Concentrations of Selected Heavy metals (Iron, Manganese, Cadmium, Lead, Chromium, and Nickel) in three fish species from Ase River at Kwale, Delta State, Nigeria

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Abstract: **The consumption of fish worldwide has increased speedily in recent years particularly with the awareness of its nutritional and therapeutic benefits. In addition to being important source of protein, fish are enriched with essential minerals, vitamins, and unsaturated fatty acids. However, fish normally accumulate heavy metals from food, water bodies like rivers, lake, stream etc., and sediments and this is a good indicator of heavy metals contamination in water. Concentration of Heavy metal namely Fe, Mn, Cd, Pb, Cr and Ni were found in dominant fish species in Ase River at Kwale. The heavy metal was analyzed by Atomic Absorption Spectrophotometer (iCE 3400 AAS, Thermo Fisher Scientific, USA). It was observed that the relative abundance of the heavy metals was as follows Fe >Mn > Cd>Pb>Cr>Ni. The level of Fe, Mn, Cd, Pb and Cr are higher than WHO Limit for food. High concentration of the heavy metals calls for constant monitoring since the level were found to represent future risk to man who is the consumer. It was revealed that *Clarias garepinus* (African sharp tooth Catfish) and *Channa channa* (Snake head fish) accumulated more heavy metals than *Tilapia mariae* (Tilapia fish).**

***Keywords*: Biomagnification, Biomonitoring, Ecosystem, Fish species, Heavy metals, Pollutants.**

I. INTRODUCTION

Heavy metal pollution in rivers gives threat to public water supplies and also to consumer of fishery sources [1]. Heavy metals constitute a core group of aquatic pollutants via its bio-accumulative and non-biodegradable properties in food [2]. Human may be contaminated by organic and inorganic pollutants associated to aquatic systems by consumption of contaminated fish and other aquatic foods from this environment [3]. Studies on bioaccumulation of pollutants in fish are important in determining different content of trace metal in fish species from bio-magnifications of food chains, metabolic capability and feeding habits [4]. In order to protect aquatic biota, it is necessary to determine contamination levels of trace elements through chemical biomonitoring and evaluation of biomarkers that represent early indicators of biological effect [5]. Certain fish species may be better bioindicators of specific heavy metal contamination compared to others [6,7].

Two main ways by which heavy metals enter the aquatic food chain are by direct consumption of water and food through the digestive tract and non-dietary routes across permeable membranes such as the muscles and gill [8]. Therefore, levels in fish usually reflect levels found in sediment and water of the particular aquatic environment from which they are sourced and time of exposure [5,9]. Absorption through skin contact, for example from contact with soil, is another potential source of heavy metal contamination [10]. Bioaccumulation of any metal above its threshold level invariably result in stress often leading to irreversible physiological conditions [11]. The objective of this research work was to ascertain concentration of the selected heavy metals (iron, manganese, cadmium, lead and chromium) in fish species from Ase river, Delta state, Nigeria and to verify that fishes in the Ase river are fit for human consumption.

Study Area

The area of study is River Ase in Kwale Southern Nigeria. River Ase is located at approximately on Latitudes 5^o 17 and 5^o 53 North of the Equator and Longitude 6^o17 and 6^o 31 East of the Greenwich Meridian [12]. The river is approximately 292 kilometres in length and flows through such settlement as Obekwele Osemele, Iselegu in Delta North Senatorial district to Ivrogbo, Ibredeni, Ase, Kwale and Asaba-Ase in Delta State South Senatorial district.River Ase is a tributary of the Forcados River, the Western branch of River Niger in the Niger Delta region of Southern Nigeria [13].

