Predisposing Factors that Promote Prevalence of heavy metals assimilation and bioaccumulation in aquatic medium and amongst fishes

Abstract

The degree of heavy metals assimilation and bioaccumulation in fish tissues (muscles, gills, liver, and kidneys), amongst scale-less fishes- *Chrysichthys macrotis*, *Chrysichthys nigrodigitatus*, *Clarias gariepinus*, and *Heterobranchus longifilis*, *-scaly fishes- Cynoglossus senegalensis*, *Oreochromis aureus*, *O. niloticus*, *Lutjanus fulgens*, *Pomadasys rogeri*, and *Tilapia galilea*, water columns and sediments, were investigated. Heavy metals assimilation and bioaccumulation varied among organisms with or without scales, tissue types, and fish location (water column & sediments) and pollution level. Fishes with scales had lower concentrations of heavy metals than scale- less fishes. The scalier the fish, the lower the metal assimilation and bioaccumulation. As expected, trace metals were generally lower in muscles than liver, and kidney. Liver had highest followed by kidney, gills and then muscles. Fish trophic level (water column or sediments) and water pollution levels affected heavy metal concentrations. Concentrations were always more in sediments than water column or tissues. The more polluted the water, the more the assimilation and accumulation of trace metals.

Key words: Heavy metals, Predispose, prevalence, bioaccumulation, fish scales, scaleless, sediments.

Introduction

Heavy metals concentrations have been studied extensively in different parts of the globe (Elnabris, Muzyed, & El-Ashgar, 2013). Majority of these studies dwelt mainly on the heavy metals in the edible part (fish muscles). Besides, other studies reported the distribution of metals in different organs like the kidney, liver, heart, gonads, brain, bone, and digestive tract (El-Moselhy, Othman, El-Azem, & El-Metwally, 2014).

Metal bioaccumulation by fish and subsequent distribution in organs is majorly inter-specific. Many factors like sex, age, size, reproductive cycle, swimming patterns, feeding behaviour and living environment (geographical location) can influence metal uptake (Mustafa & Guluzar, 2003; Zhao, Feng, Quan, Chen, Niu, & Shen, 2012; El-Moselhy, Othman, El-Azem, & El-Metwally, 2014). More often than naught, muscles usually possess the lowest concentrations of all metals. While the liver could be the target organ for Cu, Zn, and Fe accumulation, Pb and Mn often dominate in the gills (EL-Moselhy, Othman, EL-Azem, & EL-Metwally, 2014). Metal bioaccumulation among fish is both inter-specific and intra-specific and could be geographically and seasonally dependent (Idodo-Umeh, 2007; Ajah, 2013; El-Moselhy, *et al.*, 2014). Metal concentrations differences might be related to diet and feeding habits of benthic and pelagic fish species.

The present research unravels the location where heavy metals are predominant and the physiological and morphological factors that promote or predispose easier assimilation and bioaccumulation.

Materials and Methods

Fish, water and sediment samples were drawn from three locations namely, Mbaa River (05^{o}25’04”0.14”” N. 07^{o}6’.5”0.45”” E)in Imo State, Nigeria (ST1= Inyishi Beach, ST2= Oziri Beach, St3= Umuoziri Beach); Lemna slaughterhouse (Latitude 04^{o}15’ N & longitude 08^{o}25’E), Ikot Effanga Mkpa stream, Calabar Municipality, and Calabar estuary, Cross River State, Nigeria. At Lemna slaughterhouse, sediments, water, and fish samples were collected from three sampling points- SP1, SP2 and SP3 at 50, 120 and 150 meters respectively from the slaughterhouse. Fish samples (*Chrysichthys nigrodigitatus* & *Cynoglossus senegalensis*) were collected randomly from fishermen on landing at the three sampling points (SP1-3) during the raining season, from May to July 2021. Fish samples were collected into well labeled plastic containers, and preserved in an ice chest box before transferring to MIFOR Environmental Laboratory for heavy metals analysis.

Heavy metals concentrations, namely, Fe, Mn, Cu, Cr, Pb, Co, Zn, Al Ar, Hg, Cd, were analyzed using atomic absorption spectroscopy (AAS) following Unicam 919 Solar System. Sediment samples were collected from the sampling points for three months, from May to July 2021, using Ekman grab, which was lowered into the river and the samples collected. After collection, the sediments were preserved in a plastic polythene bag and put in an ice box to preserve from any external factor that might alter the heavy metal concentration and thereafter transferred to Laboratory for heavy metals analysis.

Heavy metals analysis of the fish samples

In the laboratory, the fish specimens were properly washed with distilled water and put in a clean plastic bag, stored and frozen until analysis is carried out. Prior to the digestion of the samples, the tissues of the fish samples were oven dried at 109^{o} C and grinded. One gram of the prepared and ground fish tissues was subjected to digestion by adding 10ml of freshly prepared 1:1 concentrated $CHNO_3$ – $HCLO_3$ in a beaker, covered with a water glass till initial reaction subsided in about 1 hour and gently heated at 160 ^{o}C in a sand bath on a hot plate till reduction of the volume to 2-5 ml. The digest was allowed to cool and transferred to 25 ml volumetric flasks and made up to the mark with de-ionized water. The digest was then kept in plastic bottles and later the concentration of heavy metals like manganese, iron, nickel, lead, chromium, zinc, copper, and silver etc. were measured using an atomic absorption spectrophotometer (AAS) following Unicam 919 Solar) in mg/kg.

Heavy metals analysis of water

The ice chest preserved water samples were allowed to normalize and assume the normal temperature of the laboratory (28^{o} C). About 25 millilitres of water sample were digested with three millilitres 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 to distilled water of 50 ml, before analyzing for manganese, iron, nickel, lead, chromium, zinc, copper, and silver etc using atomic absorption spectrophotometer to the nearest mg/l (APHA, 1995).

