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Evaluation of the abiotic accumulation factor of some heavy metals in muscles of *Clarias gariepinus* from QUA IBOE River, south-eastern Nigeria

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Abstract

The study was carried-out over a six months period. Seventy-two adult of *Clarias gariepinus*, thirty-six water and sediments samples were collected throughout. Lead was not detected in the muscles through-out the study. The accumulation of Cr and Ni in *Clarias gariepinus* muscles came mainly from sediments, Cu from both sediments and water, Fe mainly from sediments and slightly from water and Zn slightly from both sediment and water as shown by the different relationship between metals in muscles and the abiotic factors (water and sediments). Fish muscles were slightly polluted with Cr, Fe, Ni and Mn, while the water shows slightly polluted with Mn, Cd and Ni, and sediments shows slightly polluted with Cr, Cd, Ni and Fe, making it unsafe. It is important for regulatory agencies to monitor and enforce policies against some careless activities in the River, and also to fund more environmental related studies in this area.

Keywords: heavy metals, abiotic factor, accumulation, *clarias gariepinus*, qua iboe river

1. Introduction

Pollution is defined as the production or introduction by man either directly or indirectly of substances or energy sources into the environment (atmospheric, terrestrial or aquatic) resulting in deleterious effects which could jeopardize human health, harm other living resources in the environment and damage or impede the use of amenities or other legal use of the environment [1]. Water pollution has continued to create unpleasant implications for health and economic development in Nigeria [2]. Chemical analysis of the environmental matrix such as biological organisms, water and sediments are the most direct approach to expose the heavy metal pollution status of the environment [3]. To expose the presence of pollutants and to evaluate their toxic effects, biological indicators can be used [3]. The importance and relevance of bio-indicators rather than man-made equipment is well documented by [4], where he explained that "There is no better indicator of the status of species or a system than the species or system itself or both". Fishes are one of the most reliable metal pollution indicators in fresh water systems. Fish reveals both the past and present heavy metal exposures [5]. These metals are incorporated through the gills, skin or food [6]. Heavy metal contamination destabilizes the ecological balance of any environment. Heavy metal pollution is more pronounced in sediments, macrophytes and aquatic animals of aquatic eco-systems than in water [7]. Data obtained from sediments can give a wider knowledge on the impacts of human activity in the environment, and this serves as archives of the recent environmental changes [8, 9] reported water as the abiotic factor responsible for most of the Fish accumulation of metals and not sediments. This study was aimed at assessing the pollution levels of heavy metals in water, sediments and muscles of *Clarias gariepinus* from Qua Iboe River and also to reveal the abiotic factor (water, sediments or both) responsible for the levels of each heavy metal in the muscles of *Clarias gariepinus*.

2. Materials and Methods

2.1 Description of Study Area

Qua Iboe River flows across different communities of Abia State and through its estuary in Ibeno, and empties into the Atlantic Ocean [10]. The river lies between latitude 4°40' N and longitude 7°55' E (Fig. 1) [11]. It is about 150 to 180km in distance covered. The River runs along the Eket, Ibeno, Una and Mbo Local Government Areas axis of Akwa Ibom State, and then empties into the Atlantic Ocean. Its estuary is very close to the terminal point of Exxon-Mobil. Various human induced waste like; municipal waste, urban run-off, industrial discharges from food processing industries, garbage's, metal scraps are emptied into the river, mainly at the Atabong, Marina and Iwuochang stations of the River [11]. The River is characterized with a long period of rainy season, usually between April and November, as well as a brief dry season period, between December and March [10]. The main occupations of the inhabitants of this River are fishing, construction of boat, Ferryboat transportation, dredging, logging of woods and farming. The river also serves as the main source of water to the rural communities around the river [11].

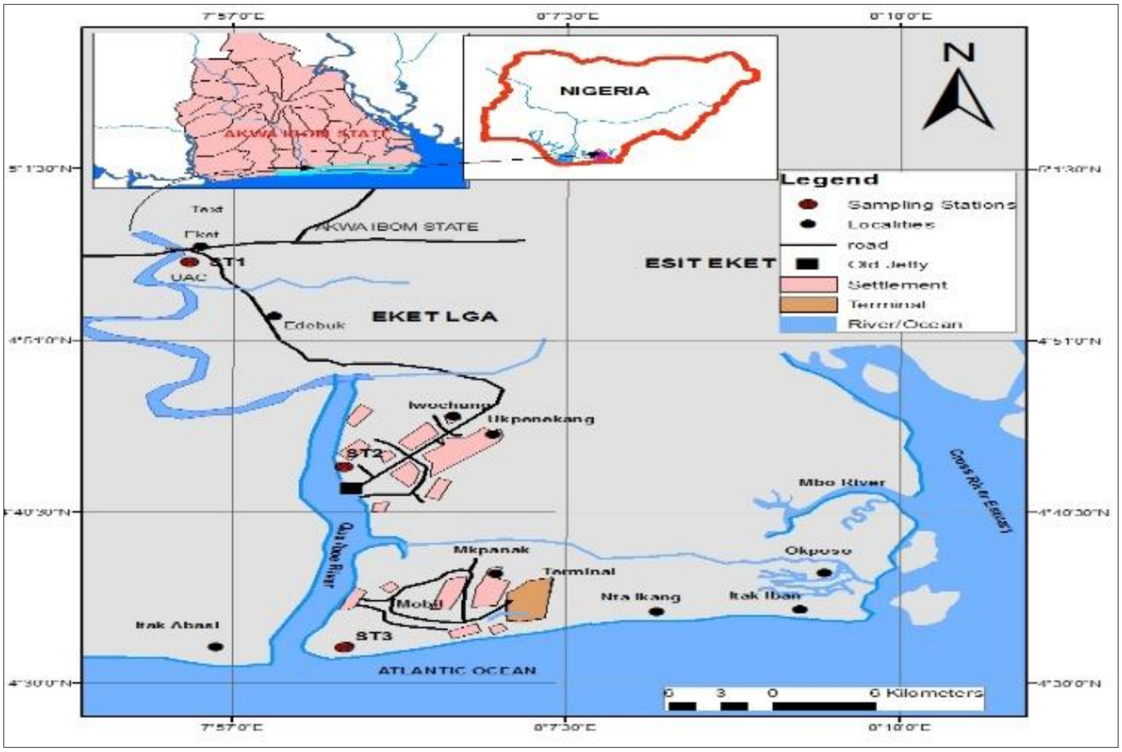

Fig 1: Map showing the sampling stations along Qua Iboe River.

