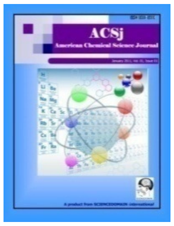

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Determination of Heavy Metals in Fish (*Clarias gariepinus*) Organs from Asaba Major Markets, Delta State, Nigeria

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Authors' contributions

This work was carried out in collaboration between all authors. Author KHI designed the study. Author NEO performed the statistical analysis. Authors KHI and NEO wrote the protocol, and wrote the first draft of the manuscript. Authors KHI, NEO, OVU and IFC managed the analyses of the study. Authors KHI and NEO managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Aim: To determine and compare the bioaccumulation of selected heavy metals- zinc, lead, cadmium, copper, mercury, and cobalt in organs of *Clarias gariepinus* obtained from fish sellers in the three major markets in Asaba.
Place and Duration of Study: Department of Chemistry Education Laboratory, Federal College of Education (Technical), Asaba between June and August 2013.
Methodology: Catfish, *Clarias gariepinus* sold commercially, were bought in replicates from three major markets in Asaba. The samples were dissected and the various organs dried separately at 110ºC to constant weight. The ground samples were digested with aqua regia solution and the heavy metals concentrations determined by AAS machine.
Results: The result revealed that the gills contained the highest total concentration (11.363 ppm)representing 27.70% of the detected heavy metals followed by the liver (11.267 ppm) representing 27.46% followed by the heart (10.303 ppm) representing 25.11% while the muscle

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had the lowest concentration (8.095) representing 19.73%. The difference in the bioaccumulation in the various organs however, did not differ significantly (P = 0.990). The overall accumulation pattern for the three markets was: Ogbeogonogo - Zn > Hg > Cu >Pb> Cd > Co; Cable - Zn > Cu > Hg >Pb> Co > Cd; and Abraka - Zn > Cu > Hg > Cd > Co >Pb. Zn mean concentration differs significantly (P =.000) from those of other metals. Mean concentrations of Pb, Cd, and Co were significantly the same but differ from those of Cu and Hg whose mean concentrations were statistically the same. The total concentrations in ppm of Zn (35.995, 32.336, and 36.292); Cu (1.587, 4.189, and 3.496) and Co (0.016, 0.070, and 0.088) in the three markets were below the permissible limits of 150 ppm, 10 ppm, and 0.15 – 1.0 ppm respectively stipulated by FAO/WHO. Also, the concentrations of Pb, 0.139 in Cable and 0.000 in Abraka; and Cd, 0.042 in Ogbeogonogo and 0.031 in Cable were below the permissible limits 0.5 ppm for Pb and 0.05 ppm for Cd. However, the concentrations in ppm of Pb, 0.949 in Ogbeogonogo, Cd, 0.673 in Abraka, and Hg in all three markets were above the permissible limits of 0.5 ppm, 0.05 ppm and 0.5 ppm in fish and food substances.

Conclusion: The consumption of *Clarias gariepinus* sold in these markets poses serious health threat to humans especially pregnant women.

Keywords: Heavy metals; Clarias gariepinus; organs; bioaccumulation; digestion; permissible limit.

1. INTRODUCTION

In recent years, there have been keen concerns about the contamination of the environment and the attendant consequences on human health. The high rise in civilization and the progress of industries have led to increased emission of pollutants into the ecosystems. Some of these pollutants, which include heavy metals, are directly discharged by industrial plants and municipal sewage treatment plants; others come from polluted runoff in urban and agricultural areas [1]. Phosphate fertilizers derived from phosphate ore in addition to phosphate minerals contain a wide range of impurities including heavy metals and naturally occurring radionuclides [2]. In a study conducted by Greenpeace Research Laboratories, fertilizer samples analyzed contained significant concentrations of a number of heavy metals [2]. Study by [3] showed that urea and superphosphate fertilizers sold commercially in Nigeria contains considerable amount of heavy metals.

Many dangerous chemical elements such as heavy metals, if released into the environment, accumulate in the soil and sediments of water bodies. The lower aquatic organisms absorb and transfer them through the food chain to higher trophic levels, including fish. Potential of heavy metal ions to accumulate in seafood, including fish living in waters polluted with heavy metals, is rather high [4]. Heavy metals, which especially accumulate in organs of fish, such as internal organs, kidneys, and spleen, can be transmitted to and accumulated in various organs of human body by their consumption [5,6].

