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Research Article

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Determination of Selected Heavy Metals and Human Health Risk Assessment in Fishes from Kiri Dam and River Gongola, Northeastern Nigeria

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Abstract

Atomic Absorption Spectrometry was used to analyze the concentrations of heavy metals (Pb, Cd, Cr, Fe and As) in the Catfish and Tilapia from Kiri Dam and River Gongola, Northeastern Nigeria. Analysis of these selected heavy metals in the fish samples reveals that these selected heavy metals are higher in Catfish than Tilapia irrespective of the location. Assessment of the health risks due to consumption of these fishes suggests that both fishermen and the general populace are not subjected to a significant potential health risk. The results of this study regarding metal contents in fishes from the study areas also suggest that the consumption of catfish and tilapia from the study area is not free of risks. And that the complex THQ and TTHQ parameters used in health risk assessment of heavy metals provides a better image than using only a simple parameter like the content of the metals in the samples.

Keywords: Heavy metals; Atomic absorption spectrometry; Fish; Health risk; Kiri Dam; River Gongola

Introduction

In aquatic ecosystems, heavy metals have received considerable attention due to their toxicity and accumulation in biota. Some of these elements are toxic to living organisms even at quite low concentrations, whereas others are biologically essential and natural constituents of the aquatic ecosystems and only become toxic at very high concentrations [1]. In fish, the toxic effect of heavy metals may influence physiological functions, individual growth rates, reproduction and mortality [2-6]. Heavy metals may enter fish bodies in three possible ways: through the body surface, the gills or the digestive tract [2]. Fish is generally appreciated as one of the healthiest and cheapest source of protein because it has amino acid compositions that are higher in cysteine than most other source of protein [7]. Fish is recommended for heart disease prevention because it is low in total and saturated fats, high in protein and essential trace minerals, and contains long-chain omega-3 fatty acids [EPA (eicosapentaenoic acid) and DHA (docosahexaenoic acid)] [2-7]. Tilapia and catfish are the most common examples of lower-fat fish that provide more of these heart-healthy nutrients than hamburger, steak, chicken, pork or turkey [7]. Catfish and Tilapia are among the most popular fish consumed in the Nigeria mainly due to their taste and relatively low cost. Studies have shown that heavy metals affect the physiological balance and other processes in fish. Also, the physical and chemical environment in which the fish resides appears to influence the rate of bioaccumulation of these trace elements in them. The effects of exposure to any hazardous substance depend on the dose, the length of time, the mode of exposure, personal habits, traits, and whether other chemicals are present [2-5]. The studies of some authors indicated different concentrations of heavy metals in different fish species. The heavy metal concentrations in the fish were attributed to chemical characteristics of water from which fish were sampled, ecological differences, metabolism and feeding patterns of fish [5,8-10]. Bioaccumulation of metals in fish can be considered as an index of metal pollution in aquatic ecosystems [5,11-14]. In Nigeria, the levels of concentration of toxic and non-biodegradable heavy metals in fish samples have been reported for some dams and lakes including Kainji Dam, Oguta Lake, Asa Dam, Ureje Dam, Alau Dam, Kusalla Dam [12,15,16] among others. Milam et al. investigated heavy metal pollution in benthic fishes from Kiri Dam (one of the areas under study in this work). They reveal that Pb, Cd, Cu, Zn, Ni and Fe are present in all fish species collected from Kiri Dam and also discovered that the gills of fishes contained higher concentration of the heavy metals compared to their muscles (flesh). Thus, despite the valuable nutritional constituents of fish, their ability to bioaccumulate toxic and non-biodegradable heavy metals in their edible body parts calls for an adequate assessment of the metal levels in them at regular intervals, so as to safeguard the safety of the consumers. The objective of this study is to determine and compare the levels of bioaccumulation of heavy metals in the two-fish species; determine if there is any significant difference between levels of heavy metals in each specie and estimate the potential human health risk associated with the consumption of these fishes from the area.

