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Assessment of Radionuclides and Heavy Metals Concentration of Some Selected Fish Samples in River Komadugu of Gashua, Yobe State, Nigeria

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Abstract

This study investigates the concentrations of heavy metals (Pb, Cd, Fe, Zn) and the activity concentrations of naturally occurring radionuclides (^{226}Ra, ^{232}Th, and ^{40}K) in fish samples from the Komadugu River. Gamma spectrometry, coupled with a sodium thallium iodide (NaI(Tl)) detector, and atomic absorption spectrometry (AAS) were employed to assess the levels of these contaminants. The mean activity concentrations of the radionuclides were found to range as follows: ^{40}K (61.54 ± 2.70 Bq/kg), ^{232}Th (24.98 ± 3.57 Bq/kg), and ^{226}Ra (17.90 ± 2.71 Bq/kg). Health risk assessment indices, including radium equivalent activity (Raeq), were below the permissible limit, while the annual effective dose (AED) and excess lifetime cancer risk (ELCR) exceeded the acceptable thresholds in some samples. The concentration of heavy metals in the fish samples varied as follows: Zn (245.25–145.0 mg/kg), Fe (1774.75–341.0 mg/kg), Cd (28.75–1.00 mg/kg), and Pb (162.75–3.5 mg/kg). The mean concentrations of heavy metals were: Fe (796.05 mg/kg), Zn (192.45 mg/kg), Pb (89.90 mg/kg), and Cd (10.65 mg/kg), with Fe being the most abundant, followed by Zn, Pb, and Cd. These findings highlight potential health risks associated with the consumption of fish from the Komadugu River, emphasizing the need for ongoing monitoring and risk management of aquatic food sources in the region.

Introduction

The Earth's crust contains abundant naturally occurring radioactive elements, and humans are continuously exposed to these radionuclides through contact with soil, crops, food, water, and air (Online *et al*., 2024). Natural radiation exposure results primarily from radionuclides such as uranium-238 (^{238}U), thorium-232 (^{232}Th), and potassium-40 (^{40}K), whose concentrations in soil, sediments, water, food, and rocks depend on the geological characteristics of each region (Ogundele.k.T, *et al*., 2020). Aquatic organisms can accumulate both natural and artificial radionuclides through direct absorption from water and feeding processes. Consequently, humans may be internally exposed to radiation through the consumption of contaminated aquatic species such as fish (Michael *et al*., 2018).

Natural and artificial radiations from the ground, building materials, water, air, food, cosmic sources, atomic bomb tests, and nuclear accidents are major contributors to human radiation exposure. The presence of active uranium mines in the Niger Republic one of the major catchment areas of the River Yobe raises concerns about potential radioactive contamination in aquatic ecosystems (Abba *et al*., 2017). Hence, it is necessary to measure the levels of radionuclide contamination in fish samples from the Komadugu River, given the high local consumption of fish from this water body.

Exposure to radionuclides and heavy metals poses serious health risks, including cancer and systemic poisoning. Although low-level exposure occurs naturally, industrial and anthropogenic activities have significantly increased human exposure to these toxic substances (Yakubu & Dankawu, 2024). Heavy metal pollution in rivers has become a global concern over recent decades—not only because of threats to potable water but also due to hazards associated with the consumption of contaminated fish. Heavy metals from natural sources, industrial discharges, sewage, agricultural runoff, and domestic wastewater are continually released into aquatic systems. Their toxicity, persistence, and tendency to bioaccumulate and biomagnify through the food chain make them particularly dangerous (Biosci *et al.,* 2013).

Bioaccumulation and biomagnification can elevate metal concentrations in aquatic organisms to hazardous levels, leading to nutrient imbalances and various health disorders such as Parkinson's disease, cancer, skin conditions, respiratory abnormalities, gastrointestinal distress, neurological damage, hematological disorders, and reproductive failure. Acute exposure to high concentrations of heavy metals can cause nausea, anorexia, vomiting, gastrointestinal irritation, and dermatitis (Dagari *et al*., 2024).