Station one

UAC beach is considered as the upstream and control station because very minimal fishing, fire wood activities and human activities take place in the station. UAC beach is located along Eket Local Government Area axis of Qua Iboe River in Akwa Ibom State. Geographically, UAC beach lies between latitude 04^0 55' 56'' N and longitude 07^o55' 32.0'' E.

Station two

Iwuochang beach is located along Ibeno Local Government Area axis of Qua Iboe River. Geographically, Iwuochang beach lies between latitude 04^o 43' 23.6'' N and longitude $08^0$00' 28.3'' E. Station two (Iwuochang) is about 22.5km from station One (UAC Beach). This station is consistently influenced by various human activities like: intensive commercial fishing, market, domestic waste disposal, boatyard, open defecation, high level Fire wood activities, bathing, washing and so on.

Station three

Mkpanak beach is located along the Ibeno Local Government axis of Qua Iboe River. Geographically, Mkpanak beach lies between latitude 04^o32' 16.0'' N and Longitude 08^0 00' 29.2''E. Station three (Mkpanak Beach) is about 21.2km from Station two (Iwuochang Beach). Several human activities introduce a lot of energy into the beach. Some of the activities are: urban and drainage discharge, abattoir, high level commercial fishing, market, fire wood activities, open defecation, domestic waste disposal, bathing, washing and so on.

2.2 Collection of Fish Samples

A total of 72 Samples of *Clarias gariepinus* were purchased alive from fishermen in the 3 sampling stations of Qua Iboe River. Fish were sampled on a monthly basis over a six months period; between January and June, 2015. The fish samples were caught alive at the time of each sampling across each station by the fisherman. The samples were put into an ice chest immediately after samples collection, in order to keep the specimens as fresh as possible to prevent tissue decay. The fish samples were transported immediately to the Ministry of Science and Technology Laboratory, Uyo, Akwa Ibom State, where the samples were preserved in the freezer while awaiting dissection and preparation of tissues for Spectrophotometric metal analysis.

2.3 Collection of Water Samples

Water samples were collected using a one litre plastic container. The container was always rinsed thoroughly twice before use. The container were dipped into the water at about two centimeters below water surface and covered appropriately after collection of samples. Once the water samples were collected, they were put in an ice chest in order to prevent any alterations in the heavy metal concentration in the water samples due to microbial activities. The Ice chest helps inhibit microbial activities. Water samples were collected at three (3) different points of each sampling stations, and were then mixed to form a composite sample for each station. Water was sampled on a monthly basis over a six months period; between January and June, 2015, and 36 composite samples of water were collected in total. Once collected, samples of water were transported immediately to the Ministry of Science and Technology Laboratory, Uyo, Akwa Ibom State, where the samples was preserved in the freezer while awaiting Spectrophotometric heavy metal analysis.

2.4 Collection of Sediments Samples

The collection of Sediment samples was carried-out using polythene bag. Prior to the sediments samples collection, 10 percent of nitric acid was used to treat the polythene bag. Ekman Grab was used to collect the Sediment samples. Immediately after the sediments are collected, they were preserved in an ice chest. Sediments samples were collected at three (3) different points of each sampling stations, and were then mixed to form a composite sample for each station. Sediments were sampled on a monthly basis over a six months period; between January and June, 2015, and 36 composite samples of sediment were collected in total. Once collected, samples of the sediments were transported immediately to the Ministry of Science and Technology Laboratory, Uyo, Akwa Ibom State, where the samples were preserved in the freezer while awaiting Spectrophotometric heavy metal analysis.

2.5 Processing and Spectrophotometric Metal Analysis of Fish Samples

In the Science and Technology Laboratory, the fish samples preserved in ice were allowed to thaw first and assume a normal temperature of the laboratory (20ºC - 27ºC).The muscles of the fish will be oven-dried and grinded into powder separately. Two grammes of grinded samples were put into Teflon, and then digested with four milliliters of concentrated nitric acid (HNO_3). The Teflon tubes was closed and placed in stainless steel bomb, which was then heated to a temperature of 110ºC for one hour and then to 150ºC for three hours. The samples were cooled by adding distilled water, and were then opened to allow for proper cooling. The samples were then analysed in mg/kg for cadmium, copper, zinc, chromium, iron, manganese, nickel and lead concentrations spectrophotometrically [12].

2.6 Processing and Spectrophotometric Metal Analysis of Water Samples

The ice chest preserved water samples were allowed to normalize and assume the normal temperature of the laboratory (i.e. 28ºC). About 25 milliliters of water sample was digested with three milliliters of concentrated hydrochloric acid (HCL). A steam bath was then used to heat the digest for 30 minutes before allowing it to cool. The digest was added distilled water of 50 ml, before the heavy metal analysis using atomic spectrophotometer [13].

2.7 Processing and Spectrophotometric Metal Analysis of Sediments Samples

The ice chest preserved sediments samples were allowed to normalize and assume the normal temperature of the laboratory (i.e. 28ºC). Oven-drying of the sediments samples was carried-out at 106 ºC temperature and the sieved accordingly after. About ten grams of the sieved sediment sample were then digested with 3ml of concentrated hydrochloric acid. The samples were then heated in a stream bath for about 30 minutes and then allowed to cool. 50ml of distilled water were then added to the sample digest. The resulting digest was analysed for cadmium, copper, zinc, chromium, iron, manganese, nickel and lead using atomic spectrophotometer [13].