Fish has been recognised as an important food source for the human body. Fish provides essential fatty acids like Omega 3, proteins, vitamins, and minerals [7]. However, despite its nutritional value, consumption of fish contaminated with heavy metals brings many times a potential hazard concern for the human consumers. It has been reported that prolonged consumption of unsafe concentrations of heavy metals through foodstuff may lead to the chronic accumulations of the metals in the kidney and liver of humans causing disruption of numerous biochemical processes, leading to cardiovascular, nervous, kidney and bone diseases [8,9], as heavy metals bioaccumulate. Bioaccumulation is the gradual build up over time of a chemical in a living organism. This occurs either because the chemical is taken up faster than it can be used or because the chemical cannot be broken down for use by the organism. The rate of bioaccumulation of heavy metals in aquatic organisms depends on the ability of the organisms to digest the metals and the concentration of such metal in the water body. Also, it has to do with the concentration of the heavy metal in the surrounding soil sediments as well as the feeding habits of the organism [10]. Aquatic animals (including fish) bioaccumulate trace metals in considerable amounts and stay over a long period. Fishes have been recognized as good accumulator of organic and inorganic pollutants [11]. Age of fish, lipid content in the tissue and mode of feeding are significant factors that affect the accumulation of heavy metals in fish [10].

In Asaba the capital city of Delta state, there is no proper waste management system because successive governments in the state have not been able to design a sanitation blueprint for the city since it became the capital of the state in 1991 [12]. Thus, there is indiscriminate dumping of waste materials, which can result to contamination of the soil by heavy metal containing waste such as batteries. During rain, this can result to polluted heavy metal urban runoff. This polluted urban runoff empties into the surrounding water bodies. Moreover, Asaba is just a few kilometres away from Onitsha- a highly industrialized town where waste management is a serious problem. The Niger River, which serves as a source of fish in the area separates Asaba and Onitsha towns. Another potential source of heavy metals in this area is inorganic fertilizer used by farmers. Over the years, there has been increasing awareness of the environmental and health impacts that are associated with `heavy metal toxicity; however, there is dearth of information on heavy metal levels in fish sold in Asaba markets. It is in the light of this that this study was undertaken. The results from this study will provide answers as to whether there is any health risk associated with the consumption of the fish sold in Asaba markets.

In this study, levels of some heavy metals, including Zn, Pb, Cd, Cu, Hg, and Co were measured by FAAS in 9 different samples of *Clarias gariepinus* bought from Ogbeogonogo, Cable, and Abraka markets in Asaba, Delta State in June, 2013. Aqua regia digestion technique was used for the preparation of fish samples to measurement step by FAAS. The results were discussed by comparing with previous studies reported in the literature as well as standard values in Food and Agriculture Organization (FAO), World Health Organization (WHO), and Federal Environmental Protection Agency (FEPA).

2. MATERIALS AND METHODS

2.1 Sampling Area and Sample Collection

Samples were collected in accordance with USEPA [13] guidelines for assessing chemical contaminants data for use in fish advisories. Replicate fish samples were purchased from three spatially located markets in Asaba namely; Ogbeogonogo, Cable, and Abraka markets between 3rd and 6th June, 2013. Asaba is located at 6°11' 0" North, 6°45' 0" East. The fishes were rinsed with ambient water to remove foreign matter, examined for breaks or lacerations, and put in well-labelled pre–cleaned polyethene bags and immediately stored frozen in icebox. The fish samples were transported to the laboratory, stored in the refrigerator at – 20℃ prior to pre-treatment and analysis.

2.2 Sample Preparation and Analysis

Adult fish samples varying in weight from 374.43 g to 787.14 g and length 41.50 cm to 45.00 cm were dissected using sterile knife to separate organs into heart, muscle, gills, and liver in accordance with standard methods provided by USEPA [13]. Digestion of samples was done using aqua regia solution 14]. The organs were dried separately in an oven at 110ºC to constant weight. Each organ from the various markets was thereafter ground to powder using a porcelain mortar and pestle and sieved through a sieve of 5 mm. 1 g each of the separated organs was digested with aqua regia (HNO_3 and HCl in the ratio 1:3) in a beaker cleaned with 10% HNO_3 and rinsed severally with deionised water. The mixture was heated to 100℃ in a water bath until the solute dissolved completely. Each solution was allowed to cool and then diluted with15 mL of deionised water. The diluted solutions were filtered through Whatman No. 1 filter papers into pre–cleaned beakers. The filtrates were stored in previously cleaned sample bottles until analysis by atomic absorption spectrophotometer. The concentrations of Zn, Pb, Cd, Cu, Hg, and Co were determined by flame atomic absorption spectrometry (FS240 AA) with detection limit of 0.001 ppm. Analytical-grade reagents (Spectrascan standards) of the various metals were used to prepare standard solutions of different concentrations for each metal. Measurements were performed for each of the triplicates of fish samples and for each market under study. The accuracy of the instrumental methods and analytical procedures and the precision of the results of the samples were checked by performing the measurements in triplicate. The average absorbance of each sample was calculated by referring to the appropriate calibration curve drawn by the in-built computer interface. The concentrations were equally read out from the computer print-out in ppm.

