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Assessment of Trace Metal Contamination of Catfish (*Clarias gariepinus*) and Tilapia (*Oreochromis niloticus*) obtained from Choba and Aluu Axis of New-Calabar River, Rivers State Nigeria

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Abstract:
This study investigated trace metal contamination in the muscle of two fish species: Catfish (*Clarias gariepinus)*) and Tilapia (*Oreochromis niloticus)* obtained from the Choba axis (Downstream) and Aluu axis (Upstream) of New Calabar River in Rivers State. The fish species were dried, ashed and analysed for trace metals such as Zn, Pb, Cd and Cu using the Atomic Absorption Spectrophotometer Model Unican Solar 969. The results obtained showed that Pb values ranged from 0.097 to 0.655 mg/kg with the highest obtained in *Oreochromis niloticus* at the Choba axis. There was no significant difference in the Pb values between the two fish species. Copper ranged 17.7-58.2 mg/kg, highest value obtained in *Clarias gariepinus* at the Aluu axis. Zinc values ranged from 28.5 to 52.1mg/kg. At Aluu, Cd was not detected in the two fish species, values obtained at Choba were 0.17mg/kg for *Clarias gariepinus* and 1.39mg/kg for *Oreochromis niloticus*. Zinc and Cu levels in the two fish species at the upstream end exceeded the FAO permissible limits. Also Pb and Cd values in *Oreochromis niloticus*, at the Choba end exceeded FAO permissible limit. The mean trace metal concentration of the water samples ranged from Zn: 1.145±0.01mg/l-2.58± 0.1mg/l, Cu:0.55±0.02mg/l-1.2±0.04mg/L, Pb: 0.018± 0.01mg/l and Cd: 0.034mg/l. Pb and Cd were not detected at Choba axis. The risk assessment for daily intake of consumers of fish from the river indicated that the non-carcinogenic risk tends to become significant with exposure duration of 30 years mainly for Cd, Zn and Cu exposure since the indices exceeded the acceptable limits of non-cancer hazard quotient.

Keywords: Trace metal, fish species, risk assessment, bioconcentration

1.0 Introduction:
The pollution of the aquatic environment with heavy metals has become a worldwide problem in the recent time, due to the fact that they have ability to bioaccumulate in bio-systems (Goldstein, 1990), indestructible and are toxic on organisms. Heavy metals may enter aquatic systems from different natural and anthropogenic (human activities) sources, including industrial or domestic wastewater, application of pesticides and inorganic fertilizers, storm runoff, leaching from landfills, shipping and harbour activities, geological weathering of the earth crust and atmospheric depositions (Yilmaz, 2009). Trace metal contamination may have devastating effects on the ecological balance of the recipient environment and on the diversity of aquatic organisms (Ashraj, 2005). Fish and shellfish species are directly affected by heavy metal contaminants (Clarkson, 1998). Thus, are widely used to evaluate the health of aquatic ecosystems with respect to chemical pollution.

Trace Metals exhibit toxicity by forming complexes with organic compounds and active sites of enzymes. The impact of anthropogenic perturbation is most strongly felt by estuarine and coastal environments, adjacent to urban areas (Nouri, *et, al*., 2008). Depending upon their concentration they may exert beneficial or harmful effects on plant, animal and human life (Forstner and Wittman, 1981). Some of these metals are toxic to living organisms even at low concentrations, whereas others are biologically essential and become toxic at relatively high concentrations. When ingested in excess amounts heavy metals combine with body's bio-molecules, like proteins and enzymes to form stable bio-toxic compounds, thereby mutilating their structures and hindering them from their normal bio-reactions (Duruibe *et al*., 2007). Some trace metals may be very essential for the survival of living organisms due to the important physiological role they play (Forstner and Wittman, 1981). However, beyond certain threshold levels they can be very toxic to humans and other organisms that depend on them and can result in various illnesses and eventually death (Debelius, *et al.,* 2009,). Heavy metals may be non-essential for biological functioning and toxic to organisms even at very minute concentrations (Fosmire, 1990). All known metals can be harmful to organisms at a particular concentration no matter how important the metal may be (Forstner and Wittman, 1981). For a metal to be considered toxic, or to provoke a biological effect, it must interact with a biological structure (Campbell, *et al.,* 2002). The level at which metals can be harmful or toxic to organisms depends on their concentration (Allen and Hansen, 1996.), their physico-chemical forms which drive their bioavailability (dissolved or particulate, ionic or elemental – species) (Paqum, *et al.,* 2002), the nature of the containing medium (e.g. pH) (Kozelke, 2002.), and the ability of the metal to form complexes with other chemical compounds (Allen and Hansen, 1996).

