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Health Risk Assessment of Heavy Metals in Fish Samples Obtained along River Benue and IBI Trough

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Abstract:

The aquatic ecosystems are being contaminated by harmful chemicals materials most of which include heavy metals. The source of contamination is either from wastewater discharged from urban, industrial, and agricultural facilities. Contaminated water contains hazardous amounts of chemicals causing deleterious impacts on marine life and humans. This research work focus on the environmental and health risk associated with heavy metals in fish from both river Benue (Makurdi) and river Ibi. The analysis of heavy metals in fish samples obtained from both river Ibi and river Makurdi as presented in Table 14 revealed the presence of the following heavy metals; Mn, Fe, Zn, Cu, Pb, Cd, Co, Cr, As, and Hg. Result for Makurdi revealed the heavy metal concentration varies from 99.370 to 0.001ppm with Zn and As having the highest lowest concentrations respectively while result of Ibi revealed that the concentration of the heavy metals varies between 70.780 to 0.002ppm with Fe and Pb having the highest and lowest concentrations respectively. analysis for the Bioaccumulation Factor of heavy metals in fish samples obtained at both river Ibi and river Benue (Makurdi) sampling locations is presented in Table 4.23. For fish samples obtained from river Benue (Makurdi), the Bioaccumulation Factor ranges between 5.035 to 0.029 with Zn and Cd having the highest and lowest Bioaccumulation factors respectively. on the other hand, the Bioaccumulation Factor for fish samples obtained from river Ibi ranges between 2.965 to 0.000 with Zn and As having the highest and lowest Bioaccumulation Factors respectively. Result analysis for Hazard Quotient (HQ) and Hazard Index (HI) associated with the consumption of heavy metal contaminated fish from both river Ibi and river Benue (Makurdi) evaluated in both adult and children is presented in Table 4.24. HQ evaluated in adult from fish samples collected at the river Benue sampling location ranges between 0.4543 to 0.0002 with Cu and As having the highest and lowest HQ values respectively while that in children ranges between 1.3629 to 0.0005 with Cu and As having the highest and lowest HQ's respectively. the HI values for fish samples in river Makurdi are 1.0317 and 3.0958 respectively. HQ evaluated in adult from fish samples collected at the Ibi river sampling location ranges between 0.2210 to 0.0000 with Mn and As having the highest and lowest HQ values respectively while that in children ranges between 0.6631 to 0.0000 with Mn and As having the highest and lowest HQ's respectively. the HI values for fish samples in river Ibi are 0.6479 and 1.9437 respectively. Non carcinogenic risk assessment yielded hazard index above one across all sampling site both in river Benue and river Ibi thus implying domestic utility of water from these water bodies may pose severe health challenges ranging from cardiovascular, and non-carcinogenic health related challenges.

Introduction

In recent years, there has been a global increase in fish consumption due to the growing recognition of their nutritional and therapeutic benefits. Fish are a valuable source of protein, essential minerals, vitamins, and unsaturated fatty acids (Mederos *et al*., 2012). The American Heart Association recommends consuming fish at least twice a week to obtain sufficient omega-3 fatty acids (Kris-Etherton *et al*., 2002). Heavy metals enter the aquatic food chain through direct consumption of water and food, as well as non-dietary routes through permeable membranes like the muscle and gills (Oliveira *et al*., 2005). Fish tend to accumulate heavy metals in their tissues from the surrounding environment, reflecting the sediment and water levels of their habitat (Annabi et al., 2013). This accumulation can exceed environmental concentrations due to their absorption along the gills, kidney, liver, and gut (Annabi *et al*., 2013). Heavy metal accumulation can be passive or selective, resulting from differences in assimilation or egestion (Egila and Daniel, 2011). Non-essential heavy metals like Cadmium (Cd), Mercury (Hg), and Lead (Pb) are extremely toxic even at low exposure levels and pose a threat to all forms of life, especially human health (Järup, 2003). Toxic effects occur when the organism's excretory, metabolic, storage, and detoxification mechanisms cannot counter the uptake of heavy metals, leading to physiological and histopathological changes (Georgieva *et al*., 2014). Fish species can vary significantly in their levels of non-essential heavy metal accumulation within the same freshwater body (Annabi et al., 2013). To protect aquatic life, it is essential to monitor trace element contamination levels through chemical biomonitoring and biomarkers that indicate early biological effects (Annabi *et al*., 2013). Some fish species are better bio-indicators of specific heavy metal contamination (Burger and Gochfeld, 2011). Water chemistry and sediment play a crucial role in the accumulation of heavy metals in fish (Petrovic *et al*., 2013). Although fish is a vital part of the human diet due to its high nutritional quality (Sioen *et al*., 2007), the bioaccumulation of non-essential trace elements in fish tissues poses a concern (Zhang and Wang, 2012). Heavy metals in fish can counteract their beneficial effects and pose serious threats to human health, leading to conditions like renal failure, liver damage, cardiovascular diseases, and even death (Rahman *et al*., 2012). Consequently, international monitoring programs assess fish quality for human consumption and the health of aquatic ecosystems (Meche *et al*., 2010). Metal bioaccumulation and distribution in fish organs vary significantly between species, and several factors can influence metal uptake, including sex, age, size, reproductive cycle, swimming patterns, feeding behavior, and geographical location (Rashed, 2001). Fish are considered reliable indicators of heavy metal contamination in coastal environments.

