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Analysis of Bio-Accumulation of Heavy Metals in Cultured and Wild Fish from Niger and Kaduna State in Nigeria

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ABSTRACT

Accumulation of some heavy metals iron manganese copper lead and zinc in the muscle, gills, intestine were determine in some fishes (clarias garinepinus and oreochromis niloticus). They were bought from fishermen at the landing site of Shiroro dam and Tagwai dam. and also purchased from Danjeo farm and Federal University Of Technology farm minna (Water Resources and Aquaculture Department Farm).The Sample were collected once monthly for a period of six months Prior to digestion, samples were rinsed with flowing water and dissected with sterile dissection tools to get rid of the gills, muscle and intestine. Wet method of digestion was used to carry out the analysis. The weight of the two fish species was taken and 1 g of each sample was first weighted.1g of each sample was dissolved in 10ml nitric acid and was boiled to complete the dissolution using hotplate .After digestion samples were filtered using filter paper number 41 and obtained precipitate was make up to 20ml with distilled water and transferred into 25ml volumetric flask and then analyzed by atomic absorption spectrophotometer (AAS). The accumulation of the heavy metals in different organs showed significance difference ($p<0.05$) except lead accumulation. Zinc concentrations in the cultured fish species were in the range of 0.6 to 2.6 mg/L whereas in the wild species values varied between 0.8 and 2.1 mg/L. The greatest zinc concentration was found in the intestine of Clarias gariepinus and Oreochromisniloticus from Danejo farm. Zinc concentration in the gill of Clarias gariepinus and Oreochromis niloticus from Danejo farm was statistically similar to those in the intestine of Clarias gariepinus and Oreochromis niloticus from FUT minna farm and Shiroro dam, as well as gill and intestine of Clarias gariepinus and Oreochromis niloticus from Tagwai dam.

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Introduction

Pollution of aquatic environment with heavy metals have become a worldwide problem and of scientific concern because the metals are indestructible and most of them have toxic effects on organisms [1]. Heavy metals enter rivers and lakes from a variety of sources that include the rocks and soils directly exposed to surface water, in addition to the discharge of various treated and untreated liquid wastes to the water bodies [2].There are over ten (10) heavy metals such as cobalt (Co), lead (Pb), mercury (Hg), arsenic (As), thallium (Tl), nickel (Ni),manganese (Mn), zinc (Zn), cadmium (Cd) andchromium (Cr) that have a particular significance in ecotoxicology, since they are highly persistent [3]. The levels of metals such as Mn, Zn, and Cr are toxic beyond a certain limit, whereas Pb, Ni and Cd are toxic even in trace amounts [4]. Toxicity is realized when these heavy metal levels are higher than the recommended limit which is different for individual elements in drinking water. These heavy metals: Pb, Ni, Mn, Zn, Cd and Cr have the following WHO recommended limits: 0.01 mg/l, 0.07 mg/l, 0.4 mg/l, 3.0 mg/l, 0.003 mg/l and 0.05 mg/l respectively for drinking water and 2.0 mg/kg in fish for Pb and Ni [5]. Exposure to high levels of these heavy metals can among many effects, severely damage the brain and kidneys, cause miscarriage in pregnant women, damage the organs responsible for sperm production in men and it may ultimately cause death [6]. Fish have been considered as one of the most significant indicators in water systems for the estimation of metal pollution level [7]. Living organisms require trace amounts of certain heavy metals such as, iron, cobalt, copper, magnesium and zinc amongst others. If these metals are taken up excessively it may be detrimental to aquatic organisms [8]. Other heavy metals such as cadmium, lead and mercury do not have any beneficial effects on living organisms. Thus the accumulation of these metals to very high toxic levels could cause severe ecological impact on organisms without any visible signs [9]. Since the control of reproduction in fishes is complex and affected by a wide range of environmental factors as well as hormones, even low levels of pollution could affect reproduction. Hence, at low levels, even though fish might not show any ill effects, it can lead to long term decline in fish supply. Exposure to these heavy metals could ultimately lead to health risks associated with the consumption of fish by humans. Some of these health risks such as renal failure and liver damage can be caused by exposure to lead (Pb). Prolonged exposure to Pb can lead to mental retardation, coma and eventual death [10]. Fish populations exploited by man often live in coastal area environments that contain high levels of heavy metals, coming from human activities such as industrial and agricultural wastes. A problem to deal when using fishes as bio¬-monitors of heavy metals is the relationship existing between metal concentration

and several intrinsic factors of the fish such as organism size, genetic composition and age of fish against this factor the study seek to find the Assessment of bioaccumulation of heavy metals (Copper, Zinc, Iron, Manganes, Lead) in fish, in the wild and culture medium.

Materials and Methods

Sampling Area and Sample Collection

The study areas are Tagwai dam is located at Latitude 60 39' to 60 44'East and longitude 90 34 to 90 37 North to South West of Minna Suleja Road, Shiroro dam is located on River Kaduna, Nigeria between latitude 090 58'N and longitude 060 50'E and Danjeo farm is located in Suleja Niger Sate, between latitude 90 37'N to 9033' of the equator and longitude 60 39' E. Two species of fish sample of different sizes were bought from the fishermen at the landing site of Tagwui and Shiroro dam respectively and also from FUT Minna fish farms and Danjeo farms for six months (three months of dry season and three months of raining season). These include Clarias gariepinus commonly called cat fish, and Oreochromis niloticus.

