Risk Assessment of Human Exposure to some Heavy Metals in Blackchin Tilapia (*Oreochromis niloticus*) from *Anyia-Ogologo* River, Mgbuosimini Community, Rivers State

G. K. Amadi, C. C. Obunwo, N. J. Maduelosi and J. L. Konne
Department of Chemistry Rivers State University Port- Harcourt
Corresponding author: gloria.amadi3@ust.edu.ng +2348067267913
gloria.amadi3@ust.edu.ng

D.O.I: 10.56201/ijccp.v9.no4.2023.pg58.72

Abstract

Samples of Blackchin Tilapia (Oreochromis niloticus) from Anyia-Ogologo River, Mgbuosimini Community were collected, preserved and analyzed. The sampling covers a period of one year (wet and dry seasons). Atomic Absorption Spectrophotometric technique for heavy metals and Health Risk Assessment showed that the high levels of heavy metals Ni, Pb, Cd, and Co pose probable high toxic and carcinogenic risks in adults and children.

Introduction

Fish are at the top of the aquatic food chain and can concentrate large amounts of metals from water (Mansour and Sidky, 2002). Furthermore, fish are one of the most important factors in freshwater systems, particularly for the estimation of the potential risk associated from human consumption (Habib *et al.,* 2022; Fazio *et al.,* 2022). Fish is a good source of protein; is high in vitamins, unsaturated fatty acids, and essential minerals (Rajeshkumar and Li, 2018). Heavy metals taken up are distributed to different organs of the fish because of the affinity between them (Fevzi *et al,* 2007). Fish accumulate heavy metals in higher concentrations in their tissues, mainly through ingestion of contaminated food or by environmental absorption along the gill surface, with metals being accumulated mainly in metabolically active tissues including gills, liver, kidney, and digestive tract (Yilmaz *et al*., 2007). The gills are uptake site of waterborne ions, where metal concentrations increase mostly at the start of exposure, before the metal enters other parts of organism (Annabi and Saidkand, 2013; Souza *et al*., 2018). Fish liver is the storage organ and thus was mostly used because of the fact that it accumulates the highest level of heavy metals and is proportional to those present in the environment (Topić *et al.,* 2023). Heavy metals enter the aquatic food chain either directly through the gastrointestinal tract or indirectly through other pathways, such as gills and muscles (Rajeshkumar and Li, 2018). Consequently, there is a correlation between the concentrations of heavy metals found in fish with those found in the water and sediment of the water bodies from which they are drawn (Annabi and Saidkand, 2013). If the concentration of heavy metals in fish tissues are above permissible limits, it may result in health risk to humans. For example, metals like Cd, Cr, Hg, and Pb can damage the nervous system, kidneys and liver (Ali and Khan, 2019); and consequently, have significant impact on the human (Habib *et al*., 2022).

Igwemmar *et al*. (2013) had detected heavy metal in Tilapia and Titus fishes sold in Gwagwalada market, Abuja, with mean concentration of the heavy metals was within the ranges (0.07 – 0.23), (3.65 – 6.12), (1.89 – 3.74) and (0.05 – 0.40) mg/L, for Cu, Fe, Zn and Mn respectively. Akpanyung *et al*. (2014) carried out an investigation on the levels of heavy metals in kidney, heart, gills and liver of silver catfish (*Chrysichthys nigrodigitatus*) obtained from two fishing sites in Akwa Ibom State, Nigeria, and found that the levels of Zn, Cu, Pb, Cr and As in the fish bought at Ibaka were above permissible limits while those bought at Ifiayong (with the exception of Zn and Cu) were significantly lower. Osakwe *et al*. (2014), in their study using African catfish (*Clarias gariepinus*) from Imo River, Nigeria, found the Target hazard quotients (THQ) for individual heavy metal and the hazard index (HI) values determined based on the levels of Cd, Cu, Zn, Ni, Pb, and Fe were all less than one, indicating that health risk associated with the intake of a single heavy metal or combined metal through consumption of this catfish for children and adult was relatively low at the moment.

Anyia-Ogologo River is exceptionally important to the inhabitants of Mgbuosimini community in Rumueme, Port-Harcourt as it serves as a drainage system, important ecological functions, provides coastal protection, recreation, resources as sea food, energy, tourism and economic development. There has been an increase in water body pollution due to the numerous human activities such as dredging, drainage constructions, waste disposal from mechanic workshops and homes, building construction, etc. The presence of these pollutants at elevated levels has protracted destructive effects on aquatic biota and also ends self-purification processes of water and the behaviour of plants and animals present in the receiving aquatic medium and other beneficial uses to which water may be applied (Isaiah *et al*., 2019). Thus, the objective of this study is to assess the concentration of Cd, Pb, Ni, and Co in samples of Blackchin Tilapia (*Oreochromis niloticus*) from *Anyia-Ogologo* River, Mgbuosimini Community as well as the potential risk to human health due to their consumption.

2.0 Materials and Methods

2.1 Study Area

The study was carried out in *Anyia-Ogologo* River in Mgbuosimini Community of PortHarcourt, Rivers State Nigeria. The community covers a landarea of about 4.2 km^2 and the length of the study path on the river stretches to about 1.14 km^2, with an average elevation of 4 m and an average slope of 0.8%. The local people use the river for mainly fishing, washing and other municipal activities. The river headwater runs behind the community into which urban drainage empties, there is also evidence of dumping of waste products from homes on the river. The *Anyia-Ogologo* River plays host toa fish market which is important to the community. Fish farming and marketing are part of the culture of the inhabitants of the area.
The sampling stations were selected using a Global Positioning System (GPS) tool, and five (5) sampling stations were initially identified. The choices of sample points were based on;

i. accessibility to the river
ii. Hydrodynamics of the water body
iii. Degree of direct human influence.

The sampling stations and their geographical coordinates using Geographical Positioning System (GPS) are presented in Table 1.