2.3 Statistical Analysis

Results are presented as mean ± standard deviation; n equals 3, the number of replicate measurements. Results from the different markets were compared using one-way analysis of variance (One-Way ANOVA) at the 95% confidence level (α = .05). $P \leq .05$ was considered to indicate significant difference. Where the means differ significantly, Duncan Multiple Range Test was used to separate the significantly different means.

3. RESULTS AND DISCUSSION

Zinc is an important trace element in human metabolism and nutrition and plays a major role in functioning of many biochemical processes [4]. However, intake of excess Zn may cause side effects [15]. The mean concentrations of zinc (ppm) in the various organs of *Clarias gariepinus* obtained from the three markets: Ogbeogonogo, Cable, and Abraka are presented in Table 1. The result revealed that the concentration of zinc in the organs of fish samples follows the order liver > gills > heart > muscle, muscle > gills > heart > liver and heart > liver > gills > muscle for Ogbeogonogo, Cable and Abraka respectively. Concentration of zinc (ppm) ranged from 1.669 in the muscle of fish samples from Abraka to 12.756 in the liver of fish samples from Ogbeogonongo market. The muscle had the overall lowest mean concentration of 6.816 while the gills had the highest (9.586 ppm). [10] reported mean concentrations of 7.05 mg/kg in gills and 3.85 mg/kg in muscle tissue of *Clarias gariepinus* obtained from River Benue. Abraka market had a higher mean concentration of 9.073 ppm than the other markets. The order of bioaccumulation in organs of fish samples from Ogbeogonogo market agrees with findings of other researchers such as [12-22]. Apart from Cable market, the lowest levels of zinc were detected in muscle because muscle is not an active tissue for uptake of heavy metals [10,23-27]. Generally, accumulation depends on metal concentration, time of exposure, way of metal up take, environmental conditions (water temperature, pH, hardness, salinity) and intrinsic factors (fish age, feeding habits, body size) [21,22]. Various metals show different affinity to fish tissues. Most of them accumulate mainly in liver, kidney, and gills. Fish muscles, compared to the other tissues; usually contain the lowest levels of metals [22].

Zn concentration in all organs of fish used in this study was below the permissible limit of 150 ppm stipulated by FAO/WHO [28]. Daily tolerable amount of Zn based on body weight of 60 kg was specified as 60 mg by FAO/WHO [29]. Zn concentration therefore poses no risks to potential consumers of these fish.

Lead is considered to be one of the most dangerous metals for human health because it affects the central nervous system, causes anaemia and gastrointestinal damage, and is associated with alterations in genetic expression [30–32]. Lead concentrations were in the range of 0.000 to 0.695 ppm as shown in Table 2. The muscle had the lowest mean concentration of 0.000 ppm while the liver had the highest (0.232 ppm). Ogbeogonogo market mean concentration of 0.237 ppm was higher than the other two markets. The order of bioaccumulation of lead was liver > heart > gills > muscle for Ogbeogonogo; apart from the gills of fish obtained from Cable market with Pb concentration of 0.139 ppm, lead concentration was below the detection limit (0.001 ppm) in all analyzed fish organs from Cable and Abraka markets. The values of Pb obtained in this study were lower than those recorded by [10] who reported 1.28 mg/kg in the gills and 0.801 mg/kg in the muscle tissue of *Clarias gariepinus* from River Benue; 0.03 ppm in the muscle of *Clarias gariepinus* from Ogun Coastal water reported by [33] and (0.73 -.4.12) ppm reported by [34]. The mean concentrations (ppm) of Pb in the heart and gills were however, slightly higher than the 0.01 ppm reported by [33]. Pb concentrations in all organs of fish analyzed apart from the liver of fish samples from Ogbeogonogo market, which had a concentration of 0.695 ppm were below the permissible limit of 0.5 ppm by FAO/WHO [35]. The consumption of all organs of *Clarias gariepinus* sold in the sampled markets with the exception of liver of fish samples from Ogbeogonogo market is safe in terms of Pb concentration.