Materials and Methods

Study area

The Kiri Dam is in Guyuk local government area of Adamawa State in the northeast of Nigeria, damming the Gongola River (Figures 1a and 1b). It is a 1.2 km long and 20 m high zoned embankment with an internal clay blanket. It is located between latitudes 9.50°N and 10.10°N and longitudes 11.90°E and 12.04°E near the town of Kiri. The dam was largely completed in 1982. The reservoir has a capacity of 615 million

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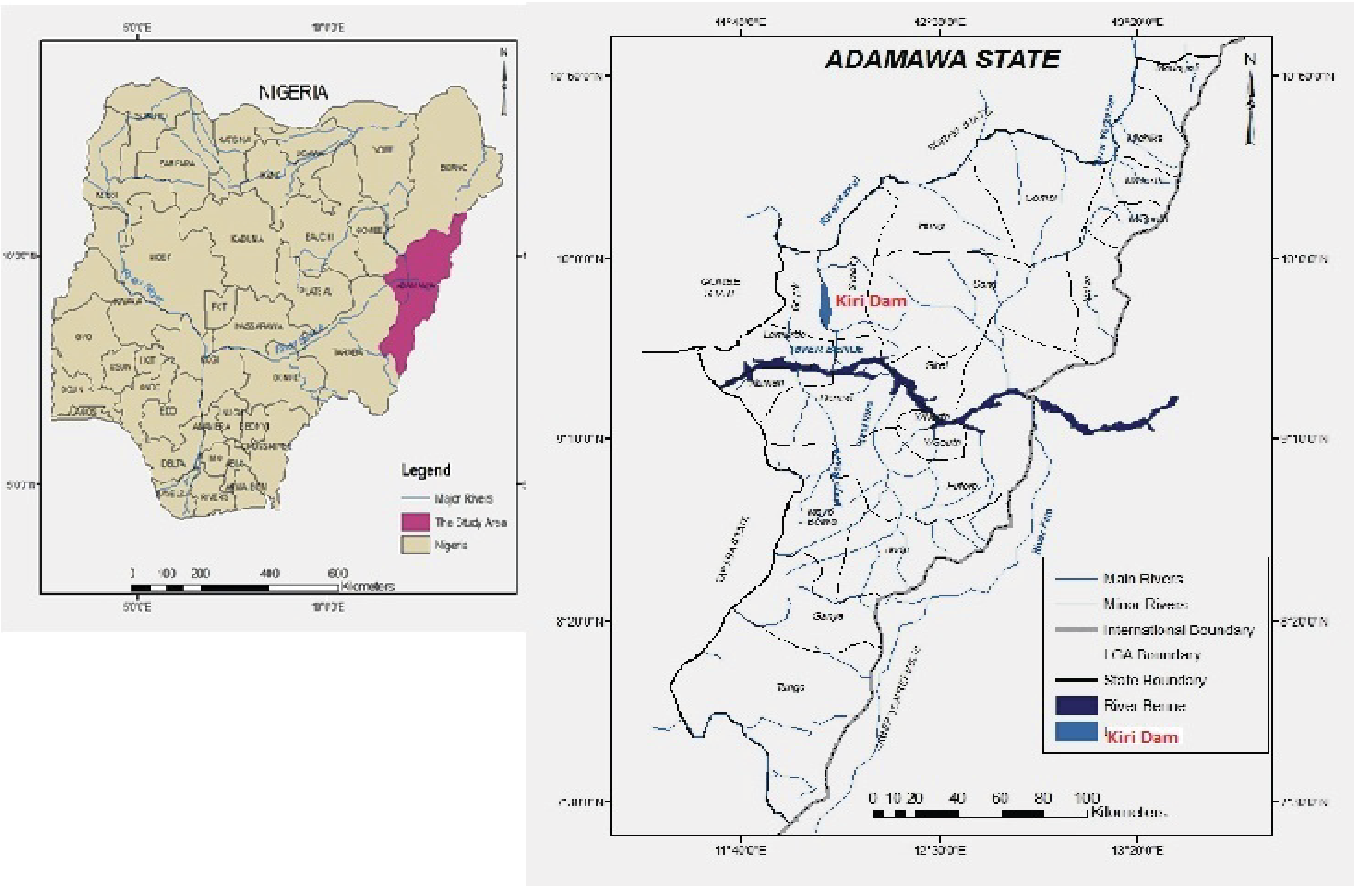

Figure 1a: Map of Nigeria and Adamawa state showing the study area.

