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Heavy Metals Concentration in Water, Sediment, and Fish around Escravos River, Nigeria

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Abstract— **This study investigates heavy metals concentration in water, sediment, and fish around Escravos River, Delta State, Nigeria. Health risks to human via consumption of *Clarias gariapinus* were assessed through mean daily dose and allowable weekly intake. Twenty-seven (27) surface water, sediment and fish samples were collected from three locations over a 3 months period. The results of heavy metals concentration in water, sediments and fish ranges from 0.058 ± 0.001 - 0.121 ± 0.002 mg/L for Zn, 0.054 ± 0.04 to 0.092 ± 0.003 mg/L for Cu, 0.014 ± 0.02 to 0.032 ± 0.001 for Cd, 0.008 ± 0.001 to 0.077 ± 0.001 mg/L for Pb, 0.043 ± 0.001 to 0.065 ± 0.001 mg/L for Ni, 0.110 ± 0.00 to 0.161 ± 0.003 mg/L for Fe respectively. High Fe concentration was noticed in sediment 383.5 ± 0.71 to 509.0 ± 1.41 mg/kg and in fish 320.8 ± 1.06 to 403.2 ± 2.82 mg/kg, respectively. The results show that Hazard quotient (HQ) values for Cu, Cd, Pb, Fe, Mn and Cr were greater than 1 (HQ>1). Furthermore, cancer risk values observed for Pb, in fish samples were below allowable limit of 1.0×10^{-4} indicating no chance of carcinogenic effects. However, cancer risk for Cd, Ni and Cr were above allowable limit of 1.0×10^{-4} indicating chance of carcinogenic effects. These findings show that there are appreciable health risks associated or connected with consuming *Clarias gariapinus*, ingestion of surface water and sediment.**

Index Terms- **Heavy Metals, Fish, Sediment, Health risk.**

I. Introduction

Heavy metals though they occur naturally, are increasing in the environment as a results of anthropogenic activities such as burning of fossils fuels, agricultural practices, mining and various other industries [1]. Heavy metals are regarded as a very common pollutants, and because of their toxicity, persistence and bioavailability they pose serious risk to human health and the environment [2]. Oil spill has been recognized as a likely source of heavy metals pollution [3]. Within the Nigerian economy oil production has continued to play dominant roles and oil spills are a frequent occurrence, particularly because of the extensive use of oil and petroleum products in our daily lives [4]. Accurate evaluation of the heavy metal contamination caused by oil spills is more urgent than that of organic pollution since heavy metals are toxic and persistent [5]. Water bodies and sediments suffer impacts from many of these sources and can carry pollutants to other sites [6]. Sediments which usually act as reservoir of these pollutants, interact directly with the environment, thus can serve as an important indicator of the effects caused by pollution and human activities [6]. Sediment is major component within the aquatic biological system which is a sink for heavy metals which are introduced into the aquatic environs. Consequently, sediment, where heavy metals tend to concentrate, could be a great source of contamination within the aquatic body [7]. Heavy metals are always present in waters from disintegration and due to run-off from anthropogenic sources [8]. Within the water body fish are also a major sink for heavy metals. They ingest and amasses heavy metals through bio-magnifications [9]. Within the aquatic environs, metals are exchanged to the fish through food chain which eventually is consumed by humans. Since, there are obviously high probabilities of bioconcentration and biomagnifications of heavy metals within the tissues of sea-going natural life, it is subsequently fundamental to access the concentrations of heavy metals in commercial fish to find out the hazard associated with human consumption. Heavy metal bioaccumulation can hugely harm both oceanic (aquatic) including earthly (terrestrial) environments [10]. Fish are utilized as bio-indicator of sea-going biological systems for estimation of heavy metal contamination and potential hazard for human utilization [11]. Several authors have studied heavy metal spatial distribution, impact to topsoil and vegetation around those point sources for establishing measures and estimating potential risks [12]. This study investigated heavy mental contamination to sediment, water and fish around an oil producing community and its impact on human health.

II. Materials and Methods

A. Study Area

The Study River is Escravos River (5°30'N, 5°5'E) of the Niger River within the western Niger delta, southern Nigeria. The area is mainly mangrove swamps and coastal sand edges. There are no ports on the waterway, but Escravos is connected by a labyrinth of interconnected conduits to the Forcados, Warri, Benin, and Ethiopia waterways and gets well over 4,000 mm (157.5 in) of rainfall annually. The main occupation of the residents is fishing and with a population of about 6000 people who are of Itsekiri ethnic group.