Determination of Heavy Metals

Samples were poured into auto analyzer cups and concentration of heavy metals (lead, copper, iron, zinc and manganese) were determined using Atomic Absorption Spectrophotometer (AAS). The values of the heavy metal concentrations in the tissues were calculated based on dry weights as this discounts the variability due to inner parts differences in the moisture content of organisms.

Digestion of Sample

Samples were rinsed with flowing water and dissected with sterile dissection tools to get rid of the gills, muscle and intestine. Wet method of digestion was used to carry out the analysis. The weight of the two fish species was taken and 1 g of each sample was first weighted.1g of each sample was dissolved in 10ml nitric acid and was boiled to complete the dissolution using hotplate .After digestion samples were filtered using filter paper number 41 and the obtained precipitate was make up to 20ml with distilled water and transferred into 25ml volumetric flask and then analyzed by atomic absorption spectrophotometer (AAS).

Determination of Heavy Metals Using Atomic Absorption Spectrophotometer (Aas)

2.8766g of KMnO4 was dissolved to make manganese stock solution in distilled water and made up to 1 litre. 10ml of stock was dissolved to get a standard solution in distilled water and was measured up to 1 litre. Stock was also prepared to get over disturbance if there might be any, using stock calcium reagent. Various standard solution concentrations were prepared and ascertained for manganese using manganese cathode lamp at 279.4mm with AAS which was utilized to ascertain manganese concentration in them. Manganese can be computed using the equation:

Mn (Mg/1) = Reading from the curve x D

$$\text{Where } D = \frac{\text{ml Sample + ml water + 1ml acid}}{\text{1 ml of sample}}$$

Copper (Cu)

Stock copper solvent was made by the dissolution 3.9296g of copper sulphate hydrate in distilled water and which was measured up to 1 litre. Standard solution was also prepared up to 1 litre. Dissolving 5ml of stock solution in 100ml of distilled water from where various concentrations were done from the range of 5ml – 20mg resulted to the standard solution analysis was done by the use of AAS to determine what the absorbance grade will be by utilizing copper cathode lamp at 324.7nm and the calibrat5ion was made from this.

the use of AAS to determine what the absorbance grade will be by utilizing copper cathode lamp at 324.7nm and the calibrat5ion was made from this.

The samples were also too be analyzed for the determination of the concentration of copper with AAS. It can be computed using equation:

Cu (Mg/1) = Reading from the curve x D

$$\text{Where } D = \frac{\text{ml Sample + ml water + 1ml acid}}{\text{1 ml of sample}}$$

Zinc (Zn)

Stock zinc solution was done by the dissolution of clean 100mg of zinc metal in 1ml HCL and this was measured up to 1 litre with distilled water. The measure of zinc solution was done by preparing 10ml of zinc stock solution to 1 litre with distilled water. Various concentrations were made from standard solution in the grade 0.1 – 0.5mg/l which was drawn from the results to ascertain the concentration. Analyse of the samples were also done for the concentration of Zinc using the equation below:

Zn (mg/1) = Reading from the curve x DX

$$\text{Where } \frac{D = \text{ml Sample + ml water + 1ml acid}}{\text{1 ml of sample}}$$

Iron (Fe)

A 5.0503g iron (H) ammonium sulphate, Fe (NH4)2 (SO4)2 in 1 litre distilled water was dissolved to make stock iron solution. Standard iron solution was made from stock solution by the dissolution of 20ml of stock solution in 1 litre of water from where various concentrations were done and to ascertain for the concentration of iron with AAS using iron cathode lamp at 248.3mm. the samples were also analyzed with the AAS to determine the concentration of iron and the outcome were inferred from the calibration curve. Iron was computed using the equation:

Fe (Mg/1) = Reading from the curve x D

$$\text{Where } D = \frac{\text{ml Sample + ml water + 1ml acid}}{\text{1 ml of sample}}$$

Lead (Pb)

The lead stock solution was made by the dissolution 1.598g lead nitrate, Pb (NO3)2 in 1litre distilled water. Standard lead solution done by the dissolution of 10ml lead stock solution in 1 litre of distilled water. Similar method used as described above was adopted in ascertaining the lead accumulation in the samples but with the use of lead cathode lamp at 283.3nm wavelength.

Pb (Mg/1) = Reading from the curve x D

$$\text{Where } D = \frac{\text{ml Sample + ml water + 1ml acid}}{\text{1 ml of sample}}$$

Data Analysis

Results presented as means ± SEM, where n equals the number of fish samples from which tissues were isolated. Results from all the specimens were compared using ANOVA and $P < 0.05$ was

considered to indicate statistical significance. Means of significant differences were separated using Duncan's Multiple Range Test.