Heavy metals analysis in sediments

Sediment samples were collected in plastic bags and transported to the laboratory for analysis. The sediments were air dried first at room temperature, then ground, sieved and digested with concentrated nitric acid and hydrochloric acid in the ratio of 2:1 respectively using a hot plate at 70 ^{o}C (Yahia *et al.*, 2012). After complete digestion, the solution was filtered using an acid-resistant filter paper in 25 ml volumetric flask and filled up to the mark using distilled water. The solution was then kept in airtight-stoppered bottle until they are analyzed for chromium, cadmium, mercury, lead, and iron using electron spectrophotometer in mg/kg.

Statistical analysis

Data obtained for heavy metals in water, sediment, and fishes were subjected to descriptive statistics (mean, standard deviation, and ranges). Analysis of variance (ANOVA) was used to assess the significant difference in the concentration of heavy metals in sediments, water, and fish between the 3 sampling points. All analysis were carried out using SPSS software at 0.05 level of significance and at their relevant degree of freedom.

Results and Discussion

Table 1, shows the mean values of heavy metals contamination on three fish species, namely, *Heterobranchus longifilis, Oreochromis niloticus* and *O. aureus* tissues (muscle) obtained from Mbaa River in Ikeduru, Imo State, Nigeria with Iron (Fe) in tissues as 0.625±0.340, 0.683±0.336 and 0.602±0.331 mg/kg, Manganese 0.047±0.219, 0.048±0.023 and 0.042±0.230 mg/kg; Copper 0.020±0.010, 0.020±0.010 and 0.019±010 mg/kg; Chromium 0.012±0.004, 0.011±0.005 and 0.012±0.005; Lead (Pb) 0.008±0.001, 0.007±0.001, and 0.007±0.000; Cobalt 0.032±0.058, 0.009±0.005 and 0.010±0.005, and Zinc 0.032±0.018, 0.037±0.21 and 09.036±0.021 mg/kg, respectively. Aluminum was not detected (ND) in the fish samples across the three stations.

Table 1. Mean, Standard deviation and Ranges in parenthesis of Heavy metals in tissues (muscle) (mg/kg) from Mbaa (Inyishi) River during the study period.

Metals (Range)	*Heterobranchus longifilis*	*Oreochromis niloticus*	*Oreochromis aureus*	Mean Value	F-Value	P-Value	Sign. Test	Inference
Iron (Fe)	0.625±0.340 (0.382-1.230)	0.683±0.336 (0.404-1.210)	0.602±0.331 (0.381-1.190)	0.637±0.317 (0.381-1.230)	0.093	0.912	P > 0.05	NS
Manganese (Mn)	0.047±0.219 (0.031-0.086)	0.048±0.023 (0.028-0.084)	0.042±0.230 (0.026-0.081)	0.046±0.022 (0.26-0.086)	0.101	0.905	P > 0.05	NS
Copper (Cu)	0.020±0.010 (0.011-0.037)	0.020±0.010 (0.012-0.036)	0.019±0.010 (0.013-0.036)	0.019±0.009 (0.011-0.037)	0.009	0.991	P > 0.05	NS
Chromium (Cr)	0.012±0.004 (0.009-0.020)	0.011±0.005 (0.006-0.019)	0.012±0.005 (0.007-0.020)	0.012±0.004 (0.006-0.020)	0.235	0.794	P > 0.05	NS
Lead (Pb)	0.008±0.001 (0.007-0.008)	0.007±0.001 (0.006-0.008)	0.007±0 (0.007-0.007)	0.007±0.001 (0.006-0.008)	0.200	0.829	P > 0.05	NS
Cobalt (Co)	0.032±0.058 (0.002-0.150)	0.009±0.005 (0.003-0.014)	0.010±0.005 (0.002-0.014)	0.017±0.034 (0.002-0.150)	0.901	0.427	P < 0.05	S
Zinc (Zn)	0.032±0.018 (0.008-0.052)	0.037±0.021 (0.010-0.060)	0.036±0.021 (0.008-0.057)	0.035±0.019 (0.008-0.060)	0.098	0.907	P > 0.05	NS
Aluminum (Al)	ND	ND	ND	ND				

Mean ± S.D, Ranges in parenthesis, Significant at P < 0.05, NS = Not Significant. WHO= World Health Organization, FMEnv= Federal Ministry for Environment. ST1= Inyishi Beach, ST2= Oziri Beach, St3= Umuoziri Beach.

Fe, Mn, Cu, Pb, Co, and Zn were all higher in scale-less *Heterobranchus longifilis* than *Oreochromis aureus* though none except cobolt (Co) which was significantly different (Table 1). Equal amount of Cr existed between them. Only Zn was lower in *H. longifilis* than *O. aureus* and *O. niloticus*. Cr, Pb, Co, were higher in scale-less *H. longifilis* than scalely *O. niloticus* while Mn, Cu, were of equal values with only Fe being higher in *O. niloticus* than *H. longifilis*. *H. longifilis* had a total mean value of 0.776 mg/l, *O. niloticus* 0.815 mg/l and *O. aureus* 0.728 mg/l.

The heavy metals in muscles of scaleless *Chrysichthys macrotis* and *Clarias gariepinu*s had more Ar, Fe, Hg, Zn, Cr than those in scalely *Lutjanus fulgens* and *Pomadasys rogeri* (Tables 2,3, 4 & 5). Cr and Mn were also more in scale-*less C. gariepinus* than in scalely *L. fulgens*. Cd and Pb were the opposite wherein the scaly fishes had more than scale-less fishes. *P. rogeri* had more Mn than *L. fulgens* while *C. gariepinus* had more Mn metals than *C. macrotis.* Total average value of all metals was 0.320 mg/l, 0.450mg/l, 0.078 mg/l and 0.068 mg/l in muscles of scaleless *Chrysichthys macrotis,* (Table 2) *Clarias gariepinus,* (Table 3) scalely *Lutjanus fulgens* (Table 4) and *Pomadasys rogeri* (Table 5), respectively, an indication that heavy metals were always higher in the muscles of scaleless fishes than scalely fishes.

