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Heavy Metals Accumulation in Water, Sediments and Catfish (*Clarias gariepinus*) from Two Fishing Settlements along River Kaduna in Niger State, Nigeria

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

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ABSTRACT

Water, sediments and catfish (*Clarias gariepinus*) samples obtained from two fishing settlements along River Kaduna at Shiroro and Zungeru in Niger State, Nigeria were analyzed for some selected heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) using Buck Scientific Model 210 VGP atomic absorption spectrophotometer. The data obtained were then, analysed using one-way analysis of variance (ANOVA) statistical analysis. All heavy metals analyzed were detected in all the samples except Pb, not detected in water and catfish samples and also, Cd was not detected in sediments sample. The highest heavy metal concentrations were found in the sediments compared to the water and catfish this is because sediments are known to be major depository of metals present in the system. Zungeru fishing settlement has higher concentration of the following metals: 0.72±0.84 mg/L Fe in the water; 1331.00±46.98 mg/kg Fe and 160.83±12.18 mg/kg Zn in the catfish;

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7447.33±139.07 mg/kg Fe and 164.67±7.63 mg/kg Mn in the sediments than the values from Shiroro site. Shiroro fishing settlement has the highest concentration of Fe in water 5.86±0.11 mg/L, highest Fe in catfish 1482.83±99.50 mg/kg, highest in sediment 26629.50±487.97 mg/kg. The heavy metals in the water from Shiroro River follow the ranking: Fe > Cu > Cr > Zn > Mn > Cd > Ni; while the metals in the fish from Zungeru follow the order: Fe > Zn > Mn > Cr > Cu > Cd > Pb, Ni. Variable results were obtained from the two fishing settlements, but results obtained for some metals in different samples (water, catfish and sediments) were within maximum permissible limits for water, sediments and fish as recommended by WHO/USEPA, while other metals were higher than the recommended limits. Regular monitoring of these heavy metals in water, catfish and sediments on these fishing settlements is recommended.

Keywords: Sediment; fish; heavy metals; shiroro; zungeru; water.

1. INTRODUCTION

Heavy metals are pollutants of the aquatic environment because of their capability to poison humans and build-up in marine organisms [1]. The toxicity effects of these heavy metals causes' serious problems on the health of man due to their easy absorption into the food chain and bioaccumulation processes [2,3]. Metals are not decomposable but undergo biogeochemical cycles with considerably different residual time in diverse spheres areas and compartment of the environment. Heavy metals such as Fe, Mn, Zn, Co and Cr play biochemical functions in living cells of aquatic organisms in minute amounts but in high concentrations however they become toxic [4].

Potential toxic metals may be generated from many diverse origins in rural and urban settlements and other activities such as vehicular emissions and industrial discharges [5,6]. Heavy meals are natural constituent of our environment produced from an array of natural and anthropogenic origin [7].

In recent years, anthropogenic activities have created ecological pressure in natural habitats and have seriously increased the atmospheric deposition of heavy metal pollutant even in places far away from close human impact [8,1]. Numerous studies have confirmed that substantial amounts of chemical elements are leached from refuse dumps into ground water, streams and rivers [5]. Consequently, variety of species of aquatic organism becomes limited with the level of heavy metal pollution [9].

Aquatic environment is one of the receiving ends of heavy metals which go back into the food chain through bioaccumulation and bio-magnification in marine animals and man respectively [7]. Bio-magnification is swayed by metal absorption or contaminants which could be shifted through the numerous tropic levels in an ecosystem [10]. Contaminants exist in low level in water and at substantial concentration in sediments and biota [11]. Sediments and water are often used as pointers for the nature of pollution of the ecosystem [12]. Also, fish is well-thought-out as one of the most essential pointers in freshwater systems for assessment of metal pollutant levels [11].

Heavy metals are classified as: potentially poisonous or non-essential such as Al, As, Cd, Pb and Hg; semi-essential like Ni, V and Co and essential like Cu, Zn and Se [13]. Associated health risks of environmental chemical element have led to a foremost change in global interest toward determent of heavy metal build-up [8]. Mercury, lead, cadmium and nickel are amid the highly harmful metallic pollutants [9].

The United States environmental action group has asserted that the world's main contaminated areas endanger the health of above 10 million people in many lands. Thus the rising tendency in concentration of heavy metals in the environment has established substantial awareness among ecologists and scientist worldwide during the last period [14].

Accumulations of heavy metals in water systems can twice as increase the human consumption through food chain besides through drinking water [8]. The significant contamination of marine animals with heavy metals due to polluted soil and water has been examined and has been introduced via the sea, river and even irrigation canals. Afterwards, the intake of polluted products forms a significant route of human and animal exposure [15,16].

Therefore, to check the growing cases of food contamination and health risk factors, it is important that informed research into sources and modes of heavy metal pollution should be undertaken so that toxic metals which pose a menace to human well-being can be minimized. The results attained from this finding will provide data on the background levels of metals in sediments of the rivers and water in the studied area and enable the effective monitoring of both environmental quality and the health of the organisms inhabiting the ecosystem.

2. MATERIALS AND METHODS

2.1 Study Area

Shiroro River is located on latitude 9°58` 25`` North and Longitude 6°50` 6`` East. It is situated at a dam known as Shiroro dam, owned by Power Holding Company of Nigeria (PHCN) and located 550 meters downstream of the confluence of Kaduna River with its tributary, the Dinya. The people of the study area are engaged in trading, farming and fishing as means of livelihood.

River Kaduna at Zungeru Bridge is next to Akusu and is located on latitude 9°49` 38.45`` North and longitude 6°9` 13.63`` East. The people of the study area are also engaged in trading, farming and fishing as their means of livelihood [17].

2.2 Sample Collection and Pre-treatment

Samples were collected during the month of May-June, 2014 by random systematic sampling. Three sediment samples were collected in polythene bags from the two different locations of the rivers (the up and downstream). Samples of water were collected using a bailer at up and downstream points of the rivers. At each point, three samples were collected and made into a composite in a 2 litre plastic container prewashed with 2 moldm^{-3} HNO_3 in order to stabilize the metal ions and prevent precipitation. Three samples were collected from each location, tightly corked, brought to the laboratory and kept refrigerated for further analysis. The collected sediment samples were air-dried and large unwanted particles removed by hand-picking. The dried samples were then ground with an agate mortar and pestle and then sieved with a 2 mm mesh size sieve before storing for further analysis. Fresh fish samples newly caught were bought from the local fishermen at each sampling location. They were kept in a cooler packed with ice block so as to retain their freshness and then conveyed to the laboratory for segmentation of the organs to be analysed. After washing with distilled water, the parts were separated into gills, intestine and tissue and dried in an oven at 105°C for 48 hours. All parts of the dried fish were pounded together to fine sizes and sieved with a 2 mm sieve mesh before keeping for further analysis.

