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# Comparative Assessment of Heavy Metal Accumulation in Two Commercial Fish Species (*Clarias Gariepinus* and *Chrysichthys Nigrodigitatus*) from Amansea River, Nigeria

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#### ABSTRACT

This study evaluated species-specific patterns of heavy metal bioaccumulation in two economically important fish species from Amansea River, southeastern Nigeria. Samples of water, sediment, and fish tissues (*Clarias gariepinus* and *Chrysichthys nigrodigitatus*) were collected from three locations between November 2023 and April 2024. Concentrations of lead (Pb), mercury (Hg), arsenic (As), cadmium (Cd), and chromium (Cr) were quantified using Inductively Coupled Plasma Mass Spectrometry. Results revealed distinct bioaccumulation patterns between species. *C. nigrodigitatus* demonstrated significantly higher accumulation of Cd ( $0.045 \pm 0.004 \text{ mg/kg}$  vs.  $0.032 \pm 0.003 \text{ mg/kg}$ ; p = 0.010) and Cr ( $0.055 \pm 0.004 \text{ mg/kg}$  vs.  $0.006 \pm 0.004 \text{ mg/kg}$ ; p < 0.001) compared to *C. gariepinus*. Bioaccumulation Factors (BAFs) showed *C. nigrodigitatus* had substantially higher capacity to accumulate Pb (BAF = 11.556) and Cr (BAF = 2.200) compared to *C. gariepinus* (BAF = 0.778 and 0.240, respectively). In contrast, *C. gariepinus* exhibited greater mercury accumulation tendencies (BAF = 0.447 vs. 0.206). Human health risk assessment indicated mercury posed potential health concerns (Target Hazard Quotient = 1.063), with species-specific risks varying considerably. The observed accumulation differences likely reflect disparate feeding ecologies and habitat utilization, with the benthic-feeding *C. nigrodigitatus* accumulation gariepinus showed enhanced mercury bioaccumulation. These findings demonstrate the importance of considering species-specific accumulation patterns in biomonitoring programs and developing targeted consumption advisories to protect public health.

Keywords: Bioaccumulation Factor, Fish biomonitoring, Human health risk, Mercury, Target Hazard Quotient

## **1. INTRODUCTION**

Anthropogenic activities have significantly increased heavy metal contamination in aquatic ecosystems worldwide, with particularly severe impacts in developing nations undergoing rapid industrialization [1,2]. These metals represent persistent environmental contaminants that accumulate in aquatic biota and potentially transfer to humans through consumption pathways [3]. The non-biodegradable nature of heavy metals, coupled with their capacity for bioaccumulation and biomagnification in food webs, raises substantial ecological and human health concerns [4,5].

Recent investigations have documented increasing heavy metal pollution in African freshwater systems, particularly in Nigeria's urbanizing regions where regulatory frameworks often lag behind industrial expansion [6,7]. The Amansea River in southeastern Nigeria exemplifies these challenges, serving as both a critical resource for local communities and a recipient of various anthropogenic inputs. This waterway supports substantial artisanal fisheries activity, with *Clarias gariepinus* (African sharptooth catfish) and *Chrysichthys nigrodigitatus* (silver catfish) representing economically important species widely consumed by local populations [8].

These fish species occupy distinct ecological niches within the same ecosystem. *C. gariepinus* displays omnivorous feeding habits and utilizes both benthic and pelagic zones, while possessing accessory breathing organs that enable exploitation of oxygen-depleted environments [9]. Conversely, *C. nigrodigitatus* primarily exhibits benthic feeding behaviors, foraging on bottom-dwelling invertebrates and organic detritus in close association with sediments [10]. These ecological differences potentially translate to distinct exposure patterns and bioaccumulation profiles for environmental contaminants.

While numerous studies have examined heavy metal contamination in Nigerian aquatic systems [11,12,13], comparative assessments that specifically address species-specific differences in bioaccumulation patterns remain limited. Understanding these differences is crucial for several reasons: (1) accurately assessing ecological risks in multi-species communities, (2) selecting appropriate bioindicator species for monitoring programs, and (3) developing targeted consumption advisories that reflect species-specific contamination profiles.

