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Health risk assessment of heavy metals in *Coptodon zillii* and *Parachanna obscura* from a tropical reservoir

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ABSTRACT

In this study, the concentrations of trace metals were examined in commercially important fish, Coptodon zillii and Parachanna obscura from Osu reservoir. These were with a view to providing baseline information on the levels of heavy metals and its associated risks to human health through fish consumption. Fish samples were collected fortnightly for five months using fish traps and gill nets with the assistance of local fisherman. They were brought into the laboratory in an ice chest for identification. The fish samples were dissected and the gills, fillet and liver kept in freezer and later analyzed for heavy metals based on Atomic Absorption Spectrophotometric (AAS) method. The data collected were subjected to appropriate statistical software packages. The results revealed that the concentration of the heavy metals in P. obscura and C. zillii across the tissues were not significantly different (p > 0.05) from each other. Also, the mean concentration of heavy metals in the fish were below the recommended limits of FAO and WHO. The target hazard quotient (THQ) for each heavy metals were below one (1) while the estimated hazard index (HI) for C. zillii and P. obscura showed no threat to human health risk through the consumption of the fish species. However, continuous consumption of the fish could probably cause health risk to the consumers of the fish. According to the study's findings, human consumption of fish species with low concentration of heavy metals at the current accumulating level is safe.

1. Background

Freshwater pollution has become a serious concern due to industrial activities, agricultural and domestic application [1,2]. This issue arises as a result of the quality of inland waterbodies and aquatic environment being destroyed due to human or anthropogenic activities. It has been estimated that 100 million people are at risk of toxic pollution at levels that exceed international health guidelines [3]. Heavy metals are among the most harmful contaminants in the environmental pollutants, and they are also particularly sensitive indicators of changes in the aquatic environment [4,5]. Their toxicity and ability accumulate in living organisms thereby causing a major problem with significant ecological implications [6,7,8]. The mechanisms and channels of toxins from one energy level to another are described by heavy metals bioaccumulation and biomagnification in living organisms (Q [9,10,11,12]. They differ from other noxious waste with their lengthy return phases, decomposition inappropriateness and their rising concentrations of buildup alongside the food chain [13]. Based on Food and Agriculture Organization (FAO), marine and freshwater fishes are the most vital

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O.E. Obayemi et al.

fishery product, monitored by ice-covered and tinned fish. Fish consumption have been increasing yearly because of its nutritional and medicinal benefits.

Fish can be considered top consumers in aquatic habitat and could concentrate enormous amount of heavy metals from the water thus they serve as bio-indicators of the habitat [14,5,15]. Gills are medium of gaseous exchange while the liver serves as deamination of toxic wastes and the fillet are the main edible part of the fish. These organs play vital role in the life history of the fish and the fillet through consumption by human being can be used to investigate direct transfer of heavy metals. Heavy metals tissue specificity are metabolically active tissues that bioaccumulate large levels of metal in fish such as the liver and gills, but metabolic activity in muscles is lesser, hence heavy metals accumulate in lower concentrations [16,17,18]. Research have revealed that bioaccumulation of heavy metals in a fleshy tissue is mostly reliant on its concentrations in the aquatic environment and its exposure period as well as ecological influences play substantial roles in their accumulation [19,20,21].

Understanding heavy metals in aquatic organisms through bioavailability helps to assess the level of heavy metals that can be ingested by human body [22]. The bio-accumulation of these metals by aquatic species, on the other hand, is a useful bio-indicator of exposure and have been used to determine contamination concentrations in polluted environments [23]. Kidney and bone damage, neurological issues, endocrine disruption, cardiovascular malfunction, and carcinogenic consequences are among the health risks posed by toxicity of heavy metals [24]. *Coptodon zillii* and *Parachanna obscura* were selected due to their consumption rate within the country. The criteria for selection of these heavy metals were based on their essential and non-essential importance in the environment as trace and toxic metals and also its possible harmful effect on human health.

Health risk assessment is used to assess the nature and likelihood of harmful health consequences on people who may be exposed to chemicals in polluted environmental media in the present or the future [25]. The methods of target hazard quotient that are utilized in analyzing exposure to pollutants and toxicity data, are employed in risk assessment [26]. Because there are no quantitative principles for calculating the likelihood of non-cancer effects from toxin exposure. There have been various research on the amounts of heavy metals in fish and their risk evaluation [27,28,29].