B. Research Design

Samples of sediment, water and fish were collected from three communities along Escravos flow stations. The sampling stations were chosen based on several oil related operations and proximity of the flow station to the communities. Heavy metals were measured with bulk scientific Atomic Adsorption Spectrophotometry (AAS). Statistical analysis was done using computer statistical packages.

C. Collection of water Samples

The study involved the use of 1L plastic containers and 500

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ml amber bottles for collection of water samples for heavy metals analysis. A total of twenty-seven (27) samples were collected consisting of three (3) samples from each study station from July – September 2018. The samples were fixed in-situ with Concentrated Nitric acid. All samples were stored in an icebox at 4 ^{o}C and transported to laboratory for extraction and analyses.

D. *Collection of Sediment Samples*

Three sample each were collected from locations close to three operating stations from July to September,2018. Samples were collected in plain sterile polyethylene packs employing a plastic pipe to scoop sediment. The sacks were sealed and transported in an ice chest to laboratory.

E. *Collection of Fish Samples*

Samples of fish (Clarias gariepinus) were collected directly from the water body around the Escravos waters utilizing fish nets in Delta State, Nigeria. Three samples per station environs were collected over a period of 3 months. The fish were named with a recognizable proof number and transported to the laboratory on the same day and stored at 4 ^{o}C.

F. *Digestion procedure for water sample*

Metal digestion was carried out using the milestone acid assimilation technique. Five millilitres of each water sample were pipetted into 20ml Teflon tube. Concentrated acids, 6 ml HNO3, 65%, 3ml HCl, 37% and 0.25ml H2O2 were added to each sample. The samples were set in ETHOS 900 microwave digester for 30min. After absorption, the samples were cooled. The fluid concentrate was then used for the heavy metal analysis using VARIAN AA240FS Fast Sequential AAS under prescribed instrument parameters.

G. *Digestion procedure for sediment sample*

Sediment samples (1.5g) were weighed into a 20 ml Teflon tube and concentrated acids of 6 ml HNO_3, 65%, 3 ml HCl, 37% and 0.25ml H_2O_2 were added to each sample. The specimen was set in an ETHOS 900 microwave digester in 30min and cooled. 5 ml of refined water was added to each sample which was filtered through a pipe with a Whatman No. 41 channel paper into 20 ml Teflon tube. The fluid concentrate was then utilized for heavy metal analysis using VARIAN AA240FS Fast Sequential AAS under prescribed instrument parameters.

H. *Fish Digestion*

The fish samples were washed with distilled water and dried for 24 hours at 105°C. After drying the fish samples, the bones and scales were removed while the muscle, head, tail, eyes, gills were utilized for the analysis. They were processed with a mortar and pestle before digestion. 2 g of the grounded fish samples was mixed with 5 ml of HNO3 and 2 ml of HCLO4 and was subjected to heat on a hot plate for 30 minutes at 85 °C. Digested samples were cooled and put into a 50 ml volumetric tube where distilled water were added. The filtrate was analysed using AAS.

I. *Health Risk Assessment*

Health risk assessments for heavy metals was calculated for mean daily dose, non-cancer danger index and cancer danger using procedures described in [13][14][15].

$$ADD = C * FIR * ED * EF / BW * AT \quad (1)$$

Where.
ADD (mg kg^{-1} day^{-1}) = the average dose contacted through ingestion.
EF = Exposure frequency 365 days/year.
ED = Exposure time equivalent to mean lifetime (60 years).
FIR =Fish Ingestion Rate
C = amount of metal contains in fish mg/kg.
BW = Body Weight
AT = average time of exposure of time.

Non-cancer Hazard Index

$$HQ = ADD / Rfd \quad (2)$$

Where;
HQ = Hazard quotient
Rfd = Reference dose factors

Cancer Risk (CR)

$$CR = ADD * SF \quad (3)$$

Sf = Slope Factor (1/mg/kg/day)

J. *Steady State Bioaccumulation Factor (BAF)*

Bioaccumulation factor (BF) was used to ascertain the amount of heavy metal accumulated in fishes using formula based on Babatunde et al., [16].

$$BAF = Concentration\ of\ metal\ in\ fish / Concentration\ of\ metal\ in\ sediment \quad (4)$$

BF is the ratio of metals concentration in fish to the concentration in sediment calculated using Microsoft Excel 2016. If the transfer factor is greater than 1.0 then bioaccumulation for metal occurs by fish species [17][18].