This study aims to quantify and compare the bioaccumulation patterns of five priority heavy metals (Pb, Hg, As, Cd, and Cr) in *C. gariepinus* and *C. nigrodigitatus* from the Amansea River. Specific objectives include: (1) determining metal concentrations in water, sediment, and fish tissues; (2) calculating and comparing species-specific Bioaccumulation Factors; (3) evaluating potential health risks associated with fish consumption using the Target Hazard Quotient approach; and (4) identifying implications for biomonitoring and public health protection. By elucidating species-specific accumulation patterns, this research contributes to improved environmental monitoring strategies and more effective human health risk management in the region.

## 2. MATERIALS AND METHODS

#### 2.1 Study Area Description

This investigation was conducted along a 5 km stretch of the Amansea River (6°12'N 7°03'E), located in Awka North Local Government Area, Anambra State, southeastern Nigeria. The river represents a tributary of the larger Niger River system and provides essential ecosystem services to surrounding communities, including water for domestic use, irrigation, and fisheries resources. The watershed experiences a tropical climate with distinct wet (April-October) and dry (November-March) seasons, with annual rainfall averaging 1800-2000 mm.



Fig 1: Map of study area

Three sampling locations were strategically selected to represent varying degrees of anthropogenic influence:

- Site 1 (S1): Upstream location characterized by relatively minimal human impact
- Site 2 (S2): Midstream section adjacent to areas with increased agricultural and residential activity
- Site 3 (S3): Downstream location potentially affected by cumulative pollution loads

### 2.2 Sample Collection and Processing

Sample collection occurred between November 2023 and April 2024, encompassing both dry and early wet season conditions. At each site, the following samples were collected:

#### 2.2.1 Water Samples

Triplicate water samples were collected at each site using pre-cleaned 2L polyethylene bottles following protocols described in APHA Method 3010B [14]. Bottles were rinsed with site water before collection, then samples were taken approximately 30 cm below the water surface. Samples were preserved with ultrapure nitric acid to pH < 2 and transported to the laboratory in coolers maintained at 4°C.

#### 2.2.2 Sediment Samples

Surface sediment samples (0-10 cm depth) were collected in triplicate at each site using an Ekman grab sampler following USEPA Method 823-B-01-002 [15]. Samples were placed in polyethylene bags, transported on ice to the laboratory, air-dried at room temperature, homogenized using a porcelain mortar and pestle, and sieved through a 2 mm nylon mesh. For heavy metal analysis, a portion was further sieved to  $<63 \mu m$  to focus on the fine fraction.

#### 2.2.3 Fish Samples

Adult specimens of *C. gariepinus* (n=9, three per site) and *C. nigrodigitatus* (n=9, three per site) were collected using gill nets (mesh size: 50-70 mm) with assistance from local fishermen. Fish were immediately euthanized following ethical guidelines, measured for total length and weight (Table 1), and transported to the laboratory in ice-filled coolers. In the laboratory, muscle tissue was carefully excised from the dorsal region using stainless steel tools, freeze-dried, homogenized, and stored in airtight containers until analysis.

Table 1: Biological characteristics of fish species sampled from Amansea River (Mean  $\pm$  SEM)

Species	n	Total Length (cm)	Weight (g)	<b>Condition Factor</b>
C. gariepinus	9	$42.5\pm3.6$	$756.3\pm68.2$	$\boldsymbol{0.98\pm0.08}$
C. nigrodigitatus	9	$31.2\pm2.8$	$523.7\pm54.5$	$1.71 \pm 0.13$

#### 2.3 Laboratory Analysis

#### 2.3.1 Analytical Procedures

All samples were analyzed for five priority heavy metals (Pb, Hg, As, Cd, and Cr) using Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Agilent 7700x). Water samples were filtered through 0.45  $\mu$ m membrane filters prior to analysis following USEPA Method 200.8 [16]. Sediment samples were digested using aqua regia (HCl:HNO<sub>3</sub>, 3:1 v/v) in a microwave digestion system following USEPA Method 3051A [17]. Fish tissue samples were digested using a mixture of HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> in a microwave digestion system following USEPA Method 3052 [18].