The same trend was seen in both the kidney and the liver with total average of all the metals in the kidney as 0.299 mg/l, 0.379 mg/l, 0.097 mg/l and 0.068 mg/l for *Chrysichthys macrotis, Clarias gariepinus, Lutjanus fulgens* and *Pomadasys rogeri,* respectively (Tables 7) and 0.404 mg/l, 0.548 mg/l, 0.186mg/l and 0.152 mg/l for *C. macrotis, C. gariepinus, L. fulgens* and *P. rogeri* respectively (Table 8). Thus, whether it has to do with the muscles, kidneys or liver, the scaleless fishes always had more trace metals compared to the scalely fishes.

The organs of greater prevalence were as follows- liver (0.185mg/l)>kidney (0.097 mg/l) > muscles (0.078 mg/l) (Table 4) for *L. fulgens,* while *P. rogeri*, in Table 5 followed the same trend of liver (0.090 mg/l) > kidney (0.068 mg/l) > muscle (0.067 mg/l). Consequently, the liver was the organ of greatest accumulation of the heavy metals for both the scalely fishes and scaleless. *Chrysichthys macrotis* in table 2 also had 0.402mg/l, 0.299 mg/l and 0.316 mg/l, for the liver, kidney, and muscle respectively. However, in *Clarias gariepinus,* the organ of greatest impart was the muscle (0.452 mg/l), followed by the kidney (0.378 mg/l) and lastly the liver with 0.359 mg/l (Table 3). Significant differences (P<0.05) were observed in the heavy metal concentrations in all the three organs -muscles, kidneys, and livers amongst the fish species.

TABLE 2. Heavy metal levels in the muscle, kidney and liver of *Chrysichthys macrotis*

Heavy Metal	Muscle	Kidney	Liver	P-Value
Ar	0.013± 0.003[a]	0.002±0.000[b]	0.012±0.001[c]	0.017
Fe	0.021±0.001[a]	0.019±0.001[a]	0.020±0.000[a]	0.729
Hg	0.120±0.001[c]	0.112±0.001[b]	0.116 ±0.001[c]	0.0002
Zn	0.146±0.003[a]	0.152±0.001[a]	0.149±0.001[a]	0.206
Cu	0.001±0.000[a]	0.001±0.000[b]	0.001±0.000[c]	0.00013
Cr	0.012±0.001[a]	0.011±0.000[b]	0.102±0.000[c]	0.0009
Cd	0.002±0.001[a]	0.001±0.000[a]	0.001±0.000[a]	0.492
Pb	0.000±0.000	0.000±0.000	0.000±0.000	
Mn	0.001±0.001[a]	0.001±0.000[a]	0.001±0.000[a]	1.000
Total Av	0.316	0.299	0.402	

* Values represents the mean of the triplicate experimental data and mean with the same superscript are not significantly different (P>0.05)

TABLE 3:Heavy metal levels in the muscle, kidney, and liver of *Clarias. gariepinus*

Heavy Metal	Muscle	Kidney	Liver	P-Value
Ar	0.001± 0.001^{a}	0.000±0.000^{a}	0.002±0.000^{a}	0.171
Fe	0.012 ±0.001^{a}	0.001±0.000^{b}	0.010±0.000^{c}	0.00005
Hg	0.084±0.036^{a}	0.111±0.000^{a}	0.121±0.009^{a}	0.491
Zn	0.012 ±0.000^{a}	0.056±0.029^{a}	0.011±0.000^{a}	0.175
Cu	0.210±0.001^{a}	0.170±0.030^{a}	0.180±0.030^{a}	0.534
Cr	0.111±0.001^{a}	0.012±0.000^{b}	0.010±0.001^{c}	0.00001
Cd	0.010±0.000^{a}	0.011±0.000^{b}	0.013±0.001^{c}	0.013
Pb	0.001±0.000^{a}	0.006±0.003^{a}	0.001±0.000^{a}	0.139
Mn	0.011±0.000^{a}	0.011±0.001^{a}	0.011±0.000^{a}	1.000

* Values represents the mean of the triplicate experimental data and mean with the same superscript are not significantly different (P>0.05)

TABLE 4:Heavy metal levels in the muscle, kidney and liver of *Lutjanus fulgens*

Heavy Metal	Muscle	Kidney	Liver	P-Value
Ar	0.001± 0.000^{a}	0.002±0.001^{b}	0.013±0.001^{c}	0.0001
Fe	0.011±0.000^{a}	0.019 ±0.001^{b}	0.012±0.001^{c}	0.0003
Hg	0.011±0.001^{a}	0.012±0.000 ^{a}	0.011±0.001^{a}	0.174
Zn	0.012±0.001^{a}	0.011±0.000^{b}	0.101±0.000^{c}	0.00016
Cu	0.007±0.003^{a}	0.011±0.000^{a}	0.012±0.000^{a}	0.212
Cr	0.002±0.000^{a}	0.004±0.003^{b}	0.012±0.000^{c}	0.027
Cd	0.022±0.000^{a}	0.020±0.001^{b}	0.010±0.001^{c}	0.0002
Pb	0.002±0.000^{a}	0.010±0.000^{b}	0.002±0.001^{c}	0.0003
Mn	0.010±0.001^{a}	0.008±0.003^{a}	0.012±0.000^{a}	0.362

* Values represents the mean of the triplicate experimental data and mean with the same superscript are not significantly different (P>0.05)

