

Health risk assessment of exposure to heavy metals in fish species consumed in Aba, Abia State, Nigeria

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Abstract. The concentrations of heavy metals (Pb, As, Cr, Cu, Cd and Fe) were determined in the gills, liver and muscles of thirty-five fishes, water and sediment samples from Aba River using atomic absorption spectrophotometer. Heavy metal concentrations varied markedly among fish species and organs. Results revealed that Pb, Cr, Fe had maximum concentration levels of 0.63 ± 0.01 , 0.81 ± 0.01 and 16.91 ± 0.20 mg/kg in Chrysichthys nigrodigitatus respectively. As and Cd recorded the highest concentration of 0.18±0.03 and 0.87±0.02 mg/kg in *Malapterurus electricus* respectively, while Trachurus trachurus had 1.05±0.03 mg/kg of Cu. Orenchromis niloticus, Tilapia ziili and Malapterurus electricus had higher concentrations of As and Cr in the liver compared to gills and muscles. The gills had higher concentrations of these heavy metals than liver and muscles in the rest of fish species studied. The concentrations of Cd, Pb and As in freshwater samples were higher than the standard maximum permissible limit. The sediments had higher concentrations of these metals than in fish and water samples. Heavy metal concentrations in fish species exceeded the standard guideline limit in food substances for human consumption. Malapterurus electricus, Parachanna obscura and Chrysichthys nigrodigitatus had bioaccumulation factors for Cd which ranged from 1.069 -1.663, indicating potential Cd poisoning or contamination of the three fish species. The estimated daily intake in both adult and children ranged from 8.611×10^{-7} to 9.72 x 10⁻³ mg/kgbw/day and were within the standard limit of daily intake for the human population. The hazard quotient for adult and children populations ranged from 0.0041 -1.3972 and 0.000287 - 0.2080 respectively. The hazard quotient was less than one in most of the metals except for iron, but hazard index was greater than one, indicating potential chronic health hazards. Incremental life cancer risk for the adult population was within safe limits.

Keywords: fish species; heavy metal; hazard quotient; hazard index; cancer risk.

1. Introduction

Fish is one of the very important sources of easily digestible animal proteins and essential nutrients required for the healthy growth of the body [1]. The availability of fish communities in any stream or river depends largely on the region, water temperature, water velocity, clarity, alkalinity and the presence of already existing habitat. Fish constitutes over 60% of the total protein intake in adults, especially in rural areas [2]. The quality of fish tissue varies among different species but depends on their body compositions and energy values [3].

Heavy metal pollution of the aquatic environment has become a global problem in recent years. Heavy metals are introduced into the water body through a natural process, weathering, erosion, mining, the process of metal ores, and effluents of metallic compounds which are often used in industrial pigments for leather, textiles and paper industries. Acid rains containing trace metals as well as suspended particulate matter inputted to the water body will cause water pollution. Agricultural discharge containing residual pesticides, herbicides and fertilizers which contain metals is another source of water pollution [4].

Heavy metals are not biodegradable but are persistent and toxic to living organisms if their concentrations are higher than the permissible values [5]. Sediments are significant sinks for several pollutants such as pesticides and heavy metals but play a vital role in the remobilization of pollutants in aquatic systems, especially in very favorable conditions. The most significant indicators for the estimation of metal pollution in freshwater systems are fish samples [6]. Heavy metals are found to bioaccumulate in fishes at concentrations much higher than present in water or sediments, consequently, fish is used for marine pollution monitoring [7, 8]. Heavy metals gradually accumulate through the process of absorption on fish tissues, gills, liver and other organs. Gills are thought to be the foremost site for contaminant uptake in fish due to their anatomical and physiological properties which take full advantage of absorption efficiency in the aquatic environment [9]. Acute and chronic disease conditions may arise as a consequence of ingesting fish polluted with toxic metals. These disease conditions

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include renal failure, liver dysfunction, cardiovascular diseases, neurotoxicity, carcinogenic effect and ultimately death [10-12].

Some studies have been done on the pollution status of Aba River where focus was placed on the levels of heavy metals in the freshwater [13-15]. Ogoko and Donald attempted to use fish as an indicator for the estimation of metal pollution in Imo River but observed that the heavy metal concentrations were higher in sediments than in fish tissue and water respectively [10]. They also noted significantly high levels of lead, copper, zinc and manganese and stated that Imo River was contaminated and not suitable for drinking. Mgbemena and Onwukeme observed significantly higher levels of Cr, Co, V, Mn, Ni, Hg and As contamination in Aba River [16]. However, there is very scanty report in the literature on levels of heavy metals in sediments from Aba River. Besides, a previous study reported higher levels of heavy metals in Aba River [16]. Nevertheless, due to increasing anthropogenic activities and the discharge of industrial effluents to Aba River as a consequence of increased industrialization and commercialization of the city, it then became imperative that the environmental conditions of Aba River should be continuously monitored.

The study is aimed at determining the heavy metal concentrations of water, fish and sediment samples from Aba River, and health risk assessment of exposure to heavy metals in fish species consumed. The results of heavy metal concentrations in the organs of fishes were compared with the standard maximum permissible limit to ascertain the overall quality of fish for consumption. The study also makes available an evaluation on the suitability of the surface water for drinking purposes.

2. Experimental

2.1. Site of study

Aba River is a river situated in southern Nigeria. The river runs through Aba metropolitan area and it is an offshoot of the Imo River. The heart of the river is at Okpu-Umuobo in the Ngwa land which extends to Aba City. Aba River is at a coordinate of 4.8230° N, 7.4910° E and serves as a major source of water for the city. Industrial effluents and abattoir waste are emptied into the river which is currently an environmental concern to the state.



