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Assessment of Heavy Metals and Total Hydrocarbon Content in Tilapia *(Oreochromis Aureus)* from Ibaka River, Nigeria

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Abstract: *This study was carried out to assess the concentrations of Pb, Fe, Cd, V, Hg and Total Hydrocarbon Content (THC) in Tilapia (oreochromis aureus) from Ibaka river during 2018 wet season. The fish specimens (60) collected were processed and analyzed for Heavy metals and Total Hydrocarbon content using atomic absorption spectrophotemetry (AAS) and GC – FID respectively. The Chronic Daily Intake (CDI) and Hazard Quotient (HQ) of heavy metals concentrations were evaluated using standard equations. Generally, level of metal concentrations (mg/kg) forFe (0.69 + 0.04 – 0.98 + 0.12), Pb (0.49 + 0.10 – 0.92 + 0.14), Ni (0.47 + 0.01 – 0.95 + 0.34), V (0.01 + 0.00 – 0.0 + 0.01), Cd (1.027 + 0.35 – 1.092 + 0. 45), Hg (0.01 + 0.00 – 0.01 + 0.00) in the fish far exceeded the WHO and FAO maximum and permissible limits. Only the Hazard Quotient (HQ) of Cd (1.046 – 1.091) in all species of tilapia was greater than 1 (Cd>1) and this may pose serious health problems to consumers of fishes from Ibaka river. The mean level of total hydrocarbon content (THC) (0.952 + 0.21 – 1.065 + t0.25) pp$_m$ in tilapia specie, were persistent and significant (P>0.05) higher between locations especially from the month of August to October, 2018. Thus tilapia specie from Ibaka river for now may not be safe for human consumption. The Government should as of a matter of urgent importance and national concern ban chemical fishing and put a stop to indiscriminate disposal of organic and inorganic pollutants into Ibaka environment.*

1. INTRODUCTION

Tilapia species may face severe extinction in Ibaka River in future probably due to metal and oil pollutions. These type of pollutions hold a major potential hazard to surface water and fish and consequently to all living things. According to Davies *et al* (1983), heavy metals pollution can alter quality of water bodies by increasing the odour, colour, pH, BOD and $P0_4^{3-}$ and make them unfit for drinking. Heavy metals on the other hand can disrupt natural quality of fish and fish tissue (Abu*et al* 2012), increase fish disease and mortality (Saxena *et al* 2018), influence physiological rates of fish reproduction (Korisiakpere and Ubogu, 2001).

The results of heavy metals bioaccumulation in various species of tilapia fish – *Heterotis niloticus, orechromis niloticus, clarius niloticus, orechromis aureus* reporled within Niger Delta show the pollution level as manifesting higher presence of Ni, Pb, Hg, Cd, V, Fe, Zn, As (Udosen 2014, Chinda *etal* 2005, Alinor 2009, Akpanyung *et.al* 2016, Edem *et.al* 2009, Ayotunde*etal* 2012). These results indicated the possibility that deleterious impacts could evolve after a long period of consumption. Heavy metal normally degradesasthey are persistent, stable, toxic and non-biodegradable. Except Ni, Fe, Zn, others such as Hg, Cd, Pb have no known biological functions in living organism whatsoever, thus in fish they exhibit extreme toxicity at low concentration (Hu, 2002), and can cause health problems and death. Construction firms, boatyard, commercial trading posts, naval base and modern seafood market dotted along Ibaka river bank may be the main source of metal generating wastes that tend to impact negatively on Ibaka river environment. Waste from these sources can bi-concentrate in seafood species, and in fishes to levels in excess of public health standard and can present a health hazard to those eating them.

Oil pollution of Ibaka river may have occurred through oil spillage, crude oil production, cleaning of storage tanks. Total Hydrocarbon Content (THC) consists of a mixture of Aliphatic Hydrocarbon (AH) and Poly Aromatic Hydrocarbon (PAH). Aliphatic Hydrocarbon contains phenol, hexene, toluene, xylene, naphthalene etc. (ATSDR, 1999) while Poly Aromatic Hydrocarbon has 21 components out of which 7 of them are classified carcinogenic. These are benz(0)anthracene, benz (0) pyrene Bap, Indo [1,2,3, - Cd] Pyrene (IND) dibenz (a, b), anthiacene [DBahA] with BAP as always highest in causing cancer risk. Some of the exposure pathways to cancer risk are through inhalation, fish ingestion and food ingestion. PAH and phenols are one of the ubiquitous sets of chemicals which result from crude oil and abound in the environment. Adult fish may experience reduced growth, reproductive impairment when exposed to crude oil. After all oil related activities leads to elevated levels of total hydrocarbon in seafood from Bonny estuary (Amadi and Braide 2003, Benson *etal* 2001), whereas volatile components like benzene, toluene and other light hydrocarbon are capable of triggering pneumonia, damaged red blood cells, suppress immune system, strain liver, spleen and kidney (Okeogbu, 2006).