K. *Statistical Analysis*

Heavy metal results were analysed for simple descriptive (i.e mean, standard deviation, minimum and maximum values) and inferential statistics (Duncan Multiple Range Test, DMRT and correlation analysis) using SPSS for Windows (version 20.0).
Table 1 shows estimated reference values for RfD and SF while Table 2 is the risk assessment criteria.

Table 1 Estimated Reference Dose Factors (RfD) and Slope Factors (SF) [19]

Metals	RfD (mg/kg/day)	*SF $[(mg/kg/day)]^{-1}$
Arsenic (AS)	0.0003	1.5E+0
Cadmium (Cd)	0.0005	15
Magnesium (Mn)	0.14	-
Nickel (Ni)	0.011	9.1E-01
Lead (Pb)	0.0035	8.5E-03
Iron (Fe)	0.0026	-
Chromium (Cr)	0.003	5.0E-01
Copper (Cu)	0.04	-

Table 2 Levels and values of assessment standards

Risk grades	Range if risk value	Acceptability
Grade I	$<10^{-6}$	Completely accept
Grade II	10^{-6}, 10^{-5}	Not willing to handle risk
Grade III	10^{-6}, 5×10^{-5}	Do not consider risk
Grade IV	5×10^{-5}, 10^{-4}	Consider risk
Grade V	10^{-4}, 5×10^{-4}	Consider and willing to handle it
Grade VI	5×10^{-5}, 10^{-3}	Give close regard to risk and act to solve the issue
Grade VII (Extremely high risk)	$>10^{-3}$	Reject risk and must be solve

III. RESULT AND DISCUSSION

A. Heavy metals Distribution in water samples

The results obtained on the concentration of heavy metals in water samples are presented in Table 3. The concentration of Zinc (Zn) ranges from 0.059 ± 0.001 to 0.122 ± 0.002 mg/L while the concentration of Copper (Cu) ranges from 0.055 ± 0.04 to 0.094 ± 0.003 mg/L. The concentration of Cadmium (Cd) ranges from 0.013 ± 0.02 to 0.031 ± 0.001 mg/L with the lowest concentration observed in august at Station I while the highest was observed in August and September at Station II.

The mean concentration of lead (Pb) ranges from 0.008 ± 0.001 to 0.077 ± 0.001 mg/L while Nickel (Ni) ranges from 0.044 ± 0.001 to 0.063 ± 0.001 mg/L. Similarly, the amount of iron (Fe) ranges from 0.110 ± 0.00 to 0.161 ± 0.003 mg/L with the most elevated concentration recorded in September at Station II whereas the least was recorded in September at Station I. However, amount of As and Hg were below detection limit while amount of Vanadium was only detectable in two of the three sampled stations; Station II and Station III.

The mean comparison shows significant ($p<0.05$) differences in concentration of analysed heavy metals across the stations, Table 3.

B. Heavy Distribution in Sediment samples

The concentration of heavy metals in sediment samples recorded in study area are presented in Table 4. The concentration of Pb ranges from 10.3 ± 0.001 to 15.2 ± 0.1 mg/L while that of Cu ranges from 9.22 ± 0 .24 to 12.25 ± 0.35 mg/L, while the concentration of Cd ranges from 1.51 ± 0.01 to 2.56 ± 0.01 mg/L with the lowest concentration observed in August at Station I.. Average concentration of Pb ranged from 3.41 ± 0.01 to 5.05 ± 0.07 mg/L while Ni ranges from 4.11 ± 0.01 to 6.15 ± 0.07 mg/L. Similarly, amount of Fe ranges from 384.5 ± 0.71 to 509.0 ± 1.41 mg/L with highest recorded in July at Station II whereas lowest was recorded in July at Station III. Result also reveals concentration Mn in sediment sample ranges from 8.60±0.14 to 12.15 ± 0.21 mg/L. However, concentration of As and Hg were below detection limit while concentration of V ranges from 0.04 ± 0.00 to 0.085 ± 0.01 mg/L. The highest concentration V was seen in July at Station I whereas lowest was recorded in September at Station III.

The mean comparison shows significant ($p<0.05$) differences in amount of analysed heavy metals across the stations Table 4.

C. Heavy metals Distribution in Clarius garipinus.

The concentration of heavy metals in Clarius garipinus collected from the area studied are presented in Table 5. The concentration of Zn observed in fish samples ranges from 3.85 ± 0.07 to 7.15 ± 0.07 mg/L while the concentration of Cu ranges from 3.5 ± 0.00 to 5.3 ± 0.28 mg/L with the lowest observed in August at Station III while the highest was observed in August at Station I. However, the concentration of Cd was below recognition limit.