Methodology

Sampling site

Sampling site 1

Makurdi town, the study area, serves as the headquarters of Makurdi Local Government, established in 1970. It is situated on both banks of River Benue, positioned between latitudes 7°45`N and longitudes 8°26`E, 8°36`E (Wikipedia, 2009). River Benue is one of Nigeria's major rivers, originating from the Cameroonian mountains and flowing westwards through Makurdi until it meets the River Niger at Lokoja in Kogi State. The river's tributaries include Rivers Donga, Katsina-Ala, Bantaji, and Taraba. Makurdi's New Bridge spans 1.194 km across the river, with an average depth and cross-sectional area measuring 7.82m and 4608.42m^2, respectively. The valley surrounding the river comprises meta-sediments and lies below 300m above sea level. This floodplain with extensive swamps is suitable for dry season irrigated farming. Despite its significance, the River Benue faces various pollution sources within the vicinity of Makurdi. Industrial wastes from Benue Brewery Limited (BBL) and Nigeria Bottling Company (NBC) are discharged into the river. Additionally, wastes from markets and abattoirs are washed into the water. Human and animal feces, along with chemical runoff from fertilizers and crop fields near the riverbanks, further contribute to the pollution (Madison, 1985). In September 2012, the situation exacerbated when the River Benue overflowed due to the release of excess water from the Lagdo Dam in Cameroon. This resulted in the displacement of over 5000 people and the submersion of 800 houses in Makurdi and its surrounding areas. The incident increased the level of pollution in the river.

Water from River Benue is needed for domestic, industrial and agricultural purposes to supplement the existing surface source in areas not covered by the current distribution network (Anhwange *et al*., 2012). Considering the fact that, Makurdi is growing and River Benue is the major source of water supply for the inhabitants, incidences of water related diseases in this area has necessitated the decision to study its raw water quality parameters especially as it affects man.

Sampling site 2

Ibi, town and river port, Taraba state, east-central Nigeria, on the south bank of the Benue River, opposite the mouth of the Shemankar River. Ibi lies on both bank of River Ibi; within latitudes 5°65`N and longitudes 9°36`E, 8°36`E (Wikipedia, 2009). Most of the inhabitants of river Ibi are normally engaged in fishing. Ibi is a collecting point for sesame seeds and soybeans. Salt extraction, a traditional occupation of the women in the vicinity, has been eclipsed by imported European salt.

Source: google maps/retrieved 2022: Map showing River Benue and River Ibi

Materials

All materials and reagent used for this experiment were of analytical standard

3.2 Sample Collection

Approximately, 1kg fish samples were purchased from fisher men from both river Makurdi and river Ibi respectively.

