ISSN No:-2456-2165

Assessment of Selected Heavy Metals (Cd, Cr, Cu, Ni And Pb) Concentration in *Oreochromis Niloticus* and *Chrysichthys Nigrodigitatus* From Great Kwa River, Calabar, Cross River State, Nigeria

*[1]Jimmy, E. U., [2]Monica,U. D., [2]Paul, S. U., [2]Uwanna, K., [1]Keyiye, O., [2]Robert, O., and [1]Excellence, O.
[1]Department of Zoology and Environmental BiologyUniversity of Calabar, Calabar (UNICAL), Nigeria
Department of Marine Biology, Akwa Ibom State University, (AKSU), Nigeria

Abstract:- Assessment of heavy metals concentration in O. niloticus and C. nigrodigitatus was carried out in Calabar, Cross River State.The people of Cross River State depend on fish and other aquatic products for their source of protein, thus the need to verify the safety of some commonly consumed fish which are significant food in Calabar. Samples were purchased from artisanal fishermen from the landing sites of Great Kwa River at EsukAtu and Anantigha beach and the concentrations of heavy metals (Nickel, Copper, Chromium, Cadmium and Lead) inliver; gill and muscle were analyzed using Atomic Absorption Spectrophotometry (AAS). Results obtained from the analysis of trace metals in the organs in O. niloticusshowed the presence of the metals in different organs of the fish at different levels of concentration. The sequence of accumulation of heavy metals in Kwa river Station in the muscles, gills and liver showed similar trend of Cu > Ni > Cr > Cd >Pb while in Anantigha station muscles and the Gills were in the order; Cu > Ni > Cd > Cr >Pb, while in liver, the order was Cu > Ni > Cr > Cd >Pb. In Chrysichthys nigrodigitatus, heavy metals in Kwa river Station in all the tissues were in the order of Cu > Ni > Cr > Cd >Pb while in Anantigha were in the order of Cu > Cr > Ni > Cd >Pb in mg/kg respectively. In general, a comparison of the sequence of accumulation in all the organs from the two stations were Oreochromis niloticus>Chrysichthysnigrodigitatus. The levels of heavy metals concentration in the muscles, gills and liver of studied organisms analyzed were below the recommended limits set by WHO/FAO with no foreseeable adverse effect from consumption. However, continuous monitoring is encouraged.

Keywords:- *Heavy metal, pollution, Oreochromis niloticus, Chrysichthys nigrodigitatus and Great Kwa River.*

I. INTRODUCTION

Pollution may be defined as the release of any substances or energy, directly or indirectly, by man into the environment, which has deleterious effects on human health, harmful to living resources and ecological systems, causes inconvenience, and encumbers the use of the environment. The substances or energy (pollutants) that are introduced affect both the biotic and abiotic components of the ecosystem, thereby, posing a serious threat. Anthropogenic activities are the chief cause of environmental, natural cause is to a lesser extent.

Environmental monitoring of substances with underlying adverse effects on both the environment and their biotic composition is inadequate in most developing nations. Recently, the contamination of the aquatic environment with varieties of impurities has come to be a matter of great concern (Dahunsi *et al.* 2012). In Nigeria, the introduction of waste products into the aquatic ecosystem is a common phenomenon. This is because some people still believe that water bodies have a limitless capacity to absorb increasing quantities and assorted wastes and energy from our civilization (Abu and Egenonu 2008). Among these environmental pollutants, heavy metals specifically are of great anxiety due to their persistent nature and poisonous effects when exposed at certain levels (Ekperusi *et al.* 2016). According to Keepax *et al.* (2011), heavy metals are metals of high density usually greater than 5.00 to 6.00 g/cm³. They are at least five times denser than water and may have harmful effects on plants and animal environments when present above concentrations found naturally. Heavy metals are recalcitrant to degradation and as such hazardous, with long biological half-life (James *et al*., 2013; Olgunoglu *et al*., 2015). The existence of contaminants such as metals in freshwater upsets the stability of the aquatic ecosystem and its accumulation in fish can lead to toxic levels, even in low concentrations (Eneji *et al.,* 2011). Interestingly, most of these toxic metals do not contribute to the proper functioning of the body but they tend to accumulate in the body tissues faster than the body's detoxification pathways (Ekpo *et al*., 2008).

In recent times, heavy metal contamination over the natural load has posed a more serious threat than anyone could have envisaged. This situation is attributed to urbanization and expansion of industrial activities as well as the lack of or poor environmental regulation policies (Morais *et al*., 2012). Accumulation of heavy metals in the aquatic environment occurs mainly from two sources; natural sources, for example, erosion and weathering of rocks, and anthropogenic activities; among these two sources, anthropogenic activities are the prime source of aquatic pollution that affect the ecosystem and ultimately to the human being through the food chain.

In a small amount, heavy metals are normal parts of aquatic habitat and organisms in water but when at a higher concentration level, they bring to bear a range of toxic effect that alters the organisms' normal metabolic, physiologic, behavioral, and economic (Uneke and Aloh, 2015). The bio-accumulation and bio-magnification tendencies of these elements enhance their toxic effect on the tissues of a living organism (Biswas *et al.,* 2012).

The increased use of heavy metals in industries has done great damage to the environment through the discharge of largely untreated effluents of anthropogenic origin (Mohanta *et al*., 2020). The toxicity and accumulative properties of heavy metals in a living organism in an aquatic ecosystem make the metals of particular concern (Miller *et al.,* 2002; Akan *et al.*, 2012) in addition to their persistence in the natural setting (Zhao *et al.*, 2012). Essential metals such as Cu, Na, K, Ca, Mn, Se, Fe, Cr3+, and Zn have normal physiological functions (Hogstrand and Hanx, 2001) but may also bioaccumulate and reach toxic levels.

