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ASSESSMENT OF HEAVY METALS IN FISHES (Ictalurus Punctatus) FROM RIVER NUN WITHIN TOMBIA AND POLAKU AXIS, BAYELSA STATE

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Abstract: The concentration of the following heavy metals (Fe, Pb, Cd, Cu, & Cr) in fishes (Ictalurus Punctatus) from River Nun within the Tombia and Polaku axis located in Bayelsa State Nigeria was studied. The gills, Kidney, liver, bones and flesh of the fishes after oven dried for 72 hours were ground together into powder. One gram of the ground sample was weighed and digested using aqua regia in the ratio of 3:1 (HNO_3 and H_2SO_4). The sample was then filtered and run in an AAS. The following results were observed and presented in mean ± SEM. For Tombia Fish; Fe recorded a concentration of 1.910± 0.001mg/kg, lead recorded 0.707 ± 0.001mg/kg, Chromium = 0.451 ± 0.001mg/kg, Copper = 0.246 ± 0.001mg/kg, and Cadmium = 0.070 ± 0.001mg/kg. While for Polaku Fish, Fe = 0.128 ± 0.001mg/kg, Pb = 0.004 ± 0.001mg/kg, Cu = 0.002 ± 0.001mg/kg, Cr and Cd were below detection limit. According to the maximum permissible limits stipulated by World Health Organization (WHO), the two fishes from River Nun within the axis of Polaku and Tombia Community are within the range and fit for consumption by humans. But in comparing the two fishes within these two communities (Tombia and Polaku), there is an increase in lead and cadmium (Pb and Cd) for Tombia compared to Polaku which might be as a result of the domestic activities carried out at the bank of Tombia river.

1. Introduction

Fish products are widely consumed in many parts of the world because it has high protein content, low saturated fatty acids, calcium, phosphorus, iron, and trace elements such as copper as well as a fair proportion of the group B vitamins to support good health. Fish accumulate toxic chemicals

such as heavy metals directly from water and diet, and contaminant residues may ultimately reach concentrations hundreds or thousands of times above those measured in water, sediment and food (Goodwin *et al.*,2003; Labonne*et al*.,2001; Osman et al.,2007).

Fish products now account for 30% of the human protein supply in Asia, 20% in Africa, and 15% in Latin America and the Caribbean. Because they are neutrally buoyant, most fishes have less need for a supporting skeleton, and consequently have a higher ratio of muscle to bone than land animals. This characteristic as well as having high levels of protein, essential fatty acids, minerals and vitamins makes them a very valuable and healthy alternative to other meats (Mozaffarian and Eric, 2006).

Fish accumulate toxic chemicals such as heavy metals directly from water and diet, and contaminant residues may ultimately reach concentrations hundreds or thousands of times above those measured in the water, sediment and food. According to Atuanya *et al.,* (2012), the concentration of heavy metals varies with variation in fish species. Also, the concentrations of these elements in the fish could be related primarily to their feeding habit (Farkas*et. al.,* 2003). Cadmium (Cd) is one of the principal heavy metals responsible for causing kidney damage, renal disorder, high blood pressure, bone fracture and destruction of red blood Cells. Human beings have reported to have nausea and vomiting at a level of 15 mg/L of cadmium (Nkpaa et al., 2013).

Lead (Pb) is one of the most dangerous pollutants in our environment which accumulates in the body due to its low rate of elimination. Lead enters aquatic systems from urban, mining and agricultural runoff, atmospheric precipitation, plating processes, and gasoline containing lead that leaks from fishery boats and a variety of natural sources. Pb is known to induce renal tumours, reduce cognitive development, and increase blood pressure and in adults. Other symptoms of Pb toxicity include gastrointestinal disorders and some liver impairment (Strömgren, T. 1998).