3.3 Sample preparation and extraction

Extraction of heavy metals in fish was done according to the method developed by Therdteppitak and Yammang (2002) with some little modifications. Ten (10.0) g of homogenized fish sample was placed into a 100 mL conical flask and 20.0 g of activated anhydrous sodium sulfate were added and mixed. Then 30 mL of 2:1 (v/v) hexane/acetone mixture were added and thoroughly mixed by shaking. The sample was then sonicated for 20 min using Bransonic

Ultrasound Sonicator. The supernatant was filtered into a 250 mL round bottom flask. The extraction was repeated two more times and all the supernatants combined and concentrated at 40 °C to near dryness using a Vacuum Rotary Evaporator (Buchi rotavapor R-200, Buchi heating bath B-490).

Determination of heavy metals in water, sediments and fish samples

The water, sediments, and fish samples were digested using concentrated Analar Nitric acid according to Zhang (2017). The UNICAM Solaar 969 atomic absorption spectrometer (AAS) which uses acetylene-air flame was used for the determination of Heavy Metals.

Statistical analysis

All the results were statistically analysed using single factor ANOVA and Least Significant Difference (LSD) test was performed to determine the location of significant differences.

Governing equations for health risk assessment

Estimation of Exposure to Humans and Risk from Fish Consumption

The estimated daily exposure (Ems) of individuals to pesticide residues and heavy metals from each fish of both river Benue and river Ibi was determined using Equation the equation below;

$\mathrm{Em} = \frac{\mathrm{Cm \times CR}}{\mathrm{Bw}}$..........................1

where Cm, CR° and Bw represent concentration of chemical contaminant in the muscle portion of fish (mg/kg), mean daily consumption rate of fish (kg/d) (Ahmad and Afzal, 2020) and body weight of an individual consumer (kg) (Boobis *et al*., 2006). Human health assessment of consumers of pesticide residue contaminated fish was characterized using health risk index (HI). The estimated HIs were obtained by dividing the estimated exposure by its corresponding reference dose by as shown in the Equation;

$\mathrm{HI} = \frac{\mathrm{Em}}{RfD}$…………………….2

When HI is less than 1.0 it can be concluded with great certainty that there is essentially no probability of population or community level effect. However, if the ratio exceeds 1.0 then there is a potential for adverse effect of either carcinogenic or non-carcinogenic risk. Carcinogenic risk (CR) were estimated using the Equation;

$\mathrm{CR} = \mathrm{Em \times SF}$…………………3

where Em and SF represents the estimated exposure and slope factor.

Result and Discussion

The analysis of heavy metals in fishes obtained from both river Ibi and river Makurdi as presented in table 1 revealed the presence of the following heavy metals; Mn, Fe, Zn, Cu, Pb, Ni, Cd, Co, Cr, As, and Hg. Result for Makurdi revealed the heavy metal concentration varies from 99.370 to 0.001ppm with Zn and As having the highest and lowest concentration respectively while result from river Ibi revealed that the concentration of the heavy metals varies between 70.780 to 0.002ppm with Fe and Pb having the highest and lowest concentrations respectively.

Table 1; Heavy metal concentrations in fish samples obtained from River Benue and River Ibi

Parameters (ppm)	River Makurdi	River Ibi	**WHO**
Mn	63.780 ± 0.002^{a}	56.470 ± 0.001^{a}	0.050
Fe	92.970 ± 0.002^{b}	70.780 ± 0.001^{a}	0.300
Zn	99.370 ± 0.003^{b}	57.790 ± 0.003^{a}	5.000
Cu	33.160 ± 0.055^{b}	14.970 ± 0.002^{a}	1.500
Pb	0.003 ± 0.001^{a}	0.002 ± 0.002^{a}	0.050
Cd	0.002 ± 0.000^{a}	0.003 ± 0.000^{a}	0.005
Co	0.003 ± 0.000^{a}	0.002 ± 0.000^{a}	0.010
Cr	0.007 ± 0.001^{a}	0.006 ± 0.000^{a}	0.050
As	0.001 ± 0.000^{a}	ND	0.050
Hg	0.121 ± 0.001^{a}	0.100 ± 0.005^{a}	0.002

Result presented as mean ± standard deviation. Result within the same row with the same superscript indicate no significance differences while result with the different superscript within a row indicate level of significance ($p > 0.005$). Where, M site: Makurdi site and I site: Ibi site; Mn: Manganese; Fe: Iron; Zn: Zinc; Cu: Copper; Pb; Lead; Cd; Cadmium; Co: Cobalt; Cr: Chromium; As: Arsenic; Hg; Mercury.