Results and Discussion

Accumulation of Heavy Metals in the Organs of Clarias Gariepinus and Oreochromis Niloticus in the Cultured and Wild Environment

There was no significant ($p>0.05$) difference in the concentration of copper, iron and manganese between cultured and wild Clarias gariepinus (Table 1). However, higher concentrations of copper and iron were detected in wild than cultured species. In contrast, there was no difference in the concentration of zinc between cultured and wild species. In Oreochromis niloticus, copper concentration was significantly ($p<0.05$) higher in the wild than cultured species. In spite of higher iron and manganese concentrations in the wild than cultured Oreochromis niloticus, the difference was not significant. Zinc concentration was higher in cultured and wild Oreochromis niloticus but the difference was not significant. Lead was not detected in any organ of both cultured and wild fish species.

Table 1: Accumulation of Heavy Metals in the Cultured and wild Clarias Gariepinus and Oreochromis Niloticus

Species	Copper (mg/L)	Iron (mg/L)	Manganese (mg/L)	Zinc (mg/L)
Clarias				
Cultured	1.3±0.2[a]	22.1±2.8[a]	2.1±0.6[a]	1.6±0.2[a]
Wild	1.5±0.2[a]	22.7±3.0[a]	1.7±0.2[a]	1.6±0.2[a]
±SE	0.2	2.9	0.4	0.2
Oreochromis niloticus				
Cultured	1.6±0.2[b]	20.9±2.5[a]	2.2±0.6[a]	1.5±0.2[a]
Wild	2.5±0.4[a]	26.5±3.3[a]	2.6±0.7[a]	1.2±0.1[a]
±SE	0.2	3.0	0.6	0.2

Means having similar superscript letter within the same column are not significantly different at $p\leq0.05$according to the Lest Significant Difference (LSD)

The highest iron concentration was observed in the intestine of Clarias gariepinus and Oreochromis niloticus from Shiroro dam. This was closely followed by iron concentration in the intestine Clarias gariepinus and Oreochromis niloticus from Danejo farm. There were no significant differences in the concentration of iron in the gill and muscle of Clarias gariepinus and Oreochromis niloticus from Danejo farm, gill of Clarias gariepinus and Oreochromis niloticus from FUT Minna farm, muscles of Clarias gariepinus and Oreochromis niloticus from Shiroro dam and Clarias gariepinus from Tagwai dam. The lowest Iron concentration was found in the muscle of Clarias gariepinus and Oreochromis niloticus in FUT Minna farm. Manganese concentrations differed significantly in various fish organs. The highest concentration was found in the intestine of Clarias gariepinus and Oreochromis niloticus from FUT Minna farm whereas the lowest was observed in the muscle of Clarias gariepinus and Oreochromis niloticus in Danejo farm. However, there was no significant difference between the manganese concentration in the muscle of Clarias gariepinus and Oreochromis niloticus and the remaining fish organs. Zinc concentrations in the organs of cultured Clarias gariepinus varied between 0.8 and 2.6 mg/L whereas in the wild fish a range of 0.6 to 2.8 mg/L was found. The difference in zinc concentration between the intestine of Clarias gariepinus and Oreochromis niloticus from FUT Minna farm and Shiroro dam was not significant. Similarly, zinc concentration observed in the gill of Clarias gariepinus and Oreochromis niloticus from Danejo farm was statistically comparable with those in the gill of Clarias gariepinus and Oreochromis niloticus from Shiroro dam and Tagwai dams.

In Oreochromis niloticus, there were no significant differences in copper concentrations across the fish organs but the highest was found in the intestine of Clarias gariepinus from Shiroro and Tagwai dams. The lowest concentration was detected in the muscle of Clarias gariepinus and Oreochromis niloticus from FUT Minna farm. In cultured fish, iron concentration ranged between 9.5 and 36.6 mg/L whereas in the wild species, values varied from 8.2 to 46.3 mg/L. The greatest concentration of iron was found in the intestine of Clarias gariepinus and Oreochromis niloticus from Shiroro dam while the lowest was found in the muscle of Clarias gariepinus and Oreochromis niloticus from Tagwai dam. Iron concentration in the gill of Clarias gariepinus and Oreochromis niloticus from Danejo farm was not significantly different from those detected in the intestine of Clarias gariepinus and Oreochromis niloticus of FUT Minna farm, gill and muscle of Clarias gariepinus and Oreochromis niloticus from Shiroro dam, as well as gill of Clarias gariepinus and Oreochromis niloticus from Tagwai dam. Similarly, there were no significant differences in iron concentrations among observed in the muscle and gill of Clarias gariepinus and Oreochromis niloticus from Danejo farm and FUT minna farm, respectively as well as intestine of Clarias gariepinus and Oreochromis niloticus from Tagwai dam. In the cultured Oreochromis niloticus, manganese concentrations varied between 0.7 and 5.1 mg/L while a range of 0.9 to 7.8 was found in the wild Orechromis niloticus. The highest and lowest concentration was obtained from the intestine and muscle of Clarias gariepinus and Oreochromis niloticus from Shiroro dam and muscle of Clarias gariepinus and Oreochromis niloticus from FUT Minna farm, respectively. In spite of this, manganese concentration in the intestine of Clarias gariepinus and Oreochromis niloticus from Danejo farm was statistically comparable to Clarias gariepinus and Oreochromis niloticus from FUT Minna farm. Non-significant manganese differences were also observed among the other fish organs.