On the other hand, heavy metal pollution has turned into a major problem in the ecosystem, it is extending to every part of the world, because it cannot easily be degradable and also it affects the aquatic organisms due to their toxic effects. For the assessment of the level of metal pollution, fish and water sample can be considered as major source in the aquatic environment. The bioaccumulation of heavy metals in the fish samples may be due to the industrial, domestic and agricultural effluents thrust in near water bodies.

There are essential metals and non- essential metals which are toxic to aquatic organisms such as fish. The essential metals are copper, iron, zinc, manganese, while mercury, lead and cadmium are highly toxic metals. Because of high consumption of fish, the heavy metals from the fish sample will penetrate in human body; if it is present at high concentration they will cause many adverse and toxic effects. So the analysis of heavy metal concentration should be very important in commercial and edible fish and water sample to evaluate the various disturbances or serious diseases for human health. Water, temperature, water velocity and clarity, alkalinity and accessible habitation are the most important factors which affect the fishes from one area to another area. Therefore, this study was undertaken to make available information on the proximate values and the current level of heavy metal contamination of fishes in river nun within the viscinity of Tombia and Polaku Community.

2. Materials and Methods

2.1 Study Area

The sampling areas for this study are indicated in the Figures below. Polaku Community is found in the region of Bayelsa located in Nigeria, 468Km south of Abuja, the country's capital. Its geographical coordinates are 5.030287N, 6.281078E.Polaku's Climate is classified as tropical.

There is significant rainfall in most months of the year. The short dry season has little effect on the overall climate. The Koppen-Geiger climate classification is Am. The average annual temperature is 26.7^{o}C in Polaku. In a year, the average rainfall is 2820mm. precipitation is the lowest in January, with an average of 37mm. with an average of 468mm; the most precipitation falls in September. The driest month is January with 37mm of rainfall. With an average of 468mm, the most precipitation falls in September.

Tombia is also situated in Bayelsa State, Nigeria and its geographical coordinates are; 5.001998N, 6.265784E. It has almost the same climatic features as Polaku. It has a tropical climate with significant rainfall in most months of the year. The average annual temperature is 26.5^{o}C in Tombia and average annual rainfall is 2601mm.

2.2 Collection of samples

The Fishes were collected from Polaku and Tombia Community respectively on the 26th of January 2018 around 7am in the morning. They were transported to the Department of Chemical Sciences, Niger Delta University. These fishes were dried in the oven for 72 hours before digestion.

2.3 Names of the fish

The native name of the fish is “Ikpoki”. The common name is “Cat Fish” while the zoological name is “IctalurusPunctatus”