In the aquatic environment, fish is at the top of the food chain and may receive large quantity of these metals from the surrounding waters. The sources through which heavy metals enter into water bodies include; chemical weathering of rocks and soil, agricultural runoffs, industrial waste discharge, mining batteries, lead-based paint, gasoline, and improper domestic waste discharge into waterways. The behaviour of heavy metals in organs has been studied extensively using fish(Oladimeji *et al.,* 2013). According to Kelle *et al*., (2015), the exposure of fish to sub-lethal concentrations of other metals such as zinc may also cause an increase in the hepatic levels of copper by yet to be understood mechanism.

There have been several surveys and reports on heavy metals accumulation in fish of some Nigerian Rivers (Alinnor and Obiji, 2010; Olowu *et al.*, 2010; Babatunde *et al,* 2013; Edward *et al.*, 2013; Adeosun *et al.*, 2015, Amina *et al.*, 2021). The presence of unacceptable levels of Hg and Pb in the tissues of silver catfish *(Chrysichthysnigrodigitatus)* from River Niger has been reported (Omeregie *et al.*, 2002). They reported enhanced levels of Pb, Copper, and Zinc in *Oreochromis niloticus* (Nile Tilapia) from river Delimi. Higher concentrations of cadmium, (Cd), copper (Cu), iron (Fe), manganese (Mn), and zinc (Zn) have been shown to bio-accumulate in muscle, liver, and gill tissues of *Oreochromis niloticus*, and *Chrysichthysnigrodigitatus*. Given the above, this study looks into heavy metal concentration levels in Nile tilapia *(Oreochromis niloticus)* (scaly fish) and African mud catfish *Chrysichthysnigrodigitatus* (non-scaly fish) from the two landing sites of the Great Kwa River.

II. MATERIALS AND METHOD

A. *Description of the study area*

The Great Kwa River is located in Cross River State, Nigeria draining the east side of the city of Calabar. The river lies between longitude 80^{o} 15' E and 80^{o} 30' E and latitude 4^{o} 45' N and 5^{o} 15' N (Figure 1). The river originates from the Oban hills, in the Cross River National Park and flows southwards to the Cross River estuary (Akpan *et al., 2011).* The climate of the study area is characterized by a long wet season from April to October and a dry season lasting from November to March, with a short period of drought referred to as "August break" which rarely occurs in the wet season while a cold, dry and dusty period, the harmattan season, usually occurs between December and January each year. Essentially, Calabar falls within the tropical rain forest of Nigeria with dense vegetation cover of fall trees and thick under growth which most have disappeared due to urbanization. Human activity in the Great Kwa basin has traditionally been limited to small scale farming aquaculture and artisanal fishers, mainly for shrimps.

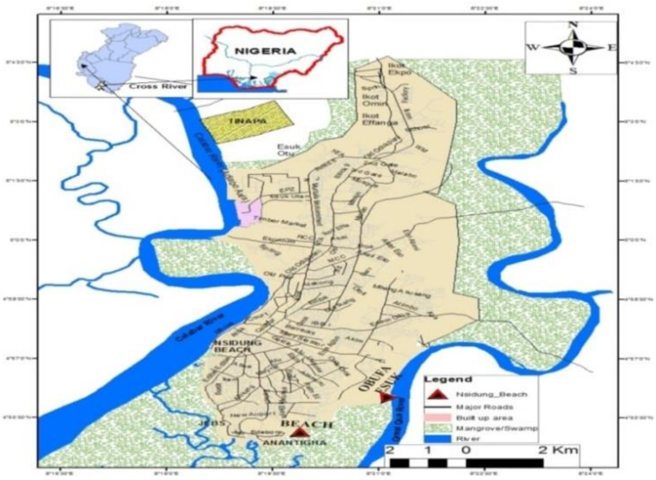

Fig. 1: Map of the study area

B. *Sample Collection*

Samples of two popular species of fish namely; Nile Tilapia *Oreochromis niloticus* (scaly) and Silver catfish *Chrysichthysnigrodigitatus* (non-scaly) were bought from artisanal fishers from the landing site at EsukAtu and Anantigha beach. Samples were transported to the Biochemistry laboratory, University of Calabar, Calabar in an ice chest. The fieldwork was embarked on a monthly basis from March to August 2021.

C. *Digestion Procedure of Fish Sample*

The collected fish samples were dried in an oven at 105^{0}C and prior to this, both specimens were processed by separating the different parts (gill, bones, liver and muscles). After drying, the samples were moved to the oven and were completely dried at 550°C. With the use of an electric grinder, the dried sample was crushed and made ready for digestion process. About 0.5g of the powdered fish sample was placed in a 100ml round bottom flask with ground glass joint and mineralized under reflux using a mixture of 6.0ml nitric acid (70% spectrosol) and 4.0ml hydrogen peroxide (35% Riedel-de Haen). The digestion procedure took about five hours to get clear solution. A triplicate digestion was done for each of the samples and finally transferred to 25ml volumetric flask and diluted to final volume.

D. Analysis of Heavy Metal Element in Standard and Sample Solution

The heavy metals such as cadmium, chromium, copper, nickel and lead were analyzed from the diluted digest of the fish samples using a fast sequential Atomic Absorption Spectrophotometer (AAS) with an aqueous calibration standards prepared from the stock standard solutions of the respective element.

E. Data Analysis

Apart from routine calculations of means and standard deviations;data were subjected to one-way analysis of variance (ANOVA), to assess whether samples varied significantly between species($p<0.05$) were considered statistically significant. All results were presented in charts and table.

III. RESULTS

The concentrations of heavy metals; cadmium, chromium, copper, nickel and lead in muscles, gills and liver from Kwa River station (Figure 2 and 3) and Anantigha station (Figure 4 and 5) respectively, are presented below. The mean of total length was 21.138±2.68cm and weight of 229±81.85g in *O. niloticus* was 21.138±2.68cm and 229±81.85g respectively, while that of *C. nigrodigitatus* was 34.9±10.5cm and 308.9±87.4g respectively.