The mean concentration of Pb also ranges from 0.15 ± 0.00 to 0.31 ± 0.01 mg/L while Ni ranges from 2.85 ± 0.07 to 4.20 ± 0.00 mg/L. Similarly, concentration of Fe ranges from 320.75 ± 1.06 to 403.2 ± 2.82 mg/L with the highest and lowest value recorded in July and August respectively at Station II. Results also reveals concentration of Mn in the analysed fish samples ranges from 4.91 ± 0.02 to 7.23 ± 0.04 mg/L while Cr ranges from 2.06 ± 0.03 to 3.30 ± 0.28 with the least observed in August at Station II, and the highest in September at Station II. However, concentration of V, As and Hg were below detection limit across the study stations.

The mean comparison shows significant ($p<0.05$) differences in amount of analysed heavy metals across the stations Table 5.

D. Health Risk Assessment of Heavy Metals in Fish

The results of Mean Daily Dose, Non-carcinogen risk and Carcinogen risk (CR) assessment of the analysed metals in fish samples are shown in Table 6.

The ADD was evaluated from mean concentration of metals obtained in fish samples and calculation assumed that an adult weighed 60 kg consumes 24.7g fish daily in Nigeria [22].

The risk assessment showed Fe as the most dose (1.44E + 01 Mg^{-1} Kg^{-1} day^{-1} $bodyweight^{-1}$). This implies that an adult would have consumed 1.01 Mg^{-1} kg^{-1} day^{-1} $bodyweight^{-1}$ of Fe in one week.

Table 3 Concentration of heavy metals in water samples

	Station I			Station II			Station III		
Parameter (mg/L)	July	August	September	July	August	September	July	August	September
Zinc (Zn)	0.072±0.03^{b}	0.071±0.001^{b}	0.082±0.001^{c}	0.094±0.003^{d}	0.122±0.002^{e}	0.084±0.002^{c}	0.064±0.002^{a}	0.063±0.001^{a}	0.059±0.001^{a}
Copper (Cu)	0.063±0.001^{cd}	0.055±0.04^{b}	0.063±0.003^{cd}	0.094±0.003^{f}	0.013±0.001^{a}	0.086±0.001^{e}	0.069±0.005^{d}	0.062±0.001^{cd}	0.061±0.002^{bc}
Cadmium (Cd)	<0.001^{a}	0.013±0.02	<0.001^{a}	0.025±0.001^{b}	0.031±0.001^{b}	0.031±0.007^{b}	<0.001^{a}	<0.001^{a}	<0.001^{a}
Lead (Pb)	0.041±0.001^{b}	0.055±0.01^{c}	0.039±0.002^{b}	0.077±0.001^{f}	0.008±0.001^{a}	0.071±0.002^{e}	0.056±0.001^{c}	0.066±0.002^{de}	0.064±0.002^{d}
Nickel (Ni)	0.05±0.003^{ab}	0.06±0.00^{de}	0.063±0.001^{e}	0.052±0.001^{bc}	0.055±0.007^{bc}	0.052±0.001^{bc}	0.044±0.001^{a}	0.057±0.001^{cde}	0.051±0.001^{bc}
Iron (Fe)	0.124±0.001^{a}	0.144±0.002^{ef}	0.11±0.00^{b}	0.147±0.002^{f}	0.152±0.002^{g}	0.161±0.003^{h}	0.125±0.001^{c}	0.141±0.001^{e}	0.131±0.001^{d}
Magnesium (Mn)	0.049±0.004^{a}	0.053±0.001^{ab}	0.07±0.014^{c}	0.069±0.004^{c}	0.054±0.001^{ab}	0.057±0.002^{ab}	0.051±0.003^{ab}	0.054±0.001^{ab}	0.064±0.002^{bc}
Chromium (Cr)	0.009±0.00^{abcd}	0.02±0.014^{d}	0.005±0.001^{a}	0.017±0.001^{bcd}	0.02±0.001^{d}	0.018±0.001^{cd}	0.006±0.00^{ab}	0.006±0.001^{ab}	0.008±0.00^{abc}
Vanadium (V)	<0.001^{a}	<0.001^{a}	<0.001^{a}	0.006±0.001^{d}	0.005±0.00^{cd}	0.004±0.00^{bc}	0.003±0.001^{b}	0.005±0.00^{cd}	0.01±0.00^{a}
Arsenic (As)	<0.001^{a}	<0.001^{a}	<0.001^{a}	<0.001^{a}	<0.001^{a}	<0.001^{a}	<0.001^{a}	<0.001^{a}	<0.001^{a}
Mercury (Hg)	<0.001^{a}	<0.001^{a}	<0.001^{a}	<0.001^{a}	<0.001^{a}	<0.001^{a}	<0.001^{a}	<0.001^{a}	<0.001^{a}

