


Ecological Risk Assessment of Heavy Metals in Some Commercially Important Fish Species from River Asse in the Niger Delta Area of Nigeria

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Abstract

*The heavy metal content in freshwater fishes in Nigeria has received a lot of attention in recent years, owing to the potential health impacts of such metals in man. The paucity of ecotoxicological data on the heavy metal status in fish from River Asse in the Niger Delta area of Nigeria warranted this research. The objective of the research was principally to carry out an ecological risk assessment of cadmium (Cd), copper (Cu), zinc (Zn) and lead (Pb) in some commercially important fish species from River Asse. The research was achieved via Atomic Adsorption Spectrometric technique. The summary statistics for mean heavy metal concentrations (mg/kg) in fish species from River Asse ranged from 0.23 (Cd) in *Synodontis eupterus* to 32.25 (Zn) in *Oreochromis niloticus* while the summary statistics for mean heavy metal concentrations (mg/kg) in fish species according to stations ranged from 0.21 for Cd in *S. eupterus* at station 1 (Upstream) to 34.09 for Zn in *O. niloticus* at station 3 (Downstream) with significant differences ($p < 0.05$) in the mean concentrations of Cd, Cu, Zn and Pb in fish species between stations. The hazard quotient (HQ) values ranged from 0.2 (Cu) in *S. eupterus* to 10.60 (Cd) in *O. niloticus* while the estimated daily intake (EDI) values (mg/person/day) for heavy metals ranged from 0.00011 (Cd) in *S. eupterus* to 0.02 (Zn) in *O. niloticus*. Overall, the fish species were found unsuitable for human consumption owing principally to excess concentrations of Cd and Pb. It was recommended that the river be regularly monitored along with public awareness aimed at protecting the natural resource of the river and safe guarding human health in the long run.*

Keywords: Fish, Heavy metals, Hazard quotient, Estimated daily intake

1. Introduction

Heavy metals in freshwater fishes in Nigeria has received a lot of attention in recent years, owing to their long-term and often irreversible adverse effects on human health (Wangboje *et al.*, 2018). In addition, studies around the world have uncovered vital information about the presence of heavy metals in food including fish and vegetables and their increasing risk to human health (Chowdhury *et al.*, 2024). Heavy metals, so called owing to their peculiar atomic weight and densities, enter the aquatic environment mainly from industrial and agricultural discharges and subsequently become deleterious to living aquatic resources while impairing the quality of water (Sumit *et al.*, 2021). Heavy metals are well known for their ecotoxicological effects and given the high consumption of fish in several parts of the world due to their medicinal and nutritional benefits, it becomes absolutely necessary to identify potential toxicities associated with these metals especially in edible fish parts (Zamboli *et al.*, 2023). Owing to the continued menace of heavy metals on aquatic ecosystems, research to produce simple and eco-friendly approaches to their control and mitigation in environmental matrices, is ongoing such as the recent production of silver nanoparticles (AgNPs) for the removal of heavy metals such as iron (Fe), zinc (Zn), manganese (Mn) and copper (Cu) from organically rich effluents (El-Shehawey *et al.*, 2023). Elsewhere, it has been suggested

that a hybrid approach to the removal of heavy metals from polluted aquatic environments be adopted to include both conventional and modern technologies (Vrinda *et al.*, 2023).

2. Related Works

The trophic transfer and biomagnification potential of heavy metals has been investigated and observed to be influenced by the tissue and metabolism of an organism as well as the overall length of the food chain (Saidon *et al.*, 2024). Both processes of bioaccumulation and biomagnification of heavy metals in food chains have been observed to have serious consequences for fish and human health as greater levels of both may imply a higher level of risk emanating from heavy metals (Khan *et al.*, 2023). The intake of heavy metals by man via food has been observed to be influenced by his dietary habits and that chronic elemental exposure may manifest negative impacts on his health status (Sree *et al.*, 2023). Sener *et al.*, (2023) observed that apart from fish, water and sediment can also be appraised for heavy metals in order to ascertain the anthropogenic impact of such metals and to reveal the quality of sediment which serve as a bank for heavy metals (Sener *et al.*, 2023). Silva *et al.*, (2023) suggested that an effective strategy for assessing the presence of heavy metals in rivers could involve bioaccumulation studies which should encompass both field and laboratory work.

2.1 Theoretical Review

Literature search on River Asse, in the Niger Delta area of Nigeria, shows that research by Ushurhe and Ohwohere-Asuma (2013), investigated the quality of water from the river with a view to assessing its suitability for irrigation purposes. However, there is paucity of ecotoxicological information on the heavy metal content in commercially important fish species from this river which this research sought to provide thereby filling an existing gap in knowledge. The target fish species were *Oreochromis niloticus* Linnaeus 1758, *Heterotis niloticus* Cuvier 1829 and *Synodontis eupterus* Boulenger 1901, as they are usually present in the catch at landing sites of the river and are of commercial appeal. The heavy metals quantified were cadmium (Cd), copper (Cu), zinc (Zn) and lead (Pb). Cadmium and Pb are non-essential elements that have carcinogenic properties and are therefore not desirable in food including fish meant for human consumption (Genchi *et al.*, 2020). Copper and Zn on the flipside, are essential elements needed by the human body for a variety of metabolic and enzymatic roles but can easily become toxic when recommended levels are surpassed (Karim, 2018). Results from this research are expected to produce data on the heavy metal content in the aforesaid fish species with the ultimate view of protecting the health of potential consumers.