Figure 1. Google map showing Aba River

2.2. Sample collection

Thirty-five fishes of seven different species (Orenchromis niloticus, Tilapia ziili, Malapterurus

electricus, Parachanna obscura, Chrysichthys nigrodigitatus, Scomber scombrus, Trachurus trachurus) were considered for the study. Five fish species of 25 samples (Orenchromis niloticus, Tilapia ziili, Malapterurus electricus, Parachanna obscura, and Chrysichthys nigrodigitatus) were collected alive from Aba River and five samples each of two other species (Scomber scombrus and Trachurus trachurus respectively) were bought frozen from Aba (Osisioma) market. The fish species of lengths which ranged from 24 to 34 cm were randomly collected in May 2021 with the aid of fishing gear. The fish samples were then taken in an ice-cold box to the appropriate laboratory and maintained at -20 °C before analysis [17]. Freshwater samples from Aba River were collected at four different sampling points and stored in a transparent 1 L polyethylene container at 4 °C in a refrigerator. Sediment samples were also collected at four different points in each sampling site. Sediment samples from the four points were then pooled together to form composite samples. The composite sediment samples were dried, ground to a fine powder and then stored in well-labeled polyethylene bags before analysis.

2.3. Heavy metal analysis

Previously defrosted fish sample was dissected, while the muscles, livers, and gills were collected for analysis of heavy metal. 2 g of each of the muscles, livers, and gills were dried and crushed into powder. The ground body parts of fish sample were then digested with concentrated HNO3 and HCl acid in the ratio of 3:1 at water boiling point (100 °C) for 35 minutes in a water bath until an observable color change appears. The resultant solution was filtered and the filtrate was diluted with distilled water up to the 50 ml mark of a standard volumetric flask [18]. Pb, As, Cr, Cu, Cd and Fe were determined with the aid of a flame furnace Atomic Absorption Spectrophotometer (Schdmazu AA-6800, Tokyo, Japan), with a detection limit of 0.001 ppm. The samples were analyzed in triplicates and assays of Pb, As, Cr, Cu, Cd, and Fe were performed at the corresponding wavelengths of 217, 193.7, 357.9, 324.8, 228.9 and 248.3 nm. The reagents used, HCl and HNO₃. were of analytical grade and 99% purity. A Blank was prepared for each sample and adjustment was made accordingly by reference to the blank. Results were then appropriately expressed in mg kg dry weight of fish, using the formulae:

Concentration
$$\left(\frac{\text{mg}}{\text{kg}}\right) = \frac{\text{Concentration}\left(\frac{\text{mg}}{\text{L}}\right) \times \text{V}}{\text{W}}$$
 (1)

where: V = final volume of sample solution; W = initial weight of sample measured

2.4. Method validation

Spiking samples with 0.5 mg/L of standard solutions of the respective metals before digestion were appropriated to establish the accuracy of the analysis. Spiked samples were subsequently exposed to similar analytical conditions as the test sample. Percentage recovery was then calculated using the formulae:

$\% Recovery = \frac{Concentration of the spiked sample - Concentration of unspiked sample}{Actual spike concentration}$ (2)

Recovery percentages of results for Cd, Pb, As, Cr, Cu, and Fe ranged from 92 - 102 %.

The correlation coefficient of most of the values of metals analyzed in the present study lies within 0.9970 - 0.9980. Triplicate measurements of samples for each metal were done while the precision of each measurement was expressed as the mean \pm standard deviation. The performance of the method concerning precision is as in the recovery study.

2.5. Data analysis

Interpretation of data obtained was done by the use of standard deviation and application of chemometric models such as pollution index, bioaccumulation factor, estimated daily intake and hazard quotient to assess the health risk to humans through consumption of fish.

2.5.1. *Estimated daily intake*. The estimated daily intake (mg/kg/day) is given by the equation below:

$$EDI = \frac{CR}{BW}$$
(3)

where: CR is the mean concentration of heavy metal in fish samples (mg/kg), IR and BW represent the daily fish consumption rate and the mean bodyweight of Nigerians respectively. 21.6 kg and 63 kg were the average body weights of Nigerian children and adults respectively [19]. The daily ingestion rate of fish protein in children (0-9 years) is 0.00186 kg/day (1.86 g/ day) while that of adult Nigerians is 13.3 kg per capita income per year or 36.438 g per day [20-21].

2.5.2. *Hazard quotient*. Noncarcinogenic health risks for each of these heavy metals in fish samples were estimated by computing the hazard quotient (HQ) as in the following equation [22-24]:

$$HQ = \frac{EDI}{RfD}$$
(4)

where RfD is the oral reference dose which refers to the estimated maximum permissible health risk associated with daily human consumption or contact with heavy metals, expressed in mg/kg/day.

The aggregate contribution of the effect of two or more of these heavy metals to the overall potential risk to human health is appropriately described by the hazard index. The hazard index (HI) can be expressed mathematically thus:

 $HI = \sum HQ$ (5)

The assumption made here was that the potential health risk is proportional to the combined effects of several heavy metals on the same target organ. HI < 1, indicates no potential health risk, whereas HI > 1 reveals potential chronic risk.

2.5.3. Carcinogenic risk. Incremental lifetime cancer risk: One index to evaluate the carcinogenic risk is the incremental lifetime cancer risk. Incremental lifetime cancer risk (ILCR) is expressed by the equation below:

$$ILCR = CDI \times CSF$$
(6)

where CDI is the chronic daily intake of carcinogenic chemical substance (mg/kg bw/day). CSF is the cancer slope factor, which defines the risk inherent in a lifetime average dose of 1 mg/kg bw/day of contaminant [25-28]. But,

$$CDI = \frac{EDIxEFx ED}{AT}$$
(7)

where EF is the expose frequency in days/year, which is equivalent to 365 days per year. ED refers to the exposure duration in years which is equivalent to life expectancy. Life expectancy for adult Nigerians is 54 years [23-25]. AT in the above equation refers to the average time or period of exposure, which is equivalent to 365 days per year multiplied by 54 years (i.e. average expectancy) = 19,710 days.

3. Results and discussion

The concentration of different metals in the gills, liver and muscles of seven fish species are presented in Table 1.

