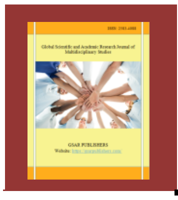

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Seasonal variation in concentrations of heavy metals in catfish (*Clarias buthupogon*) from River Oluwa and River Owena, Southwestern, Nigeria

BY

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Abstract

Fish represents one of the main sources of the exposure of people to heavy metal toxicity, and it is the main source of trace elements in the human diet. Most of the human health risk related to fish consumption is associated with metal-contaminated fish. In this study, concentrations of Fe, Cu, Mn, Cr, Zn, Hg, Pb, Cd, Ni, and Ni were determined in catfish (Clarias buthupogon) collected from River Oluwa and River Owena in the dry season and rainy season, to investigate the status of heavy metal contamination. Samples were analyzed using the AAS using GBC Avanta PM ver 2.02. The concentrations of most of the metals were higher in the dry season than in the rainy season. Fe, Cu, Zn, Cd, Ni, and V concentrations were lower than the maximum permissible by ingestion. However, the mean concentration of Mn was 7.10 ppm in the dry season and 3.14 ppm in the rainy season while the mean concentration of Cr in the rainy season was 3.26 ppm, 2.81 ppm in the dry season, and 2.54 ppm in the rainy season which were higher than the allowed levels for human consumption proposed by Food and Agriculture Organization (FAO) (1983). Catfish from River Oluwa and River Owena should be consumed with caution.

Keywords: *Catfish, heavy metal, contamination, season, concentration*

I. Introduction

Anthropogenic activities such as industry, agriculture, mining, and the natural deposit of minerals have significantly impacted the environment and increased the naturally occurring amounts of heavy metals in the environment, including the marine ecosystem. Fish and other seafood can accumulate these metals to potentially toxic concentrations (Djedjibegovic et al., 2020). Fish represents one of the main sources of the exposure of people to metals toxicity, and it is the main source of trace elements in the human diet. Most of the human health risk related to fish consumption is associated with metal-contaminated fish (Hosseini et al., 2015). Clarias *buthupogon* is catfish that belongs to the species of Clarias which is characterized by having an elongated, body, lively, and have the ability to live for long periods out of water. Indices of weight and volumetric occurrences indicated that Clarias *buthupogon* eats aquatic insects, crustaceans, oligochaetes, mollusks, and animal and plant debris (Mahamba 2019). Pollution of the aquatic environments is a major threat to marine fish populations all over the world. Natural mineral deposits, dumping of toxic waste into the sea, and emptying of ballast water from ships into the sea are other human activities polluting the aquatic environment. In Nigeria, the sources of pollution of the aquatic environment are natural mineral deposits such as bitumen, industrial waste, raw/untreated domestic sewage, run-off of fertilizers and pesticides, sand mining, construction of canals, and oil spills (Adeyemo, 2003; Fagbote and Olanipekun, 2014). Polythene bags and other types of nonbiodegradable debris that have been washed by rainwater into the aquatic environment constitute new threats to marine fisheries (Olaoye and Ojebiyi, 2018)Studies on the spatial distribution and condition factors of Clarias buthupogon and Heterobranchus longifilis from the polluted Asa River, Ilorin, Nigeria was conducted by Akinloye and Olubanjo (2017). Their results showed that more fishes were caught in the rainy season than in the dry season, and the fish populations were more concentrated in the downstream, and *C. buthupogon* and *H. longifilis* were not in good physiological condition in the river. Bassey and Chukwu (2019) carried out a health risk assessment of heavy metals in fish (Chrysichthys nigrodigitatus) from Two Lagoons in Southwestern Nigeria. The Total Hazard Quotient (THQ) for all metals (THQ) had no adverse health effects from fish consumption. However, the Target Cancer Risk (TR) due to Pb and Ni exposure through fish consumption may increase the probability of developing cancer in the future. Pazou et al., 2020 carried out an assessment of heavy metal's in Atlantic sea fish sold in Benin and found out that consumption