A. Heavy Metals in Muscles, Gills and Liver in Tilapia (mg/kg)

The concentration of Cadmium in the muscles was 0.07±0.03mg/kg, which were the lowest followed by 0.08±0.06mg/kg in the liver and the highest (0.12±0.04mg/kg) in the gills in Kwa River station (Figure 2). In Anantigha, the highest (0.12±0.0mg/kg) was recorded in gills followed by the liver (0.08±0.01mg/kg) and the least (0.00±.03mg/kg) was observed in the muscles (Figure 3).

In Kwa River station Chromium concentration recorded the highest (0.11±0.09mg/kg) value in the gills followed by the muscles (0.04±0.02mg/kg); the least (0.04±0.03mg/kg) was obtained in the liver (Figure 2). Similarly, in Anantigha River station, muscles recorded 0.04±0.02mg/kg as the least value obtained followed by the liver (0.05 ±0.02mg/kg) and the highest (0.10±0.05mg/kg) concentration in was gotten in the gills (Figure 3).

Copper concentration 0.21±0.01mg/kg recorded in the liver followed by muscles (0.024±0.01mg/kg) and the highest (0.29±0.02mg/kg) was recorded in the gills in Kwa River for *O. niloticus* (Figure 2). However 0.27±0.02mg/kg was obtained in the gills, followed by the muscles (0.23±0.04mg/kg) and the least 0.21±0.01mg/kg was recorded in the liver of *O. niloticus* in Anantigha River (Figure 3).

The mean concentration of Nickel in *O. niloticus* from in Kwa River were 0.11±0.05mg/kg, 0.13±0.06mg/kg and 0.16±0.09mg/kg for live, muscles and gills respectively, while in Anantigha River recorded 0.11±0.05mg/kg, 0.13±0.03mg/kg and 0.17±0.07mg/kg for liver, muscles and gills respectively.

Slight variations were observed in the concentrations of lead between the two stations. Kwa River station recorded lead concentration of 0.01±0.00mg/kg for liver and muscles and 0.03±0.02mg/kg for gills. However in Anantigha station, Lead concentration of 0.01±0.00mg/kg was in the liver, 0.03±0.01mg/kg for muscles and 0.03±0.01mg/kg for gills respectively. The above results show that Cu content was the highest and that of Lead (Pb) was the lowest in the two stations for *Oreochromis niloticus* were in the order of Cu > Ni > Cr > Cd >Pb.

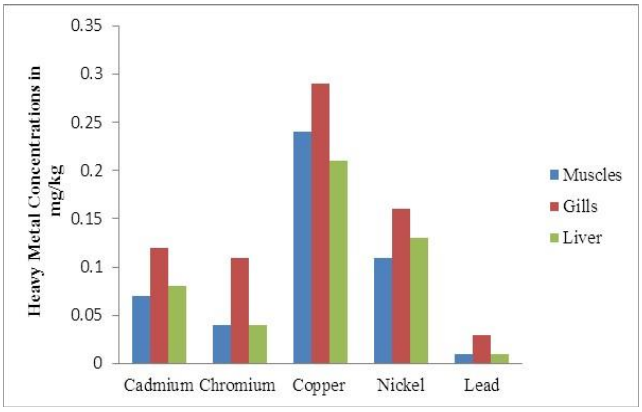

Fig. 2: Heavy Metals Concentrations (mg/kg) in *Oreochromis niloticus* in Kwa River Station

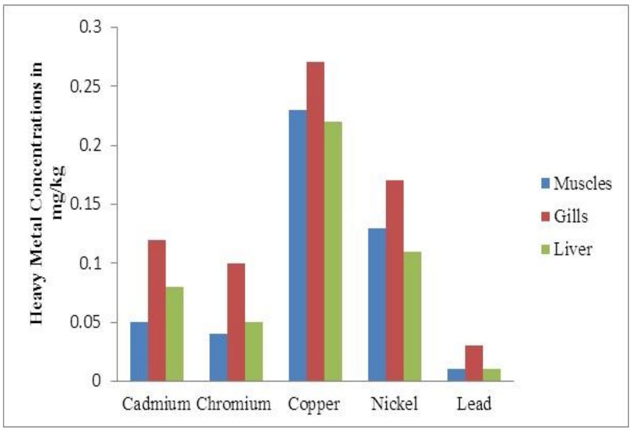

Fig. 3: Heavy Metal Concentrations (mg/kg) in *Oreochromis niloticus* in Anantigha Station

B. Heavy Metals in Muscles, Gills and Liver of Chrysichthys nigrodigitatus

A summary of the Heavy metals in the muscles, gills and liver tissues of *C. nigrodigitatus* are shown in figure 4 and 5. Cadmium was not detected in the muscles; 0.01±0.00mg/kg concentration was recorded in the gills and liver in Kwa River station. Cadmium was not also detected in the muscles in Anantigha station but the values 0.01±0.00mg/kg was the concentration recorded in liver and gills during the study.

The concentrations obtained for chromium show that muscles had the lowest (0.01±0.00mg/kg) followed by the liver (0.03±0.02mg/kg) and the highest (0.08±0.03mg/kg) recorded in the gills while liver and gills had the same concentration of 0.03±0.0 mg/kg in Anantigha river station. The mean concentration of 0.06±0.02mg/kg was observed in muscles for copper, followed by 0.07±0.03mg/kg in the liver and the gills accounted for 0.13±0.01mg/kg in Kwa river station while liver had the least 0.01±0.02mg/kg mean concentration in Copper followed by muscles and gills which has the same concentration 0.11±0.01mg/kg.

Nickel concentration of 0.02±0.01mg/kg was recorded in the muscles, 0.05±0.02mg/kg in the gills and 0.06±0.01mg/kg in the liver respectively in Kwa River station. Moreover the lowest mean and standard error of 0.02±0.00 was obtained in the liver while the gills and muscles the concentration of 0.04±0.02mg/kg in Anantigha Station.