Cadmium is 10 times more toxic than lead, and is an element to which humans are readily exposed due to its large industrial use. This metal has been associated with problems in respiratory pathways, including lung cancer [36–38] and problems in the gastrointestinal system [39]

Table 1. Mean concentration (ppm) of zinc in the organs of fish samples from different markets in Asaba town

Market/organ	Heart	Muscle	Gills	Liver	Mean
Ogbeogonogo	8.195±0.056	6.073±1.793	8.971±0.048	12.756±0.098	8.999±1.795
Cable	6.939±0.032	12.707±0.049	8.314±0.081	4.377±0.039	8.084±0.050
Abraka	11.593±0.093	1.669±2.882	11.474±0.175	11.556±0.056	9.073±0.082
Mean	8.909±0.060	6.816±1.575	9.586±0.101	9.563±0.064	

Table 2. Mean concentration (ppm) of lead in organs of fish from different markets in Asaba

Market/organ	Heart	Muscle	Gills	Liver	Mean
Ogbeogonogo	0.141±0.026	ND	0.113±0.003	0.695±0.046	0.237±0.019
Cable	ND	ND	0.139±0.017	ND	0.035±0.004
Abraka	ND	ND	ND	ND	
Mean	0.047±0.009		0.081±0.007	0.232±0.015	

Table 3 shows the mean concentrations (ppm) of cadmium in different organs of fish samples analyzed. The concentrations of cadmium were in the range of 0.000 to 0.656 ppm. The muscle had the highest mean concentration of 0.219 ppm while the heart had the lowest (0.000 ppm) among the organs. Abraka market had highest mean concentration of 0.168 ppm followed by Ogbeogonogo with a mean concentration of 0.011 ppm. The order of bioaccumulation is gills > heart/muscle/liver for Ogbeogonogo and Cable markets and muscle > liver > heart/gills for Abraka market. Mean values of 0.325 ppm in the gills and 0.269 ppm in the muscle [10], 0.29 ppm in the gills and 0.00 ppm in the muscle [33] were obtained in earlier researches on *Clarias gariepinus* from Nigerian rivers. The mean concentrations of Cd in the gills by both [10] and [33] are higher than the value (0.024 ppm) observed in the present study. Mean concentrations of 0.26 ppm and 0.25 ppm respectively were found in the heart of *Clarias gariepinus* in earlier studies by [33,34]. The concentrations of Cd in the heart of fish samples used in this study were below the detection limit (0.001 ppm). The result reported by [33] and the present study indicate that the gills accumulate cadmium than the heart. Cd concentration (0.656 ppm) in the muscle of fish samples from Abraka market was above the permissible limit of 0.05 ppm in fish and food substances set by FAO/WHO [35] while those of the muscles from the other two markets and all other organs analyzed were below. In terms of Cd concentration, the consumption of *Clarias gariepinus* sold in Ogbeogonogo and Cable markets poses no health threat to consumers.

Copper exists in the nervous system and has an important role during biological electron transfer. Furthermore, Cu is vital for synthesis of red blood cells [4]. Copper concentrations ranged from 0.136 ppm in the muscle to 2.797 ppm in the gills as shown in Table 4. The gills had the highest mean concentration of 1.267 ppm while the muscle had the lowest (0.327 ppm). Among the markets, Cable had the highest mean concentration (1.047 ppm) while Ogbeogonogo had the least (0.397 ppm). The bioaccumulation of copper followed the order: liver > gills > heart > muscle, gills > muscle > heart > liver and heart > liver > gills > muscle for Ogbeogonogo, Cable, and Abraka markets respectively. Earlier research by [10] showed that the gills and muscle tissue of *Clarias gariepinus* from River Benue contained 2.07 and 1.56 ppm of copper respectively. Permissible Cu concentration allowed by FAO/WHO [36] was specified as 10 ppm. Therefore, Cu concentration in the respective fish organs in this study is below legal limits. Daily tolerable amount of Cu on the basis of body weight of 60 kg was determined as 3 mg by FAO/WHO [29].

Mercury is one the most lethal heavy metals. Its toxicity effects vary from the chemical form, dose, and route of ingestion, and with the exposed organism's species, sex, age, and general condition [40]. Mercury instantly damages every cell it touches and causes organ dysfunction, being particularly destructive to the brain, kidney, and liver [41].