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Sample	Fish Parts	Pb	As	Cr	Cu	Cd	Fe
	Gills	0.03 ± 0.01	0.05 ± 0.00	0.08 ± 0.01	0.40 ± 0.06	0.12 ± 0.01	10.02±0.02
Orenchromis niloticus	Liver	0.02 ± 0.01	0.07 ± 0.01	0.10 ± 0.02	0.40 ± 0.01	0.11 ± 0.01	9.81 ± 0.30
	Muscles	0.01 ± 0.00	0.04 ± 0.01	0.08 ± 0.01	0.40 ± 0.01	0.10 ± 0.01	9.02±0.05
	Gills	0.01±0.00	0.06 ± 0.01	0.07±0.01	0.50 ± 0.01	0.14 ± 0.01	6.01 ± 0.10
Tilapia ziili	Liver	0.01 ± 0.00	0.07 ± 0.01	0.09 ± 0.01	0.51 ± 0.01	0.14 ± 0.01	6.15 ± 0.01
	Muscles	0.01 ± 0.00	0.06 ± 0.01	0.07 ± 0.01	0.50 ± 0.01	0.14 ± 0.01	6.00 ± 0.10
	Gills	0.51±0.01	0.16±0.03	0.05 ± 0.01	0.79±0.01	0.84±0.02	10.0±0.01
Malapterurus electricus	Liver	0.53 ± 0.02	0.18±0.03	0.04 ± 0.01	0.81±0.02	0.87 ± 0.02	11.0±0.05
	Muscles	0.50 ± 0.01	0.16 ± 0.01	0.04 ± 0.01	0.75 ± 0.01	0.84 ± 0.02	10.0±0.02
	Gills	0.44 ± 0.01	0.12±0.01	0.70±0.01	0.68±0.02	0.54 ± 0.01	11.01±0.03
Parachanna obscura	Liver	0.43 ± 0.01	0.13±0.01	0.65 ± 0.00	0.60 ± 0.02	0.54 ± 0.01	11.03±0.03
	Muscles	0.40 ± 0.01	0.10 ± 0.01	0.62 ± 0.01	0.62 ± 0.02	0.54 ± 0.01	10.90±0.03
	Gills	0.63±0.01	0.14 ± 0.01	0.81±0.01	0.38±0.01	0.81±0.01	16.81 ± 0.01
Chrysichthys nigrodigitatus	Liver	0.61 ± 0.01	0.11 ± 0.01	0.63 ± 0.01	0.35 ± 0.01	0.81±0.02	16.81 ± 0.02
	Muscles	0.60 ± 0.01	0.10 ± 0.01	0.73±0.01	0.35 ± 0.01	0.81 ± 0.01	16.91 ± 0.20
	Gills	0.02 ± 0.00	0.04 ± 0.01	0.08 ± 0.01	0.85 ± 0.01	0.28±0.02	11.81 ± 0.10
Scomber scombrus	Liver	0.01 ± 0.00	0.02 ± 0.00	0.05 ± 0.01	0.72 ± 0.02	0.31±0.01	10.01 ± 0.05
	Muscles	0.01 ± 0.00	0.02 ± 0.00	0.03 ± 0.00	0.70±0.03	0.22 ± 0.01	11.05 ± 0.21
Trachurus trachurus	Gills	0.01±0.00	0.06±0.00	0.01±0.00	0.95±0.01	0.14±0.01	13.01 ± 0.23

Table 1. Heavy metal composition in some organs of the fish species (mg/kg)

Sample	Fish Parts	Pb	As	Cr	Cu	Cd	Fe
	Liver	0.01±0.00	0.07±0.01	0.04 ± 0.00	1.05±0.03	0.15±0.02	13.58 ± 0.50
	Muscles	0.01 ± 0.00	0.06 ± 0.00	0.01 ± 0.00	1.00 ± 0.02	0.13±0.01	13.41 ± 0.46
WHO		0.01	0.01	0.05	0.50	0.03	
NAFDAC		0.01	0.01	0.05	1.00	0.03	

In Orenchromis niloticus, there was an observable higher concentration of Pb in the gills (0.03±0.01 mg/kg) than in the liver (0.02 \pm 0.01 mg/kg). The lead had the lowest concentration of 0.01±0.00 mg/kg in the muscles. Arsenic had the highest concentration (0.07±0.01 mg/kg) in the liver and the lowest concentration $(0.04\pm0.01 \text{ mg/kg})$ in the muscles. A higher concentration (0.10±0.02 mg/kg) of Cr was observed in the liver but a lower concentration $(0.08\pm0.01 \text{ mg/kg})$ was obtained in the gills and muscles respectively. There was no discrepancy in the concentrations of Cu in the gills, liver and muscles, but Cd was in higher concentration in the gills than in other tissues. Fe had the highest concentration in the gills $(10.02\pm0.02 \text{ mg/kg})$ than in the liver $(9.81\pm0.30 \text{ mg/kg})$ followed by the muscles $(9.02\pm0.05 \text{ mg/kg})$.

In *Tilapia ziili*, the three tissues had the same concentration $(0.01 \pm 0.00 \text{ mg/kg})$ of Pb. The liver had the highest concentration of arsenic $(0.07\pm0.01 \text{ mg/kg})$ while the gills and muscles recorded lower concentrations $(0.06\pm0.01 \text{ mg/kg})$ comparatively to the liver. Cr had a higher concentration $(0.09\pm0.01 \text{ mg/kg})$ in the liver and a lower concentration $(0.07\pm0.01 \text{ mg/kg})$ in the gills and muscles respectively. There was no difference in the concentrations of copper and cadmium in the gills, liver and muscles respectively. Copper and cadmium had mean concentrations of $0.51\pm0.01 \text{ mg/kg}$ and $0.14\pm0.01 \text{ mg/kg}$ in the three tissues respectively. Results show that there was no marked discrepancy in the concentrations of Fe in gills and muscles, however, liver had a slightly higher concentration.

The lead had the highest concentration in the liver $(0.53\pm0.02 \text{ mg/kg})$, followed by gills $(0.51\pm0.01 \text{ mg/kg})$, and then the muscles $0.50\pm0.01 \text{ mg/kg}$ in *Malapterurus electricus*. The concentrations of arsenic were found to be $0.18\pm0.01 \text{ mg/kg}$ in the liver and 0.16 mg/kg in gills and muscles respectively. The liver recorded the highest values of Cu, Cd and Fe whereas the muscles and gills had $0.84\pm0.02 \text{ mg/kg}$ and $10.0\pm0.01 \text{ mg/kg}$ of Cd and Fe in *Malapterurus electricus* respectively.