3. Materials and Methods

3.1 Description of the study area

The research was carried out along a stretch of River Asse (Figure 1) with GPS co-ordinates of Latitude 5°25'55.0"N and Longitude 6°21'02.3"E. It is a popular river that flows through Isoko South Local Government Area of Delta State, Nigeria. The river is approximately 292 km in length and is a tributary of the Forcados River, in the Niger Delta region of Southern Nigeria. Three sampling stations were established based on the level of human activities, accessibility and the nature of mixed effluents reaching the river. A brief description of the stations is given below.

Station 1 (Upstream):

The GPS location for this station is Latitude 5°25'30.6"N and Longitude 6°20'41.9"E. Observable human activities at this point include fishing, laundry, bathing, swimming and dredging.

Station 2 (Midstream):

The GPS location for this station is Latitude 5°25'53.7"N and Longitude 6°20'56.2"E. Observable human activities at this point include the operation of cassava processing mills and an abattoir. It is about a kilometer from station 1.

Station 3 (Downstream):

The GPS location for this station is Latitude 5°26'02.9"N and Longitude 6°21'09.4"E. Observable human activities at this point include laundry, fishing, swimming and the operation of boats. It is located about 1.5 kilometers from the midstream station.

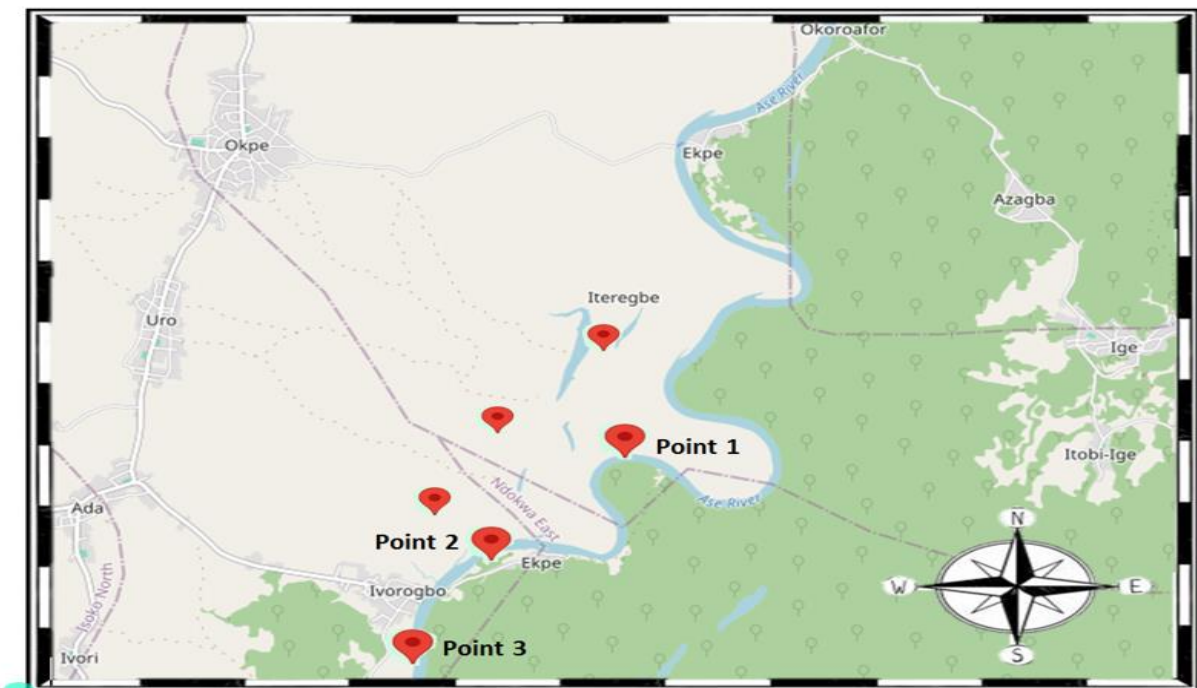


Figure 1: Map of the River Asse showing the specific sampling stations

3.2 Collection of Bioindicators

Fifteen (15) samples each of three commercially important fish species namely, Nile Tilapia (*Oreochromis niloticus*, mean total length 22.96 ± 2.71 cm, mean weight 586.25 ± 2.62 g), Bony tongue (*Heterotis niloticus*, mean total length 30.26 ± 1.62 cm, mean weight 945.35 ± 1.96 g), and Upsidedown catfish (*Synodontis eupterus*, mean total length 26.77 ± 0.98 cm, mean weight 731.26 ± 1.78 g), were netted with the assistance of artisanal fishermen between January and May, 2024. The identities of fish samples were verified *in-situ* using a key (Idodo-Umeh, 2003) and a field guide (Olaosebikan and Raji, 2013). The total lengths (cm) of fish samples were measured with a calibrated wooden board while their respective weights (g) were determined using a battery-powered compact electronic scale (A & D®, EK-AEP series). The fish samples were placed in labeled polythene bags and conveyed to the laboratory within 24 hours in a Thermolineo® ice chest for further studies.

3.3 Ex-situ Work and Laboratory Assay

The muscle tissue was excised with a stainless-steel dissecting lancet from the flanks of fish specimens, while working on a wooden board. Excised tissue was dried with a Uniscope® SM 9023 Laboratory oven (Surgifield® Medicals, England) to a constant weight, at a temperature of 80°C. This was followed by milling using a porcelain mortar and pestle. The milled product was stored in airtight plastic vials prior to digestion. The mixed acid digestion method using 65 % Nitric acid and 37 % Hydrochloric acid was applied as described and detailed by Mohammed *et al.*, (2017). The digested samples were diluted with 20 ml of distilled water and then filtered to remove undigested materials with a Whatman® filter paper (#42). Blanks were prepared using the same quantity of mixed acids but without the samples. All reagents used were of analytical grade (BDH, Poole, England). Digested samples were analyzed for cadmium (Cd), copper (Cu), zinc (Zn) and lead (Pb), using an Atomic Absorption Spectrophotometer (UNICAM® 969 Series, Belgium) equipped with solar software using air acetylene flame as an oxidant. The concentrations of heavy metals were expressed in mg/kg.

