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Heavy Metal Analysis of Selected Estuarine Fish Species from Oron River, Oron Local Government Area, Akwa Ibom State, Nigeria

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Abstract: Environmental pollution is a worldwide problem, heavy metals belonging to the most important pollutants. The progress of industries has led to increased emission of pollutants into ecosystems. Oron River is one of the most important aquatic environment, which receives effluents discharges from heavily industrialized and highly populated settlements. Metals tend to accumulate in water and move up through the food chain. So, studies to ascertain the level of heavy metals in environment and determine potentially hazardous levels for human are necessary. In this study heavy the heavy metals profile [Lead (Pd), Zinc (Zn), Chromium (Cr), Cadmium (Cd), Iron (Fe)], in sea food with special reference to selected fishes *Hydrocynus lineatus* (African tiger fish), *Chrysichthys aluuensis* (Catfish), *Distichodus rostratus* (Grass eater), *Tilapia guieensis* (Tilapia), *Arius gigas* (Giant sea catfish) using Atomic Absorption spectrophotometer. The heavy metal profile was observed in the order of intestine, gills, skin and Lead, Cadmium, Chromium, Iron and Zinc respectively. Most of the metals were below the maximum allowable levels set by WHO, FEPA and USEPA except Chromium with 1.02 on the gills. This indicates that an urban and industrial waste discharged into Oron River has a significant effect on the ecological balance of the river, which shows that the fish species and seafood from the river are safe for consumption. In conclusion, the levels of heavy metals observed in the fish and water samples can be considered as a serious matter. More safe and economic methods for the elimination of heavy metals from contaminated waters are needed and continuous assessment of the level of pollution of the lake waters and fish with heavy metals is also necessary. Safe disposals of domestic sewage and industrial effluents as well as enforcement of laws enacted to protect our environment are therefore advocated.

Keywords: Environmental Pollution, Heavy Metal, Estuarine Fish Species, Atomic Absorption Spectrophotometer, Oron River, Nigeria

1. Introduction

Heavy metal pollution is of widespread concern for ecological management of streams and rivers. Drainage water from both active and abandoned mines may be the major source of heavy metal contamination in mountain streams. Most field studies of the effects of heavy metals on aquatic organisms, including benthic macro invertebrates, have been conducted in mountain streams of Europe and the Americas, e.g., in Sweden [34], Ireland [22], Spain [41], Colorado [14], Idaho [33], Virginia [15], and Bolivia [46]. In China, the effects of heavy metal pollution are underestimated due to limited research in high mountain areas [21]. There is, however, a pressing need for ecological risk assessments to protect and manage aquatic ecosystems in these areas.

Biomonitoring approaches have been used to assess the effects of contaminants on aquatic organisms since the early 1900s [11]. Most of these researches have focused on responses of benthic macro invertebrates [12]. Benthic macro invertebrate assemblages contain species with various

sensitivities to contaminants and have been widely used to evaluate the ecological impacts of metal contamination in streams [33]. Metal contamination can reduce benthic macro invertebrate species richness, as well as density, growth and production [22, 33]. Heavy metals can be accumulated in the gut and tissues of individuals [41], which can affect predator-prey interactions in macro invertebrate [13] and even fish communities [19] through the food web. The effects of heavy metals on macro invertebrates are highly variable among taxa [30].

Due to their toxicity and accumulation in biota determination, the level of heavy metals in commercial fish species have received considerable attention in different countries. [27, 23]. There has been an increasing interest in the utilization of fishes as bio-indicator of the integrity of aquatic environmental systems in recent years [33, 37]. Fish lie at the top of the aquatic food chain and may concentrate large amounts of some metals from the water. Fish take heavy metals from the primary route for the uptake of water borne pollutants and accumulate them in their tissues [5].

Pollutants accumulation in aquatic areas possess threat to aquatic plant and animals which is the reason for fish population decline in Nigeria [8, 20]. The fish diet is another source of these pollutants in the tissues. It has been reported [41] that copper toxicity in fish is taken up directly from the water via gills and stored in the liver. Therefore they are the most indicative factors for the estimation of pollution and risks potential of human consumption [8, 14]. The concentration of heavy metals were found to be higher in the liver, kidney and gills than in the gonad and muscle tissues of fish species [28, 34, 9].