TABLE 5:Heavy metal levels in the muscle, kidney and liver of *Pomadasys rogeri*

Heavy Metal	Muscle	Kidney	Liver	P-Value
Ar	0.007± 0.001	0.000±0.000	0.006±0.001	
Fe	0.001±0.000	0.012±0.001	0.013±0.000	
Hg	0.011 ±0.001^{a}	0.009±0.001^{a}	0.012± 0.000^{a}	0.098
Zn	0.001±0.000	0.011±0.000	0.012±0.000	
Cu	0.000 ±0.000^{a}	0.001±0.000^{a}	0.005±0.003^{a}	0.244
Cr	0.010±0.001^{a}	0.001±0.000^{b}	0.004±0.002^{c}	0.023
Cd	0.012±0.000^{a}	0.011±0.000^{a}	0.030±0.034^{a}	0.082
Pb	0.013±0.003^{a}	0.012±0.000^{a}	0.011±0.001^{a}	0.752
Mn	0.012±0.001^{a}	0.011±0.001^{a}	0.009±0.001^{a}	0.164
Total Av.	0.089	0.068	0.102	

* Values represents the mean of the triplicate experimental data and mean with the same superscript are not significantly different (P>0.05)

Table 6:Heavy metal levels in the muscle in relation to species from Cross River Estuary

Heavy Metal	*C. macrotis*	*C. gariepinus*	*L. fulgens*	*Lutjanus sp at Egyptian Red sea*	*P. rogeri*	P-value
Ar	0.013±0.003[a]	0.001±0.001[a]	0.001±0.000[a]	-	0.007±0.000[a]	0.003
Fe	0.020±0.001[a]	0.012±0.001[a]	0.011±0.000[a]	2.05±0.26	0.002±0.000[a]	0.000001
Hg	0.120±0.001[a]	0.084±0.036[a]	0.011±0.001[a]	-	0.011±0.001[a]	0.006
Zn	0.146±0.003[a]	0.012±0.000[a]	0.012±0.000[a]	2.08±0.28	0.001±0.000[a]	0.000002
Cu	0.006±0.000[a]	0.210±0.001[a]	0.007±0.003[a]	0.24±0.11	0.000±0.000[a]	0.00001
Cr	0.012±0.000[a]	0.111±0.001[a]	0.002±0.001[a]	-	0.010±0.002[a]	0.00004
Cd	0.002±0.001[a]	0.010±0.000[a]	0.022±0.001[a]	0.03±0.02	0.012±0.001[a]	0.000012
Pb	0.000±0.000[a]	0.001±0.000[a]	0.002±0.001[a]	0.57±0.05	0.013±0.003[a]	0.002
Mn	0.001±0.001[a]	0.011±0.000[a]	0.010±0.001[a]	0.10±0.03	0.012±0.001[a]	0.000003
Total Av.	0.320	0.450	0.078		0.068	

* Values represents the mean of the triplicate experimental units and means with the same superscript were not significantly different (P>0.05). *Lutjanus* from Egyptian Red Sea adopted from El-Moselhy *et al* 2014.

The dominance trend is as follows: Zn>Hg>Ar>Cr>Fe>Cd>Mn>Pb

TABLE 7. Heavy metal levels in the Kidney in relation to species from Cross River Estuary

Heavy Metal	*C. macrotis*	*C. gariepinus*	*L. fulgens*	*P. rogeri*	P-value
Ar	0.002±0.000[a]	0.000±0.000[a]	0.002±0.001[a]	0.000±0.000[a]	0.015
Fe	0.019±0.001[a]	0.001±0.000[a]	0.019±0.001[a]	0.012±0.000[a]	0.00001
Hg	0.112±0.001[a]	0.111±0.000[a]	0.012±0.000[a]	0.009±0.001[a]	0.00003
Zn	0.152±0.000[a]	0.056±0.029[a]	0.011±0.000[a]	0.011±0.000[a]	0.000001
Cu	0.001±0.000[a]	0.171±0.030[a]	0.011±0.000[a]	0.001±0.000[a]	0.00032
Cr	0.011±0.000[a]	0.012±0.000[a]	0.004±0.003[a]	0.001±0.000[a]	0.004
Cd	0.001±0.003[a]	0.011±0.000[a]	0.020±0.001[a]	0.011±0.000[a]	0.00007
Pb	0.000±0.000[a]	0.006±0.003[a]	0.010±0.000[a]	0.012±0.000[a]	0.003
Mn	0.001±0.000[a]	0.011±0.001[a]	0.008±0.002[a]	0.011±0.001[a]	0.006
Total Av.	0.299	0.379	0.097	0.068	

* Values represent the mean of the triplicate experimental data and mean with the same superscript are not significantly different (P>0.05)

The dominance trend is as follows: Zn>Hg>Fe>Cr>Ar>Cd, Cu, Mn>Pb

TABLE 8:Heavy metal levels in the Liver in relation to species in Cross River Estuary

Heavy Metal	*C. macrotis*	*C. gariepinus*	*L. fulgens*	*Lutjanus sp at Egyptian Red sea*	*P. rogeri*	P-value
Ar	0.012±0.001[a]	0.002±0.000[a]	0.013±0.001[a]	-	0.006±0.001[a]	0.00002
Fe	0.020±0.000[a]	0.010±0.000[a]	0.012±0.001[a]	322.55+58.1	0.013±0.000[a]	0.000001
Hg	0.110±0.001[a]	0.121±0.009[a]	0.011±0.001[a]	-	0.012±0.001[a]	0.000003
Zn	0.149±0.001[a]	0.012±0.000[a]	0.101±0.000[a]	36.02+0.26	0.012±0.001[a]	0.00001
Cu	0.009±0.000[a]	0.180±0.030[a]	0.012±0.000[a]	4.41+0.36	0.005±0.003[a]	0.00004
Cr	0.102±0.001[a]	0.010±0.001[a]	0.012±0.001[a]	-	0.004±0.003[a]	0.000005
Cd	0.001±0.000[a]	0.013±0.001[a]	0.010±0.001[a]	0.86+0.01	0.080±0.034[a]	0.042
Pb	0.000±0.000[a]	0.001±0.000[a]	0.002±0.001[a]	0.83+0.03	0.011±0.002[a]	0.000033
Mn	0.001±0.000[a]	0.011±0.000[a]	0.012±0.000[a]	1.29+0.12	0.009±0.001[a]	0.000021
Total Av.	0.404	0.548	0.186		0.152	

* Values mean of the triplicate experimental data and mean with the same superscript are not significantly different (P>0.05). *Lutjanus* from Egyptian Red Sea adopted from El-Moselhy *et al* 2014.