The concentration of Lead in *C. nigrodigitatus* in Kwa River station was 0.01±0.00mg/kg in the gills, while in the muscles and liver it was below detectable limit. However the concentration of lead was not detectable in Anantigha station. The above results show that Cu content was the highest and that of Lead (Pb) was the lowest in the two stations in *C. nigrodigitatus*. Heavy metal in Kwa river Station were in the other of Cu > Ni > Cr > Cd >Pb while in Anantigha were in the order of Cu > Cr > Ni > Cd >Pb.

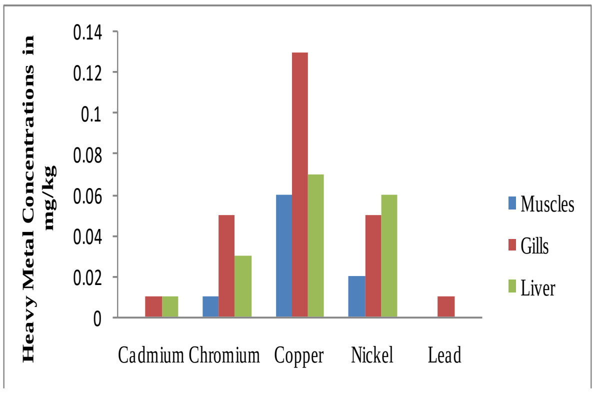

Fig. 4: Heavy Metal Concentration (mg/kg) in *Chrysichthys nigrodigitatus* in Kwa River Station

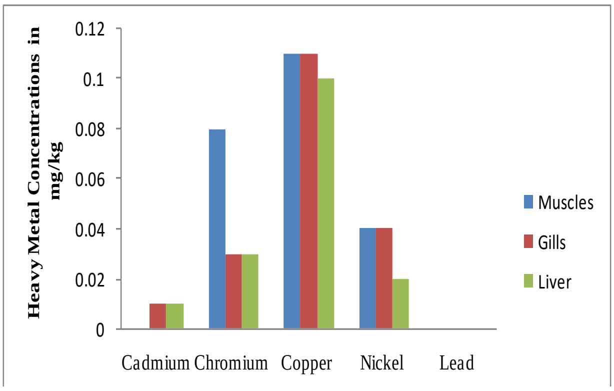

Fig. 5: Heavy Metal Concentration (mg/kg) in *Chrysichthys nigrodigitatus* in Anantigha Station

C. Comparison of Selected Heavy Metals Concentration (mg/kg) in Oreochromis niloticus and Chrysichthys nigrodigitatus

Table 1 compares the differences inconcentrations of heavy metals in tilapia and catfish species during the sampling period. The concentrations of Cdfound in the two fish species ranged between0.05mg/kg to 0.12mg/kg in Kwa River Station and 0.01mg/kg to 0.12mg/kg in Anantigha Station. The maximumconcentration was detected in *O. niloticus*was 0.12mg/kg in both stations while the minimum was 0.05 mg/kg and 0.01mg/kg in Catfish.

The Cr concentration in the two fish species ranged from 0.01mg/kg to 0.11mg/kg in Kwa River and 0.03mg/kg to 0.10mg/kg in Anantigha Station. The highest concentration was *O. niloticus*while the minimum concentration was recorded in *C. nigrodigitatus* (Table 1). The Cu levels ranged from 0.06mg/kg to 0.29mg/kg in Kwa River Station and 0.10mg/kg to 0.27mg/kg in Anantigha Station.

Heavy Metals (mg/kg)	Kwa River	Anantigha	WHO/FAO Standards (2011)
Cadmium (Cd)	0.05-0.12	0.01-0.12	0.2
Chromium (Cr)	0.01-0.11	0.03-0.10	1.0
Copper (Cu)	0.06-0.29	0.10-0.27	-
Nickel (Ni)	0.02-0.16	0.02-0.17	80
Lead (Pb)	0.01-0.03	BDL	1.5

Table 1: Shows the Range of Heavy Metal Concentration (mg/kg) in the Tissues of *Oreochromis niloticus* and *Chrysichthys nigrodigitatus* in Kwa River Station and Anantigha Station during the Period of Study

The highest and lowest level of concentration was recorded inTilapia and Catfish respectively. The concentration of Nifound in the two fish species ranged between0.02mg/kg to 0.16mg/kg in Kwa River Station and 0.02mg/kg to 0.17mg/kg in Anantigha Station. The maximumconcentration was detected in *O. niloticus*in both stations while the minimum was recordedin *C. nigrodigitatus*. Pb were still below detectable limits in *C. nigrodigitatus* in Anantigha but were in the ranged of 0.01mg/kg to 0.03mg/kg in Kwa River Station. The descending order of the heavy metals accumulated in tissues of the two fish species was Cu > Ni > Cd > Cr >Pb.

IV. DISCUSSION

In recent times, the high cost of meat cannot be afforded by most Nigerians, hence the increase in fish consumption which serves as compliment for meat (Oladimeji*et al.*, 2013). The presence of contaminants especially the heavy metals in excess of natural loads in aquatic environment has become a problem of increasing concern. Fish absorbs these heavy metals into their body tissues; however, since fish are important in human nutrition, it is necessary to ensure that high level of these toxic heavy metals are not being transmitted to human through consumption (Edward *et al.*, 2013). The toxicity of heavy metals causes histomorphological changes, deformities, biochemical alterations and sometimes death in the organism and also have other health implications (More *et al*., 2003).