In natural aquatic ecosystems, metals occur in low concentrations. As they cannot be degraded, they are deposited, assimilated or incorporated in water, sediment and aquatic animals and thus, causing heavy metal pollution in water bodies (Abdel-Baki, 2011). In fish, which is often at the higher level of the aquatic food chain, substantial amounts of metals may accumulate in their soft and hard tissues (Mansour and Sidky, 2002). Pollutants enter fish species through a number of routes: via skin, gills, oral consumption of water, food and non-food particles. Once absorbed, pollutants are transported in the blood stream to either a storage point (i.e bone) or to the liver for transformation and/or storage (Obasohan, 2008). Studies on heavy metals in rivers, lakes, fish and sediments have been a major environmental focus especially during the last decade (Ozmen *et al*., 2004; Pote *et al*.,2008). Sediments have been reported to form the major repository of heavy metal in aquatic system while both allochthonous and autochthonous influences could make concentration of heavy metals in the water high enough to be of ecological significance (Oyewo and Don-Pedro, 2003). Bioaccumulation and magnification is capable of leading to toxic level of these metals in fish, even when the exposure is low. The presence of metal pollutant in fresh water is known to disturb the delicate balance of the aquatic systems. Fish species are notorious for their ability to concentrate heavy metals in their muscles and since they play important role in human nutrition, they need to be carefully screened to ensure that high level of toxic trace metals are not transferred to man through fish consumption (Adeniyi and Yusuf, 2007).

Increasing amounts of chemicals may be found in predatory species resulting from biomagnifications, which is the concentration of chemicals in the body tissue of organisms along the food chain. (Tomori *et al.,* 2004). Metals could be accommodated in water, sediment, and organisms in the aquatic environment. Fishes have been recognized as good bio-accumulators of organic and inorganic pollutants (King and Jonathan 2003). Trace metals gain access into the aquatic system from natural and anthropogenic sources and get distributed in the water body, suspended solids and benthic sediments during the course of their transportation (Olajire and Imeokparia, 2000). The Oil exploration activities in and around Choba and Aluu communities are increasing. Waste from these exploration activities flow into the New-Calabar River. Kakulu, (1985) observed high concentrations of trace metals, Fe, Zn, Cu, Pb and Hg in the Nigerian crude. Crude-oil-induced bio-concentration of heavy metals in waterand fish species in the Niger-Delta is well documented (Ezemonye, 1992; Agada, 1994). Choba and Aluu communities depend on the River for domestic use and fishing. It is therefore necessary to assess the heavy metal content of the river and fish species. The objective of the present study was to assess the presence of Zinc (Zn) , Cadmium (Cd), Lead(Pb) and Copper (Cu) in Catfish (*Clarias gariepinus*) and Tilapia (*Oreochromis niloticus*) obtained from New Calabar River.

2.0 Materials and Methods:

2.1 Description of the Study Area:

The New Calabar River lies between longitude 006° 53' 53.086"E and latitude 04° 53' 19.020"N in Choba, Rivers State, Nigeria (Fig. 1). Aluu on the other hand is upstream of the river, about 2 km away from Choba location. However, the entire river course is situated between longitude 7° 60'E and latitude 5° 45'N in the coastal area of the Niger Delta and empties into the Atlantic Ocean (Sidney, et al., 2014). The river watershed experiences medium to high urban activities such as abattoir, poultry, a fabrication company, oil exploration and market. It is also used as routes and harbor for boats and barges of Oil and Oil Servicing Companies.

2.2 Sample Collection:

Samples were collected from two locations namely: Choba, Downstream (Location A) and Aluu, Upstream (Location B) of New Calabar River in rivers State, Nigeria (Fig. 3). Two fish species (Fig. 2), Catfish *(Clarias gariepinus)* and Tilapia *(Oreochromis niloticus)*, were purchased from the fishermen at the two locations. The fish samples were kept in the ice pack and later taken to the Laboratory for drying and analysis. Replicate water samples (0.5 l) were collected from both ends of New Calaba river; Choba axis, (downstream) and Aluu axis (upstream). All samples were collected in polyethylene bottles, which were pre-washed with de-ionized water. The bottles were immersed to about 20 cm below the water surface to prevent contamination of heavy metals from air. Samples were labeled, iced and transported to the laboratory.