2.8 Statistical analysis

Analysis of variance (ANOVA) was used to test for the significant difference in the liver, muscle and gills tissues of *Clarias gariepinus* metal concentration between each sampling station. Also, ANOVA was used to test for the significant of differences in the concentration of heavy metals between the different tissues. Correlation was carried out between metal concentration in fish muscle and water, as well as between fish muscle and sediment, in order to determine the actual abiotic factor (water or sediment) responsible for metal accumulation. Mean and standard deviations was carried out for metal concentration in water, fish, and sediment. All the statistical analysis was carried out using Predictive Analytical Software (PASW, version 20).

3. Results

Summary of the variations in mean concentrations of metals in *Clarias gariepinus* muscles across the three sampling stations during the study is shown in Table 1. At UAC beach, the copper concentrations in the muscle of *Clarias gariepinus* ranged from 1.10-2.00 mg/kg, having a mean and standard deviation of 1.515 ± 0.515 mg/kg. Chromium had a concentration range of 0.014-0.032 mg/kg, having a mean and standard deviation of 0.021 ± 0.851 mg/kg. Zinc had a concentration range of 8.90-10.92 mg/kg, having a mean of 9.435 ± 0.747 mg/kg. Iron had a concentration range of 0.100-0.126 mg/kg, having a mean and standard deviation of 0.114 ± 2.583 mg/kg. Manganese had a concentration range of 0.22-0.39 mg/kg, having a mean and standard deviation of 0.302 ± 1.222 mg/kg. Cadmium had a concentration range of 0.24-3.92 mg/kg, having a mean of 2.042 ± 1.975 mg/kg. Lead was not detected at all in the muscle of *Clarias gariepinus*. Nickel had a concentration range of 0.28-0.38 mg/kg, having a mean and standard deviation of 0.332 ± 3.019 mg/kg. The mean metal concentrations in muscle of *Clarias gariepinus* from UAC beach showed a decreasing trend of Zn>Cd>Cu>Ni>Mn>Fe>Cr (Table 1).

At Iwuochang, the copper concentrations in the muscle of *Clarias gariepinus* ranged from 2.48-5.30 mg/kg, having a mean of 3.496 ± 1.281 mg/kg. The chromium concentrations had a range of 0.14-0.80 mg/kg, having a mean and standard deviation of 0.387 ± 0.279 mg/kg. Zinc had a concentration range of 10.21-14.52 mg/kg, having a mean of 11.597 ± 1.682 mg/kg. Iron had a concentration of 21.11-28.21 mg/kg, having a mean of 24.717 ± 2.965 mg/kg. Manganese had a concentration range of 10.38-12.47 mg/kg, having a mean of 11.372 ± 1.074 mg/kg. Cadmium had a concentration range of 0.48-4.18 mg/kg, having a mean of 2.397 ± 1.913 mg/kg. Lead was not detected at all in the muscle of *Clarias gariepinus*. The nickel concentrations ranged from 16.20-21.48 mg/kg, with a mean and standard deviation of 18.470 ± 2.383 mg/kg. The mean metal concentrations in muscle of *Clarias gariepinus* from Iwuochang beach showed a decreasing trend of Fe>Ni>Zn>Mn>Cu>Cd>Cr (Table 1). At Mkpanak beach, the copper concentrations in the muscle of *Clarias gariepinus* ranged from 2.07-5.22 mg/kg, having a mean of 3.685 ± 1.521 mg/kg. Chromium had a concentration range of 0.22-0.85 mg/kg, having a mean and standard deviation of 0.436 ± 0.245 mg/kg. Zinc had concentration range of 11.00-18.62 mg/kg, having a mean of 12.397 ± 3.052 mg/kg. Iron had a concentration range of 24.10-29.32 mg/kg, having a mean of 25.227 ± 2.046 mg/kg. Manganese had a concentration range of 10.01-13.62 mg/kg, having a mean of 11.498 ± 1.574 mg/kg. Cadmium had a concentration range of 0.92-4.09 mg/kg, having a mean of 2.488 ± 1.686 mg/kg. Lead was not detected at all in the muscle of *Clarias gariepinus*. The nickel concentrations ranged from 18.11-24.10 mg/kg, with a mean and standard deviation of 20.247 ± 2.558 mg/kg. The mean metal concentrations in muscle of *Clarias gariepinus* from Mkpanak beach showed a decreasing trend of Fe>Ni>Zn>Mn>Cu>Cd>Cr (Table 1). Various distributions of the different metals in muscles across the stations are presented in Table 1. However, statistically, copper, chromium, zinc, manganese and cadmium did not show any significant difference in their mean concentrations in muscles across UAC, Iwuochang and Mkpanak beaches (P>0.05), while iron and nickel showed significant difference in their mean accumulation in muscles across UAC, Iwuochang and Mkpanak beaches (P<0.05) (Table 1). Mean concentration of copper in *Clarias gariepinus* muscle through-out the study ranged from 1.10-5.30 mg/kg, having a mean and standard deviation of 2.898 ± 0.626 mg/kg. Chromium had a mean concentration range of 0.01-0.85 mg/kg, having a mean and standard deviation of 0.281 ± 0.050 mg/kg. Zinc had a concentration range of 8.90-18.62 mg/kg, having a mean of 11.140 ± 1.526 mg/kg.