Superscripts with the same letters across the row are not significantly ($p < 0.05$) different (DMRT)

Table 4 Amount of heavy metals in Sediment samples

	Station I			Station II			Station III		
Parameter (mg/L)	July	August	September	July	August	September	July	August	September
Zn	13.93±0.05^{d}	12.3±0.14^{b}	14.5±0.00^{e}	10.3±0.28^{a}	14.01±0.12^{d}	12.2±0.14^{b}	15.2±0.1^{f}	12.73±0.29^{c}	12.2±0.14^{b}
Cu	11.2±0.91^{c}	10.24±0.01^{b}	11.32±0.01^{c}	9.22±0.02^{a}	10.2±0.28^{b}	10.32±0.13^{b}	12.25±0.35^{d}	11.4±0.28^{c}	10.37±0.21^{b}
Cd	1.53±0.04^{a}	1.51±0.01^{a}	1.61±0.01^{a}	4.15±0.07^{d}	1.54±0.03^{a}	1.49±0.05^{a}	2.15±0.21^{b}	2.56±0.01^{c}	1.54±0.02^{a}
Pb	4.03±0.11^{d}	3.8±0.07^{cd}	3.69±0.23^{bc}	5.05±0.07^{e}	3.98±0.04^{d}	3.7±0.07^{bc}	3.41±0.01^{a}	3.53±0.01^{bc}	3.74±0.02^{bc}
Ni	4.24±0.04^{a}	5.25±0.21^{bc}	4.11±0.01^{a}	6.15±0.07^{d}	4.26±0.01^{a}	4.95±0.21^{b}	4.37±0.19^{a}	4.17±0.09^{a}	5.3±0.14^{c}
Fe	404.3±0.41^{c}	421.5±2.12^{ef}	391±1.41^{b}	509±1.41^{g}	404.0±0.42^{c}	420.3±0.42^{e}	384.5±0.71^{a}	424.0±1.41^{f}	411.0±1.41^{d}
Mn	9.44±0.02^{b}	10.3±0.28^{c}	12.15±0.21^{e}	8.6±0.14^{a}	9.49±0.05^{b}	10.35±0.21^{c}	11.25±0.35^{d}	10.48±0.05^{c}	9.6±0.04^{b}
Cr	3.23±0.03^{b}	3.15±0.07^{ab}	3.41±0.01^{c}	4.53±0.03^{e}	3.23±0.04^{ab}	3.13±0.04^{a}	4.14±0.06^{d}	3.23±0.04^{ab}	3.13±0.04^{a}
V	0.085±0.01^{c}	0.05±0.00^{b}	0.075±0.01^{c}	0.045±0.001^{a}	0.09±0.01^{c}	0.055±0.01^{b}	0.005±0.001^{a}	0.085±0.01^{c}	0.04±0.00^{b}
As	<0.01^{a}	<0.01^{a}	<0.01^{a}	<0.01^{a}	<0.01^{a}	<0.01^{a}	<0.01^{a}	<0.01^{a}	<0.01^{a}
Hg	<0.01^{a}	<0.01^{a}	<0.01^{a}	<0.01^{a}	<0.01^{a}	<0.01^{a}	<0.01^{a}	<0.01^{a}	<0.01^{a}

Superscripts with the same letters across the row are not significantly ($p < 0.05$) different (DMRT)