2.3 Digestion of Fish, Sediment and Water Samples:

The stored frozen fish samples were allowed to thaw at ambient room temperature, and then wrapped in foil and oven dried at 105°C until constant weight. 3g of each dried fish samples was placed in a crucible and ashed in a muffle furnace at temperatureof 650^{o}C for 5hours. Each of the ashed fish sample was placed in a Teflon beaker and digested with concentrated hydrochloric acid and the clear digest was diluted with deionised water, filtered and made up to 50ml. Two grams sediment sample was digested in a 250ml conical flask by adding 10ml of Aqua Regia composed of (2:1) Hydrochloric Acid and Nitric Acid and then heated on a hot plate until volume remains about 7-12ml. The digest was filtered using Whatman No 42 filter paper and volume made up to 50ml volumetric flask. The digested samples were then analyzed for lead, cadmium, copper and zinc using Atomic Absorption Spectrophotometer (Unican Solar 969).

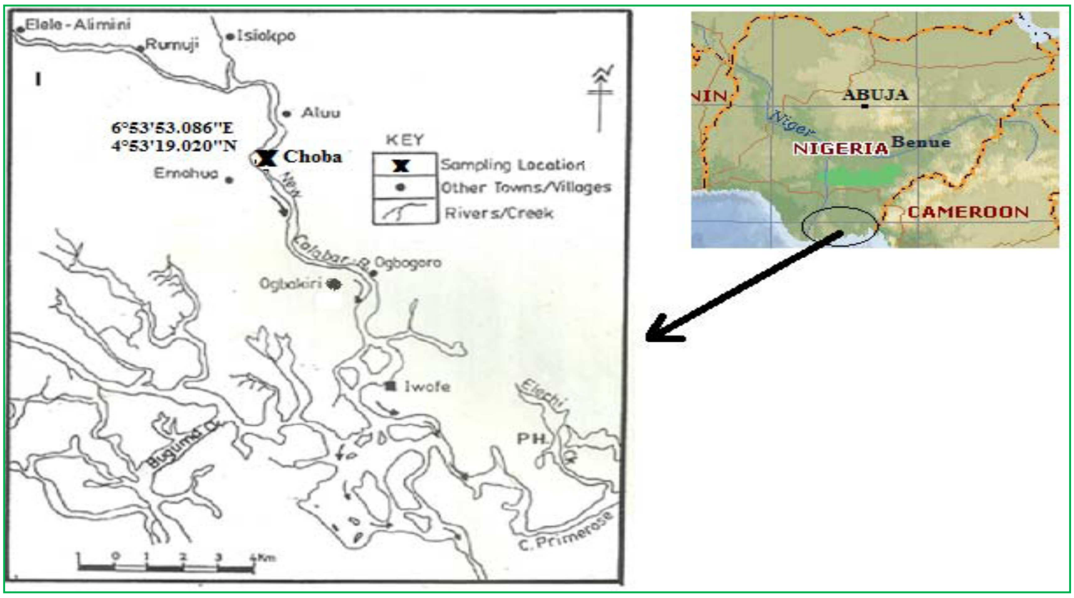

Fig 1: Map of the Study Area and the location of the study area in Nigeria

Fig. 2: Catfish *Clarias gariepinus and* Tilapia *(Oreochromis niloticus)*

Fig. 3: New Calabar River, Choba axis (Downstream) Aluu axis (Upstream)

2.4 Statistical Analysis:

All data obtained were analyzed using one and two-way ANOVA with Minitab Statistical software version. 16 and significant ($p<0.05$) means were separated using Tukey pairwise comparison.

3.0 Results and Discussion:

The result of water samples from the two sampling locations are presented in Table 1. The total zinc concentration in the New Calabar river was 3.725 mg/l, Aluu axis had 2.58 mg/l. Total Copper concentration was 1.75mg/l , Pb and Cd were 0.018 mg/l and 0.034 mg/l, respectively. However, at Choba axis, Pb and Cd were below detection limit. The trace metal concentration in the water decreased in the sequence of Zn>Cu>Cd>Pb.