Table 1: Heavy metals concentration in muscles of *Clarias gariepinus* from different stations of Qua Iboe River

Metals	UAC	Iwuochang	Mkpanak	Mean	WHO Limit
Cu	1.515±0.515[a] (1.10-2.00)	3.496±1.281[a] (2.48-5.30)	3.685±1.521[a] (2.07-5.22)	2.898±0.626 (1.10-5.30)	3.0
Cr	0.021±0.851[a] (0.01-0.03)	0.387±0.279[a] (0.14-0.80)	0.436±0.245[a] (0.22-0.85)	0.281±0.050 (0.01-0.85)	0.05
Zn	9.435±0.747[a] (8.90-10.92)	11.597±1.682[a] (10.21-14.52)	12.397±3.052[a] (11.00-18.62)	11.140±1.526 (8.90-18.62)	10-75
Fe	0.114±2.583[a] (0.10-0.12)	24.717±2.965[b] (21.11-28.21)	25.227±2.046[c] (24.10-29.32)	16.686±2.297 (0.10-29.32)	0.3
Mn	0.302±1.222[a] (0.22-0.39)	11.372±1.074[a] (10.38-12.47)	11.498±1.574[a] (10.01-13.62)	7.724±0.891 (0.22-13.62)	0.5
Cd	2.042±1.975[a] (0.24-3.92)	2.397±1.913[a] (0.48-4.18)	2.488±1.686[a] (0.92-4.09)	2.307±0.236 (2.04-4.18)	3.0
Pb	BDL	BDL	BDL	BDL	-
Ni	0.332±3.019[a] (0.28-0.38)	18.470±2.383[b] (16.20-21.48)	20.247±2.558[c] (18.11-24.10)	13.016±2.203 (0.31-24.20)	0.6

Values are in Mean ± standard deviation (Ranges in Parenthesis), BDL – Below detectable limit
*Means with the same superscript are not significantly different (P>0.05).

The mean iron concentrations ranged from 0.10-29.32 mg/kg, with a mean and standard deviation of 16.686 ± 2.297 mg/kg. The mean manganese concentrations ranged from 0.22-13.62 mg/kg, having a mean of 7.724 ± 0.891 mg/kg. The mean cadmium concentrations ranged from 0.24-4.18 mg/kg, having a mean of 2.307 ± 0.236 mg/kg. Lead was not detected at all in the muscle of *Clarias gariepinus*. The mean nickel concentrations ranged from 0.31-24.10 mg/kg, with a mean and standard deviation of 13.016 ± 2.203 mg/kg. The mean concentrations of the metals in *Clarias gariepinus* muscle were all above the WHO limits, except copper, zinc and cadmium. The overall mean concentrations of the different metals in *Clarias gariepinus* muscle from Qua Iboe River showed a decreasing trend of Fe>Ni>Zn>Mn>Cu>Cd>Cr (Table 1).

Summary of the mean concentrations of metals in water of UAC, Iwuochang and Mkpanak Beaches of Qua Iboe River is shown in Table 2. At UAC beach, the copper concentrations in water had a range of 0.19-0.28 mg/l, having a mean and standard deviation of 0.222 ± 0.033 mg/l. Chromium had a concentration range of 0.01-0.01 mg/l, having a mean and standard deviation of 0.010 ± 0.000 mg/l. Zinc had a concentration range of 0.17-0.29 mg/l, having a mean of 0.213 ± 0.046 mg/l. Iron had a concentration range of 0.03-0.09 mg/l, having a mean and standard deviation of 0.056 ± 0.019 mg/l. Manganese had a concentration range of 0.32-0.48 mg/l, having a mean and standard deviation of 0.402 ± 0.758 mg/l. Cadmium had a concentration range of 0.02-0.06 mg/l, having a mean and standard deviation of 0.030 ± 0.015 mg/l. Lead had a concentration range of BDL-0.01 mg/l, having a mean and standard deviation of 0.010 ± 0.000 mg/l. Nickel had a concentration range of 0.01-0.05 mg/l, having a mean and standard deviation of 0.028 ± 0.383 mg/l. Mean concentrations of metals in UAC beach water were below the WHO and FMENV permissible limits. Mean concentrations of metals in water from UAC showed a decreasing trend of Mn>Cu>Zn>Fe>Cd>Ni>Cr=Pb (Table 2). At Iwuochang beach, the copper concentrations in water had a range of 0.23-0.67 mg/l, having a mean and standard deviation of 0.465 ± 0.192 mg/l. Chromium had a concentration range of 0.02-0.02 mg/l, having a mean and standard deviation of 0.020 ± 0.000 mg/l. Zinc had a concentration range of 0.19-0.46 mg/l, having a mean and standard deviation of 0.322 ± 0.109 mg/l. Iron had a concentration range of 0.33- 0.61 mg/l, having a mean and standard deviation of 0.478 ± 0.092 mg/l. Manganese had a concentration range of 0.96-2.23 mg/l, having a mean and standard deviation of 1.392 ± 0.432 mg/l. Cadmium had a concentration range of 0.27-0.46 mg/l, having a mean and standard deviation of 0.372 ± 0.071 mg/l. Lead had a concentration range of 0.24-0.46 mg/l, having a mean and standard deviation of 0.325 ± 0.080 mg/l. Nickel had a concentration range of 0.25-0.35 mg/l, having a mean and standard deviation of 0.310 ± 0.035 mg/l. Mean metal concentrations in water from Iwuochang beach were all below the WHO and FMENV permissible limits except for iron and lead which were both above the WHO and FMENV permissible limits, and manganese and cadmium which were above WHO permissible limit. The mean metal concentrations in Iwuochang water showed a decreasing trend of Mn>Fe>Cu>Cd>Pb>Zn>Ni>Cr (Table 2). In Mkpanak beach, the copper concentrations in water had a range of 0.31-0.72 mg/l, having a mean and standard deviation of 0.488 ± 0.188 mg/l. Chromium had a concentration range of 0.02-0.03 mg/l, having a mean and standard deviation of 0.023 ± 0.005 mg/l. Zinc had a concentration range of 0.23-0.53 mg/l, having a mean and standard deviation of 0.335 ± 0.120 mg/l. Iron had a concentration range of 0.29-0.51 mg/l, having a mean and standard deviation of 0.430 ± 0.084 mg/l. Manganese had a concentration range of 0.89-2.01 mg/l, having a mean and standard deviation of 1.460 ± 0.446 mg/l. Cadmium had a concentration range of 0.21-0.51 mg/l, having a mean and standard deviation of 0.415 ± 0.108 mg/l. Lead had a concentration range of 0.17-0.27 mg/l, having a mean and standard deviation of 0.210 ± 0.035 mg/l. Nickel had a concentration range of 0.22-0.46 mg/l, having a mean and standard deviation of 0.375 ± 0.097 mg/l. Mean metal concentrations in water from Mkpanak beach were all below the WHO and FMENV permissible limits except for iron and lead which were both above the WHO and FMENV permissible limits, and manganese and cadmium which were above WHO limit. The mean metal concentrations in Mkpanak water showed a decreasing trend of Mn>Cu>Fe>Cd>Ni>Zn>Pb>Cr (Table 2).