In Kwa River, among the heavy metals analyzed, only Copper was an essential element, its concentration was in the range of 0.06-0.29mg/l and 0.10-0.27mg/l in Kwa river station and Anantigha station respectively. On the contrary, toxicologically relevant metals, such as cadmium, chromium, nickel, and lead, are not biologically important and their concentrations in fish tissues examined were generally low as seen in Figures 2 and 3. Increasing levels of As, Cd, Pb, Cu, and Hg in the body can cause damage to the immune, circulatory, endocrine, and enzyme systems (Chen *et al*., 2015) hence the reason they are classified as toxic and a maximum human consumption limit have been set for these metals (Zhao *et al*., 2012). Though the quantity of these toxic metals recorded in fish species at Kwa River are insignificant, nevertheless, it is important to note that the metals may be substantial in the River but the values were low due to poor accumulation by the fish and also to a greater extend their ability to regulate their body metal concentration to a certain degree. This could account for low values concentrations recorded in their organs, as excretion of metals can occur through the gills, bile (via feaces), kidneys, and skin (Mehmood, 2017; Zhuang, 2013).

Some environmental and biological factor influences the rate of heavy metal accumulation, hence the dissimilarities between individual and species in bioaccumulation of heavy metals. Also, different levels of the metals accumulated in various tissues depend on the biochemical features of the metal (Farkas *et. al*., 2000). Generally, in fishes, the gill is the tissue that is more often found to have high heavy metal concentrations (Farkas *et. al*., 2000) This account for the high levels of all the heavy metals recorded in the gills of both *Chrysichthysnigrodigitatus and Oreochromis niloticus* as shown in Figure 2 and 3. On the other hand, feeding habits of the fish and the levels of heavy metal concentrations in the environment may also be responsible for metal accumulation in various tissues in fishes (Farkas *et. al*., 2003).

Furthermore, this study revealed in the gill, the levels of the heavy metal concentration was higher than those in the muscle tissues signifying that the gill was the main route of metal uptake. Thus, the levels of metals in the fish gill reflects its levels in the water, where the fish species lives (Zhuang, 2013; Edward *et al*., 2013). Antal *et al*. (2013) reported that the gills of fishes unswervingly interact with water and bio-accumulate heavy metals. In addition, heavy metal accumulations in tissues are mostly found to be species-specific. Malik *et al.*, (2014) observed that the differences between the metal concentrations in fishes may be related to their feeding habits and the bio-concentration capacity of each species.

Low concentration of Cadmium, Chromium, Nickel, and Lead (Figs. 2, 3, 4, and 5) was found to have been deposited in the liver and muscles of *O. niloticus* and *C. nigrodigitatus*. Naturally, Cd concentration in the earth's crust is about an average of 0.1 mg/kg and, higher levels exist in sedimentary rocks. Cd contains about 15 mg/kg in marine phosphates in addition to non-point pollution sources from Calabar city. Reports from WHO (1992) and Environmental Protection Administration (1991) revealed high content of Cd in Municipal refuse which is obtained batteries and plastics containing cadmium pigments and stabilizers. Also, the system of burning refuse is a major source of atmospheric cadmium release at the country, regional, and worldwide levels. Similarly, cadmium upon getting into the environment as reported by WHO (1992) mingles with the calcium metabolism of animals and in fish thereby causing hypocalcaemia, perhaps by preventing calcium uptake from the water. However, high calcium concentrations in the water protect fish from cadmium uptake by competing at uptake sites (Opaluwa *et al.*, 2012).

Although, the concentration of copper was below the permissible limit, the reason for this low concentration compare to WHO standards is attributed to high alkalinity of the Kwa River. Copper is an essential element which is necessary for synthesis of hemoglobin, but at high level, Cu can result in adverse health problems for the living organism (Sivaperumal *et al.*, 2007). Svobodova *et al*., (1993) reported that in waters with high alkalinity, copper forms hydroxides of low solubility, also in waters with a high bicarbonate/carbonate, copper precipitates as poorly soluble or insoluble cupric carbonate. This is because compounds that are slow to dissolve are unlikely to be taken up to any extent into the fish body, so their toxicity to fish may be low. Adeosun *et al. (*2015) revealed that increase in water hardness and alkalinity, leads to increased uptake and toxicity of copper in freshwater organisms. Conversely, *O. niloticus* bio-accumulated copper most, though the values were within the WHO standard, however, the value is a pointer to the gradual concentration of copper in the Kwa river which may eventually constitute a burden to the aquatic system. Anim *et al*., 2011 reported the bioaccumulation of Cu in tissues of *Clariasgariepinus* collected from the Densu River.

The foods we consume, it processing and to a lesser extend natural sources are the primary source of Ni for humans (Nas-NRC, 1975). There have been several reports on incidence of lung cancer and nasal cavity as a result of high intake of Ni in some Ni smelting workers. In this study, the highest concentration of Ni (0.17mg/kg) was recorded in the gill of *O. niloticus*, while the lowest level of 0.02mg/kg was detected in the muscles and liver of *C. nigrodigitatus*. The estimated maximum permissible limit for Ni is 80 mg/kg (WHO/FAO, 2011). Therefore, the levels of Ni in all the samples were far below the stipulated limit.

Cadmium is a toxic non-essential metal with little or no role in biological process in living organisms. Thus, even at its low concentration, Cd could be harmful to living organisms (Tsui and Wang, 2004). The highest cadmium concentrations of 0.12mg/kg were detected in the gills of *O. niloticus*. It was not discovered in the muscle and liver tissues of *O. niloticus*. The mean concentration of cadmium in both fish species was above the WHO/FAO Maximum Permissible Limit of 0.2mg/kg for food samples and this may have severe health risk implication in fish consumers.

Literature review shows that Cadmium that accumulates in the human body through food negatively affects internal organs such as; liver, kidney, lung, bones, placenta, brain and the central nervous system (Chouba*et al.,* 2007). In addition, Cd can cause reproductive and development toxicity, hepatic, haematological and immunological effects. In this study, Cd levels recorded in the studied organisms may be attributed to industrial and agricultural operations and alleged lateral inflow of leachates from damaged geomembranes/textile of adjacent landfill sites in the considered area.