3.1 Trace Metals in Fish:

Lead values ranged from 0.097 to 0.655 mg/kg with the highest obtained in Tilapia at Choba axis. The values did not differ in the fish species.The highest value of Cu (58.2mg/kg) was obtained in Catfish at Aluu axis while the least value of (17.7 mg/kg) was obtained in Catfish at Choba axis (Table 2). Zn values ranged from 28.5 to 52.1mg/kg with the highest obtained in Tilapia at Choba axis while the least value was obtained in Catfish. At Aluu axis Cd was not detected in the two fish species, values obtained at Choba axis were 0.17mg/kg for Catfish and 1.39mg/kg for Tilapia. Pb and Cd levels in the fish species did not differ irrespective of the sample location.

Table 1: Trace metal concentration of New Calabar River at the sampling locations

Water Samples	Zn(mg/l)	Cu(mg/l	Pb(mg/l)	Cd(mg/l)
Choba area	1.145± 0.12a	0.55±0.1a	ND	ND
Aluu	2.58±0.1a	1.2±0.02a	0.018±0.02a	0.034±0.02a
Total metal conc	3.725	1.75	0.018	0.034

Same letters within columns are not significantly different at 5% probability level

Table 2: Trace metal concentration of Tilapia and catfish obtained from New Calabar River around Aluu community

Fish species	Zn (mg/kg)	Cu(mg/kg)	Pb(mg/kg)	Cd(mg/kg)
Catfish (*Clarias gariepinus)*	48.9± 2.3a	58.2±8.2a	0.45± 0.2a	ND
Tilapia (Oreochromis niloticus)	30.8±3.4a	37.4±5.2b	ND	ND
**FAO/WHO limit*	40	30	0.5	0.5
Total metal concentration	79.67	95.64	0.45	ND

Same letters within columns are not significantly different at 5% probability level, *= FAO/WHO, (1989).

Table 3: Trace metal concentration of Tilapia and catfish obtained from New Calabar River around Choba community.

Fish species	Zn(mg/kg)	Cu(mg/kg)	Pb(mg/kg)	Cd(mg/kg)
Catfish (*Clarias gariepinus*)	28.5±2.3b	17.7±4.5b	0.097±0.11b	0.17±0.32a
Tilapia (*Oreochromis niloticus*)	52.1±4.5a	25.7±2.9a	0.655±0.63a	1.39±0.23a
**FAO/WHO limit*	40	30	0.5	0.5
Total metal concentration	80.5	43.5	0.752	1.56

Same letters within columns are not significantly different at 5% probability level, *= FAO/WHO, (1989).

The accumulation of metals in a single species showed significant inter-specific variations in all metals (Table 3). Furthermore, Cu and Cd accumulation in fish species significantly varied in the two locations.

Table 4: Two-way ANOVA showing variations in metals between locations and different species

Metal	Source	df	F	P-value
Cu	Location	1	223.2	0.001
	Species	1	45.3	0.003
Zn	Location	1	123	0.32
	Species	1	69.4	0.34
Pb	Location	1	453.2	0.12
	Species	1	231.9	0.26
Cd	Location	1	432.2	0.02
	Species	1	231.7	0.001

3.2 Bioconcentration Coefficient (BC):

Bioconcentration coefficients (BC_{metal}) were calculated on a dry weight basis by dividing the metal concentration in the fish (mg /kg) by the metal concentration in the river (mg/l). Bioconcentration coefficients of fish species were greater than 1 except Pb (0.097) and Cd (0.17) in Catfish and Tilapia Cd (0.655) (Table 5.0). The Bioconcentration coefficients from water to fish in case of Catfishwas in the order of Cu > Zn >Cd > Pb in Choba axis and Cu > Pb > Zn in Aluu axis. Copper was the greatest metal accumulated by Catfish, while Pb was the least.

3.3 Trace metal Pollution Index (TPI):

The Trace metal pollution index (TPI) was used to compare the total metals accumulation level in fish samples at the two sampling locations. The (TPI) was determined using the equation by Usero *et al*., 1997

$$TPI= (TC_1 * TC_2 * TC_3 \ldots\ldots TC_n)^{1/n} \ldots\ldots 1$$

whereTC is the total concentration of n trace metals in fish samples.

The concentrations of most of the metals in the two fish species studied varied depending on the location of the sampling sites (Table 4).Trace metal pollution index (TPI) for the two locations are 3.641 and 3.352 in Aluu and Choba ,respectively indicating higher pollution index in Aluu axis (table 6).

Table 5: Bioconcentration coefficient (BC) of fish species of trace metals in the river.