Therefore, this study assessed the risk assessment through consumption of *C. zillii* and *P. obscura*. As a consequence, heavy metals in water bodies are probably to build up in fish and signify a potential risk for the fish and also fish consumers, especially humans [30,31, 32,1]. The tropical reservoir is surrounded by farmlands and is close to major highways. The importance of this study is to provide preliminary investigation on the health risk associated with consuming *C. zillii* and *P. obscura* in Osu reservoir.

The following were the study's objectives.

- (i) determine the levels of heavy metal in Coptodon zillii and Parachanna obscura,
- (ii) compare the levels of heavy metal with FAO, WHO, ROPME, FDA and EC standards; and



Fig. 1. Map of osu reservoir in atakumosa west local government, osu.

(iii) evaluate the target cancer risk, target hazard quotient, and the hazard index of these metals

through the consumption of C. zillii and P. obscura.

2. Methods

2.1. Study area, samples collection and preparation

The area of study is an impounded Osu reservoir in a semi-urban community of Osun state. The reservoir was created by the damming of River Sasa in 2006 and is surrounded by a number of villages which include Agbao, Alatise etc. Osu reservoir is mainly for domestic water production for rural dwellers. Osu reservoir lies approximately on Latitude 007°58′48′ N to 007°58′85′ N and Longitude 04°64′76′ E to 04°64′77′ (Fig. 1). The reservoir is surrounded by agricultural farmlands and close to two major highways, these could serve as source of pollution. Fish samples were collected from different section of Osu reservoir using gill nets and traps through the help of a professional fisherman from April to August 2012. The samples were brought to the laboratory in an ice chest for further analysis. The fishes were identified using standard keys prepared by Ref. [33]. Total and standard lengths of the fifty-two (52) fishes were taken using meter-rule in centimetres and the sex of each fish samples were determined by visual inspection of the gonads. Weights of the fish were taken using Denward weighing balance instrument calibrated in grams.

The fish tissues weighing 0.5 g of gills, fillet and liver were carefully removed, dried and powdered samples were weighed and digested with aqua regia, a mixture of HNO_3 and HCl in ratio 3:1 [34]. To each sample, 5 mL of HNO_3 and 15 mL of HCl was added and the mixture was allowed to slowly react for an hour, it was then heated at 60 °C until near dryness. Also, 3 mL of HNO_3 was again added for total dissolution while 10 mL of distilled water was added and boiled to remove the excess acid, this process was repeated again and boiled until the volume in the flask reduces to about 5 mL. It was allowed to cool, filtered and transferred into a volumetric flask and made up to 50 mL mark with distilled water and poured into sample bottle for AAS analysis [35]. PG 990 Atomic absorption spectrophotometer (AAS) was used for the analysis of heavy metals.

2.2. Quality assurance and quality control

To avoid sample mix-ups at the laboratory, all of the sample vials were meticulously labeled in the field. All determinations were made using analytical grade reagents, with the majority of the analyses being done in duplicate and the focus being on precision and accuracy monitoring. Also in the laboratory, apparatus were cleansed through soaking in 10% vol/vol HNO₃ for 24 h before analysis while stocked chemical solutions were certified for purity and concentration [36]. Twenty thousand (20,000) ng/L of the standard solution of heavy metals were added to the fish sample for precision method analysis. The values of the fish sample were recorded before and after the addition. In order to ensure quality control of the metals in fish samples, the NIST SRM® 1946-Lake Superior Fish Tissue was used as the standard reference. The limit of detection (LOD) for the instrument were 1 ng/g, 1 ng/g, 2 ng/g and 1 ng/g for Pb, Cu, Zn and Cd while As, Cr, Ni, Mn and Fe had LOD of 1 ng/g, 1 ng/g, 1 ng/g, 1 ng/g and 2 ng/g respectively.

2.3. Health risk determination

2.3.1. Target hazard quotient

This computation determines the non-carcinogenic risk limit related to pollutant exposure. It was determined using the USEPA region III risk-based level table to estimate human health risk of ingesting metal-contaminated fish species. The calculation was done using the equation [37] below:

$$THQ = \frac{EF \ x \ ED \ x \ FIR \ x \ Cf \ x \ CM}{WAB \ x \ ATn \ x \ RfD} \ x \ 10^{-3}$$

Where.

THQ = Target hazard quotient

EF = Exposure frequency (365 days/year)

ED = Exposure duration (30 years for non-cancer risk was used)

FIR = Fish ingestion rate (20.8 g/person/day [38]).

Cf = Conversion factor (0.0208) to convert fresh weight (Fw) to dry weight (Dw) considering 79% of moisture content in fish

CM = Concentration of heavy metals in fish species (mg/kg d. w.)