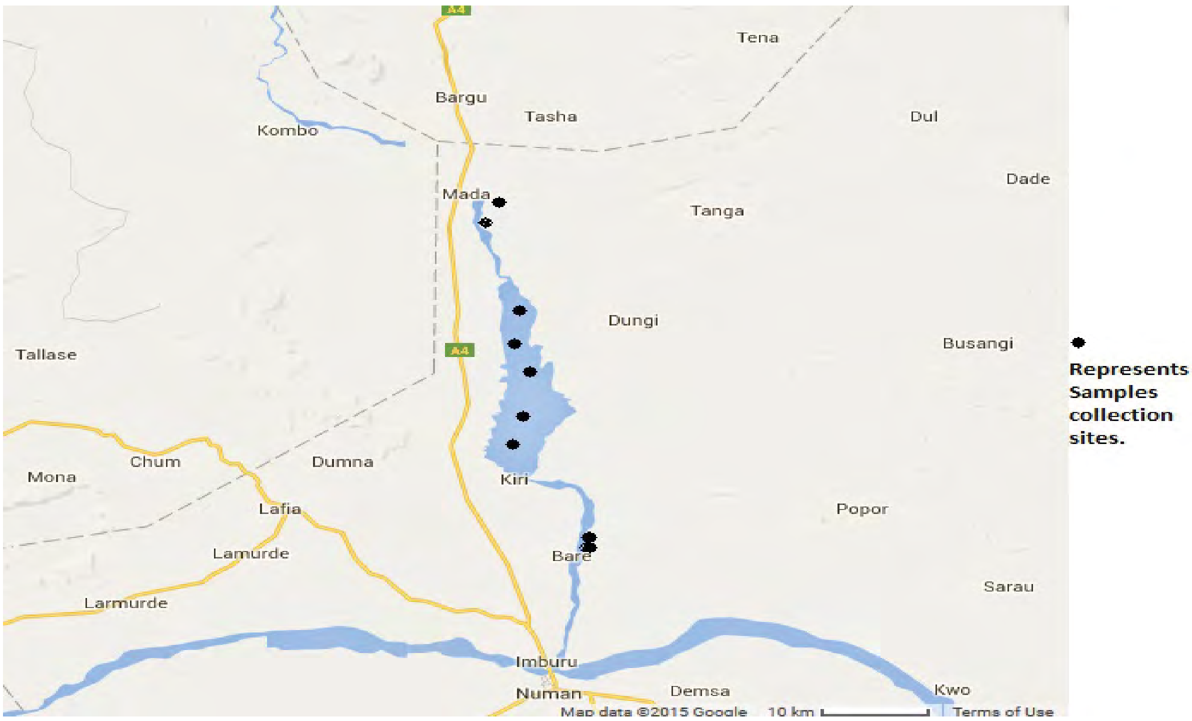

Figure 1b: Google Map showing the study areas and sample collection points.

m^3. The dam was built to supply electricity and irrigation needs of the Savannah Sugar Company (SSC) at Numan, a large-scale sugarcane plantation and processing company set up as joint venture between Nigerian Government and Commonwealth Development Corporation (CDC). It provides daily water supply for domestic and industrial use to SSC and environs from the reservoir, which includes the sugar plantation, fisheries production, flood control and flow regulation along the Gongola and Benue Rivers [16,17]. On the geology of Adamawa state, Ref. [18] described the geology to encompass parts of an ancient craton that was tectonically active in geologic past. A rift was created from one of such tectonics in the cretaceous and was filled with series of sedimentary deposits. This rift divides the State into almost two equal halves resulting into four main classes of rocks. The first is the alluvial or sedimentary deposit within the rift. The second rock type is the cretaceous continental deposit. Next is the hard crystalline cratonic basements and the tertiary/quaternary deposit.