Fish species	Trace metal	Choba	Aluu
Catfish *(Clarias gariepinus*)	Zn	25	18.9
	Cu	32.2	48.5
	Cd	0.17	ND
	Pb	0.097	25
Tilapia *(Oreochromis niloticus)*	Zn	45.7	11.9
	Cu	46.7	31.1
	Cd	0.655	ND
	Pb	1.39	ND

Table 6: Trace metal Pollution Index (TPI) in New Calabar River

Location	Zn	Cu	Pb	Cd	TPI
Choba	80.5	43.5	0.752	1.56	3.352
Aluu	79.67	95.64	0.45	ND	3.641

3.4 Health-Risk (Non-carcinogenic) Assessment for Fish Consumption (Consumption Safety):

The current study‘s risk assessment was based on EPA’s (2000) Guidance for Assessing Chemical Contaminant Data for use in Fish Advisories. The level of exposure resulting from the consumption of a particular chemical in fish samples can be expressed by an estimation of daily intake levels (Table 7) with the following equation:

Average Daily Dose (mg/kg^{-1}*day)* $ADD= (C \times IR \times EF \times ED)/ (BW \times AT)$ 2

Where:

C = Mean total metal concentration in fish species
IR = Mean ingestion rate of fish
EF = Exposure frequency
ED = Exposure duration (years) over lifetime
BW = Body weight
AT = averaging time (days)

The average daily dose expresses the average daily intake of a specific chemical over a certain period of time. Estimating hazard levels, the mean and maximum total chemical concentrations, were determined from the data from the two fish species. The Exposure frequency (EF) represents the average per capita number of meals by the population based on a long term average contact rate (EPA 1992). For all calculations, an average adult body weight (BW) of 70kg, standard exposure duration (ED) of 30 years, and average time (AT) of 365 days were assumed, to keep with the default values provided in EPA (1987) Exposure Factor’s Handbook.

Hazards were quantified by the calculation of a Hazard quotient (HQ). The Hazard quotient is a ratio of the average daily dose (ADD) divided by the reference dose (RfD) of the chemical of concern equation 3.

$HQ= ADD/ RfD$ 3

The oral route is the route of exposure observed in this study; therefore, oral RfD values from the EPA’s IRIS (2009) database were used. Oral chronic reference dose for assessing non-carcinogenic health effects was for Cadmium 0.001(mg/kg/day), Lead 0.3(mg/kg/day), Copper 0.04mg/kg/day and Zinc 0.02(mg/kg/day). Also the hazard index *(HI)* can be expressed by the sum of the hazard quotients in the following equation:

$HI = HQ_{Cd} + HQ_{Pb} + HQ_{Cu} + HQ_{Zn}$ 4

When the intake exceeds the reference dose and thus the *HQ* is greater than or equal to one, it is probably that non-carcinogenic adverse health effects will be observed.The mean values of ADD in this study are greater than the recommended oral reference dose (RfDs) stipulated except for Pb (EPA, 2009) (Table 7). The sequence of the magnitude of the ADD is Zn>Cu>Cd> Pb (Table 8). Reference Dose (RfD) is an amount of daily exposure to toxic compound that does not show the symptoms of toxic effects from the exposed organism.Where, HQ is known as the magnitude of quantifiable potential for developing non-carcinogenic health effects after averaged exposure period. Total potential for non-cancer risk to humans was derived by summing the HQ values of metals.

Table 7: Mean Trace metals in fish species of upstream and downstream (mg/kg)

Fish species	Zn	Cu	Pb	Cd
Catfish (*Clarias gariepinus)*	38.7	37.95	0.547	0.17
Tilapia (Oreochromis niloticus)	41.45	31.55	0.655	1.39

Table 8: Average trace metals Daily Dose (ADD) (mg/kg/day)

Fish species	Zn	Cu	Pb	Cd
Catfish (*Clarias gariepinus)*	0.497	0.487	0.007	0.0021
Tilapia (*Oreochromis niloticus)*	0.532	0.405	0.0084	0.0178

Table 9: Hazard Quotients (HQ) and Hazard Index (HI).

