.15 \text{ mg}/\text{kg}$ for the gills, 15.60 ± 1.91 , 0.32 ± 0.16 , 0.20 ± 0.16 , 2.47 ± 1.29 , $<0.08 \pm 0$, 2.56 ± 0.65 , 1.41 ± 0.66 , 2.17 ± 0.12 , $2.18 \pm 0.77 \text{ mg}/\text{kg}$ for the muscles and 34.18 ± 13.27 , 13.59 ± 4.67 , 0.64 ± 0.16 , 1.97 ± 1.04 , $<0.08 \pm 0$, 4.08 ± 0.28 , 0.64 ± 0.35 , 2.46 ± 0.25 , $2.69 \pm 0.47 \text{ mg}/\text{kg}$ for the bones respectively.

Table-6: Mean metal concentrations in Tilapia fish (gill, bones and muscles)/ mg/kg

METALS FISH	RANGE	MEAN \pm SD	REFERENCE
Fe			
Gills	31.32 – 93.20	50.46 \pm 24.99	-
Muscle	12.44 – 17.24	15.60 \pm 1.91	
Bones	19.92 – 58.56	34.18 \pm 13.27	
Mn			0.5 (WHO, 1985) [54]
Gills	5.08 – 18.0	12.61 \pm 4.82	
Muscle	0.08 – 0.92	0.32 \pm 0.36	
Bones	7.04 – 18.92	13.59 \pm 4.37	
Cu			30(WHO, 1989) [55]
Gills	0.12 – 0.56	0.35 \pm 0.18	
Muscle	0.12 – 0.48	0.20 \pm 0.16	
Bones	0.44-0.92	0.64 \pm 0.16	
Pb			0.5(FAO/WHO, 1989) [55]
Gills	1.52 – 5.24	2.91 \pm 1.47	
Muscle	0.72- 4.12	2.47 \pm 1.29	
Bones	0.60- 3.60	1.94 \pm 1.04	
Cd			0.5 (FAO/WHO, 1989) [55]
Gills	<0.08 - <0.08	<0.08 \pm 0	
Muscle	<0.08 - <0.08	<0.08 \pm 0	
Bones	<0.08 - <0.08	<0.08 \pm 0	
Cr			12-13(USFDA, 1993a) [50]
Gills	2.28 – 3.84	3.20 \pm 0.68	
Muscle	1.6 – 3.28	2.56 \pm 0.65	
Bones	3.64 – 4.4	4.08 \pm 0.28	
Co			
Gills	0.04 – 2.32	1.25 \pm 0.82	
Muscle	0.88 – 2.48	1.41 \pm 0.66	
Bones	0.04 – 1.0	0.64 \pm 0.35	
Zn			40(FAO/WHO, 1989) [55]
Gills	2.04 – 3.96	2.97 \pm 0.76	
Muscle	2.0 – 2.28	2.17 \pm 0.12	
Bones	2.12 – 2.72	2.46 \pm 0.25	
Ni			70-80 (USFDA1993b) [51]
Gills	1.04 – 4.0	2.77 \pm 1.15	
Muscle	1.24 – 3.12	2.18 \pm 0.77	
Bones	2.08 – 3.0	2.69 \pm 0.47	

DISCUSSION

Physicochemical parameters

The values obtained in this study were within the acceptable levels of physiology, survival and metabolism of aquatic organisms in the waterbody. Plant growth could either be affected positively or negatively by the temperature of the water. A plant grows well under water temperature between 20-35°C. Plants decay and growth regression can be observed as result of temperature over 30°C [16].

The measured pH at the Afram River compares quite favourably with studies conducted by Opoku-Duahet *al.*, [17] who conducted studies on the determination of water requirements for producing irrigated rice and other crops in the Afram River Valleybottom at Afram, Ghana

The pH value of 6.01 was the lowest whereas the highest pH of 6.51 was obtained. The pH values ranged from 6.01 – 6.51. WHO [18] limit for pH is 6.5 to 8.5. According to PCTU [19], a pH that is not within this limit reduces biological diversity in a river. The obtained pH values was with the acceptable limit. When pH is low, it becomes harmful to immature fish and insects and extreme also make a river hostile to life in the river [20].

A study by Amakye [21] revealed maximum TDS and conductivity values of 69.4 mg/L and 142 compared to the maximum TDS and conductivity values of 56.9 mg/L and 112.1 recorded in this study. When the Electrical Conductivity is high, then contaminants are present [22]. In this study the mean EC was 110.4 \pm 1.61 μ S/cm. This was below the WHO [18] limit of 700 μ Scm⁻¹ for drinking potable water. Based on this parameter, this river is suitable for

domestic use. The levels recorded could be attributed to anthropogenic activities such as farming, road construction, charcoal burning and municipal waste disposal. Temperature affects conductivity, the warmer the water, the higher the conductivity [19].