#### 2.3.2 Quality Assurance/Quality Control

Rigorous quality control procedures were implemented throughout the analytical process. These included:

- Analysis of procedural blanks with each batch of samples
- Calibration using multi-element standards (Agilent Technologies)
- Analysis of certified reference materials (DORM-4 for fish tissue, PACS-3 for sediment)
- Triplicate analysis of 10% of the samples
- Determination of method detection limits for each element

Recoveries for certified reference materials ranged from 93-105% for all metals analyzed, validating the analytical procedures employed.

#### 2.4 Data Analysis and Calculations

#### 2.4.1 Bioaccumulation Factors

Bioaccumulation Factors (BAFs) were calculated for each metal and fish species following the method described by McGeer et al. [19]:

#### BAF = Cf / Cw

Where: Cf represents the metal concentration in fish tissue (mg/kg dry weight), and Cw represents the metal concentration in water (mg/L).

#### 2.4.2 Human Health Risk Assessment

Health risk assessment was conducted using the Target Hazard Quotient (THQ) approach following USEPA methodology [20]. The process involved calculating:

1. Estimated Daily Intake (EDI):  $EDI = (C \times IR \times EF \times ED) / (BW \times AT)$ 

Where:

- C = metal concentration in fish (mg/kg)
- IR = fish ingestion rate (0.068 kg/day, based on local consumption patterns)
- EF = exposure frequency (365 days/year)
- ED = exposure duration (30 years)
- BW = body weight (65 kg, representing average adult weight in the study area)
- AT = averaging time (10,950 days)
- 2. Target Hazard Quotient (THQ): THQ = EDI / RfD

Where RfD represents the oral reference dose for each metal [20]:

- Pb: 3.5 × 10<sup>-3</sup> mg/kg/day
- Hg: 3.0 × 10<sup>-4</sup> mg/kg/day
- As: 3.0 × 10<sup>-4</sup> mg/kg/day
- Cd: 1.0 × 10<sup>-3</sup> mg/kg/day
- Cr: 3.0 × 10<sup>-3</sup> mg/kg/day

A THQ value greater than 1 indicates a potential health risk to consumers.

#### 2.4.3 Statistical Analysis

Statistical analyses were performed using R software version 4.1.2 [21]. Data normality was verified using the Shapiro-Wilk test, and homogeneity of variance was assessed using Levene's test. Independent t-tests were employed to compare metal concentrations between the two fish species. Pearson's correlation coefficients were calculated to examine relationships between metal concentrations in different environmental compartments. Statistical significance was established at  $\alpha = 0.05$ .

## 3. RESULTS AND DISCUSSION

#### 3.1 Heavy Metal Concentrations in Water and Sediment

The concentrations of heavy metals in water and sediment samples from the Amansea River are presented in Table 2. Water analysis revealed concerning levels of several metals, with mercury showing the highest mean concentration  $(0.167 \pm 0.109 \text{ mg/L})$ , followed by cadmium  $(0.031 \pm 0.003 \text{ mg/L})$ , lead  $(0.024 \pm 0.011 \text{ mg/L})$ , arsenic  $(0.023 \pm 0.006 \text{ mg/L})$ , and chromium  $(0.016 \pm 0.006 \text{ mg/L})$ . When compared with World Health Organization drinking water guidelines [22], mean concentrations of lead, mercury, arsenic, and cadmium exceeded the recommended limits, with mercury demonstrating the most substantial exceedance at 27.8 times the guideline value.

Table 2: Mean concentrations of heavy metals in water and sediment samples from Amansea River

Metal (ppm)	Water (mg/L)	WHO (mg/L)	Guideline	Exceedance Factor	Sediment (mg/kg)	USEPA TE (mg/kg)	Ľ
Pb	$0.024\pm0.011$	0.01		2.4	$0.029\pm0.020$	35.0	
Hg	$0.167\pm0.109$	0.006		27.8	$0.068\pm0.010$	0.17	
As	$0.023\pm0.006$	0.01		2.3	$0.054\pm0.003$	5.9	
Cd	$0.031\pm0.003$	0.003		10.3	$0.053\pm0.003$	0.596	
Cr	$0.016\pm0.006$	0.05		0.32	$0.038\pm0.009$	37.3	

Values represent mean ± SEM of nine replicates (three per site) TEL: Threshold Effect Level; USEPA: United States Environmental Protection Agency