2.3 Methods

The procedure involving the use of trioxonitrate (V) acid as described by AOAC was employed [18]. To each 50 cm^3 triplicate samples of water in 250 cm^3 conical flask, 10 cm^3 of HNO_3 was added and then heated at 200°C for 1 hour. In each case, 2 cm^3 of hydrogen peroxide was added and the sample was further heated for about 30 minutes. The remaining mixture obtained was then made to 20 cm^3 mark with distilled water and filtered into a 50 cm^3 volumetric flask and made up to the mark. A blank determination was also carried out.

To each 1.0 g triplicate sample in 250 cm^3 conical flasks, 20 cm^3 of a mixture of perchloric acid and trioxonitrate (V) acid at a 2:1 ratio (v/v) was added and heated at 200°C on a hot plate to near dryness. To each triplicate sample, 20 cm^3 of 0.5 moldm^{-3} trioxonitrate (V) acid was added and filtered into 50 cm^3 volumetric flask through Whatman No 42 filter paper. The filtrate obtained was made up to 50 cm^3 mark with distilled water and stored in pre-cleaned polyethylene bottles for heavy metals analysis using Atomic Absorption Spectrometer (Buck Scientific model 210 VGP) [19,20].

1.0 g portion of the ground samples was weighed using a digital weighing balance (sensitive to ± 0.01g). To each 1.0 g triplicate sample of catfish in 250 cm^3 conical flask, 10 cm^{3}trioxonitrate (V) acid and 2 cm^3 perchloric acid added and then heated at 200ºC for 2 hours. After complete digestion, the residue was dissolved and diluted using 0.2% v/v trioxonitrate (V) acid to 20 cm^3 volumes and then filtered into a 50 cm^3 volumetric flask and made up to the mark [21].

2.4 Statistical Analysis

One-Way Analysis of variance ANOVA was used as a statistical inference for the comparison of results obtained from each settlement. The identification of the relationship was carried out by using Pearson correlation matrix and Duncan

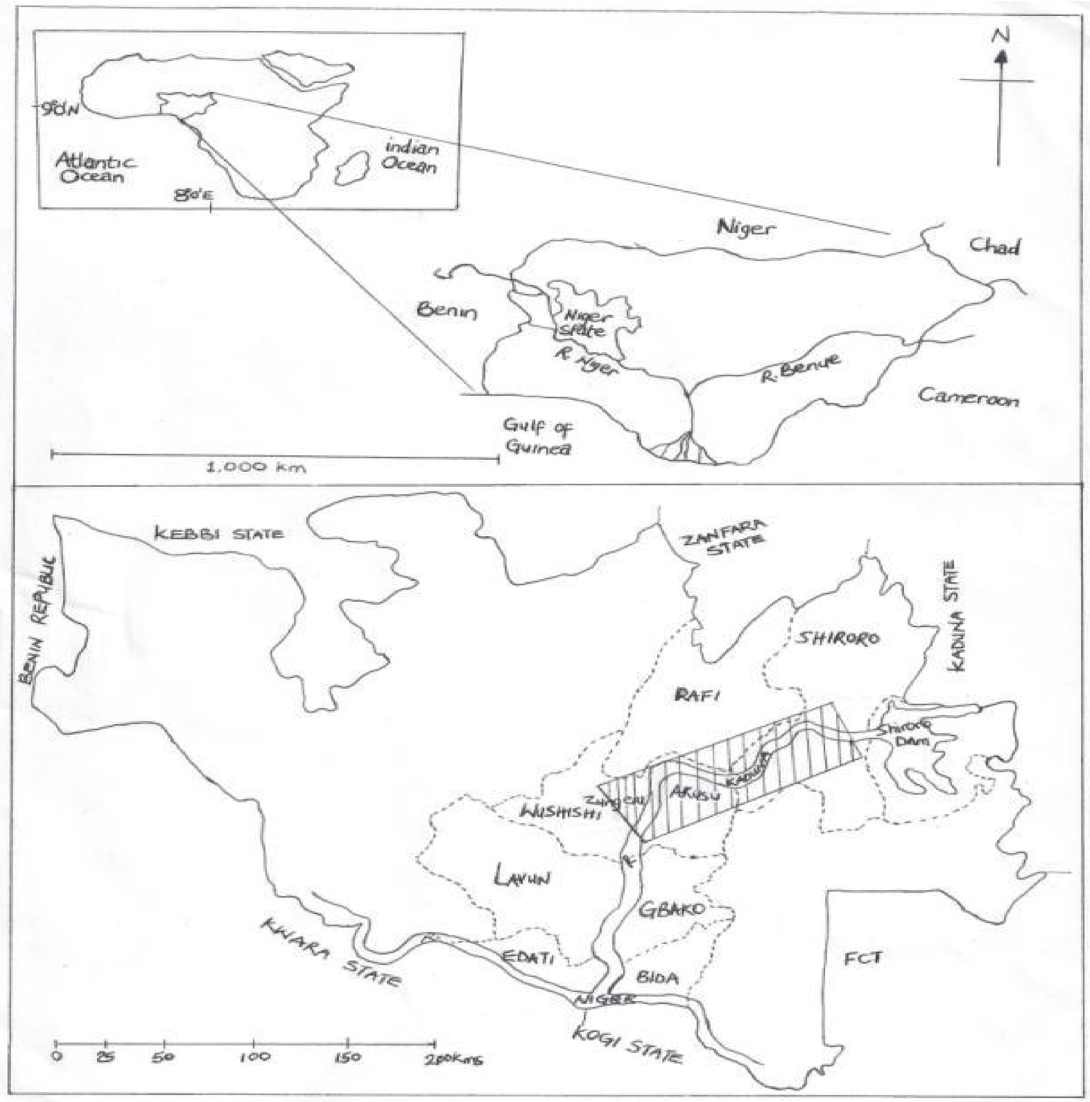

Fig. 1. Base map of Niger state showing local government areas along river Kaduna and the sample site

multiple range test. The samples were analyzed using ANOVA test in the Statistical Package for Social Science (SPSS) software [22]. The 95% confidence intervals ($P < 0.05$) were used to determine error margin and also significant differences between the different sampling point and settlement and the accuracy of the data obtained from the analysis.

3. RESULTS AND DISCUSSION

3.1 Heavy Metals in Water

From the results in Table 1 and Figs. 2 and 3, the concentration of Mn in the water samples ranged from 0.10±0.00 to 0.27±0.08 mg/L from the two locations. Higher concentrations of 0.21±0.02 to 0.27±0.08 mg/L of Mn were obtained for water samples from Zungeru compared to water samples from Shiroro which were 0.10±0.00 to 0.11±0.01 mg/L of Mn. Thus, indicating higher contamination of Mn in water samples from Zungeru. Similar values were obtained from Zayandeh Rood River in Isfahan-Iran (0.037 to 0.072 mg/L) reported by Sanayei et al. [2]. However, the obtained result is lower than those recorded by Edward et al. [7] with concentrations of 0.78 – 0.80 mg/L in Odo-Ayo River in Ado-Ekiti, Ekiti-State Nigeria. Nonetheless, a reported result in this study were above the permissible limits of 0.05 mg/L Mn in describing water by WHO/FEPA, and indicates pollution by Mn [23].