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of fish could have no negative effect on the population's health. Matouke and Abdullahi (2020) carried out the assessment of heavy contamination and human health risk in Clarias gariepinus (Burchell, 1822) collected from Jabi Lake, Abuja, Nigeria. The Hazard Index (HI) values revealed no adverse health risk. Studies on heavy metals and fish health indicators in Malapterurus electricus from Lekki Lagoon, Lagos, Nigeria was carried out by Kuton et al. (2021), and their results showed that Metals analyzed in the fish tissues were generally low and below regulatory limits. It has been observed that reports of heavy metals in catfish (*Clarias buthugon)* are limited in Nigeria. Fish consumption has increased tremendously across Nigeria, especially in the Western part of the country. Okitipupa and Owena communities where the fish samples depend mainly on fishing as their main occupation. These communities also consume fish to a large extent. However, several studies also show that fish in rivers bio-accumulate heavy metals to a large extent that can cause health consequences (Mieiro et al., 2012; Bashir, et al., 2013; Abubakar et al., 2014). Therefore, this study assessed the concentration of heavy metals in Catfish (*Clarias buthugon*).

II. Materials and method

Study Sites

River Oluwa lies between Latitude 7°2' 00" and Longitude 4° 31' 30" from Osun State through Ondo State before discharging into the Atlantic Ocean at Ayetoro (Omoniyi et al., 2011; Akinsorotan, 2013; Talabi et al. 2017). River Owena is located about four kilometers from Joseph Ayobabalola University Ikeji Arakeji along the Ilesha-Akure expressway, at Latitude 6°33' 53" N and Longitude 5° 8' 52" E (Kolawole et al., 2019).

Sample Collection

Catfish (Clarias *buthupogon*) was collected from River Oluwa at Okitipupa and River Owena at Owena, Kilometer 10, Akure – Ondo Road, Western Nigeria. Samples were taken to the laboratory on the day of collection and preserved

Heavy Metal Determination

The tissues were placed in watch glasses and oven-dried at 105 °C until the weight is constant and later cooled in the desiccators. A representative sample (2.5g) of the plant was accurately weighed and was subjected to nitric, perchloric, and sulphuric acid digestion (wet oxidation). Digestion was carried out with nitric, perchloric, and sulphuric acid mixture in ratio 10:4:1 at a rate of 5 mL/per 0.5 g of sample and was placed on a hot plate at 100˚C temperature. Digestion was continued until the liquor becomes clear. All the digested liquors were filtered and diluted to 25 mL with distilled water of the element in the sample solution times 20 as an additional factor in µg/g dry weight. The entire digest was made up of 25mls for analysis in the AAS using GBC Avanta PM ver 2.02. Blank samples were run to avoid contamination during the analysis (IITA, 1979; ASTM, 1981; Akan, et al., 2012; Hosseini et al., 2015).

The data were statistically analyzed using the statistical package, IBM SPSS Statistics 25.0. The Pearson correlation coefficient was used to examine the significant differences at $p < 0.05$ for each metal in the dry and rainy seasons and River Oluwa and River Owena.

III. Results and Discussion

TABLE 1: RIVER OLUWA – CATFISH *(Clarias buthopogon)*

Heavy Metal	Dry Season Mean Conc (ppm)	SD	Rainy Season Mean Conc (ppm)	SD	Maximum Permissible Level (ppm) (FAO, 1983)	Standard/Guideline (ppm) (CEFAS, 1998)
e	88.90	±10.60	58.81	±9.9	180	na
Cu	2.00	±0.50	0.86	±0.46	10	20
Mn	7.10	±0.25	3.14	±0.50	0.5	na
Cr	0.86	±0.12	3.51	±0.60	1	na
Zn	62.50	±10.50	12.32	±3.26	100	50
Hg	BDL	#DIV/0!	BDL	#DIV/0!	0.5	0.3
Pb	1.72	±0.22	1.7	±0.45	1.5	2
Cd	0.80	±0.20	0.39	±0.07	0.5	1
Ni	0.62	±0.32	1.88	±0.35	0.05-5.5	na
V	0.16	±0.04	0.181	±0.06	0.5	na