Sample collection and preparation

Collection: Before samples were collected, a collection protocol was established which was strictly followed. This involves establishing a collection procedure (catching of fishes using a fisherman hook and net), obtaining appropriate containers, and utilizing the appropriate methods of preservation in order to reduce the effect of adsorption or biodegradation. Measurements carried out *in-situ* include conductivity, pH and temperature of the water. A total of 30 samples were collected from the study areas. At each location, 5 samples each of Catfish and Tilapia were collected from Kiri Dam, Mada (upstream) and Bare (downstream) along river Gongola the dam's major source of water. All the samples collected were identified and grouped according to their type and location. The samples were placed in ice, brought to the laboratory, washed, separated by species and then stored frozen prior to analysis.

Reagents: All reagents used were of analytical grade. Working standards of Lead, cadmium, chromium, arsenic and iron were prepared by diluting concentrated stock solutions (Merck, Germany) of 1000 mg/l in ultra-pure water (MilliQ, Millipore-USA) [19].

Sample preparation: The edible portions of the meat from the samples were removed, homogenized and about 2.5 ± 0.5 g was taken for analysis. Ten milliliters of nitric acid-perchloric acid (10:4) mixture were added to the sample, covered and left overnight at room temperature. Then the samples were digested, using a microwave digester. The completely digested samples were allowed to cool to room temperature, filtered (glass wool), and made up to 25 ml in a 25 ml standard flask which was finally transferred into plastic reagent bottle for Atomic Absorption Spectrometry [1]. The Atomic Absorption Spectrometry is a spectro-analytical procedure for the quantitative determination of chemical elements using the absorption of optical radiation (light) by free atoms in the gaseous state. The technique measures the concentrations of elements in digested samples down to parts per million (ppm) in a sample. The Atomic Absorption Spectrometry was carried out at ROTAS Soil-Laboratory in Ibadan using Buck Scientific Model 210 VGP Atomic Absorption Spectrophotometer.

Results and Discussion

Physio-chemical parameters of water samples collected from Kiri, Bare and Mada

The pH of the water samples from kiri ranged from 6.7 ± 0.1 to 7.5 ± 0.3 with an average value of 7.0 ± 0.2 which represent neutral water (neither acidic nor alkaline in nature). The mean pH of water samples from Bare (downstream) and Mada (upstream) are 7.0 ± 0.1 and 6.7 ± 0.1 respectively (Table 1). This range of values obtained is well within the WHO range of 6.5-8.5 for domestic and portable water. The electrical conductivity ranges between 370.0 ± 2.0 and 386.0 ± 3.2 with mean value of 381.0 ± 2.9 µS/cm for kiri water. The mean EC values for Bare and Mada were 360.5 ± 2.1 and 388.5 ± 2.1 µS/cm respectively. This shows that EC level of all the locations did not exceed the permissible limit of 500 µs/cm set by WHO. EC is an indicator of water quality; hence the water may be very suitable for aquatic animals and also good for domestic and agricultural use in terms of the EC value. The temperature of the water is relatively constant ranging between 29°C and 30°C. All these parameters have their own importance. For example, the pH is a measure of acid-base equilibrium achieved by water dissolved compounds as well as extent of flocculation and coagulation process of chemicals. Similarly electrical conductivity gives an idea about the concentration of electrolytes in water and is the limiting factor. It is a measure of water's ability to conduct an electric current is related to the amount of dissolved minerals in water, but it does not give an indication of which element is present.