Metals such as copper (Cu), iron (Fe), lead (Pb), and zinc (Zn) are essential trace elements required for various metabolic processes, while others—such as cadmium (Cd), nickel (Ni), and mercury (Hg)—are highly toxic even at trace concentrations. Notably, even essential metals become harmful when present above optimal levels. Heavy metal contamination of aquatic environments thus represents a critical ecological and public health issue due to the toxicity and bioavailability of these metals in aquatic habitats. River Yobe is one of the major water bodies in Yobe State, Nigeria, and its contamination poses significant risks to local communities (El-ishaq *et al.*, 2016)

Fish are vital components of human diets and should be routinely monitored to ensure that heavy metal concentrations remain within safe limits (kumar *et al*., 2018). As bioaccumulators of both organic and inorganic pollutants, fish serve as effective bioindicators for assessing the ecological health of aquatic ecosystems (State *et al*., 2013). The presence of toxic substances in soil and water facilitates their entry into the food chain, thereby increasing human exposure through diet. In Nigeria, fish constitute a major source of animal protein, with national consumption estimated at approximately 3.32 million metric tons annually (FAO, 2018). Therefore, assessing the concentrations of toxic metals and radionuclides in fish is essential for managing their potential impact on human health and ensuring food safety (Online *et al.*, 2024).

Study Area

The Yobe River, also known as the Komadugu Yobe, flows through West Africa, reaching Lake Chad via Nigeria and Niger. Originating in Gashua, Yobe State (12º52'N, 10º58'E), the river spans 320 km, with key tributaries like the Hadejia, Jama'are, and Komadugu Gana Rivers. It forms part of the border between Nigeria and Niger. The river supports the livelihoods of hundreds of thousands, particularly in agriculture and commerce along its 200 km stretch in northern Yobe, covering seven local government areas. However, concerns about changes in river flow, ecology, and the economy arise due to upstream dams, notably the Tiga Dam in Kano and the proposed Kafin Zaki Dam in Bauchi. Notable towns along the river include Gashua, Geidam, and Damasak in Nigeria, and Diffa in Niger (Dagari *et al*., 2024)

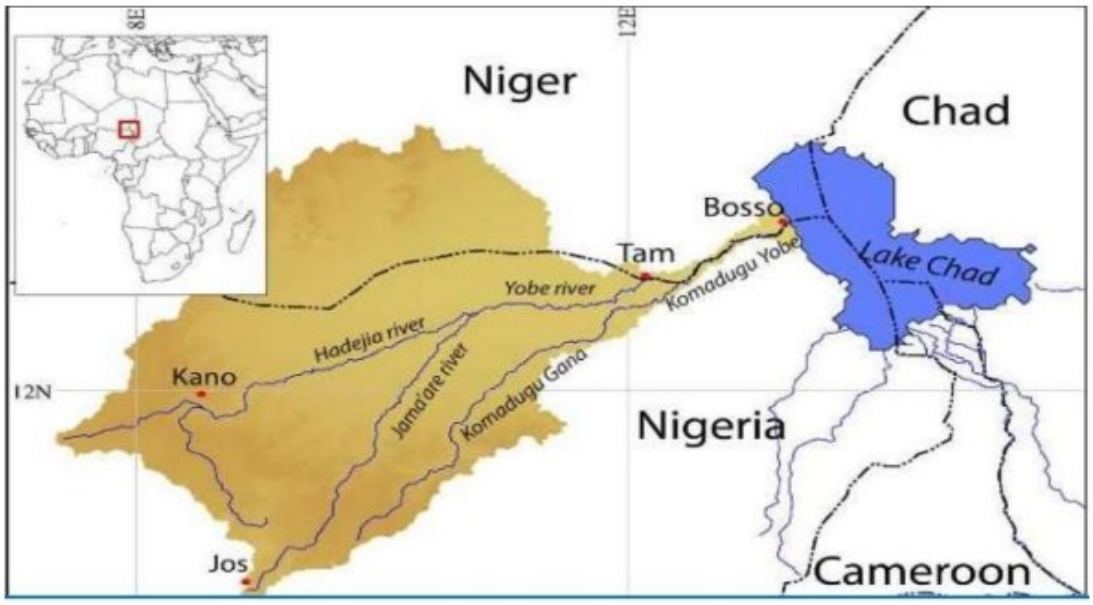

Figure 1 Map of the study area showing the sampling location

Sample Collection

Five different samples of fish species were collected from fishermen along the Komadugu River axis in Gashua. The samples were promptly placed in an ice container and transported to the