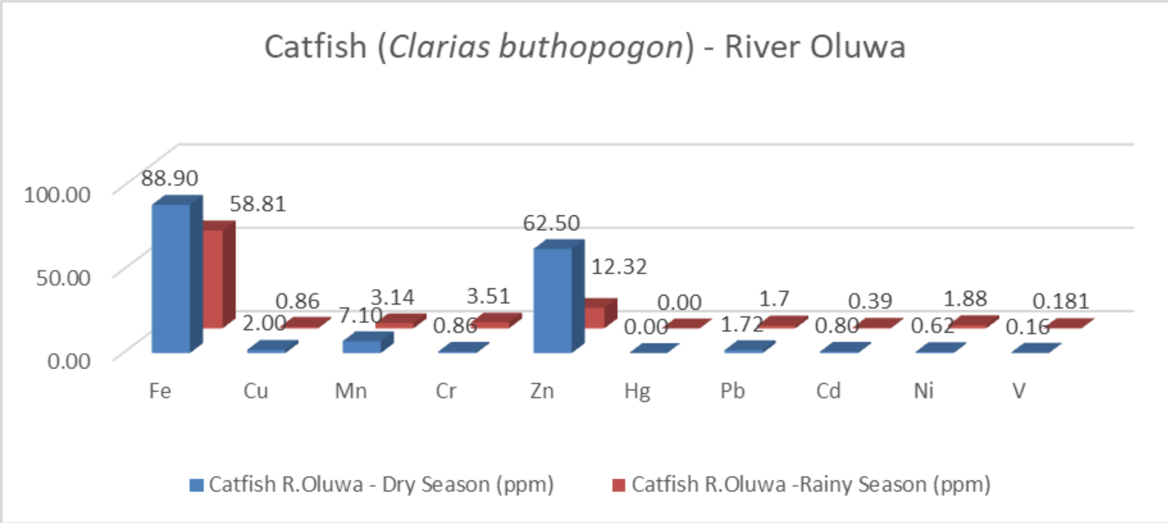

Fig. 1: River Oluwa - Catfish *(Clarias buthupogon)*

TABLE 2: RIVER OWENA – CATFISH *(Clarias buthopogon)*

Heavy Metal	Dry Season Mean (ppm)	SD	Rainy Season Mean (ppm)	SD	Maximum Permissible Level (ppm) (FAO, 1983)	Standard/Guideline (ppm) (CEFAS, 1998)
Fe	62.13	±18.55	49.76	±6.38	180	na
Cu	1.71	±0.67	0.52	±0.15	10	20
Mn	5.37	±1.24	2.21	±0.65	0.5	na
Cr	2.81	±0.68	2.54	±0.77	1	na
Zn	35.85	±4.45	12.69	±3.89	100	50
Hg	BDL	#DIV/0!	BDL	#DIV/0!	0.5	0.3
Pb	1.67	±0.55	1.52	±0.31	1.5	2
Cd	0.77	±0.25	0.25	±0.08	0.5	1
Ni	1.20	±0.60	1.24	±0.58	0.05-5.5	na
V	0.13	±0.07	0.12	±0.08	0.5	na

