Assessment of Heavy Metals in Selected Dried Consumer Fish Species Sold in Some Markets in Port Harcourt Metropolis, Rivers State, Nigeria

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Abstract
The concentrations of some heavy metals which include Cadmium-Cd, Lead-Pb, Mercury-Hg, Arsenic-As, and Zinc-Zn were examined in some dried consumer fish samples, obtained from three daily markets: Choba, Rumuokoro, and Mile 1, located in Port Harcourt metropolis of Rivers State, Nigeria. The investigated fish samples include: stock fish (Gadus morhua), horse mackerel (Trachurus trachurus), and African catfish (Clarias gariepinus). In each of the selected markets, three samples of each fish species were procured from the sellers and taken to the laboratory for analysis. The metal concentrations were determined in the sampled fish by Atomic Absorption Spectrophotometry (Buck Scientific, 200A Model). Levels of heavy metals were expressed in mg/Kg dry weight. The data obtained from the study were collated and analyzed using Statistical Package for Social Sciences (SPSS 22.0). According to the findings, the species Gadus morhua had the highest concentrations of: cadmium (0.23±0.01), lead (0.08±0.02), mercury (0.07±0.01), and arsenic (0.03±0.00), whereas C. gariepinus had the lowest concentrations of cadmium (0.06±0.01), lead (0.03±0.01), mercury (0.01±0.00), and arsenic (0.01±0.00). Nonetheless, T. trachurus has the highest concentration of zinc (5.97±0.23), followed by G. morhua (5.89±0.66), while C. gariepinus (3.22±0.66) has the lowest. Within the species, there were significant differences in metal concentrations ($p>0.05$). The fish utilized in this study were deemed safe for human consumption because their heavy metal levels were below the range established by the World Health Organization (WHO). Given the low concentrations of heavy metals found in the smoked fish samples examined in this study, monitoring of aquatic species should be done on a regular basis in the study area to determine when the amounts of heavy metals will rise above the permissible limits for safe consumption.

***Keywords**: Heavy metals, Fish food, Environmental pollution, Markets*

INTRODUCTION

The discharge of elements that are detrimental to living organisms into the atmosphere, water, or soil is commonly referred to as environmental pollution [1]. Given their toxicity to humans and environmental persistence, heavy metals are common contaminants in urban settings that are of immediate concern [2]. Heavy metals can harm aquatic ecosystems, the food chain, and human health. They can enter the aquatic environment through a range of man-made and natural methods [3]. The integrity of the environment has been threatened by anthropogenic input of heavy metals, particularly when it comes to aquatic living resources like fish species [4]. It has been documented that heavy metals alter the genetic, physiological, biochemical, and behavioral characteristics of fish and other aquatic organisms [5]. Since fish are significant sources of protein for humans and are perhaps the best-understood organisms in the aquatic environment, they have been the most often chosen species to test for heavy metals [6]. Because heavy metals are extremely persistent, indestructible, and have the capacity to bio-accumulate, their pollution of aquatic environments is an issue that is becoming worse on a global scale [7]. Because they vary in size and trophic level, fish are often used to assess the health of aquatic ecosystems and are good markers of heavy metal contamination [8]. Fish are indicators of pollution and water quality since they are at the bottom of the aquatic food chain. After consuming aquatic organisms, metals from the environment build up in the food chain and can affects the ecosystem and human health [9]. Therefore, keeping an eye on fish tissue pollution is crucial as an early warning sign of water quality issues and aids in taking appropriate action for the sake of the environment and public health [10].

Since trace metals develop in suspended particulates and sediments [11] and are not eliminated from aquatic environments by self-purification [12], their toxicity has long been a concern. This could endanger ecosystems and human health through the food chain [13]. Assessing the ecological risk posed by trace elements has so gained popularity in recent years [14]. Aquatic ecosystems, the food chain, and human health may all be negatively impacted by heavy metals, which can enter the aquatic environment through a range of anthropogenic and natural processes [15, 16]. A complex interplay of biological and ecological factors determines the concentration of heavy metals in biological compartments, including fish muscle [17]. These factors can lead to histopathological changes in the skin, gills, liver, spleen, and kidneys of fish, as well as growth and reproductive abnormalities [18]. Given the popularity of smoked fish products among the local population, the lack of updated and consistent data on the amounts of heavy metals in smoked fishes offered in Port Harcourt metropolis numerous markets made this study necessary.