The elevated mercury concentrations warrant particular attention, as they significantly surpass acceptable limits for aquatic environments. These findings align with observations reported by Zhang et al. [23] in river systems affected by industrial discharges. The notably high mercury levels in this study may reflect inputs from upstream artisanal gold mining activities, which frequently employ mercury for amalgamation processes, as documented by Esdaile and Chalker [24] in similar tropical riverine environments. Interestingly, while water samples showed concerning levels of metal contamination, sediment analysis revealed concentrations below both the Threshold Effect Level (TEL) and Probable Effect Level (PEL) established by the USEPA [25]. This pattern diverges from the typical relationship where sediments serve as primary repositories for heavy metals in aquatic systems [26]. This discrepancy might be attributed to several factors, including: (1) relatively recent metal inputs that have not yet fully partitioned to sediments, (2) hydrological characteristics of the river that limit sediment deposition, or (3) resuspension and mobilization of sediment-bound metals due to seasonal flow variations. The spatial distribution of metals showed distinct patterns across the three sampling sites (Fig. 1). Lead concentrations peaked at the midstream site (S2:  $0.043 \pm 0.075 \text{ mg/L}$ ), while mercury demonstrated a decreasing gradient from upstream to downstream (S1:  $0.349 \pm 0.460 \text{ mg/L}$ ; S2:  $0.122 \pm 0.003 \text{ mg/L}$ ; S3:  $0.030 \pm 0.009 \text{ mg/L}$ ). These spatial variations likely reflect different contamination sources along the river continuum, with potential point sources of lead contamination near S2, and possible mercury inputs from activities upstream of the study area.

#### 3.2 Species-Specific Heavy Metal Accumulation in Fish

Analysis of muscle tissue revealed significant interspecies differences in metal accumulation patterns (Table 3, Fig. 2). *C. nigrodigitatus* exhibited significantly higher concentrations of cadmium (t = -4.648, p = 0.010) and chromium (t = -16.971, p < 0.001) compared to *C. gariepinus*. The difference was particularly pronounced for chromium, with *C. nigrodigitatus* containing approximately nine times higher concentrations ( $0.055 \pm 0.004$  mg/kg) than *C. gariepinus* ( $0.006 \pm 0.004$  mg/kg).

Metal	C. gariepinus	C. nigrodigitatus	t-value	p-value	FAO/WHO Limit
Pb	$0.007\pm0.012$	$0.104\pm0.089$	-1.846	0.139	0.3
Hg	$0.156\pm0.202$	$0.072\pm0.005$	0.713	0.515	0.5
As	$0.043\pm0.006$	$0.043\pm0.003$	0.164	0.878	0.1
Cd	$0.032\pm0.003$	$0.045\pm0.004$	-4.648	0.010*	0.05
Cr	$0.006\pm0.004$	$0.055\pm0.004$	-16.971	<0.001*	0.1

Table 3: Heavy metal concentrations (mg/kg wet weight) in muscle tissue of fish species from Amansea River

Values represent mean  $\pm$  SEM of nine replicates; \*indicates statistically significant difference (p < 0.05)

Though not statistically significant, notable differences were also observed for lead and mercury. *C. nigrodigitatus* contained substantially higher lead concentrations  $(0.104 \pm 0.089 \text{ mg/kg})$  compared to *C. gariepinus*  $(0.007 \pm 0.012 \text{ mg/kg})$ , while mercury showed the opposite pattern with higher concentrations in *C. gariepinus*  $(0.156 \pm 0.202 \text{ mg/kg})$  than in *C. nigrodigitatus*  $(0.072 \pm 0.005 \text{ mg/kg})$ . Arsenic concentrations were nearly identical between the two species (0.043 mg/kg).

When compared with FAO/WHO guidelines for maximum permissible limits in fish [27], all measured concentrations fell below the established thresholds. However, cadmium in *C. nigrodigitatus* (0.045 mg/kg) approached the guideline value (0.05 mg/kg), suggesting a need for continued monitoring. The calculation of Bioaccumulation Factors (BAFs) provided further insight into species-specific accumulation tendencies (Table 4, Fig. 3). *C. nigrodigitatus* demonstrated remarkably higher BAFs for lead (11.556) and chromium (2.200) compared to *C. gariepinus* (0.778 and 0.240, respectively). Conversely, *C. gariepinus* exhibited a higher BAF for mercury (0.447) compared to *C. nigrodigitatus* (0.206). Both species showed identical BAFs for arsenic (1.265), consistent with their equal tissue concentrations.