Table 2: Heavy metals concentration in water from different stations of Qua Iboe River.

Metals	UAC	Iwuochang	Mkpanak	Mean	WHO	FMENV, 2003
Cu	0.222±0.033[a] (0.19-0.28)	0.465±0.192[b] (0.23-0.67)	0.488±0.188[c] (0.31-0.72)	0.392±0.192	1.0	-
Cr	0.010±0.000[a] (0.01-0.01)	0.020±0.000[b] (0.02-0.02)	0.023±0.005[c] (0.02-0.03)	0.018±0.006	0.05	0.05
Zn	0.213±0.046[a] (0.17-0.29)	0.322±0.109[a] (0.19-0.46)	0.335±0.120[a] (0.23-0.53)	0.290±0.108	5.0	5-15
Fe	0.056±0.019[a] (0.03-0.09)	0.478±0.092[b] (0.33-0.61)	0.430±0.084[c] (0.29-0.51)	0.322±0.206	0.3	1.0
Mn	0.402±0.758[a] (0.32-0.48)	1.392±0.432[b] (0.96-2.23)	1.460±0.446[c] (0.89-2.01)	1.084±0.451	-	0.05-0.5
Cd	0.030±0.015[a] (0.02-0.06)	0.372±0.071[b] (0.27-0.46)	0.415±0.108[c] (0.21-0.51)	0.272±0.192	0.05	-
Pb	0.010±0.000[a] (BDL-0.01)	0.325±0.080[b] (0.24-0.46)	0.210±0.035[c] (0.17-0.27)	0.216±0.130	0.05	0.01-1.0
Ni	0.028±0.383[a] (0.01-0.05)	0.310±0.035[b] (0.25-0.35)	0.375±0.097[c] (0.22-0.46)	0.237±0.112	0.07	0.05

Values are in Mean ± standard deviation (Ranges in Parenthesis), BDL – Below detectable limit
*Means with the same superscript are not significantly different (P>0.05)

The distribution of various metals in water across the stations is presented in Table 2. However, statistically, zinc did not show any significant difference in their Mean concentrations in water from UAC, Iwuochang and Mkpanak beaches (P>0.05), while copper, chromium, iron, manganese, cadmium, lead and nickel showed significant difference in their mean accumulation in water from UAC, iwuochang and mkpanak beaches (P<0.05). The mean concentrations of metals and their standard deviations in water were; 0.392 ± 0.192, 0.018 ± 0.006, 0.237 ± 0.112, 0.322 ± 0.206, 1.084 ± 0.451, 0.272 ± 0.192, 0.216 ± 0.130 and 0.290 ± 0.108 mg/l for copper, chromium, nickel, iron, manganese, cadmium, lead and zinc respectively. Mean metal concentrations in the study area water showed a decreasing trend of Mn>Cu>Fe>Zn>Cd>Ni>Pb>Cr. Overall iron and lead mean concentrations in Qua Iboe River water were above WHO permissible, but within FMENV permissible limits. Manganese was above FMENV permissible limits. Nickel was above WHO and FMENV permissible limits, while cadmium was above WHO limits. The remaining metals were within the WHO and FMENV permissible limits (Table 2).

The summary of the mean heavy metal concentrations in sediments from UAC, iwuochang and mkpanak beaches of Qua Iboe River is shown in Table 3. At UAC beach, the copper concentrations in sediments ranged from 3.36-6.50 mg/kg, having a mean and standard deviation of 5.102 ± 1.488 mg/kg. The chromium concentrations had a range of 0.04-0.09 mg/kg, having a mean and standard deviation of 0.065 ± 0.124 mg/kg. Zinc had a concentration range of 5.36-9.28 mg/kg, having a mean of 7.580 ± 1.891 mg/kg. Iron had a concentration range of 60.33-83.66 mg/kg, having a mean of 71.212 ± 9.791 mg/kg. Manganese had a concentration range of 20.26-30.89 mg/kg, having a mean of 28.608 ± 4.116 mg/kg. The cadmium concentrations had a range of 0.35-0.68 mg/kg, having a mean and standard deviation of 0.493 ± 0.149 mg/kg. Lead had a concentration range of 1.01-1.18 mg/kg, having a mean of 1.085 ± 0.072 mg/kg. Nickel had a concentration range of 15.08-20.28 mg/kg, having a mean of 18.001 ± 2.043 mg/kg. The mean metal concentrations in sediments from UAC beach were all below the WHO and SQG (sediments quality guidelines) permissible limits. The mean metal concentrations in UAC water showed a decreasing trend of Fe>Mn>Ni>Zn>Cu>Pb>Cd>Cr (Table 3).
At Iwuochang beach, copper concentrations in sediment ranged from 4.06-9.24 mg/kg, having a mean of 7.223 ± 2.292 mg/kg. The chromium concentrations had a range of 0.59-0.84 mg/kg, having a mean and standard deviation of 0.717 ± 0.119 mg/kg. Zinc had a concentration range of 6.98-12.61 mg/kg, having a mean of 9.996 ± 2.518 mg/kg. Iron had a concentration range of 70.11-188.94 mg/kg, having of 137.643 ± 52.986 mg/kg. Manganese had a concentration range of 30.12-49.01 mg/kg, having a mean of 40.570 ± 9.292 mg/kg. The cadmium concentrations had a range of 0.42-0.96 mg/kg, having a mean and standard deviation of 0.730 ± 0.235 mg/kg. Lead had a concentration range of 3.29-5.72 mg/kg, having a mean of 4.560 ± 0.941 mg/kg. Nickel had a concentration range of 17.34-22.56 mg/kg, having a mean of 20.407 ± 1.819 mg/kg. The mean metal concentrations in sediments from Iwuochang beach were all below the WHO and SQG permissible limits except for chromium which was both above the WHO permissible limits, and cadmium and nickel were above the SQG permissible limits. The Mean Metal concentrations in Iwuochang sediment showed a decreasing trend of Fe>Mn>Ni>Zn>Cu>Pb>Cd>Cr (Table 3).
At Mkpanak beach, the copper concentrations in sediments ranged from 3.99-9.41 mg/kg, having a mean of 7.253 ± 2.414 mg/kg. The chromium concentration had a range of 0.62-0.89 mg/kg, having a mean and standard deviation of 0.742 ± 0.107 mg/kg. Zinc had a concentration range of 7.21-12.32 mg/kg, having a mean of 9.895 ± 2.482 mg/kg. Iron had a concentration range of 62.53-180.62 mg/kg, having a mean of 122.492 ± 57.951 mg/kg. Manganese had a concentration range of 33.21-48.67 mg/kg, having a mean of 42.762 ± 6.759mg/kg. The cadmium concentrations had a range of 0.39-0.92 mg/kg, having a mean and standard deviation of 0.690 ± 0.245 mg/kg. Lead had a concentration range of 3.21-5.21 mg/kg, having a mean of 4.467 ± 0.847 mg/kg. Nickel had a concentration range of 18.28-