The concentrations of Fe as shown in Table 1 were 5.47±0.34 to 5.86±0.11 mg/L for water samples from Shiroro and 6.68±0.46 to 7.02±0.84 mg/L for Zungeru water samples. This indicates that, concentration was high in the latter than the former. There is no distinct pattern in the distribution of Fe since a lower concentration of 5.47±0.34 mg/L was from the upstream area of Shiroro while a lower concentration of 6.68±0.46 mg/L was obtained in the downstream area of Zungeru (Figs. 2 and 3). The value obtained corresponds to those reported for concentration in water samples from Odo-Ayo River in Ado-Ekiti, Ekiti-State, Nigeria (5.87 mg/L) by Edward et al. [7]. Nonetheless, the reported result was higher than the permissible limits of 0.3 mg/L Fe in drinking water by WHO, and indicates pollution by Fe [24].

The distribution of Cu content in the water samples from Table 1 were 0.03±0.00 to 0.53±0.02 mg/L. Significant variation was visible in the results with minimum concentrations of 0.03±0.00 mg/L obtained from the upstream of Zungeru and maximum concentration of 0.08±0.03 mg/L obtained from the downstream (Fig. 3). While from Shiroro, the downstream gave a lower concentration of 0.04±0.00 mg/L and the upstream, a higher concentration of 0.53±0.02mg/L (Fig. 2). This discrepancy could be attributed to dilution factor of the rivers. Mean values of 0.84 mg/L obtained by Edward et al. [7] from Odo-Ayo River in Ado-Ekiti, Ekiti-State, Nigeria was slightly higher than the obtained values in the study. The results obtained from the study were all lower than the permissible limits of 1.00 to 2.00 mg/L recommended by WHO, indicating non pollution of this metal in the studied sample [24].

The concentration of Zn in all water samples were 0.27±0.08 mg/L (SU); 0.24±0.02 mg/L (SD); 0.34±0.09 mg/L (ZU) and 0.34±0.05 mg/L (ZD) with no significant difference at $P \leq 0.05$ (Table 1). Higher concentration of Zn was obtained in water sample from Zungeru as compared to water samples from Shiroro, with the distribution in the upstream and downstream of each interchange; Shiroro had more Zn concentration in water samples from the downstream while the reverse was the case in Zungeru (Figs. 2 and 3). Values obtained from the present study are lower than 3.19 mg/L reported for water samples from Uke Stream, Nasarawa State, Nigeria by Opaluwa et al. [12]. Results from the present study were within the acceptable limits for drinking water of 3.0 mg/L recommended by WHO [24].

The concentration of Cr contents ranges from 0.18±0.05 to 0.33±0.03 mg/L in all samples in Table 1. The highest concentration of 0.33±0.03 mg/L was obtained from upstream of Shiroro and the downstream of Zungeru respectively while the lowest concentration of 0.18±0.05 mg/L in water sample was obtained downstream of Shiroro (Figs. 2 and 3). These results were compared with the 2.08 mg/L reported by Olatunji and Osibanjo, for Inland Fresh Water from River Niger and River Osara in North-Central Nigeria [25] which is higher than the present study while values obtained from Bara River, Nowshera, KPK province, Pakistan for surface water contamination in the range of 0.16 to 0.29 mg/L by Amir Waseem et al. [26] compares favourably with present study. Concentrations obtained for the samples, however, did not exceed maximum permissible value of 0.05 mg/L as recommended by WHO [24].

From Table 1, cadmium concentrations in water samples were obtained from downstream areas of both Shiroro and Zungeru (Figs. 2 and 3). This could be as a result of activities from the Shiroro Dam which flow downstream. In Zungeru, it was observed that vehicles and motorcycle washed from upstream flows downstream could have led to the release of Cd based contaminants into the water. Thus, the concentration of Cd in Shiroro was within the maximum permissible limit of 0.003 mg/L [27], but slightly above the permissible limit in Zungeru. The concentrations of Cd in both rivers however, were within the permissible limit for irrigation water of 0.01 mg/L [28].

The concentration of lead in all the water samples as shown in Table 1 and Figs. 2 and 3 were below detection limits (BDL), indicating minimum contamination from Pb. Findings by Opaluwa et al. [12], Ali et al. [29] and Mwegoha and kihampa [30] in Uke Stream Nasarawa State, Red Sea at Jeddah Islamic Port Coast and Dares Salaam City, Tanzania reported values of 0.04 mg/L, 1.20 mg/L and 0.08 mg/L respectively. This shows that the levels of Pb concentrations are sometimes determined by anthropogenic sources or by environmental factors. Permissible limit of Pb in drinking water is 0.01 mg/L as recommended by WHO [24].

From Table 1, nickel contents was only present in minimum amount downstream of Shiroro with a mean value of 0.01±0.00 mg/L while it was absent from Zungeru (Figs. 2 and 3). Reason for the absence of Ni upstream of Shiroro is unclear but dilution factor is suggested. Olatunji and Osibanjo reported a mean concentration of 0.78±0.12 mg/L for Inland Fresh Water from River Niger and River Osara in North-Central Nigeria [25] which were greater than those reported from downstream of Shiroro in the present study. Amir Waseem et al. [26] reported values ranging from <0.001 to 1.52 mg/L in surface water in Pakistan which were within the values obtained from the present study. The obtained values are however within the maximum permissible limit for water of 2.00 mg/L [24].

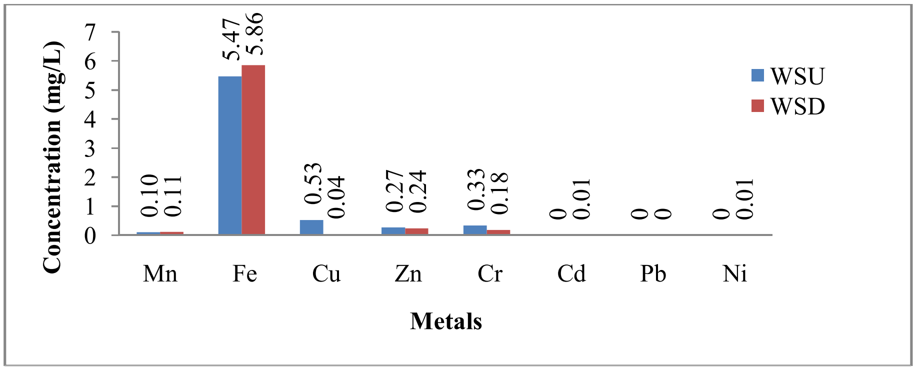

Fig. 2. Mean concentrations of heavy metal in water sample from Shiroro fishing settlement

Table 1. Concentration of heavy metals in water samples collected from Shiroro and Zungeru fishing settlements (mg/L)