In Parachanna obscura, the mean concentration of lead and arsenic in the three tissues were 0.423±0.01 and 0.117 ± 0.01 mg/kg respectively. However, the gills had the highest lead and arsenic concentrations of 0.44 ± 0.01 mg/kg and 0.12±0.01 mg/kg but the lowest concentrations of both metals were found in the muscles $(0.40\pm0.01 \text{ mg/kg} \text{ and } 0.10\pm0.01 \text{ mg/kg})$ respectively. The mean concentration of chromium and copper in the three tissues were 0.657±0.01 mg/kg and 0.633 mg/kg respectively. Though, the gills had the highest chromium and copper concentrations of 0.70±0.01 mg/kg and 0.68 ± 0.02 mg/kg while lowest concentrations of both metals were found in the muscles (0.62±0.01 mg/kg and 0.62±0.02 mg/kg) respectively. There were no significant differences in the

concentrations of Cd and Fe in the three tissues respectively.

Chrysichthys In nigrodigitatus, the mean concentration of lead and arsenic in the three fish tissues were 0.613±0.01 and 0.117±0.01 mg/kg respectively. The gills had the highest lead and arsenic contents $(0.63\pm0.01 \text{ mg/kg} \text{ and } 0.12\pm0.01 \text{ mg/kg})$ respectively. The muscles had the lowest lead and arsenic contents (0.60±0.01 mg/kg and 0.10±0.01 mg/kg) respectively. Chromium recorded the highest concentration in the gills (0.81±0.01 mg/kg) and the lowest concentration in the liver (0.63±0.01 mg/kg). There was no difference in concentration of copper in the liver and muscles, nevertheless, the highest concentration of 0.38±0.01 mg/kg was obtained in gills. There was no marked difference in the concentration of cadmium and iron in all three tissues examined respectively.

The mean concentrations of Pb, As, Cr, Cu, Cd and Fe in the three tissues (gills, liver and muscles) of *Scomber scombrus* were 0.013 ± 0.00 , 0.027 ± 0.00 , 0.053 ± 0.01 , 0.75 ± 0.01 , 0.27 ± 0.01 , and 11.11 ± 0.12 mg/kg respectively. It was observed that the gills had the highest concentrations of these metals.

The mean concentrations of Pb, As, Cr, Cu, Cd and Fe in the three tissues of *Trachurus trachurus* assessed were 0.01 ± 0.00 , 0.063 ± 0.00 , 0.01 ± 0.00 , 1.00 ± 0.02 , 0.14 ± 0.01 and 13.30 ± 0.33 mg/kg respectively. Results revealed that gills had the highest concentrations of these metals.

Heavy metal pollution of the aquatic ecosystem has been widely documented [29-33]. Fishes are vital biomonitors in the estimation of heavy metal contamination of aquatic ecosystems [34]. Varying concentrations of heavy metals were detected in Aba River ecosystem which supports claims from previous studies of the presence of Pb, As, Cr, Cu, Cd and Fe [35]. The fact that the vicinity of Aba River is an old habour for scraps vehicles, old dumpsites for refuse, the presence of several auto mechanic workshops where metals are welded and the presence of these metals in the aquatic ecosystem may not have come as a surprise. Furthermore, several industries discharge their effluents directly into Aba River without prior treatment, which may have contributed mainly to the pollution state of the aquatic ecosystem [16]. Heavy metal tends to accumulate in the organs and tissues of fishes in the polluted aquatic ecosystem. The discrepancy in the levels of metals in the different fish species can be attributed to variation in metabolic rate [17], and the extent of food consumption. Other factors that can influence metal concentrations in fishes are age, feeding habits and microbial activities in the immediate environment of water [36]. The ability of fishes to actively interact with the environment could also be another factor. Lead is a non-essential element that is potentially hazardous to life even in minute quantities [26]. Other heavy metals are also hazardous to live in

very small concentrations, however, Pb, As, Cr, Cu, Cd and Fe were detected in all the fish species assessed. However, Parachanna obscura, Chrysichthys nigrodigitatus, Scomber scombrus and Trachurus trachurus had comparatively higher concentrations of these heavy metals in the gills than liver and muscles. Gills have a large surface area made up of filaments [9], and blood vessels which enhance the diffusion of gaseous and metal elements [37]. Lower concentration of heavy metals in the liver compared to the gills in some fish species could be a result of the ability of the liver to detoxify toxicants. Higher concentration of lead and other metals in the gills has been well-documented in previous studies [38, 39]. On the other hand, arsenic and chromium had higher concentrations in the liver compared to the gills and muscles of Orenchromis niloticus and Tilapia ziili while arsenic, chromium, lead, cadmium and iron recorded copper, higher concentrations in the liver of *Malapterurus electricus*. The concentration of Cd in the fish species was higher than the standard recommended limits WHO [40, 41].

The concentration of metals in water samples from Aba River is presented in Table 2. The mean concentrations of Cd, Pb, Cu, As, Cr, and Fe were $0.05\pm0.01, 0.21\pm0.02, 1.01\pm0.01, 0.07\pm0.01, 0.03\pm0.01$, and 0.32 ± 0.01 mg/L respectively. The concentrations of Cd, Pb, and As in water samples appeared to be higher than the WHO-recommended maximum permissible limits of 0.01 mg/L respectively.

The heavy metal contents in sediment were determined and values are presented in Table 3. Pb had a value as high as 2.11 ± 0.05 mg/kg whereas Cd had 0.505 ± 0.02 mg/kg. Similarly, the mean concentrations of Cu, As, Cr, and Fe were 14.98 ± 0.09 , 1.03 ± 0.10 , 2.13 ± 0.24 and 5.43 ± 1.10 mg/kg respectively.