Table 3: Estimated Daily Intake (EDI) values of heavy metals in fish samples obtained from both river Benue (Makurdi) and river Ibi

Sampling Sites				
	Makurdi		**Ibi**	
Heavy metals	Adult	**Children**	**Adult**	**Children**
Mn	0.034900	0.104900	0.030900	0.092800
Fe	0.050900	0.152800	0.038800	0.116400
Zn	0.054500	0.163400	0.031700	0.095000
Cu	0.018200	0.054500	0.008200	0.024600
Pb	0.000001	0.000005	0.000001	0.000003
Ni	0.000005	0.000015	0.000004	0.000013
Cd	0.000001	0.000003	0.000001	0.000005
Co	0.000002	0.000005	0.000001	0.000003
Cr	0.000004	0.000012	0.000003	0.000009
As	0.000005	0.000002	ND	ND
Hg	0.000066	0.000199	0.000054	0.00020

Mn: Manganese; Fe: Iron; Zn: Zinc; Cu: Copper; Pb; Lead; Cd; Cadmium; Co: Cobalt; Cr: Chromium; As: Arsenic; Hg; Mercury.

Result of Bioaccumulation Factor (BAF) of heavy metals in fish samples obtained in both Ibi and Benue (Makurdi)

Result analysis for the Bioaccumulation Factor of heavy metals in fish samples obtained at both river Ibi and river Benue (Makurdi) sampling locations is presented in Table 4.23. For fish samples obtained from river Benue (Makurdi), the Bioaccumulation Factor ranges between 5.035 to 0.029 with Zn and Cd having the highest and lowest Bioaccumulation factors respectively. on the other hand, the Bioaccumulation Factor for fish samples obtained from river Ibi ranges between 2.965 to 0.000 with Zn and As having the highest and lowest Bioaccumulation Factors respectively.

Table 4; Bioaccumulation Factor (BAF) of heavy metals in fish samples obtained in both Ibi and mkd

Heavy metals	**BAF in fish in Makurdi**	**BAF in fish in Ibi**
Mn	0.631	0.565
Fe	1.346	1.037
Zn	5.035	2.965
Cu	2.933	1.340
Pb	0.070	0.084
Cd	0.029	0.023
Co	0.078	0.013
Cr	3.889	0.022
As	0.051	0.000
Hg	33.611	0.740

Bioaccumulation greater than 1 implies the substances have accumulated in an undesirable amount capable of causing harm or negative effect to humans when consumed. Mn: Manganese; Fe: Iron; Zn: Zinc; Cu: Copper; Pb; Lead; Cd; Cadmium; Co: Cobalt; Cr: Chromium; As: Arsenic; Hg; Mercury.

Hazard Quotient and Hazard index associated with the Consumption of Fish contaminated with Heavy metals from both river Benue (Makurdi) and river Ibi.

Result analysis for Hazard Quotient (HQ) and Hazard Index (HI) associated with the consumption of heavy metal contaminated fish from both river Ibi and river Benue (Makurdi) evaluated in both adult and children is presented in Table 4.24. HQ evaluated in adult from fish samples collected at the river Benue sampling location ranges between 0.4543 to 0.0002 with Cu and As having the highest and lowest HQ values respectively while that in children ranges between 1.3629 to 0.0005 with Cu and As having the highest and lowest HQ's respectively. the HI values for fish samples in river Makurdi are 1.0317 and 3.0958 respectively. HQ evaluated in adult from fish samples collected at the Ibi river sampling location ranges between 0.2210 to 0.0000 with Mn and As having the highest and lowest HQ values respectively while that in children ranges between 0.6631 to 0.0000 with Mn and As having the highest and lowest HQ's respectively. the HI values for fish samples in river Ibi are 0.6479 and 1.9437 respectively.