Figure 1: Tombia and Polaku fish (IctalurusPunctatus) from left

Figure 2: Tombia and Polaku River from left

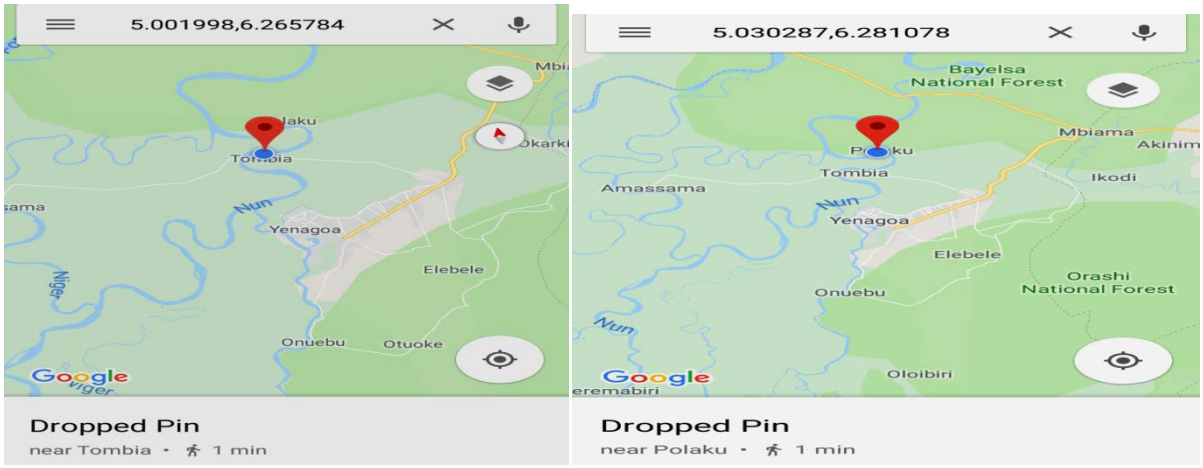

Figure 3: Map Showing the sample location; from left Tombia and Polaku

2.4 Community

Heavy Metals to be determined includes; Chromium (Cr), Lead (Pb), Cadmium (Cd), Iron (Fe), and Copper (Cu).

2.5 Materials and Instruments

They include;Sample (Fish from Polaku and Tombia River), Plastic Container ,Oven, Mortar, Pestle, Spatula, Weighing Balance, Digestion Flask, Digestion Block, Hot Plate, Volumetric Flask, Plastic Bottles, Whatman filter paper, Timer, Atomic Absorption Spectrophotometer (GBC Avanta PM A6600 AAS).
Reagents used are concentrated nitric acid (HNO_3) and Sulphuric acid (H_2SO_4)

2.6 Sample preparation

Fish samples were taken to the laboratory on that day itself. The fish scales were removed where applicable and washed with running tap water to remove sticky substances. The whole body of the different fish, were then separately oven dried at temperature of 70^{o}C for 72 hours.
After drying, portion of the gills, liver, kidney, bones and flesh were mixed together for mastication. These portions were ground thoroughly after which about 1gram of the ground sample was digested with 20ml aqua regia (mixture of nitric acid and sulphuric acid) in the ratio of 3:1 in a 100ml digestion flask and placed on the digestion block in the fume cupboard. This was heated until a clear solution was obtained.
The digested sample was then diluted with 20ml of distilled water and filtered with whatman filter paper; the filtrate was then taken for AAS (Atomic Absorption Spectroscopy) analysis.

3. Results and Discussion

After the sample was analyzed in an AAS (Atomic Absorption Spectrophotometer), the following results were obtained and represented in the table below;

Table 1: Triplicate Values of Heavy Metals Concentration (mg/kg) for fish within the viscinty of Tombia (punctatusIctalurus)

Heavy Metals	**Concentrations (mg/kg) and their triplicate values**		
	First	**Second**	**Third**
Copper (Cu)	0.247	0.244	0.246
Chromium (Cr)	0.450	0.452	0.450
Iron (Fe)	1.912	1.908	1.910
Lead (Pb)	0.709	0.706	0.706
Cadmium (Cd)	0.072	0.068	0.071

3.1 Discussion

From the above data, the mean, mean deviation, variance, standard deviation and standard error were derived and the following mean concentration values were calculated: Thus; results are presented as means ± SEM, and the mean concentration values for Tombia Fish is as follows.

Table 2: Mean Concentration Values of Fish within the viscinity of Tombia (punctatusIctalurus)

Heavy Metals	**Mean Concentration Values (mg/kg)**
Copper (Cu)	0.246 ± 0.001
Chromium (Cr)	0.451 ± 0.001
Iron (Fe)	1.910± 0.001
Lead (Pb)	0.707 ± 0.001
Cadmium	0.070 ± 0.001

From the above data, it was observed that Iron (Fe) has the highest mean concentration in the fish sample with a value of 1.910± 0.001. Iron (Fe) is an essential element in human diet; it forms part of haemoglobin, which allows oxygen to be carried from the lungs to the tissues. Severe Iron (Fe) deficiency causes anaemia in humans. Lead (Pb) recorded a high concentration value after Iron (Fe) with a mean concentration value (ppm) of 0.707 ± 0.0008 followed by Chromium that recorded 0.451 ± 0.0006 and copper (Cu) having a value of 0.246 ± 0.0008. Cadmium (Cd) had the lowest record with a mean concentration value of 0.070 ± 0.0010.