Hydrocynus lineatus (African tiger fish), Chrysichthys aluuensis (catfish), *Distichodus rostratus* (Grasseater), Tilapia guieensis (Tilapia), Arius gigas (Giant sea catfish), are fresh water fishes they carry out all their activities in fresh water and Oron River, which is the case study is an example of their habitat. The fishes vary in size in their different species and they also vary in their appearances example colour of skin, shape of mouth, dentition, feeding mood and feeding period example *Distichodus rostratus* (Grasseater), some feed on other fingerlings example Hydrocynus lineatus (African tiger fish). All these fish are choice food in Akwa Ibom State, Nigeria.

2. Literature Review

Heavy metal concentrations in fish provide useful and important information with respect to nature of management and human consumption of fish. Generally, heavy metal concentrations in the tissue of freshwater fish vary considerably among different studies [21], possibly due to differences in metal concentrations and chemical characteristics of water from which fish were sampled, ecological needs, metabolism and feeding patterns of fish and also the season in which studies were carried out. In the river, fish are often at the top of the food chain and have the tendency to concentrate heavy metals from water (Carliste and Clement, 2003). Therefore, bioaccumulation of metals in fish can be considered as an index of metal pollution in the aquatic bodies [44] that could be a useful tool to study the biological role of metals present at higher concentrations in fish [33].

The environmental factors affect the uptake and accumulation of metals in fish. According to [24]. Water temperature may cause the differences in metals deposition in various organs. Higher temperatures promote accumulation of cadmium especially in the most burdened organs: Kidneys and Liver [3]. Increased accumulation of metals by fish at higher temperatures probably results from higher metabolic rate, including higher rate of metal uptake and binding. Many data indicate that water acidification directly affect metal accumulation rates by the fish. Comparison of the data concerning metals in fishes from various lakes indicates that the concentrations of cadmium and lead but not zinc are considerably higher in the fish from acidified lakes [4, 18, 2].

Accumulation of cupper is also higher at lower pH [19], we may conclude that water acidification affects bioaccumulation by the fish in an indirect way, by changing solubility of metal compound or directly due to damage of epithelia which become more permeable to metals on the other hand, competitive uptake of H+ ions may inhibit metal absorption. According to [31], enrichment of water with calcium reduced copper accumulation in the gills. Calcium might compete with other metals for binding sites on the gill surface, [31].

Similarly as hardness, also Salinity reduces uptake and accumulation of metals by the fish. According [35], seawater adopted species (fishes) showed lower copper concentration than fresh water-adopted species. Natural waters are usually contained with mixtures of metals and other toxic compounds. Accumulation of certain metals in fish may altered in presence of the others [42, 5, 6, 32].

According to [21] he observed that predatory fish species accumulated more mercury but the benthivores contains more cadmium and zinc. Various species of fish from the same water body may accumulate different amount of metals. Interspecies differences in metals accumulation may be related to living and feeding habits.

In fish, concentrations of most metals (except for mercury) are usually inversely related to the age and size. Measurements of bioaccumulation of Iron, maganese, zinc, copper, nickel and lead by a fish species from a non-polluted impoundment revealed that there was an inversely relationship between metals concentrations and body mass of fish [12].

According to [6], an inverse correlation occurred between the age and size of fish species. Increase in body mercury level with fish age and size is probably related to the affinity of this metal to the muscle tissue [17].

Many authors indicate that metals show different affinity to various organs. The major part of total body loads accumulated at different concentrations of metals in the water and at various exposure times are found in liver, kidney and gills. Also some considerable amounts of concentrations of

metals in the digestive tracts of fishes from natural water bodies [7] such organs as the gonads, bones and brain may also show high metal levels while the muscle comparing to the other tissues usually show low concentrations of metals but are often examined for metal content due to their use for human consumption.

The obvious sign of highly polluted water results in dead fishes but the sub lethal pollution might result only in unhealthy fish. Very low-levels of pollution may have no apparent impact on the fish itself, which would show no obvious sign of illness but it may decrease the fecundity of fish populations leading to a long-term decline and eventually extinction of this important natural resource. [25, 10].