WAB = Mean body weight (bw) (70 kg),

ATn = When describing non-cancer risk, the average exposure time for non-carcinogens (EFED) (365 days per year for 30 years, or ATn = 10,950 days)

RfD = The reference dose of the metal (an estimate of the amount of exposure per day to which the general public might be constantly exposed for a lifetime without a detectable risk of adverse effects).

A THQ below 1 implies that the fish can be considered safe for consumption with no potential associated risks [39].

O.E. Obayemi et al.

2.3.2. hazard index

The total of the hazard quotients is used to determine the hazard index (HI) from THQs (USEPA, 2011).

$$HI = THQ(Cd) + THQ(Fe) + THQ(Zn) + THQ(Cu) + THQ(Pb) + THQ(As) + THQ(Mn) + THQ(Cr) + THQ(Ni)$$

Where.

HI = The hazard index

THQ (Cd) = The target hazard quotient for Cadmium intake.

2.3.3. Target cancer risk

The target cancer risk (TR) was used to denote concerns over carcinogenic issues. The technique for measuring TR is also presented in the USEPA Region III Risk-Based Concentration Table [37]. The following is the model for estimating TR (Bonsignore et al., 2018):

 $TR = \frac{EF \ x \ ED \ x \ FIR \ x \ CF \ x \ CM \ x \ CPSo}{WAB \ x \ ATc} \ x \ 10^{-3}$

Thus.

TR = Target cancer risk CM = Concentration of heavy metals in fish species (ng/g) FIR = Fish ingestion rate (g/day) CPSo = The carcinogenic potency slope, oral (mg/kg bw/day) ATc = The averaging time, carcinogens (365 days/year for 70 year as used by Ref. [37]. The CPSo values for Ni = 1.7, As = 1.5, Cd = 0.01, Cr = 0.5 and Pb = 0.38 [40], so TR values for their intake of these metals were computed.

*Note: Inorganic As was used for health risk calculation from 10% of total As.

2.3.4. Statistical analysis

The statistical tool SPSS 25.0 was used to analyze all of the data (SPSS, USA). The mean heavy metal concentrations in fish species and standard deviations were calculated. One-way ANOVA was used to determine the significant differences between heavy metal concentrations in the different tissues while tukey post hoc test was used to separate the means. T-test was used to determine the significance in the concentration of heavy metals between the fish species. Probability level at p = 0.05 was used to indicate statistical significance. Nanograms of each heavy metal were calculated for each gram of dry weight of the metals (ng/g dry weight).

3. Results

3.1. Morphometric measurements

The range of standard lengths, total lengths and weights with the mean and standard deviation of *Coptodon zillii* and *Parachanna obscura* in Osu reservoir are presented in Table 1. The mean standard lengths values of *C. zillii* varied between 16.3 and 22.2 cm, while the standard length was between 19.8 and 27.5 cm. Similarly, the weight varied from 176 to 280 g. The mean total length, standard length and weight of *P. obscura* were 32.3 ± 7.68 cm, 38 ± 9.5 cm and 556 ± 333 g respectively (Table 1).

3.2. Heavy metals

The mean concentration of heavy metals in the gills, fillet and liver of *Coptodon zillii* are shown in Table 2. The levels of heavy metals in the gills of the fish increased from As < Pb < Cr < Ni < Mn < Cd < Zn < Fe < Cu whereas in the fillet of the same fish, the trend was Ni < As < Cd < Pb < Mn < Cr < Zn < Cu < Fe. The concentrations of Ni and Zn in the gills and liver was significantly higher when compared to the concentrations in the fillets. The one-way ANOVA showed that there was a significant difference (p < 0.05) in heavy metals between the fish tissues except in Cd, Zn, Pb, As, and Cr (Table 2).

Table	

Standard length (SL), total length (SL) and weight of Coptodon zillii and Parachanna obscura

Parameters	Species			
	Coptodon zillii	Parachanna obscura		
Standard Length Range (cm)	16.3–22.2	22.3-42.8		
Mean \pm SD (cm)	18.9 ± 2.01	32.3 ± 7.68		
Total Length Range (cm)	19.8–27.5	26.5-51.3		
Mean \pm SD (cm)	23.6 ± 2.61	38 ± 9.5		
Weight Range (g)	176–280	128-848		
Weight±SD (g)	217 ± 40.7	556 ± 333		