Table 3. Mean concentration (ppm) of cadmium in the organs of fish samples from different markets in Asaba

Market/organ	Heart	Muscle	Gills	Liver	Mean
Ogbeogonogo	ND	ND	0.042±0.011	ND	0.011±0.003
Cable	ND	ND	0.031±0.019	ND	0.008±0.005
Abraka	ND	0.656±1.118	ND	0.017±0.018	0.168±0.284
Mean		0.219±0.373	0.024±0.010	0.006±0.006	

Table 4. Mean concentration (ppm) of copper in organs of fish samples from different markets in Asaba

Market/organ	Heart	Muscle	Gills	Liver	Mean
Ogbeogonogo	0.260±0.050	0.177±0.049	0.387±0.042	0.763±0.010	0.397±0.039
Cable	0.385±0.433	0.667±0.366	2.797±0.019	0.340±0.010	1.047±0.282
Abraka	1.808±0.031	0.136±0.010	0.617±0.021	0.935±0.031	0.874±0.023
Mean	0.818±0.171	0.327±0.142	1.267±0.027	0.679±0.049	

Mercury mean concentrations (ppm) are shown in Table 5. Concentrations of mercury were in the range of 0.109 to 1.233 ppm. The highest mean concentration of mercury (0.767 ppm) was observed in the liver while lowest value of 0.392 ppm was found in the gills. Ogbeogonogo market had the highest mean concentration of 0.655 ppm among the markets. The order of bioaccumulation in the fish organs were liver > muscle > heart > gills, liver > muscle > heart > gills and gills > muscle > heart > liver for Ogbeogonogo, Cable and Abraka markets respectively. The result of this study revealed that mercury accumulates more in the liver. Hg concentrations in majority of fish organs – muscle and liver from Ogbeogonogo; heart, muscle and liver from Cable and muscle and gills from Abraka were above the permissible limits, 0.5 ppm in fish and food substances set by FAO/WHO [35]. The muscle tissue is the most consumed part of fish. In view of the high concentration of mercury in muscle tissues of fish used in this study, the consumption of *Clarias gariepinus* sold in the sampled markets poses serious health threat to the consumers.Majority of the studies on heavy metals concentrations in fish samples in Nigeria have not involved mercury. [42] in his research on catfish, *Synodontis membrane* from Asa River in Kwara State found that the muscle contained <0.01 ppm mercury. The result obtained by [43] showed that the muscle of small sized D. labrax contained 0.21 ppm of mercury. Mercury deposition in a given area depends on mercury emitted from local, regional, national, and international sources [44]. The high concentration of mercury recorded in this study could be attributed to both natural and anthropogenic sources. Naturally occurring mercury in the soil, atmospheric deposition, burning of coal, indiscriminate disposal and/or burning of mercury-containing waste as well as production of chlorine, metals and alkali are possible sources of mercury in the area where the samples were obtained. Asaba is a few kilometres away from Onitsha- a high industrial and commercial centre where various wastes are dumped indiscriminately on land. These wastes could be washed off into water bodies in surrounding localities. Moreover, several coal mines were operated on commercial scale in Delta State and other neighbouring states between 1909 and 1999.The burning of coal over these years could have released a substantial amount of mercury into the environment.

Cobalt is an element that is not easily found in free form in the environment, but is known for being introduced into the food chain due to its absorption by plants in the forms of fertilizers and industrial pollutants [45,46]. Exposure to cobalt can cause damage to respiratory pathways and to the lungs, heart and thyroid [47,48]. Cobalt concentrations ranged from 0.000 to 0.039 ppm as shown in Table 6. The liver had the highest mean concentration of 0.020 ppm while the mean concentrations of muscle and gills were lowest (0.010 ppm). Abraka market had the highest mean concentration of 0.022 ppm among the markets. The order of bioaccumulation were liver > gills > heart/muscle; muscle > liver > heart > gills and heart > liver > gills > muscle for Ogbeogonogo, Cable and Abraka markets respectively. [33] reported the mean values of 0.00 ppm in the muscle, 0.55 ppm in the heart and 0.06 ppm in the gills of *Clarias gariepinus* from Ogun Coastal water. Co concentrations in fish organs analyzed in this study were below the permissible limit of 0.15 – 1.0 ppm allowed by FAO/FEPA [49,50].

Table 5. Mean concentration (ppm) of mercury in organs of fish samples from different markets in Asaba

Markets/organs	Heart	Muscle	Gills	Liver	Mean
Ogbeogonogo	0.391±0.060	0.746±0.000	0.250±0.062	1.233±0.232	0.655±0.039
Cable	0.641±0.318	0.853±0.184	0.109±0.107	0.782±0.120	0.596±0.182
Abraka	0.498±0.221	0.570±0.221	0.818±0.122	0.287±0.218	0.543±0.196
Mean	0.510±0.200	0.723±0.134	0.392±0.097	0.767±0.140	

Table 6. Mean concentration (ppm) of cobalt in organs of fish samples from different markets in Asaba