Fish species	**Hazard Quotients (HQ)**				**Hazard Index (HI)**
	Zn	Cu	Pb	Cd	
Catfish (*Clarias gariepinus)*	24.85	12.175	0.023	2.1	39.148
Tilapia (*Oreochromis niloticus)*	26.6	10.125	0.028	17.8	54.55

Total HQ is referred to as the Hazard Index (HI) Table 9. It has been suggested that, if HQ is equal to or less than one (≤1) it indicates no appreciable health risk. From Table 9 HQ value for Pb is < 1 while Zn, Cu and Cd HQ values are > 1. Hazard index or Σ HQs value of less than one (<1) suggests no risks either from any chemical or in combination with others. From Table 8, the Hazard indexes (HI) of the fish species are > 1. Characterization of the risk of individual heavy metals showed that Zn, Cd and Cu portend greater toxic hazards of oral exposure (Table 8) (HQ= 26.6, 17.8 and 12.18 respectively).

3.5 Accumulation of Metals By Fish Species:

Trace metal in the body of the river was significantly low especially Pb and Cd. These metal species probably have settled at the sediment since they are denser than water. The accumulation of essential metals in the muscle is likely linked to its role in metabolism (Zhao , 2012); high levels of Zn and Cu in tissues are usually related to a natural binding proteins such as metallothioneins (MT) (Gorur , 2012) which act as an essential metal store (i.e., Zn and Cu) to fulfill enzymatic and other metabolic demands (Roesijadi, 1996 , Amiard , 2006). Kamaruzzaman, *et al*.,(2010), noted that there were relationship between metal concentration and several intrinsic factors of fish such as organism size, genetic composition and age of fish.

In the present study, fish species were collected from different locations. The results showed that fish species exhibited wide inter-specific variations in metals accumulated. Many studies attributed high metal accumulation to the feeding habit of the fish species. For instance, Khaled (2004) argued that because *S. rivulatus* is a herbivore, it accumulated higher concentrations of metals in their muscles than the carnivore *Sargussargus;* This suggestion was not a reasonable cause for low metal accumulation in the current study since tilapia (a herbivore) recorded low concentration of metals in most cases during the study, while the other species Catfish (an Omnivore) showed minor variations. It is suggested that benthic fish are likely to have higher heavy metal concentrations than fish inhabiting the upper water column because they are in direct contact with the sediments and their greater uptake of heavy metal concentrations from zoobenthic predators (Yi 2011). However, results from several studies did not support this suggestion or even contradict it; Zhao *et al*.(2012) found that *Cynoglossus gracilis* had the lowest level of metal accumulation among investigated species despite that it is a typical benthic fish. Also, Bustamante *et al*. (2003) did not find segregation between pelagic and benthic fish in their accumulation of metals in the liver and kidneys. Results of the present study provide weak or no support for this suggestion, where no variations existed between pelagic and benthic organisms. Although fish are mostly migratory and seldom settle in one place, metal accumulation in fish organs provides evidences of exposure to contaminated aquatic environment and could be used to assess the health condition of the area from which they were collected (Qadir (2011).

To asses public health risk of the New Calabar River fish consumption, we compared metal levels in muscles of the current study with the maximum permissible limits (MPL) for human consumption established by (FAO/WHO 1989). At the Aluu axis of the river, catfish had Zn (48.9 mg/kg) and Cu (58.2 mg/kg) exceeding maximum permissible limit as well as Tilapia that had Cu (37.4mg/kg) (Table 2). Similarly, at the Choba axis, Tilapia had Zn, Pb and Cd exceeding maximum permissible limits (Table 3). Generally, in the present study, concentrations of non-essential elements (Cd and Pb) in fish species were lower than those of essential metals (Zn, and Cu) (Table 2 and Table 3). This result is consistent with the report of Huang *et al*. (2003) that the accumulation levels of the essential metals in fish are generally higher and more homeostatic than the non-essential metals.

3.6 Bioconcentration Coefficient (BC):

The result of the bioconcentration coefficient showed higher transfer factors >1 except lead and cadmium in Catfish upstream which indicated trace metal accumulation in the two fish species. This result agrees with many previous studies. Rashed, (2001), determined transfer factors for Co, Cr, Cu, Fe, Mn, Ni, Sr and Zn from water, sediment and plant in *Tilapia nilotica* fish in Nasser lake, results indicated that only transfer factors from water for all metals were >1.00, which means that fish accumulated metals from water .