multi-user laboratory at the Faculty of Science and the Center for Energy Research and Training (CERT) at Ahmadu Bello University in Zaria, Nigeria, for analysis.

Estimating activity concentration of radionuclides

The activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K in fish samples were measured using a NaI (TI) gamma spectrometer at the Centre for Energy Research and Training, Ahmadu Bello University, Nigeria. The detector's resolution (8% at 662 keV) was sufficient to distinguish the relevant gamma-ray peaks for the radionuclides. Activity of 226Ra was estimated from the ^{214}Bi peak (1760 keV), ^{232}Th from the ^{208}Tl peak (2615 keV), and ^{40}K from its 1460 keV gamma emission. Fish samples were analyzed for 8 hours, with background interference subtracted to determine net activity concentrations.

Sample analysis for heavy metals

Atomic Absorption Spectroscopy (AAS) begins by digesting the sample to liberate metals into a solution. Next, the solution is fed into an AAS instrument, where the metals are vaporized and subjected to light at precise wavelengths. The degree of light absorption by the metals correlates directly with their concentration in the sample. By employing a calibration curve, the metal concentrations are precisely quantified. Rigorous quality control protocols are applied to guarantee result accuracy. In summary, AAS is a highly sensitive and accurate technique for assessing heavy metal levels across diverse sample types (Yakubu *et al.*, 2024)

Radium equivalent activity index (Raeq)

Radium Equivalent Activity (Raeq): The Radium Equivalent Activity (Raeq) was calculated using the following formula:

$$Ra_{eq} = A_{Ra} + 1.43_{Th} + 0.077_{k} \quad (1)$$

where A_{Ra}, A_{Th} and A_K are the specific activities of ^{226}Ra, ^{232}Th and ^{40}K (in Bq/kg).*(Mustapha et al.,* 2024)

Absorbed dose rate (D)

The absorbed dose rates in outdoor (D) due to gamma radiations in the air at 1m above the ground surface for the uniform distribution of the naturally occurring radionuclides (^{226}Ra, ^{232}Th, and ^{40}K) when calculated based on guidelines provided by (UNSCEAR, 2000). The conversion factors used to compute absorbed gamma (γ) dose rate (D) in air per unit activity concentration in Bq/kg (dry-weight) corresponds to 0.462 ηGyh-1 for ^{226}Ra (of U series), 0.621 ηGyh-1 for ^{232}Th and 0.0417 ηGyh-1 for ^{40}K(Kareemah *et al*, 2024)

$$D_R(nGyh^{-1}) = 0.462_{Ra} + o.621_{Th} + 0.0417_{k} \quad (2)$$

Radiation Hazard Index

These indices were used to estimate the level of gamma radiation hazard associated with the natural radionuclide in the fish samples. The external (H_{ext}) and internal (H_{int}) radiation hazard (H_{int}) indices were calculated using equations 3 and 4, respectively.(Michael *et al*, 2018)

$$H_{ext} = \frac{C_{Ra}}{370} + \frac{C_{Th}}{259} + \frac{C_k}{4810} \quad 3$$

$$H_{int} = \frac{C_{Ra}}{185} + \frac{C_{Th}}{259} + \frac{C_k}{4810} \quad 4$$

Representative Gamma Index (Iγ)

The Gamma Index (Iγ) calculated using equation 5 is used to estimate the gamma radiation hazard associated with the natural radionuclide in the specific investigated samples

$$I\gamma = \frac{C_{Ra}}{150} + \frac{C_{Th}}{100} + \frac{C_k}{1500} =\leq 1 \quad 5$$