		Sample	Sites		
Metals	**SU**	**SD**	**ZU**	**ZD**	**Standard limit**
Mn	0.10±0.00[a]	0.11±0.01[a]	0.27±0.08[b]	0.21±0.02[b]	0.05 WHO/FEPA 2003
Fe	5.47±0.34[a]	5.86±0.11[ab]	7.02±0.84[c]	6.68±0.46[bc]	0.30 WHO 2008
Cu	0.53±0.02[ab]	0.04±0.00[ab]	0.03±0.00[a]	0.08±0.03[c]	1.00-2.00 WHO 2008
Zn	0.27±0.08[a]	0.24±0.02[a]	0.34±0.09[a]	0.34±0.05[a]	3.00 WHO 2008
Cr	0.33±0.03[a]	0.18±0.05	0.22±0.09[a]	0.33±0.02[a]	0.05 WHO 2008
Cd	BDL	0.01±0.00[a]	BDL	0.03±0.00[b]	0.01 USEPA 1986
Pd	BDL	BDL	BDL	BDL	0.01 WHO 2008
Ni	BDL	0.01±0.00	BDL	BDL	2.00WHO 2008

Values are mean ± SD of three determinations. Samples with the same superscripts across row are not significantly different at P ≤ 0.05 while sample with different superscripts across row are significant difference at P ≤ 0.05. WSD: Shiroro Downstream, SU: Shiroro Upstream, ZU: Zungeru Upstream, ZD: Zungeru Downstream, BDL = Below Detectable Limit. mg/L: milligram per litre

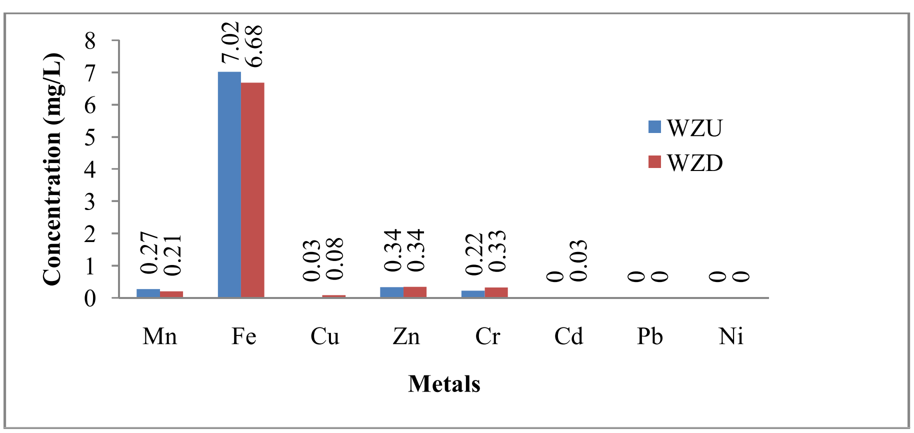

Fig. 3. Mean concentrations of heavy metal in water sample from Zungeru fishing settlement

3.2 Heavy Metals in Sediment

Table 2, shows that sediment sample for Mn from Shiroro had higher concentration of 370.17±27.10 mg/kg in downstream and 402.33±32.08 mg/kg upstream, while sediment sample from Zungeru had lower concentration of 116.83±4.69 mg/kg at upstream area and 164.67±7.63 mg/kg at the downstream area (Figs. 4 and 5). The current study is high when compared with sediment concentrations obtained from River Kubanni Zaria in Nigeria (184.5 to 293.25 mg/kg) as reported by Butu and Iguisi [5]. Maximum allowable limit for Mn as recommended by the USEPA is 300 mg/kg [31], implying that there was major Mn contamination in Shiroro sediments while that for Zungeru were within acceptable limits.

The concentration of Fe (Table 2) in sediments obtained from Shiroro had higher concentration of 26629.50 ± 487.97 mg/kg at the downstream area and 15546.11±310.90 mg/kg at the upstream area. Samples from Zungeru had Fe concentration of 7447.33±139.07 mg/kg at the downstream and a concentration of 5446.33±118.49 mg/kg at the upstream area which is lower than the former (Figs. 4 and 5). The higher concentration from Shiroro could be due to anthropogenic sources of contamination, especially at the downstream area. These results were compared with those obtained from sediments collected in Panama (17788.12 mg/kg) by Greany [32]. However, the Fe concentrations from the present study were all higher than 20000 mg/kg as recommended by CBSQG for sediments [33].

From Table 2, a higher concentration of 30.17±5.80 mg/kg Cu was obtained from the upstream of Shiroro and 24.50±1.32 mg/kg from the downstream, while Zungeru recorded 2.0±0.86 mg/kg upstream and 4.33±0.29 mg/kg downstream (Figs. 4 and 5). Similar values were obtained by Edward et al. [7] and Sabo et al. [34] from River Delimi in Jos and Odo-Ayo River in Ado-Ekiti with 1.98±0.18 and 0.83 to 0.84 mg/kg, which compares with the results obtained from Zungeru in the study. A study by El-Zokm et al. [1] compares favourably with the results obtained from Shiroro of between 34 mg/kg and 270 mg/kg. The concentration of Cu in samples from Shiroro was above permissible limit of 18.70 mg/kg as recommended by USEPA, while those from Zungeru were within permissible limits [31].

From Table 2 and Figs. 4 and 5, Zn concentration in sediment samples from Shiroro downstream gave 84.33±3.88 mg/kg and upstream 103.33±3.08 mg/kg. Similar values were obtained for Stream Sediments of the South Dry Sac River (89.0 to 123 mg/kg) by Gwenda [35]. However, all the results obtained for Zn in sediments from the sample were lower than the 124.00 mg/kg recommended by USEPA for sediments [31].

The concentration of Cr as shown in Table 2 ranged from 5.17±0.40 to 16.33±1.60 mg/kg in all samples. A mean concentration of Cr 16.33±1.06 mg/kg was obtained at the upstream area of Shiroro, which was twice the concentration, obtained from the downstream area of 8.83±0.17 mg/kg. However, Zungeru recorded 5.17 ± 0.40 and 7.17±0.16 mg/kg at the upstream and downstream area respectively (Figs. 4 and 5). Results obtained were less, compared to 52.34 to 311.69 mg/kg reported by Barakat et al. [36] in Morocco and Oyakhilome et al. [37] for Sediment

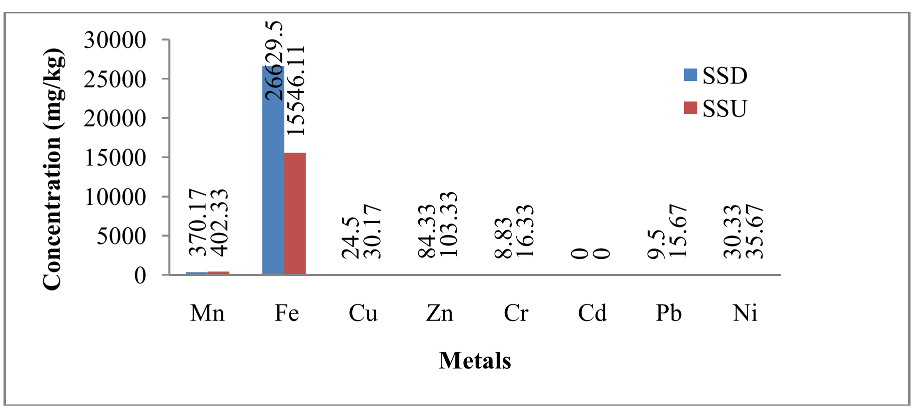

Fig. 4. Mean heavy metal concentrations in sediment samples from Shiroro fishing settlement