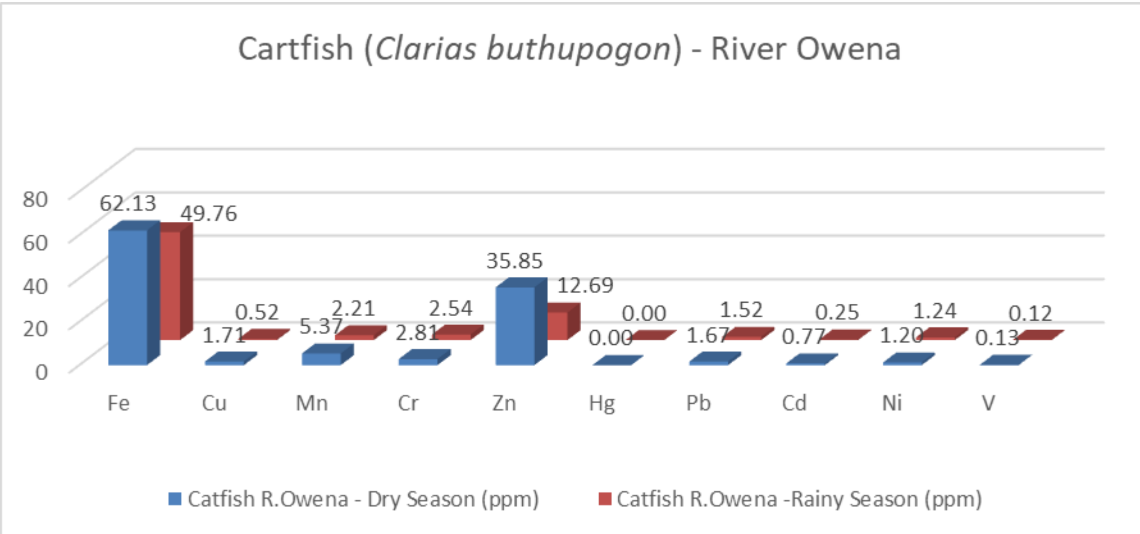

Fig. 2: River Owena - Catfish *(Clarias buthupogon)*

TABLE 3: THE PEARSON CORRELATION COEFFICIENT USING SPSS 25.0

		Cu	Mn	Cr	Zn	Fe	Pb	Cd	Ni	V
Cu	Pearson Correlation	1	.988*	-0.64	0.935	0.857	-0.384	.992**	-0.68	0.152

	Sig. (2-tailed)		0.012	0.36	0.065	0.143	0.616	0.008	0.32	0.848
	N	4	4	4	4	4	4	4	4	4
Mn	Pearson Correlation	.988*	1	-0.736	.974*	0.924	-0.387	.960*	-0.739	0.198
	Sig. (2-tailed)	0.012		0.264	0.026	0.076	0.613	0.04	0.261	0.802
	N	4	4	4	4	4	4	4	4	4
Cr	Pearson Correlation	-0.64	-0.736	1	-0.87	-0.828	0.636	-0.556	.950*	0.062
	Sig. (2-tailed)	0.36	0.264		0.13	0.172	0.364	0.444	0.05	0.938
	N	4	4	4	4	4	4	4	4	4
Zn	Pearson Correlation	0.935	.974*	-0.87	1	0.943	-0.51	0.888	-0.862	0.104
	Sig. (2-tailed)	0.065	0.026	0.13		0.057	0.49	0.112	0.138	0.896
	N	4	4	4	4	4	4	4	4	4
Fe	Pearson Correlation	0.857	0.924	-0.828	0.943	1	-0.232	0.787	-0.718	0.407
	Sig. (2-tailed)	0.143	0.076	0.172	0.057		0.768	0.213	0.282	0.593
	N	4	4	4	4	4	4	4	4	4
Pb	Pearson Correlation	-0.384	-0.387	0.636	-0.51	-0.232	1	-0.384	0.831	0.793
	Sig. (2-tailed)	0.616	0.613	0.364	0.49	0.768		0.616	0.169	0.207
	N	4	4	4	4	4	4	4	4	4
Cd	Pearson Correlation	.992**	.960*	-0.556	0.888	0.787	-0.384	1	-0.627	0.102
	Sig. (2-tailed)	0.008	0.04	0.444	0.112	0.213	0.616		0.373	0.898
	N	4	4	4	4	4	4	4	4	4
Ni	Pearson Correlation	-0.68	-0.739	.950*	-0.862	-0.718	0.831	-0.627	1	0.323
	Sig. (2-tailed)	0.32	0.261	0.05	0.138	0.282	0.169	0.373		0.677
	N	4	4	4	4	4	4	4	4	4
V	Pearson Correlation	0.152	0.198	0.062	0.104	0.407	0.793	0.102	0.323	1
	Sig. (2-tailed)	0.848	0.802	0.938	0.896	0.593	0.207	0.898	0.677	
	N	4	4	4	4	4	4	4	4	4

*** Correlation is significant at the 0.05 level (2-tailed)**

Comparison of Concentration of heavy metals in catfish *(Clarias buthopogon)* with standards

The concentrations of the heavy metals in catfish *(Clarias buthopogon)* from River Oluwa and River Owena are shown in Table 1, Figure 1, Table 2, and Figure 2.