Tabla 2	Concentration	of heavy	metals in	Water from	Aba River	(ma/I)
I able 2.	Concentration	of neavy	metals m	water from	Aba Kiver	(IIIg/L)

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Parameter	Station1	Station 2	Station 3	Station 4	Mean	WHO
Cd (mg/L)	0.04 ± 0.01	0.06 ± 0.01	0.05 ± 0.01	0.05 ± 0.00	0.05 ± 0.01	0.01
Pb (mg/L)	0.18 ± 0.01	0.20 ± 0.01	0.22 ± 0.02	0.23 ± 0.02	0.21 ± 0.02	0.01
Cu (mg/L)	1.01 ± 0.01	1.01 ± 0.01	0.96 ± 0.01	1.06 ± 0.24	1.01 ± 0.01	1.0
As (mg/L)	0.06 ± 0.01	0.06 ± 0.01	0.07 ± 0.00	0.08 ± 0.00	0.07 ± 0.01	0.01
Cr (mg/L)	0.02 ± 0.00	0.04 ± 0.01	0.01 ± 0.00	0.03 ± 0.01	0.03 ± 0.01	0.05
Fe (mg/L)	0.30 ± 0.01	0.24 ± 0.01	0.41 ± 0.01	0.32 ± 0.01	0.32 ± 0.01	0.3

Table 3. Concentration of neavy metals in the sediment sample (mg/kg)									
Parameter	Station1	Station 2	Station 3	Station 4	Mean				
Cd (mg/kg)	0.50 ± 0.01	0.49±0.02	0.52±0.02	0.51±0.02	0.505 ± 0.02				
Pb (mg/ kg)	2.01 ± 0.02	2.10 ± 0.01	2.20 ± 0.12	2.134 ± 0.12	2.11 ± 0.05				
Cu (mg/ kg)	14.80 ± 0.10	15.10 ± 0.01	15.00 ± 0.12	15.01 ± 0.11	$14.98{\pm}0.09$				
As (mg/ kg)	1.00 ± 0.01	0.80 ± 0.10	1.20 ± 0.10	1.10 ± 0.10	1.03 ± 0.10				
Cr (mg/ kg)	2.11 ± 0.20	2.08 ± 0.20	2.16 ± 0.25	2.18 ± 0.30	2.13 ± 0.24				
Fe (mg/ kg)	5240 ± 0.40	5410 ± 0.90	5504 ± 2.00	5564 ± 1.20	$5,429 \pm 1.10$				

The mean level of arsenic in the freshwater and sediment was found to be 0.07±0.01 mg/L and 1.03±0.01 mg/kg respectively, which accounts for the values of arsenic in the five freshwater fishes. The concentration of chromium in freshwater (0.03±0.01 mg/L) by conversion to mg/kg is small compared to the level of chromium accumulated in the seven fish species. However, the sediment which recorded higher mean values in these metals than freshwater, appeared to be the major source of the metal in all the fish species. There was decreasing ease for the different metal ions to remain in the aqueous phase, hence this accounts for the very low concentration of heavy metals in fresh water when compared to sediment. This observable trend can further be explained using the thermodynamics principle, where the system tends to equilibrium with the infinitesimal Gibbs free energy of the system at time, t. As the sorption capacity becomes appreciable on the sediment, the metal precipitates as sulfides, sulfates, oxides, phosphate, or as free ions based on the prevailing environmental conditions. The partitioning between the water and the sediment could be largely affected by some factors such as sediment mineral crystallinity, surface site density, reactive surface areas, carbon content, mineralogy, sulfide production and redox process. Partitioning between the water and the sediment is measured by the partition coefficient (K_d). The greater the K_d value the greater the sediment will draw metals out of the water. As the sediment pulls metals out of the freshwater, the greater is the partition coefficient [10].

The values of computed mean pollution index of heavy metals in water are presented in Table 4.

	Table 4. Pollution index								
Parameter	Station1	Station 2	Station 3	Station 4	Mean				
Cd (mg/L)	4.00	6.00	5.00	5.00	5.00				
Pb (mg/L)	18.00	20.00	22.00	23.00	21.00				
Cu (mg/L)	1.01	1.01	0.96	1.06	1.01				
As (mg/L)	6.00	6.00	7.00	8.00	7.00				
Cr (mg/L)	2.00	4.00	1.00	3.00	3.00				
Fe (mg/L)	3.00	2.40	4.10	3.20	3.20				

The pollution index of Cd, Pb, Cu, As, Cr and Fe ranged from 4.00 to 6.00, 18.00 to 23.00, 0.96 to 1.06,

6.00 to 8.00, 1.00 to 4.00 and 2.40 to 4.10 respectively. Values of the pollution index were far higher than the

threshold value of 1.0 for all the metals investigated except for Cu. This revealed partly that the levels of metals in freshwater were far above standard recommended limits and also that the aquatic ecosystem was polluted with these toxic metals with exception of copper.

The ratio of the contaminants in the different fish species to the concentration in the immediate environment where the contaminant was taken in with food through ingestion or direct contact is appropriately described as a bioaccumulation factor [26].

The levels of bioaccumulation factor are presented in Table 5. Bioaccumulation factors of Pb, As, Cr, Cu, Cd and Fe ranged from 0.0047-0.299, 0.039-0.175, 0.005-0.380, 0.002-0.070, 0.237-1.663 and 0.001-0.003 respectively. Values of bioaccumulation factor were less than 1.0 in all the metal elements investigated except for Cd. *Malapterurus electricus, Parachanna obscura* and *Chrysichthys nigrodigitatus* had bioaccumulation factors for Cd which ranged from 1.069 to 1.663, indicating potential Cd poisoning or contamination. There was no wide disparity in the capacities to bioaccumulate heavy metals between the imported fish species sold in Aba market (*Trachurus trachurus* and *Scomber scombrus*) and the other five fish species obtained from Aba River.

The toxicity of these toxic metals has been well reported. Chronic exposure to inorganic arsenic may result in serious damage to the nervous system [3]. Hexavalent chromium is very toxic and mutagenic if inhaled and is highly carcinogenic. Long-term exposure to chromium could result in liver, kidney circulatory and nervous tissues disorder [42, 43]. Cd has been found to be toxic to fish and other organisms in aquatic ecosystems. Cd in higher concentration can cause renal and testicle dysfunction, damage to red blood cells and cancer of the lungs [44].