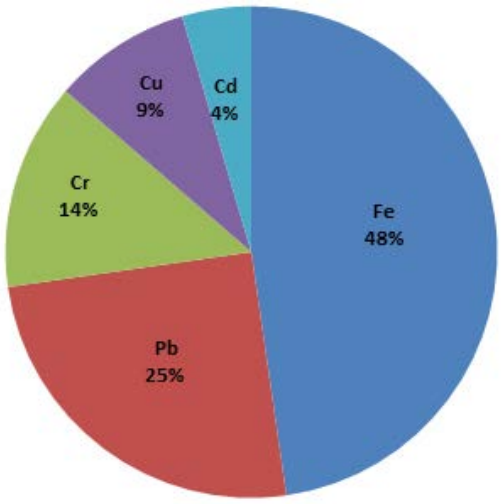

Figure 4: Percentage Concentration Values for Tombia Fish (Ictalurus Punctatus)

Table 3: Triplicate Values of Heavy Metals Concentration (mg/kg) for Fishwithin the viscinity of Polaku(punctatusIctalurus)

Heavy Metals	Concentrations (mg/kg) and their triplicate values		
	First	**Second**	**Third**
Copper (Cu)	0.002	0.004	0.001
Chromium (Cr)	-0.002	-0.001	-0.002
Iron (Fe)	0.128	0.130	0.126
Lead (Pb)	0.003	0.005	0.004
Cadmium (Cd)	-0.001	-0.002	-0.000

Using the above expressions, the same procedure was employed in calculating for the mean, standard deviation and standard error for the Polaku Fish, and all values are expressed in milligram per kilogram (mg/kg).

Table 4: Mean Concentration values for Polaku Fish (punctatusIctalurus)

Heavy Metals	Mean Concentration Values (mg/kg)
Copper (Cu)	0.002 ± 0.001
Chromium (Cr)	BDL
Iron (Fe)	0.128 ± 0.001
Lead (Pb)	0.004 ± 0.001
Cadmium (Cd)	BDL

From the above data, Iron (Fe) recorded the highest concentration with mean value of 0.128 ± 0.001mg/kg in fish within the viscinity of Polaku community, followed by lead having a mean value of 0.004 ± 0.001mg/kg and copper (Cu) having the least mean concentration value of 0.002 ± 0.001mg/kg. Both Chromium and Cadmium were below detection limit ie (they were not detected by the atomic absorption spectrophotometer) and that is the reason why both Chromium (Cu) and Cadmium (Cd) are having negative (-) signs.

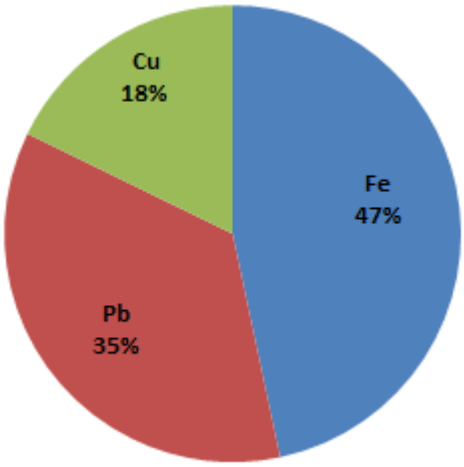

Figure 5: Percentage Concentration Values for Polaku Fish (Ictalurus Punctatus)

Note: Both Cadmium and Chromium were below detection limit (BDL)

3.2 Comparing the Mean Concentrations of Heavy Metals Found in Fishes within the Axis of Polaku and Tombia Community

The variability of the heavy metals in Fish within the axis of Polaku and Tombia community was determined by comparing their mean concentrations using the table below;