Table 2. Concentration of heavy metals in sediment samples from Shiroro and Zungeru fishing settlements (mg/kg)

Metal	Sample	Sites			Standard limit
	SU	SD	ZU	ZD	
Mn	402.33±32.08^{b}	370.17±27.10^{b}	116.83±4.69^{a}	164.67±7.63^{a}	300.00 USEPA 2004
Fe	15546.11±310.90^{c}	26629.50±487.97^{d}	5446.33±118.49^{a}	7447.33±139.07^{b}	20000.00 CBSQG 2003
Cu	30.17±5.80^{c}	24.50±1.32^{b}	2.00±0.86^{a}	4.33±0.29^{a}	18.70 USEPA 2004
Zn	103.33±3.08^{b}	84.33±3.88^{b}	21.33±1.37^{a}	17.33±4.73^{a}	124.00 USEPA 2004
Cr	16.33±1.06^{a}	8.83±0.17^{a}	5.17±0.40^{a}	7.17±0.16^{a}	43.00 CBSQG 2003
Cd	BDL	BDL	BDL	BDL	0.68 USEPA 2004
Pb	15.67±9.80^{b}	9.50±5.41^{ab}	BDL	BDL	30.20 USEPA 2004
Ni	35.67±7.01^{b}	30.33±3.51^{b}	1.67±0.07^{a}	8.50±0.50^{a}	23.00 CBSQG 2003

Values represent mean ± SD of triplicate results. Samples with the same superscripts across row are not significantly different at P ≤ 0.05 while sample with different superscripts across row are significant difference at P ≤ 0.05. SU: Shiroro Upstream, SD: Shiroro Downstream, ZU: Zungeru Upsteam, ZD: Zungeru Downstream and BDL: Below Detectable Limit. mg/kg: milligram per kilogram

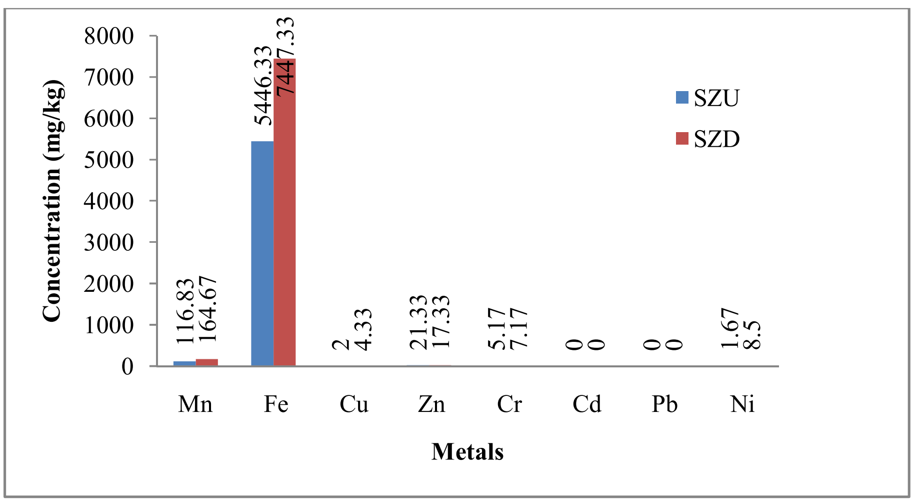

Fig. 5. Mean heavy metal concentrations in sediment samples from Zungeru fishing settlement

Samples (0.29 to 0.41 mg/kg) from Owena Multi-Purpose Dam, Ondo State, Nigeria. Concentration of Cr in this study did not exceed the limit of 43.00 mg/kg recommended by CBSQG [33].

The Cd concentration was below detection limits (BDL) in both Shiroro and Zungeru, as shown in Table 2. Thus, indicating a little or no toxicity of the metal. This finding differed from results for sediment samples reported by Gwenda of 1.3 mg/kg [35] and in normal soil to contaminated soil which ranged between 0.02 and 184 mg/kg in various regions of Pakistan by Amir Waseem et al. [26]. The values were below recommended maximum permissible limit (0.68 mg/kg) of Cd reported by USEPA [31].

The Pb concentrations was below detection limit (BDL) in sediment samples obtained from Zungeru, however, downstream area of Shiroro had mean Pb concentration of 9.50±5.41 mg/kg as indicated in Table 2, while concentration of 15.67±13.80 mg/kg was obtained from the upstream area (Figs. 4 and 5). These values were however lower than values obtained in various coastal regions of Pakistan in the coastal sediments of the Arabian sea along the urban Karachi of Pb 121 mg/kg and from surficial sediments of Lyari River of Pb 49.5 mg/kg by

Amir Waseem et al. [26]. The increased level of Pb in the upstream area could be as a result of human activities as evident at this point and further diluted in process of flow towards the downstream area. A permissible limit of 30.20 mg/kg Pb in sediments as recommended by USEPA was however not exceeded from the obtained result [31].

The sediment samples Shiroro had higher concentration of Ni as compared to sediment samples from Zungeru (Table 2). Concentrations of Ni 30.33±3.51 and 35.67±7.01 mg/kg were obtained in sediment samples from downstream and upstream areas of Shiroro respectively, while Ni concentrations of 1.67±0.07 mg/kg was obtained for upstream and 8.50±0.50 mg/kg at the downstream area (Figs. 4 and 5). Studies by Oyakhilome et al. [37] reported the concentrations ranging between 1.24 mg/kg to 2.07 mg/kg from Owena Multi-Purpose Dam, Ondo State, Southern Nigeria which was similar to results obtained from Shiroro and Zungeru. A permissible limit of 23.00 mg/kg Ni in sediments samples as recommended by CBSQG was however not exceeded from the result obtained in Zungeru but was exceeded by results obtained from Shiroro from the present study [33].

3.3 Heavy Metals in Fish

From results in Table 3, it can be observed that the concentration of Mn in catfish samples from Shiroro was 56.50±1.21 mg/kg while catfish samples collected from Zungeru was 38.67±1.79 mg/kg Mn, indicating higher Mn levels in samples from Shiroro (Fig. 6). Studies by Eneji et al. [21] and Sen et al. [38] reported a maximum concentration of 6.18 mg/kg in fish, from River Benue, North-Central Nigeria and 5.14 mg/kg in River Yamuna (Delhi), India respectively. These values were lower than this present study. Findings of Saeed and Shaker are between 26.13 mg/kg and 42.12 mg/kg for Mn in Northern Delta Lakes, Egypt, however compares favourably with this present study [39]. The result from the study exceeded the permissible limits of 2.0 to 9.0 mg/kg as recommended by FAO/WHO [40].