The dominance trend is as follows: Zn>Hg>Cr>Fe>Ar>Cu>Cd>Pb

TABLE 9. Heavy metals concentration in water from Ikot Effanga Mkpa stream during the study

Heavy metals (mg/l)	Sampling point 1	Sampling point 2	Sampling point 3	Mean	WHO (2008)
Fe	1.078 ± 0.014[a] (1.06 – 1.08)	1.009 ± 0.012[b] (1.00 – 1.02)	1.271 ± 0.062[c] (1.21 – 1.33)	1.119± 0.122 (1.00 – 1.33)	0.03
Ni	1.156 ± 0.051[a] (1.12 – 1.21)	1.124 ± 0.183[a] (1.01 – 1.33)	1.025 ± 0.153[a] (0.91 – 1.20)	1.101± 0.136 (0.91 – 1.33)	0.07
Pb	0.897 ± 0.080[a] (0.81 – 0.97)	0.819 ± 0.003[a] (0.81 – 0.82)	0.776 ± 0.041[a] (0.73 – 0.81)	0.831± 0.069 (0.73 – 0.97)	0.01
Cr	0.079 ± 0.014[a] (0.06 – 0.09)	0.070 ± 0.005[a] (0.06 – 0.09)	0.076 ± 0.016[a] (0.06 – 0.09)	0.075± 0.011 (0.06 – 0.09)	0.05
Zn	1.120 ± 0.015[a] (1.10 – 1.13)	1.076 ± 0.064[a] (1.00 – 1.12)	1.036 ± 0.023[a] (1.01 – 1.06)	1.077± 0.050 (1.00 – 1.13)	5.0
Cu	0.610 ± 0.004[a] (0.60 – 0.61)	0.627 ± 0.014[b] (0.61 – 0.64)	0.518 ± 0.004[c] (0.51 – 0.52)	0.585± 0.052 (0.51 – 0.64)	1.0
Mn	0.528 ± 0.028[a] (0.50 – 0.55)	0.412 ± 0.003[b] (0.40 – 0.41)	0.337 ± 0.028[c] (0.31 – 0.36)	0.425± 0.086 (0.31 – 0.55)	0.40
Ag	0.077 ± 0.011[a] (0.06 – 0.08)	0.072 ± 0.004[a] (0.06 – 0.07)	0.084 ± 0.005[a] (0.07 – 0.08)	0.078± 0.008 (0.06 – 0.08)	-

Values are in mean ± standard deviation; ranges in parenthesis ( ) Total av.5.291

Values with different superscript across sampling points are significantly different ($p<0.05$) The dominance trend is as follows: Ni>Zn>Fe>Pb>Cu>Mn>Cr>Ag

TABLE 10.Heavy metals concentration in sediments from Ikot Effanga Mkpa stream during the study

Heavy metals (mg/l)	Sampling point 1	Sampling point 2	Sampling point 3	Mean	WHO (2008)
Fe	7.063 ± 0.021[a] (7.04 – 7.08)	6.981 ± 0.622[b] (6.30 – 7.52)	5.874 ± 0.506[c] (5.31 – 6.29)	6.639 ± 0.701 (5.31 – 7.52)	1.90
Ni	1.927 ± 0.093[a] (1.82 – 1.99)	1.585 ± 0.050[b] (1.52 – 1.62)	1.517 ± 0.008[c] (1.50 – 1.52)	1.676 ± 0.197 (1.50 – 1.99)	18
Pb	1.333 ± 0.102[a] (1.22 – 1.43)	1.118 ± 0.008[b] (1.10 – 1.12)	1.102 ± 0.001[c] (1.10 – 1.104)	1.184± 0.122 (1.10 – 1.43)	<20
Cr	0.107 ± 0.001[a] (0.10 – 0.11)	0.102 ± 0.002[b] (0.10 – 0.104)	0.095 ± 0.002[c] (0.09 – 0.10)	0.101± 0.005 (0.09 – 0.11)	0.10
Zn	14.729± 0.603[a] (14.18 – 15.38)	14.132 ± 0.094[b] (14.04 – 14.23)	13.221 ± 0.021[c] (13.20 – 13.24)	14.027± .725 (13.2015.38)	50 - 300
Cu	4.309 ± 0.279[a] (4.08 – 4.62)	4.059 ± 0.114[a] (3.92 – 4.13)	3.796 ± 0.342[a] (3.40 – 4.02)	4.055 ± 0.318 (3.40 – 4.62)	20
Mn	2.778 ± 0.039[a] (2.74 – 2.82)	2.595 ± 0.087[a] (2.50 – 2.67)	2.432 ± 0.271[a] (2.13 – 2.66)	2.602 ± 0.208 (2.13 – 2.82)	9.30
Ag	0.094 ± 0.003[a] (0.09 – 0.10)	0.081 ± 0.010[b] (0.07 – 0.09)	0.073 ± 0.007[c] (0.06 – 0.08)	0.082 ± 0.011 (0.06 – 0.09)	-

Values are in mean ± standard deviation; ranges in parenthesis ( ) Total av.trace metals 30.366