Table 1: Identification of Sampling Stations with Geographical Coordinates

Station Name	Geographical Coordinates
STN1	4° 48' 27.6" N; 6° 58' 03.108" E
STN2	4° 48' 26.8" N; 6° 58' 02.202" E
STN3	4° 48' 24.0" N; 6° 58' 02.102" E
STN4	4° 48' 14.0" N; 6° 58' 01.66" E
STN5	4° 48' 11.5" N; 6° 58' 01.58" E

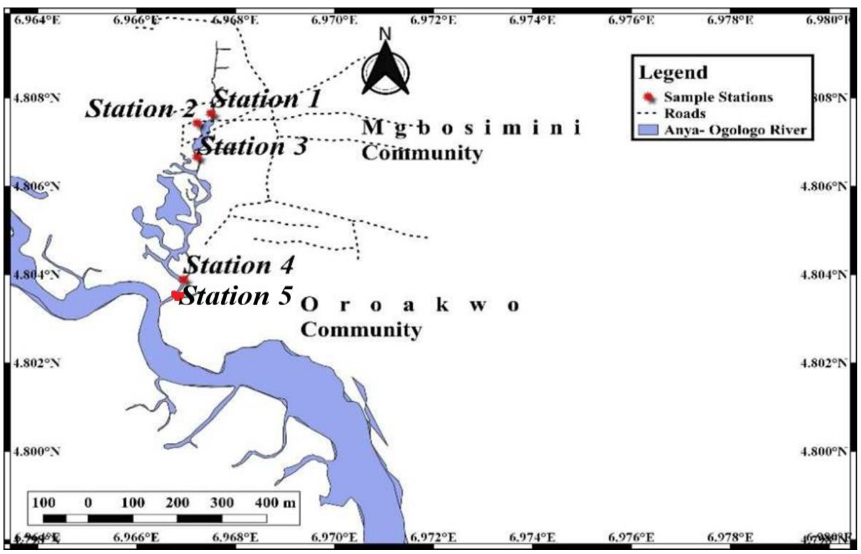


Fig. 1: Map of the Study Area

2.2 Sample Collection

Sample collection employed for fish (*Oreochromis niloticus)* is the active collection method [37]. With the aid of a boat. fishermen and fishing traps and baited hooks, fifteen (15) fishes were sampled during low tide around ≈250m radius of each sample point. Sampling was carried out monthly for twelve months, April 2022 to March 2023, covering the dry and wet seasons. Samples were collected and put into a cooler with ice and transported immediately to the laboratory for sample preparation and analysis.

2.3 Sample Preparation and Analysis

Heavy metal content from each fish was determined using the acid digestion method. The fish were cut into pieces, placed in a conical flask and dried at 45 ºC for 8 hours on a hot plate in a furnace. On cooling, the sample was ground to fine powder using a porcelain mortar. For the analysis, 2 g of the dried samples were used. The digestion of the samples was done by adding 20 cm^3 aqua regia (which is a mixture of HCl and HNO_3 in a ratio of 3:1) and 10 cm^3 of 30% H_2O_2. In order to avoid overflow which will lead to loss of material from beaker, H_2O_2 was added in small portions. The digestion was done in high borosilicate glass vessel on a hot plate at a temperature of 45 ºC for 3 hrs. The digested sample was allowed to cool at room temperature. After digestion, the sample was diluted to 30 mL with distilled water and thereafter, each metal ion (Ni, Co, Cd and Pb) was determined using Perkin Elmer Analyst 200 Atomic Absorption Spectrometer (AAS) with appropriate lamps and standard.

2.4 Data Analysis

2.4.1. Human Health Risk Assessment

Human health risks- Average Daily Dose (ADD), Hazard Quotient (HQ), Hazard Index (HI) and Carcinogenic Risk (CR_{ing}) associated with the exposure to fish via ingestion and dermal pathways, as influenced by the various heavy metals was calculated using the following equations:

$$\mathrm{ADD}_{ing}(\mathrm{mg^{-1}L^{-1}day^{-1}}) = \frac{(\mathrm{C}_x \times \mathrm{Ir} \times \mathrm{Ef} \times \mathrm{Ed})}{(\mathrm{Bwt} \times \mathrm{At})} \quad (1)$$

$$\mathrm{ADD}_{derm}(\mathrm{mg^{-1}L^{-1}day^{-1}}) = \frac{(\mathrm{C}_x \times \mathrm{Sa} \times \mathrm{Pc} \times \mathrm{Et} \times \mathrm{Ef} \times \mathrm{Ed} \times \mathrm{Cf})}{(\mathrm{Bwt} \times \mathrm{At})} \quad (2)$$

Where ADD is the Average Daily Dose, C_x is the concentration of metals (Ni, Co, Cd and Pb) (mg/L), *Ir* is the ingestion rate per unit time (L/day), *Ed* is the Exposure Duration (years), which is equal to the life expectancy of a resident Nigerian, *Ef* is the exposure frequency (days / year), *Bwt* is body weight (kg), and *At* is the Averaging Time (*Ed* x *Ef*). For the conversion factor from years to days, 365 days was used; *Sa* is the total Skin Surface Area (cm^3), *Cf* is the Volumetric Conversion Factor for water (1 L/1000 cm^3), *Et* is the Exposure Time (h/day), *Pc* is the Chemical-Specific Dermal Permeability Constant (cm/h), *Ef* is the Exposure Frequency (days / years, *Ed* is the Exposure Duration (years), and *Bwt* is the Body Weight.

The hazard index (HI) and carcinogenic risk (CR) due to fish consumption with the metals were determined using equation (3) and (4)

$$\mathrm{H}Q_{ing} = \frac{\mathrm{ADD}_{ing}}{\mathrm{RfD}_{ing}} \quad (3)$$

$$\mathrm{H}Q_{derm} = \frac{\mathrm{ADD}_{derm}}{\mathrm{RfD}_{derm}} \quad (4)$$

$$HI = HI_{ing} + HI_{derm} \quad (5)$$

$$CR_{ing} = \frac{ADD_{ing}}{SF_{ing}} \quad (6)$$

Where RfD = reference dose of the heavy metal

SF = cancer slope factor of heavy metal.

