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EVALUATION OF THE ACCUMULATION OF SOME HEAVY METALS AND TOTAL HYDROCARBON CONTENT (THC) IN *CHRYSICTHYS NIGRODIGITATUS* FROM CALABAR RIVER, CROSS RIVER STATE, NIGERIA.

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ABSTRACT

Adult *Chrysichthys nigrodigitatus* (Silver catfish) were obtained from Calabar River from a station bordering the NNPC depot and were analyzed for some heavy metals – Lead (Pb), Zinc (Zn), Copper (Cu), Iron (Fe), and Vanadium (V) and hydrocarbons in their tissues (bone, gills, liver, kidney and muscles) using Atomic Absorption Spectrophotometer (AAS) and UV AAS respectively. All the tissues analyzed contained varying concentrations of the metals; Fe (0.097mg/l), Zn (O.0288mg/l), Pb (0.0234mg/l), Cu (0.0116mg/l), and Ni (0.0006mg/l). V was undetected in all the tissues of the fish. Hydrocarbons were found to accumulate in the muscles and gills (0.051mg/l and 0.011mg/l respectively) but were absent in the liver, kidney and bone. The levels recorded for the metals present in the various tissues of the test fish samples were significant and may constitute a source of poisoning to humans when consumed. Calabar River should therefore be protected from heavy metal and hydrocarbon pollution by ensuring strict compliance with environmental laws by companies operating around the river. The concentration and accumulation patterns of heavy metals and hydrocarbons with their implications on the aquatic ecosystem and human consumption of the fish are discussed in the text.

Keywords: *Chrysichthys nigrodigitatus*, Hydrocarbons, Heavy Metals, Bio-magnification, Bio-accumulation, Food chain.

1. INTRODUCTION

The discharge of contaminants into aquatic ecosystems is a common occurrence in Nigeria. It is estimated that about 15% of the total petroleum input to aquatic systems is from natural sources and the remaining 85% is due to anthropogenic causes, Ghosh *et al*., (2006).

Hydrocarbons are the major components of crude oil and its by-products. Other components include heavy metals, sulphides, phenols, naphthalenic acids arid other chemicals (Lief *et al*., 2004). These components are ubiquitous organic contaminants of aquatic systems. They are used as indicators of the presence and fate of petroleum products as well as the changes in chemical composition of the system where they are found (Wang *et al*. 1998). They are highly toxic to the aquatic organisms (Pandey and Madhuri, 2014).

There have been reported cases world over, where large volumes of crude oil and its by-products have been emptied into water bodies either resulting from accidents on the seas or through spillage emanating from exploration activities. The quantity is estimated in the range of 2 to 20 million tons per annum (Nef, 1990). This threatens the existence of aquatic organisms particularly the fishes occupying the surface layer (Khan, 1999). Examples of cases of oil pollution to the water bodies include; Exxon Valdez spill which released about 258,000 barrels of oil into the sea, the Iraq –Iranian war estimated to have resulted in the release of 6million barrels into the high sea, the Gulf war recorded that 711 million barrels of oil was emptied into the sea, while about 85,000 tons of oil was introduced into water bodies from the Braer oil spill (Maki, 1991, Alam, 1993, Ritchie and O'Sullivan, 1994).

Several investigations have shown positive correlation between pollutions from petrochemical effluents and the health of aquatic organisms. The presence of pollutants have been associated with reproductive abnormalities like decreased fertility in fish, altered immune function, increase susceptibility of aquatic animals to various diseases, (Pandey and

Madhuri, 2014). Prolonged exposure to water pollutants even in very low concentrations induce morphological, histological and biochemical alterations in the tissues which may critically influence fish quality. Some chronic effects of diesel oil fractions on gill, liver and spleen have been reported (Alkindi *et al.,* 1996).

Malims (1982) reviewed the structural effects of crude oil and petroleum hydrocarbons on marine fishes and reported increase in the hepatocellular vacuolization in the rough endoplasmic reticulum of the liver, gill damage (for example, epithelial lifting, chloride cell damage and fusion of the secondary lamellae); hyperplasia of the olfactory epithelium, degeneration of olfactory mucosal tissue and development abnormalities.

The rate of hydrocarbon uptake is affected by exposure concentration, molecular weight of the hydrocarbons and the amount of lipid in the fish, which depends on the species, age, season and reproductive state as well as feeding rate and oxygen uptake (Falk-Peterson *et al.*, 1982; Rice, 1985). Interaction of hydrocarbon with lipids could lead to the accumulation of these hydrocarbons in the structural lipids of membranes and disturb the membrane function.