Market/organ	Heart	Muscle	Gills	Liver	Mean
Ogbeogongo	ND	ND	0.007±0.007	0.009±0.011	0.004±0.005
Cable	0.017±0.016	0.021±0.021	0.013±0.022	0.019±0.018	0.018±0.019
Abraka	0.039±0.019	0.008±0.011	0.010±0.018	0.031±0.012	0.022±0.015
Mean	0.019±0.012	0.010±0.016	0.010±0.016	0.020±0.014	

Tables 7 a – c present the mean concentrations (ppm) of heavy metals in organs of *Clarias gariepinus* from each of the three markets. The pattern of heavy metal accumulation in the various organs of *Clarias gariepinus* across the three markets are as follows: Ogbeogonogo; Zn > Hg > Cu >Pb> (Cd and Co) in the heart; Zn > Hg > Cu > (Pb, Cd and Co) in the muscle; Zn > Cu > Hg >Pb> Cd > Co in the gills; and Zn > Hg > Cu >Pb> Co > Cd in the liver; Cable: Zn > Hg > Cu > Co > (Pb and Cd) in the heart, muscle, and liver; Zn > Cu >Pb> Hg > Cd > Co in the gills; Abraka: Zn > Cu, > Hg > Co > (Pb and Cd) in the heart; Zn > Cd > Hg > Cu > Co >Pb in the muscle; Zn > Hg > Cu > Co > (Pb and Cd) in the gills and Zn > Cu > Hg > Co > Cd >Pb in the liver. The trend observed by [33] in their work on *Clarias gariepinus* from Ogun Coastal water was: gills - Cd > Co >Pb; heart - Co > Cd >Pb and muscle – Co >Pb> Cd. It was observed from this work that different metals are accumulated at different concentrations in various organs of fish. Other workers such as [10] and [33] observed the same trend. The differences in the physiological role of each organ primarily account for the difference in the levels of heavy metals accumulation in different organs of fish [10]. Other factors such regulatory ability, behaviour and feeding habits of fish may also play a significant role in the accumulation differences in the different organs [51]. In addition, the chemical nature of the metals, ionic strength, and pH tends to be a master variable in the accumulation process [10]. The results of this present study showed that Zn was consistently the most accumulated heavy metal in all organs of *Clarias gariepinus* sampled from the three markets. The mean concentration of Zn in each market differs significantly [(P = .000) for Ogbeogonogo, Cable, and Abraka] from those of the other heavy metals. However, the mean total of all the analyzed metals were significantly the same in all three markets [(P = .922, .891 and .844) for Ogbeogonogo, Cable, and Abraka respectively].

Table 7a – c. Average concentration of heavy metals (ppm) in the organs of *Clarias gariepinus* obtained from Ogbeogonogo, Cable, and Abraka markets in Asaba town

Table 7a. Ogbeogonogo market

Metal/organ	Heart	Muscle	Gills	Liver	Mean
Zn	8.195±0.056	6.073±1.793	8.971±0.048	12.756±0.048	$8.999±1.795^a$
Pb	0.141±0.026	ND	0.113±0.003	0.695±0.046	$0.237±0.019^b$
Cd	ND	ND	0.042±0.011	ND	$0.011±0.003^b$
Cu	0.260±0.050	0.177±0.049	0.387±0.042	0.763±0.010	$0.397±0.039^b$
Hg	0.391±0.060	0.746±0.000	0.250±0.062	1.233±0.232	$0.655±0.039^b$
Co	ND	ND	0.007±0.007	0.009±0.011	$0.004±0.005^b$
Mean	1.498±0.100	1.166±1.794	1.628±0.090	2.576±0.242	

Means with different superscripts differ significantly at α = .05

Table 7b. Cable market

Metal/organ	Heart	Muscle	Gills	Liver	Mean
Zn	6.939±0.032	12.707±0.049	8.314±0.081	4.377±0.039	8.084±0.050[a]
Pb	ND	ND	0.139±0.017	ND	0.035±0.004[b]
Cd	ND	ND	0.031±0.019	ND	0.008±0.005[b]
Cu	0.385±0.433	0.667±0.366	2.797±0.019	0.340±0.010	1.047±0.282[b]
Hg	0.641±0.318	0.853±0.184	0.109±0.107	0.782±0.120	0.596±0.182[b]
Co	0.017±0.016	0.021±0.021	0.013±0.022	0.019±0.018	0.018±0.019[b]
Mean	1.330±0.538	2.375±0.413	1.900±0.140	0.919±0.128	