Values of some parameters for the heavy metals are shown in Table 2

Table 2: Standard Values of some Parameters for Heavy Metals (USEPA, 2004)

Pdvarameters	Cd	Ni	Pb	Co
Dermal Permeability Coefficients (cm/h)	1 x 10^{-3}	2 x 10^{-4}	1 x 10^{-4}	4 x 10^{-4}
Slope Factor (mg/L/day)	6.12	8.4 x 10^{-1}	8.51 x 10^{-3}	9.8
Reference Dose (ingestion) (mg/L/day)	5.0 x 10^{-4}	2.0 x 10^{-2}	1.4 x 10^{-3}	2.0 x 10^{-2}
Reference Dose (dermal) (mg/L/day)	2.5 x 10^{-5}	5.4 x 10^{-3}	4.2 x 10^{-3}	5.70 x 10^{-6}

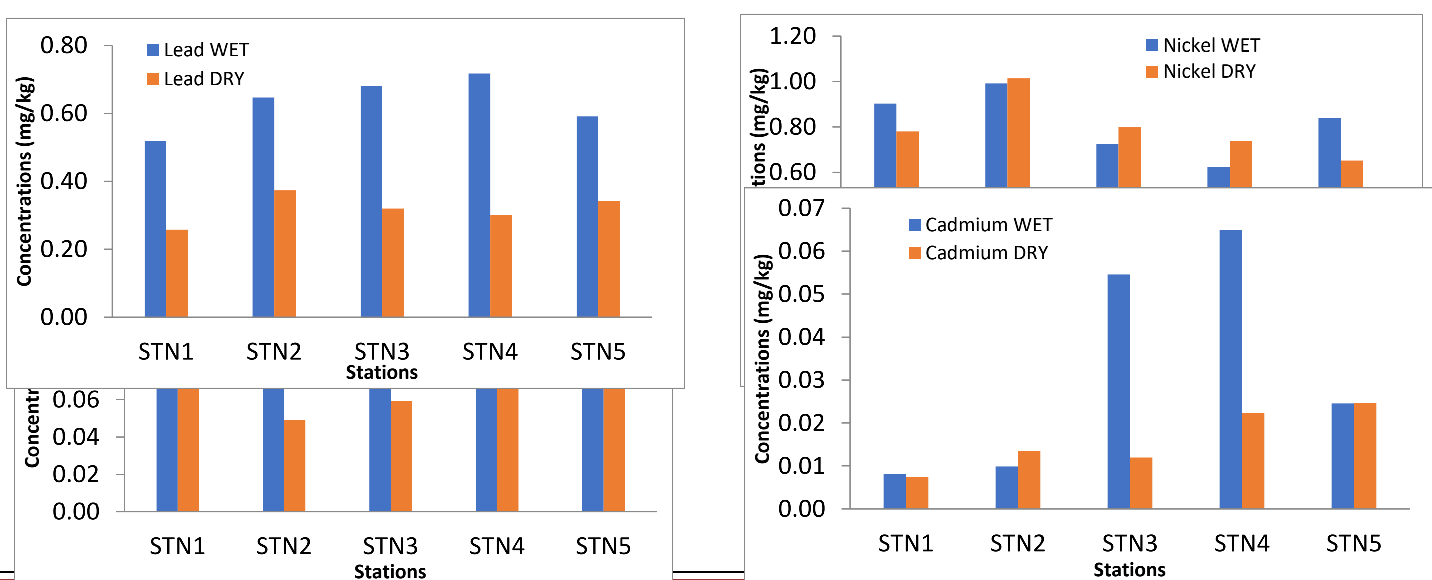
3.0 Results

3.1 Levels of Heavy Metals in Fish Samples

Mean levels of heavy metals in the fish samples for the wet and dry seasons are shown in Fig.2.

Nickel ions in fish ranged from 0.62±0.42 mg/kg to 0.99±0.77 mg/kg in wet season and 0.65±0.32 mg/kg to 1.02±0.41 mg/kg in dry season. Cobalt ions in fish ranged from 0.09±0.04 mg/kg to 0.14±0.06 mg/kg in wet season and 0.05±0 mg/kg to 0.07±0.02 mg/kg in dry season Cadmium ions in fish ranged from 0.01±0 mg/kg to 0.06±0.02 mg/kg in wet season and 0.01±0.01 mg/kg to 0.02±0 mg/kg in dry season. Lead ions in fish ranged from 0.52±0.33 mg/kg to 0.72±0.35 mg/kg in wet season and 0.26±0.12 mg/kg to 0.37±0.19 mg/kg in dry season

Fig. 3: Mean Levels of Heavy Metals in Fish



3.2 Human Health Risk Analysis

The results of the health risk assessment of heavy metals for wet and dry seasons in water and biota (fish) samples from the study area are presented in Table 4.10 to Table 4.18 for water and Table 4.19 to Table 4.27 for fish respectively.

Cobalt Hazard Quotient levels via the ingestion pathway (HQ_{ing}) in wet season fell between 1.42×10^{-1} and 1.77×10^{-1} mg/L/day for adults; 5.42×10^{-1} and 6.75×10^{-1} mg/L/day for children. Cobalt Hazard Quotient levels via the ingestion pathway (HQ_{ing}) in dry season fell between 7.73×10^{-2} and 1.17×10^{-1} mg/L/day for adults; 4.03×10^{-1} and 4.48×10^{-1} mg/L/day for children. Cobalt Hazard Quotient levels via the dermal pathway (HQ_{derm}) in wet season fell between 9.45×10^{-1} and 1.18 mg/L/day or adults, and 2.79 and 3.48 mg/L/day for children. Cobalt Hazard Quotient levels via the dermal pathway (HQ_{derm}) in dry season fell between 5.15×10^{-1} and 7.82×10^{-1} mg/L/day for adults; 1.52 and 2.31 mg/L/day for children. Hazard Index levels in wet season for adults fell between 1.09 and 1.36 mg/L/day; 3.33 and 4.15 mg/L/day for children. Hazard index levels in dry season for adults fell between 5.92×10^{-1} and 9.00×10^{-1} mg/L/day in adults; 1.81 and 2.76 mg/L/day for children.