Heavy metals are non-biodegradable and once they enter the environment, bio-concentration occurs in the organisms' tissue which comes in contact with them, (Wicklund-Glynn, 1991). Metal contamination of aquatic ecosystem has been recognized as a serious pollution problem. When fish are exposed to elevated levels of metals in a polluted aquatic ecosystem, they tend to take these metals up directly from their environment (Seymore, 1994). A typical example of such metal is lead which does not break down at all and the body treating it as calcium, incorporates it into bones and teeth. Heavy metal contamination may have devastating effects on the ecological balance of the recipient environment and the diversity of aquatic organisms (Farombi *et al.*, 2007).

Heavy metals such as cadmium, lead, copper, and more specifically, mercury are potentially harmful to most organisms even in very low concentrations and have been reported as hazardous environmental pollutants able to accumulate along food chain with severe risk for animal and human health (Wicklund-Glynn, 1991). Maret and Skinner (1998) reported that bioaccumulation of heavy metals in fish can be at least three orders of magnitude greater than the same element in aqueous phase because the trace elements often sorb to particles surface.

Smol (2002) also reported that older fishes tend to have higher concentration of heavy metals which indicates that animals at higher trophic level of food chain tend to have more concentration of heavy metals in their tissue than those at lower trophic levels. Hill (2007) showed the bio-magnification of organic pollutants PCBs in the Great Lakes food web. Phytoplanktons, a one-celled plants at the base of the food chain bio-accumulated PCBs to a concentration of 0.025ppm. Zooplankton ate enough phytoplankton to accumulate PCBs to levels (0.123ppm) higher than those in phytoplankton. In turn, smelt (small fish) eat enough zooplankton that their PCB level (1.04ppm) was greater than that of the zooplankton. The Lake trout that ate the smelt had higher levels (4.83ppm) still. The eggs of Herring gull (a predatory bird) that ate the fish had a PCB concentration higher than that recorded for the Lake trout, and dramatically greater than that in the phytoplankton (5.25ppm), where the food web was traced from.

Based on these observations, it was concluded that predators of fish, including humans could show very high PCB levels following consumption of contaminated fish. This multiplication would continue throughout the food web until high levels of contaminants are biomagnified in the top predator such that negligible concentration of pollutants that may not have been toxic enough to cause any damage at the lowest level of food chain may become very dangerous at a higher trophic level following bio-magnifications.

The silver catfish, C*hrysichthys nigrodigitatus* is an important, high valued and ubiquitous rainy season fish and sought after for its flavour and taste, Olarinmoye *et al.*, (2009). A research on the species by Lawal *et al.* (2010) in Epe Lagoon showed the percentage food sources of silver catfish to include; diatoms (47.91%), green algae (18.23%), blue-green algae (12.23%), crustacean (9.37%), mollusk (8.92%), plant materials (1.9%), fish parts (1.32%), detritus and unidentified mass were 38.45% and 35.86% respectively. This indicates that *C. nigrodigitatus* is an omnivorous feeder. The wide food spectrum of *C. nigrodigitatus* is an indication of flexibility in trophic level which gives the fish ecological advantage to feed effectively on different categories of diet based on availability of food items (Offem *et al.*, 2009) and hence a higher tendency to bio-accumulate petroleum compounds including heavy metals in their tissues which may bio-magnify over time.

This paper therefore present the heavy metal bioaccumulation capability and hydrocarbon content of the silver catfish from Calabar River, Cross River State.

2. MATERIALS AND METHOD

2.1 Description of study site.

Calabar River is a tributary of the larger Cross River, it is located geographically between longitude 8˚18'E and latitude of 4˚58'3N (Eze and Effiong, 2010) and flows from the northern part of Cross River through the city of Calabar, about 8km south and empties into the main Cross River Course (Cross River National Park, 2010). There are a group of villages surrounding and utilizing the river for fishing and water for agricultural and domestic uses (Eze and Effiong, 2010). The river also serves for transportation of persons and goods to other parts of the country boosting local economy and trade (Otong *et al.*, 2010). Petroleum products are also transported via this route to the neighboring Cameroun.

2.2 Sample collection

ten adults *C. nigrodigitatus* were obtained from different points along the course of the river in the areas bordering the NNPC depot. These samples were preserved in an ice chest to retain their quality. They were taken to Pure and Applied Chemistry Laboratory of University of Calabar.

2.3 Laboratory analysis

2.3.1 Heavy Metals analysis

The fish samples were dissected and eviscerated with knife to separate the bone, gills, kidney, liver and muscles. Each of the separated organs was placed on a foil paper and oven dried at 60°C for 2 days. Dried samples were ground into powder using glass mortar and pestle.