Table 5 Amount of heavy metals in *Clarius gariepinus*

Parameter (mg/L)	Station I			Station II			Station III		
	July	August	September	July	August	September	July	August	September
Zn	6.04 ± 0.02^{d}	5.23 ± 0.04^{b}	4.1 ± 0.14^{a}	3.85 ± 0.07^{a}	6.02 ± 0.001^{d}	7.15 ± 0.07^{f}	6.65 ± 0.21^{e}	5.65 ± 0.21^{c}	6.02 ± 0.01^{d}
Cu	4.27 ± 0.02^{c}	5.3 ± 0.28^{d}	3.10 ± 0.14^{a}	3.35 ± 0.21^{ab}	4.19 ± 0.13^{c}	4.20 ± 0.14^{c}	4.1 ± 0.00^{c}	3.5 ± 0.00^{b}	4.28 ± 0.00^{c}
Cd	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.07	<0.05	<0.05
Pb	0.17 ± 0.02^{ab}	0.24 ± 0.02^{d}	0.31 ± 0.01^{e}	0.22 ± 0.02^{cd}	0.17 ± 0.03^{ab}	0.18 ± 0.02^{abc}	0.17 ± 0.01^{ab}	0.19 ± 0.01^{bcd}	0.15 ± 0.00^{a}
Ni	3.69 ± 0.37^{de}	4.2 ± 0.00^{f}	3.54 ± 0.03^{cd}	3.43 ± 0.03^{bcd}	3.98 ± 0.04^{ef}	3.29 ± 0.08^{bc}	3.15 ± 0.07^{ab}	2.85 ± 0.07^{a}	4.00 ± 0.07^{ef}
Fe	335.94 ± 1.05^{b}	358.7 ± 9.17^{c}	372.6 ± 3.68^{d}	403.2 ± 2.82^{e}	335.6 ± 3.68^{b}	320.75 ± 1.06^{c}	320.8 ± 1.06^{a}	322.1 ± 2.89^{a}	335.6 ± 0.79^{b}
Mn	6.14 ± 0.01^{e}	7.23 ± 0.04^{f}	5.15 ± 0.07^{d}	5.95 ± 0.21^{e}	6.11 ± 0.02^{e}	4.91 ± 0.02^{c}	4.55 ± 0.07^{b}	4.20 ± 0.14^{a}	6.18 ± 0.07^{e}
Cr	2.07 ± 0.04^{a}	2.53 ± 0.03^{c}	2.37 ± 0.04^{bc}	2.1 ± 0.00^{ab}	2.06 ± 0.03^{a}	3.30 ± 0.28^{e}	2.75 ± 0.07^{d}	2.35 ± 0.21^{abc}	2.06 ± 0.03^{a}
V	$<0.05^{a}$	$<0.05^{a}$	$<0.05^{a}$	$<0.05^{a}$	$<0.05^{a}$	$<0.05^{a}$	$<0.05^{a}$	$<0.05^{a}$	$<0.05^{a}$
As	$<0.01^{a}$	$<0.01^{a}$	$<0.01^{a}$	$<0.01^{a}$	$<0.01^{a}$	$<0.01^{a}$	$<0.01^{a}$	$<0.01^{a}$	$<0.01^{a}$
Hg	$<0.01^{a}$	$<0.01^{a}$	$<0.01^{a}$	$<0.01^{a}$	$<0.01^{a}$	$<0.01^{a}$	$<0.01^{a}$	$<0.01^{a}$	$<0.01^{a}$

Superscripts with the same letters across the row are not significantly ($p < 0.05$) different (DMRT)

Table 6 The Health Risk Assessment (HRA) of heavy metals in Clarius garipinus

Metal	Mean	RfD (Mg/kg/day)	*Sf*	ADD	HQ	CR	PTWI
Zn	5.68	0.3		2.34E-01	7.79E-01		1.64E+00
Cu	4.06	0.0011		1.67E-01	1.52E+02		1.17E+00
Cd	0.07	0.0005	15	2.88E-03	5.76E+00	4.32E-02	2.02E-02
Pb	0.20	0.00014	8.50E-03	8.10E-03	5.78E+01	6.88E-05	5.67E-02
Ni	3.57	0.02	9.10E-01	1.47E-01	7.36E+00	1.34E-01	1.03E+00
Fe	348.95	0.00026		1.44E+01	5.53E+04		1.01E+02
Mn	5.61	0.14		2.31E-01	1.65E+00		1.62E+00
Cr	2.36	0.003	5.00E-01	9.71E-02	3.24E+01	4.86E-02	6.80E-01

** USFDA, 1993 *CDQW – Canadian Drinking Water Quality Standard, W.H.O [21].

Table 8 Heavy Metals Standards in Water, Sediment and Food

Parameter	Sediment/Soil WHO/FEPA [18][20] (mg/kg)	Fish FAO/WHO/FEPA [18][20](mg/kg)	Water CDQW/WHO [18]
Pb	0.04/0.5	0.3	0.05
Cd	0.006	0.2	0.003
Ni	2.0	80	0.02
Cu	0.025	30	1.0*
Mn	2	5	0.5
Fe	500	43	0.3*
Zn	0.3	30	2.0
Cr	0.1	0.13**	0.002