Table 4: Bioaccumulation Factors (L/kg) for C. gariepinus and C. nigrodigitatus from Amansea River

Metal (ppm)	BAF C. gariepinus	BAF C. nigrodigitatus	Ratio (C.n/C.g)
Pb	0.778	11.556	14.85
Hg	0.447	0.206	0.46
As	1.265	1.265	1.00
Cd	0.941	1.324	1.41
Cr	0.240	2.200	9.17

BAF: Bioaccumulation Factor; Ratio (C.n/C.g): Ratio of C. nigrodigitatus BAF to C. gariepinus BAF

These striking differences in bioaccumulation patterns likely reflect the distinct ecological characteristics of the two species. *C. nigrodigitatus* is predominantly a benthic feeder, consuming sediment-dwelling organisms and organic detritus in close association with bottom substrates [10]. This feeding strategy increases exposure to metals that preferentially accumulate in sediments and benthic invertebrates, including lead, cadmium, and

chromium [28,29]. The higher BAFs for these metals in *C. nigrodigitatus* align with this ecological niche. Conversely, *C. gariepinus* exhibits more varied feeding habits, consuming prey from multiple trophic levels including smaller fish, making it more susceptible to biomagnification processes [9]. This may explain its enhanced mercury accumulation, as methylmercury (the predominant form in fish tissue) efficiently biomagnifies through aquatic food webs [30,31]. Eagles-Smith et al. [30] similarly reported higher mercury levels in predatory fish compared to species at lower trophic positions across multiple aquatic ecosystems. Correlation analysis between water and fish tissue concentrations provided additional evidence of species-specific relationships with environmental metal levels. A strong and statistically significant positive correlation was observed between mercury concentrations in water and *C. gariepinus* tissues (r = 0.999, p = 0.030), while no such relationship was found for *C. nigrodigitatus* (r = 0.756, p = 0.454). This suggests that *C. gariepinus* mercury levels more directly reflect water column concentrations, potentially making it a more suitable bioindicator for aqueous mercury contamination. These findings are consistent with observations by Zhao et al. [32], who demonstrated that feeding strategy and habitat use were strong predictors of metal concentrations in fish tissues, and with Liu et al. [33], who reported significant interspecies differences in metal accumulation related to ecological characteristics. The contrasting accumulation patterns observed between these commercially important species emphasize the need for species-specific approaches in both biomonitoring programs and human health risk assessments.

#### 3.3 Human Health Risk Assessment

Cr

TTHO

8.36E-05

To evaluate potential health implications for consumers, Target Hazard Quotients (THQs) were calculated for each metal based on average concentrations in fish muscle tissue (Table 5). Mercury was the only metal with a THQ exceeding unity (1.063), indicating a potential health risk associated with regular consumption of fish from the Amansea River. The Total Target Hazard Quotient (TTHQ), representing cumulative non-carcinogenic risk from all metals, was 1.640, further suggesting potential health concerns from combined metal exposure.

Metal	EDI (mg/kg/day)	RfD (mg/kg/day)	ТНQ	Risk Level	
Pb	1.54E-04	3.50E-03	0.044	Low	
Hg	3.19E-04	3.00E-04	1.063	Elevated	
As	1.19E-04	3.00E-04	0.397	Low	
Cd	1.08E-04	1.00E-03	0.108	Low	

3.00E-03

Table 5: Estimated Daily Intake (EDI) and Target Hazard Quotient (THQ) for heavy metals through fish consumption

EDI: Estimated Daily Intake; RfD: Reference Dose; THQ: Target Hazard Quotient; TTHQ: Total Target Hazard Quotient

Species-specific THQ calculations (Table 6) revealed distinct risk profiles between the two fish species. The THQ for mercury was substantially higher for *C. gariepinus* (1.733) compared to *C. nigrodigitatus* (0.800), reflecting the higher mercury concentrations observed in *C. gariepinus*. Conversely, *C. nigrodigitatus* showed higher THQ values for lead (0.099 vs. 0.007), cadmium (0.150 vs. 0.107), and chromium (0.061 vs. 0.007). The Total THQ was elevated for both species, with values of 2.332 for *C. gariepinus* and 1.588 for *C. nigrodigitatus*.