Concentration of Fe as seen from Table 3 gave a mean value of 1482.83 ± 99.50 mg/kg for catfish from Shiroro. This value was higher than that obtained values from Zungeru of 1331.00±46.98 mg/kg (Fig. 6). There is no variation in result at $P \leq 0.05$ level. Results from present study is far greater than those reported by Oyakhilome et al. [37] and Ismaniza and Idaliza [10] ranging from 20.11 to 37.99 mg/kg form Owena Multi-Purpose Dam, Ondo State, Southern Nigeria and 31.90 to 743.0 mg/kg for Tasik Mutiara, Puchong respectively. The levels of Fe concentration in the catfish samples from both rivers are far greater than the permissible limits of 43.00 mg/kg as recommended by FAO/WHO [40]. This variation could be attributed to high residual Fe in sediments found in water which may have led to their accumulation in fish through interaction in water with possibly mild contribution from anthropogenic influences.

The concentrations of Cu in the catfish samples as shown in Table 3 and Fig. 6 were 5.67±0.76 mg/kg and 4.00±0.50 mg/kg for catfish samples from Shiroro and Zungeru respectively. There was no significant variation in result at $P \leq 0.05$ level. Values obtained by Oyakhilome et al. [37] for Cu (1.42 mg/kg) from Owena Multi-Purpose Dam, Ondo State, Southern Nigeria are slightly lower than the present study. However, Ismaniza and Idaliza obtained results of 0.01 to 20.80 mg/kg in fish from Tasik Mutiara, Puchong, which compared favourably with the present study [10]. The levels of Cu obtained in the present study were higher than the permissible limit of 3.00 mg/kg as recommended by FAO/WHO [40].

The concentrations of Zn in the catfish samples (Table 3 and Fig. 6) were 75.5±6.22 mg/kg for Shiroro and 160.83±12.18 mg/kg for Zungeru with significant variation in values at $P \leq 0.05$. Zhang et al. [41], reported a mean concentration of 10.4±5.3 mg/kg in the muscles of fish samples analysed in Banan Section of Chongqing from Three Gorges Reservoir, China while Edward et al. [7], reported mean concentration of 0.95 mg/kg in fish samples from Odo-Ayo River in Ado-Ekiti, Ekiti-State, Nigeria respectively. These concentrations fall short of the present study, however, it compares favourably with results reported by Benzer et al. [13] which ranged between 33.24 – 224.59 mg/kg from Mogan Lake (Turkey). However, levels of Zn in the present study were higher than the permissible limit of 60.00 mg/kg recommended by FAO/WHO [40].

From Table 3, the concentration of Cr was higher in the catfish samples from Zungeru compared to the catfish samples from Shiroro with each having concentrations of 5.00±0.23 mg/kg and 1.17±0.02 mg/kg respectively (Fig. 6). These concentrations compares well with the values obtained by Benzer et al. [13] of 1.57 mg/kg and 6.45 mg/kg for fish samples from Mogan Lake (Turkey). Shabanda and Itodo recorded 0.47 mg/kg in muscles of fish which was lower than that of the present study [42]. The finding of Eneji et al. [21] obtained range value of 29.8 mg/kg to 31.6 mg/kg in Tissue and Gills of Fish Samples from River Benue, North-Central, Nigeria which were greater than the values in the present study. The maximum permissible limits of 2.30 mg/kg for Cr in food recommended by WHO was however exceeded in fish samples from Zungeru but were within limit for fish sample from Shiroro [24].

Concentrations for Cd in catfish samples as shown in Table 3 and Fig. 6, indicates that lower concentration of 0.17±0.09 mg/kg was obtained in catfish samples from Shiroro, while higher concentration of 2.83±0.69 mg/kg was obtained in catfish samples from Zungeru with significant variation in results at $P \le 0.05$ level. Ozturk et al. [11] also obtained concentration ranging from 0.17±0.01 to 0.79±0.33 mg/kg from Avsdar Dam Lake in Turkey which compares favourably with the catfish samples collected from Shiroro but lower than the catfish samples from Zungeru. Also, Ackacha et al. [43] reported Cd concentrations ranging from 0.33 to 2.68 mg/kg in various species of fish analysed from Mediterranean Sea (Libyan coastline) which compares favourably with the present study. Results of both samples from Shiroro and Zungeru exceed the permissible limits of 0.03 mg/kg as recommended by WHO, thus, indicates Cd pollution [24].

From Table 3, it can be observed that Pb is below detectable limits (BDL) for fish samples from both Shiroro and Zungeru indicating the absence of the metal (Fig. 6). This study compares well with that reported by Ismaniza and Idaliza and Shabanda and Itodo of BDL and 0.015 mg/kg respectively [10,42]. Other study by Oyakhilome et al. and Ackacha et al. however, were greater than the present study and ranged between 0.15 to 0.19 mg/kg and 0.07 to 2.39 mg/kg in Owena Multi-Purpose Dam, Ondo State, Southern Nigeria and Mediterranean Sea (Libyan coastline), respectively [37,43]. Therefore, the concentration of Pb from the present study falls within WHO permissible limit of 0.30 mg/kg for fish and edible foods [24].

Table 3. Concentration of heavy metals in Catfish (*Clarias gariepinus*) samples from Shiroro and Zungeru fishing settlement (mg/kg)

	Sample	Sites	
Metals	**FS**	**FZ**	**Standard limit**
Mn	56.50±1.21^{b}	38.67±1.79^{a}	2.0-9.0 FAO/WHO 1999
Fe	1482.83±99.50^{a}	1331.00±46.98^{a}	43.00 FAO/WHO 1999
Cu	5.67±0.76^{a}	4.00±0.50^{a}	3.00 FAO/WHO 1999
Zn	75.50±6.22^{b}	160.83±12.18^{a}	60.00 FAO/WHO 1999
Cr	1.17±0.02^{b}	5.00±0.23^{a}	2.30 WHO 2008
Cd	0.17±0.09^{b}	2.83±0.69^{a}	0.03 WHO 2008
Pb	BDL	BDL	0.30 WHO 2008
Ni	0.33±0.08^{b}	BDL	0.30 WHO 2008

Values are means ± SD of three determinations. Samples with the same superscripts across row are not significantly different at $P \le 0.05$ while sample with different superscripts across row are significant difference at $P \le 0.05$. FS: Fish Shiroro, FZ: Fish Zungeru and BDL: Below Detectable Limit. mg/kg: milligram per kilogram