Values with different superscript across sampling points are significantly different ($p<0.05$). The dominance trend is as follows: Zn>Fe>Cu>Mn>Pb>Ni>Cr>Ag

TABLE 11. Heavy metals concentration in *Chrysichthys nigrodigitatus* from Ikot Effanga Mkpa stream during the study

Heavy metals (mg/l)	Sampling pt 1	Sampling pt 2	Sampling pt 3	Mean	WHO (2008)
Fe	1.186 ± 0.017[a] (1.16 – 1.19)	1.167 ± 0.005[b] (1.16 – 1.17)	1.141 ± 0.012[c] (1.12 – 1.15)	1.164±0.022 (1.13– 1.19)	0.30
Ni	0.027 ± 0.004[a] (0.02 – 0.03)	0.021 ± 0.002[b] (0.02 – 0.024)	0.017 ± 0.001[c] (0.01 – 0.02)	0.022±0.005 (0.01– 0.03)	0.6
Pb	0.781 ± 0.044[a] (0.73 – 0.82)	0.691 ± 0.061[b] (0.62 – 0.73)	0.635 ± 0.039[c] (0.61 – 0.68)	0.703±0.076 (0.61– 0.82)	1.5
Cr	0.041 ± 0.010[a] (0.03 – 0.05)	0.026 ± 0.002[b] (0.02 – 0.03)	0.021 ± 0.003[c] (0.01 – 0.02)	0.029±0.010 (0.02– 0.05)	0.05
Zn	1.163 ± 0.019[a] (1.14 – 1.18)	1.122 ± 0.020[b] (1.10 – 1.14)	1.038 ± 0.039[c] (1.01 – 108)	1.108± .059 (1.01– 1.18)	10 - 75
Cu	0.546 ± 0.064[a] (0.50 – 0.62)	0.407 ± 0.075[a] (0.33 – 0.48)	0.360 ± 0.105[a] (0.28 – 0.48)	0.438±0.110 (0.28– 0.62)	3.0
Mn	0.442 ± 0.029[a] (0.41 – 0.46)	0.344 ± 0.050[b] (0.30 – 0.40)	0.310 ± 0.004[c] (0.03 – 0.32)	0.366±0.066 (0.30– 0.46)	0.5
Ag	0.083 ± 0.002[a] (0.08 – 0.09)	0.076 ± 0.002[b] (0.07 – 0.09)	0.057 ± 0.009[c] (0.05 – 0.07)	0.072±0.012 (0.05– 0.09)	-

Values are in mean ± standard deviation; ranges in parenthesis ( )

Values with different superscript across sampling points are significantly different (p<0.05). The dominance trend is as follows: Fe>Zn>Pb>Cu>Mn>Ag>Cr>Ni

TABLE 12.Heavy metals concentration in *Cynoglossus senegalensis* from Ikot Effanga Mkpa stream during the study

Metals (mg/l)	Sampling pt 1	Sampling pt 2	Sampling pt 3	Mean	WHO (2008)
Fe	0.921 ± 0.011[a] (0.91 – 0.93)	0.852 ± 0.034[b] (0.82 – 0.89)	0.810 ± 0.004[c] (0.80 – 0.81)	0.861 ± 0.052 (0.80 – 0.81)	0.30
Ni	0.018 ± 0.001[a] (0.01 – 0.02)	0.017 ± 0.001[b] (0.01 – 0.02)	0.014 ± 0.002[c] (0.01 – 0.02)	0.016 ± 0.002 (0.01 – 0.02)	0.6
Pb	0.719 ± 0.020[a] (0.69 – 0.73)	0.670 ± 0.036[b] (0.64 – 0.71)	0.587 ± 0.042[c] (0.53 – 0.62)	0.658 ± 0.065 (0.53 – 0.73)	1.5
Cr	0.036 ± 0.003[a] (0.03 – 0.04)	0.029 ± 0.001[b] (0.02 – 0.03)	0.026 ± 0.002[c] (0.02 – 0.03)	0.308 ± 0.004 (0.02 – 0.04)	0.05
Zn	1.107 ± 0.004[a] (1.10 – 1.11)	1.102 ± 0.002[b] (1.10 – 1.11)	1.080 ± 0.016[c] (1.06 – 1.09)	1.096 ± 0.015 (1.06 – 1.11)	10 - 75
Cu	0.443 ± 0.026[a] (0.41 – 0.47)	0.392 ± 0.032[b] (0.36 – 0.42)	0.350 ± 0.043[c] (0.31 – 0.39)	0.395 ± 0.050 (0.31 – 0.47)	3.0
Mn	0.439 ± 0.030[a] (0.40 – 0.46)	0.394 ± 0.010[a] (0.38 – 0.41)	0.334 ± 0.032[c] (0.30 – 0.37)	0.389 ± 0.050 (0.30 – 0.46)	0.5
Ag	0.086 ± 0.002[a] (0.08 – 0.09)	0.075 ± 0.003[b] (0.07 – 0.08)	0.070 ± 0.001[c] (0.06 – 0.08)	0.077 ± 0.007 (0.06 – 0.09)	-

Values are in mean ± standard deviation; ranges in parenthesis (   )

Values with different superscript across sampling points are significantly different ($p<0.05$). The dominance trend is as follows: Zn>Fe>Pb>Cu>Mn>Ag>Cr>Ni

Metal Concentrations in Water and Sediments

The data presented in table 1 show the values of heavy metals obtained from Mbaa River throughout the study period. The average heavy metal concentration was ranked as follows Fe > Mn > Zn > Cu > Cr > Pb > Co > Al. The concentration of the individual parameters as recorded varied between station 1, 2 and 3. The range of the heavy metals was as follows- Fe (0.042-0.272 mg/l), Mn (0.014-0.063), Zn (0.005-0.028 mg/l), Cu (0.006-0.027 mg/l), Cr (0.003-0.014 mg/l), Pb (0.001-0.004 mg/l), Co (0.001-0.002 mg/l), and Al (ND). Comparing same to Table 9 (slaughter water) that is more polluted shows far higher values that Mbaa River in also parameters tested.