Table 2		

Heavy metals	Tissues					
	Gills	Fillet	Liver			
	Mean \pm SD	Mean \pm SD	Mean \pm SD			
Cd	$3.8\pm1.9^{ m a}$	$1.8\pm1.9^{ m a}$	$1.8\pm1.2^{\rm a}$			
Fe	$1.37\pm4.4^{\mathrm{a}}$	7 ± 5.4 $^{\mathrm{ab}}$	3.6 ± 3.1 $^{\rm b}$			
Zn	$5.5\pm2.7^{\rm a}$	$3.8\pm1.9^{ m a}$	$4\pm2.8^{\mathrm{a}}$			
Cu	$1.53\pm3.2^{\rm a}$	5.3 ± 2.4 $^{ m b}$	3.7 ± 2.4 $^{ m b}$			
Pb	$1.2\pm1.2^{\rm a}$	$1.8\pm0.9^{\rm a}$	$1.3\pm0.8^{\rm a}$			
As	$1.0\pm0.8^{\rm a}$	$1.3\pm0.8^{\rm a}$	$1.2\pm0.7^{\rm a}$			
Mn	$3.5\pm2.1^{\rm a}$	$2.7\pm1.4~^{\rm ab}$	1.2 ± 0.9 $^{ m b}$			
Cr	$1.8\pm1.1^{\rm a}$	$3.2\pm1.9^{ m a}$	$2.8\pm1.6^{\rm a}$			
Ni	$3.2\pm1.2^{ m a}$	0.7 \pm 0.5 $^{\mathrm{b}}$	2.7 ± 1.4^{a}			

Concentration of mean heavy metal (ng/g) in the tissues of Coptodon zillii.

* row means with the same superscript are not statistically different (p > 0.05) among tissues.

The mean heavy metal concentrations in the tissues of *Parachanna obscura* are shown in Table 3. The levels of heavy metals in the gills increased from As < Pb < Mn < Ni < Cr < Cd < Zn < Cu < Fe while similar pattern was recorded in the liver as < Cr < Pb < Ni < Mn < Cd < Zn < Cu < Fe and the fillet showed an increasing order of Mn < As < Cr < Pb < Cd < Ni < Zn < Cu < Fe. The one-way ANOVA revealed that there was no significant difference (p > 0.05) in the level of heavy metals between the fish tissues.

There was no significant (p < 0.05) difference between the mean heavy metals concentration of *C. zillii* and *P. obscura* (Table 4.). The levels of heavy metals in the fish fillets of *C. zillii* and *P. obscura* were evaluated in comparison to regulated requirements for human consumption (Table 5). The concentration of heavy metals recorded in *C. zillii* were lower than FAO, 200, [41,42]. Hence, the levels of heavy metals in the fillets of *C. zillii* did not exceed the regulatory limitations for [43,44] and NOAA, 2009 (Table 5).

3.3. Assessment of health risks

To calculate the target hazard quotient, assumptions were used in the health risk assessment. The excess likelihood of acquiring cancer over a 70-year period was used to express the health risk associated with carcinogenic impacts of specific heavy metals. In this study, by analyzing the consumption of each heavy metal, the target hazard quotient (THQ) was determined for *C. zillii* and *P. obscura* as shown in Table 6. The satisfactory regulatory value for THQ = 1, according to Ref. [37]. THQ values < 1 for *C. zillii* and *P. obscura* which indicated no non-carcinogenic health risk from ingesting of any metals through the consumption of the fish. In *C. zillii*, Pb (0.34) had the highest THQ value while Cd (0.009) recorded the lowest value. The levels of THQ for the metals was Cd < Cr < Zn < Fe < As < Cu < Mn < Ni < Pb. The THQ for *P. obscura* showed that Mn had the highest value of 0.28 followed by Pb (0.27) with the lowest value recorded in Cd (0.007). The increasing order of THQ in the fish was Cd < Zn < Cr < As < Fe < Ni < Cu < Pb < Mn. Also, the THQ for each metal was in agreement with the acceptable limit while the joint heavy metals was less than 1. The Hazard Index (HI) for *C. zillii* (1.04 ng/g) was significantly higher than that of *P. obscura* that recorded HI value of 0.81 ng/g.

In this study, Ni, Mn, Cd and Pb contributed the most in the hazard index of *C. zillii* and *P. obsura* collected from Osu reservoir (Fig. 2). Also in order to determine the target risk, the metals with known carcinogenic effects were used to determine the target risk values. The target risk (TR) values for Cd, Pb, As, Cr and Ni varied from 0 to 3.4 ng/g in *C. zillii* while TR ranged between 0 and 1.2 ng/g in *P. obscura*. In *C. zillii*, Ni had the highest TR of 3.4 ng/g when compared to Cr that had the highest value in *P. obscura*. In both fish species, Pb had the least TR value (Table 7). The screening level for ingestion of *C. zillii* and *P. obscura* for non-carcinogenic is as shown in Table 8. In *C. zillii*, the increasing order for each heavy metal was Cd < Cr < Zn < Fe < Cu < As < Mn < Ni < Pb while the decreasing order for individual heavy metal was Pb > Mn > Ni > As > Cu > Fe > Cr > Zn > Cd in*P. obscura*.