Table 5; Hazard Quotient and Hazard index associated with the Consumption of Fish contaminated with Heavy metals from both river Benue (Makurdi) and river Ibi

Parameter	Makurdi		Ibi	
Heavy metals	Adult	Children	Adult	Children
Mn	0.2497	0.7490	0.2210	0.6631
Fe	0.0728	0.2183	0.0554	0.1662
Zn	0.1815	0.5445	0.1056	0.3167
Cu	0.4543	1.3629	0.2051	0.6153
Pb	0.0005	0.0014	0.0003	0.0009
Cd	0.0011	0.0033	0.0016	0.0049
Co	0.0041	0.0123	0.0027	0.0082
Cr	0.0013	0.0038	0.0011	0.0033
As	0.0002	0.0005	0.0000	0.0000
Hg	0.0663	0.1989	0.0548	0.1644
Hazard index	1.0317	3.0958	0.6479	1.9437

Hazard Index (HI) and Hazard Quotient (HQ) >1 implies health risk. Where Mn: Manganese; Fe: Iron; Zn: Zinc; Cu: Copper; Pb; Lead; Cd; Cadmium; Co: Cobalt; Cr: Chromium; As: Arsenic; Hg; Mercury.

The presence of heavy metals in the environment poses a direct threat to public health as they can accumulate and magnify through the food chain, leading to potential hazards (Hussain *et al.*, 2012). In the examination of fish samples collected from both river Ibi and river Makurdi, the analysis presented in separate tables confirmed the presence of the following heavy metals; Mn, Fe, Zn, Cu, Pb, Cd, Co, Cr, As, and Hg.

Mammals can experience toxic effects when exposed to high levels of manganese (Tufan and Canan, 2020). Furthermore, excessive exposure to manganese can lead to spasms, resulting in conditions like tremors and mental disorders. Another study found that children born to pregnant women with high manganese intake were more likely to develop behavioral disorders (Dural *et al*., 2007). Despite these toxic effects of Mn, there is no report of any ML at neither the FAO nor the TFC (Tufan *et al*., 2020). Fish, the concentration of Mn in fish obtained at the Makurdi river was at 63.780ppm while that of the Ibi river was at 56.470ppm. However, the concentration of on Mn at both river Ibi and Benue at Makurdi are however greater than the WHO approved or recommended maximum permissible limits in fish samples.

The concentration of Fe in fish samples obtained from river Makurdi was at 92.970ppm while that of fish in river Ibi was at 70.780ppm. The concentration of Fe in fish samples obtained from both river Ibi and Benue at Makurdi are however greater than the WHO approved or recommended maximum permissible limits in fish samples thus implying toxicity.

Arsenic is known to cause a variety of diseases, including skin cancer, circulatory disorders, heart failure, chronic poisoning, extreme fatigue, and cancer. Initially, arsenic accumulates in the liver by binding to thiol groups and subsequently in keratin-rich tissues (Habibun *et al*., 2016). The concentration of As in fish samples obtained from river Makurdi was 0.001ppm while that from fish samples in river Ibi was not detectable. The concentration of As in fish samples obtained from Benue at Makurdi are however far lesser than the WHO approved or recommended maximum permissible limits in fish samples thus implying none or lesser toxicity, similarly, no amount or quantity of As was detected in fish samples obtained at the Ibi river.

Cadmium, while having benefits in various product manufacturing, poses significant risks to human health. It stands as one of the most hazardous heavy metal pollutants in the ecosystem (Tufan and Canan, 2020) and is highly toxic to living organisms. Compounds containing cadmium are also extremely toxic. In batteries, cadmium has shown carcinogenic effects. Unlike some essential elements for biological functions, cadmium is not essential (Tufan and Canan, 2020). The adverse effects of cadmium exposure on human health are extensive, including associations with lung diseases, prostate cancer, tissue damage, central nervous system and immune system problems, anemia, diarrhea, chronic issues, adrenal gland damage, abdominal pains, vomiting, bone disorders, reproductive system problems, infertility, prostate problems, psychological issues, damage to the brain and spinal cord, and triggering DNA damage leading to cancer (Turkmen et al., 2009).The concentration of Cd in fish samples obtained from river Makurdi was at 0.002ppm while that in fish samples in river Ibi was at 0.003ppm findings from this study were in consonance with that recorded by Ayeloja *et al.*, (2014) and Badr *et al.*, (2014) who reported Cd concentration of 0.020±0.006 ppm and 0.123±0.04 ppm respectively in fish. However, findings from this research are not in agreement with reports of Tajiri *et al.* (2011); Stancheva *et al*., (2013) and Shreadah *et al.*, (2015) who detected cadmium in fish samples with higher concentrations (0.011ppb,0.012±0.002 and 0.08 ppb for them, respectively and with those of Turkmen *et al.,* (2011) who detected higher levels (0.49 ± 0.05 ppm) and with those of Adeosun *et al.,* (2015) who failed to detect it in all examined samples of fish.