Zinc concentrations in the cultured fish species were in the range of 0.6 to 2.6 mg/L whereas in the wild species values varied between 0.8 and 2.1 mg/L. The greatest zinc concentration was found in the intestine of Clarias gariepinus and Oreochromis niloticus in Danejo farm. Zinc concentration in the gill of Clarias gariepinus and Oreochromis niloticus of Danejo farm was statistically similar to those in the intestine of Clarias gariepinus and Oreochromis niloticus from FUT minna farm and Shiroro dam, as well as gill and intestine of Clarias gariepinus and Oreochromis niloticus from Tagwai dam. Similarly, there were no significant differences with respect to zinc accumulation in the muscle of Clarias gariepinus and Oreochromis niloticus from Danejo dam and the remaining fish organs. In all, the lowest zinc concentration was found in the muscle of Clarias gariepinus and Oreochromis niloticus from FUT Minna farm.

Heavy Metals Accumulation in Different Organs of the Cultured and wild Clarias Gariepinus in Dry and wet Seasons

There was no significant effect of dry season on copper accumulation in different organs of Clarias gariepinus as indicated in (Table 2). However, the greatest amount of iron was found in the intestine of Clarias gariepinus from Shiroro dam, followed by the intestine of Clarias gariepinus from Tagwai dam. The lowest copper concentration was detected in the gill of Clarias

gariepinus from FUT Minna farm. Significant differences occurred among the organs with respect to iron concentration during the dry season. The highest amount of it was found in the intestine of Clarias gariepinus from Shiroro dam. Iron accumulation was also high in other organs including the intestine of Clarias gariepinus from Danejo farm and FUT Minna farm. Furthermore, there were no significant differences in the concentration of iron across muscle of Clarias gariepinus from Danejo farm, gill and intestine of Clarias gariepinus from FUT Minna farm, gill of Clarias gariepinus from Shiroro and Tagwai dam respectively, as well as intestine and muscle of Clarias gariepinus in Tagwui dam. Manganese concentrations in various organs of Clarias gariepinus differed significantly. The highest value was found in the intestine of Clarias gariepinus from FUT Minna farm. Manganese concentrations were comparable among the remaining fish organs but the lowest was observed in the muscle of Clarias gariepinus in danjeo farm. The differences in zinc concentrations were not significant but the intestine of Clarias gariepinus from FUT minna farm and Tagwai dam had the highest and lowest concentration, respectively.

Table 2: Accumulation of Heavy Metals in Different Organs of The Cultured and Wild Clarias and Oreochromis Niloticus at Different Locations

Clarias					Oreochromis niloticus			
Site/ Fish organ	Cu (mg/L)	Fe (mg/L)	Mn (mg/L)	Zn (mg/L)	Cu (mg/L)	Fe (mg/L)	Mn (mg/L)	Zn (mg/L
DGCUL	1.8±0.4^{ab}	13.7±5.2^{de}	1.4±0.6^{b}	1.9±0.5^{a-d}	1.6±0.3^{a}	20.7±5.6^{abc}	1.1±0.3^{b}	2.0±0.4^{ab}
DICUL	1.5±0.4^{b}	40.9±6.3^{ab}	1.0±0.4^{b}	2.4±0.6^{ab}	2.1±0.7^{a}	36.6±8.3^{ab}	3.8±2^{ab}	2.6±0.9^{a}
DMCUL	0.8±0.3^{b}	15.5±5.0^{de}	0.5±0.2^{b}	0.8±0.2^{cd}	1.6±0.9^{a}	17.6±4.5^{bc}	0.9±0.3^{b}	0.7±0.2^{b}
FGCUL	0.9±0.2^{b}	17.3±3.3^{de}	1.6±0.7^{b}	1.0±0.2^{bcd}	1.2±0.5^{a}	11.4±3.5^{bc}	0.8±0.3^{b}	1.0±0.2^{b}
FICUL	1.7±0.3^{ab}	37.3±6.3^{abc}	5.9±2.7^{a}	2.6±0.6^{a}	2.1±0.6^{a}	30.0±4.9^{abc}	5.1±2.0^{ab}	2.0±0.4^{ab}
FMCUL	0.9±0.5^{b}	7.6±1.2^{e}	0.7±0.3^{b}	1.0±0.3^{bcd}	0.7±0.2^{a}	9.5±1.4^{bc}	0.7±0.3^{b}	0.6±0.2^{b}
SGWLD	0.9±0.2^{b}	21.2±4.0^{cde}	2.6±0.9^{b}	1.6±0.3^{a-d}	2.5±0.7^{a}	34.3±5.9^{abc}	2.2±0.8^{b}	0.9±0.1^{b}
SIWLD	2.9±0.9^{a}	49.2±8.5^{a}	2.0±0.4^{b}	2.8±0.6^{a}	3.3±1.0^{a}	46.3±7.9^{a}	7.8±4.3^{a}	2.1±0.4^{ab}
SMWLD	0.8±0.4^{b}	9.0±1.9^{de}	0.9±0.3^{b}	0.7±0.2^{d}	3.0±1.1^{a}	27.2±5.0^{abc}	2.1±1.0^{b}	0.8±0.1^{b}
TGWLD	1.2±0.3^{b}	15.0±2.7^{de}	1.8±0.5^{b}	1.4±0.3^{a-d}	1.7±0.7^{a}	27.5±10.3^{abc}	1.4±0.4^{b}	1.3±0.3^{ab}
TIWLD	1.9±0.4^{ab}	30.0±6.4^{bcd}	2.3±0.5^{b}	2.3±0.5^{abc}	3.3±1.6^{a}	15.6±5.7^{bc}	1.8±0.6^{b}	1.4±0.4^{ab}
TMWLD	1.0±0.4^{b}	12.0±3.4^{de}	0.6±0.2^{b}	0.6±0.2^{d}	1.1±0.5^{a}	8.2±2.4^{c}	0.9±0.3^{b}	0.8±0.3^{b}
±SE	0.8	4.8	1.2	0.4	0.6	5.9	0.3	1.2