Health-risk of these heavy metals through the consumption of fish was assessed via noncarcinogenic risk and carcinogenic risks using Equations 3-7 above. The estimated daily intake of fish by both adults and children (0 –9 years) are presented in Tables 6a and 6b respectively.

Sample	Pb	As	Cr	Cu	Cd	Fe
Orenchromis niloticus	0.0095	0.0485	0.038	0.002	0.237	0.002
Tilapia ziili	0.047	0.058	0.038	0.034	0.277	0.001
Malapterurus electricus	0.251	0.175	0.023	0.053	1.663	0.002
Parachanna obscura	0.211	0.117	0.033	0.045	1.069	0.002
Chrysichthys nigrodigitatus	0.299	0.136	0.380	0.023	1.604	0.003
Scomber scombrus	0.0047	0.039	0.038	0.057	0.61	0.002
Trachurus trachurus	0.0047	0.058	0.005	0.070	0.30	0.003

Table 6a. Estimated Dai	ly Intake (EDI)) for adults (m	g/kgbw/day)
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Sample	Fish parts	Pb	As	Cr	Cu	Cd	Fe
Orenchromis	Gills	0.000017	0.000029	0.000046	0.000231	0.000069	0.0058
niloticus	Liver	0.000012	0.000041	0.000058	0.000231	0.000064	0.0057
	Muscles	0.000050	0.000023	0.000046	0.000231	0.000058	0.0053
Tilapia ziili	Gills	0.0000058	0.000035	0.000041	0.000289	0.000081	0.00350
	Liver	0.0000058	0.000041	0.000052	0.000295	0.000081	0.00360
	Muscles	0.0000058	0.000035	0.000041	0.000289	0.000081	0.00346
Malapterurus	Gills	0.000295	0.000093	0.000029	0.000457	0.000486	0.005784
electricus	Liver	0.000305	0.00011	0.000023	0.000469	0.000503	0.006362
	Muscles	0.000288	0.000093	0.000023	0.000434	0.000486	0.005784
Parachanna	Gills	0.000253	0.000069	0.000405	0.000393	0.000312	0.006368
obscura	Liver	0.000248	0.000075	0.000376	0.000347	0.000312	0.006380
	Muscles	0.000231	0.000058	0.000359	0.000359	0.000312	0.006305
Chrysichthys	Gills	0.000364	0.000081	0.000469	0.000220	0.000469	0.009723
nigrodigitatus	Liver	0.000353	0.000063	0.000364	0.000203	0.000469	0.009723
	Muscles	0.000347	0.000058	0.000422	0.000203	0.000469	0.009781
Scomber	Gills	0.000012	0.000023	0.000046	0.000492	0.000162	0.006831
scombrus	Liver	0.0000058	0.000012	0.000029	0.000417	0.000179	0.005790
	Muscles	0.0000058	0.000012	0.000017	0.000405	0.000127	0.006391
Trachurus	Gills	0.0000058	0.000035	0.000006	0.000550	0.000080	0.007524
trachurus	Liver	0.0000058	0.000041	0.000023	0.000607	0.000086	0.007855
	Muscles	0.0000058	0.000035	0.000006	0.000578	0.000075	0.007756

RfD = *Cd* (0.001); *Cr* (0.003); *As* (0.0003); *Ni* (0.02); *As* (0.0003); *Hg* (0.0001); *Pb* (0.00143); *Cu* (0.040) Source: USEPA 2011 [45].

Table 6b. Estimated Daily Intake (EDI) for children (mg/kg	gbw/day)
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Sample	Fish parts	Pb	As	Cr	Cu	Cd	Fe
Orenchromis niloticus	Gills	2.583 E-6	4.305 E-6	6.888E-6	3.444E-5	1.03 E-5	8.628E-4
	Liver	1.722 E-6	6.028 E-6	8.611E-6	3.444E-5	9.472 E-6	8.4475E-4
	Muscles	8.611 E-7	3.444E-6	6.888E-6	3.444E-5	8.611E-6	7.767 E-4
Tilapia ziili	Gills	8.611 E-7	5.166 E-6	6.028 E-6	4.306E-5	1.205E-5	5.175 E-4
	Liver	8.611 E-7	6.028 E-6	7.750E-6	4.391E-5	1.205E-5	5.296E-4
	Muscles	8.611 E-7	5.166 E-6	6.028 E-6	4.306E-5	1.205E-5	5.166 E-4

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Sample	Fish parts	Pb	As	Cr	Cu	Cd	Fe
Malapterurus electricus	Gills	4.391 E-5	1.377 E-5	4.305 E-6	6.802E-5	7.233 E-5	8.611 E-4
	Liver	4.563 E-5	1.55 E-5	3.444E-6	6.975E-5	7.491 E-5	9.472 E-4
	Muscles	4.305 E-5	1.377 E-5	3.444E-6	6.458E-5	7.233 E-5	8.611 E-4
Parachanna obscura	Gills	3.789 E-5	1.03 E-5	6.028E-5	5.855E-5	4.650E-5	9.481 E-4
	Liver	3.702 E-5	1.119 E-5	5.597 E-5	5.167E-5	4.650E-5	9.498 E-4
	Muscles	3.444 E-5	8.611E-6	5.339 E-5	5.339E-5	4.650E-5	9.386 E-4
Chrysichthys nigrodigitatus	Gills	5.425 E-5	1.205E-5	6.975E-5	3.272 E-5	6.975E-5	1.448E-3
	Liver	5.252 E-5	9.472E-6	5.425E-5	3.014 E-5	6.975E-5	1.447 E-3
	Muscles	5.166 E-5	8.611E-6	6.286E-5	3.014 E-5	6.975E-5	1.456 E-3
Scomber scombrus	Gills	1.722 E-6	3.444E-6	6.888E-6	7.319E-5	2.411 E-5	1.016E-4
	Liver	8.611 E-7	1.722 E-6	4.305 E-6	6.200E-5	2.669 E-5	8.619E-4
	Muscles	8.611 E-7	1.722 E-6	2.583 E-6	6.027 E-5	1.89 E-5	9.515 E-4
Trachurus trachurus	Gills	8.611 E-7	5.166 E-6	8.611E-7	8.180 E-5	1.205E-5	1.120E-3
	Liver	8.611 E-7	6.028 E-6	3.444E-6	9.042 E-5	1.291 E-5	1.169 E-3
	Muscles	8.611 E-7	5.166 E-6	8.611E-7	8.611 E-5	1.119 E-5	1.155E-3