Table 10: The trace metal concentrations (mg/l) in New Calabar River and comparison with water quality Guidelines

Guidelines	Zn (mg/l)	Cu(mg/l)	Pb (mg/l)	Cd (mg/l)	References
WHO	-	2	0.01	0.003	WHO, 2003
EPA	-	1.3	0.05	0.01	EPA, 2002
New Calabar River	1.14 - 2.58	0.55-1.2	0.018	0.034	

Since water quality is the major factor in the sustainability of aquaculture (Abdel-Baki**,** *et al.***,** 2011) the lead, copper, zinc and cadmium concentration in the river water were compared with national and international standards (Table 10).The result showed that Lead and Cadmium exceeded WHO (World Health Organization, 2003) guidelines, and Cadmium concentration also exceeded EPA limit (Environmental Protection Agency, 2002).

3.7 Potential Health Risk Assessment:

So far, few studies have investigated the non-carcinogenic effects induced by the metals in New Calabar River, and limited information is available about the toxicity effects caused by these metals. On the basis of the experimental results, a non-carcinogenic risk assessment was performed on the metals in the two fish species consumed by human. Fish has been identified as a significant source of human exposure to various compounds. However fish consumption rates could vary in different subpopulations, children may consume larger quantities compared to their body masses than adults, prenatal exposure may occur through pregnant women; these subpopulations are considered as potential high risk groups (G.O.A, 2009. The HQs of Pb exposure through oral ingestion that were less than 1, suggested that the fish consumers of the study area are not exposed to any potential non-carcinogenic risk of Pb from oral ingestion of Pb-contaminated fish. Nevertheless, Inhalation and ingestion are the two routes of exposure to Pb and the effects from both are the same (Wuana and Okieimei, 2011). Copper is indeed essential to humans but in high doses especially above RfDs, it can cause anaemia, liver and kidney damage, and stomach and intestinal irritation (Wuana and Okieimei, 2011). In this study, consumers of fish from the river happened to be prone to health risk from Cu toxicity due to the daily oral ingestion estimate that was greater than oral chronic RfD (0.04 mg/kg/day) (Table 7). This later translated into HQ that was greater than unitary which possess high non-carcinogenic risk when acceptable limit is considered.

There is great risk of complications resulting from Cd toxicity in the exposed population of the consumers of fish from the river. The daily oral intake estimates (Table 7) for the consumers was more than twice the RfD (0.001 mg/kg/day; EPA, 2009) which made the HQ to be in the multiples of moderate hazard threshold (Lemly, 1996). This is a serious situation because of the high risk of renal toxicity in the exposed consumers; renal NOAEL (the dose of chemical at which there were no statistically or biologically significant increase in the frequency or severity of adverse effects seen between the exposed population and an appropriate control) for Cd is 0.0021mg/kg/day (Nogawa *et al.*, 1989) which was reported in this study to be far below the daily oral intake of the consumers. This indicated that the consumers are exposed to high risk of renal toxicity from Cd oral ingestions. Considering the HI for Cd also calls for serious attention because of the severity of the risk of the consumers to non-carcinogenic toxicity of Cd.

Zn is an essential element with a recommended daily allowance ranging from 5 mg for infants to 15 mg for adults (RAIS, 2008). It is important to note that too little Zn can cause health problems and too much Zn is also harmful; but according to RAIS (2008) harmful effects generally begin at levels in the 100 to 250 mg/day range. The present Zn content of fish samples in this study (Table 7 & Table 8) are below threshold limits, hence there is no toxic risk of Zn exposure to consumers.

3.8 Comparison of Metals Concentrations with Other Studies:

In order to have a clear judgment about the level of pollution in fish consumed by people along New Calabar River at Choba and Aluu axis, the observed values were compared with other literature data obtained from similar studies in the country and from different areas of the world. Table 11 shows a comparison between the concentrations of metals in the present study with concentrations in other studies conducted on the same fish species in several countries. The concentrations of Zn, Cu in fish samples in the present study gave a reasonable level comparing with other results. Zn concentrations in both Catfish and Tilapia from present study were close to values obtained from Kubanni river, Northern Nigeria. Also, Cu concentration in Tilapia from Aluu axis was close to the value obtained from River Niger, Nigeria. The highest Zn values 292.22mg/kg and 132.82mg/kg were from WadiHaneffah, Riyadh, Saudi Arabia and Tekeze River Dam, Tigray, Northern Ethiopia respectively (Lemly, 1996). Similarly, the highest Pb and Cd values were from River Niger in Nigeria. Pb concentration in Catfish at Choba axis is lower than other studies except the value from Okumeshi River in Delta state. Also, Cd concentration in Catfish at Choba is lower than other studies except the concentration in Owah Abbi (Ethiope) river, Delta state. Moreover, its concentration in Tilapia at Choba axis was close to values obtained from Tekeze River Dam, Tigray, Northern Ethiopia and WadiHaneffah, Riyadh, Saudi Arabia. Generally, concentrations of non-essential metals (Cd, Pb) in *Catfish* and *Tilapia* showed low levels in this study and other studies in (Table 3).The variations of heavy metal concentrations in fish from different areas of the world may be due to differences in metal concentrations and chemical, physical characteristics of water from which fish were sampled (Bahnasawy, *et al.,* 2009).