Like Zn, copper (Cu) is an important element for organisms, including humans and is needed in small amounts in our diet to ensure good health. Copper (Cu) is an essential element for living organisms, including humans, but excessive ingestion of copper can indeed lead to serious toxicological concerns. This condition is known as copper toxicity or copper poisoning. Symptoms of copper toxicity can include vomiting, diarrhea, stomach cramps, nausea, and in severe cases, it can even lead to death. Long-term exposure to high levels of copper can also cause liver and kidney damage. To prevent copper toxicity, it's important to ensure that copper intake remains within safe limits. This is usually achieved through a balanced diet that provides the necessary copper for normal bodily functions without exceeding harmful levels. For public health and environmental safety, it's important for regulatory bodies and industries to monitor and control the release of copper and other heavy metals into the environment to prevent contamination of water resources and food chains. Regular monitoring of copper levels in fish and other food sources can help identify potential health risks and guide appropriate measures to protect consumers and ecosystems (Habibun *et al*., 2016). The concentration of Cu fish samples obtained from river Makurdi was at 33.160ppm while it concentration in fish samples obtained from the Ibi river was at 14.970ppm. The concentration of Cu in fish samples obtained from both river Ibi and Benue at Makurdi are however greater than the WHO approved or recommended maximum permissible limits in fish samples (1.500ppb) thus implying toxicity.

Cobalt (Co) is a significant transition metal that has a dual impact on human beings, with both harmful and beneficial effects. Its increased utilization, especially Co(II), in various industries like nuclear power plants, petrochemical, metallurgical, electroplating, battery, dye, mining, and electronic industries, results in the generation of substantial amounts of effluent. As a consequence, surface and groundwater become contaminated due to the discharge of these effluents (Habibun *et al*., 2016). Although, a minute amount of Co is needed for the formation of vitamin B12, excessive exposure can be hazardous (Habibun *et al*., 2016). Excessive levels of Cobalt (Co) in water can lead to a variety of physical and mental health problems, including vomiting, nausea, diarrhea, asthma, pneumonia, kidney congestion, skin degeneration, and weight loss. These adverse effects highlight the importance of controlling and monitoring Cobalt levels in water sources to ensure human well-being (Habibun *et al*., 2016). The concentration of Co in fish samples obtained from river Makurdi was 0.003ppm while the mean average concentration of Co in fish samples from the Ibi river was at 0.002ppm. The concentration of Co in fish samples obtained from Benue at Makurdi and river Ibi respectively are however lesser than the WHO approved or recommended maximum permissible limits in fish samples thus implying none or lesser toxicity, similarly, no amount or quantity of Co was detected in fish samples obtained at the Ibi river.

Chromium (Cr) is extensively used in electroplating, leather tanning, metal finishing, nuclear power plant, dying, photography industries and textile industries. In an aqueous solution, it exists in both the Cr(III) and Cr(VI) forms. Hexavalent chromium, which is more toxic, alters human physiology, accumulates in the food chain and causes severe health problems ranging from simple skin irritation to lung cancer (Habibun *et al*., 2016). Cr concentration in fish samples from the Makurdi river was 0.007ppm while the Cr concentration from the fish samples obtained from river Ibi was 0.006ppm. The concentration of Cr in fish samples obtained from Benue at Makurdi and river Ibi respectively are however lesser than the WHO approved or recommended maximum permissible limits in fish samples thus implying none or lesser toxicity.