At TDS levels greater than about 1000 mg/L, drinking water becomes notably and increasingly unpleasant to taste. TDS greater than 1200 mg/L may cause consumers to reject the water source and could have some effects for those who need to control their daily salt intake e.g renal dialysis [23]. The TDS range, 54.4 mg/L to 56.9 mg/L was far below 1000 mg/L and is therefore suitable for domestic use. According to Dhembareet *al.*, [24], dissolved solids in the water may be due to inorganic salt, organic matter and dissolved gas. The levels recorded for the study could be attributed to municipal waste disposal and farming activities along the river.

Metal concentration in water sample

The findings of this study (Zn, Cu and Cd in water) appear to be in conformity with the findings of Hagan *et al.*, [25] who conducted studies at the Densu River Basin. The heavy metal concentrations of Zn, Cu and Cd in water was within the WHO recommended limits for drinking water, similar to the findings of this research. Karikari *et al.*, [26] also reported that the heavy metal levels in the Densu River were below WHO guideline (Cu, Zn,) hence there was no danger with respect to these metals.

Akotoet *al.*, [27] conducted studies in the streams serving the Owabi reservoir. The concentrations of Copper were similar to the finding of this research in almost all the sampling. The metals found in this research were in traces and values below WHO [28] recommended values for freshwater (table-5).

Heavy metals could be introduced into the river as a result of the intense river fishing activities from sources such as fuel leakages and fumes from outboard motors of the fishing boats.

The metals lead and Nickel were higher than the levels specified by WHO [28] for water sources utilized for various purposes. It was observed that Pb exceeded the fisheries and aquatic life recommended values for drinking water, 0.007 - 0.01 mg/L [29].

The mean Pb value was 0.455 ± 0.16 mg/L. This exceeded the limit. The high level of lead could be attributed to the paint coatings on the fishing boats which are used for fishing and as a means of transport on the river. Paint chips, used ammunition, fertilizers, pesticides and lead-acid batteries or other industrial products and atmospheric lead (primarily from automobile emissions) are the major sources of lead going into an ecosystem [30]. Expectant and Pregnant

women who use the water sources are at serious risk. In drinking water, the high levels of lead may cause abortion in some cases and can be detrimental to developing foetus. Prolonged use of the affected water samples can cause risk of children and babies in the area, developing neurological problems and hearing impairment [31].

The value obtained for Copper in this study was 0.012 mg/ L and this was below the WHO [28] threshold of 2 mg/L. ATSDR [32] attributes it to the fact that in running water, levels of copper tend to be low than in standing water. This suggests that any adverse health effect arising from domestic use of the water is not expected. At excessive levels, it can cause anaemia, liver damage and disorders of bone although it is an essential element in human metabolism [33].

The metal Cobalt (Co) had low mean concentration of 0.77 ± 0.31 mg/ L. Natural sources such as weathering of rocks by the action of water and decomposition of plant waste may have resulted in the level recorded [34].

Heavy metals like Cu and Co at low concentrations are for many biological processes and enzymatic activity and are essential metals [35].

Metal concentration in sediment

Heavy metal levels in the sediment samples were higher than the overlying water. This is because sediment is a major depository of metals, in some cases holding up to 99% of the total amount of metals present in a system [36]. The highest concentration of 167.03 ± 0 mg/kg was recorded for the metal Iron, Fe in the sediment. This may be due to the fact that Fe is highly abundant in the earth crust. According to Vuori [37], it is found everywhere in all freshwater environments and in water and sediments, it often reaches appreciably high concentrations. Vertebrate studies have shown that high cellular concentration of Iron, Fe particularly ferrous iron, may cause degeneration [37].

The findings of this study appear to be in conformity with the findings of Tayet *al.*, [38] who conducted studies on the heavy metals levels in water and sediment from the Sakumono II and Muni Lagoons. The concentrations recorded for Iron was the highest with respect to the other metals zinc, lead, cadmium and manganese. This was similar to the finding of this research in all the sampling. All the metals were however below IAEA recommended values.

In the river sediments, the Levels of trace metals measured could be attributed to the discharge of domestic waste. The levels of Co could be attributed to debris from run-off and discharge of municipal waste into the river. These may be carried to the river as runoff or by eroding soil or percolating or leaching through the soil [39].

Cadmium concentrations in sediment were the lowest. Cadmium is an important factor in aquatic monitoring studies, because it has been found to be toxic to fish and other aquatic organisms [40]. Thus, the indiscriminate dumping of refuse into the river in the catchment area could have accounted for the levels measured.

The concentration of Nickel was also low and the possible sources of Ni in surface water include old battery wastes, components of automobiles, old coins, and many other items containing stainless steel and other Ni alloys [39].