Such low level pollution could have an impact on reproduction, either indirectly via accumulation in the reproductive organs, or directly on the free gametes which are released into the water. Control of reproduction in fish is complex and regulated by a wide range of factors and low-level pollution could affect any part of this pathway. Steroid hormones are very important and play essential roles in maintaining reproductive functions [22, 11]

3. Materials and Methods

3.1. Study Area

The work was carried out in Oron River in Oron Local Government Area, Akwa Ibom State, Nigeria. The river situated within Oron is a major source of water. It serves the people in terms of fishing and farming which is their predominant occupation. There are also deposits of solid minerals such as Iron, Silica or Glass sand and gravels, seafoods such as crayfish, snipers, oyster, periwinkle, fishes, richly in the coastal area.

3.2. Sample Collection

The fish samples hydrocynus lineatus, chrysichthys aluuensis, distichodus rostratus, tilapia guieensis and arius gigas were collected from fresh landing from the artisan fishermen at Oron River. The samples were taken to the laboratory in container with ice blocks to avoid deterioration. The fishes were dissected and their vital organs like the skin, gills and intestine were separated. The Atomic Absorption Spectrophotometer Machine was used to determine the level of Heavy Metals present in each of them.

3.3. Preparatory Procedures

Preparation of Fish Sample
The fish samples were dissected and the vital organs (gills, intestine and the skin) were removed from the fish for analysis, according to the method described by [13]. The various parts were dehydrated in a ventilated drying oven at 100°C until constant weight was attained, then ground into ashes. This is to ensure an increase in the surface area of the fish samples during digestion.

3.4. Digestion Process

The chemical for digestion process was aquarager, it is prepared by a mixture of hydrochloric acid and citric acid in a ratio of 3:1 respectively, prepared in a fume hood to avoid it toxic smell. 0.5g – 2.0g of the ashed samples were dissolved in aquarager and heated on a plate. The solution was filtered and made up to 30 cl with distilled water. The filtrate was used for the determination of trace metals in the Atomic Absorption Spectrophotometer (AAS).

3.5. Statistical Analysis

The obtained data were subject to one-way analysis of variance the (ANOVA) and Duncan's.

Multiple Range Test (DMRT) was used to assess whether heavy metal concentrations varied significantly between stations [29].

4. Results

The result presented in tables 1 and Figure 1 below shows that the heavy metal analysis conducted on the vital organs (skin, gills and intestines) of the following species, *Hydrocynus lineatus* (African tiger fish), *Chrysichthys aluuensis* (catfish), *Distichodus rostratus* (Grasseater), *Tilapia guieensis* (Tilapia), *Arius gigas* (Giant sea catfish), their values indicates that there are trace metals present in Oron River where their activities are carried out.

In *Hydrocynus lineatus*, the intestine has the greatest concentration of lead with 0.04 values while the gills have the less concentration. Cadmium (Cd) affects the skin most (0.04), Chromium (Cr) has greatest effect on gills (1.02) and Iron (Fe) has the most effect on gills (0.62) and Zinc (Zn) on gills (0.04). In *Chrysichthys aluuensis* the greatest concentration of lead is on the intestine (0.05), Cadmium (Cd) affects the intestine most (0.06), Chromium (Cr) has effects on skin (0.08), Iron (Fe) is more concentrated in the intestine (0.52), Zinc (Zn) is more concentrated on the gills (0.06). In *Distichodus rostratus*, the highest level of concentration of level is on the skin (0.11), Cadmium (Cd) is on the skin (0.12), Chromium (Cr) is on gills (0.06), Iron (Fe) is on skin (0.25), Zinc (Zn) is on gills (0.4). In *Tilapia guieensis*, the greatest level of concentration of lead is on skin (0.05), Cadmium (Cd) is on the gills (0.04), Chromium (Cr) is on skin (0.11), Iron (Fe) is on gills (0.82), Zinc (Zn) is on gills (0.62).