** USFDA, 1993 *CDQW – Canadian Drinking Water Quality Standard, W.H.O [21].

Table 7 Bioaccumulation factor of heavy metals in fish sample

	Station I			Station II			Station III		
Parameter	July	August	September	July	August	September	July	August	September
Zn	0.43	0.43	0.29	0.39	0.43	0.58	0.45	0.45	0.49
Cu	0.36	0.50	0.28	0.38	0.43	0.42	0.34	0.31	0.42
Cd	-	-	-	-	-	-	-	-	-
Pb	0.04	0.07	0.08	0.05	0.04	0.04	0.05	0.05	0.04
Ni	0.93	0.82	0.86	0.56	0.93	0.64	0.69	0.68	0.73
Fe	0.83	0.84	0.96	0.79	0.83	0.85	0.84	0.77	0.82
Mn	0.65	0.69	0.43	0.72	0.65	0.47	0.42	0.39	0.65
Cr	0.63	0.81	0.71	0.47	0.63	1.00	0.70	0.68	0.66
V	-	-	-	-	-	-	-	-	-
As	-	-	-	-	-	-	-	-	-
Hg	-	-	-	-	-	-	-	-	-

The HQ values of metals calculated from fish tests shows HQ of Zn (7.79E-01) from fish utilization within the sampled area to be less than 1 (HQ<1) which indicates no non-carcinogenic antagonistic impacts. HQ values for Cu, Cd, Pb, Fe, Mn and Cr were more prominent than 1 (HQ>1) which show non-carcinogenic antagonistic impact.

Furthermore, the cancer chance values estimated for Pb were underneath the constrain value of 1.0×10^{-4} showing no conceivable carcinogenic impacts while the cancer hazard for Cd, Ni and Cr were over the restrain value of 1.0×10^{-4} showing conceivable carcinogenic effects.

E. Bioaccumulation Factor

The bioaccumulation factor of heavy metals from fish and sediments is shown in Table 7. The results showed the order of bioaccumulation of metal in *C.gariapinus* from sediment in Station I, II and III to be Fe > Ni > Cr > Mn > Cu > Zn > Pb

IV. Discussion

Heavy metal contaminant concentrations can be evaluated by measuring the intensity of the metals in the sea water, residue and the biota in water system. Past studies demonstrated that concentration is ordinarily lower in water but tend to increase within sediment and biota water-based system [23]. Table 8 shows heavy metals standards in Water, Sediment and Food. Concentrations of Zn in all the fish tests were below the FAO limit of 30 mg/Kg of Zn for secure human utilization [24]. The concentrations of Zn found in the fish samples cannot cause any harm to the fish themselves as well as to humans who consume them. Zn is an indispensable trace metal for both animals as well as humans. Zn toxicity is somewhat rare, but at concentrations up to 40 mg/Kg, Zn may stimulate toxicity, characterized by way of symptoms of irritability, muscular stiffness and pain, loss of appetite, combined with nausea [22]. The observed values of Zn in water sample across the stations were within allowable limit of 2.0 mg/L. Similar results was observed in work of [25], who reported low zinc concentration in water which resulted in mortality, reduced growth, cardiovascular, developmental and immunological effect which is reduced using drugs and food that contains zinc. Zinc is valuable to human and other ecological entities, however, high amount zinc could be toxic to biological systems of humans. Additionally, symptoms of zinc toxicity in human include vomiting, dehydration, electrolyte imbalance, adnominal pain. High Zn concentration recorded in sampled sediment demonstrated that, heavy metals amount is actually higher in the sediment than that of the water which may well be due to the fact that suspended sediment will retain toxins from water and will have a lower concentration of the metals within the water column [25]. Copper is a basic part of a few chemicals and it is fundamental for amalgamation of hemoglobin but can cause harm at reasonably high concentrations [26]. The observed values of Cu in water were within allowable limit of 1.0 mg/L. The most sources of copper in provincial water bodies comes from companies' effluents, household wastewater, disinfection and agro-based chemicals and breaking-down of copper bearing rocks. Like other harmful metals, long term contact to copper can cause bothering of sense organs which could result in cerebral pain, stomachache, tipsiness, heaving and loose bowels alongside other wellbeing dangers [27]. According to WHO [18] recognized limits for Cu in fish as 30.0 mg/L for human health risk concerns, the concentrations of Cu in these samples were far below maximum permissible limit therefore, regular consumption of fish with such low concentration of Cu could not lead to any serious health risk.