Fish, among other animal species, are the inhabitants of aquatic environments that are unable to avoid the harmful effects of heavy metal contaminants [19]. Fish are frequently used to assess the health of aquatic ecosystems because contaminants accumulate in the food chain and have negative impacts on fish welfare in aquatic environments [20]. The majority of freshwater fishes are restricted to particular microhabitats within the networked river/stream ecosystem. When heavy metals contaminate such an ecosystem, fish species either die off or relocate to less polluted areas of the river or stream habitat, which eventually disrupts the food chains [21]. High concentrations of heavy metals appear to be fatal and have long-term consequences on fish [22]. As a result, fish have become increasingly popular in recent years for evaluating environmental conditions in aquatic ecosystems [23]. Proper understanding in the level of heavy metals is necessary to evaluate the health effects of these metals when consumed through fish. This will contribute to existing literatures, the study will also help to increase proper understanding of the nature of water bodies and the fishes in this area as well as serve as a source of information for those who need it. Very little research has been done on smoked fish within the state to determine the concentration of heavy metals on smoked fish and their impact on human life [23].This study therefore assess the heavy metal concentrations in some smoke dried fish from selected markets in Port Harcourt metropolis of Rivers State, Nigeria.

MATERIALS AND METHODS

Study Location

The study was carried out in three local daily markets namely: Choba Junction market, Rumuokoro main market, and Mile 1 market. These markets were all located in Port Harcourt metropolis, Rivers State, Nigeria.

Sample collection

The dried consumer fish samples commonly consumed by the local populace in Port Harcourt metropolis, Rivers State, Nigeria were procured from three selected markets on three occasions. The species were: Stock fish (Cod) - *Gadus morhua*; Horse mackerel (Shina) – *Trachurus trachurus* ; and African Catfish - *Clarias gariepinus.* Three samples of each fish species were purchased directly from the retailers in each of the selected markets, making a total of twenty seven samples.

Heavy Metal Analysis

The muscles from each of the sampled fish were rinsed with distilled water to remove dust and other external adherents. They were then dried in an oven at 105^0c. They were later homogenized using mortar and pestle. 10g of the homogenate was digested as described by APHA [24]. The sample was digested using 1:5:1 mixture of 70% perchloric acid, concentrated nitric acid and sulphuric acid at 80^0c in a fume chamber until a colourless liquid was obtained. The metal concentrations which include Hg, Cr, Pb, Cd and As were determined by Atomic Absorption Spectrophotometry (Buck Scientific 200A model). Levels of heavy metals were expressed in mg/Kg dry weight.

3.4. Statistical Analysis

The data obtained from the study were collated and analyzed using Statistical Package for Social Sciences (SPSS 22.0). A one way analysis of variance (ANOVA) was employed to reveal significant differences in measured variables. When a difference was detected ($P < 0.05$), Tukey's multiple comparison test was applied to identify differences between the means.

RESULTS

Heavy metals in some dried consumer fish sold in Choba Junction Market, Port Harcourt metropolis are presented in Table 1. The results showed the concentrations of heavy metals compared with the World Health Organization (WHO) / Food and Agriculture Organization (FAO) acceptable limits. The result of the study revealed that *G. morhua* has the highest concentration of cadmium (0.20±0.01), followed by *T. trachurus* (0.11±0.02), and *C.gariepinus* had the lowest value of 0.06±0.01. In lead, *T. trachurus* has the highest concentration of 0.07±0.02, while *C. gariepinus* has the lowest of 0.04±0.01 . Mecury was highest in *G. morhua* (0.03±0.00), followed by *T. trachurus (*0.02±0.00), and *C. gariepinus* was the least. Highest concentration of Arsenic was observed in *T. trachurus* (0.02±0.00), while Zinc has the highest