3.4 Determination of Hazard Quotient (HQ) for Heavy Metals

The hazard quotient (HQ) expresses the possibility of a contaminant being an ecological risk or a contaminant of potential ecological concern (Purchase 2000). The HQ is expressed as:

$$HQ = \frac{\text{Measured concentration of contaminant}}{\text{Toxicity reference value or selected screening benchmark}}, \tag{1}$$

where $HQ \geq 1$ = Implies possibility of ecological risk indicated or a contaminant of potential ecological concern (COPEC).

3.5 Determination of Estimated Annual Intake (EAI) and Estimated Daily Intake (EDI) for Heavy Metals

The EAI (*mg/person/year*) is expressed as:

$$EAI = \frac{\text{Concentration of heavy metals in fish} \times \text{per capital figure}}{\text{Adult body weight (Assumed to be 70kg)}}, \tag{2}$$

where: Per capital figure is 13.3 kg/person/year for Nigeria (World Fish Center, 2023).

The EDI is expressed as:

$$EDI (mg/person/day) = \frac{EAI}{365 \text{ days}}. \tag{3}$$

3.6 Determination of Total Toxicity of Mixtures (TTM) Index for Heavy Metals

Whether or not a mixture of heavy metals in a particular medium exceeds the quality guideline value for the medium, can be determined by applying the TTM index (ANZECC/ARMCAN, 2000). The TTM index is given by

$$TTM = \sum \frac{CI}{GVI}, \tag{4}$$

where *CI* = Concentration of the ‘ith’ component of mixture; *GVI* = Guideline value for the “ith” component; $TTM > 1$, it implies the mixture has exceeded the guideline value.

3.7 Determination of Condition Factor for Fish

The condition factor expresses the fatness, wellbeing, and relative robustness of fish. It is believed that a heavier fish of a given length is in better condition than a lighter fish of the same length (Nikolsky, 1963).

$$\text{Condition factor} = 100 \times W/L^3, \tag{5}$$

where W = Weight of fish (g) and L = Total length of fish (cm).

3.8 Statistical Analysis

Data obtained from the study were analyzed using GENSTAT computer software (Version 12.1 for windows). One-way Analysis of Variance (ANOVA) was used to test for significant differences ($p < 0.05$) between mean values of heavy metals while the Duncan Multiple Range Test (DMRT), was used for separating significant means. Microsoft Excel (for Windows 2010), was used for all graphical features.

4. Results

The summary statistics for mean heavy metal concentrations (mg/kg) in fish species from River Asse ranged from 0.23 (Cd) in *S. eupterus* to 32.25 (Zn) in *O. niloticus* as shown in Table 1 while the typical heavy metal profile (mg/kg) in fish species ranged from 0.36 (Cd) to 23.83 (Zn) as presented in Figure 2. The summary statistics for mean heavy metal concentrations (mg/kg) in fish species from River Asse according to stations ranged from 0.21 for Cd in *S. eupterus* at station 1 (Upstream) to 34.09 for Zn in *O. niloticus* at station 3 (Downstream) with significant differences ($p < 0.05$) in the mean concentrations of Cd, Cu, Zn and Pb in fish species between stations (Table 2). The hazard quotient (HQ) values ranged from 0.2 (Cu) in *S. eupterus* to 10.60 (Cd) in *O. niloticus* as shown in Figure 3. The estimated annual intake (EAI) values for heavy metals in mg/person/year, ranged from 0.04 for Cd in *S. eupterus* to 6.12 for Zn in *O. niloticus* (Figure 4) while the estimated daily intake (EDI) values for heavy metals in mg/person/day, ranged from 0.00011 for Cd in *S. eupterus* to 0.02 for Zn in *O. niloticus* (Figure 5). The total toxicity of mixtures (TTM) values ranged from 7.28 in *S. eupterus* to 19.57 in *O. niloticus* (Figure 6) while the spatial total (mg/kg) for heavy metals ranged from 24.33 for *S. eupterus* at station 3 (Downstream) to 46.22 for *O. niloticus* also at station 3(Downstream) as shown in Figure 7. The typical percent (%) quota for heavy metals in fish species ranged from 1.07 % for Cd to 71.35 % for Zn as shown in Figure 8 while the condition factor values ranged from 3.41 for *H. niloticus* to 4.84 for *O. niloticus* as presented in Figure 9.