Lead Hazard Quotient levels via the ingestion pathway (HQ_{ing}) in wet season fell between 1.16×10^{1} and 1.53×10^{1} mg/L/day for adults; 4.44×10^{1} and 5.83×10^{1} mg/L/day for children. Lead Hazard Quotient levels via the ingestion pathway (HQ_{ing}) in dry season fell between 5.79 and 8.38 mg/L/day for adults; 2.21×10^{-1} and 3.20×10^{-1} mg/L/day for children. Lead Hazard Quotient levels via the dermal pathway (HQ_{derm}) in wet season fell between 1.84×10^{-2} and 2.14×10^{-2} mg/L/day for adults, and 5.43×10^{-2} and 7.13×10^{-2} mg/L/day for children. Lead Hazard Quotient levels via the dermal pathway (HQ_{derm}) in dry season fell between 9.96×10^{-3} and 1.33×10^{-2} mg/L/day for adults, and 2.70×10^{-2} and 3.91×10^{-2} mg/L/day for children. Hazard Index levels in wet season for adults fell between 1.17×10^{1} and 1.53×10^{-1} mg/L/day; 4.45×10^{1} and 5.84×10^{1} mg/L/day for children. Hazard index levels in dry season for adults fell between 5.80 and 8.39 mg/L/day, and 2.21×10^{1} and 3.20×10^{1} mg/L/day for children. Lead Carcinogenic Risk (CR_{ing}) levels in wet season for adults fell between 1.92 and 2.51 mg/L/day;7.31 and 9.59 mg/L/day for children. Lead Carcinogenic Risk (CR_{ing}) levels in dry season for adults fell between 9.53×10^{-1} and 1.38 mg/L/day; 3.64 and 5.26 mg/L/day for children.

Nickel Hazard Quotient levels via the ingestion pathway (HQ_{ing}) in wet season fell between 1.14 and 1.56 mg/L/day for adults; 4.35 and 5.95 mg/L/day for children. Nickel Hazard Quotient levels via the ingestion pathway (HQ_{ing}) in dry season fell between 1.02 and 1.59 mg/L/day for adults; 3.91 and 6.09 mg/L/day for children. Nickel Hazard Quotient levels via the dermal pathway (HQ_{derm}) in wet season fell between 4.00×10^{-3} and 5.48×10^{-3} mg/L/day for adults, and 1.18×10^{-2} and 1.62×10^{-2} mg/L/day for children. Nickel Hazard Quotient levels via the dermal pathway (HQ_{derm}) fell between 3.60×10^{-3} and 5.60×10^{-3} mg/L/day for adults, and 1.06×10^{-2} and 1.65×10^{-2} mg/L/day for children Hazard Index levels in wet season for adults fell between 1.14 and 1.56 mg/L/day; 4.36 and 5.97 mg/L/day for children. Hazard index levels in dry season for adults fell between 1.03 and 1.60 mg/L/day, and 3.92 and 6.10 mg/L/day for children. Nickel Carcinogenic Risk (CR_{ing}) in wet season levels for adults fell between 2.71×10^{-2} and 3.71×10^{-2} mg/L/day; 1.04×10^{-1} and 1.42×10^{-1} mg/L/day for children. Nickel Carcinogenic Risk (CR_{ing}) in dry season levels for adults fell between 2.44 and 3.80 mg/L/day; 9.31×10^{-2} and 1.45×10^{-1} mg/L/day for children.

Cadmium Hazard Quotient levels via the ingestion pathway (HQ_{ing}) in wet season fell between 5.15×10^{-1} and 3.05 mg/L/day for adults; 1.47and 1.78 mg/L/day for children. Cadmium Hazard Quotient levels via the ingestion pathway (HQ_{ing}) in dry season fell between 4.65×10^{-1} and 1.40 mg/L/day for adults; 1.78 and 5.36 mg/L/day for children. Cadmium Hazard Quotient levels via the dermal pathway (HQ_{derm}) in wet season fell between 4.89×10^{-2} and 2.90×10^{-1} mg/L/day for adults; 1.44×10^{-1} and 8.56×10^{-1} mg/L/day for children. Cadmium Hazard Quotient levels via the dermal pathway (HQ_{derm}) in dry season fell between 4.41×10^{-2} and 4.33×10^{-1} mg/L/day for adults, and 1.30×10^{-1} and 3.93×10^{-1} mg/L/day for children. Hazard Index levels in wet season for adults fell between 5.64×10^{-1} and 3.34 mg/L/day; 2.11 and 1.25 mg/L/day for children. Hazard index levels in dry season for adults fell between 5.09×10^{-1} and 1.54, and 1.91 and 5.75 mg/L/day for children. Cadmium Carcinogenic Risk (CR_{ing}) levels for adults fell between 4.21×10^{-5} and 2.49×10^{-4} mg/L/day; 1.61×10^{-4} and 9.52×10^{-4} mg/L/day for children. Cadmium Carcinogenic Risk (CR_{ing}) levels for adults fell between 3.80×10^{-5} and 1.15×10^{-4} mg/L/day; 1.45×10^{-4} and 1.38×10^{-4} mg/L/day for children.

4.0 Discussion

4.1 Heavy Metal Levels

The levels of Ni in the fish samples were above FAO/WHO (2003) acceptable limits of 0.2 mg/kg. The results also show that the highest levels occurred in station 2 for both seasons. Similar findings were reported by Olatunji *et al.* (2011). Nickel, when accumulated in the body via chronic exposure, may result in lung fibrosis, kidney and cardiovascular diseases and cancer of the respiratory tract (McGregor *et al*., 2000; Seilkop and Oller, 2003). IARC (2012) classified soluble and insoluble nickel compounds as Group 1 (carcinogen to humans), and nickel and alloys as Group 2B (possibly carcinogenic to humans). The levels of Co in the fish samples were below WHO acceptable limits of 0.5 mg/kg. The results also show that the highest levels occurred in the wet season when compared to dry season in all stations. These results similar with the findings of Uffah *et al.* (2021). The levels of Cd in the fish samples were below FAO/WHO (2003) acceptable limits of 0.1 mg/kg in both seasons. Cd can be enriched and accumulate in fish and transferred into the human body when ingested, causing damage to the cardiovascular, immune, reproductive, and nervous systems in the body (Mielcarek *et al.,* 2022). It disrupts the cell cycle and DNA replication and repair at the cellular level (Liu *et al.,* 2013; Liao *et al*., 2021). Fish are very sensitive to Cd pollution and if they are exposed to Cd pollution for a long time, absorption and bioaccumulation of Cd will occur in their tissues, thus affecting the structure and function of the gills and liver (Liu *et al*., 2022). The levels of Pb in the fish samples, in the wet season, were above FAO/WHO (2003) acceptable limits of 0.5 mg/kg. The results also show the dry season recorded levels below the permissible limit in all stations. High concentrations of Pb in fish tissues can affect the health of humans if taken up through the diet and can adversely affect the liver, brain, nervous system, kidneys, and reproductive system (Ishaque, 2020). Bioaccumulation is the primary mechanism responsible for Pb-induced toxicity in fish exposed to toxicants (Lee *et al*., 2019).