concentration of 5.97±0.44 in *T. trachurus*. The values of heavy metals in some dried consumer fish sold in Rumuokoro market compared with the World Health Organization (WHO) / Food and Agriculture Organization (FAO) acceptable limits are presented in Table 2. The results obtained indicated that *G. morhua* has the highest concentration of cadmium (0.23±0.01), *T.trachurus* has the highest concentration (0.05±0.01) of lead, while *G. morhua* has the concentration (0.07±0.01) of mercury. The highest concentrations of arsenic (0.03±0.00) and Zinc (5.88±0.82) were observed in the specie *G. morhua*, Table 3 represents the concentration of heavy metals in some dried consumer fish sold in Mile 1 Market. The results of the study revealed that the values of Cadmium were within the same range with no significant difference (P>0,05). In lead, the specie *G. morhua* has the highest concentration of 0.08±0.02, while *T. trachurus* has the lowest of 0.03±0.01. The value of mercury was highest in *G. morhua* (0.04±0.01), followed by *T. trachurus (*0.02±0.00), and *C. gariepinus* was the least value of 0.01±0.00. Highest concentration of Arsenic (0.03±0.00) was observed in *G. morhua* , while Zinc has the highest concentration of 5.88±0.44 in *T. trachurus*
The comparative values of Cd in some dried consumer fish sold in three markets in Port Harcourt Metropolis is shown in Figure 1. The results indicated that that the highest value of Cd (0.25) was observed in the specie *G. morhua* at Rumuokoro market, while the lowest value 0.05 was observed in *C. gariepinus* at Choba market .The comparative values of Lead in some dried consumer fish sold in Port Harcourt Metropolis is shown in Figure 2. The results indicated that that the highest value of 0.18 was observed in the specie *G. mrhua* in Mile one market, while the lowest value of 0.04 was observed in *C. gariepinus* in Rumuokoro market .The comparative values of mercury in some dried consumer fish sold in three markets in Port Harcourt metropolis is shown in Figure 3. The results indicated that that the highest value 0.04 was observed in the specie *G. morhua* in mile one market, while the lowest value of 0.01 was observed in *C. gariepinus* in all the markets .The comparative values of Arsenic in some dried consumer fish sold in three markets in Port Harcourt Metropolis is shown in Figure 4. The results indicated that that the highest value of 0.03 was observed in the specie *G. morhua* in mile 1market, while the lowest value of 0.01 was observed in *C. gariepinus* in all the markets .The comparative values of Zinc in some dried consumer fish sold in three markets in this study are presented in Figure 5. The results indicated that that the highest value of 5.97 was observed in the specie *T trachuru* in Choba market, while the lowest value of 3.22 was observed in *C. gariepinus* in Rumuokoro market.

Table 1: Heavy Metals in Some Dried Consumer Fish Sold in Choba Junction Market, Port Harcourt Metropolis (Mean± SD)

	Heavy metals in Fish Species (mg/Kg)			**FAO/WHO Limits**
Metals	***G. morhua***	***T. trachurus***	***C. gariepinus***	**FAO/WHO [25]**
Cadmium	0.20±0.01^{c}	0.11±0.01^{b}	0.06±0.01^{a}	0.50
Lead	0.05±0.01^{a}	0.07±0.02^{b}	0.05±0.01^{b}	0.50
Mercury	0.02±0.00^{a}	0.02±0.00^{a}	0.01±0.00^{a}	0.50
Arsenic	0.01±0.00^{a}	0.02±0.01^{a}	0.01±0.00^{a}	0.05
Zinc	5.89±0.66^{b}	5.97±0.44^{b}	3.66±0.19^{a}	99.40

Means with the same row with different superscripts are significantly different (P<0.05)

Table 2: Heavy Metals in Some Dried Consumer Fish Sold in Rumuokoro Market, Port Harcourt Metropolis (Mean± SD)

	Heavy metals in Fish Species (mg/Kg)			**FAO/WHO Limits**
Metals	***G. morhua***	***T. trachurus***	***C. gariepinus***	**FAO/WHO [25]**
Cadmium	0.23±0.01^{c}	0.11±0.01^{a}	0.15±0.02^{b}	0.50
Lead	0.04±0.01^{a}	0.05±0.01^{b}	0.03±0.01^{a}	0.50
Mercury	0.07±0.01^{b}	0.03±0.01^{a}	0.01±0.00^{a}	0.50
Arsenic	0.02±0.00^{a}	0.02±0.01^{a}	0.01±0.00^{a}	0.05
Zinc	5.88±0.82^{b}	5.62±0.77^{b}	3.22±0.66^{a}	99.40

Means with the same row with different superscripts are significantly different (P<0.05)

Table 3: Heavy Metals in Some Dried Consumer Fish Sold in Mile 1 Market, Port Harcourt Metropolis (Mean± SD)