Table 3

Mean heavy meta	l concentrations	(ng/g)	in the	tissues	of Pa	ırachanna	obscura
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Heavy metals	Tissues		
	Gills	Fillet	Liver
	Mean \pm SD	Mean \pm SD	Mean \pm SD
Cd	$2.3\pm1.5^{\rm a}$	$2.5\pm1.4^{\rm a}$	2.7 ± 2^{a}
Fe	$12.8\pm4.2^{\rm a}$	$10.2\pm4.2^{\mathrm{a}}$	$12.7\pm4.1^{\rm a}$
Zn	3.8 ± 2.5^{a}	6.3 ± 3.6^{a}	5 ± 3.3^{a}
Cu	13.3 ± 3.4^{a}	$8.5\pm4.0^{\mathrm{a}}$	$11.2\pm3.13^{\rm a}$
Pb	$1.8\pm1.5^{\rm a}$	2.3 ± 1.5^{a}	$1.2\pm0.9^{\mathrm{a}}$
As	$1.8\pm1.3^{\rm a}$	$1.7\pm1.2^{\mathrm{a}^{\scriptscriptstyle m \circ}}$	$0.8\pm0.4^{\rm a}$
Mn	$2\pm1.4^{\mathrm{a}}$	$1.5\pm1.1^{\rm a}$	$2\pm1.8^{\rm a}$
Cr	$2.3\pm1.2^{\rm a}$	$2.2\pm1.5^{\rm a}$	$1\pm0.9^{\mathrm{a}}$
Ni	$\textbf{2.2}\pm \textbf{1.2}^{a}$	$2.7\pm2.1^{\rm a}$	$1.8\pm1.0^{ m a}$

* row means with the same superscript are not statistically different (p > 0.05) among tissues.

Table 4

Heavy metal concentrations (ng/g) in Coptodon zillii and Parachanna obscura of osu reservoir.

Heavy metals	C. zillii	P. obscura	р	t
Cd	2.5	2.5	0.50	2.92
Fe	8.1	11.9	0.15	2.92
Zn	4.4	5.1	0.33	2.92
Cu	8.1	11	0.20	2.92
Pb	1.5	1.8	0.16	2.92
As	1.2	1.4	0.25	2.92
Mn	2.4	1.8	0.24	2.92
Cr	2.6	1.8	0.19	2.92
Ni	2.2	2.2	0.48	2.92

* Significant (p < 0.05).

Heavy metals	Standards	Standards						
	C. zillii	P. obscura	FAO	WHO	ROPME	FDA	EC	
Cd	2.5	1.8	0.5	0.5	0.01-0.75	4	0.5	
Fe	10.2	7	180	109	200			
Zn	6.3	3.8	100	100				
Cu	8.5	5.3	30	30	0.05-19.5			
Pb	2.3	1.8	2	0.5	0.01 - 1.28	1.7	1	
As	1.7	1.3						
Mn	1.5	2.7	0.5	0.5				
Cr	2.2	3.2	0.5	0.5				
Ni	2.7	0.7	55	30	0.01-0.75	70	40	
References	This Study	This Study	FAO, 2000	[42]	[41]	[44]	[43]	

Table 6

Target Hazard Quotient (THQ) (ng/g) for Heavy Metals and its Hazard Index (HI). From Ingestion of Coptodon zillii and Parachanna obscura in Osu Reservoir.

 $THQ = \frac{EF \ x \ ED \ x \ FIR \ x \ Cf \ x \ CM}{WAB \ x \ ATn \ x \ RfD} \quad x \ 10^{-3}$

Heavy metals	RfD (ng/g)	Target hazard quotient (THQ)		
		C. zillii	P. obscura	
Cd	5	0.009	0.007	
Fe	7	0.053	0.036	
Zn	5	0.023	0.014	
Си	20	0.13	0.079	
Pb	200	0.34	0.27	
As	300	0.038	0.029	
Mn	140	0.16	0.28	
Cr	9	0.015	0.021	
Ni	140	0.28	0.073	
Hazard index (HI)	830	1.04	0.81	