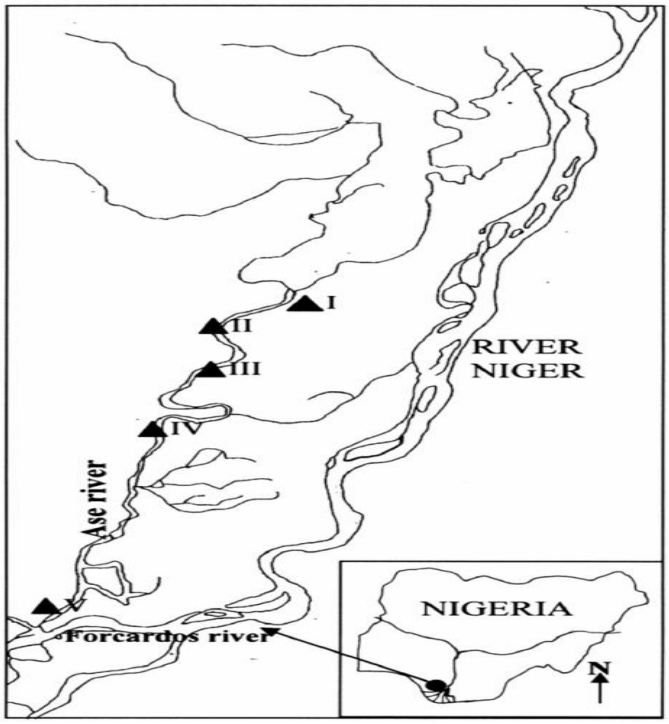

Fig 1: Map of the Ase river showing sampling points.

II. MATERIAL AND METHOD

Equipment

The equipment's are as follows; Conical flasks (Lanexo), beakers (Lanexo), Beam balance (Merck), Electric Oven (Thermocool) Fume cupboard, busen burner, Atomic Absorption Spectrophotometer (iCE 3400 AAS, Thermo Fisher Scientific,USA) Refrigerator (LG), Mortar and pestle.

Reagents

Reagents were analytical grade which include Trioxonitrate(V)acid (HNO_3), Perchloric Acid ($HCLO_4$), $KMNO_4$ (from Sigma Aldrich).

Sample Collection

The Sampling sites were established from the upstream section to downstream section of the river;

Site I (Obetim OB): It represent the upstream section, the visible activities in the site are basically swimming, washing and fermentation of cassava.

Site II (Kwale KW): This point is used s jetty by the Nigeria Agip oil company to ferry their crude oil and petroleum products across the river.

Site III (Ashaka AS): The most visible activities in the site are basically washing, fermentation of cassava, motor car mechanic spots at the bank of the river and swimming. The site was used as inland port in 18^{th} and earlier 19^{th} century.

Site IV (Igbuku IG): The primary activities in this site are commercial sand dredging, washing and fermentation of cassava.

Site V (Asaba ASE): This is downstream section of the river; it serves as local jetty for transportation of goods from the inland area to the deep coastal area of the Niger Delta. This point is also used as jetty by local petroleum dealers in the coastal zone. The traffic densities of speed boats are quite high in this site.

5 Samples of each fish species was collected using gill net from October to November 2015. Each fish was washed with river water to remove adhering debris. The collected fish species were *Clarias garepinus, Channa channa and Tilapia mariae.* The fish species represent different biotopes (Table 3) were immediately preserved on ice in an ice chest and transferred to the laboratory where they were classified, weighed, with total length recorded and kept frozen at -20^0 C until further analysis. Identification of fish to species was done by a specialist from Department of Fisheries, Delta State University Abraka (DELSU), Delta State, Nigeria.

Determination of Metal Concentration

The fish samples were rinsed with distilled water and scales of *Tilapia Mariae* was removed and digested by the method described by Voegborlo *et al* [14]. The fish samples were pounded using mortar and pestle. 2g portion was weighed into a beaker. The beakers were labeled according to the samples it contained. 20ml of concentrated nitric acid (HNO_3) was added to each of the samples. After 5 minutes, 2ml of concentrated per chloric acid ($HClO_4$) were added to each of the sample at ratio (10:1) i.e., HNO_3(65%) and $HCLO_4$ (30%). The mixture was heated at 60^oC for 30 minutes with constant stirring, in a fume cupboard to attain a uniform mixture with the liberation of nitrous gas (NO_2). The complete digest was then cooled down to room temperature and made up to 100ml scale with distilled water and analyzed for Fe, Mn, Cd, Pb and Ni using Atomic Absorption Spectrophotometer (iCE 3400 AAS, Thermo Fisher Scientific, USA)

Quality Assurance

All the reagents used were of analytical grade. Glass wares were soaked in 10% nitric acid for 24 hrs. and rinsed with distilled water followed by 0.5% (w/v) $KMNO_4$ solution and finally with distilled water. Accuracy and precision were verified by using reference material (CRM IAEA 407) provided by the International Atomic Agency (IAEA). Analytical results of the quality control samples indicated a satisfactory performance of heavy metal determination within the range of certified values 95–101% recovery for the metals studied.

Statistical Analysis

All analyses were performed in triplicate. Statistical data analyses of the results were performed using GRAPH PAD INSTAT AND PAST WINDOWS 2010 (computer package).