Table 11: Trace metal concentrations (mg/kg) in fish species from other studies

Fish Species	Location	Cu	Zn	Cd	Pb	References
Catfish	Northeast axis of Lagos Lagoon site 3	10.66	15.71	ND	2.11	Ugwu *et al.,* (2012)
	WaliHaneffah, Saudi Arabia	18.71	178.91	2.12	3.05	Shahid *et al.,* (2013)
	Tekeze river dam, Tigray,Ethiopia	2.71	126.30	2.58	1.44	Mulu *et al*., (2012)
	Usuma River, Abuja, Nigeria	0.50	0.20	ND	ND	Ugwu *et al.,* (2012)
	Gwagwalada market, Abuja, Nig.	0.12	2.93	-	ND	Igwemmar *et al*., (2013)
	OwahAbbi (Ethiope) River,Delta State.	0.44	0.54	0.15	0.42	Omuku, (2008)
	River Benue.	5.89	17.8	0.927	2.78	Ishaq, *et al.,* (2010)
	Okumeshi River, Delta state, Nigria			0.24	0.01	Ekeanyanwu *et al.,*(2010)
	Kubanni River, Northern Nigeria.	19.3	49.56	0.21	0.28	Uzairu *et al.,* (2008)
	River Niger, Nigeria	23.50		14.20	0.90	Nwajei *et al.,* (2011)
	New Calabar River, Aluu axis	58.2	48.9	ND	0.45	Present Study
	New Calabar River, Choba axis	17.7	28.5	0.17	0.097	
Tilapia	Northeast axis of Lagos Lagoon site 3					Ugwu *et al.,* (2012)
	WaliHaneffah, Saudi Arabia	25.11	292.22	1.88	3.48	Shahid *et al.,* (2013)
	Tekeze river dam, Tigray,Ethiopia	3.29	132.82	1.12	2.12	Mulu *et al*., (2012)
	Usuma River, Abuja, Nigeria	0.68	0.63	ND	ND	Ugwu *et al*., (2012)
	Gwagwalada market, Abuja, Nig.	0.19	3.74		ND	Igwemmar *et al.,* (2013)
	OwahAbbi (Ethiope) River,Delta State.	0.41	0.31	0.19	0.34	Omuku, (2008)
	River Benue.	9.99	18.1	0.994	3.58	Ishaq, *et al*., (2010)
	Okumeshi River, Delta state, Nigria			0.915	0.01	Ekeanyanwu *et al.,(*2010)
	Kubanni River, Northern Nigeria.	40.11	65.72	0.40	0.76	Uzairu *et al*., (2008)
	River Niger, Nigeria	33.20		12.10	4.30	Nwajei *et al.,* (2011)
	New Calabar River, Aluu axis	37.4	30.8	ND	ND	Present Study
	New Calabar River, Choba axis	25.7	52.1	1.39	0.665	

4.0 Conclusion:

The health status of New Calabar River with respect to the contamination by Cu, Zn, Pb and Cd in the river and quality of two fish species: Catfish and Tilapia were evaluated in this study. Generally, fish species in this study accumulated essential metals in higher levels than non-essential metals. There was evidence of contamination of fish species by metals exceeding FAO/WHO limits except Cd. Human health risk for carcinogens from consumption of fish in the river were low compared with US EPA permissible limits. However, mean Zn, and Cu levels in the two fish species exceeded the FAO guidelines. Also Pb and Cd values in Tilapia, downstream exceeded FAO and CCFAC guidelines. Cu concentration in the two fish species upstream and Zn value in Tilapia downstream also exceeded WHO and FAO limits respectively. Thus there may be some concern for individuals consuming fish from the New Calabar river. The risk assessment for daily intake of consumers of fish from the river indicated that the non-carcinogenic risk tends to become significant with exposure duration of 30years mainly for Cd, Zn and Cu exposure since the indices exceeded the acceptable limits of non-cancer hazard quotient.

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