Where, C_{Ra}, C_{Th}, and C_K are the radioactivity concentration of ^{238}U, ^{232}Th and ^{40}K in the fish samples. Values of Iγ of ≤ 2 correspond to a dose rate criterion of 0.3 mSv/year, whereas Iγ≤ 6 corresponds to a 1 mSv/year criterion. Thus, Iγ should be used for screening samples and samples with Iγ > 6 should be avoided completely (Michael *et al*,2018)

Annual effective ingestion dose of plants (AEDing)

The annual ingestion of radionuclides to humans from fish was estimated from the activity concentration of individual radionuclides as shown in equation (6).

$$AEDing(mSvy^{-1}) = AR \times IR_{ing} \times DCF_{ing} \quad 6$$

Where AR is the activity concentration of the radionuclides in a sample, IRing is the consumption rate per year, and DCF_{ing} is the effective dose coefficient for the ingestion of ^{226}Ra (3.58 × 10-4 $mSvBq^{-1}$), ^{232}Th (2.30 × 10-4 $mSvBq^{-1}$) and ^{40}K (6.20 × 10-6 $mSvBq^{-1}$)

The Excess Lifetime Cancer Risk

Excess Lifetime Cancer Risk (ELCR): Excess lifetime cancer risk (ELCR) is calculated using the formula

$$ELCR = AEDE \times DL \times RF \quad 7$$

Where AEDE, DL, and RF are annual effective dose equivalent, duration of life (70 years) and risk factor (0.05 Sv^{-1}), respectively.(Mustapha *et al*., 2024)

Health Risk Assessment

Health risk assessments for heavy metals was calculated for mean daily dose, non-cancer danger index and cancer danger using procedures described in (Membere & Abdulwasiu, 2020)

$$ADD = \frac{C \times IR \times EF \times ED}{AT \times BW} \quad 8$$

Where. ADD (mg kg-1 day-1) = the average dose contacted through ingestion. EF = Exposure frequency 365 days/year. ED = Exposure time equivalent to mean lifetime (60 years). FIR =Fish Ingestion Rate C = amount of metal contains in fish mg/kg. BW = Body Weight AT = average time of exposure of time.

Non-cancer Hazard Index

$$HQ = \frac{ADD}{Rfd} \quad (9)$$

Where;

HQ = Hazard quotient, R*fd* = Reference dose factors

Cancer Risk (CR)

$$CR = ADD \times SF \quad (10)$$

S*f* = Slope Factor (1/mg/kg/day)

Activity Concentration of Radionuclides in Fish Samples

The Gamma spectrometry method was used to determine the activity concentration of radionuclides in fish samples, as shown in Table 1

Table 1 Activity Concentration of Radionuclide in Fish Sample at Gashua

SAMPLE ID	K-40 (Bk/Kg)	Ra-226 (Bk/Kg)	Th-232 (Bk/Kg)
A	33.0327	19.1033	23.1417
B	47.9471	15.0602	19.3843
C	48.3670	18.9990	38.5405
D	70.1340	19.1844	27.8221
E	108.2430	17.1455	15.9977
Min	**33.0327**	**15.0602**	**15.9977**
Max	108.2430	19.1844	38.5405
Average	**61.5447**	**17.8985**	**24.9782**

The Gamma spectrometry method was used to determine the activity concentration of **^{40}K, ^{226}Ra,** and **^{232}Th** in fish samples. The results showed that all samples contained these radionuclides, with **^{40}K** having an average concentration of **61.5447 ± 2.6966 Bq/kg, Ra-226** at **17.8985 ± 2.7062 Bq/kg,** and **Th-232** at **24.9783 ± 3.5701 Bq/kg, which is shown in Figure 2**. These results indicate typical levels of natural radionuclides, with the standard deviations suggesting minimal variation across the samples, implying consistent environmental exposure.