In this study, the levels of Chromium measured may have originated from weathering of rock, wet precipitation and the dry fallout from the atmosphere.

The levels of Manganese recorded in the sediment may be due to the fact that, manganese occurs naturally in most surface waters and in soils that may erode into waters [39].

It has also been reported that metals such as Cd, Cu, Pb and Zn have a high tendency to binding tenaciously to the organic matter contained in the soil, sediment and suspended particles within the water column [41].

Metal concentration in fish

The gills recorded the highest concentration of Fe in fish samples. This could be attributed to the fact that the function of respiration is carried out by the gills and are directly in touch with water and pollutants that may be present in water. Thus, the concentration of trace metals in gills reflects the concentration of the trace metals in the water where the fish lives [42].

The presence of Mn may be due to natural geochemical processes such as weathering of Mn bearing minerals and rocks [43]. In addition, it's been used as a fuel additive for motor vehicles which is normally used along the coast for commercial or recreational activities and this could contribute to its presence. Other sources such as refuse dump sites and dust from the atmosphere cannot be overlooked for its contribution to the Mn levels.

The findings of this study appear to be in conformity with the finding of Animet *et al.*, [44] who conducted studies on the accumulation profile of heavy metals in fish samples from Nsawam, along the Densu River. The concentrations of iron, zinc, nickel, cadmium, cobalt and chromium were similar to the finding of this research in almost all the sampling. The metals were in below WHO [28] recommended values for fresh water except for manganese which recorded

high concentration above the WHO limit similar to this study.

The low levels of concentrations, 1.25 ± 0.82 mg/kg, 1.41 ± 0.66 mg/kg and 0.64 ± 0.35 mg/kg in the gills, muscles and bones respectively could be attributed to its high affinity to organic particles in solution [45].

The concentration of Cd in all fish samples was very low, <0.08 mg/kg in the fish gills, bones and muscles. However, it fell below the FAO [46] limit of 0.5 mg/kg. According to Sivapermal *et al.*, [47], cadmium ingestion between 10 to 326 mg records severe toxic symptoms.

The lowest concentration of 1.94 ± 1.04 was recorded for Pb in the fish bones whereas the highest concentration of 2.91 ± 1.47 was recorded in fish gills. This was above the FAO [46] guideline of 0.5 mg/kg (table-6). Accumulation of Lead in fish can be attributed to the fact that lead is naturally occurring on the surface water due to weathering of materials and soil erosion [48]. Lead is mainly from storage batteries, type metal and antiknock compound in petrol [49].

The mean concentration of Cr in fish samples (gills, muscle and bones) ranged from 2.50 – 4.08 mg/kg. The maximum guideline by USFDA [50] is 12-13 mg/kg. In all the fish samples, the Cr concentrations measured was lower than this limit.

The highest concentration, 2.77 ± 1.15 mg/kg was measured in gills of the fish with the lowest detectable concentration 2.18 ± 0.77 mg/kg measured in muscle. The USFDA [51] limit for Ni is 70-80 mg/kg. In all the samples, the concentrations of Ni were far below the acceptable limit. The presence of Nickel could be attributed to the fact that nickel is naturally found on surface water due to weathering of materials and soil erosion [48].

Excluding Cd and in relation to the other heavy metals, recorded very low concentration in the fish samples (gills, bones and muscle). It could be due to decomposition and plant residues [52].

The highest concentration, 2.97 ± 0.76 mg/kg was measured in Tilapia fish gills and the lowest concentration of 2.17 ± 0.12 mg/kg in the fish (*Oreochromis niloticus*) muscle. This was below the FAO/WHO acceptable limit of 40 mg/kg. Health complications such as neutropenia, fatigue and dizziness may occur due to continual use over a long time [53].

CONCLUSION

Generally, the heavy metals in the water, fish and sediment were all below the regulatory standards. The average levels of Pb and Ni in the water and Pb and Mn in the fish (*Oreochromis niloticus*) were higher than the WHO, FAO standards. However, Cu, Co, Cd, Cr,

Zn and Fe were within the limit. In the sediments, Fe recorded the highest concentration of 167.03 mg/kg whilst Cd recorded the least concentration of less than 0.027 (< 0.027). The high levels of Pb, Ni and Mn could be attributed to the paint coatings on the fishing boats which are used for fishing and as a means of transport on the river, fertilizers, pesticides and lead-acid batteries or other industrial products, atmospheric lead primarily from automobile emissions and natural geochemical processes such as weathering of Mn bearing minerals and rocks.

The physicochemical parameters such as pH, conductivity, temperature and TDS which were measured for the water were also within the limit. This makes it safe for drinking and for domestic purposes.

ACKNOWLEDGEMENT

We are grateful to the Ghana Atomic Energy Commission for allowing us to use types of equipment in their laboratory for this research work.

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