In *Arius gigas*, the greatest level of concentration of lead is on skin (0.06), Cadmium (Cd) is on skin (0.07), Chromium (Cr) is intestine (0.08), Iron (Fe) on skin (0.42) Zinc (Zn) on skin (0.12). The different species, the Skin of Distichodus rostratus has the highest level of Lead (Pb) concentration (0.11), *Distichodus rostratus* skin has the highest concentration of Cadmium (Cd) (0.2), gills of *Hydrocynus lineatus* has the highest concentration of Chromium (Cr) (1.02) gills of *Tilapia guieensis* has the greatest concentration of Lead (Fe) (0.82) while the greatest Zinc (Zn) concentration is on *Tilapia guieensis* (0.62). Thus indicating

that   different   metals   have   their   different   level   of   concentration in different species of fishes.

Table 1. *Heavy Metal profile in the different Fish Species in Oron River, Oron, Akwa Ibom State. Nigeria.*

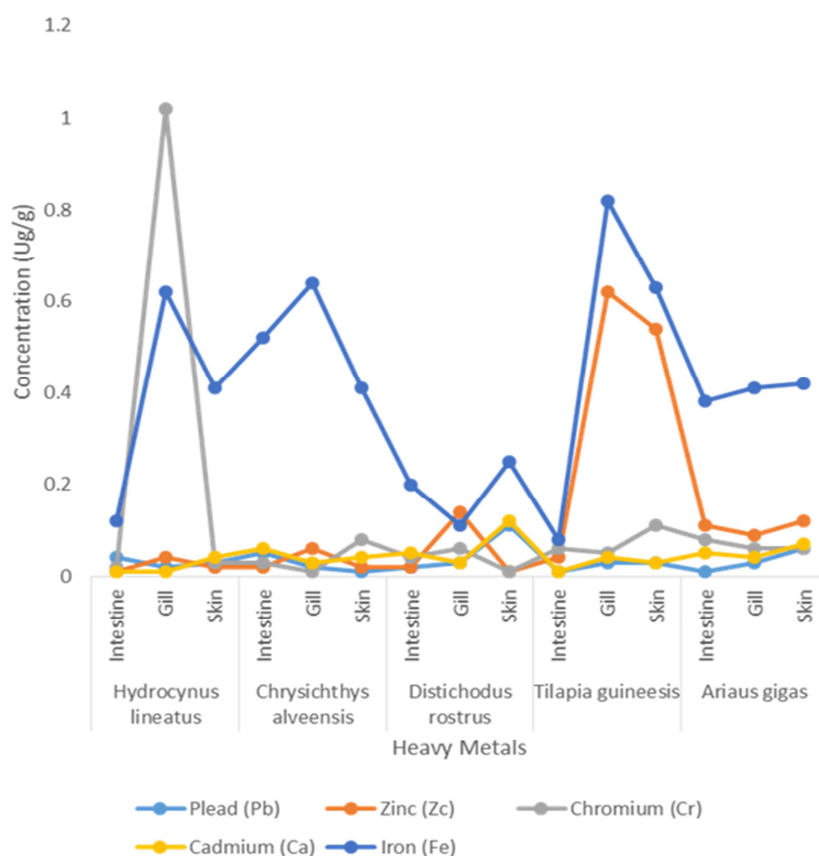| S/N	Fish Species	Organs	Plead (Pb) µg.g⁻¹	Zinc (Zc) µg.g⁻¹	Chromium (Cr) µg.g⁻¹	Cadmium (Ca) µg.g⁻¹	Iron (Fe) µg.g⁻¹
		Intestine	0.04	0.01	0.02	0.01	0.12
1	*Hydrocynus lineatus*	Gill	0.02	0.04	1.02	0.01	0.62
		Skin	0.03	0.02	0.03	0.04	0.41
		Intestine	0.05	0.02	0.03	0.06	0.52
2	*Chrysichthys alveensis*	Gill	0.02	0.06	0.01	0.03	0.64
		Skin	0.01	0.02	0.08	0.04	0.41
		Intestine	0.02	0.02	0.04	0.05	0.20
3	*Distichodus rostrus*	Gill	0.03	0.14	0.06	0.03	0.11
		Skin	0.11	0.01	0.01	0.12	0.25
		Intestine	0.01	0.04	0.06	0.01	0.08
4	*Tilapia guineesis*	Gill	0.03	0.62	0.05	0.04	0.82
		Skin	0.03	0.54	0.11	0.03	0.63
		Intestine	0.01	0.11	0.08	0.05	0.38
5	*Ariaus gigas*	Gill	0.03	0.09	0.06	0.04	0.41
		Skin	0.06	0.12	0.06	0.07	0.42
	WHO (WHO 1985) Specification		0.05	5.00	0.15	0.005	0.30
	FEPA (FEPA 2003) Specification		<1.0	<1.0	-	<1.0	-
	USEPA (USEPA 1987) Specification		0.0058	0.0766	0.05	0.008	0.1