Monitoring of Total Hydrocarbon Content and Heavy Metal in tilapia from Ibaka river has never been reported. Thus continuous monitoring and assessment of both inorganic and organic pollutants in tilapia fish from Ibaka river form the basis of this work.

2. Study Area

Ibaka river lies from latitude 4038' 0" N to 40 42' 0" N and longitude 80 18' 0" E to 80 19' 0" E coordinates within Mbo Local Government Area (Fig I) of Akwa Ibom State. It borders vertically the eastern flank of Cross River and occupies a considerable length of littoral portion of Atlantic Ocean far beyond the low water mark.

The area is characterized by dry season (November – April) and wet season (May – October). Along the coast, the rainfall is heavy above 3000mm than along the fringe that records 2000mm. The area experiences an average temperature which varies between 26oc and 28oc with a maximum temperature of 30.3oc and a minimum of about 4.1oc. The relative humidity varies between 75% and 85% while salinity fluctuates significantly. Ibaka river has a natural depth of (11-16m), water current velocity (6.2-9.5cmsec-1) and water transparency (30.30-52.81cm) as reported by Umar (2012). Ibaka river also has a long stretch that opens into gulf or Guinea and the water is brackish and highly saline. Ibaka river contributes significantly to food availability and security, trade and improved living standard as well as preservation of biodiversity. It is a good nursery ground for cultivation of tilapia and breeding of different fish and sea food species for fishermen.

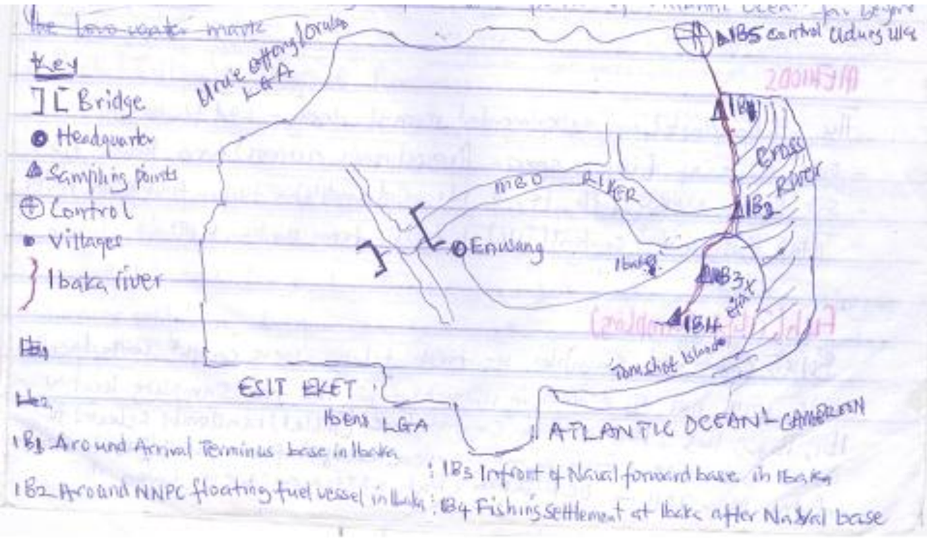

Fig1. *Showing Sampling Locations*

Table1. *Sampling Locations and Their Coordinates on Ibaka River for Fish Samples*

Locations	Code	Samples	Sampling Coordinates	Parameter Measured	Human Activities
Around arrival terminus base in Ibaka.	IB_1	Tilipia	No. 4^{o}39 09.2" E 008^{o} 18' 53.5"	Heavy metal/THC	Dumpsites, fuels stations,abattoirboat and oil operating companies.
Around NNPC floating fuel vessel in Ibaka	IB_2	Tilipia	N 04 39.04.7" E 008 19.23.7"	Heavy metal/THC	Chemical fishing, fuel supply.