	Heavy metals in Fish Species (mg/Kg)			**FAO/WHO Limits**
Metals	***G. morhua***	***T. trachurus***	***C. gariepinus***	**FAO/WHO [25]**
Cadmium	0.15±0.02^{a}	0.16±0.01^{a}	0.14±0.01^{a}	0.50
Lead	0.08±0.02^{b}	0.03±0.01^{a}	0.05±0.01^{a}	0.50
Mercury	0.04±0.01^{b}	0.02±0.00^{a}	0.01±0.00^{a}	0.50
Arsenic	0.03±0.00^{a}	0.02±0.01^{a}	0.01±0.00^{a}	0.05
Zinc	5.07±0.11^{b}	5.88±0.44^{b}	4.66±0.02^{a}	99.40

Means with the same row with different superscripts are significantly different (P<0.05)

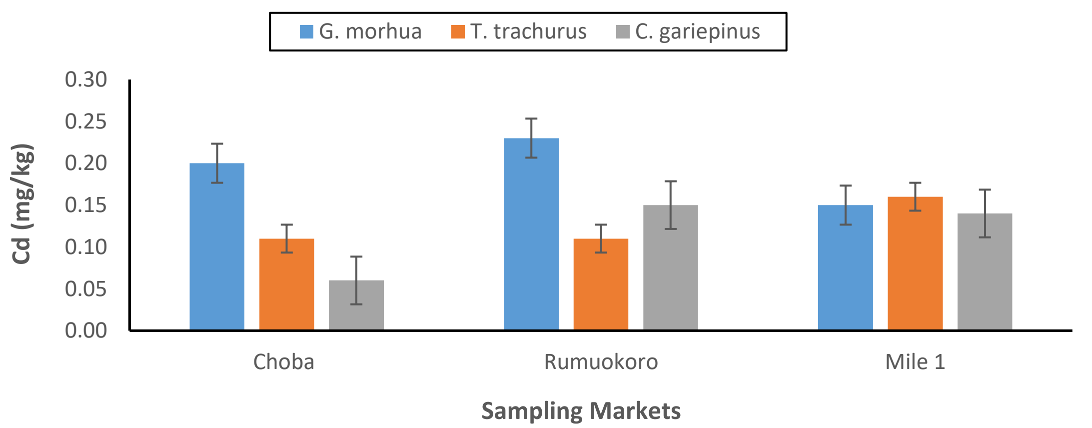

Figure 1: Concentrations of Cadmium (Cd) in some dried consumer fish sold in three markets located in Port Harcourt metropolis

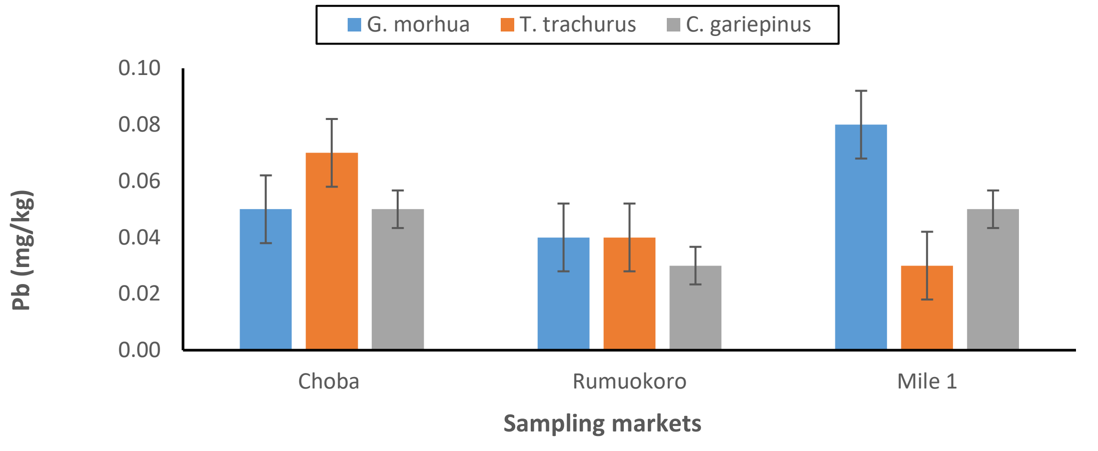

Figure 2: Concentrations of Lead (Pb) in some dried consumer fish sold in three markets located in Port Harcourt metropolis