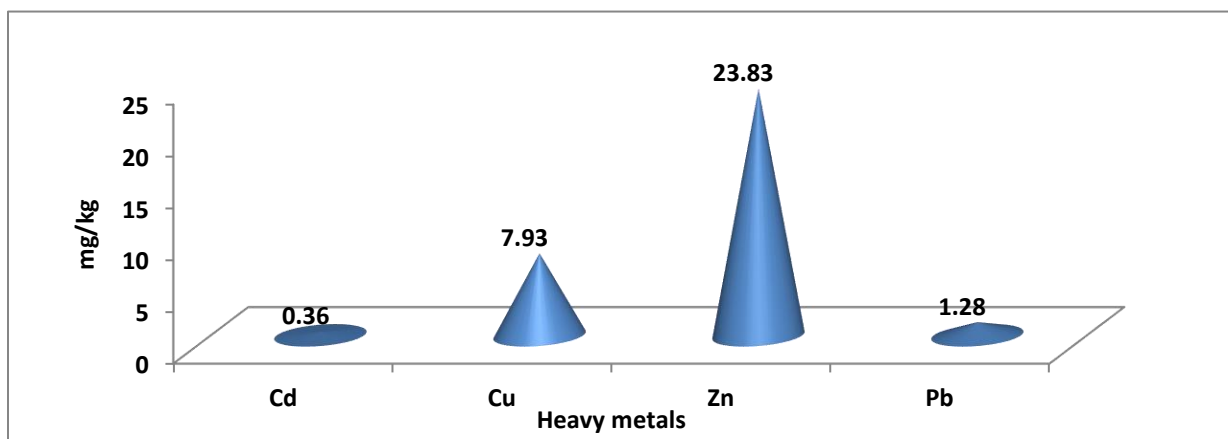


Figure 2: Typical heavy metal profile (mg/kg) in fish from River Asse

Table 1: Summary statistics for mean heavy metal concentrations (mg/kg) in *Oreochromis niloticus*, *Heterotis niloticus* and *Synodontis eupterus* from River Asse

Heavy metal	Fish species	Mean (mg/kg)	Minimum (mg/kg)	Maximum (mg/kg)	Threshold (mg/kg)
Cd	<i>O. niloticus</i>	0.52	0.50	0.59	0.05**
	<i>H. niloticus</i>	0.35	0.30	0.40	0.05**
	<i>S. eupterus</i>	0.23	0.20	0.25	0.05**
Cu	<i>O. niloticus</i>	9.78	8.50	10.33	30*
	<i>H. niloticus</i>	8.05	7.80	8.20	30*
	<i>S. eupterus</i>	5.96	5.80	6.20	30*
Zn	<i>O. niloticus</i>	32.25	30.10	34.10	40*
	<i>H. niloticus</i>	21.32	20.08	22.40	40*
	<i>S. eupterus</i>	17.92	17.50	18.20	40*
Pb	<i>O. niloticus</i>	2.35	1.96	2.95	0.30**
	<i>H. niloticus</i>	0.83	0.78	0.85	0.30**
	<i>S. eupterus</i>	0.67	0.60	0.71	0.30**

Note: * FAO (1983); ** CODEX Alimentarius (2015) and Commission Regulation (2023).

Table 2: Summary statistics for heavy metals (mg/kg) in *Oreochromis niloticus*, *Heterotis niloticus* and *Synodontis eupterus* from River Asse according to stations

Stations	Fish species	Heavy metals (mg/kg)			
		Cd	Cu	Zn	Pb
Upstream	<i>O. niloticus</i>	0.53 ± 0.005 ^a	10.24 ± 0.122 ^a	32.40 ± 0.015 ^a	2.16 ± 0.025 ^a
	<i>H. niloticus</i>	0.34 ± 0.013 ^b	8.20 ± 0.008 ^b	22.36 ± 0.047 ^b	0.81 ± 0.015 ^b
	<i>S. eupterus</i>	0.21 ± 0.021 ^c	6.18 ± 0.023 ^b	18.16 ± 0.067 ^b	0.63 ± 0.21 ^b
Midstream	<i>O. niloticus</i>	0.50 ± 0.0057 ^a	10.02 ± 0.06 ^a	30.23 ± 0.142 ^a	1.98 ± 0.03 ^a
	<i>H. niloticus</i>	0.30 ± 0.006 ^b	8.10 ± 0.021 ^a	21.50 ± 0.03 ^b	0.79 ± 0.025 ^b
	<i>S. eupterus</i>	0.22 ± 0.01 ^c	5.90 ± 0.187 ^b	17.96 ± 0.12 ^b	0.60 ± 0.015 ^b
Down stream	<i>O. niloticus</i>	0.56 ± 0.051 ^a	8.77 ± 0.336 ^a	34.09 ± 0.021 ^a	2.90 ± 0.096 ^c
	<i>H. niloticus</i>	0.40 ± 0.007 ^b	7.80 ± 0.451 ^a	20.09 ± 0.051 ^b	0.84 ± 0.025 ^a
	<i>S. eupterus</i>	0.24 ± 0.005 ^c	5.83 ± 0.057 ^b	17.56 ± 0.067 ^b	0.70 ± 0.035 ^a
Threshold		0.05	30	40	0.30

Means with the same superscripts are not significantly different (p > 0.05). Vertical comparison only.

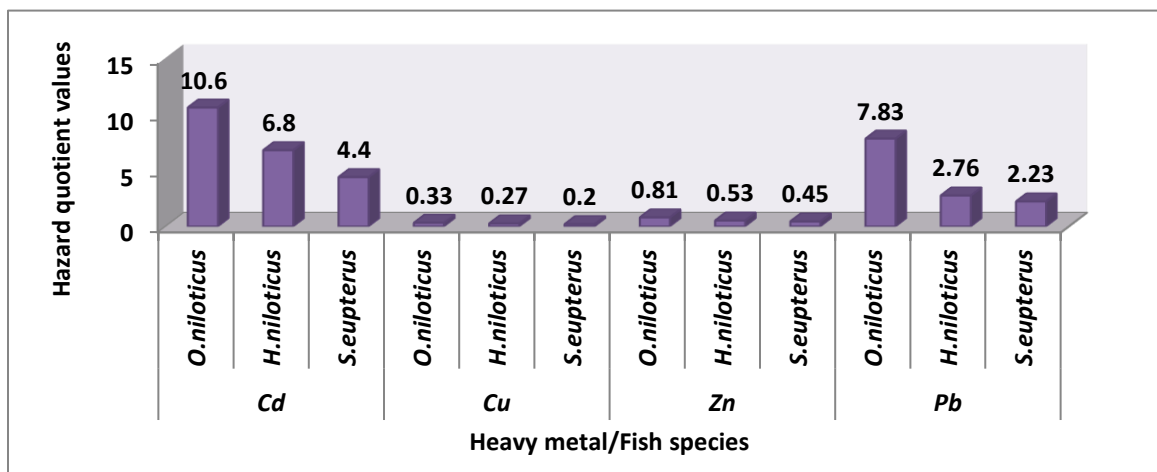


Figure 3: Hazard quotient (HQ) values for heavy metals in fish species from River Asse