The observed values of Cd in water samples were above allowable range of 0.003 mg/L in sample analysed. Cd containing items are not recycled but dumped alongside family squander, subsequently contaminating the environment. It is already observed a relationship between cadmium build-up and inveterate renal failure [27]. Intense exposure to cadmium vapour may cause flu-like side effects including chills, fever, and muscle hurt in some cases alluded to as the cadmium blues, more serious exposures can cause trachea-bronchitis, pneumonitis, and aspiratory oedema, ingestion of a critical sum of cadmium causes quick harming and harm to the liver and the kidneys [27]. The cruel concentration of Cd in fish samples were under allowable limit of 0.2 mg/Kg [22].

Water can contain broken down metals containing nickel (Ni) and chemicals normally discharged from shake and soil, which can be hurtful to people [28]. The observed values of Ni in water were over the permissible limit of 0.02 mg/L [22]. Nickel concentrations in ground water are affected by soil sort, pH level and sampling profundity [22]. Higher concentrations have been reported where potable water is contaminated with nickel waste released from chemical, industrialization activities or mining plants [29]. This result was comparable to that of Al-Najjar et al., [30], who reported a result lower than the permissible allowable limits.

The observed values of Pb in water samples were above allowable range of 0.05 mg/L in six (6) samples. Grown-ups take up to 10 to 15% of lead in nourishment and water while children may assimilate up to 50% through the gastrointestinal tract [27]. The side effects of intense lead harming are migraine, crabbiness, stomach torment and various side effects related to anxious framework. Long term lead contact in children may cause decreased mental capacity, encephalopathy, intense psychosis, concentration and learning challenges and decreased capacity to get it [31]. The observed results of lead in the sediment samples exceeds the permissible levels; 0.4 mg/kg [32] and 0.5 mg/kg [22] whereas the concentration in fish sample were under the passable limit of 0.3 mg/Kg. Lead causes renal seizure and liver harm in people [33]. Pb exposure is also known to cause musculoskeletal disorder, reproductive and developmental [34]

Iron is crucial to most life forms and to normal human physiology. In humans, iron is crucial element in proteins involved in oxygen transports from the lungs to tissues. It is equally a key element in controlling cell development and division [35]. The observed values Fe present in sampled water were above allowable limit of 0.3 mg/L. Abundance of iron in water can be dangerous to individual's health [27]. High value of iron present in sampled water has been equally observed [36]. The value is high because irons are metals that occur naturally in soils, rocks and minerals. In the aquifer groundwater meets these solid minerals dissolving them, releasing their constituents. The Fe level in fish tests were higher than the allowable limit of 43 mg/kg [22]. These possess a risk to potential consumers.

The results of Cr in water samples were over the acceptable limit of 0.002 mg/L [18]. Water containing chromium particles in large concentration may causes goiter among individuals and animals [37]. The level of Cr in fish samples were higher than USFDA, [21] limit of 0.13 mg/kg, which presents a potential hazard to consumers of the fishes from the study area. The observed values Mn2+ in water sample were within the limit of 0.5 mg/L. Magnesium could be a crucial micro-nutrient and contributes to the normal development for connective tissues. A few studies have connected manganese with human kidney, liver, and pancreas infections [38].

The observed concentration of As, V and Hg were within the allowable level. High levels of Hg in fish have been detailed to cause serious neurotoxic and genotoxic impacts [39]. Foods that are contaminated with mercury has negative impacts on the gastrointestinal tract and may cause actuate kidney harmfulness if ingested [40]. Additionally, utilization of arsenic contaminated foods over prescribed levels has been connected to hazard of skin cancer and other skin injuries, such as hyperkeratosis and pigmentation changes. WHO concludes that arsenic exposure through potable water is causally related to cancer within the lungs, kidney, bladder and skin [41].

The evaluated cancer risk from exposure to Pb, Cd, Cr, Ni was estimated as 1.0×10^{-6} to 1.0×10^{-4} which is a case of cancer per each 1,000,000 to 1 case of cancer per each 10,000. Ayenuddin et. al, [42] reported a risk factor of 1.0×10^{-3} will completely require cautious measures showing that a lifetime exposure to heavy metal concentration brings about risk of cancer to individuals.

V. CONCLUSION

The monitoring of heavy metal concentration is normally done by measuring the concentration of metal contain in sediment, water, biota in water-based system. This study ascertains heavy metals amount in fish (Clarius garipinus) and sediment and water samples collected from the three study locations. The result shows high heavy metals from surface water, sediments and fish samples. The estimated Hazard Index (HI) of metals in fish samples showed high risk for consuming fish in research area. The results suggest from this study that, utilization of fish around these zones may be hurtful due to metal poisoning.

VI. ACKNOWLEDGMENT

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VII. REFERENCES

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