Table 4.1.1: Health Risk for Cobalt in Fish Samples

STATION	Conc. (mg/L)	ADULT (mg/L/day)		CHILD (mg/L/day)		ADULT		CHILD		ADULT	CHILD
		ADDing	ADDderm	ADDing	ADDderm	HQing	HQderm	HQing	HQderm	HI	HI
WET SEASON											
STNI	0.100	3.15×10^{-3}	5.98×10^{-6}	1.20×10^{-2}	1.76×10^{-5}	1.57×10^{-1}	1.05	6.01×10^{-1}	3.09	1.21	3.69
STN2	0.090	2.84×10^{-3}	5.39×10^{-6}	1.08×10^{-2}	1.59×10^{-5}	1.42×10^{-1}	9.45×10^{-1}	5.42×10^{-1}	2.79	1.09	3.33
STN3	0.093	2.93×10^{-3}	5.56×10^{-6}	1.12×10^{-2}	1.64×10^{-5}	1.47×10^{-1}	9.76×10^{-1}	5.59×10^{-1}	2.88	1.12	3.44
STN4	0.095	2.97×10^{-3}	5.64×10^{-6}	1.13×10^{-2}	1.66×10^{-5}	1.49×10^{-1}	9.90×10^{-1}	5.67×10^{-1}	2.92	1.14	3.49
STN5	0.113	3.54×10^{-3}	6.72×10^{-6}	1.35×10^{-2}	1.98×10^{-5}	1.77×10^{-1}	1.18	6.75×10^{-1}	3.48	1.36	4.15
DRY SEASON											
STNI	0.067	2.11×10^{-3}	4.00×10^{-6}	8.06×10^{-3}	1.18×10^{-5}	1.05×10^{-1}	7.03×10^{-1}	4.03×10^{-1}	2.07	8.08×10^{-1}	2.48
STN2	0.049	1.55×10^{-3}	2.94×10^{-6}	5.90×10^{-3}	8.66×10^{-6}	7.73×10^{-2}	5.15×10^{-1}	2.95×10^{-1}	1.52	5.92×10^{-1}	1.81
STN3	0.058	1.83×10^{-3}	3.47×10^{-6}	6.98×10^{-3}	1.02×10^{-5}	9.14×10^{-2}	6.09×10^{-1}	3.49×10^{-1}	1.80	7.00×10^{-1}	2.15
STN4	0.075	2.35×10^{-3}	4.46×10^{-6}	8.97×10^{-3}	1.32×10^{-5}	1.17×10^{-1}	7.82×10^{-1}	4.48×10^{-1}	2.31	9.00×10^{-1}	2.76
STN5	0.070	2.21×10^{-3}	4.19×10^{-6}	8.43×10^{-3}	1.24×10^{-5}	1.10×10^{-1}	7.35×10^{-1}	4.22×10^{-1}	2.17	8.46×10^{-1}	2.59

Table 4.1.2: Health Risk for Lead in Fish Samples

STATION	Conc. (mg/L)	ADULT (mg/L/day)		CHILD (mg/L/day)		ADULT		CHILD		ADULT	CHILD	ADULT	CHILD
		ADDing	ADDderm	ADDing	ADDderm	HQing	HQderm	HQing	HQderm	HI	HI	CRing	CRing
WET SEASON													
STNI	0.519	1.63×10^{-2}	7.73×10^{-6}	6.22×10^{-2}	2.28×10^{-5}	1.16×10	1.84×10^{-2}	4.44×10	5.43×10^{-2}	1.17×10	4.45×10	1.92	7.31
STN2	0.647	2.03×10^{-2}	9.64×10^{-6}	7.76×10^{-2}	2.85×10^{-5}	1.45×10	2.30×10^{-2}	5.54×10	6.77×10^{-2}	1.45×10	5.55×10	2.39	9.12
STN3	0.680	2.14×10^{-2}	1.01×10^{-5}	8.16×10^{-2}	2.99×10^{-5}	1.53×10	2.42×10^{-2}	5.83×10	7.13×10^{-2}	1.53×10	5.84×10	2.51	9.59
STN4	0.615	1.93×10^{-2}	9.17×10^{-6}	7.38×10^{-2}	2.71×10^{-5}	1.38×10	2.18×10^{-2}	5.27×10	6.44×10^{-2}	1.38×10	5.28×10	2.27	8.67
STN5	0.591	1.86×10^{-2}	8.81×10^{-6}	7.09×10^{-2}	2.60×10^{-5}	1.33×10	2.10×10^{-2}	5.06×10	6.19×10^{-2}	1.33×10	5.07×10	2.18	8.33
DRY SEASON													
STNI	0.258	8.11×10^{-3}	3.85×10^{-6}	3.10×10^{-2}	1.13×10^{-5}	5.79	9.16×10^{-3}	2.21×10	2.70×10^{-2}	5.80	2.21×10	9.53×10^{-1}	3.64
STN2	0.373	1.17×10^{-2}	5.57×10^{-6}	4.48×10^{-2}	1.64×10^{-5}	8.38	1.33×10^{-2}	3.20×10	3.91×10^{-2}	8.39	3.20×10	1.38	5.26
STN3	0.316	9.92×10^{-3}	4.71×10^{-6}	3.79×10^{-2}	1.39×10^{-5}	7.08	1.12×10^{-2}	2.71×10	3.31×10^{-2}	7.10	2.71×10	1.17	4.45
STN4	0.301	9.47×10^{-3}	4.49×10^{-6}	3.61×10^{-2}	1.33×10^{-5}	6.76	1.07×10^{-2}	2.58×10	3.16×10^{-2}	6.77	2.58×10	1.11	4.25
STN5	0.342	1.08×10^{-2}	5.11×10^{-6}	4.11×10^{-2}	1.51×10^{-5}	7.69	1.22×10^{-2}	2.93×10	3.59×10^{-2}	7.70	2.94×10	1.26	4.83