Means having similar superscript letter (s) within the same column are not significantly different at p≤0.05according to Student-Newman-Keuls (SNK) test at p≤0.05

As observed in the dry season, there was no significant effect of wet season on copper concentrations in Clarias gariepinus (Table. 3). However, the greatest copper concentration was detected in the intestine of Clarias gariepinus from Shiroro dam whereas the lowest was found in the muscle of Clarias gariepinus from FUT minna farm, Shiroro dam and Tagwai dam respectively. Although significant differences were found with respect to iron concentrations in various organs, the pattern of the distribution in the dry season differed from the wet season. In the latter, the intestine of Clarias gariepinus from FUT Minna farm had the highest concentration while muscle of Clarias gariepinus from Tagwai dam contained the lowest. However, there was no significant difference in iron concentration between the intestine of Clarias gariepinus from FUT Minna farm and Danejo farm. Similarly, iron concentrations in the gill of Clarias gariepinus from Danejo farm, FUT Minna farm and intestine of Clarias gariepinus from Shiroro dam were all statistically comparable. Those in the muscle of Clarias gariepinus from Danejo farm, FUT Minna farm, gill and muscle of Clarias gariepinus from Shiroro dam, as well as gill of Clarias gariepinus from Tagwai dam were all similar.

Manganese concentrations during the wet season varied from 0.1 to 2.0 mg/L among the Clarias gariepinus organs but the differences were not significant. The highest was found in the intestine of Clarias gariepinus from Tagwai dam while the lowest was detected in the muscle of Clarias gariepinus from Danejo dam and from FUT Minna farm. Unlike in dry season, zinc concentrations varied significantly in fish organs during the wet season. The highest was found in the intestine of Clarias gariepinus from Tagwai dam which was comparable to that in the intestine of Clarias gariepinus from Shiroro dam. Similarly, the difference in zinc concentrations in the intestine of Clarias gariepinus from Danejo farm and FUT Minna farm was not significant. Also, zinc concentration in the gill of Clarias gariepinus in Danejo dam was comparable to that in the gill of Clarias gariepinus from Shiroro dam. Moreover, zinc contents in the gill and muscle of Clarias gariepinus from FUT Minna farm as well as the gill of Clarias gariepinus from Tagwai dam were statistically at par. The lowest accumulation of zinc was found in the muscle of Clarias gariepinus from Shiroro and Tagwai dams, which was not significantly different from the value observed in the muscle of Clarias gariepinus from Danejo dam.

Table 3: Accumulation of heavy metals in different organs of the cultured and wild Clarias in dry and wet seasons

	Dry season				Wet season			
Site/Fish organ	**Cu (mg/L)**	**Fe (mg/L)**	**Mn (mg/L)**	**Zn (mg/L)**	**Cu (mg/L)**	**Fe (mg/L)**	**Mn (mg/L)**	**Zn (mg/L)**
DGCUL	2.5±0.6^{a}	10.4±3.4^{c}	2.1±0.6^{b}	1.5±0.7^{a}	1.1±0.2^{a}	17.0±10.6^{abc}	0.4±0.1^{a}	2.3±0.6^{abc}
DICUL	1.2±0.3^{a}	40.1±7.1^{b}	1.2±0.7^{b}	2.0±1.1^{a}	2.0±0.5^{a}	41.7±12.2^{a}	0.9±0.5^{a}	2.8±0.4^{ab}
DMCUL	1.3±0.5^{a}	20.0±8.4^{bc}	0.6±0.1^{b}	0.8±0.4^{a}	0.4±0.1^{a}	11.0±5.9^{bc}	0.1±0.0^{a}	0.8±0.1^{c}
FGCUL	0.9±0.2^{a}	12.9±4.2^{bc}	3.0±0.5^{b}	1.0±0.4^{a}	0.9±0.3^{a}	21.7±4.2^{abc}	0.2±0.1^{a}	1.1±0.2^{bc}
FICUL	2.1±0.6^{a}	31.8±5.8^{bc}	10.6±3.9^{a}	2.5±1.4^{a}	1.4±0.2^{a}	42.8±11.5^{a}	1.3±0.4^{a}	2.8±0.5^{ab}
FMCUL	1.4±0.6^{a}	7.5±1.7^{c}	1.0±0.3^{b}	0.8±0.4^{a}	0.1±0.1^{a}	7.7±2.1^{bc}	0.1±0.1^{a}	1.2±0.5^{bc}
SGWLD	1.3±0.2^{a}	28.7±4.7^{bc}	4.6±0.5^{b}	1.4±0.5^{a}	0.6±0.3^{a}	13.7±0.9^{bc}	0.7±0.2^{a}	1.8±0.5^{abc}
SIWLD	2.9±1.2^{a}	66.1±7.7^{a}	2.6±0.5^{b}	2.4±0.9^{a}	3.1±1.7^{a}	32.3±3.7^{abc}	1.4±0.2^{a}	3.2±0.8^{a}
SMWLD	1.1±0.4^{a}	10.0±4.0^{c}	1.5±0.3^{b}	0.8±0.3^{a}	0.1±0.0^{a}	8.0±1.2^{bc}	0.3±0.2^{a}	0.5±0.2^{c}
TGWLD	1.7±0.4^{a}	19.2±4.1^{bc}	2.7±0.3^{b}	1.6±0.6^{a}	0.7±0.1^{a}	10.7±1.3^{bc}	0.9±0.5^{a}	1.2±0.1^{bc}
TIWLD	2.6±0.6^{a}	24.1±10.1^{bc}	2.7±2.8^{b}	1.3±0.2^{a}	1.3±0.2^{a}	35.8±8.2^{ab}	2.0±0.5^{a}	3.3±0.5^{a}
TMWLD	1.3±0.3^{a}	18.9±1.7^{bc}	1.0±0.2^{b}	0.7±0.4^{a}	0.1±0.1^{a}	5.0±2.7^{c}	0.3±0.2^{a}	0.5±0.1^{c}
±SE	0.5	6.0	1.2	0.6	0.6	6.0	0.3	0.4