The concentration of the individual heavy metals showed no significant difference ($P>0.05$) across the stations when the values were subjected to one way ANOVA, except Pb that showed significant difference ($P<0.05$). In table 1 iron (Fe) was found to have the highest mean concentration values while in Ikot Effanga Mkpa stream Ni was highest followed by Zn and thirdly Fe. At station 1, concentration was higher followed by station 2 and lowest at station 3. Fe metal values in Table 1 and Zn and Cu in Table 9 were found to be within the WHO (2017) and SON (2007) limit and no statistically significant difference ($P>0.05$) observed. The dominance of Fe over other heavy metals in aquatic ecosystem had been reported by Puyate, Rim-Rukeh, and Awatefe, (2007), Oribhabor and Ogbeibu (2009), Wogu and Okaka (2011). However, the slaughterhouse stream was dominated by Zn followed by Cu then Fe.

A comparative analogy of unpolluted water body (Mbaa River) and polluted stream (Effanga Mkpa-slaughter waste channel) showed steady intra and inter increases in heavy metals in sediments far above the surface water and between surface water and sediments of unpolluted and polluted water bodies. Total average trace metals in surface water of Mbaa River was 0.21 mg/l while that of Effanga Mkpa stream was 5.291 mg/l. Likewise, total average heavy metals for Mbaa River were 4.1185 mg/l compared to 30.366 mg/l in Effanga Mkpa stream. The same trend was followed on individual metals for both locations as seen in the table 13 below

Table 13.Comparative analysis of heavy metals in surface and sediments from polluted and unpolluted sources

	Mbaa River-Treated Aluminum waste channel		Effanga Mkpa Stream - slaughterhouse waste channel	
Metals	Surface water	Sediments	Surface water	Sediments
Fe	1.119±0.12 (1.00-1.33)	6.639±0.701 (5.31-7.52)	0.125±0.077 (0.242-0.272)	1.975±0.699 (0.933-3.02)
Pb	0.831±0.069 (0.73-0.97)	1.184±0.122 (1.10-1.43)	0.002±0.001 (0.001-0.004)	0.003±0.001 (0.001-0.004
Cr	0.075±0.011 (0.06-0.09)	0.101±0.005 (0.09-0.11)	0.008±0.004 (0.003-0.014)	0.020±0.019 (0.003-0.049)
Zn	1.077±0.050 (1.00-1.13)	14.027±0.725 (13.20-15.38	0.018±0.005 (0.005-0.028)	0.024±0.006 (0.009-0.030
Cu	0.585±0.052 (0.51-0.64)	4.055±0.318 (3.40-4.561)	0.016±0.007 (0.006-0.021)	0..035±0.033 (0.006-0.090)
Mn	0.425±0.086 (0.31--.55)	2.602±0.208 (2.13-2.82)	0.039±0.019 (0.014-0.061)	0.090±0.078 (0.014-0.211
Ag	0.078±-.008 (0.06-0.081)	0.082±0.011 (0.06-0.09)	ND	ND
Co	-ND	ND	0.002±0.001 (0.001-0.002	0.006±0.002 (0.003-0.009)

Table 14. Comparison of metal concentrations in fish tissues from polluted and none polluted waterbodies

Metals	Scaleless *Chrysichthys* nigro digitatus Effanga Mkpa	Scalely *Cynoglossus* Effanga Mkpa	Scaleless *Chrysichthys macrotis* CR estuary	Scalely *Pomadasys rogeri* CR estuary	Scaleless *H. longifilis* Mbaa R.	Scalely *O. aureus* Mbaa R.
Fe	1.164±0.022 (1.13– 1.19)	0.861±0.052 (0.80–.81)	0.02±0.001	0.001±0.001	0.625±0.34	0.602±0.317
Ni	0.022±0.005 (0.01 – 0.03	0.016±0.002 (0.01–.02)	-	-	-	-
Pb	0.703±0.076 (0.61– 0.82)	0.658±0.065 (0.53–.73)	0.000±0.000	0.013±0.003	0.008±0.001	0.007±0.007
Cr	0.029±0.010 (0.02 – 0.05	.308±0.004 (0.02– .04)	0.012±0.000	0.010±0.002	0.012±0.004	0.012±0.004
Zn	1.108±0.059 (1.01– 1.18)	1.096±0.015 (1.06– .11)	0.146±0.003	0.001±0.000	0.032±0.018	0.036±0.021
Cu	0.438±0.110 (0.28– 0.62)	0.395±0.05 (0.31– .47)	0.006±0.000	0.000±0.000	0.020±0.01	0.019±0.01
Mn	0.366±0.066 (0.30– 0.46)	0.389±0.050 (0.30– .46)	0.001±0.001	0.012±0.001	0.047±0.219	0.042±0.23
Ag	0.072±0012 (0.05– 0.09)	0.077±0.007 (0.06– .09)	-	-		

The high levels of Mn in sediments from the sample locations agree with the concept that sediments contain higher concentration of metals than that of overlying water (Depinto & Martin 1980; Shabanda, *et al.*, 2012).

Ruqia *et al.*, (2015), noted that lead as a soil contaminant is a widespread issue, it accumulates with age in bones, aorta, kidney, liver, and spleen and can enter the human body through uptake of food (65%), water (20%) and air (15%). Usman (2011), working on Asa River in Ilorin Metropolis of Kwara state of Nigeria reported high concentration of Pb in the sediment with mean value of 370.40 ng/g. The high level of Pb concentration in Asa River sediment was attributed to slow movement of the river water and the high level of absorption by sediment. Lead in the environment is strongly absorbed by sediments. These findings were collaborated by the higher values of Pb in benthic catfish compared to the pelagic scalely *Oreochromis*. The concentration of Pb from Mbaa River in both sediment and water showed significant differences ($P<0.05$) when the values were subjected to one way ANOVA. River sediments act as reservoir which may either concentrate metals from the water or release them into the water, (Mayerson, *et al*., 1981).