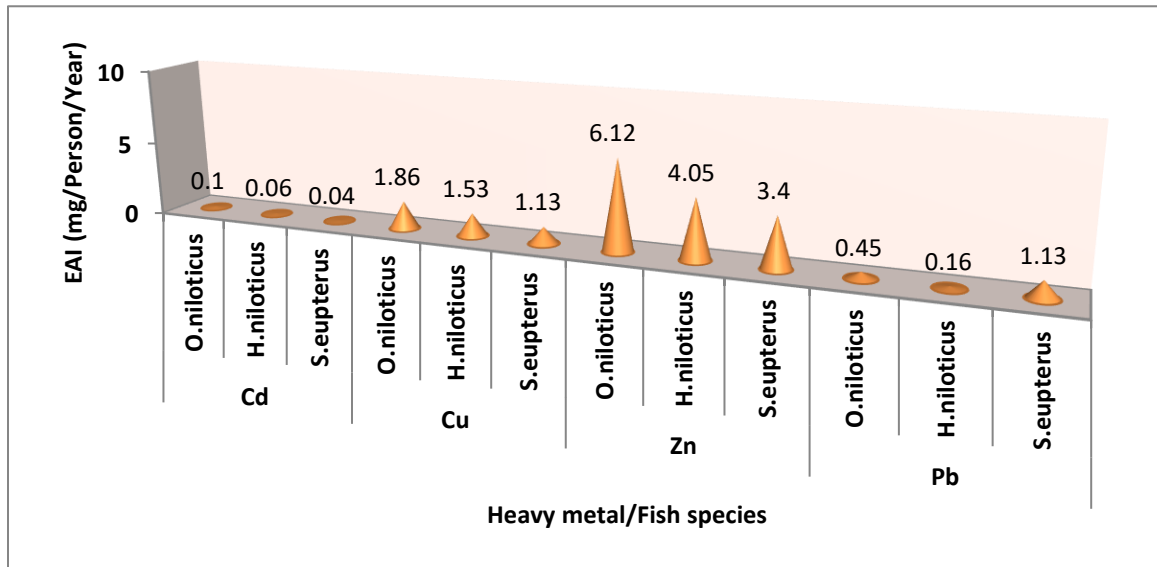


Figure 4: Estimated annual intake (EAI) values for heavy metals from fish species