Table 4.1.3: Health Risk for Nickel in Fish Samples

STATION	Conc. (mg/L)	ADULT (mg/L/day)		CHILD (mg/L/day)		ADULT		CHILD		ADULT	CHILD	ADULT	CHILD
		ADDing	ADDderm	ADDing	ADDderm	HQing	HQderm	HQing	HQderm	HI	HI	CRing	CRing
WET SEASON													
STNI	0.902	2.83×10^{-2}	2.69×10^{-5}	1.08×10^{-1}	7.94×10^{-5}	1.42	4.98×10^{-3}	5.41	1.47×10^{-2}	1.42	5.43	3.37×10^{-2}	1.29×10^{-1}
STN2	0.992	3.12×10^{-2}	2.96×10^{-5}	1.19×10^{-1}	8.73×10^{-5}	1.56	5.48×10^{-3}	5.95	1.62×10^{-2}	1.56	5.97	3.71×10^{-2}	1.42×10^{-1}
STN3	0.725	2.28×10^{-2}	2.16×10^{-5}	8.70×10^{-2}	6.38×10^{-5}	1.14	4.00×10^{-3}	4.35	1.18×10^{-2}	1.14	4.36	2.71×10^{-2}	1.04×10^{-1}
STN4	0.873	2.74×10^{-2}	2.60×10^{-5}	1.05×10^{-1}	7.68×10^{-5}	1.37	4.82×10^{-3}	5.24	1.42×10^{-2}	1.38	5.25	3.27×10^{-2}	1.25×10^{-1}
STN5	0.839	2.64×10^{-2}	2.50×10^{-5}	1.01×10^{-1}	7.39×10^{-5}	1.32	4.64×10^{-3}	5.04	1.37×10^{-2}	1.32	5.05	3.14×10^{-2}	1.20×10^{-1}
DRY SEASON													
STNI	0.780	2.45×10^{-2}	2.33×10^{-5}	9.36×10^{-2}	6.86×10^{-5}	1.23	4.31×10^{-3}	4.68	1.27×10^{-2}	1.23	4.69	2.92×10^{-2}	1.11×10^{-1}
STN2	1.015	3.19×10^{-2}	3.03×10^{-5}	1.22×10^{-1}	8.93×10^{-5}	1.59	5.60×10^{-3}	6.09	1.65×10^{-2}	1.60	6.10	3.80×10^{-2}	1.45×10^{-1}
STN3	0.897	2.82×10^{-2}	2.68×10^{-5}	1.08×10^{-1}	7.89×10^{-5}	1.41	4.96×10^{-3}	5.38	1.46×10^{-2}	1.41	5.40	3.36×10^{-2}	1.28×10^{-1}
STN4	0.738	2.32×10^{-2}	2.20×10^{-5}	8.86×10^{-2}	6.50×10^{-5}	1.16	4.08×10^{-3}	4.43	1.20×10^{-2}	1.16	4.44	2.76×10^{-2}	1.05×10^{-1}
STN5	0.652	2.05×10^{-2}	1.94×10^{-5}	7.82×10^{-2}	5.73×10^{-5}	1.02	3.60×10^{-3}	3.91	1.06×10^{-2}	1.03	3.92	2.44×10^{-2}	9.31×10^{-2}

Table 4.1.4: Health Risk for Cadmium in Fish Samples

STATION	Conc. (mg/L)	ADULT (mg/L/day)		CHILD (mg/L/day)		ADULT		CHILD		ADULT	CHILD	ADULT	CHILD
		ADDing	ADDderm	ADDing	ADDderm	HQing	HQderm	HQing	HQderm	HI	HI	CRing	CRing
WET SEASON													
STNI	0.008	2.57×10^{-4}	1.22×10^{-6}	9.83×10^{-4}	3.6×10^{-6}	5.15×10^{-1}	4.89×10^{-2}	1.97	1.44×10^{-1}	5.64×10^{-1}	2.11	4.21×10^{-5}	1.61×10^{-4}
STN2	0.010	3.10×10^{-4}	1.47×10^{-6}	1.18×10^{-3}	4.34×10^{-6}	6.20×10^{-1}	5.88×10^{-2}	2.37	1.73×10^{-1}	6.78×10^{-1}	2.54	5.06×10^{-5}	1.93×10^{-4}
STN3	0.049	1.53×10^{-3}	7.24×10^{-6}	5.83×10^{-3}	2.14×10^{-5}	3.05	2.90×10^{-1}	1.17×10	8.55×10^{-1}	3.34	1.25×10	2.49×10^{-4}	9.52×10^{-4}
STN4	0.022	6.98×10^{-4}	3.31×10^{-6}	2.66×10^{-3}	9.77×10^{-6}	1.40	1.32×10^{-1}	5.33	3.91×10^{-1}	1.53	5.72	1.14×10^{-4}	4.35×10^{-4}
STN5	0.017	5.34×10^{-4}	2.54×10^{-6}	2.04×10^{-3}	7.48×10^{-6}	1.07	1.01×10^{-1}	4.08	2.99×10^{-1}	1.17	4.38	8.73×10^{-5}	3.33×10^{-4}
DRY SEASON													
STNI	0.007	2.33×10^{-4}	1.10×10^{-6}	8.88×10^{-4}	3.26×10^{-6}	4.65×10^{-1}	4.41×10^{-2}	1.78	1.30×10^{-1}	5.09×10^{-1}	1.91	3.80×10^{-5}	1.45×10^{-4}
STN2	0.014	4.25×10^{-4}	2.02×10^{-6}	1.62×10^{-3}	5.95×10^{-6}	8.51×10^{-1}	8.07×10^{-2}	3.25	2.38×10^{-1}	9.31×10^{-1}	3.49	6.95×10^{-5}	2.65×10^{-4}
STN3	0.010	3.29×10^{-4}	1.56×10^{-6}	1.26×10^{-3}	4.61×10^{-6}	6.58×10^{-1}	6.24×10^{-2}	2.51	1.84×10^{-1}	7.20×10^{-1}	2.70	5.38×10^{-5}	2.05×10^{-4}
STN4	0.022	7.02×10^{-4}	3.33×10^{-6}	2.68×10^{-3}	9.83×10^{-6}	1.40	1.33×10^{-1}	5.36	3.93×10^{-1}	1.54	5.75	1.15×10^{-4}	4.38×10^{-4}
STN5	0.008	2.45×10^{-4}	1.16×10^{-6}	9.36×10^{-4}	3.43×10^{-6}	4.90×10^{-1}	4.65×10^{-2}	1.87	1.37×10^{-1}	5.37×10^{-1}	2.01	4.01×10^{-5}	1.53×10^{-4}