22.06 mg/kg, having a mean of 20.893±1.362mg/kg. The mean metal concentrations in sediment from Mkpanak beach were all below the WHO and SQG permissible limits except for chromium which was above the WHO limits, and nickel and cadmium which were above SQG permissible limits. The mean metal concentrations in Mkpanak sediments showed a decreasing trend of Fe>Mn>Ni>Zn>Cu>Pb>Cr>Cd (Table 3).

Distribution of various metals in sediments across the stations is presented in Table 3. However, statistically, copper, zinc, iron, cadmium and nickel did not show any significant difference in their mean concentrations in sediments from UAC, Iwuochang and Mkpanak beaches (P>0.05), while chromium, manganese and lead showed significant difference in their mean accumulation in sediments from UAC, Iwuochang and Mkpanak beaches (P<0.05). The overall mean metal concentrations and standard deviation in sediments from Qua Iboe River were; 6.526 ± 2.233, 0.508 ± 0.191, 19.767 ± 0.459, 110.449 ± 51.934, 37.313 ± 9.208, 0.638 ± 0.228, 3.371 ± 1.800 and 9.157 ± 2.459 mg/kg for copper, chromium, nickel, iron, manganese, cadmium, lead and zinc respectively. Overall mean concentration of metals in Qua Iboe River sediments were all below WHO and SQG permissible limits except for chromium which was above WHO permissible limits, and cadmium and nickel which were above SQG limits, showing a decreasing trend of Fe>Mn>Ni>Zn>Cu>Pb>Cd>Cr (Table 3).

Table 3: Heavy metals concentration in sediments from different stations of Qua Iboe River

Metals	UAC	Iwuochang	Mkpanak	Mean	WHO limit	SQG
Cu	5.102±1.488[a] (3.36-6.50)	7.223±2.292[a] (4.06-9.24)	7.253±2.414[a] (3.99-9.41)	6.526±2.233	20	35.7
Cr	0.065±0.124[a] (0.04-0.09)	0.717±0.119[b] (0.59-0.84)	0.742±0.107[c] (0.62-0.89)	0.508±0.191	0.10	-
Zn	7.580±1.891[a] (5.36-9.28)	9.996±2.518[a] (6.98-12.61)	9.895±2.482[a] (7.21-12.32)	9.157±2.459	50-300	123
Fe	71.212±9.79[a] (60.33-83.66)	137.643±52.986[a] (70.11-188.94)	122.492±57.95[a] (62.53-180.62)	110.449±51.934	-	-
Mn	28.608±4.116[a] (20.26-30.89)	40.570±9.292[b] (30.12-49.01)	42.762±6.759[c] (33.21-48.67)	37.313±9.208	-	-
Cd	0.493±0.149[a] (0.35-0.68)	0.730±0.235[a] (0.42-0.96)	0.690±0.245[a] (0.39-0.92)	0.638±0.228	-	0.6
Pb	1.085±0.072[a] (1.01-1.18)	4.560±0.941[b] (3.29-5.72)	4.467±0.847[c] (3.21-5.21)	3.371±1.800	<20	35
Ni	18.001±2.04[a] (15.08-20.28)	20.407±1.819[a] (17.34-22.56)	20.893±1.362[a] (18.28-22.06)	19.767±0.459	-	18

Values are in Mean ± standard deviation (Ranges in Parenthesis)
*Means with the same superscript are not significantly different (P>0.05)

The summary of the co-relation values and co-relation equation between the concentration of heavy metals in muscle of fish against the concentration of metals in Sediments and Water is shown in Table 4a and 4b respectively. The Copper and Iron concentrations in muscle of the fish positively related significantly (Strong relationship) with Copper and Iron concentrations in sediments (r = 0.84 and 0.84 respectively) at P<0.05, while concentrations of Nickel, Chromium and Zinc in Fish muscle positively and slightly related significantly (Positive Slightly Strong relationship) with the Chromium, Nickel and Zinc concentrations in sediments (r = 0.71, 0.73 and 0.56 respectively) at P<0.05. Cadmium concentrations in Fish muscle related negatively and significantly (Negative Strong Relationship) with the Cadmium concentrations in Sediments (-0.99). Manganese concentrations in Fish Muscle had a Slight negative Strong relationship with that of Sediments (r = -0.62) at P<0.05 (Table 4a). The concentrations of Copper in Fish muscle positively related significantly (Strong relationship) with Copper concentrations in Water (r = 0.87) at P<0.05, while the concentrations of Iron and Zinc in Fish muscle positively and slightly related significantly (Positive slightly strong relationship) with Iron and Zinc concentrations in Water (r = 0.60 and 0.60 respectively) at P<0.05. Cadmium concentrations in Fish Muscle had a Slight negative Strong relationship with that of Water (r = -0.70) at P<0.05 (Table 4b). Chromium and Nickel concentrations in Fish muscle came from mainly sediments, while Copper concentrations in Fish muscle came from both sediments and Water. Iron concentrations in Fish Muscle came mainly from sediments and slightly from water. Zinc concentrations in Fish Muscle came slightly from both sediments and water (Table 4c).