Table 9 showed the carcinogenic screening levels (SL) for *C. zillii* and *P. obscura* based on individual heavy metal. The highest SL in *C. zillii* was observed in Ni while As had the least SL value. Similarly, As recorded the lowest SL in *P. obscura* with the maximum value observed in Cr. The results obtained for the relationship amongst the heavy metal in the organs of *C. zillii* is as shown in Fig. 3. The cluster analysis showed three major groupings among the heavy metals. The clustering showed the differences in the grouping based on trace and toxic metals in the fish. At significant level ($p \le 0.05$) Zinc and Cadmium clustered with each other. At $p \le 0.01$, Lead and Nickel clustered with Arsenic and Chromium while at $p \le 0.001$, Copper clustered with Iron and Manganese. Fig. 4 showed the relationship amongst the different selected heavy metals in the organs of *P. obscura*. The cluster analysis showed three major groupings among the heavy metals of *P. obscura*. The cluster analysis showed three major groupings and the organs of *P. obscura*. The cluster analysis showed three major groupings among the beavy metals in the organs of *P. obscura*. The cluster analysis showed three major groupings among the heavy metals. At significant level ($p \le 0.05$) Ni clustered with Mn, Zn, Cd, Cu and Fe. At $p \le 0.01$, Mn clustered with Zn, Cd, Cu and Fe while at $p \le 0.001$, Pb clustered with As and Cr.

Thus.

THQ = Target hazard quotient



Fig. 2. Hazard index (HI) of selected heavy metals in fish species at osu reservoir.

Table 7

Target Cancer Risk (ng/g) of *Coptodon zillii* and *Parachanna obscura* based on Selected Heavy Metals.

Heavy metals	Target cancer risk (TR)		
	C. zillii	P. obscura	
Cd	0.7	0.51	
Pb	0	0	
As	0.19	0.15	
Cr	0.82	1.2	
Ni	3.4	0.9	

Table 8

Coptodon zillii and Parachanna obscura ingestion screening levels for non- carcinogenic (ng/g) of selected heavy metals.

$$SL = \frac{THQ \ x \ AT \ x \ ED \ x \ BW}{\left(\frac{1}{RfDo}\right) x \ EF \ x \ ED \ x \ IRFI}$$

Heavy metals	RfD (ng/g)	Screening Level for Non-Carcinogenic		
		C. zillii	P. obscura	
Cd	5	0.007	0.005	
Fe	7	0.053	0.037	
Zn	5	0.017	0.01	
Cu	20	0.36	0.23	
Pb	200	9.8	7.67	
As	300	1.63	1.25	
Mn	140	3.13	5.64	
Cr	9	0.019	0.028	
Ni	140	5.64	1.46	

EF = Exposure frequency (365 days/year)

ED = Exposure duration (30 years for non-cancer risk was used)

FIR = Fish ingestion rate (20.8 g/person/day [38].

Cf = Conversion factor (0.0208) to convert fresh weight (Fw) to dry weight (Dw) considering 79% of moisture content in fish CM = Concentration of heavy metals in fish species (mg/kg d. w.)

WAB = Mean body weight (bw) (70 kg),

Table 9

Coptodon zillii and Parachanna obscura ingestion screening levels for carcinogenic (ng/g) of selected heavy metals.

$$SL = \frac{TR \ x \ AT \ x \ LT \ x \ BW}{CPFo \ x \ EF \ x \ ED \ x \ IRFI}$$

Heavy metals	Screening Level for Carcinogenic		
	C. zillii	P. obscura	
Cd	716.8	516.1	
Pb	659.4	516.1	
As	48.7	37.3	
Cr	630.8	917.5	
Ni	774.1	200.7	



Fig. 3. Relationship among selected heavy metal concentrations in the tissues of Coptodon zillii.

ATn = When describing non-cancer risk, the average exposure time for non-carcinogens (EFED) (365 days per year for 30 years, or ATn = 10,950 days) [37].

RfD = The reference dose of the metal (an estimate of the amount of exposure per day to which the general public might be constantly exposed for a lifetime without a detectable risk of adverse effects).

Thus.

TR = Target cancer risk

CM = Concentration of heavy metals in fish species (ng/g)

FIR = Fish ingestion rate (g/day)

CPSo = The carcinogenic potency slope, oral (mg/kg bw/day)

ATc = The averaging time, carcinogens (365 days/year for 70 year as used by USEPA, 2011). Since CPSo values were known for Ni, AS, Cr, Cd, and Pb, so TR values for their intake of these metals were computed [45].

$$TR = \frac{EF \ x \ ED \ x \ FIR \ x \ CF \ x \ MC \ x \ CPSo}{WAB \ x \ ATc} \ x \ 10^{-3}$$

Thus.