Means with different superscripts differ significantly at α = .05

Table 7c. Abraka market

Metal/organ	Heart	Muscle	Gills	Liver	Mean
Zn	11.593±0.093	1.669±2.882	11.474±0.175	11.556±0.056	9.073±0.082[a]
Pb	ND	ND	ND	ND	0.000±0.000[b]
Cd	ND	0.656±1.118	ND	0.017±0.018	0.168±0.284[b]
Cu	1.808±0.031	0.136±0.010	0.617±0.021	0.935±0.031	0.874±0.023[b]
Hg	0.498±0.221	0.570±0.221	0.818±0.122	0.287±0.218	0.543±0.196[b]
Co	0.039±0.019	0.008±0.011	0.010±0.018	0.031±0.012	0.022±0.015[b]
Mean	2.323±0.059	0.507±3.099	2.154±0.215	2.139±0.052	

Means with different superscripts are significantly different at α = .05

Fig. 1 shows overall the average concentrations (ppm) of heavy metals in organs of *Clarias gariepinus* samples from the three markets. The gills contained the highest total concentration (11.363 ppm) representing 27.70% of the detected heavy metals followed by the liver (11.267 ppm) representing 27.46% followed by the heart (10.303 ppm) representing 25.11% while the muscle had the lowest concentration (8.095) representing 19.73%. The difference in the bioaccumulation in the various organs however, did not differ significantly (P = .990). The general order of bioaccumulation of heavy metals in the various organs of the fish samples analyzed was: Gills > Liver > Heart > Muscle. This is in agreement with the results of other workers such as [10,33]. Higher metal concentrations in the gills could be due to the element complexion with the mucus that is virtually impossible to completely remove from the gill lamellae before being prepared for analysis [42]. Gill tissues play an important role in interface with the environment in performing its functions in gas exchange, ion regulation, acid balance, and waste excretion while muscle on the other hand is not an active tissue in bioaccumulation [52,53,54]. Gills have been reported as metabolically active site and can accumulate heavy metals in higher level [33]. This is evidenced by the position that the gills occupied in the accumulation pattern for the heavy metals. Furthermore, the adsorption of metals onto the gills surface as the first target for pollutants in water could also be a significant influence in the total metal levels of the gill. Target organs such as gills, liver, heart, kidney, and intestine are metabolically active parts that can accumulate heavy metals in higher levels as shown in the works of [10,33] and also in the present study. [55] reported that metal may be in high concentrations in gill, lung, and digestive gland because of relatively high potential for metal accumulation.

Table 8 shows the total concentrations in ppm of the determined heavy metals in Ogbeogonogo, Cable and Abraka markets, the mean values of the three markets, and the WHO/FAO permissible limit for each metal. The concentrations in ppm of Zn (35.995, 32.336, and 36.292); Cu (1.587, 4.189 and 3.496) were below the permissible limits of 150 ppm, and 10 ppm respectively stipulated by FAO/WHO [28], and those of Co (0.016, 0.070 and 0.088) and 0.15 – 1.0 ppm were below the permissible limit allowed by FAO/FEPA [49, 50] in all three markets. Also, the concentrations of Pb, 0.139 in Cable and 0.000 in Abraka; and Cd, 0.042 in Ogbeogonogo and 0.031 in Cable were below the permissible limits 0.5 ppm for Pb and 0.05 ppm for Cd set by [39]. However, the concentrations in ppm of Pb, 0.949 in Ogbeogonogo, Cd, 0.673 in Abraka, and Hg, 2.620- Ogbeogonogo, 2.385- Cable and 2.173- Abraka were above the permissible limits of 0.5 ppm, 0.05 ppm and 0.5 ppm in fish and food substances set by FAO/WHO [35]. The