In front of naval forward base in Ibaka.	IB_3	Tilipia	N 04 43.23.9” E 008 16.56 22”	Heavy metal/THC	Naval, and maritime operations, lumbering activities.
Fishing settlement immediately afternaval base.	IB_4	Tilipia	N 04 39 13.2” E 008 19 50 9”	Heavy metal/THC	Boat construction, chemical fishing, sand excavation.
Nung Uko.	IB_5(control)	Tilipia	N 0E 37 13.5” E 008 22 40.8”	Heavy metal/THC	No fishing, calm water.

3. Material and Methods

3.1. Materials

The instruments include; 6890 Angilant Gas Chromatograph Induction Detector and a computerized inductively coupled plasma spectrometer (ICP) Optima 300 Permer Elmer). All reagents were of Analar grade.

3.2. Methods

The study adopted an experimental research design and focused on;

- One type of tilapia specie (*Oreochromis aureus*) from Ibaka river
- Six heavy metals (Pb, Fe, V, Ni, Cd and Hg) in tilapia from Ibaka river.
- Total Hydrocarbon content (THC) of tilapia from Ibaka river.

3.2.1. Fish (Tilapia Sampling)

Sixty (60) samples of fresh tilapia were caught with locally made wire net of 2.5mm in diameter from the four sampling locations IB1, IB2, IB3, IB4 and a control IB5 (Table 1) randomly selected to cover Ibaka river. Fish samples were caught from Ibaka in wet season from May 2018October 2018. Fish specimen were taken in polythene bags and stored in a deep freezer at 10oC in a fishery store for proper identification. The length of tilapia species varies between 20.4 and 29.5cm SL and mass from 210 and 340g were measured and weighed respectively prior to treatment and analysis.

3.2.2. Fish (Tilapia Samples) Treatment

The tilapia samples were allowed to defrost and the whole body chopped with a clean stainless steel knife on a wooden cutting board and mixed to homogeneity. The samples were dried to constant weight in an oven at 105oC and crushed in clean mortar with piston.For metal extraction quantities 5g each of whole fish samples were digested using 0.02 MHNO3 and HCl in the ratio 1:3 (aqua regia) in a fumed cupboard at 80oC. For total hydrocarbon extraction about 5g of each dried and ground sample spiked with squalene and C32 – alkane were serially extracted with methyl isobutyl ketone (Analargrade). The solvent was allowed to settle and later centrifuged and decanted. The extracts were concentrated on a rotary evaporator and maintained at 20oC to volume of about 5mL.

3.2.3. Fish (Tilapia) Laboratory Analysis

Parameter	Standard Analytical Procedures	Author/Bodies Describing the Procedures
Heavy metals	Digestion, Extraction, Filtration Atomic Absorption Spectrophtometry using Computerised inductively coupled plasma spectrometer (ICP) optima 3000 (Perkins Elmer) model.	ASTM (1964), AOAC (1996)
Total Hydrocarbon content	6890 Gas Chromatograph Flame Induction Detector (GC – FID).	ASTM (1964)

Heavy metals Pb, Fe, V, Ni, Cd and Hg in whole tilapia specimens were analyzed using a computerized inductively coupled plasma spectrometer (ICP) optima 3000 (Perkins Elmer) model while Total Hydrocarbon Content were analyzed using 6890 Angilant Gas Chromatograph induction detector (GC – FID): Concentrations of Total Hydrocarbons Contents were quantified relative to the total peaks and were converted to weights using hydrocarbon standard calibration. Blank analyses were carried out and all the values, were computed for corrections.

3.2.4. Fish (Tilapia) Statistical Analysis

The data obtained were collected and subjected to mean, standard deviation and one way analysis of variance. The ANOVA and Duncan's Multiple Range Test (DMRT) was used to assess whether heavy metals concentrations varied significantly between locations, while the Chronic Daily Intake (CDI) and the Hazard Quotient (HQ) of heavy metals in tilapia species were evaluated using standard equations.