The results in table 14 agree with Mohammadi, (2011) and other studies that the bioaccumulation of heavy metals in the gills and livers of fishes were higher than the concentrations of heavy metals in the muscles of fishes.

The increasing order of iron from scaled to scaleless fish agrees with this research. *P. annectens* (West African lung fish) (fw) (40-50 scales between the operculum and the anus and 36-40 around the body) and scaleful *Gymnarchus niloticus* whereas *Clarias gariepinus* is scaless.

A comparison of fish from polluted and none polluted waterbodies show a remarkably higher concentrations of metals in the more polluted water than less polluted water. *Lutjanus* sp from higher polluted Shalateen area of Egyptian Red Sea (El.Moselhy, *et al* 2014, Tables 6, 8) had higher concentrations of metals in both the muscles and livers than the less polluted Cross River Estuary. Likewise, the highly polluted Effanga Mkpa slaughter site had higher metals in fishes than those in Egyptian Red Sea while the estuary had higher values than the unpolluted Mbaa River. Furthermore, using *Epinephelus* sp, *Caranx sp* and *Synodus* sp., in El-Moselhy, *et al*., each of which occurred in two locations as a case study, Zn in muscle and Fe in liver were higher in Hurghada region than at Shalateen with *Epinephelus*. All other values were higher in Shalateen than in Hurghada at the three organs--muscle, liver, and gills. The reverse was the case with *Caranx* sp where almost all values except Cu at gills, Pb, Fe and Mn at muscle were lower, the rest values were higher at Hurghada than Shalateen, while at Suez location, only Cd, Fe and Mn were lower than Shalateen in all three organs-muscle, liver, and gills of *Synodus* sp, the rest did not follow any defined pattern. Thus, heavy metals can vary based on location (water body) or species which agrees with the findings in this research (Table14) where *Chrysichthys sp.* From the highly polluted slaughter site had much higher metals compared to *Chrysichthys* from the less polluted estuary.

A comparative analogy of all 14 benthic and pelagic scalely fish species from three locations -Shalateen, Hurghada and Suez in Egyptian Red Sea, namely, *Scarus gibbus, Sardinella sp, Synodus sp, Lutjanus bohar, Sargocentron spiniferum, Lethrinus sp , Epinephelus sp, Caranx sp, Nemipterus* japonicas, *Carangoides bajad, Thunnus albacores, Gerres oyena, Siganus rivalatus* and *Trachurus mediterraneus,* (El-Moselhy, *et al*, 2014), though not the thrust of their research shows that all 14 species had lower values of metals than their scaleless counterparts - *Chrysichthys macrotis, Clarias gariepinus* and *Heterobranchus longifilis* in our study.

The level of heavy metals and major elements contamination of *Heterobranchus longifilis, Oreochromis niloticus* and *Oreochromis aureus* tissues obtained from stations 1, 2, 3 of Mbaa River in Ikeduru, Imo state Nigeria. The concentration of Fe was seen to be higher than that of other metals. Alinnor *et al*., (2014) working on Nkisa River reported Fe concentration mean values of 174.66, 194.33 and 346.00mg/kg in scalely fish species

Protopterus annectens, *Gymnarchus niloticus* (scalely) and scaleless *Clarias gariepinus* respectively. Again, there is clear evidence of much more higher concentration of Fe (trace metals) in scaleless *C. gariepinus* compared to scalely *P. annectens* and *G. niloticus*..

Copper concentration from Mbaa River was low compared to other findings from related studies. Obodo (2002), working on lower reaches of River Niger reported concentration of mean value 8.33mg/kg in *Synodontis membranaceus*. Copper in scaled *Oreochromis* was found to be slightly lower than that of *Heterobranchus*.

Obodo (2002), reported zinc concentration of mean values 72.33 and 65.33mg/kg in *Synodontis membranaceus* and *Tilapia zilli*, respectively showing higher concentrations in scaly tilapia compared to the scaleless *Synondontis*. Alinnor (2005), also reported that zinc concentration has effect on the hepatic distribution of other trace metals in fish.

Possible reasons for the high concentrations of Mn, Fe, Cu, Zn, Ar, Hg, Cd, and Pb in tables 6-12 in different fish species and sample sites put simply, the saltier or polluted the water, the heavier the metals concentrations in water columns, tissues, and sediments. Metal concentration also decreases with decrease from point of discharge. Thus, the farther away from point source, the lesser the metal concentrations. Again, even amongst the same species of either scaleless/scaly fishes, metals bioaccumulate and assimilate more where salt concentrations are higher though the time of abode in such habitat equally affects the degree. The three most dominant metals were Zn, Fe and Hg with Zn almost always taking the lead except in tables 1, where it came third and second to Ni and Fe in tables 9 and 11 respectively.

Conclusion

This research sought to find out the level of impact of effluent discharges in Mbaa River on the water quality, sediments, and aquatic organism and factors that predispose or prevent aquatic organisms from assimilating and accumulating heavy metals in their organs and the organs of greatest impart of heavy metals amongst scaly and scaleless fishes. It is logical to say that the high concentration of heavy metals in Lemna slaughterhouse and Calabar estuary becomes accumulated in the sediments and in due course gets transferred to the fishes. In virtually all heavy metals assessed, the scaleless fishes were found to accumulate higher metals than scaly fishes implying that scales have a way of lowering bioaccumulation and bio.assimilation of heavy metals in fishes.

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