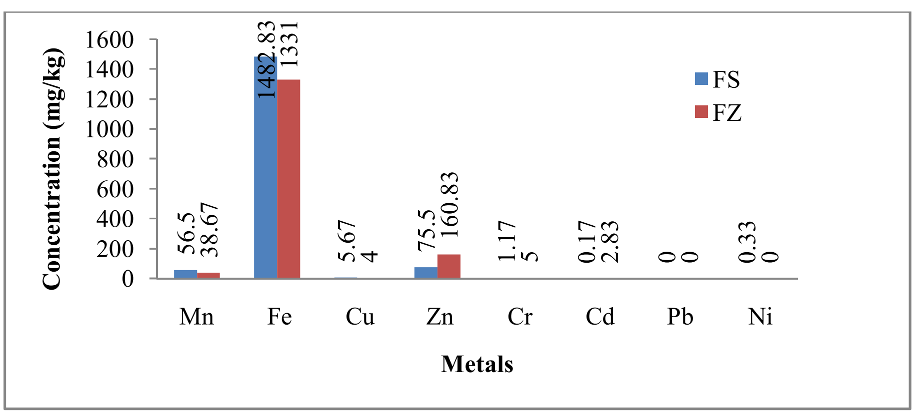

Fig. 6. Mean heavy metal concentrations in Catfish (*Clarias gariepinus*) samples from Shiroro and Zungeru fishing settlements

The concentration of Ni was present in only catfish samples from Shiroro with concentration of 0.33±0.08 mg/kg while Ni was below detectable limit (BDL) in catfish samples from Zungeru as shown in Table 3 and Fig. 6. Aderinola et al. [44] reported Ni concentration of 0.01±0.00 mg/kg in fish from Lagos Lagoon which compares with samples obtained from Zungeru while Amirah et al. [45] obtained concentrations ranging from 3.84±0.41 to 3.97±0.17 mg/kg which was higher than the present study. Similarly, Mohammadi et al. [9] also reported concentrations ranging between 0.59±0.01 mg/kg and 1.43±0.03 mg/kg in fish from Karoon and Dez Rivers of Khuzestan, Iran, which compares with results obtained from Shiroro. However, maximum permissible limit for Ni (0.30 mg/kg) does not exceed for all samples WHO [24].

4. CONCLUSION

Heavy metal accumulation in water, catfish and sediment from this study should be of major concern to the people of Shiroro and Zungeru. Although, health guidelines were not exceeded for water samples except Fe; for heavy metals in catfish, Mn, Fe, Cu and Cd exceeded permissible limit, while elevated values of Mn, Fe and Cu exceeded maximum limits recorded in sediments. In the results obtained for water samples, it was observed that mean metal concentrations were higher in Zungeru than in Shiroro except for Ni and Cu which were highest at Shiroro. Pb was absent in both sites. Results from Shiroro also showed that average contaminations were higher at the upstream area compared to the downstream area and this could be attributed to the high activity experienced in this area due to the local market. There was a similar trend recorded at Zungeru which might be due to the flow direction of the river. The pattern of heavy metal concentration from Shiroro was in the decreasing order of Fe > Cu > Cr > Zn > Mn > Cd > Ni while for Zungeru it was in decreasing order of Fe > Zn > Cr > Mn > Cu > Cd > Pb, Ni respectively. Catfish (*Clarias gariepinus*) from Shiroro contained higher levels of Mn, Fe, Cu and Ni while catfish from Zungeru had higher levels of Zn, Cr and Cd with no Pb present in catfish from both site as evidence in the water samples. Results also showed that Mn, Fe, Cu and Cd exceeded permissible limits set by relevant bodies for catfish samples from both sites, while Cr was above allowable limits for catfish from Zungeru. Accumulation of metals was in decreasing order of Fe > Zn > Mn > Cu > Cr > Ni > Cd > Pb for catfish from Shiroro and Fe > Zn > Mn > Cr > Cu > Cd > Pb, Ni for catfish from Zungeru respectively. Therefore it shows that this catfish caught from the two rivers may cause health hazards for consumers. Accumulation of metals was in decreasing order of Fe > Mn > Zn > Ni > Cu > Cr > Pb > Cd for sediment samples from Shiroro and Fe > Mn > Zn > Cr > Ni > Cu > Pb, Cd for sediment sample from Zungeru respectively. Concentrations of heavy metal in sediment samples were higher in Shiroro for all metal analysed than sediment samples from Zungeru which may be due to heavy machinery and other equipment used to generate electricity from the Shiroro dam. Also, it could be as a result of its proximity to a local market located close to the river side.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. El-Zokm GM, El-Gohary SEI, Abd-El-Khalek DE. Studies of some heavy metals in water and sediment in el-max fish farm, Egypt. World Applied Sci. J. 2012;18(2):171-180.
2. Sanayei Y, Norli I, Talebi SM. Determination of heavy metals in zayandeh rood river, Isfahan-Iran. World Applied Sci. J. 2009;6(9):1209-1214.
3. Tabari S, Seyed SSS, Gholamali AB, Atena D, Mohammad S. Heavy metals (Zn, Pb, Cd and Cr) in fish, water and sediments sampled form Southern Caspian Sea, Iran. Toxicology and Ind. Health. 2010;26(10):649-656. DOI:10.1177/0748233710377777.
4. Akoto O, Bruce TN, Darko G. Heavy metals pollution profiles in streams serving the Owabi Reservoir. African J. of Environ. Sci. Tech. 2008;2(11):354-359.
5. Butu AW, Iguisi EO. Heavy metal concentration in soil and sediment along river Kubanni Zaria, Nigeria. Compre. J. Environ. Earth Sci. 2013;2(2):26-34.
6. Ekpete OA, Festus C. Heavy metal distribution in soil along Iwofe Rumuolumeni road. Int. J. Sci. Tech. 2013;8(1):450-455.
7. Edward JB, Idowu EO, Oso JA, Ibidapo OR. Determination of heavy metal concentration in fish samples, sediment and water from odo-ayo River in Ado-Ekiti,