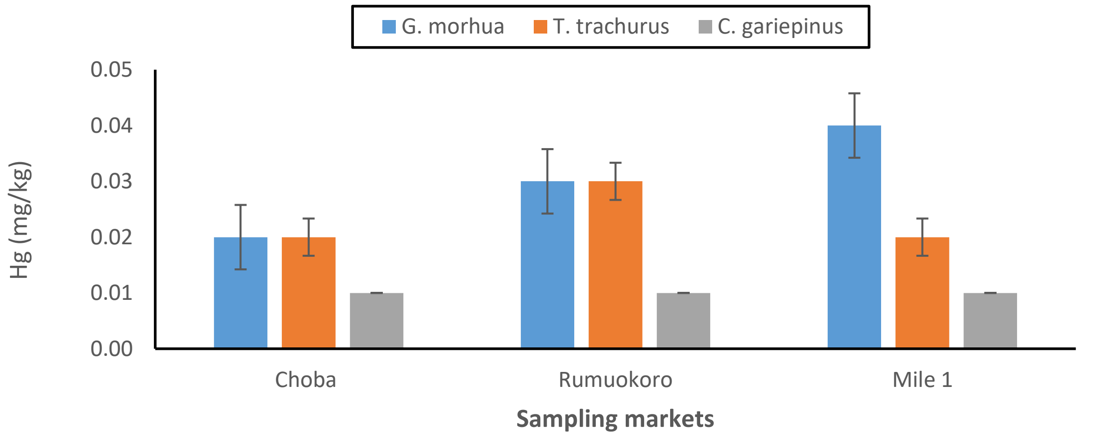

Figure 3: Concentrations of Mercury (Hg) in some dried consumer fidh sold in three markets located in Port Harcourt metropolis

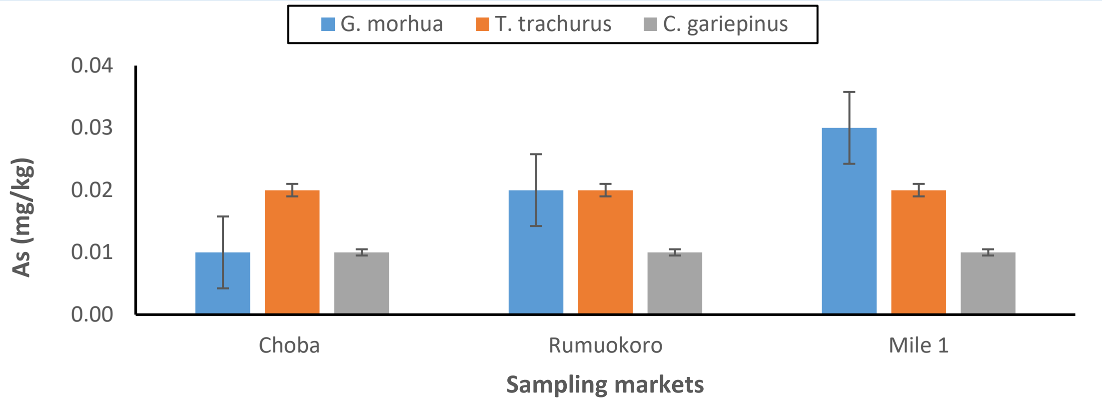

Figure 4: Concentrations of Arsenic (As) in some dried consumer fish sold in three markets located in Port Harcourt metropolis

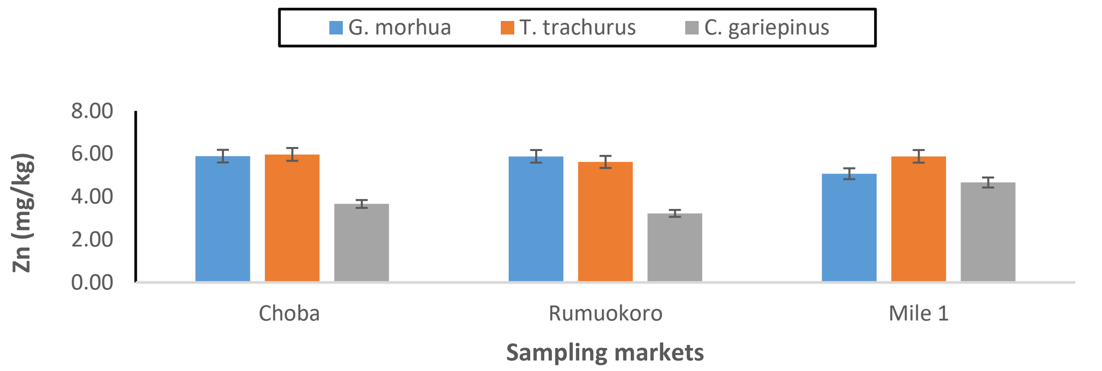

Figure 5:Concentrations in Zinc (Zn) in some dried consumer fish sold in three markets located in Port Harcourt metropolis