One gram (1g) each of the ground samples was digested with 40% nitric acid and 80% sulphuric acid solutions at ratio of 3:1 mixture. Gentle heat was applied to the mixture on a sand bath and allowed to dry. Cooled digested sample was washed with de-ionized water and filtered. The digested samples were analyzed for the following; Lead (Pb), Iron (Fe), Nickel (Ni), Zinc (Zn), Vanadium (V) and Copper (Cu) using the Perkin Elmer (A Analyst 200) version 6.0 Atomic Absorption Spectrophotometer in the Institute of Oceanography laboratory, University of Calabar. The experiment was replicated thrice.

2.3.2 Total Hydrocarbon Content (THC)

A measurement of 0.2g of ground sample was taken and placed in a test-tube and extracted with 10cm^3 of n-hexane. The set up was allowed to boil for 5mins at 100 °C in a beaker and allowed to cool and separated into layers. The supernatant fraction was analyzed for THC using UV AAS at 430nm wavelength.

2.4 Statistical analysis:

The experiment was laid out in a complete randomized design (CRD). The data obtained were analyzed using ANOVA and descriptive statistics.

3. RESULT

All the samples subjected to both heavy metals and THC analysis recorded varying values for each of the fish sample parts analyzed.

The result of the analysis showed that the concentration of the metals in the organs in the following trend Fe > Pb > Zn > Cu > Ni. The concentrations of V in the organs of the sampled fishes were below equipment detection limit.

4. DISCUSSION

Accumulation of heavy metals was observed to be in the order: Fe > Zn > Ni > Cu > Pb while V was absent in all the organs.

The statistical analysis reveals that there are significant differences in the accumulation of heavy metals in the organs of *C. nigrodigitatus*. This means that all the organs of *C. nigrodigitatus* had affinity for all but one (valadium) of the heavy metals examined. Therefore, consumption is not restricted to a particular organ but then activities that introduce high amounts of heavy metals into the Calabar River should be controlled.

From the results, it is observed that the muscle accumulated the highest concentration of hydrocarbons followed by the gill. In bone, liver and the kidney, no significant concentrations were observed or detected. According to Moe and Skeie (1994), petroleum hydrocarbons in sediments or water may rapidly be taken up by fish, either by transport across cell membranes-of skin and gills, or dietary by contaminated food.

Accumulation of hydrocarbons in the muscle and gill of *C. nigrodigitatus* could be attributed to its diet or feeding habits and trophic significance. This indicates that significant quantities of hydrocarbons enter the Calabar River and one of the sources is the oil depot around the river. However, these organs (muscle and gills) can act as indicators of exposure to hydrocarbons.

5. CONCLUSION and RECOMMENDATION

Chrysichthys nigrodigitatus, an important food fish prevalent in the Calabar River accumulates significant levels of heavy metals and hydrocarbons in its tissues and organs to the detriment of its development and reproductive processes and human consumers.

Calabar River should therefore be protected from heavy metal and hydrocarbon pollution by ensuring strict compliance by Companies to environmental laws.

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Table 1: Mean concentrations of some heavy metals in tissues of C*hrysichthys nigrodigitatus* from Calabar river

Organs	Metals					
	Cu	Fe	Pb	Zn	Ni	V
Bone	0.005 ± 0.002^{a}	0.050 ± 0.030^{a}	0.011 ± 0.003^{a}	0.026 ± 0.002^{a}	BDL	BDL
Gill	0.007 ± 0.003^{b}	0.061 ± 0.040^{a}	0.016 ± 0.002^{b}	0.012 ± 0.001^{b}	0.003 ± 0.002	BDL
Kidney	0.016 ± 0.001^{c}	0.062 ± 0.030^{a}	0.033 ± 0.003^{c}	0.034 ± 0.003^{c}	BDL	BDL
Liver	0.021 ± 0.002^{d}	0.104 ± 0.135^{a}	0.043 ± 0.001^{d}	0.036 ± 0.001^{d}	BDL	BDL
Muscle	0.009 ± 0.002^{e}	0.053 ± 0.001^{a}	0.014 ± 0.005^{e}	0.036 ± 0.006^{e}	BDL	BDL
Mean	0.011 ± 0.064	0.066 ± 0.056	0.023 ± 0.013	0.028 ± 0.009	-	-
Who Limit	3.0	0.3	-	10 -75	0.6	NA

Values are in mean ± standard deviation, BDL – Below Detection Limit
Means with the same superscript are not significantly different ($p> 0.05$).

Table 2: Total hydrocarbon content in the different organs of C*hrysichthys nigrodigitatus* from Calabar river.

Organs	Concentration (Mg/l)
Bone	-
Gill	0.011
Kidney	-
Liver	-
Muscle	0.015

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