Heavy Metals	Mean Concentrations (mg/kg)		Maximum Permissible limits (mg/kg)
	Tombia	Polaku	
Iron (Fe)	1.910± 0.001	0.128 ± 0.001	0.8 (JECFA 2000), 0.5 (WHO 2003)
Lead (Pb)	0.707 ± 0.001	0.004 ± 0.001	2.0 (WHO 1983, FEPA/FAO 2003)
Chromium (Cr)	0.451 ± 0.001	BDL	1.0 (WHO 1983, FEPA/FAO 2003)
Copper (Cu)	0.246 ± 0.001	0.002 ± 0.001	0.5 (JECFA 2000)
Cadmium (Cd)	0.070 ± 0.001	BDL	0.5 (FAO 1983) 2.0 (Int&Nat. Std 2011)

In comparing the order of heavy metal concentrations for the two fishes (Tombia and Polaku), the increasing order for Tombia is; Fe >Pb> Cr > Cu > Cd, while the increasing order for Polaku fish is; Fe >Pb> Cu > Cr > Cd

According to Joint Expert Committee for Food Additives (JECFA), the maximum permissible limits in milligram per kilogram (mg/kg) for Iron (Fe) is 0.8mg/kg (JECFA 2000) and 0.5mg/kg (WHO 2003) and from the data set, analysis showed that the mean concentration of Iron (Fe) in fish within the viscinity of Tombia community is more compared to Polaku community with mean value of 1.910± 0.001mg/kg and this concentration is more than the maximum permissible limit slated by JECFA. But the mean concentration value for Polaku fish is within the maximum range with a mean concentration of 0.128 ± 0.001mg/kg and this value is fit and recommended for human consumption.

Lead (Pb) is classified as one of the most toxic heavy metals; excess of this heavy metal causes renal failure and liver damage in humans. The Maximum permissible limits in milligram per kilogram (mg/kg) for lead (Pb) given by the World Health Organization (WHO 1983), FEPA/FAO (2003) was 2.0mg/kg. From the data above, analysis done showed that mean concentrations of the heavy metal for both fishes (Tombia and Polaku) are within the range slated by these organizations (WHO 1983), FEPA/FAO (2003) with concentration values of 0.707 ± 0.001 and 0.004 ± 0.001mg/kg respectively. But in comparison, Tombia has a higher mean concentration of the heavy metal than Polaku.

Chromium (Cr) is an essential trace metal and the biologically usable form of Cr plays an essential role in glucose metabolism. But when in excess could have an undesirable lethal effect on fish and wildlife (Akan et al., 2009). Deficiency of Chromium (Cr) results in impaired growth and disturbances in glucose, lipid and protein metabolism (Calabrese et al., 1985). The maximum permissible limits given by (WHO 1983), FEPA/FAO (2003) for Chromium to be present in fish is 1.0mg/kg and from the data set above, the mean concentration of Tombia fish is within the range given by (WHO 1983), FEPA/FAO (2003), with mean value of 0.451 ± 0.001mg/kg. But for the case of Polaku fish, the heavy metal (Cr) was below the detection limit during analysis and that is the reason for the presence of the negative sign via the concentration value.