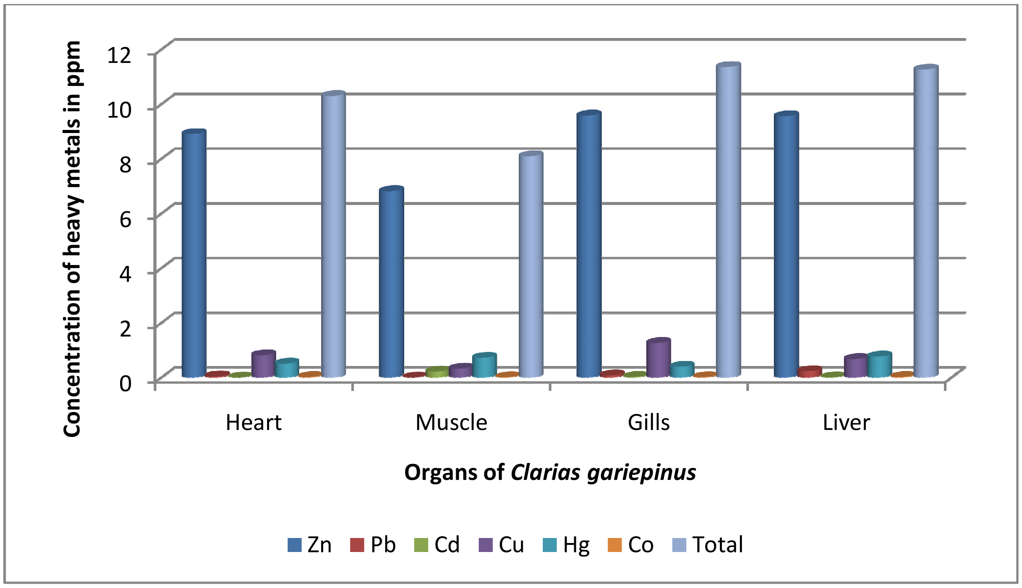

Fig. 1. Average concentrations of heavy metals in organs of *Clarias gariepinus* obtained from Ogbeogonogo, Cable, and Abraka markets (each value is a mean of the values from the three markets)

Table 8. Total concentration of heavy metals in *Clarias gariepinus* obtained from different markets in Asaba and FAO/WHO Permissible Limit (PL)

Metal/market	Ogbeogonogo	Cable	Abraka	Mean	PL
Zn	35.995±1.795	32.336±0.107	36.292±2.889	34.872±1.597^{a}	150
Pb	0.949±0.053	0.139±0.017	0.000±0.000	0.363±0.023^{b}	0.5
Cd	0.042±0.011	0.031±0.019	0.673±1.118	0.248±0.383^{b}	0.05
Cu	1.587±0.065	4.189±0.567	3.496±0.050	3.091±0.227^{c}	10
Hg	2.620±0.248	2.385±0.401	2.173±0.400	2.392±0.350^{c}	0.5
Co	0.016±0.013	0.070±0.039	0.088±0.031	0.058±0.028^{b}	0.15 – 1.0
Mean	6.868±0.364	6.525±0.192	7.119±0.748		

Means with the same superscripts are statistically the same at α = .05

concentrations of Zn and Cu in *Clarias gariepinus* samples from River Benue reported by [10] were 17.4 and 5.89 ppm respectively. The concentration of Zn in the present study is higher while that of the Cu is lower than that of [10]. Concentrations of Pb in *Clarias gariepinus;* 2.73 ppm [10], 0.210 ppm [56], 0.480 [57]; Cd 0.927 [10] 0.183 [58], 0.030 [57], and 0.190 [56] have been previously reported. The overall accumulation pattern for the three markets was: Ogbeogonogo - Zn > Hg > Cu >Pb> Cd > Co; Cable - Zn > Cu > Hg >Pb> Co > Cd; and Abraka - Zn > Cu > Hg > Cd > Co >Pb. One-way ANOVA of the mean concentrations of the heavy metals revealed a statistically reliable difference (*P* =.000) between Zn and other metals. Mean concentrations of Pb, Cd, and Co were significantly the same but differ from those of Cu and Hg whose mean concentrations were statistically the same. However, the total mean concentrations in ppm of the analyzed heavy metals (i.e Zn + Pb + Cd + Cu + Hg + Co) across the markets sampled; Ogbeogonogo (6.868), Cable (6.525) and Abraka (7.119) showed no significant difference (*P* =.997).

The variations in the pattern of heavy metal bioaccumulation across the markets could be linked to differences in source as fish sold in the markets are harvested from different locations. The high level of Hg in the present study makes all the fish samples unsafe for human consumption.

4. CONCLUSION

The study revealed that the concentrations of zinc, cobalt, and copper in all organs of the samples of *Clarias gariepinus* analyzed were lower than the permissible limits of 150 ppm, 0.15-1.0 ppm and 10 ppm respectively. However, the concentrations of lead in the liver and cadmium in the muscle of fish samples from Ogbeogonogo and Abraka respectively were higher than the permissible limits. The concentrations of mercury in fish samples from the three markets were above the permissible limit of 0.5 ppm for mercury in fish and food substances stipulated by FAO/WHO. The results from the present study indicate that African catfish sold in Asaba markets are unsafe for human consumption due to the high levels of these toxic elements. The observed high levels of cadmium, lead, and mercury in this study could be attributed to anthropogenic sources such as fossils fuels combustion, indiscriminate disposal of domestic waste and industrial effluents on land and water bodies. Adoption of alternative renewable energy sources such as biogas and biodiesel, proper waste disposal strategies, as well as enforcement of environmental protection laws are imperative to ensure safety of aquatic organisms.

COMPETING INTEREST

The authors declare that there is no competing interest. The research was solely funded by the researchers.

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