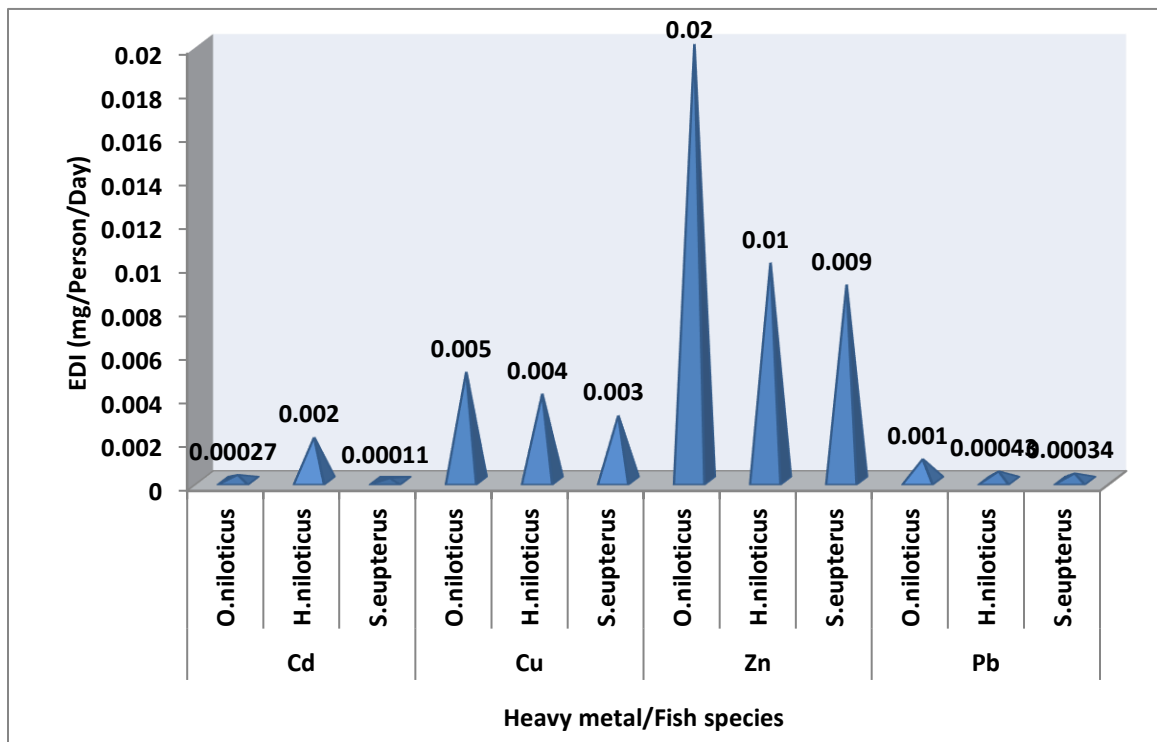


Figure 5: Estimated daily intake (EDI) values for heavy metals from fish species

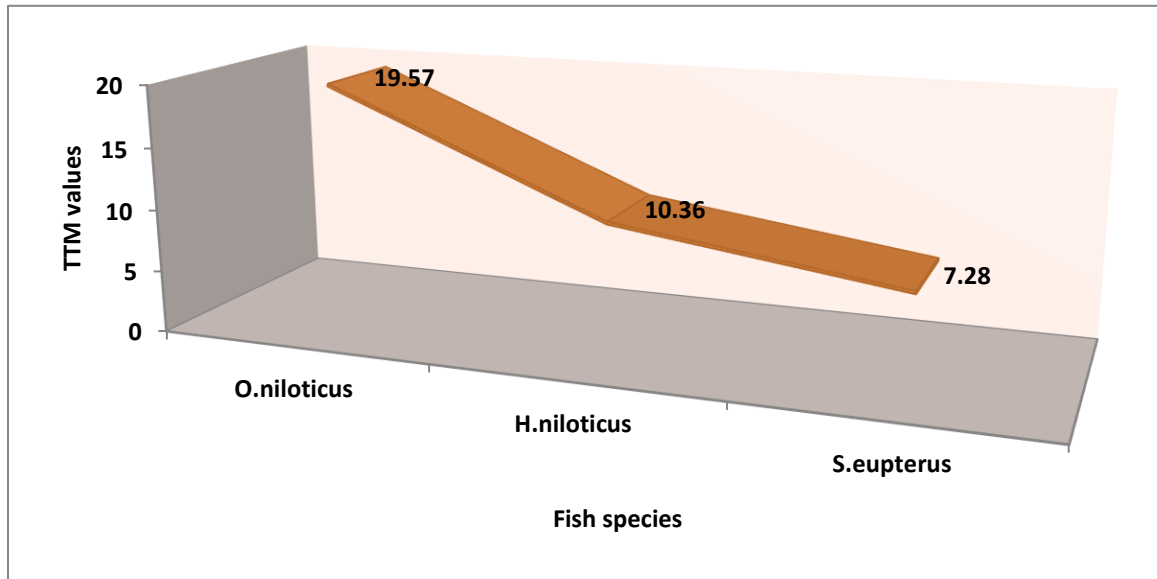


Figure 6: Total toxicity of mixtures (TTM) values for heavy metals in fish species from River Asse

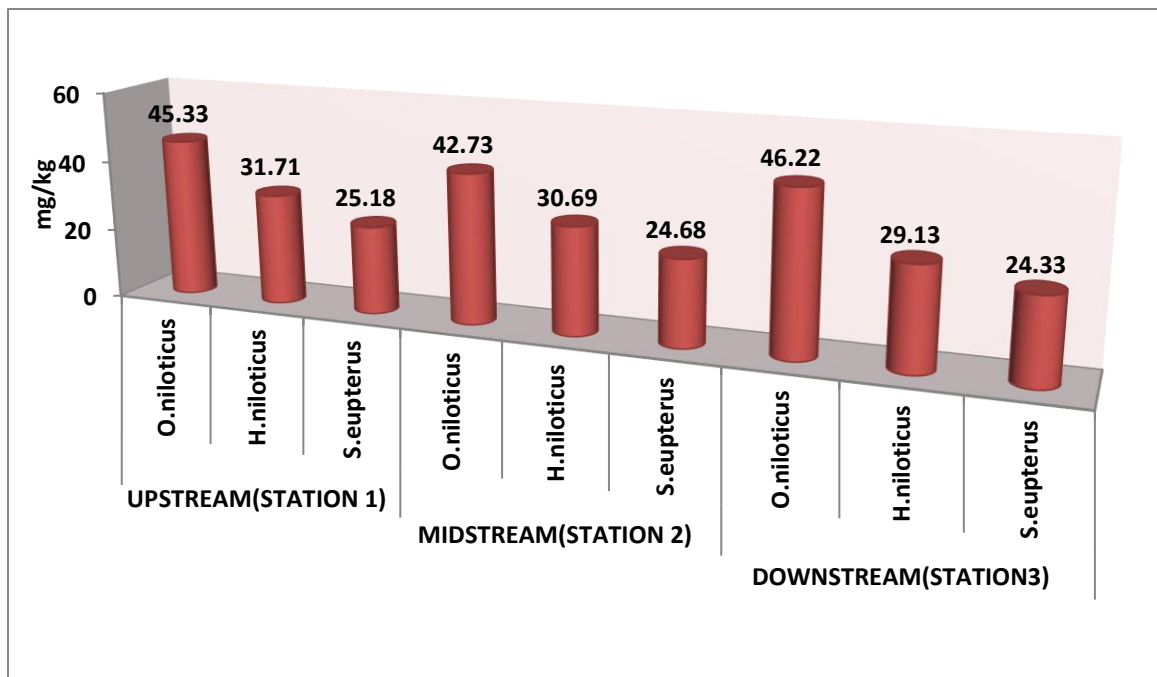


Figure 7: Spatial total values (mg/kg) for heavy metals in fish species from River Asse