Chromium is recorded as a poisonous heavy metal. Its hexavalent form may cause ulcerations, dermatitis, and allergic skin responses. Inhalation of hexavalent chromium compounds can result in perforation of the mucous membranes of the nasal septum, irritation of the pharynx and larynx, asthmatic bronchitis, bronchospasms and edema. Respiratory symptoms may include coughing and wheezing, shortness of breath, and nasal itch (Patil& Ahmed, 2011). This study indicated that the concentration of Cr in all the fish tissues were below the prescribed limit (1.0 mg/Kg).

Udiba*et al.*, (2012a) revealed that Pb is a protoplasmic poison that is slow-acting and subtle in nature. Exposure to lead within a short period of time may lead to damage of the brain, gastrointestinal problems, anaemia and paralysis (lead palsy). Additionally, chronic effects of Pb can damage the kidney, immune, nervous and reproductive systems (Ogwuebgu&Muhanga, 2005; Leon & Pacheco, 2020). The most dangerous consequence of low-level Pb exposure is on intellectual growth in young children (Udedi, 2003). Pb concentration in all the fish samples examined were below the prescribed limit of 1.5 mg/Kg.

Accumulation of heavy metals can result in structural lesions and functional disturbances in fish itself (Jezierska and Wieteska, 2001). High level of accumulation may exert cumulative toxic effect and results in lethal disturbances. Also, fish being top in the food chain, may pose potential health risk for predatory fish and other animals such as; birds and mammals, feeding on the contaminated fish. Fish muscles are the main edible part and can influence the human health directly. Therefore, different regulatory bodies have established toxicological limits for heavy metals in seafood (Agah*et al*., 2009). Regular consumption of fishes containing heavy metals beyond prescribed limit by human may impair body metabolism (Ambedkar&Muniyan 2012;Paurang*et al*., 2009; Udiba*et al.*, 2012a).

Assessment of the concentrations of Cd, Cr, Cu, Ni, and Pb in the tissues of the *O. niloticus* and *C. nigrodigitatus* has provided a baseline information and data on the pollution level of the Kwa River. This data will guide researchers and environmental scientist in recognizing future anthropogenic impacts in the study area in relation to the studied metals, and in monitoring changes from the existing levels. The availability of the studied metals in the fish samples suggests the capability of the fish to absorb these metals from their environments. This is an important factor that calls for further research.

V. CONCLUSION

The result of this study shows that the fish species of interest have preferences to retain the heavy metals analyzed in their internal organs more than other metals. It also indicates no health risk when consumed and therefore prevention of risk of occurrence should be focused on reducing the level of heavy metals discharged from municipal, agricultural and industrial wastes into the catchment area.

To maintain the 'clean' state of the Kwa River, it is important that waste introduced into the catchment area have to be controlled by environmental agencies to ensure that existing approaches are not aggravated. Professional bodies within the field of public health and the environment should be aggressively involved. Also, there should be an awareness and enlightenment program for the artisanal fishermen, sellers, and fish consumers that purchase their fish supply from the Kwa River on the potential health risks of Cd, Cr, Cu, Ni, Pb, and other heavy metals from fish and other food samples such as vegetables from the water source to reduce the possible health risks of consuming contaminated food samples.

REFERENCES

[1.] Abu G. O. and Egenonu C. (2008) The current pollution status of the new Calabar River in the Niger Delta region of Southern Nigeria: A survey of antibiogram profiles of its bacterial isolates. *Afr. J. Environ. Sc. Technol.* 2(6):134-141.

[2.] Adeosun, F.I., Akinyemi, A. A., Idowu, A. A., Taiwo, I. O., Omoike, A. and Ayorinde, B. J. O. (2015). The effects of heavy metals concentration on some commercial fish in Ogun River, Opeji Ogun State, Nigeria.*Africa Journal of Environmental Science and Technology*, 9(4): 365-370.

[3.] Agah, H., Leermakers, M., Elskens, M., Fatemi, S. M. R. and Baeyens, W. (2009) *Accumulation of trace metals in the muscles liver tissues of five fish species from the Persian Gulf*. Environmental Monitoring and Assessment, 157: 499-514.

[4.] Akan, J. C., Mohmoud, S., Yikala, B. S., and Ogugbuaja, V. O. (2012).Bioaccumulation of Some Heavy Metals in Fish Samples from River Benue in Vinikilang, Adamawa State, Nigeria.*Am. J. Analytical Chemistry*, 13: 727-736.

[5.] Akpan, J.O., Offem, A. E. and Nya (2011).*Baseline ecological studies of the Great kwa river Nigeria*. Physio-chemical studies, 5 (6):120-125.

[6.] Alinnor, J. and Obiji, I. A. (2010) Assessment of trace metal composition in fish samples from Nworie River. *Pakistan Journal of Nutrition*, 9(1): 81 - 85.

[7.] AmbedkarG., and Muniyan M. (2012), Analysis of heavy metals in water, sediments and selected freshwater fish collected from gadilam river, tamilnadu, india, *InternationalJournal of Toxicology and Applied Pharmacology*, 2(2), pp. 25–30.

[8.] Amina M. M., Adamu Y. U., and Zainab M. (2021) Assessment of heavy metal levels in fish tissues, water and sediment from Epe lagoon, Lagos, Nigeria, *Science World Journal Vol. 16(4):* 1597-6343

[9.] Anim, A. K., Ahialey, E. K., Duodu, G. O., Ackah, M. and Bentil, N. O., (2011).Accumulation profile of heavy metals in fish samples from Nsawam, along the Densu River, Ghana. *Research Journal of Environmental and Earth Sciences*, 3(1), 56-60.

[10.] Antal, L., Halasi-Kovacs, B., and Nagy, S. A. (2013) Changes in fish assemblage in the Hungarian section of river Szamos/Someş after a massive cyanide and heavy metal pollution.*North western Journal of Zoology*, 9(1), 131–138.