4. Results

In (Table 2) the results of heavy metals presence in tilapia shows average bioaccumulation levels as Fe (0.83 + 0.21mg/kg), Pb (0.7+ 0.19mg/kg), V (0.1 + 0.00 mg/kg) Ni (0.67 + 0.15 mg/kg), Cd (0.59 + 0.12mg/kg) and Hg (0.01 + 0.00mg/kg).

Table2. *Average concentration of Heavy Metals (mg/kg) in Tilapia from Ibaka River caught in Wet Season at all locations.*

Sampling Periods	Iron M+-SD	Lead M+-SD	Cadmium M+-SD	Vanadium M+-SD	Nickel M+-SD	Mercury M+-SD
April 2018	0.77+ 0.20	0.51+0.10	0.59+0.10	<0.0+0.00	0.62+0.20	<0.01+ 0.00
May 2018	0.69+0.20	0.49+0.10	0.37+0.05	<0.01+0.00	0.55+0.20	<0.01+ 0.00
June 2018	0.74+0.20	0.68+0.10	0.46+0.04	<0.01+0.00	0.47+0.10	<0.01+ 0.00
July 2a018	0.70+0.20	0.72+0.20	0.59+0.20	<0.01+0.00	0.62+0.20	<0.01+ 0.00
August 2016	0.97+0.30	0.84+0.30	0.54+0.20	0.01+0.00	0.71+0.20	0.01+ 0.00
September 2018	0.96+0.30	0.81+0.30	0.78+0.30	0.01+0.00	0.74+0.20	0.02+ 0.00
October 2018	0.98+0.30	0.92+0.35	0.92+0.30	0.01+0.00	0.95+0.30	0.03+ 0.00
Mean	0.83+ 0.21	0.71+ 0.19	0.59+ 0.12	0.01+ 0.00	0.67+0.15	0.01+ 0.00
IB_5(Control) max. Limit	0.28+0.04	0.04+ 0.01	0.42+ 0.08	<0.01	0.25+0.01	<0.01
WHO max. Limit (2011)	0.30		0.2		0.4	<0.01
FAO (2007)		0.05	0.5	<0.01	0.4	<0.01

Average values are of triple determinations + SD, N=3

Table3. *Risk Assessment values of Cd in Tilipia from Ibaka River in the Wet Season between locations*

SAMPLING PERIOD	**LOCATIONS**				
	IB_1	IB_2	IB_3	IB_4	IB_5 (control)
Early wet season (2018).HQ	1.081	1.059	1.080	1.046	0.523
Late wet season (2018).HQ	1.091	1.065	1.087	1.051	0.525

Note: HQ > 1 pose high risk, HQ < 1 pose little or no risk (Yi *et al* 2011).

Standard Equations used are:

$$CDI = \frac{EF \times ED \times FIR \times C \times 10^{-3}}{EW \times AT} \quad (1)$$

$$HQ = \frac{CDI}{RFD} \quad (2)$$

Where CDI = Chronic Daily Intake

HQ = Hazard Quotient.

RFD = Oral Reference Dosage of Cd (mg/kg / day) = 5 x 10^4 (USEPA, 2005).

EF = Exposure frequency, Ingestion rate = IR

ED = Exposure duration Concentration = C

BIO = Average body height, AT = Average time for non-carcinogens.

HQ for Fe, Pb, V, Ni and Hg calculated were all less than 1 and so posed little or no threat, but the standard equations showed that only Cd recorded Hazard Quotient greater than 1 i.e HQ>1 for all species of tilapia (Table 3).

TABLE4.*Concentrations (P^{pm}) of Total Hydrocarbon Content (Thc) in Tilapia Fish from Ibaka River Caught in Wet Season 2018.*

SAMPLING			**LOCATIONS**		
Periods	**IB_1**	**IB_2**	**IB_3**	**IB_4**	**IB_5 (Control)**
April 2018	1.046 + 0.24	0.964 + 0.20	0.953 + 0.15	1.041 + 0.20	0.001 + 0.000

May 2018	1.045 + 0.22	0.963 + 0.20	0.950 + 0.20	1.040 + 0.25	0.003 + 0.001
June 2018	1.065 + 0.24	0.961 + 0.17	0.941 + 0.15	1.062 + 0.30	0.005 + 0.001
July 2018	1.042 + 0.20	0.958 + 0.15	0.944 + 0.20	1.038 + 0.18	0.003 + 0.001
August 2018	1.081 +0.025	0.976 + 0.16	0.965 + 0.25	1.074 + 0.20	0.004 + 0.002
Sept. 2018	1.087 + 0.30	0.969 + 0.18	0.954 + 0.18	1.076 + 0.28	0.009 + 0.003
Oct. 2018	1.091 + 0.45	0.972 + 0.19	0.959 + 0.16	1.082 + 0.35	0.009 + 0.003
Mean	1.065 + 0.25	0.966 + 0.17	0.952 + 0.21	1.059 + 0.20	0.006 + 0.002
WHO 0.01 (PP^{m}) (2011).	0.01	0.01	0.01	0.01	0.01

Average values of triple determinations + SD, N = 3.