THQ = Target hazard quotient

AT = Average exposure time for non-carcinogens (365 days per year for 26 years)



Fig. 4. Relationship among selected heavy metal concentrations in the tissues of Parachanna obscura

ED = Exposure Duration (26 years)

BW = Body Weight (80 kg)

RfD = Reference dose of the metal (mg/kg/day)

EF = Exposure Frequency (350 days per year)

IRFI = Ingestion Rate of Fish (mg/day)

Thus [45].

TR = Target cancer risk
AT = Average exposure time for carcinogenic (365 days per year for 70 years) [37].
LT = Lifetime exposure (70 years)
BW = Body Weight (80 kg)
EF = Exposure Frequency (350 days per year)
ED = Exposure Duration (26 years)
CPSo = The carcinogenic potency slope, oral (mg/kg/day)

IRFI = Ingestion Rate of Fish (mg/day)

4. Discussion

In this study, the values of standard length, total length and weight of *C. zillii* in Osu reservoir were 16.3–22.2 cm, 19.8–27.5 cm and 176–280 g respectively, was consistent with the range recorded by Komolafe et al., 2016 [46], in *C. zillii* collected at Igun reservoir. In the same vein, *P. obscura* in Osu reservoir had standard length, total length and weight within the range of 22.3–42.8 cm, 26.5–51.3 cm and 128–848 g respectively and compared favourably with the values recorded by Refs. [47,48]. The differences in the lengths and body weight of the fishes could probably be due to environmental changes and the presence or absence of foods and nutrients in the habitat.

The mean of heavy metal concentrations in the tissues of *C. zillii* revealed that Cu $(1.53 \pm 3.2 \text{ ng/g})$, Fe $(7 \pm 5.4 \text{ ng/g})$ and Zn $(4 \pm 2.8 \text{ ng/g})$ were the most accumulated heavy metals in the gills, fillet and liver. This results is consistent with earlier studies involving heavy metals in fish species [49,50,51]. The findings showed that the distribution of heavy metals varies between fish tissues. In *C. zillii*, the Liver revealed distribution in the order As < Mn < Pb < Cd < Ni < Cr < Cu < Fe < Zn. Similar trend in the distribution of heavy metals in the fish was also recorded by Ref. [52] in fish of Cross River as well as the reports of [53] from fish of the Mediterranean coast, Damietta. High concentration of Zn and Ni in the liver compared to other tissue might be due to the metalothionein protein in the liver [54,55]. Essential heavy metals (Fe, Cu, and Zn) were shown to accumulate at higher concentrations than non-essential heavy metals in this study (Cd, Pb, As, Ni). Zinc is a vital mineral that plays a part in many metabolic processes, and a lack of it can cause a variety of symptoms, including appetite loss, development problems, and immune system problems [56,57]. Cu is a

necessary metal for organisms' health, but excessive levels can create a variety of problems [58,59]. The current study found that the mean of heavy metals concentration in the tissues of P. obscura showed that Cu (13.3 \pm 3.4 ng/g), Fe (10.2 \pm 4.2 ng/g) and Fe (12.7 \pm 4.1 ng/g) were the most accumulated heavy metals in the gills, fillet and liver respectively. These levels were low when compared with the findings of [60] in Oreochromis niloticus of Challawa river, Kano and [50] in P. obscura from Owan River, Edo State. Gills and linked proteins come into direct contact with water and have a trend for accumulating heavy metals through adsorption [61]; N [62]. Due to excessive mucous secretion and gill blockage, accumulation affinity of various organs for heavy metals has shown to be slightly lower according to different studies [63,64]. Although, the concentration of heavy metals in the fish tissues might be low, the metals could probably find their way through flooding of chemicals that are used on the farmlands into nearby streams, rivers and reservoirs. The overall mean heavy metal concentrations in the tissues of *P. obscura* were As < Cr < Mn < Pb < Ni < Cd < Zn < Cu < Fe. High level of Fe in this study were also reported by Ref. [9] in the tissues of Spanish mackerel at Karachi Fish Harbor and [65] in some organs of two commercial fish species in Kapar and Mersing Coastal Waters. The low level of pollution of C. zillii and P. obscura with non-essential heavy metals could be as a result of low environmental pollution in Osu reservoir. This was also the view of [66] that recorded low concentration of heavy metals in the tissues of Pampus chinensis and Hyporhamphus limbatus from Karnaphuli River estuary, Bangladesh. Information from previous studies has shown that concentration of heavy metals in fish tissues varied according to the fish species and locality [27,39,67]. In general, the levels of Cd, Cu, Zn, Pb and Fe in the fillet of the two fishes in this study were lower than those in Solea and Solea aurata from Iskenderun Gulf [54]. [68] recorded high levels of heavy metals of As, Cd, Pb, Hg and Al in Tilapia spp and Catfish of Lake Mariut, Egypt when compared to the values reported in this current study which was low. The difference in the levels of heavy metal in the fishes could probably due to species specific of these metals since C. zillii are mostly found at the surface column (pelagic) of the water when compared with *P. obscura* that live at the lower part of water or demersal in nature. Also, since metals migrate differently in different organ activities, different fish organs have varying capacities for storing and metabolizing heavy metals from the aquatic environment [69,70]; A. 1 [71].