Concentration of the selected heavy metals in the fish samples

The result of the heavy metal analysis in the samples of Catfish and Tillapia collected from the study area is given in Table 2. In Kiri, the concentration of Pb in Catfish ranges between 0.012-0.021 ppm with mean of 0.0156 ppm while it ranges between 0.005 and 0.012 ppm with mean of 0.0098 ppm in the samples of Tilapia. In Bare (Downstream) and Mada (Upstream) the mean concentration of Pb is 0.0135 and 0.0085 ppm for Catfish and 0.0115 and 0.0120 ppm for Tilapia. Varying concentration of Pb was observed in all the fish samples but Catfish from Kiri have the highest mean concentration (Figure 2). All the mean concentrations of Pb are below the WHO limit of 0.4-0.5 ppm for consumable fish, but Pb can bioaccumulate in Human body over years of continues consumption of these fish samples. So people should be worried of its bioaccumulation over time as higher concentrations of Pb can even cause irreversible brain damage [20-22]. Lead is a commutative poison and a possible human carcinogen. It may also cause the development of autoimmunity in which a person's immune system attacks its own cells. This can lead to joint diseases and ailment of the kidneys, circulatory system and neurons [20]. The concentration of Cd in Kiri ranges between 0.021-0.031 ppm with mean of 0.0258 ppm for Catfish and ranges between 0.008-0.014 ppm with mean of 0.0116 ppm for Tilapia (Table 3). The mean concentration of Cd in Bare and Mada is 0.0265 and 0.0275 ppm for Catfish and 0.011 and 0.0085 ppm for Tilapia respectively. Cadmium exposure has been reported to enhance kidney damage and hypertension [5,19,22]. None of the sampled fishes was found to contain Cd above the EC limit of 0.1 ppm. Humans are exposed to cadmium through food and the average daily intake for adults has been estimated to be approximately 50 mg [23]. The threshold for acute cadmium toxicity is reported to be a total ingestion of 3-15 mg. Severe toxic symptoms are reported to occur with ingestions of 10-326 mg. Fatal ingestions of cadmium, producing shock and acute renal failure, occur from ingestions exceeding 350 mg [24-27]. Chromium is an essential trace element [28] and the biologically usable form of chromium plays an essential role in glucose metabolism. It has been estimated that the average human requires nearly 1 lg/day. Deficiency of chromium results in impaired growth and disturbances in glucose, lipid, and protein metabolism [23]. It has also been reported that long term exposure to Cr can cause damage to liver, kidney circulatory and nerve tissues, as well as skin irritation [29,30]. The concentration of Cr in Kiri ranges between 0.08-

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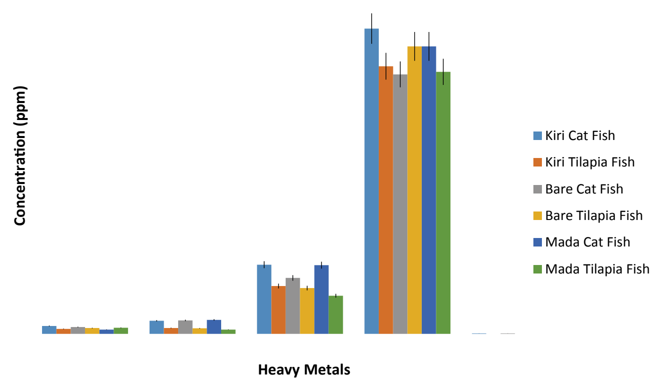

Figure 2: Concentration of the selected heavy metals in Cat-fish and Tilapia-fish.

		Water Samples		Sediment Samples	
		pH	EC (µS/cm)	pH	EC (µS/cm)
Kiri Samples	MIN	6.7 ± 0.1	370.0 ± 2.0	7.00 ± 0.1	46.80 ± 1.5
	MAX	7.5 ± 0.3	386.0 ± 3.2	8.60 ± 0.2	64.30 ± 2.0
	MEAN	7.0 ± 0.2	381.0 ± 2.9	7.72 ± 0.2	55.20 ± 1.8
Bare Samples	MIN	6.8 ± 0.1	340.0 ± 2.1	7.80 ± 0.2	60.10 ± 1.5
	MAX	7.2 ± 0.1	381.0 ± 2.0	8.40 ± 0.2	64.20 ± 2.0
	MEAN	7.0 ± 0.1	360.5 ± 2.1	8.10 ± 0.2	62.15 ± 1.8
Mada Sapmles	MIN	6.5 ± 0.1	336.0 ± 2.0	7.50 ± 0.1	46.80 ± 1.5
	MAX	6.8 ± 0.1	341.0 ± 2.1	7.80 ± 0.1	52.40 ± 2.0
	MEAN	6.7 ± 0.1	338.5 ± 2.1	7.65 ± 0.1	49.60 ± 1.8

Table 1: Physio-Chemical parameters of the samples collected from Kiri, Bare and Mada.