The total Hydrocarbon content in the tilapia specie were high and showed significant levels from August 2018 – October 2018 at $IB_1$and IB_2locations (Table 4).

5. Discussion

The present study shows that tilapia *(Oreachromis aureus*) metal bioaccumulation preferred Pb, Fe and Cd (Table2). Their concentrations in the tilapia species are significantly (p>0.05) higher than the values recorded for V, Ni and Hg. Pb accumulates most significantly as Lead nitrate (Oladimeji and Offem, 1999) while Cd even as a non – essential heavy metal is potentially toxic to most fish, wildlife particularly fresh water organisms (Eisher, 1985). The source of high level of Fe may arise from corrosion of skunked vessels or boats in the river. Another source could be from allothonous materials from offshore. The highest concentration recorded for V, Niand Hg were (0.01, 0.95 and .01) mg/kg respectively. The little presence of Hg in fish may have come from additive effects of Hg in water while oil spillage is the main source of Pb and V. The significant level of Pb, Fe and Cd in tilapia from the month of August to October 2018 could be traced to the domestic effluent and proximity of the Nigerian National Petroleum Corporation (NNPC) floating fuel vessel and the nearby on-shone oil facilities at Unygenge community. This observation agrees with the reports of Olajire and Oderinde (1993) that oil effluent is the main source of Cd.

Comparatively the metal pollution concentration declined drastically from the month of July to April 2018 at all locations especially at the control (Table 2). The comparison of the overall metal concentrations with WHO maximum permission limits shows that tilapia fish species are polluted. The study agrees with earlier work reported by Akpanyung (2006) for tilapia from Ifiayong river and by Edem*etal* (2005)for tilapia from Henshaw Town Beach in Calaber, Nigeria.However the values are lower than similar metals reported by Abidal *et al* (2009) for fishes from Madivala lake in India and for fishes from vial river system in Egypt as reported by Crafford and *Avanant (2006).*Also the Hazard Quotient (HQ) values (1.046 – 1.091) recorded (table 3) are significantly higher. Considering the carcinogenic, mutagenic nature of Cd, tilapia and other fishes may not be same for Cd consumption. However this result is consistent with Amirah *etal* (2003) work in human health risk concentration of metal pollution through consumption of fish.The mean level of Total Hydrocarbon Contents (0.952 + 0.21 – 1.065 +0.25) PP^{m}in the tilapia species investigated (Table 4) when compared with WHO recommended concentration of 0.01 mg/L (Jack *etal* 2005) where high.The elevated hydrocarbon contents at locations IB_1 (1.042 + 0.20 – 1.091 + 0.45) PP^{m} and IB_3 (0.941 + 0. 15 – 0.959 + 0.16) PP^{m} may be due to leak and spills that have occurred during ferrying of engine and gun boats across Ibaka river, usage of generators used for powering saw and fuelling woods at IB_4 (0.958 + 0.15 – 0.972 + 0.19) PP^{m}. Some high level (THC) also noticed at IB_2 (1.038 + 0.18 – 10.82 + 0.35) PP^{m}may be due to leak from storage tanks and leaks from NNPC floating vessel.

6. Conclusion

From the study tilapia fish (*oreuchromis aureus*) from Ibaka river is a metal and oil contamination pathway that could affect human health. The detection of excessive Fe, Cd, Pb and persistence of high level of hydrocarbon in tilapia species from Ibaka River above WHO (2011) maximum limitsis an indication of short and long term chronic accumulation of these pollutants. Thus tilapia fish species from Ibaka River were unsafe for consumption. Government should therefore enact and enforce necessary policies to continually check reckless release of metals effluents and spillage of oil into Ibaka environment.

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