Figure 1. *Heavy Metal in the vital Organs of selected fish species in Oron River, Oron, Akwa Ibom State. Nigeria.*

5. Discussion

The result from the research on trace metals affecting some fish species *Hydrocynus lineatus, Chrysichthys aluuensis, Distichodus rostratus, Tilapia guieensis, Arius gigas* breeding in Oron River, indicates that the river contains trace metals which are harmful to the fishes and also to some extent, human that consume them, if consumed in large quantity. The life span of the fishes, their yield, and their growth may also be affected by the presence of these metals in the water which all their activities take place, however it has not yet

been known whether the fishes in the river have been severely affected by heavy metals based on the results obtained from this study.

Hydrocynus lineatus, Chrysichthys aluuensis, Distichodus rostratus, Tilapia guieensis, and Arius gigas, were examined for Cadmium (Cd), Lead (Pb), Iron (Fe), Zinc (Zn), Chromium (Cr) and they were all present in the water thus affecting in the fishes absorbing them. This indicates pollution in the water by heavy metals caused by different natural and human activities including industrial or domestic waste water, application of pesticides and waste such as fuel, inorganic fertilizers, leaching from landfills, shipping, and harbor activities and atmospheric deposits and geological weathering of the earth crust [45] 2003). From the collected samples of *Hydrocynus lineatus*, the presence of Lead (Pd), Zinc (Zn), Chromium (Cr), Cadmium (Cd), Iron (Fe) is recorded in the intestine, skin, and gills respectively with the highest level of concentration on the gills (1.02 of Chromium) and the lowest level of concentration in the intestine (0.001µg.g-1 of Cadmium). Which is lower than the approved standard by [39, 16].

Chrysichthys aluuensis, shows no effect on heavy metals despite its presence. This is due to the quantity of the metals in the fish. Therefore, *Chrysichthys aluuensis* has met the standard of WHO and FEPA. For *Distichodus rostratus*, the skin has a higher accumulation of Cadmium (Cd) and Lead (Pd) which are above the standards of WHO and could be dangerous to consumers. *Tilapia guieensis* has the standard level of lead concentration by WHO on the skin (0.05µg-g-1) but cadmium and lead have their level of concentrations on the organs higher than the normal standard from WHO [39] and might be of effect to fishes consuming them [33]. In *Arius gigas*, the level of zinc and cadmium concentration is lower in the fish organs, lead and iron is of standard while cadmium was detected with a high level of concentration on the gills, skin, and intestine.

From the laboratory experiment on the fish samples, it is detected that the skin and the gills have the greatest effects of metal concentrations on them compared to the intestine. This is so because the skin and the gills have direct contact with the water body which is already contaminated, this results from the gills and skin being at the surface while the intestine has a little or less contact with the water body thus decreasing its contamination level. This contamination if not controlled might be of harmful effect to consumers of sea food from Oron River and it could also reduce the yield of the plants around the River.

6. Conclusion

The result showed that the Oron River, Oron, Akwa Ibom State, is polluted by minerals and heavy metals which are highly accumulated in fishes. The result shows a little or no effect on the consumers of sea food and water from this stream but the possibility of deleterious effect after long period cannot be ruled out. This is as a result of the fact that this water body serves as the receptor for domestic waste as well as runoff from agricultural lands where phosphate fertilizers and other agrochemicals are frequently used. The level of heavy metals in different fish organs are disturbing because of the health implications on the people depending locally on sea food and their requirements. There is therefore the need for continual assessment of the level of pollution of this stream with metals from the mentioned sources with a view to reducing the level of pollution by education and public enlightenment.

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