Table 4: Relationship between metal concentrations in fish muscle and metal concentrations in sediments, water

a) Sediment and fish

Sediment against Fish muscle(mg/kg)	r- value	R^2- value	Equation	Relationship Inference
Cd	-0.99	0.97	Y= -0.1071X + 0.8825	Negatively strong
Cr	0.73	0.52	Y= 0.1735X + 0.544	Slightly strong positive
Cu	0.84	0.71	Y= 1.6598X + 1.1627	Positively Strong
Fe	0.84	0.70	Y = 13.582X – 210.62	Positively Strong
Mn	-0.62	0.39	Y = -15.192X + 203.4	Slightly strong negative
Ni	0.71	0.51	Y = 0.4638X + 11.521	Slightly strong negative
Zn	0.56	0.31	Y = 0.716X + 1.1795	Slightly strong positive

b) Water and fish

Water against Fish muscle(mg/kg)	r- value	R^2- value	Equation	Relationship Inference
Cd	-0.70	0.49	Y= -0.0212X + 0.3224	Slightly strong negative
Cr	0.12	0.016	Y= 0.0007X + 0.0163	No relationship
Cu	0.87	0.76	Y= 0.1137X + 0.0227	Positively strong
Fe	0.60	0.36	Y = 0.0167X – 0.0724	Slightly strong positive
Mn	0.21	0.046	Y = 0.1827X – 0.7757	Positively Weak
Ni	-0.16	0.02	Y = -0.0069X + 0.3554	Negatively Weak
Zn	0.60	0.36	Y = 0.0291X – 0.0363	Slightly strong positive

c) Relationship comparison between fish against sediment and water

Metal Relationship Comparison	Sediment against muscle r –value	Water against muscle r-value	Abiotic metal source
Cd	-0.99	-0.70	-
Cr	0.73	0.12	Sediment
Cu	0.84	0.87	Both Sediment and Water
Fe	0.84	0.60	Mainly from sediment and slightly from water
Mn	-0.62	0.21	-
Ni	0.71	-0.16	Sediment
Zn	0.56	0.60	Slightly from both Sediment and Water

Correlation Rating: 0.75 – 0.99 (Strong), 0.50 – 0.74 (Slightly Strong), 0.15 – 0.49 (Weak), 0 – 0.14 (No Relationship).

4. Discussion

Fishes are one of the most reliable metal pollution indicators in fresh water systems. Fish reveals both the past and present heavy metal exposures [5]. Continuous environment monitoring of metals in water, sediment and aquatic fauna gives an idea with regards the sources, degree of pollution, and distribution [17]. Metal concentrations in the muscles of *Clarias gariepinus* varied across the different sampling stations, with the control station (UAC) accumulating the least heavy metals when compared to the other two stations (Iwuochang and Mkpanak). This is due to the very minimal activities around the control station (UAC beach), when compared to the intense activities observed at Iwuochang and Mkpanak beach. The accumulation of zinc, nickel, chromium, manganese, cadmium and copper in muscles of *Clarias gariepinus* in the present study were much higher than that reported by [18]. These discrepancies between the two studies could be traced to the difference in fish species used, difference in study area, difference in study period and difference in activity levels. It could also be due to differences in size, age, feeding habit, capture season of the fishes used in the two studies [19]. Also, these discrepancies could be due to difference in numbers of trophic levels of the fish, sampling location, type of pollutant [20], the length of time in water and bio-activity of a metal [21, 22]. Lead was not detected at all in the muscles of *Clarias gariepinus* from Qua Iboe River, and this could be as a result of inability for lead to enhance formation of Metallothionein in fish muscles [23]. The iron and nickel concentration varied significantly in muscles across sampling stations indicating that the various human activities affected the accumulation in muscles of *Clarias gariepinus*. The mean concentrations of the metals in *Clarias gariepinus* muscle were all above the WHO limits, except copper, zinc and cadmium. This indicates that the muscles are slightly polluted with iron, manganese, chromium and nickel, and as such unsafe for consumption. The chromium, iron, manganese and nickel concentration in the muscles of *Clarias gariepinus* of the present study was higher than that reported by [24]. The chromium, cadmium and nickel concentration of the present research were also higher than the report of [25]. The overall mean concentrations of the different metals in *Clarias gariepinus* muscle from Qua Iboe River showed a decreasing trend of Fe>Ni>Zn>Mn>Cu>Cd>Cr, which varied with the trend of Cr > Mn > Pb > Ni > Zn > Cu reported by [26], Zn > Mn = Cu > Pb > Cd reported by [27] and Cu > Fe >Zn > Cr > Pb > Cd > Co reported by [28].These discrepancies in metal concentration and metal trends between the different studies could be traced to the difference in fish species used, difference in study area, difference in study period, difference in activity levels, differences in size, age, feeding habit, sex, capture season of the fishes used [19], difference in numbers of trophic levels of the fish, sampling location, type of pollutant [20], the length of time in water and bio-activity of a metal [21, 22].