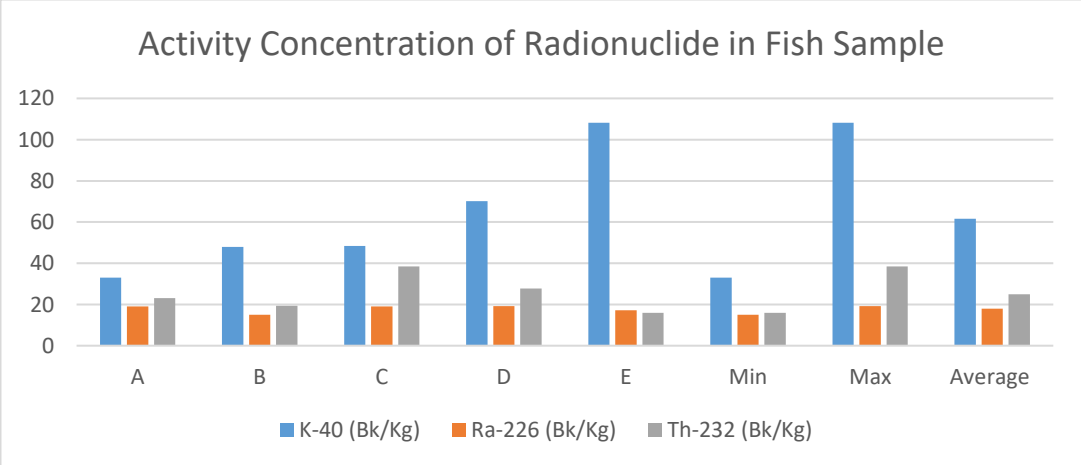

Figure 2: Activity concentration of Radionuclide in the fish sample

Comparison of mean activity concentration (Bq/kg) with other studies

Table 2: Comparison of Mean Activity (Bq/kg) with Other Studies

Country	Ra-226	Th-232	K-40	Reference
Nigeria	–	10.85 ± 1.74	30.19 ± 3.43	Michael *et al.* (2018)
Nigeria	–	26.55 ± 4.77	365.31 ± 11.36	Katherine *et al.* (2020)
Brazil	0.11 ± 0.03	–	102 ± 4	Nery *et al.* (2022)
Nigeria	37.22 ± 4.31	94.82 ± 3.82	384.98 ± 11.97	I *et al.* (2013)
Tanzania	87.96 ± 0.07	–	434.16 ± 0.24	Kazoka *et al.* (2023)
Nigeria	17.8985 ± 2.7062	24.9782 ± 3.5701	61.5447 ± 2.6966	Current Study
Permissible Limit	35	500	UNSCEAR	

The results presented in Table 2 were the average activity concentrations of ^{40}K, ^{226}Ra, and ^{232}Th from this study were compared with those from other sudies and the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) guidelines. The concentrations found in the current study for ^{226}Ra (17.8985 Bq/kg), ^{232}Th (24.9782 Bq/kg), and ^{40}K (61.5447 Bq/kg) were higher than the recommended permissible limits set by UNSCEAR, which are 35 Bq/kg for Ra-226, 500 Bq/kg for Th-232, and no specific limit for K-40.

Radiological Impact Parameters Absorbed

Table 3 This table summarizes the radium equivalent activity (Raeq), internal and external hazard indices (H_{in} and H_{ex}), absorbed dose rate (DR), and gamma index (Iγ) for each of the five fish samples, along with the overall mean values

S/N	Sample	Raeq (Bq/kg)	H_{ex}	H_{in}	DR (nGy/h)	Iγ
1	A	34.75	0.1479	0.1996	24.58	0.3809
2	B	79.70	0.1254	0.1874	20.99	0.3261
3	C	77.84	0.2102	0.2616	34.69	0.5443
4	D	64.37	0.1738	0.2257	29.07	0.4529
5	E	48.36	0.1306	0.1770	22.37	0.3464
Mean	-	**61.00**	**0.1576**	**0.2103**	**26.34**	**0.4101**