DISCUSSION

Heavy metals have become a threat because of their persistence in the natural environment, [26]. Fish intake of heavy metals in polluted aquatic media is dependent on ecological requirements, metabolism, and other factors like salinity, water pollution level, food, and sediment [27]. The concentrations of Zn, Pb, Cd, As and Hg in smoked *C. gariepinus*, *T. trachurus*, and *G. morhua* were highest in *G. morhua*, with the exception of Zn, which is higher in *T. trachurus*. This suggests that the fish species may have bioaccumulated more Zn than the other metals from its host aquatic medium. For Cd, the opposite situation might have existed in the same domain. Measurements of bioaccumulation are research or techniques used to track the absorption and retention of contaminants such as metals or biocides in the tissues of organisms like fish [28]. The movement of pollutants from one trophic level to another is described by the bioaccumulation of heavy metals in living organisms and biomagnifications [29]. Toxic metals can enter a living organism's tissues through the bioaccumulation process if they are highly available in the environment or food [30].

According to reports, smoked fish can introduce components from the surrounding water that are absorbed through the gills or by the consumption of contaminated food, and concentrations of these elements can reach dangerous levels [31]. The quantities of heavy metals in fish were found to vary significantly (P>0.05) among market places, most likely as a result of the smoked fish products coming from various wholesalers or processors. Additionally, in this study the amounts of these heavy metals varied significantly (P<0.05) among fish species, most likely due to seasonal variations in the metals' levels in fish aquatic media. The levels of several heavy metals in smoke-dried Bonga fish (*Ethmalosa fimbriata*) sold in fish markets in Warri, Niger Delta, Nigeria, were determined by Wangboje and Oghenesode [32]. Their findings were significantly higher than those found in this study.

This study found that the amounts of heavy metals from possible fish eating was highest for zinc and lowest for arsenic. Although it did not surpass the FAO limit in practice, this is not surprising given that As had the lowest concentration and consistently the lowest quota of all the metals among the fish species. As a result, potential consumers of this smoked fish are not in any way threatened by consuming this level of heavy metals. Akan *et al.* [33] state that if the concentration has surpassed the FAO limit, the exposure level might be either acute or chronic, depending on how long the exposure lasted. When heavy metals build up in soft tissues and are not broken down by the body, they become poisonous [34]. Fish consumers in the sampling markets had varying levels of these metals, according to the total heavy metal load in fish being sold in the market. This finding immediately implies that, should the limit surpass the WHO limit, future consumers of smoked fish could theoretically be exposed to a higher metal burden.

In this study, the FAO/WHO limits for heavy metals were 99.40 mg/kg for zinc and 0.05 mg/kg for Cd, Mg, As, and Pb. Since the mean concentrations of each heavy metal—Pb, Mg, As, Cd, and Zn—in fish were below the previously indicated thresholds for heavy metals in fish. There is little risk associated with eating these fish because the Pb, Cd, and Zn concentrations in this study were below the threshold. Batteries, alloys, solders, fossil fuels, plastics, and pesticides are among the natural or lithogenic sources of lead, whereas batteries, fossil fuels, fertilizers, plastics, alloys, and paints are among the sources of cadmium. Batteries, landfills, insecticides, alloys, dyes, fossil fuels, electroplating, and metallurgical processes are some of the sources of zinc [35]. It makes sense to assert unequivocally that smoked *C. gariepinus T. trachurus* and *G. morhua* should be consumed, but cautiously, due to the potential of heavy metal poisoning, particularly from mercury.

CONCLUSION AND RECOMMENDATIONS

The levels of heavy metals which include: Pb, Cd, Hg, Zn, and As in smoked *C. gariepinus*, *G. morhua* and *T. trachurus* bought from these three markets in Port Harcourt metropolis, were not above the WHO/FAO established limits as the fish were safe to be consumed. Heavy metal levels in the study area were highest in the specie *G. morhua*, followed by *T. trachurus*, and the lowest was recorded in the specie *C. gariepinus*. Given the low levels of heavy metals found in the smoked fish samples examined in this study,regular monitoring should be carried out on a regular basis to determine when the levels of heavy metals will rise higher than the thresholds safe for consumption. This is because these metals can be transferred to humans and put consumers at risk for health problems. To prevent these metals and other pollutants from entering the environment, it is important to properly dispose household wastes and industrial effluents safely and recycle them whenever feasible.

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