The means of the replicates and evaluation of significant differences between different samples were determined using descriptive statistics and analysis of variance (ANOVA), respectively. Two-way and one-way analysis of variable (ANOVA) were used to test for significant differences in the concentrations of heavy metals in the samples and the sites. For comparison of means, ANOVA test and post hoc Duncan test were used. Results of the test were considered significant if the calculated P values were ≤0.05. Pearson correlation was used to examine the relationship between the elements in fish.

III. RESULT AND DISCUSSION

The concentration of heavy metals Iron (Fe), Manganese (Mn), Cadmium (Cd), Lead (Pb), Chromium (Cr) and Nickel (Ni) in the fish species have been analyzed using AAS, the results in mg/kg shown in table below:

Table 1: Heavy metals in fish species (mg/kg) from Ase river at Kwale and FAO/WHO limit for food

Concentrations of metals (mg/kg) in different species							
Heavy metals	*C.gariepinus*	*T. mariae*	*C. channa*	FAO (2011)	FAO/WHO(2003/2011)	FAO(2003)	WHO/FAO(2011)
Fe	26.875±0.538	10.630±0.213	26.000±0.520	43	-	-	-
Mn	4.670±0.093	2.000±0.040	3.830±0.076	-	5.5	-	-
Cd	2.000±0.040	1.250±0.025	2.630±0.053	-	-	0.05	0.5
Pb	2.250±0.045	0.500±0.010	1.300±0.030	-	1.0	0.2	-
Cr	0.800±0.016	0.300±0.006	0.800±0.016	-	-	2.0	-
Ni	0.240±0.005	0.160±0.003	0.240±0.005	-	-	-	0.5-0.6

Data are presented as the mean value ±SD

Table 2: Fish Species Ecological Characteristics

Scientific name	English name	Feeding habit	Biotype complex	Number of sample	Length(cm)	Weight(g)
Tilapia mariae	Tilapia fish	Omnivorous/Herbivore	Pelagic	5	16.26- 17.01	109.34- 112.92
Clarias gariepinus	African sharp tooth catfish	Carnivores	Benthnic	5	27.80 – 41.00	150.34 – 458.03
Channa channa	Snake head fish	Carnivores	Benthnic	5	23.50 – 33.10	100.10- 416.24

The concentrations of iron, Manganese and Cadmium in the fish species obtained from Ase River are shown in decreasing order as Fe >Mn> Cd>Pb>Cr>Ni.

The study revealed that *Clarias gariepinus* and *Channa channa* accumulates more heavy metal in its tissue because of its feeding habit as a carnivorous. The fish *(Clarias gariepinus* and *Channa channa*) picked the metals up mainly from the site II (Kwale KW) and site V (Asaba ASE) where the activities of Nigeria Agip oil company in the ferrying of their crude oil and petroleum product across the river and the actions of local petroleum dealers in the coastal zone.

The intake of heavy metals in *Tilapia mariae* was low when compared with other species as a result of the feeding habit (omnivorous and herbivorous) it acquired fewer heavy metals in its tissues. Fish were collected covering different feeding habitat as shown in Table 2. The result showed that fish exhibited wide range of variation in interspecific metal concentration in all the tissues.

Iron is an essential element required for growth and survival [15]. Fish is a major source of iron in the human diet and it is reported that iron deficiency causes anemia [16]. Iron concentration in fish species from Ase river is higher in *Clarias gariepinus*(African sharp tooth catfish) at 26.875mg/kg and lowest in the *Tilapia mariae* at 10.630 mg/kg shown in the Table 1. It is below FAO limit for food [17]. The Iron concentration in the fish species analyzed ranged from 10.630 mg/kg to 26.875 mg/kg (Table 1). Iron level (44mg/kg) in the fish from Densu River at Weija District in Grater Accra Region of Ghana [18] revealed that the concentration of Iron in fish species from Ase River were lower in concentration.

Manganese is an essential trace element for both animals and man, necessary for the formation of connective tissue and bone, growth, carbohydrate and lipid metabolism, embryonic development of the inner ear, and reproductive function WHO [17] and DWAF [19]. The concentration of manganese measured in this study varied from 4.670mg/kg to 2.000mg/kg according to (Table 1). The maximum manganese value was present in *Clarias gariepinus*(4.670mg/kg). The lowest concentration was detected in *Tilapia mariae*(2.000mg/kg). For all the sample analyzed and irrespective of species the concentration of manganese in fish sample were below FAO/WHO [17,20] limit(5.5mg/kg).