The radium equivalent activity (Raeq), internal hazard index (Hin), external hazard index (Hex), absorbed dose rate (DR), and gamma index (Iγ) values for the five fish samples (A to E) are summarized as follows: Sample A had a Raeq of 34.75 Bq/kg, Hin of 0.1996, Hex of 0.1479, DR of 24.58 nGy/h, and Iγ of 0.3809. Sample B showed Raeq of 79.70 Bq/kg, Hin of 0.1874, Hex of 0.1254, DR of 20.99 nGy/h, and Iγ of 0.3261. Sample C had Raeq of 77.84 Bq/kg, Hin of 0.2616, Hex of 0.2102, DR of 34.69 nGy/h, and Iγ of 0.5443. Sample D's Raeq was 64.37 Bq/kg, Hin was 0.2257, Hex was 0.1738, DR was 29.07 nGy/h, and Iγ was 0.4529. Sample E showed Raeq of 48.36 Bq/kg, Hin of 0.1770, Hex of 0.1306, DR of 22.37 nGy/h, and Iγ of 0.3464. The overall mean values across all samples were Raeq 61.00 Bq/kg, Hin 0.2103, Hex 0.1576, DR 26.34 nGy/h, and Iγ 0.4101.

Annual Effective ingestion dose of plants (AEDing) and Excess lifetime cancer risk (ELCR) the value of Evaluated AEDing and ELCR in fish sample is presented in table 4

Table 4 Evaluated AEDing and ELCR in fish sample

				AEDing	TOTAL	
S/N	SAMPLE	^{226}Ra	^{232}Th	^{40}K	AEDing ($mSvy^{-1}$)	ELCR $X10^{-3}$
1	A	0.067	0.052	0.002	0.121	0.042
2	B	0.053	0.044	0.003	0.100	0.350
3	C	0.067	0.087	0.003	0.157	0.549
4	D	0.061	0.063	0.004	0.128	0.448
5	E	0.061	0.036	0.007	0.104	0.364
	MEAN	0.0618	0.0564	0.0038	0.122	0.3506

The values of the excess lifetime cancer risk (ELCR) calculated using equation 7 are presented in table 4 and illustrated in figure 4.The values ranged from 0.042 to 0.549 with a mean of 0.3506 respectively. The values is higher than the world average value of 0.2 ($\times 10^{-3}$) and this poses a cancer risk. The fisherman are at risk of incurring cancer and care must be taken in the consumption of these fishes.

HEAVY METAL

Table 5. Concentration of Heavy Metals fish sample

Sample ID	Fe (mg/kg)	Zn (mg/kg)	Cd (mg/kg)	Pb (mg/kg)
A	341.75	145	1	103
B	573.75	174.25	1.25	3.5
C	1774.75	245.75	28.75	92
D	472.25	201.75	6.5	88.25
E	817.75	195.5	15.75	162.75
Min	341.75	145	1	3.5
Max	1774.75	245.75	28.75	162.75
Average	796.05	192.45	10.65	89.9

The concentration of heavy metals in the fish samples from the studied area is presented in Table 6 and illustrated in **Figure 3**. The average concentrations were **796.05 mg/kg for Fe, 192.45 mg/kg for Zn, 10.65 mg/kg for Cd**, and **89.9 mg/kg for Pb.** Iron (Fe) had the highest concentration among the heavy metals, while cadmium (Cd) had the lowest. The mean concentration of the heavy metals followed this decreasing order: **Fe > Zn > Cd > Pb.** Notably, the concentration of Fe was significantly higher than the others, and the values for all heavy metals exceeded the World Health Organization (WHO) recommended limits, except for zinc (Zn), which had the lowest mean concentration compared to the WHO threshold.