0.028

1.640

Low

Elevated

Table 6: S	pecies-specifi	c Target Hazard	Ouotient	(THO) for heavy	v metals through f	fish consumption
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Metal	THQ C. gariepinus	THQ C. nigrodigitatus
Pb	0.007	0.099
Hg	1.733	0.800
As	0.478	0.478
Cd	0.107	0.150
Cr	0.007	0.061
ТТНQ	2.332	1.588

THQ: Target Hazard Quotient; TTHQ: Total Target Hazard Quotient

These findings indicate that frequent consumption of these fish species, particularly *C. gariepinus*, could potentially result in mercury exposure exceeding recommended safety thresholds. Mercury is a well-documented neurotoxicant, with developing fetuses and young children especially vulnerable to its effects [34]. Even low-level chronic exposure has been associated with developmental delays, cognitive impairment, and cardiovascular effects [35].

The observed differential risk profiles between the two species underscore the importance of developing species-specific consumption advisories. For populations dependent on these fisheries resources, selective consumption practices could meaningfully reduce exposure risks. For instance,

preferential consumption of *C. nigrodigitatus* over *C. gariepinus* could reduce mercury exposure, though this should be balanced against the relatively higher levels of other metals in *C. nigrodigitatus*.

These results align with research by Chen et al. [36], who similarly found that species-specific consumption guidelines were more effective at reducing exposure risks than general advisories. The need for targeted advisories is particularly relevant in this context, where both fish species represent important dietary protein sources for local communities.

## 4. CONCLUSION

This comparative assessment of heavy metal accumulation in *C. gariepinus* and *C. nigrodigitatus* from the Amansea River revealed significant speciesspecific differences that have important implications for environmental monitoring and public health protection. Key findings include:

- 1. *C. nigrodigitatus* exhibited significantly higher concentrations of cadmium and chromium compared to *C. gariepinus*, with Bioaccumulation Factors for lead and chromium 14.85 and 9.17 times higher, respectively, than those observed in *C. gariepinus*.
- 2. C. gariepinus demonstrated greater mercury accumulation capacity, with mercury concentrations more directly correlated with water concentrations, suggesting its potential utility as a bioindicator for aqueous mercury contamination.
- 3. Human health risk assessment identified mercury as a contaminant of concern, with a Target Hazard Quotient exceeding unity (1.063) and species-specific THQ values of 1.733 for *C. gariepinus* and 0.800 for *C. nigrodigitatus*.
- 4. The observed interspecies differences in accumulation patterns likely reflect distinct ecological characteristics, with the benthic-feeding C. nigrodigitatus accumulating sediment-associated metals, while the more predatory C. gariepinus showed enhanced mercury bioaccumulation potentially linked to biomagnification processes.

These findings emphasize the importance of species-specific approaches in both biomonitoring programs and human health risk assessments. Singlespecies monitoring may inadequately characterize overall ecosystem contamination, while general consumption advisories may fail to address speciesspecific risk profiles. We recommend:

- 1. Implementing targeted monitoring programs that incorporate multiple fish species representing different ecological niches and feeding strategies.
- 2. Developing species-specific consumption advisories that reflect the differential accumulation patterns observed, potentially limiting consumption of *C. gariepinus* to reduce mercury exposure.
- 3. Establishing continuous monitoring of water quality parameters and metal concentrations in the Amansea River, with particular attention to mercury levels that substantially exceed regulatory guidelines.

Future research should investigate seasonal variations in metal accumulation patterns, tissue-specific distribution of metals within each species, and the influence of fish size and age on bioaccumulation processes. Additional studies examining metal speciation and transformation processes would further enhance understanding of the complex dynamics of metal cycling in this tropical freshwater ecosystem.

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#### CONFLICT OF INTEREST

The authors declared that there is no conflict of interest.

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