Means having similar superscript letter (s) within the same column are not significantly different at p≤0.05according to Student-Newman-Keuls (SNK) test
DGCUL = Danejo Farm (cultured) Gills; DICUL = Danejo Farm (cultured) Intestine; DMCUL = Danejo Farm (cultured) Muscle; FGCUL = FUT MINNA Farm (cultured) Gills; FUT MINNA Farm (cultured) Intestine; FMCUL = FUT MINNA Farm (cultured) Muscle; SGWLD = Shiroro Dam (wild) Gills; SIWLD = Shiroro Dam (wild) Intestine; SMWLD = Shiroro Dam (wild) Muscle; TGWLD = Tagwai Dam (wild) Gills; TIWLD = Tagwai Dam (wild) Intestine; TMWLD = Tagwai Dam (wild) Muscle

During the wet season, copper concentrations in Orechromis niloticus organs were statistically at par. Despite this, the highest copper content was detected in the intestine of Orechromis niloticus from Shiroro dam while the lowest was found in the muscle of Orechromis niloticus from Tagwai dam. Iron concentrations during the wet season varied between 8.3 and 46.4 mg/L in Orechromis niloticus. These extreme values were observed in the muscle of Orechromis niloticus from FUT minna farm and intestine of Orechromis niloticus from Shiroro dam. However, the differences in iron concentrations in the remaining fish organs were not significant. Manganese concentrations varied significantly in different organs of Orechromis niloticus during the wet season. The highest was observed in the intestine Orechromis niloticus of FUT Minna farm whereas the lowest was found in the muscle of Orechromis niloticus from Shiroro dam. Manganese concentration in the muscle of Orechromis niloticus from Danejo dam was not significantly different from that in the muscle of Orechromis niloticus from FUT Minna farm. The differences in manganese concentrations across the other fish organs were also not significant. Zinc concentrations ranged from 0.5 to 2.3 mg/L in Orechromis niloticus during the wet season but the differences were not significant. The lowest value came from the muscle of Orechromis niloticus from FUT Minna farm while the intestine of Orechromis niloticus from Danejo farm had the highest zinc concentration.

Table 4: Accumulation of heavy metals in different organs of the cultured and wild Tilapia in dry and wet seasons