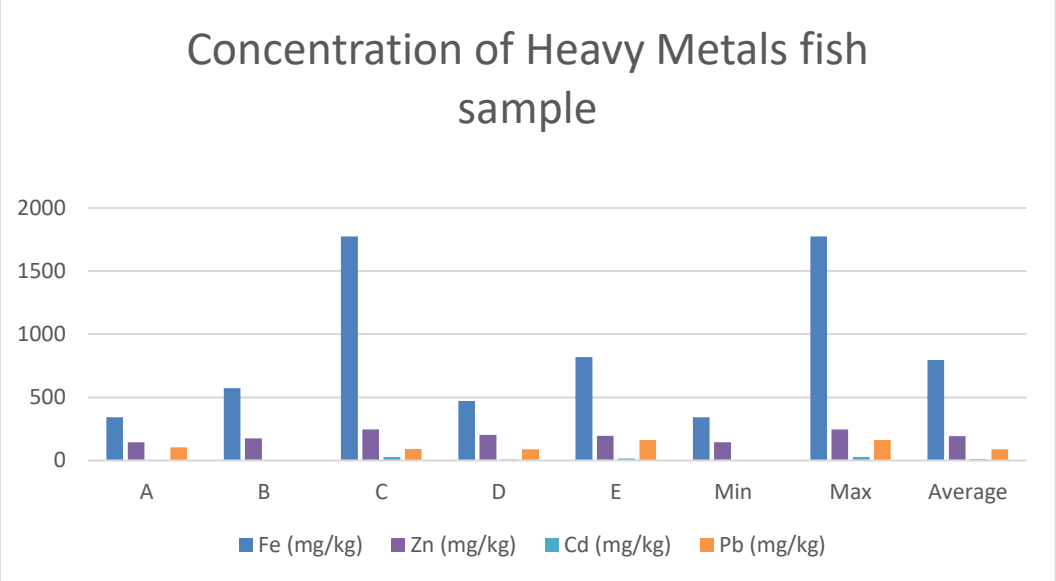

Figure 3: Concentration of Heavy Metal

Table 6: The Health Risk Assessment (HRA) of heavy metals in Fish Sample

S/N	Metal	Mean	*Rfd mg/kg/day*	*SF*	ADD	HQ	CR
1	Fe	796.05	0.00026	8.28E	123167.6	473721538.46	1.73E+06
2	Zn	192.45	0.3	9.26E+00h	29776.54	99255.13	2.76E+05h
3	Cd	10.65	0.0005	15	1647.805	3295610	3.08E+04
4	Pb	89.9	0.00014	8.5E-03	13909.39	99354571.43	1.23E+02

The degree of toxicity of heavy metal to human being depends upon their daily intake average daily dose is a function of body weight and intake. In the present study, the Highest ADD values for metals is Fe was 2.9E+04.The lowest is Cd 1.3E+04 with the mean value of 4.2E+04 ADD.

Hazard Quotient (HQ)

The hazard quotient and hazard index (HQ) values were calculated on the basis of the oral reference dose. Oral reference doses (RfDo) for heavy metal Table 6.From the result obtained, the HQ values of some of the heavy metals in fish sample were all above (1). When HQ exceeds one (1), there is concern for health effect (Chapter *et al*., 2023). The results further indicated that the population might be probably exposed to some potential health risk through the intake of heavy metals via consuming fish.

Cancer Risk

Cancer risks were computed as 1.73E+06 for highest and 2.76E+05h for lowest chances for the studied fish respectively (Tables 6). These cancer risk values indicate that consumption of fish from the study area would result in an excess of 5 cancer cases per 1,000,000 people while a previous study showed consumption of fish could result in 5 cancer cases per 100

people(Chapter *et al.*, 2023). The CR value is also higher than the USEPA recommended value of 0.0001, indicating a considerable potential risk.

Conclusion

This study measured the concentration of radionuclides and heavy metals in fish samples from the Komadugu River in Bade LG, Yobe State, Nigeria. While the activity concentrations of 226Ra, 232Th, and 40K were below the recommended limits by UNSCEAR, the concentration of heavy metals, particularly iron (Fe), exceeded the recommended levels set by WHO/FAO. The study also calculated the annual effective dose and excess lifetime cancer risk (ELCR) for fish consumption, indicating potential health risks. The findings highlight the need for public awareness regarding the potential risks associated with consuming river fish. It is recommended that guidance be provided to farmers and the public, especially regarding the use of pesticides, herbicides, and fertilizers. Additionally, actions such as monitoring sedimentation processes in the river and controlling household wastewater disposal should be implemented to mitigate the environmental and health risks.

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