Metal concentrations in water varied across the different sampling stations, with the control station (UAC) having the least heavy metals concentration when compared to the other two stations (Iwuochang and Mkpanak). This is due to the very minimal activities around the control station (UAC beach), when compared to the intense activities observed in Iwuochang and Mkpanak beach. Nickel, manganese, copper, chromium, cadmium, lead and iron varied significantly between water from the different stations, indicating human activities influenced these metals accumulation in water. The zinc, nickel, chromium, cadmium and copper concentrations were more in mkpanak water, and this could be due to increase in petroleum spills in the shores as well as domestic sewage, increase in industrial discharge as well as industrial waste, increase in dumping of decaying roofing sheets, sea vessels paints and petroleum run-off respectively [29]. Iron and lead concentrations were more in Iwuochang beach, and this could be as a result of high iron waste discharges along with increased petroleum spill as well as discharge of lead laden waste respectively [29]. The mean Iron and Lead concentrations in water from Qua Iboe River were above WHO permissible limits, but within FMENV permissible limits. Manganese was above FMENV permissible limits. Nickel was above WHO and FMENV permissible limits, while cadmium was above WHO permissible limits. The remaining metals were within the WHO and FMENV permissible limits. This indicates that the water from Qua Iboe River is slightly polluted with manganese, cadmium and nickel and as such unsafe for drinking. The accumulation of copper in the water of the present study is lower than the findings report of [30]. Zinc concentrations in water of the present study is higher than that of the report of [31], but lower than the finding reported by [30]. The concentrations of iron, lead and nickel in water of this study is smaller than the findings reported by [31] and [30]. Accumulation of cadmium in water of this study is lower than findings reported by [30]. Also, mean concentrations trend of heavy metals in water showed a decreasing trend of Mn> Cu> Fe> Zn> Cd> Ni> Pb> Cr, and this trend did not corroborate with the trends of Zn > Mn > Pb > Cu > Cd and Fe > Ni > V> Pb > Co > Zn reported by [27] and [31] respectively. These discrepancies in metal concentration and trend between the studies could be traced to the difference in study area, difference in study period, difference in the extent of pollution, difference in activity levels, difference in sampling location, type of pollutant [20], the length of time in water and bio-activity of a metal [21, 22].

Metal concentrations in Sediments varied across the different sampling stations; with the control station (UAC) having the least heavy metals concentrations when compared to the other two stations (Iwuochang and Mkpanak). This is due to the very minimal activities around the control station (UAC beach), when compared to the intense activities observed in Iwuochang and Mkpanak beach. Chromium, manganese, lead and nickel varied significantly in sediments between stations, indicating human activities influenced these metals accumulation in water. The copper, chromium and nickel concentration were more in Mkpanak sediments, and this could be due to increase in petroleum spills in the shores as well as domestic sewage, increase in industrial discharge as well as industrial waste and sea vessels paints as well as petroleum run-off respectively. Also, zinc, cadmium, iron and lead concentration were more in Iwuochang beach sediment, and this could be to increase in dumping of decaying roofing sheets discharge, sea vessels paints, increased discharge of iron laden waste and increased petroleum spill as well as discharge of lead laden waste respectively. Iron concentration is always high in Nigerian sediments, because it occurs naturally in Nigerian sediments [32]. The mean concentrations of chromium in the sediments of Qua Iboe River were above the WHO permissible limits, but cadmium and nickel was above the SQG permissible limits. All the other metals were below the WHO and SQR permissible limits. This indicates that the sediments from Qua Iboe River are slightly polluted with chromium, cadmium and nickel. The sediment concentrations of copper in this study is greater than that reported by [30]. The lead, nickel, iron and Zinc concentrations in sediments of this study are higher than that reported by [31] and [30]. Accumulation of cadmium in the sediments during this study is smaller than that reported by [30]. Also, the mean concentrations of heavy metals in sediments showed a decreasing trend of Fe> Mn> Ni> Zn> Cu> Pb> Cd> Cr, and this trend did not corroborate with the trends of Mn > Zn > Al > Cr > Cu > Pb > Co > Ni > Cd and Fe > Mn > Zn > Cu > Pb > Cd reported by [33] and [34] respectively. These discrepancies in metal concentrations and trend between the sediments of the studies could be traced to the difference in study area, difference in sediment type, difference in study period, difference in the extent of pollution, difference in activity levels, difference in sampling location, type of pollutant [20], the length of time in water and bio-activity of a metal [21, 22].

Copper and iron accumulation in fish muscle related strongly and positively with copper and iron concentrations in sediments, and this indicates that the copper and iron concentrations in fish increases with increase in these aforementioned metals in sediments. Copper and iron accumulation in fish muscle had a strong positive and slightly positive strong relationship respectively with Copper and iron concentrations in water. This shows that the increase in copper in fish increases with its increase in water, and iron in fish increases slightly with its increase in water. This indicates that copper accumulation in fish muscle came from both sediments and water, while iron came mainly from sediments and slightly from water. Chromium, nickel and zinc accumulation in fish muscle had a slightly strong positive relationship with chromium, nickel and zinc concentrations in sediments. This shows that the increase in chromium, nickel and zinc in fish increases slightly with its increase in sediments. In the case of water, Chromium, nickel and zinc accumulation in fish muscle had no relationship, negative and slightly strong positive relationship with chromium, nickel and zinc concentration in water respectively. This indicates that chromium and nickel accumulation came from sediments, while zinc accumulation in fish muscle came slightly from both sediments and water. The results of this study did not corroborate with the report of [35] and [36], who reported water as the abiotic factor responsible for accumulation of metals in fish. These variations between the studies could be due to difference in fish species, feeding habit, pollution status of study area and depth inhabited by fish (whether pelagic or bottom dwellers).

5. Conclusion

In conclusion, the study revealed that heavy metals concentrations in water, sediments and muscles of *Clarias gariepinus* varied across sampling stations, with the control station (UAC) having the least. It was also revealed that muscles of *Clarias gariepinus* was slightly polluted with chromium, iron, nickel and manganese, water was slightly polluted with manganese, cadmium and nickel, sediments were slightly polluted with chromium, cadmium and nickel. The accumulation of chromium and nickel in muscles *Clarias gariepinus* came from sediments, while the accumulation of copper in the muscles of *Clarias gariepinus* originated mainly from both the sediments and water. Iron and zinc in fish muscle came from mainly sediments as well as slightly from water and slightly form both sediments and water respectively.

6. References

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