	Dry season				Wet season			
Site/Fish organ	**Cu (mg/L)**	**Fe (mg/L)**	**Mn (mg/L)**	**Zn (mg/L)**	**Cu (mg/L)**	**Fe (mg/L)**	**Mn (mg/L)**	**Zn (mg/L)**
DGCUL	1.9±0.2^{a}	16.6±4.4^{a}	1.6±0.4^{b}	2.0±0.6^{a}	1.3±0.6^{a}	24.8±11.0^{ab}	0.7±0.3^{ab}	2.0±0.6^{a}
DICUL	3.0±1.1^{a}	44.1±12.8^{a}	7.3±3.0^{b}	2.9±1.8^{a}	1.1±0.4^{a}	29.1±11.4^{ab}	0.3±0.1^{ab}	2.3±0.5^{a}
DMCUL	2.9±1.5^{a}	19.6±7.1^{a}	1.2±0.3^{b}	0.6±0.1^{a}	0.3±0.2^{a}	15.6±7.0^{ab}	0.2±0.0^{b}	0.9±0.3^{a}
FGCUL	1.5±0.9^{a}	3.9±2.1^{a}	1.1±0.4^{b}	0.9±0.3^{a}	0.7±0.2^{a}	18.8±0.1^{ab}	0.4±0.2^{ab}	1.1±0.3^{a}
FICUL	2.5±1.3^{a}	24.2±8.3^{a}	8.3±3.0^{b}	2.5±0.6^{a}	1.7±0.5^{a}	35.7±4.1^{ab}	2.0±0.7^{a}	1.4±0.4^{a}
FMCUL	0.9±0.1^{a}	10.7±1.8^{a}	1.3±0.4^{b}	0.7±0.5^{a}	0.2±0.0^{a}	8.3±2.1^{b}	0.1±0.0^{b}	0.5±0.2^{a}
SGWLD	3.4±0.7^{a}	45.2±5.6^{a}	3.7±0.8^{b}	1.0±0.3^{a}	1.6±1.0^{a}	23.4±4.6^{ab}	0.7±0.4^{ab}	0.8±0.1^{a}
SIWLD	4.7±1.2^{a}	46.1±10.2^{a}	17.7±4.7^{a}	2.2±0.8^{a}	1.8±1.2^{a}	46.4±14.4^{a}	1.2±0.1^{ab}	2.0±0.4^{a}
SMWLD	4.4±0.9^{a}	31.4±9.2^{a}	3.4±1.0^{b}	0.9±0.3^{a}	0.8±0.5^{a}	23.0±4.5^{ab}	0.1±0.1^{b}	0.8±0.2^{a}
TGWLD	3.0±0.7^{a}	40.9±17.8^{a}	2.1±0.5^{b}	1.5±0.7^{a}	0.3±0.1^{a}	14.1±5.5^{ab}	0.8±0.3^{ab}	1.2±0.3^{a}
TIWLD	5.9±2.4^{a}	6.7±1.0^{a}	3.0±0.8^{b}	1.0±0.3^{a}	0.8±0.3^{a}	24.5±9.2^{ab}	0.7±0.2^{ab}	1.7±0.7^{a}
TMWLD	1.5±0.5^{a}	6.5±2.1^{a}	1.4±0.2^{b}	0.7±0.3^{a}	0.1±0.0^{a}	10.0±4.5^{ab}	0.3±0.2^{ab}	1.0±0.4^{a}
±SE	1.0	8.5	1.6	0.6	0.5	7.3	0.3	0.4

Means having similar superscript letter (s) within the same column are not significantly different at p≤0.05according to Student-Newman-Keuls (SNK) test
DGCUL = Danejo Farm (cultured) Gills; DICUL = Danejo Farm (cultured) Intestine; DMCUL = Danejo Farm (cultured) Muscle; FGCUL = FUT MINNA Farm (cultured) Gills; FUT MINNA Farm (cultured) Intestine; FMCUL = FUT MINNA Farm (cultured) Muscle; SGWLD = Shiroro Dam (wild) Gills; SIWLD = Shiroro Dam (wild) Intestine; SMWLD = Shiroro Dam (wild) Muscle; TGWLD = Tagwai Dam (wild) Gills; TIWLD = Tagwai Dam (wild) Intestine; TMWLD = Tagwai Dam (wild) Muscle

Relationship Among the Heavy Metals in Clarias Gariepinus and Oreochromis Niloticus

During the dry season, there was a negative correlation between copper and iron contents in cultured Clarias gariepinus but the relationship was not significant (Table.5). Positive but non-significant relationships were found among the other heavy metals. In wild Clarias gariepinus, all the heavy metals were positively correlated and a significant relationship was found between iron and zinc. During the wet season, all the heavy metals were positively correlated and the relationships were significant except between copper and manganese in both cultured and wild Clarias gariepinus (Table.6). In Cultured and wild Oreochromis niloticus, positive correlation was observed among the heavy metals during the dry season and a significant relationship was found between manganese and zinc (Table.7). During the wet season, all the heavy metals were also positively correlated in both cultured and wild Oreochromis niloticus (Table. 8). However, in the former, significant relationship was found between copper and iron as well as copper and manganese. In the latter, significant relationship was found between copper and iron only.

Table 5: Correlation Coefficients of the Heavy Metals in Cultured and Wild Clarias During the Dry Season

Cultured Clarias					Wild Clarias			
	Copper	Iron	Manganese	Zinc	Copper	Iron	Manganese	Zinc
Copper								
Iron	- 0.11852				0.76112			
Manganese	0.41138	0.35399			0.09952	0.27115		
Zinc	0.45825	0.74481	0.72582		0.7574	0.88053*	0.45213	

Table 6: Correlation Coefficients of The Heavy Metals in Cultured and Wild Clarias During the Wet Season

Cultured Clarias				Wild Clarias			
Copper	Iron	Manganese	Zinc	Copper	Iron	Manganese	Zinc
Copper							
Iron	0.90464*			0.81421*			
Manganese	0.80834	0.94754**		0.69306	0.96062**		
Zinc	0.8731*	0.84091*	0.89448*	0.84565*	0.97757**	0.94268**	

Table 7: Correlation Coefficients of The Heavy Metals in Cultured and Wild Oreochromis Niloticus During the Dry Season

Cultured Oreochromis niloticus				Wild Oreochromis niloticus			
Copper	Iron	Manganese	Zinc	Copper	Iron	Manganese	Zinc
Copper							
Iron	0.77957			0.04779			
Manganese	0.55946	0.7659		0.37038	0.49491		
Zinc	0.52262	0.78179	0.86536*	0.34662	0.62652	0.88039*	

Table 8: Correlation Coefficients of The Heavy Metals in Cultured and Wild Oreochromis Niloticus During the Wet Season