[11.] Babatunde A. M., Waidi O. A. and Adeolu A. A. (2013).*Bioaccumulation of heavy metals in fish organs in downstream Ogun coastal water*.Nigeria Department of Aquaculture and Fisheries Management.Federal University of Agriculture, Abeokuta, Nigeria. pp. 212-217.

[12.] Biswas, S., Prabhu, R. K., Hussain, K. J., Selvanayagam, M. and Satpathy, K. K. (2012). Heavy metals concentration in edible fishes from coastal region of Kalpakkam, southeastern part of India.*Environmental Monitoring and Assessment*, 184, 5097-5104. DOI:10.1007/s10661-011-2325-y

[13.] Chen, H., Teng, Y., Lu, S., Wang, Y. and Wang, J., (2015)Contamination features and health risk of soil heavy metals in China. *Science of the Total Environment*, 512-513, 143-153. DOI:10.1016/j.scitotenv.2015.01.025

[14.] Chouba, L., Kraiem, M., Njimi, W., Tissaoui, C. H., Thompson, J. R. and Flower, R. J. (2007).Seasonal variation of heavy metals (Cd, Pb and Hg) in sediments and in mullet, *Mugilcephalus*(Mugilidae), from the Ghar El Melh Lagoon (Tunisia).*Transitional Waters Bulletin.*TWB, Transit. Waters Bull. 4, 45-52.

[15.] Dahunsi SO, Oranusi SU, Ishola RO. (2012) Differential bioaccumulation of heavy metals in selected biomarkers of *Clariasgariepinus*(Burchell, 1822) exposed to chemical additives effluent. *J. Res. Environ. Sci. Toxicol.* 1(5):100-106.

[16.] Edward, J. B., Idowu, E. O., Oso, J. A. and Ibidapo, O. R, (2013). Determination of Heavy Metal Concentration in Fish Samples, Sediment and Water from Odo-Ayo River in Ado-Ekiti, Ekiti-State, Nigeria, *International Journal of Environmental Monitoring and Analysis*, 1(1): 27-33.

[17.] Ekperusi O. A., Aigbodion I. F., Iloba BN, Okorefe S. (2016). Assessment and bioremediation of heavy metals from crude oil contaminated soil by earthworms. *Ethiopian J. Environ. Study Management*. 9(2):1036-1046. doi: 10.4314/ejesm.v9i2.9S

[18.] Ekpo, K. E., Asia, I, O., Amayo, K. O., and Segede, D. A. (2008).Determination of lead, cadmium and mercury in surrounding water and organs of some species of fish from Ikpoba River in Benin City, Nigeria.*East Coast Shef. Sci.*, 59(94):601-609.

[19.] Eneji I. S., Sha.Ato R, Annune P. A. (2011). Bioaccumulation of Heavy Metals in Fish (*Tilapia Zilli*and *ClariasGariepinus)* Organs from River Benue, North Central Nigeria. Pak. *J. Anal. Environ. Chem.* 12(1 & 2): 25-31.

[20.] Environmental Protection Administration. (1991). General reports of surveys of heavy metal content of soil in Taiwan: (IV) East and island regions: I-Lan, Hualien, Taitung and Penghu counties. Environmental Protection Administration, R.O.C., Taipei, pp 47-160.

[21.] FAO/WHO, (2011)Joint FAO/WHO food standards programme codex committee on contaminants in foods, 5th session. The Hague, Netherlands.

[22.] Farkas, A., Salánki, J. and Specziár, A., (2003).Age- and size- specific patterns of heavy metals in the organs of freshwater fish *Abramisbrama*L. populating a low-contaminated site.*Water Research*, 37(5), 959-964. DOI:10.1016/s0043-1354(02)00447-5

[23.] Farkas, A., Salanki, J. and Varanka, I. (2000).*Heavy metal concentrations in fish of Lake Balaton*.Lakes Reserv. Res. Manag. 5: 271-279.

[24.] Hogstrand, C. and Haux, C. (2001).Binding and detoxicfication of heavy metal in lower vertebrates with reference to melallothiorein.*Comp. Biochem. C.*, 100:137.

[25.] James O. O., Nwaeze K., Mesagan E., Agbojo M., Saka K. L., and Olabanji D. J. (2013). Concentration of Heavy Metals in Five Pharmaceutical Effluents in Ogun State, Nigeria. Bull. *Env.Pharmacol. Life Sci.*, 2 (8): 84-90.

[26.] Jezierska, B. and Witeska, M. (2001) *Metal toxicity to fish in WydawnictwoAkademiiPodlaskiej*, Siedlce, 318.

[27.] Keepax, R. E., Moyes, L. N. and Livens, F. R. (2011). Speciation of heavy metals and radioisotopes, In: Environmental and Ecological Chemistry vol. II. Encyclopedia of Life Support Systems (EOLSS) available from http://www.eolss.net/Sample-Chapters/C06/E6-13-03-05.pdf

[28.] Kelle, H. I., Ngbede, E. O., Oguezi, V. U., and Ibekwe, F. C. (2015).Determination of Heavy Metals in Fish (*Clariasgariepinus*) Organs from Asaba Major Markets, Delta State, Nigeria *American Chemical Science Journal 5(2): 135-147*,

[29.] Leon, O. L. and Pacheco, J. M. S. (2020).Effects of Lead on Reproductive Health.*IntechOpen*, 1-19

[30.] Malik, R. N., Hashmi, M. Z., & Huma, Y. (2014).Heavy metal accumulation in edible fish species from Rawal reservoir, Pakistan. Environmental Science and Pollution Research, 21, 1188–1196.

[31.] Mehmood, M. A., Shafiq-urRehman, Ganie, S. A., Rashid, A., and Bhat, R. A. (2017) Seasonal and spatial variation in bioaccumulation of heavy metals in two commercial fish species from river Jhelum of Kasmir valley, *International Journal of Current and Advance Research*, 06 (07), 4650-4658.