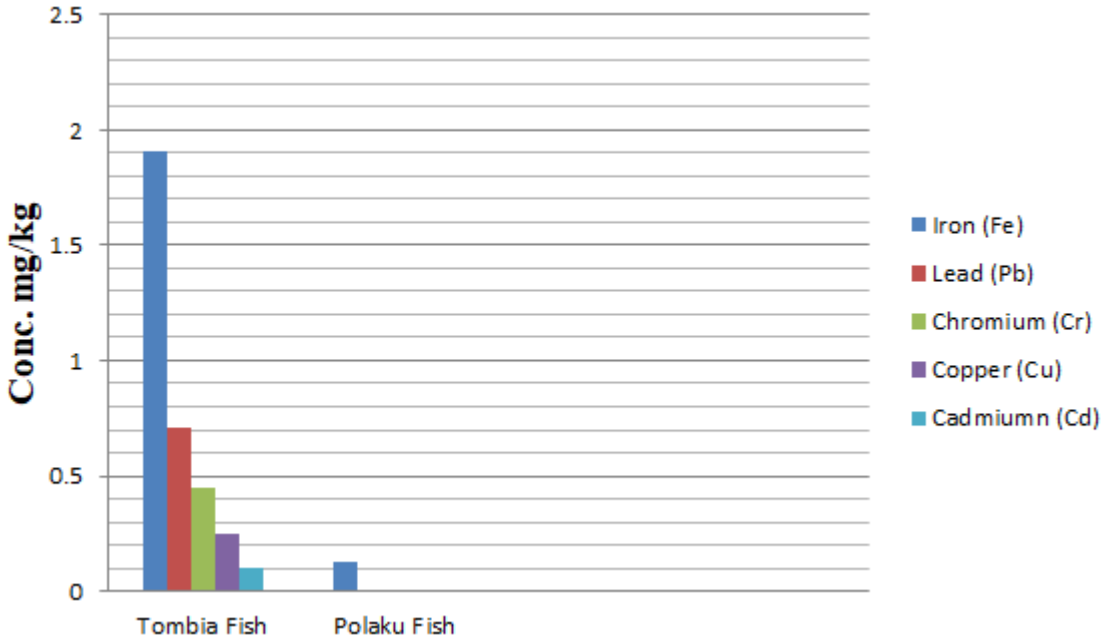

Figure 6: Fish Species (Ictalurus Punctatus)

3.3 A Chart showing the comparison between the Fishes within the Tombia and Polaku Axis

The maximum permissible limit slated by the Joint Expert Committee for Food Additives (JECFA) is 0.5mg/kg (JECFA 2000).Copper (Cu) is an essential part of several enzymes and it is necessary for the synthesis of haemoglobin. From the data set above, analysis done showed that the two fishes (Polaku and Tombia fish) are within the given range with mean concentrations of 0.246 ± 0.001mg/kg for Tombia fish and 0.002 ± 0.001mg/kg for Polaku fish although Tombia fish has a higer concentration than Polaku fish.

Analysis done during the course of this research showed that Cadmium was detected in small amount with a mean concentration of 0.070 ± 0.001mg/kg in Tombia fish while -0.003 ± 0.001mg/kg for Polaku fish signifying that Cadmium (Cd) was below detection limit. Food and Agricultural Organizations (FAO) gave a maximum permissible limit of 0.5mg/kg for the heavy metal (FAO 1983) whereas International and National Standard slated the maximum permissible amount of Cadmium to be present in fish organisms to be 2.0mg/kg (Int. & Nat. Standards 2011)

Lead (Pb) and Cadmium (Cd) are toxic elements which have no significant biological functions and show their carcinogenic effects on aquatic biota and humans even at low exposure. Lead (Pb) exposure is known to cause muscular, skeletal, renal, ocular, neurological, immunological, reproductive and developmental effects. In humans, Cadmium poisoning could lead to anemia, renal damage, bone disorder and cancer of the lungs.

4. Conclusion

In comparing the heavy metals and the maximum permissible limits given by these organizations, it was observed that the fish within the axis of Polaku community is mostly fit for consumption compared to that of Tombia community in the sense that the analyzed heavy metals are within the slated range or in small amounts. The fish caught within the Tombia Community is also fit for consumption but excess concentration of Iron (Fe), Lead (Pb) and Cadmium (Cd) has to be regulated in order to fall within the range. Excess of this heavy metal (Fe) causes life threatening

conditions such as liver disease, heart problems, and diabetes, while lead and cadmium do not have any biological significance to the aquatic ecosystem.

5. Recommendations

The trace of lead (Pb) and cadmium (Cd) in the fish within the axis of Tombia which is not required for food consumption might be as a result of domestic activities carried out in the river and this may be due to contamination of the river by the activities of bike wash operators. Such activities must be controlled in order to maintain and avoid pollution of aquatic life.

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