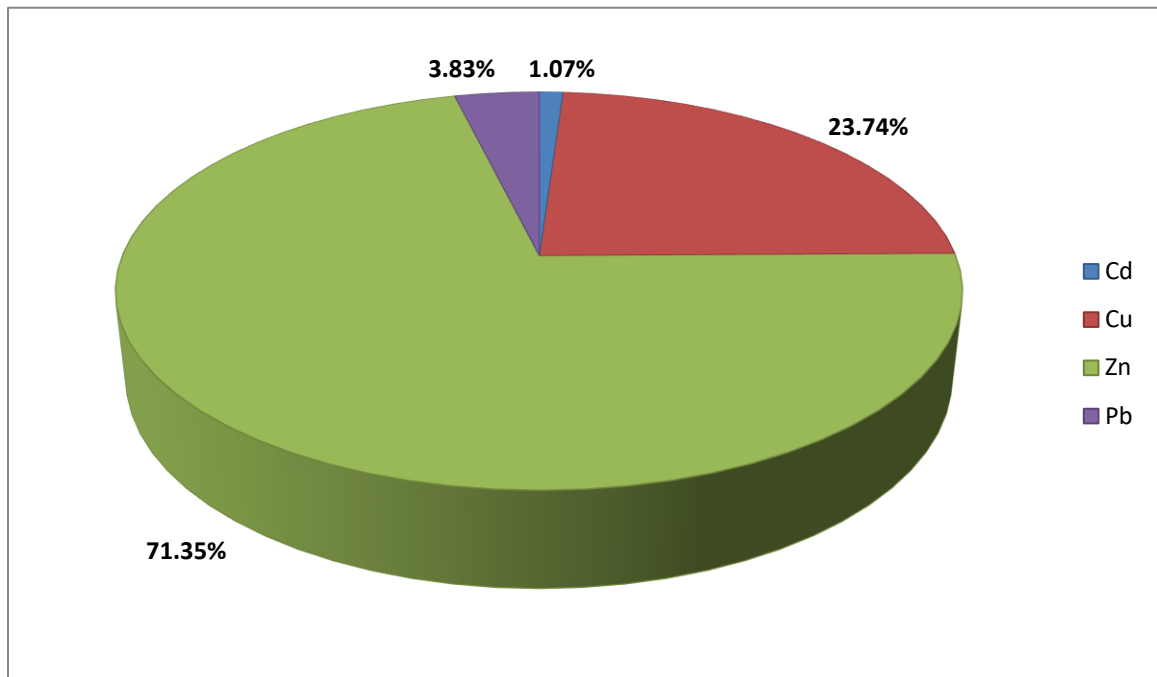


Figure 8: Typical percent (%) quota of heavy metals in fish species from River Asse

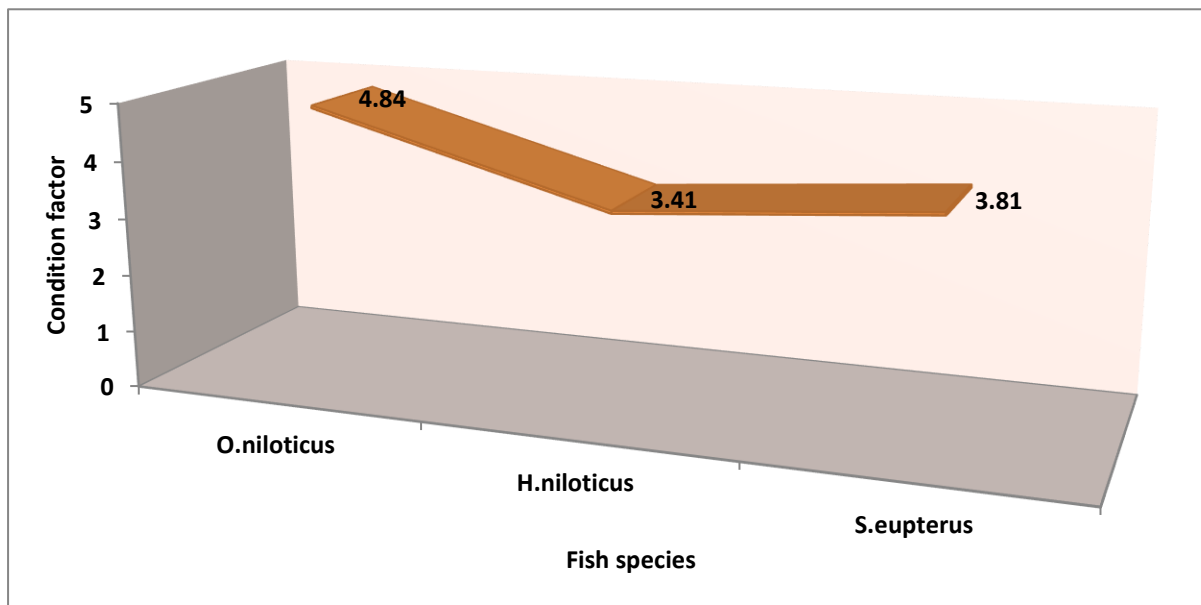


Figure 9: Condition factor values for fish species from River Asse

Table 3: Comparison of mean heavy metal levels (mg/kg) in fish species from River Asse to some selected studies