Kiri Cat Fish		Pb	Cd	Cr	Fe	As
	MIN	0.0120	0.0210	0.080	0.510	ND
	MAX	0.0210	0.0310	0.210	0.820	0.001
	MEAN	0.0156	0.0258	0.136	0.600	0.001
Bare Cat Fish	MIN	0.0120	0.0210	0.100	0.500	ND
	MAX	0.0150	0.0320	0.120	0.510	0.001
	MEAN	0.0135	0.0265	0.110	0.510	0.001
Mada Cat Fish	MIN	0.0050	0.0240	0.130	0.520	ND
	MAX	0.0120	0.0310	0.140	0.610	ND
	MEAN	0.0085	0.0275	0.135	0.565	NA

Table 2: Concentration of the selected heavy metals of Cat-fish samples collected from Kiri, Bare and Mada.

0.21 ppm with an average value of 0.136 ppm for Catfish and ranges between 0.05-0.12 ppm with an average of 0.094 ppm for Tilapia samples. The mean concentration of Cr for samples from Bare and Mada are 0.11 ppm and 0.135 ppm respectively for Catfish and 0.09 ppm and 0.075 ppm for Tilapia fish respectively (see table). For Iron (Fe) in Kiri, the concentration ranges between 0.510-0.820 ppm with an average value of 0.600 ppm in Catfish and ranges between 0.420-0.610 ppm with mean value of 0.526 ppm in Tilapia respectively (see table). For samples from downstream (Bare) and upstream (Mada) the mean concentration of Fe were found to be 0.510 ppm and 0.565 ppm for Catfish respectively and 0.565 ppm and 0.515 ppm for Tilapia respectively. Excess amount of iron (more than 10 ppm) is reported to causes rapid increase in pulse rate and coagulation of blood in blood vessels, hypertension and drowsiness [20-22]. The concentration Arsenic (As) is below the detectable limit for all the sampled Tilapia fishes from Kiri, Bare and Mada. Sampled Catfishes from Mada also follow similar trend. The concentration of As where traceable is 0.001 ppm in all the Catfishes from Kiri and Bare respectively. This is well below the accepted limit of 76 mg/kg [31]. The estimated US daily intake of arsenic is approximately 70 µg [31]. Arsenic concentrations as high as 170 mg/kg have been reported in crustaceans and other shellfish [23]. Chronic arsenic poisoning symptoms include pigmented skin lesions, gangrene of the lower extremities (blackfoot disease), along with neuritis and paralysis, anemia and disturbances of the liver and circulatory system [5,19,22,29]. From Figure 2, it is observed that the concentration of these selected heavy metals is higher in Catfish than Tilapia irrespective of the location. This is believed to be due to their difference in eating habit and metabolism. As it is well known that one of the most important factors that play a significant role in heavy metal accumulation in aquatic animals is the metabolic activity [5,19,32].

Human health risk assessment of heavy metals in from consuming fish

Determination of target hazard quotients (THQ): The Target Hazard Quotient (THQ) is defined as the ratio of the exposure and the reference doses, it expresses the risk of non-carcinogenic effects. A THQ value less than 1 means the level of exposure is less than the reference dose, implying that there will not be any obvious risk. Thus, a daily exposure at this level is not likely to cause any adverse effects during the lifetime of an individual. On the other hand, a population exposed to a dose equal to or greater than the RfD will experience health risks, and therefore calls for concern [5]. The method for the determination of THQ was provided in the United States EPA Region III risk-based concentration table (USEPA, 2000). The dose calculations were carried out using standard assumptions from an integrated United States EPA risk analysis.