[32.] Miller, J. R., Lechley, P. J., Hudson, K. A., Edwards, T. and Macklin, M. G. (2002). Lead isotopic finger printing of heavy metal contamination, RIO, Pilcomayo, Bolivia. In. allan R. AJ Horowitz and J. R miller (Eds) metal mining in the Environment, special issue. *J. Geochem, Explor. Environ. Anal,* 2 (3):225-233.

[33.] Mohanta, V.L., Naz, A. and Mishra, K.B., (2020).Distribution of heavy metals in the water, sediments, and fishes from Damodar River basin at steel city, India: A probabilistic risk assessment. *Human and*

Ecological Risk Assessment: an International Journal, 26(2), 406-429. DOI: 10.1080/10807039.2018.1511968.

[34.] Morais, S., Costa, F. G., & Pereira, M. L. (2012). Heavy metalsand human health. In J. Oosthuizen (Ed.), Environmentalhealth –emerging issues and practice (pp. 227–246).London: Intech Open Limited.

[35.] More, T. G., Rajput, R. A. and Bela, N. N. (2003).Impact of heavy metals on DNA content in the whole body of freshwater bivalve, *Lamelleidenmarginalis*.*Environmental Science Pollution Research*, 22: 605-616.

[36.] NAS-NRC (1975).(National Academy of Sciences-National Re- search Council), "Division of Medical Sciences, Medical and Environmental Effects of Pollutants Nickel," National Academic Press, Washington DC. pp342.

[37.] Ogwuegbu, M. O. C., Muhanga, W. (2005). Investigation of lead concentration in the blood of people in the Copper belt Province of Zambia. *Journal of Environment*, (1): 66 - 75.

[38.] Oladimeji, Y. U., Abdulsalam, Z. and Damisa, M. A. (2013). Socioeconomic characteristics and returns to rural artisanal fishery households in Asa and Patigi local government areas of Kwara State, Nigeria. *International journal of nature*, 4(3):445-455

[39.] Olgunoğlu M. P., Artar E., and Olgunoğlu I. A. (2015).Comparison of Heavy Metal Levels in Muscle and Gills of Four Benthic Fish Species from the Northeastern Mediterranean Sea.*Polish J. Environ. Studies*, 24(4): 1743-1748.

[40.] Olowu, R. A., Adejoro, I. A., Denloye, A. A. and Ogundajo, A. L. (2010) Determination of Heavy Metals in Fish Tissues, Water and Sediment from Epe and Badagry Lagoons, Lagos, Nigeria. *E-Journal of Chemistry*.7(1): 215-221.

[41.] Omeregie, E., Okoronkwo, M.O., Eziashi, A.C. and Zoakah, A.L. (2002). Metal concentration in water column, Benthic macro invertebrate and tilapia from Delimi, River, Niger. *Journal of Aquatic science*, 17:55-59.

[42.] Opaluwa, O. D., Aremu, M. O., Ogbo, L. O., Magaji, J. I., Odiba, I. E. and Ekpo, E. R. (2012). Assessment of Heavy Metals in Water, Fish and Sediments from UKE Stream, Nasarawa State, Nigeria.*Current World Environment*, 7(2): 213-220.

[43.] Patil G., and Ahmed I., (2011), Heavy metals contamination assesment of kanhargaon dam water near chhindwara city, *ActaChimica and PharmaceuticaIndica*, 1(1), pp. 7–9.

[44.] Paurong, M., Özözen, G., Minareci, O., Minareci, E. (2009).Determination of heavy metals in fish, water and sediments of Avsar Dam Lake in Turkey, *Iran. J. Environ. Health. Sci. Eng*. 6(2) 73-80.

[45.] Sivaperumal P, Sankar T V, Nair Viswanathan P.G. (2007), Heavy metals concentrations in fish, shellfish and fish products from internal markets of India visàvis international standards, *Food Chemistry*, 102, pp. 612–620.

[46.] Svobodova, Z., Lloyd, R., Machova, J. &Vykusova, B. (1993).*Water quality and fish healt*h. EIFAC technical paper no 54, FAO, Rome. pp. 254

[47.] Tsui, M. T. K. and Wang W. V. (2004).Uptake and elimination routes of inorganic mercury and methyl mercury in Daphnia manga.*Environ.Sci.Tecno*.38, 808-816.

[48.] Udedi, S. S. (2003). *From guinea worm scourge to metal toxicity in Ebonyi State*, chemistry in Nigeria as the New Millennium Unfolds, 2(2): 13-14.

[49.] Udiba, U. U., Ogabiela, E. E., Hammuel, C., Magomya, A. M., Yebpella, G. G., Ade-Ajayi, A. F., Odey, M. O. and Gauje, B. (2012a). Post remediation assessment of contaminants levels in soil, Dareta village, Zamfara, Nigeria. *Journal of Trends in Advanced Science and Engineering, TASE*.4 (1), 70-79.

[50.] Uneke B. I., and Aloh I. (2015). Concentration of Heavy Metals (Zn, Cd, Pb) in Kidney and Gill of Catfish (Clarias spp.) in Ebonyi River, Southeastern Nigeria.*AASCIT Journal of Bioscience.*Vol. 1, No. 2, pp. 9-14.

[51.] WHO (World Health Organization) (1992). Environmental Health Criteria Geneva, Switzerland, pp28.

[52.] Zhao, S., Feng, C., Quan, W., Chen, X., Niu, J. and Shen, Z. (2012).Role of living environments in the accumulation characteristics of heavy metals in fishes and crabs in the Yangtze River Estuary, China, *Marine Pollution Bulletin*, 64(6), 1163-1171. DOI:10.1016/j.marpolbul.2012.03.023

[53.] Zhuang, P., Li, Z., McBride, M. B., Wang, G., & Zou, B. (2013).Concentrations of heavy metals in fish from a mine affected area and potential health risk. Fresenius Environmental Bulletin, 22:2402–2408.