Fish species	Cd	Cu	Zn	Pb	Location	Reference
<i>Oreochromis niloticus</i>	0.52	9.78	32.25	2.35	RA, Nigeria	This study
<i>Heterotis niloticus</i>	0.35	8.05	21.32	0.83	RA, Nigeria	This study
<i>Synodontis eupterus</i>	0.23	5.96	17.92	0.67	RA, Nigeria	This study
<i>Hemichromis fasciatus</i>	0.25	0.86	128.87	0.05	RN, Nigeria	Wangboje and Ikhuabe (2015)
<i>Chrysichthys nigrodigitatus</i>	ND	ND	29.81	0.01	LL, Nigeria	Ukwa <i>et al.</i> , (2015)
<i>Clarias gariepinus</i>	0.05	4.27	6.04	0.17	ER, Nigeria	Membere and Abdulwasiu (2020)
<i>Oreochromis niloticus</i>	0.01	0.04	ND	ND	DKD, Nigeria	Ezekiel <i>et al.</i> , (2019)
<i>Heterotis niloticus</i>	0.39	0.15	10.18	7.12	LG, Nigeria	Bawuro <i>et al.</i> , (2018)
<i>Channa punctatus</i>	ND	0.01	0.01	ND	CR1, Pakistan	Ilyas <i>et al.</i> , (2023)
<i>Pterygoplichthys pardalis</i>	0.83	ND	ND	5.47	CR2, Indonesia	Yulyana <i>et al.</i> , (2023)
<i>Oreochromis niloticus</i>	ND	296.05	77.70	ND	YR, India	Khan <i>et al.</i> , (2020)
<i>Labeobarbus intermedius</i>	0.06	2.05	ND	ND	BR, Ethiopia	Mohammed <i>et al.</i> , (2023)

Note: ND - Not determined; RA –River Asse; RN -River Niger; LL-Lekki Lagoon; ER – Escravos River; DKD - Dadin Kowa Dam; LG - Lake Geriyo; CR1 - Chenab River; CR 2 - Ciliwung River; YR - Yamuna River; BR - Borkena River.

5. Discussion

The heavy metal profile in fish species in this research generally took the order Zn > Cu > Pb > Cd with Zn clearly dominating the profile with a typical quota of 71.35%. This observation is an indication that Zn was conceivably more available to fish in its ambient medium thus giving rise to a higher bioaccumulation potential of the metal. Rajagopal *et al.*, (2024), recognized that bioaccumulation of heavy metals by fish can occur when such metals are bioavailable for subsequent uptake. It was observed that the mean concentrations of heavy metals in fish between stations were significantly different ($p < 0.05$) which gives an indication that the influx of metals into the river varied from station to station during the course of the research. The hazard quotient (HQ) values were above unity for Cd and Pb in all the fish species giving a clear indication of potential risk to consumers of these fish species. Cadmium and Pb are thus the contaminants of potential ecological concern (COPEC) as corroborated by Purchase (2000). These two heavy metals are very toxic and have been described as cumulative poisons in the human body (Ali *et al.*, 2019). The estimated annual intake (EAI) and estimated daily intake (EDI) values for pollutants simply provide estimated intake figures on an annual and daily basis respectively assuming that the screened food items were to be consumed by man (Sherman *et al.*, 2024). In this case, the EAI and EDI values were the least for Cd and the highest for Zn owing to the fact that the mean concentrations of Cd in fish were the least while on the other hand the mean concentrations of Zn in fish were the highest in this research. It thus means that consumers of such fish would be exposed to more of Zn in their diet when compared side by side to the other heavy metals. The total toxicity of mixtures (TTM) values were all above unity signifying that the mixture had exceeded stipulated guideline values.

This observation was buttressed by the fact that the mean concentrations of Cd and Pb in the fish species were all above international threshold levels for heavy metals in fish. The thresholds applied in this research were published by the Food and Agriculture Organization of the United Nations (FAO, 1983), CODEX Alimentarius (2015) and Commission Regulation (2023). The CODEX Alimentarius contains thresholds for heavy metals and a host of other contaminants in food as jointly published by the FAO and World Health Organization (WHO) while the Commission Regulation is published by the European Union. The typical level of Cd in fish was approximately seven times above the threshold of 0.05 mg/kg while the typical level of Pb in fish was approximately four times over the threshold of 0.30 mg/kg clearly indicating that such fish is unsuitable for human consumption. To drive home the seriousness of this finding, documented adverse effects of Cd in man include lung cancer, damage to the kidneys and bone demineralization (Bernard, 2008) while the reported adverse effects of Pb include carcinogenicity, genotoxic effects, impairment of children's brain development and damage to the central nervous system (Yang, 2023). The spatial total values (mg/kg) for heavy metals revealed that the station 3 (Downstream) had the highest value indicating that fish at this station are expected to have more anthropogenic impact with regard to heavy metals when compared directly to the other stations. The condition factor (CF) values for the respective fish species were all above unity with a rank profile of *O. niloticus* > *S. eupterus* > *H. niloticus*. Clearly, all the fishes were well conditioned in their ambient environment probably due to the availability and abundance of suitable prey. It is pertinent to note that the robust nature of these fishes as confirmed by the CF values may make them attractive to prospective consumers who are unwary of the harmful levels of Cd and Pb contained in these fishes thus compounding the worrisome problem already at hand. The mean heavy metal levels in fish observed in this research compared well to the findings from some selected studies as presented in Table 3. The contaminated status of these fishes is clearly connected to the influx of effluents into the river from a combination of point and non-point sources which if not mitigated may worsen the scenario uncovered in this research.

6. Conclusion

The research successfully presented the heavy metal (Cd, Cu, Zn and Pb) profile in three commercially important fish species (*O. niloticus*, *H. niloticus* and *S. eupterus*) from River Asse in the Niger Delta region of Nigeria. The ecological risk indices revealed that Cd and Pb were the metals of immediate ecological concern while the mean concentrations of these metals in fish (typically 0.36 mg/kg and 1.28 mg/kg respectively) exceeded international thresholds thus posing such fish species as unsuitable for human consumption. It therefore becomes pertinent for River Asse to be regularly monitored for heavy metals along with the commencement and sustenance of a robust public awareness campaign aimed at protecting the natural resource of the river and safe guarding human health in the long run.

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