In adults (Table 6a), the estimated daily intake (EDI) in mg/kg/day of Pb, As, Cr, Cu, Cd and Fe ranged from 5.8E-5 to 3.64E-4, 1.2E-5 to 1.1E-4, 6.0E-6 to 4.69E-4, 2.03 E-4 to 6.07E-4, 5.8 E-5 to 5.03E-4, and 3.46E-3 to 9.78E-3 respectively. In children, the estimated daily intake (EDI) in mg/kg/day (Table 6b) for Pb, As, Cr, Cu, Cd and Fe ranged from 8.6E-7 to 5.4E-5, 8.6E-6 to 1.55E-5, 8.61E-7 to 6.98E-5, 3.01E-5 to 9.04E-5, 8.611E-6 to 7.491E-5, 1.016E-4 to 1.456E-3 respectively. The equivalent of provisional tolerable daily intake of Cd, As and Pb obtained by conversion are 0.00083, 0.0021, and 0.00357 mg/kgbw/day respectively [45, 46]. Since there is a dearth of information on the acceptable standard daily intake of

copper and chromium by standard organizations such as WHO and FAO, the oral daily intake of copper from food is 0.5 mg/kgbw/day [47]. The provisional maximum tolerable daily intake of iron is 0.8 mg/kgbw/day [46]. The estimated daily intake of cadmium, arsenic, lead, copper and iron was compared with the provisional daily intake of the corresponding metals. The estimated daily intake of Pb, As, Cu, Cd, and Fe in fish organs for both adult and children were lower than their corresponding standard values (acceptable daily intake) which presupposes no health risk. The values for hazard quotient and hazard index for both adults and children are presented in Table 7a and 7b respectively.

Table 7a. Hazard Quotient (HQ) and Hazard Index (HI) for an adult

Sample	Fish parts	Pb	As	Cr	Cu	Cd	Fe	HI
Orenchromis niloticus	Gills	0.0120	0.0967	0.0153	0.0058	0.0690	0.8285	1.0273
	Liver	0.0084	0.1367	0.0193	0.0058	0.064	0.8146	1.0488
	Muscles	0.0350	0.0767	0.0153	0.0058	0.058	0.7571	0.9479
Tilapia ziili	Gills	0.0041	0.1167	0.0137	0.0072	0.081	0.5000	0.7227
	Liver	0.0041	0.1367	0.0173	0.0074	0.081	0.5143	0.7608
	Muscles	0.0041	0.1167	0.0137	0.0072	0.081	0.4943	0.7170
Malapterurus electricus	Gills	0.2060	0.3101	0.0097	0.0114	0.486	0.8263	1.8495
	Liver	0.2132	0.3666	0.0077	0.0117	0.503	0.9089	2.0111
	Muscles	0.2014	0.3101	0.0077	0.0109	0.486	0.8263	1.8424
Parachanna obscura	Gills	0.1769	0.2300	0.135	0.0098	0.312	0.9097	1.7734
	Liver	0.1734	0.2500	0.1253	0.0087	0.312	0.9114	1.7808
	Muscles	0.1615	0.1933	0.1196	0.0090	0.312	0.9007	1.6961
Chrysichthys nigrodigitatus	Gills	0.2546	0.270	0.1563	0.0055	0.469	1.3891	2.5445
	Liver	0.2469	0.210	0.1213	0.0051	0.469	1.3891	2.4414
	Muscles	0.2427	0.1933	0.1406	0.0051	0.469	1.3972	2.4479
Scomber scombrus	Gills	0.0084	0.0767	0.0153	0.0123	0.162	0.9758	1.2505
	Liver	0.0041	0.040	0.0097	0.0104	0.179	0.8271	1.0703
	Muscles	0.0041	0.040	0.0056	0.0101	0.127	0.913	1.0998
Trachurus Trachurus	Gills	0.0041	0.1167	0.0021	0.0138	0.080	1.0748	1.2915
	Liver	0.0041	0.1366	0.0076	0.0152	0.086	1.1221	1.3716
	Muscles	0.0041	0.1167	0.0020	0.0145	0.075	1.108	1.3203

Table 70. Hazard Quotient (HQ) and Hazard Index (HI) for child

Sample	Fish parts	Pb	As	Cr	Cu	Cd	Fe	HI
Orenchromis niloticus	Gills	0.00180	0.014350	0.00230	0.000861	0.0103	0.12325	0.1529
	Liver	0.001204	0.0201	0.00287	0.000861	0.00947	0.12068	0.1552
	Muscles	0.000602	0.011480	0.00230	0.000861	0.00861	0.11095	0.1348
Tilapia ziili	Gills	0.000602	0.017220	0.00201	0.001077	0.01205	0.07393	0.1069
	Liver	0.000602	0.020093	0.00258	0.001098	0.01205	0.07565	0.1121
	Muscles	0.000602	0.017220	0.00201	0.001077	0.01205	0.0738	0.1068
Malapterurus electricus	Gills	0.03070	0.04590	0.001435	0.00170	0.07233	0.12301	0.2751
	Liver	0.03191	0.0516	0.001148	0.00174	0.07491	0.13531	0.2966
	Muscles	0.03011	0.0460	0.001148	0.00162	0.07233	0.12301	0.2742
Parachanna obscura	Gills	0.02649	0.0343	0.0201	0.00146	0.00075	0.13544	0.2185