Hg was not detectable in all tested samples. At River Oluwa, in the dry season, the order of concentrations of the metals tested in catfish *(Clarias buthopogon) is* Fe > Zn > Mn > Cu > Pd > Cr > Cd > Ni > V while the order is slightly altered in the rainy reason as follows: Fe > Zn > Cr > Mn > Ni > Cu > Cd > V. At River Owena, in the dry season, the order of concentrations of the metals tested in catfish *(Clarias buthopogon) is* Fe > Zn > Mn > Cr > Cu > Pb > Ni > Cd > V and Fe > Zn > Cr > Mn > Pb > Ni > Cu > Cd > V in the rainy season. The concentration of Fe is the highest in the catfish samples while the concentration of V is the least.

The mean values of Fe, Cu, Zn, Cd, Ni, and V obtained in catfish in the dry season and rainy season collected from River Oluwa were lower than the maximum permissible (FAO, 1983), and allowed in the standard guidelines (CEFAS, 1998). At River Oluwa, the Pb concentrations obtained were 1.72 ppm in the dry season and 1.7 ppm in the rainy season. While at River Owena, the concentrations of Pb were 1.67 ppm in the dry season and 1.52 ppm in the rainy season. These values were higher than the 1.5 ppm maximum permissible levels (FAO, 1983), but lower that 2 ppm required in the standard guidelines (CEFAS, 1998).

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However, at River Oluwa, the mean concentrations of Mn were 7.10 ppm in the dry season and 3.14 ppm in the rainy season. At River Owena, the mean concentrations of Mn were 5.37 ppm in the dry season and 2.21 ppm in the rainy season. These values were higher than the maximum permissible Level (FAO, 1983) of 0.5 ppm. Manganese is a mineral that naturally occurs in rocks, soil, groundwater, surface water, and food and is a normal part of the human diet. Potential health effects of manganese are not a concern until concentrations are approximately six times higher. Breathing high concentrations of manganese dust and fumes (e.g., welding) over the course of years has been associated with toxicity to the nervous system in workers, producing a syndrome that resembles Parkinson's disease (WHO, 2000).

At River Oluwa, the concentration of Cr in the rainy season was 3.26 ppm, while at River Owena, the mean concentration was 2.81 ppm in the dry season and 2.54 ppm in the rainy season. These values were higher than the maximum permissible level of 1 ppm. The amount of chromium in the diet is of great importance as Cr is involved in insulin function and lipid metabolism Bratakos et al., 2002; Md. Kawser et. al, 2015). Chromium(III) is recognized as a trace element that is essential to both humans and animals. Chromium(VI) compounds are toxic and carcinogenic, but the various compounds have a wide range of potencies. As the bronchial tree is the major target organ for carcinogenic effects of chromium(VI) compounds, and cancer primarily occurs following inhalation exposure, uptake in the respiratory organs is of great significance in respect of the subsequent risk of cancer in humans (WHO, 2000).

At River Oluwa and River Owena, the concentrations of most of the metals were higher in the dry season than in the rainy season probably due to higher bioconcentration of heavy metals by catfish *(Clarias buthopogon)* in the dry season.

The Pearson correlation coefficient of concentration of heavy metals in catfish *(Claris buthopogon)* at River Oluwa and River Owena in the dry and rainy seasons carried out using SPSS 25.0 showed that Mn and Cu ($r = 0.988^*$, $p < 0.05$), Mn and Zn ($r = 0.974^*$, $p < 0.05$), Mn and Cd ($r = 0.960^*$, $p < 0.05$), Cr and Ni ($r = 0.950^*$, $p < 0.05$) exhibited positively significant correlation. The positive correlation between the metals could be attributed to discharges from non-point sources of heavy metals input into River Oluwa and River Owena

IV. Conclusion

The concentrations of most of the metals were higher in the dry season than in the rainy season. Fe, Cu, Zn, Cd, Ni, and V concentrations in catfish (*Clarias buthopogon*) collected from River Oluwa and Owena were lower than the maximum permissible by ingestion. Mn concentrations were above the maximum permissible. Mn health effects, which include toxicity to the nervous system, begin to show at concentrations of about six times above the maximum permissible. Cr concentrations were also above the maximum permissible. High concentrations of Chromium (VI) is carcinogenic. Therefore, if catfish (*Clarias buthopogon*) collected from River Oluwa and River Owena cannot be avoided, it should be consumed moderately.

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