4.2 Health Risk Analysis

The hazard quotient of lead exposure via the ingestion pathway (HQing) in all fish samples in both seasons were above the safety limit of 1.0 for adults and children. The lead hazard quotient exposure via the dermal pathway (HQderm) in all fish samples were below the safety limit of 1.0 for adults and children in both seasons. The lead hazard index levels in all fish samples were above the safety limit of 1.0 for adults and children for both seasons. The lead carcinogenic risk levels in all fish samples were above the safety limit of 1.0×10^{-4} - 1×10^{-6}. for adults and children in both seasons. These results indicate that all examined fish species are not safe for consumption, and possible lead health risk related with non-carcinogenic and carcinogenic effect is high for long term consumption.

Hazard quotient of nickel exposure via the ingestion pathway (HQing) in all fish samples were above the safety limit of 1.0 for adults and children in both seasons. The nickel hazard quotient for exposure via the dermal pathway (HQderm) in all fish samples were below the safety limit of 1.0 for adults and children in both seasons. The nickel hazard index levels in all fish samples were above the safety limit of 1.0 for adults and children in both seasons. The nickel carcinogenic risk levels in all fish samples were above the safety limit of 1.0×10^{-4} - 1×10^{-6} for adults and children in both seasons. These results indicate that all examined fish species are not safe for consumption, and possible nickel health risk related with non-carcinogenic and carcinogenic effect is high for long term consumption.

Hazard quotient of cadmium exposure via the ingestion pathway (HQing) in all fish samples in wet season were above the safety limit of 1.0 for adults except station 1 (5.15×10^{-1} mg/L/day) and station 2 (6.20×10^{-1} mg/L/day) which were below the safety limit while in the dry season all fish samples were below the safety limits except in station 4 (1.40 mg/L/day) which was above the limits. Hazard quotient of cadmium for exposure via the ingestion pathway (HQing) in all fish samples in children were above the safety limit of 1.0 for both seasons. The cadmium hazard quotient for exposure via the dermal pathway (HQderm) in all fish samples were below the safety limit of 1.0 for adults and children in both seasons. The cadmium hazard index levels in all fish samples were above the safety limit of 1.0 for adults except in station 1 (5.64×10^{-1} mg/L/day) and station 2 (6.78×10^{-1} mg/L/day) which were below the limit in wet season while in dry season all fish samples were below the safety limit except station 1 (1.54 mg/L/day) which was above the limits. The cadmium hazard index levels in all fish samples were above the safety limit of 1.0 for children in both seasons. The cadmium carcinogenic risk levels in all fish samples were within the safety limit of 1.0×10^{-4} - 1×10^{-6} for adults and children in both seasons. These results indicate probable non-carcinogenic risk of cadmium toxicity to adults and high probable risk of cadmium in children population when fish is consumed. No probable carcinogenic risk levels to both adults and children were observed for fish species.

Hazard quotient levels of cobalt exposure via the ingestion pathway (HQing) in all fish samples in both seasons were below the safety limit of 1.0 for adults and children. The cobalt hazard quotient for exposure via the dermal pathway (HQderm) in all fish samples were below the safety limit of 1.0 for adults in both season except in station 1 (1.05 mg/L/day) and station 5 (1.08 mg/L/day) in wet season. The cobalt hazard quotient for exposure via the dermal pathway (HQderm) in all fish samples were above the safety limit of 1.0 for children in both seasons. The cobalt hazard index levels in all fish samples for adults in wet seasons were above the safety limit of 1.0 for adults while in dry season it was all below the safety limits. The cobalt hazard index levels in all fish samples were above the safety limit of 1.0 for children in both seasons. These results indicate probable non-carcinogenic risk of cobalt toxicity to adults and high probable risk of cobalt in children population when fish is consumed.

Conclusion

The levels of Cd, Ni, Pb and Co in fish samples and the health risks associated with consumption of the fish have been investigated in this study. Ni levels were found to be above permissible limits in the wet and dry seasons of the study, Cd levels were below permissible limits in both seasons, Pb levels were above permissible limits in the wet season only. Hazard index and carcinogenic risk levels were high for Ni and Pb in the fish samples suggesting potential health risks to humans if consumed. Lower risk levels were recorded for Cd and Co. There is need to restrict fishing activities in the river and regulate the disposal of wastes by environmental regulatory agencies.

REFERENCES

Akpanyung, E. O., Ekanemesang, U. M., Akpakpan, E. I. & Anadoze, N. O. (2014). Levels of heavy metals in fish obtained from two fishing sites in Akwa Ibom State, Nigeria. *African Journal of Environmental Science and Technology*, 8(7), 416-421.

Ali, H. and Khan, E. (2019) Trophic transfer, bioaccumulation, and biomagnification of non-essential hazardous heavy metals and metalloids in food chains/webs—Concepts and implications for wildlife and human health. *Hum Ecol Risk Assess,* 25:1353–1376. https:// doi. org/ 10. 1080/ 10807 039. 2018. 14693 98

Annabi, A. and SaidKand, M.I. (2013) Cadmium: bioaccumulation, histopathology and detoxifying mechanisms in fish Am. J. Res. Commun. 1 60–79

FAO/WHO (2003). Summary of evaluations performed by the joint FAO/WHO expert committee on food additives (JECFA 1956-2003), (First Through Sixty First Meetings). ILSI Press International Life Sciences Institute.

Fazio, F.; Habib, S.S.; Naz, S.; Ullah, M.; Nawaz, G.; Nava, V., Piccione, G. and Arfuso, F. (2022) *Withania coagulans* fruit extract: a possible useful additive in ameliorating growth and immunity of *Labeo rohita* (Hamilton, 1822). *Nat Prod Res,* 10:1–6. https:// doi. org/ 10.1080/ 14786 419. 2022. 20891 39

Fevzi, Y., Nedim, Ö., Ahmet, D. and Levent, A. T. (2007). Heavy metal levels in two fish species Leuciscus cephalus and Lepomis gibbosus. *Food Chemistry, 100*(2), 830-835.