The Mangenese level reported in fishes from Ogun River, Southwest Nigeria is high ranging from (11.48mg/kg to

5.04mg/kg) [23] when compared with the result from fish species from Ase River. The Mn level according to [21] which is 1.10mg/kg is lower when compared with the fish species from Ase river Delta State. The Manganese pollution at Ase river could be attributed to crude oil mining and industrial effluent from oil and gas companies located around the river, such as Agip oil company.

Cadmium is widely known to be a highly toxic non-essential heavy metal and it does not have a role in biological process in living organisms [18]. Thus, even at its low concentration, cadmium could be harmful to living organism [22]. Nevertheless, the level of cadmium detected in the fish species from Ase river ranged from 1.250mg/kg to 2.630mg/kg with *channa channa* (2.630mg/kg) the highest in level and *Tilapia mariae*(1.250mg/kg) lowest in concentration. Equally, the level of the cadmium in fish sample analyzed is higher than WHO/FAO [17] limit for food. The presence of cadmium in human diet could cause disorder in genes carrying chord or nerves, respiratory tract disease and bone malformation.

In this study, lead accumulation in the fish species is relatively high with less concentration in *Tilapia mariae*. However, the concentration ranges from 0.500 mg/kg to 2.250 mg/kg which exceeds WHO/FAO [17,20]. *Clarias gariepinus* had highest lead concentration than others(2.250mg/kg). Ayanda *et al* [23], reported high concentration of lead in fish from Ogun River, as 15.5 mg/kg on the gill as a result of industrial activities in Ogun State. The lead concentration according to [24] varied from 0.004 to 0.05 mg/kg from fishes in Galas River Malaysia is lower than the Pb concentration found in fish species from Ase River.

Nevertheless, non – essential metals like Cr is not known to play any metabolic function although, as a consequence to their bioaccumulation in fish, these metals can be toxic for humans, even at very low concentration [25]. Chromium concentration range from 0.300mg/kg to 0.800mg/kg which exceeds FAO limit for food [20]. The highest level is found in *Clarias gariepinus* and *Channa channa*. The lowest concentration is found in *Tilapia mariae* (0.300mg/kg) Rajeskumar S. and Li. X [25] reported that the level of Cr concentration is 1.0 mg/kg in Taihu Lake, China which is higher than the concentration of Cr found in Ase River, delta state, Nigeria.

Accumulation of heavy metal like Nickel in fish species differ in their metabolic rates, amount of food they consume and food requirement [26]. Moreover, presence of Nickel in the fish species posed no danger to human health since the concentration fall below the recommended limit by WHO for food (0.5mg/kg to 0.6mg/kg) [17]. The level ranged from 0.160mg/kg to 0.240mg/kg with *Clarias gariepinus* and *Channa channa* had the highest. According to [23] the concentration of Ni in fish species from Ogun River, Southwest Nigeria ranged from 3.88mg/kg to 1.9mg/kg which is higher than the concentration in Ase River, Delta State.

Tilapia mariae had the lowest concentration in heavy metal due to it feeding habit as omnivorous/herbivore and its biotype complex as pelagic as seen in (Table 2). *Clarias gariepinus* had the highest concentration of heavy metals because of its feeding habit as a carnivorous and its biotype complex as benthnic according to (Table 2). *Channa Channa* been a carnivorous according (Table 2) was greater than concentration of heavy metals in *Tilapia mariae* and lower than concentration in *Clarias Gariepinus*.

IV. CONCLUSION

The study revealed that among the fish analyzed *clarias gariepienus* (African sharp tooth cat fish) had the highest concentration of heavy metals, followed by *channa channa* while *Tilapia Mariae* had the lowest.

Manganese, Cadmium, Lead, Chromium are very dangerous heavy metal and their concentration in fish species from Ase River is high and above WHO limit for food. It should be seriously monitored by researchers, health workers and government agencies to curb the adverse effect of these metals on the health of the people. Iron found in the fish samples were above WHO limit for food but though lower than FAO limit for food. High concentration of heavy metal measured in fish species from Ase river were attributed to probable high influx of metals as a result of pollution by oil and gas companies working in the region and domestic waste. Though Nickel level could not be treated or accorded as harmful to human since its concentration falls below WHO recommended limit for food.

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Conflicts of Interest:

The authors declare that they have no conflicts of interest.

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