The concentration of heavy metals observed in the fillet of *C. zillii* and *P. obscura* in Osu reservoir were low when compared with permissible limits of regulatory agencies standard such as FAO, WHO and ROPME. Therefore, the fishes are suitable for human consumption. These data provides an important baseline information in order to monitor pollution in the environment. Low heavy metal concentrations may not tend to harm fish [72,73], but they can cause a reduction in fish reproduction [74,75], that can lead to population decline.

In this study, the level of heavy metals in the fillet was used for health risk assessment calculation. The hazards of heavy metals in fishes of the reservoir and its implications for human health are highlighted in this study. The THQ-based evaluation method has proven to be effective in estimating heavy metal health risks for consumers of fish [54,76,77]. The target hazard quotient for *C. zillii* and *P. obscura* in Osu reservoir was less than 1, this is also below the permissible value of 1 [39,37]. The values of THQ for each heavy metal in *C. zillii* and *P. obscura* were less than 1 which indicated no carcinogenic health risk that might be as a result of ingesting any of the heavy metal through intake of the fish. In *C. zillii*, the maximum THQ was recorded in Pb (0.34 ng/g) followed by Ni (0.28 ng/g) with least value recorded in Cd (0.009 ng/g). Also, in *P. obscura*, the combined impacts of THQ of each heavy metal were less than 1. Similar observation was also recorded by Ref. [52] in four commercially important fish species from Cross River ecosystem. Several authors have reported less than 1 in the THQ of heavy metals in fish of different waterbodies [78,79,80].

As most risk contributor, non-essential heavy metals such as Ni and Pb accounted for more than 50% of the hazard index for *C. zillii* in this study. In contrast, essential heavy metals (Mn, Cu, Zn and Fe) contributed 50.6% to the HI of *P. obscura*. The HI value for the fishes are less than 1 which indicated the fishes are safe for consumption based on health risk assessment. However, these current results was in contrast with the findings of [78] that recorded HI value greater than 1 in *Liza parsia* fish.

The use of target cancer risk values can predict the potential carcinogenic effects of a substance over an individual's lifetime and values greater than 10^{-4} are known to exert possible carcinogenic properties [81]. The target cancer risk for heavy metals (Cd, Pb, As, Cr, and Ni) with carcinogenic effects ranged from 0 to 3.4 ng/g in *C. zillii* to 0–1.2 ng/g in *P. obscura*. The TR values for the fishes were less than the values estimated by Ref. [10] in fishes from River Buriganga. These results agree with the findings of [50] that recorded TR value less than 1 in *Clarias gariepinus* and *Parachanna obscura* from the Owan River. The fish ingestion screening level for non-carcinogenic showed that the fillet of the fish species revealed no carcinogenic risk through the consumption of any of the heavy metals. The carcinogenic risk values for Cd, Pb, As, Cr and Ni in the two species in this study revealed slightly higher risks than the 10^{-6} and 10^{-4} which is considered as the acceptable limit [82].

5. Conclusions

In conclusion, the results of target risk of *C. zillii* and *P. obscura* collected from Osu reservoir indicated that excessive consumption of the fish over a long period of time could probably cause health risk to the consumers of the fish. Therefore, the consumption of the fishes could pose possible risk of cancer for the consumers at distant future.

Author contribution statement

Oluwadamilare Emmanuel Obayemi, Mary Ayoade: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Olaniyi Komolafe: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Data availability statement

Data will be made available on request.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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List of Abbreviation

FAO	Food and Agriculture Organization
WHO	World Health Organization
HCl	Hydrochloric Acid
HNO ₃	Nitric Acid
mL	milliliter
USEPA	United States Environmental Protection Agency
ANOVA	Analysis of Variance
р	Probability level
SD	Standard deviation
FDA	Food and Drug Administration
EC	European Commission
NOAA	National Oceanic and Atmospheric Administration
ROPME	Regional Organization for the Protection of the Marine Environment
RfD	Reference Dose

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