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Sample	Fish parts	Pb	As	Cr	Cu	Cd	Fe	HI
	Liver	0.02588	0.0373	0.0187	0.00129	0.00075	0.13568	0.2196
	Muscles	0.02408	0.0287	0.01779	0.00133	0.00075	0.13409	0.2067
Chrysichthys nigrodigitatus	Gills	0.03793	0.04016	0.02325	0.000818	0.06975	0.20686	0.3788
	Liver	0.03672	0.03157	0.0181	0.000754	0.06975	0.20671	0.3636
	Muscles	0.03612	0.02870	0.02095	0.000754	0.06975	0.2080	0.3643
Scomber scombrus	Gills	0.00120	0.01148	0.00230	0.00183	0.02411	0.01451	0.0554
	Liver	0.000602	0.00574	0.001435	0.00155	0.02669	0.12313	0.1592
	Muscles	0.000602	0.00574	0.000861	0.00151	0.0189	0.13593	0.1635
Trachurus trachurus	Gills	0.000602	0.01722	0.000287	0.00205	0.01205	0.16	0.1922
	Liver	0.000602	0.02008	0.001148	0.00226	0.01291	0.167	0.204
	Muscles	0.000602	0.01722	0.000287	0.00215	0.01119	0.165	0.1965

In adults, the hazard quotient of Pb, As, Cr, Cu, Cd and Fe ranged from 0.0041 to 0.2546, 0.0767 to 0.3666, 0.0020 to 0.1563, 0.0051 to 0.0152, 0.058 to 0.503 and 0.4943 to 1.3972 respectively. The hazard quotient of these metals in adults was below the threshold value of 1.0 in all the species of fish except *Chrysichthys nigrodigitatus* (1.3891 to 1.3972) and *Trachurus trachurus* (1.0748 to 1.1221), whereas iron had a slightly higher hazard quotient values across the three organs investigated.

In children, the hazard quotient of Pb, As, Cr, Cu, Cd and Fe ranged from 0.000602 to 0.03793, 0.00574 to 0.0516, 0.000287 to 0.02325, 0.000754 to 0.00226, 0.00075 to 0.07491 and 0.07565 to 0.2080 respectively. The hazard quotient of these metals in children was lower than the standard threshold value of 1.0, suggesting there is no potential health risk associated with these heavy metals through the consumption of fish. The hazard index was greater than one in the adult population (HI > 1) but less than one (HI < 1) in children indicating associated potential health risk only in adult due to the combined effect of these heavy metals through the consumption of fish.

The International Agency for Research on Cancer (IARC) has classified Ni, Cd, Cr, As and Pb as groups 1 and 2 potential carcinogenicity metals respectively while Zn, Al, Mn and Cu are designated as non-carcinogenic metals [47, 48]. Cancer slope factors for Pb, Ni and Cd are 0.009, 1.7 and 0.6 respectively [49, 50], while that of As and Cr are 1.5 and 0.501 [47, 48]. Computed values of incremental life cancer risk for the adult population are shown in Table 8. The cancer risk values for Pb, As, Cr, and Cr ranged from 5.2E-8 to 3.2E-6, 2.0E-5 to 1.9E-4, 3.0E-6 to 2.3E-4 and 3.5E-5 to 3.0E-4 respectively.

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Sample	Fish parts	Pb	As	Cr	Cd
Orenchromis niloticus	Gills	1.5E-7	4.9E-5	2.3E-5	4.1E-5
	Liver	1.1E-7	7.0E-5	2.9E-5	3.8E-5
	Muscles	4.5E-7	3.9E-5	2.3E-5	3.5E-5
Tilapia ziili	Gills	5.2E-8	6.0E-5	2.1E-5	4.9E-5
	Liver	5.2E-8	7.0E-5	2.6E-5	4.9E-5
	Muscles	5.2E-8	6.0E-5	2.1E-5	4.9E-5
Malapterurus electricus	Gills	2.7E-6	1.6E-4	1.5E-5	2.9E-4
	Liver	2.8E-6	1.9E-4	1.2E-5	3.0E-4
	Muscles	2.6E-6	1.6E-4	1.2E-5	2.9E-4
Parachanna obscura	Gills	2.3E-6	1.2E-4	2.0E-4	1.9E-4
	Liver	2.2E-6	1.3E-4	1.9E-4	1.9E-4
	Muscles	2.1E-6	9.9E-5	1.8E-4	1.9E-4
Chrysichthys nigrodigitatus	Gills	3.3E-6	1.4E-4	2.3E-4	2.8E-4
	Liver	3.2E-6	1.1E-4	1.8E-4	2.8E-4
	Muscles	3.2E-6	9.9E-5	2.1E-4	2.8E-4
Scomber scombrus	Gills	1.1E-7	3.9E-5	2.3E-5	9.7E-5
	Liver	5.2E-8	2.0E-5	1.5E-5	1.0E-4
	Muscles	5.2E-8	2.0E-5	8.5E-6	7.6E-5
Trachurus trachurus	Gills	5.2E-8	6.0E-5	3.0E-6	4.8E-5
	Liver	5.2E-8	7.0E-5	1.2E-5	5.2E-5
	Muscles	5.2E-8	6.0E-5	3.0E-6	4.5E-5

Table 8. Incremental	life cancer	risk for adult	population
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Interestingly, values of incremental life cancer risk for the adult population were within the acceptable safe limit of 1.0×10^{-4} to 1.0×10^{-6} [22]. Consequently, it may be asserted that there is no possibility of carcinogenic risk from the heavy metals in this study through the consumption of frozen and fresh fish.

4. Conclusions

The heavy metals in most of the fish samples were above the standard recommended guideline limit in food substances, fish and fisheries. Cd, Pb, and As concentrations in water samples from Aba River were higher than the permissible limits (0.01 mg/l). The bioaccumulation factor for Cd was greater than one in *Malapterurus electricus, Parachanna obscura* and *Chrysichthys nigrodigitatus*, indicating possible potential health risk. The estimated daily intake (mg/kg/day) in adult and children were within the standard limit of daily intake for the human population. The hazard quotient was less than one in most of the

metals indicating no possible potential health risk associated with each of these heavy metals through the consumption of fish. The hazard index was greater than one in the adult population indicating the associated potential health risk of these heavy metals through the consumption of fish. The hazard index of these heavy metals in the children population was less than one and does not indicate any potential health hazard through the consumption of fish. Incremental life cancer risk for the adult population was within safe limit hence there is no potential cancer risk from the consumption of these metals through fish.

Conflict of interest

Authors declare no conflict of interest.

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