Ekiti-State, Nigeria. Int. J. Environ. Monitoring Analysis. 2013;1(1):27-33.
8. Pandey J, Shubhashish K, Richa Pandey. Heavy metal contamination of ganga river at varanasi in relation toatmospheric deposition. Tropical Ecology. 2010;51(2S): 365-373.
9. Mohammadi M, Askary Sary A, Khodadadi M. Accumulation variations of selected heavy metals in Barbus xanthopterus in Karoon and Dez Rivers of Khuzestan, Iran. Iranian J. Fisheries Sci. 2012;11(2):372-382.
10. Ismaniza I, Idaliza MS. Analysis of Heavy Metals in Water and Fish (Tilapia sp.) Samples from Tasik Mutiara, Puchong. Malaysian J. Analytical Sci. 2012;16(3):346-352.
11. Ozturk M, Ozozen G, Minareci O, Minareci E. Determination of heavy metals in fish, water and sediments of Avsdar Dam lake in Turkey. Iran J. Environ. Health Sci. Eng. 2009;6(2):73-80.
12. Opaluwa OD, Aremu MO, Ogbo LO, Magaji JI, Odiba IE, Ekpo EK. Assessment of heavy metals in water, fish and sediments from UKE stream, Nasarawa State, Nigeria. Current World Environ. 2012;7(2):213-220.
13. Benzer S, Arslan H, Uzel N, Gül A, Yılmaz M. Concentrations of metals in water, sediment and tissues of *Cyprinus carpio* L, 1758 from Mogan Lake (Turkey). Iranian J. Fisheries Sci. 2013;12(1):45-55.
14. Sonawane NS, Sawant CP, Patil RV. Soil quality and heavy metal contamination in agricultural soil in and around toronmal (Triable Region) of Maharashtra. Archives of Applied Sci. Research. 2013;5(2):294-298.
15. Sajjad K, Robina F, Shagufta S, Mohammed AK, Maria, S. Health risk assessment of heavy metals for population via consumption of vegetables. World Applied Sci. J. 2009;6(12):1602-1606.
16. Tsafe AI, Hassan LG, Sahabi DM, Alhassan Y, Bala BM. Evaluation of heavy metals uptake and risk assessment of vegetables grown in Yargadama of Northern Nigeria. J. Basic Applied Sci. Research. 2012;2(7):6708-6714.
17. Yinka O, Wesler KW. Zungeru colonial settlement. Historical archaeology in Nigeria. Africa World Press. 1998;278-279.
18. Association of Analytical Chemist (AOAC). Methods of soil and water analysis. association of analytical chemist. Washington DC, USA. 2000;211-232.
19. Lacatusu R. Appraising levels of soil contamination and pollution with heavy metals. European Soil Bureau. 2000;4.
20. Aiyesanmi AF. Baseline heavy metals concentration in river sediments within Okitipupa South East belt of Nigeria bituminous sand field. J. Chem. Society Nigeria. 2008;33(2):29-41.
21. Eneji SI, Sha. Ato R, Annune PA. Bioaccumulation of heavy metals in fish (*Tilapia Zilli* and *Clarias Gariepinus*) Organs from River Benue, North. Central Nigeria. Pakistan J. Analytical Environ. Chem. 2011;12(1&2):25-31.
22. Statistical Package for Social Sciences (SPSS), SPSS for Windows version 20.0.1; 2013. SPSS Inc., Chicago, IL.
23. Federal Government Protection Agency/World Health Organization, FEPA/WHO. Guidelines and standards for environmental pollution control in Nigeria. 2003:238/Guidelines for drinking water quality. Recommendation WHO. Geneva. 2003;1:130.
24. World Health Organization, (WHO). Guidelines for drinking water quality. Third Edition Incorporating 1st and 2nd Addenda Recommendation WHO. Geneva. 2008; 1:130.
25. Olatunji OS, Osibanjo O. Comparative assessment of some heavy metals in some inland fresh water fish species from river Niger and River Osara in North-Central Nigeria. Int. J. Environ. Sci. 2012;2(3):1842-1852.
26. Amir W, Jahanzaib A, Farhat I, Ashif S, Zahid M, Ghulam M. Review Article Pollution Status of Pakistan: A retrospective review on heavy metal contamination of water, Soil, and Vegetables. BioMed Research Int., 2014;2014. Article ID 813206:29. Available:http://dx.doi.org/10.1155/2014/813206
27. Yahaya A, Adegbe AA, Emurotu JE. Assessment of heavy metal content in the surface water of oke-afa canal, Isolo Lagos, Nigeria. Achieves Applied Sci. research. 2012;4(6):2322-2326.
28. United States Environmental Protection Agency, (USEPA). Quality criteria for water. EPA. Office of water regulations and standards. Washington DC., USA; 1986. 440/5-86-001.

29. Ali AA. Elazein EM, Alian MA. Determination of Heavy Metals in Four Common Fish, Water and Sediment Collected from Red Sea at Jeddah Islamic Port Coast. J. of Applied Environ. Biol. Sci. 2011;1(10):453-459.
30. Mwegoha WJS, Kihampa C. Heavy metal contamination in agricultural soils and water in Dares Salaam city, Tanzania. African J. Environ. Sci. Tech. 2010;4(11):763-769.
31. United States Environmental Protection Agency, (USEPA). Child-Specific exposure factors handbook, EPA/600/P-00/002B; National center for environmental assessment; Washinton, DC. 2004;40.
32. Greaney KM. An assessment of heavy metal contamination in the marine sediments of Las Perlas archipelago, Gulf of Panama. Heriot-Watt University, Edinburgh; 2005.
33. Consensus Based Sediment Quality Guidelines (CBSQG). Wisconsing Department of natural resources. recommendations for use and application. Department of interior, Washington D.C. 2003;20240:17.
34. Sabo A, Gani AM, Ibrahim AQ. Pollution status of heavy metals in water and bottom sediment of river delimi in Jos, Nigeria. American J. of Environ. Protection. 2013;1(3):47-55.
35. Gwenda JS. Heavy metal concentrations in stream sediments of the south dry sac river. Available:http://courses.missouristate.edu (Access Date: May 6, 2001)
36. Barakat A, El Baghdadi M, Rais J, Nadem S. Assessment of heavy metal in surface sediments of day river at Beni-Mellal region, Morocco. Research J. of Environ. Earth Sci. 2012;4(8):797-806.
37. Oyakhilome GI, Aiyesanmi AF, Adefemi SO, Asaolu SS. Heavy metals concentration in sediment and fish samples from owena multi-purpose dam, Ondo State, Southern Nigeria. British J. Applied Sci. Tech. 2013;3(1):65-76.
38. Sen I, Shandil A, Shrivastava VS. Study for determination of heavy metals in fish species of the river Yamuna (Delhi) by Inductively Coupled Plasma-Optical emission spectroscopy (ICP-OES). Adv. in Appl. Sci. Research. 2011;2(2):161-166.
39. Saeed SM, Shaker IM. Assessment of heavy metals pollution in water and sediments and their effect on *Oreochromic Niloticus* in the Northern Delta Lakes, Egypt, 8th International Symposium on Tilapia in Aquaculture. 2008;475-490.
40. Food and Agriculture Organization/World Health Organization (FAO/WHO). Expert committee on food additives. Summary and Conclusion, 53rd meeting, Rome. 1999;1-10.
41. Zhang Z, He L, Li J, Wu ZB. Analysis of heavy metals of muscle and intestine tissue in fish – in Banan section of chongqing from three gorges reservoir, China. Polish J. Environ. 2007;16(6):949-958.
42. Shabanda IS, Itodo AU. Toxins in gills and flesh of *Synodontissorex* and *Bagrus filamentosus*. Int. J. Ecosys. 2012;2(6): 150-153.
43. Ackacha MA, Khalifa KM, Hamil AM, Al-Houni AQA. Determination of heavy metals in fish species of the mediterranean sea (Libyan coastline) using atomic absorption spectrometry. Int. J. PharmTech Research. 2010;2(2):1350-1354.
44. Aderinola OJ, Clarke EO, Olarinmoye OM, Kusemiju V, Anatekhai MA. Heavy metals in surface waters, sediments and periwinkles of Lagos lagoon. American-Eurasian J. Agric. Environ. Sci. 2009;5(5):609-617.
45. Amirah MN, Afiza AS, Faiza WIW, Nurliyana MH, Laili S. Human health risk assessment of metal contamination through consumption of fish. J. Environ. Pollution Human Health. 2013;1(1):1-5.

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