Habib, S.S; Batool, A.I; Rehman, M.F.U. and Naz, S. (2022). Comparative analysis of the haemato-biochemical parameters and growth characteristics of *Oreochromis niloticus* (Nile tilapia) cultured under different feed and habitats (biofloc technology and earthen pond system). *Aquac Res*, 53(6184–1):6192. https:// doi. org/ 10. 1111/ are. 16091

IARC (The International Agency for Research on Cancer) Nickel and nickel compounds. *IARC Monogr. Eval. Carcinog. Risk Hum.* 2012;100C:169–218.

Igwemmar, N. C., Kolawole, S. A. & Odunoku, S. O. (2013). Heavy metal concentration in fish species sold in Gwagwalada market, Abuja. *International Journal of Science and Research*, 2(11), 7-9.

Isaiah, O., Obunwo, C. C., Boisa, N. & Ihunwo, O. (2019). Quality assessment of surface waters and sediments of Anya-Ogologo River. *Journal of Water Resources and Ocean Science*, 8(5), 77-85.

Ishaque, A., Ishaque, S., Arif, A. and Abbas, H.G. (2020). Toxic effects of lead on fish and human. *Biol Clin Sci Res J,* 47. https://doi. org/10.54112/bcsrj.v2020i1.47

Lee, J.W., Choi, H., Hwang, U.K., Kang, J.C., Kang, Y.J., Kim, K.I. and Kim, J.H. (2019) Toxic effects of lead exposure on bioaccumulation, oxidative stress, neurotoxicity, and immune responses in fish: a review. *Environ Toxicol Pharmacol,* 68:101-108

Liao, Y., Zheng, H., Wu, L., He, L., Wang, Y., Ou, Y., Yang, H., Peng, S., Chen, F. and Wang, X. (2021). Cadmium cytotoxicity and possible mechanisms in human trophoblast HTR-8/SVneo cells. *Environ. Toxicol.* 36:1111–1124. doi: 10.1002/tox.23110.

Liu, Y., Chen, Q., Li, Y., Bi, L., Jin, L. and Peng, R. (2022). Toxic effects of cadmium on fish. *Toxics.* 10(10):622. doi: 10.3390/toxics10100622. PMID: 36287901; PMCID: PMC9608472.

Liu, Y., Wang, P., Wang, Y., Zhu, Z., Lao, F., Liu, X., Cong, W., Chen, C., Gao, Y. and Liu, Y. (2013). The influence on cell cycle and cell division by various cadmium-containing quantum dots. *Small,* 9:2440–2451. doi: 10.1002/smll.201300861.

Mansour, S.A. and Sidky, M.M. (2002). Ecotoxicological Studies. 3. heavy metals contaminating water and fish from Fayoum Governorate, Egypt. Food Chemistry, 78(1):15-22

McGregor, D.B., Baan, R.A., Partensky, C., Rice J.M. and Wilbourn J.D. (2000). Evaluation of the carcinogenic risks to humans associated with surgical implants and other foreign bodies- A report of an IARC Monographs Programme Meeting. International Agency for Research on Cancer. *Eur. J. Cancer,* **36**:307–313. doi: 10.1016/S0959-8049(99)00312-3.

Mielcarek, K., Nowakowski, P., Puścion-Jakubik, A., Gromkowska-Kępka, K.J., Soroczyńska, J., Markiewicz-Żukowska, R., Naliwajko, S.K., Grabia, M., Bielecka J. and Żmudzińska A. (2022). Arsenic, cadmium, lead and mercury content and health risk assessment of consuming freshwater fish with elements of chemometric analysis. *Food Chem,* 379:132167. doi: 10.1016/j.foodchem.2022.132167.

Olatunji, M. K, Ajayi, T. & Anthony, I. O. (2011). Assessment of water quality in Asa rivers Nigeria and its Indigenous *Clarius gariepines* Fish. *International Journal of Environmental Research and Public Health*, 8, 4332-4352.

Rajeshkumar, S. and Li, X. (2018). "Bioaccumulation of heavy metals in fish species from the meiliang Bay, taihu lake, China." *Toxicology Reports*, 5, 288–295.

Seilkop, S.K. and Oller, A.R. (2003). Respiratory cancer risks associated with low-level nickel exposure: An integrated assessment based on animal, epidemiological, and mechanistic data. *Regul. Toxicol. Pharm,* **37**:173–190. doi: 10.1016/S0273-2300(02)00029-6.

Souza, I.D.C, Morozesk, M., Bonomo, M.M., Azevedo, V.C., Sakuragui, M.M., Elliott, M., Matsumoto, S.T., Wunderlin, D.A., Baroni, M.V., Monferrán, M.V. and Fernandes, M.N. (2018). Differential biochemical responses to metal/metalloid accumulation in organs of an edible fish (Centropomus parallelus) from Neotropical estuaries. *Ecotoxicol Environ Saf.,* 161:260-269. doi: 10.1016/j.ecoenv.2018.05.068. Epub 2018 Jun 7. PMID: 29886313.

Topić, P. N., Čižmek, L., Babić. S., Strunjak-Perović, I. and Čož-Rakovac, R. (2023). Fish liver damage related to the wastewater treatment plant effluents. *Environ Sci Pollut Res Int*. (17):48739-48768. doi: 10.1007/s11356-023-26187-y. Epub 2023 Mar 4. PMID: 36869954; PMCID: PMC9985104.

USEPA Risk Assessment Guidance for Superfund (RAGS) (2004). Human health evaluation manual Vol. 1, [Internet]. Washington, D.C.: United States Environmental Protection Agency, Part E: Supplemental Guidance for Dermal Risk Assessment. Available from: https://www.epa.gov/risk/risk-assessment-guidance-superfund-rags-part-e

Yilmaz, F., Ozdemir, N., Demirak, A. & Tuna, A. L. (2007). Heavy metal levels in two fish species *Leuciscus cephalus* and *Lepomis gibbosus*. *Food Chemistry*, 100(2), 830-835. vc