	Cultured Oreochromis niloticus				Wild Oreochromis niloticus			
	Copper	Iron	Manganese	Zinc	Copper	Iron	Manganese	Zinc
Copper								
Iron	0.95353**				0.86707*			
Manganese	0.84578*	0.78178			0.59305	0.67324		
Zinc	0.6912	0.73191	0.21239		0.35751	0.67831	0.77349	

*Significant at p≤0.05; **Significant at p≤0.01

Discussion

During the course of this work, heavy metals like copper, iron, manganese, and zinc were detected in the four sampling sites. Lead was however, absent. It was observed that the concentration of copper, iron and manganese in cultured and wild fish were not significantly different ($p>0.05$). Similar results were obtained by who reported that it is difficult to quantify very low contaminant concentrations commonly found in natural waters [11,12]. Reported that the two major sources of zinc in water bodies are particles released from vehicle tires and brake linings. Since none of the sampling stations is located close to a major road, this may largely account for the low and no difference in the concentration of zinc between cultured and wild species. One of the species of fish sampled for heavy metal analysis in this work is Clarias gariepinus. It was observed that the difference in copper concentration in Clarias gariepinus from the wild and cultured environment was significant ($p<0.05$). The higher copper concentration of samples from the wild fish may have come from the rocky terrains where the dams are located. Slightly similar report was given by who reported weathering of rock and anthropogenic activities as some of the sources of heavy metals in natural water bodies. This same reason may account for the high iron and manganese concentration of wild Clarias gariepinus [13,14]. observed that bioavailability of metals is dependent on the chemical and physical (dissolved or particulate) forms of metals in the water column. They showed how this leads to varying levels of heavy metal concentration in different organs of fish e.g gills, intestine and muscles. This may also explains why there was high iron concentration in the intestine of species from Shiroro dam, while the lowest concentration was found in the muscles of species from FUT Minna farm. It has been established that heavy metal sources could come from the terrestrial environment into the water body, e.g surface runoff and air or from within the aquatic environment itself. Depending on the source of a metal, its concentration in a water body may be influenced by season. Those which depend largely on surface runoff to find their way into water may not be found in significant concentration in the water body under consideration. In this study, there was no significant effect of dry season on copper accumulation in different organs of Clarias gariepinus and Oreochromis niloticus. This suggests that the source of copper in this water bodies may be terrestrial and depends largely on runoff to get into the dams, hence the no effect on fish during the dry season. In contrast, significant differences occurred among the organs with respect to iron concentration during the dry season. This may not be far from the possibility of an iron source within the water body. Fish are an important source of food and represents a major part of many natural food chains. Therefore, the levels of contaminants in fish are of interest because of the potential effects of these polluting substances on the fish themselves and on the organisms that consume those including humans [15]. The result in this work showed the presence of copper, iron, manganese and zinc in all samples of Oreochromis niloticus and Clarias gariepinus obtained from these sampling sites. Moreover, the results indicated a variation between the heavy metal levels in the analyzed muscle, gills and intestinal tissues as also registered by [16]. In general, the level of heavy metal accumulation in Oreochromis niloticus and Clarias gariepinus were greater in the intestinal tissues [17]. Found higher levels of zinc and cadmium in fish livers in comparism to other organs. The liver is often used as a reference for analysis of tissue damage caused by environmental toxic compounds [18]. Furthermore, it was not possible to verify any relationship between the levels of heavy metals bioaccumulation to the sex of the analyzed fish, as has previously been reported by [19]. In this work, muscles samples with levels of manganese contamination above the safe limit for human consumption. That is, about 1.7-2.1mg/l as against the 0.4mg/l safe limit recorded (table 4-1). It was noted that in all the fish analyzed, manganese was detected including some cases of levels near the safe limit for human consumption. During the dry season of the present study, exception of copper and iron, the rest of the heavy metals detected, positively correlated in cultured and wild fish species. Furthermore, there were no exceptions during the wet season, since all the heavy metals detected correlated positively thereby confirming the theory of bioaccumulation from continuous exposure to the metal as also recorded by [20].

Conclusion and Recommendation

In conclusion, the present study provides crucial information on the distribution of heavy metals in tissues of Oreochromis niloticus and Clarias gariepinus. These fish species are of great economic importance especially in Nigeria. The information showed that the viscera (in this case, the intestinal tissues) usually contains high amounts of heavy metals, and should thus, not be considered for human consumption. Although the level of bioaccumulation of copper, iron and zinc in the analyzed samples of Oreochromis niloticus and Clarias gariepinus generally do not exceed the safe levels for human consumption, the constant presence of heavy metals in concentrations near those considered unsafe for human consumption is a reason for warning populations who regularly consume fish from Tagwai and Shiroro dams. Moreover, the results in this work indicates that in a dam network where there are connected areas with high rates of environmental pollutants, consumption of fish can be dangerous even when these fish are caught in areas considered to have low rates of contamination. Despite the fact that fish are wholesome for human consumption as far the studied metals are concerned, it should be pointed out that exposure estimates for heavy metals intake from fish consumption are based on the national average fish consumption data. This may not be appropriate for estimating the risk associated with fish consumption of a particular area or residing in specific regions and towns of the country.

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