The models for estimating THQ is given by equations 1 and 2 [3,33]:

$$THQ = \frac{EFr \times EDtot \times FIR \times C}{RfDo \times BW\alpha \times ATn} \times 10^{-3} \quad (1)$$

Where THQ is the target hazard quotient; EFr is exposure frequency (365 days/year); EDtot is the exposure duration (70 years, average lifetime); FIR is the food ingestion rate (kg/day) i.e., Nigerian per capita consumption of fish is 11.2 kg for general populace and 109.5 kg for fishermen [34]. This follows that the daily intake of fish per person is 0.031 kgd^{-1} for Nigeria; C is the heavy metal concentration in fish (mg/kg or ppm); RfDo is the oral reference dose (mg/kg/day, Table 4); BWa is the average adult body

Kiri Tila Fish		Pb	Cd	Cr	Fe	As
	MIN	0.005	0.008	0.05	0.42	0
	MAX	0.012	0.014	0.12	0.61	0
	MEAN	0.0098	0.0116	0.094	0.526	NA
Bare Tilapia	MIN	0.010	0.012	0.08	0.52	ND
	MAX	0.013	0.010	0.10	0.61	ND
	MEAN	0.0115	0.011	0.09	0.565	NA
Mada Tilapia	MIN	0.010	0.005	0.05	0.51	ND
	MAX	0.012	0.012	0.10	0.52	ND
	MEAN	0.012	0.0085	0.075	0.515	NA

Table 3: Concentration of the selected heavy metals of Tilapia-fish samples collected from Kiri, Bare and Mada.

Heavy metal	Pb	Cd	Cr	Fe	As
RfD_o (mgkg^{-1}day^{-1})	4.0×10^{-4}	1.0×10^{-3}	5.0×10^{-3}	9.0×10^{-3}	3.0×10^{-4}

Table 4: Oral Reference dose of heavy metals (USEPA).

		Pb	Cd	Cr	Fe	As	Total THQ
Kiri Cat	General Populace	0.002015	0.013330	0.014053	0.034444	0.001722	0.065565
	Fishermen	**0.019520**	**0.129129**	**0.136136**	**0.333667**	**0.016683**	**0.635135**
Tilapia	General Populace	0.001266	0.005993	0.009713	0.030196	0.000000	0.047169
	Fishermen	**0.012262**	**0.058058**	**0.094094**	**0.292514**	**0.000000**	**0.456929**
Bare Cat	General Populace	0.001744	0.013692	0.011367	0.029278	0.001722	0.057802
	Fishermen	**0.016892**	**0.132633**	**0.11011**	**0.283617**	**0.016683**	**0.559934**
Tilapia	General Populace	0.001485	0.005683	0.009300	0.032435	0.000000	0.048904
	Fishermen	**0.014389**	**0.055055**	**0.09009**	**0.314203**	**0.000000**	**0.473737**
Mada Cat	General Populace	0.001098	0.014208	0.01395	0.032435	0.000000	0.061691
	Fishermen	**0.010636**	**0.137638**	**0.135135**	**0.314203**	**0.000000**	**0.597611**
Tilapia	General Populace	0.001550	0.004392	0.007750	0.029565	0.000000	0.043256
	Fishermen	**0.015015**	**0.042543**	**0.075075**	**0.286397**	**0.000000**	**0.419030**

Table 5: Estimated Target Hazard Quotients (THQ) for individual metals and Total THQ from consumption of Cat and Tilapia fish by the general populace and fishermen in Kiri, Bare and Mada.

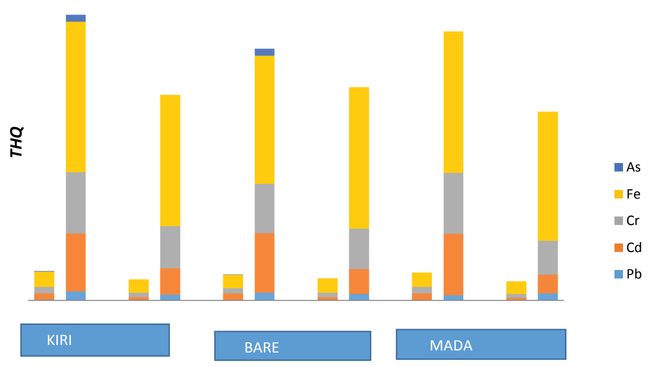

Figure 3: The relative contributions of the selected heavy metals to the total metal THQ values due to consumption of fish for general populace and fishermen for all the areas.

weight (60.0 kg); and ATn is the averaging exposure time for non-carcinogens (365 days/year x number of exposure years, assuming 70 years). The total THQ which is the sum of the individual metal THQ values is given by:

$$\text{Total THQ (TTHQ)}=\text{THQ (toxicant}_1)+\text{THQ (toxicant}_2)+ \text{---} +\text{THQ (toxicant}_n) \quad (2)$$

In the calculation of THQ, the ingested dose and the absorbed pollutant dose has been considered to be same, it has also been assumed that cooking has no effect on the pollutants. The estimated THQ of each metal due to fish consumption is less than 1 for both the general populace and the fishermen in all the areas (see Table 5), suggesting that intake of individual metals through fish consumption would pose no significant health risks. THQ values for Cat Fish were higher than comparable values for Tilapia in all the areas. This follows from the fact that the concentration of these selected heavy metals are higher in Catfish than Tilapia irrespective of the location. And as stated earlier, this is believed to be due to their difference in eating habit and metabolism [5,19,32]. The relative contributions of the selected heavy metals to the total metal THQ from fish consumptions is shown in Figure 3. Fe contributed major risk for both the general population and for fisherman in all the areas. It accounted for an average of 58% of the total THQ. Cr contributed the next highest risk, contributing an average of 20.4% to the total THQ. This is followed by Cd, Pb and As with an average of 17.7%, 2.8% and 1.1% respectively. The estimated target quotients (THQ) for individual metal decreased in following sequence: Fe>Cr>Cd>Pb>As. The total THQ for the general populace is very much less than threshold of 1. The THQ value is a relative and highly conservative index. This means in reality, a THQ>1 may not actually translate to people experiencing adverse or severe health effects instead it means that there exist a relative possibility of the adverse effects. This implies that there is no evidence of an unacceptable non-cancer risk for the general populace in all the areas. The estimated THQ for fishermen was observed to be about 9 times that of the general populace with an average of 0.52 and highest value of 0.64 in Kiri. These values are still less than 1 suggesting that the fishermen may not experience adverse health effects also. However, worry should still exist about its bioaccumulation over time as higher concentrations could potentially lead to adverse health effects.

Conclusion

Fish is generally appreciated as one of the healthiest and cheapest source of protein but despite its valuable nutritional constituents, its ability to bioaccumulate toxic and non-biodegradable heavy metals in its edible body parts calls serious concerns. In this study, we have determined and compared the levels of bioaccumulation of heavy metals in two fish species (Catfish and Tilapia), determined if there is any significant difference between levels of heavy metals in each specie and also estimated the potential human health risk associated with the consumption of these fishes from the area. Analysis of these selected heavy metals in the fish samples reveals that these selected heavy metals are higher in Catfish than Tilapia irrespective of the location. This was believed to be due to their difference in eating habit and metabolism. As it is well known that one of the most important factors that play a significant role in heavy metal accumulation in aquatic animals is the metabolic activity [5,19,32]. Assessment of the health risks associated with the consumption of these fishes suggest that both fishermen and the general populace are not liable to a significant potential health risk as a result of intake of the selected heavy metals consumed by these fishes, consequently, there is no evidence of an unacceptable non-cancer risk.

Also, in this study the results of the heavy metal contents in fishes from the study areas suggest that the consumption of catfish and tilapia from Kiri Dam and river Gongola, Northeastern Nigeria is not free of risks. And that the complex THQ and TTHQ parameters used in health risk assessment of heavy metals provides a better image than using only a simple parameter like the content of the metals in the samples. Hence, since human health risks associated with fish consumption from this area were considerably beyond negligible amounts, the sources of heavy metal pollution in the hydrosphere should be controlled [34-36].

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