Mercury (Hg) is released into the environment through the discharge from agricultural fungicide, chemicals, waste incineration, electronic materials, scientific instruments (thermometers, barometers), batteries, dental amalgams, textile, photographic and pharmaceutical industries, and fossil fuel combustion. It is a neurotoxin that can cause damage to the central nervous system. High concentrations of Hg causes the impairment of pulmonary and kidney function, chest pain and dyspnea (Habibun *et al*., 2016). The rate of mercury has increased 3 times in the environment by increasing usage of industry. There is a small amount of mercury in seafood (Topal and Canan, 2020). However, some game fish contain higher levels of mercury and, when eating these fishes regularly, they may cause accumulation of mercury in the body (Topal and Canan, 2020). The concentration of Hg in fish sample obtained from river Makurdi was 0.121ppm while that from the fish samples obtained from river Ibi was 0.100ppm findings from this studies are not in consonance with reports of Reji *et al*., who detected higher levels (2.85±1.22ppm wet weight). The concentration of Hg in fish samples obtained from Benue at Makurdi and river Ibi respectively are however greater than the WHO approved or recommended maximum permissible limits in fish samples thus implying toxicity.

The presence of inorganic lead (Pb) in natural water systems is a concern due to its toxic effects on human health. The sources of Pb contamination include industrial fuel, leaded gasoline, and mining activities, among others. Exposure to Pb can lead to acute poisoning, causing severe dysfunction in the kidneys, liver, and reproductive system. It is especially harmful to children and can cause mental retardation and other toxic symptoms like anemia, insomnia, headache, dizziness, irritability, weakness of muscles, hallucination, and renal damage.

The study found that the concentration of Pb in fish samples obtained from the Makurdi river was 0.003ppm, while in fish samples obtained from the Ibi river, it was 0.002ppm. These concentrations are relatively low and may not be consistent with previous reports in other regions, where higher levels of Pb in fish have been detected. For example, Ayeloja *et al*. (2014) reported higher mean residual levels of lead in muscle samples of Tilapia nilotica and Catfish collected from a reservoir in Nigeria. Similarly, Badr *et al*. (2014) evaluated higher mean lead values in muscle samples of O. niloticus fish collected from the River Nile. On the other hand, the concentration of Cr (chromium) in fish samples obtained from both Makurdi and Ibi rivers was found to be below the WHO approved or recommended maximum permissible limits in fish samples, indicating that there is no significant toxicity concern associated with Cr in these fish samples. It's important to consider that heavy metal contamination can vary based on geographic location, environmental factors, and industrial activities in the area. Therefore, findings from different studies can differ, and it is crucial to continue monitoring and conducting further research to assess the potential risks associated with heavy metal contamination in different regions.

Zn is one of the most common pollutants for surface and groundwater as it has versatile uses (Habibun *et al*., 2016). Again, due to its non-biodegradability and acute toxicity, Zn-containing liquid and solid wastes are considered as hazardous wastes. An excessive amount of Zn exposure can cause well-known health problems such as stomach cramps, skin irritations, vomiting, nausea and anemia (Habibun *et al*., 2016). The concentration of Zn in fish samples obtained from river Makurdi was 99.370ppm while it concentration in fish samples obtained from river Ibi was 57.790ppm. The concentration of Zn in fish samples obtained from both river Ibi and Benue at Makurdi are however greater than the WHO approved or recommended maximum permissible limits in fish samples (5.00ppb) thus implying toxicity.

Estimation of Bioaccumulation factor of heavy metals in fish

The result of the estimated bioaccumulation factor of heavy metals in fish is presented in table 28**;** the result depict the fish obtained from Makurdi has the highest bioaccumulation rate or concentration as more of the heavy metals tend to bioaccumulate more in fish samples in Makurdi than Ibi. Zn was observed to have the highest bioaccumulation factor of Hg 33.611 in Makurdi followed by Zn, Cr, and Cu respectively while for fish samples analyzed in Ibi, the highest bioaccumulation factor was noticeable in Zn followed by Cu however, the lowest bioaccumulation factor was noticeable in as for both Makurdi and Ibi. The bioaccumulation of these heavy metals in the fish samples at the different sampling locations depict the toxicity associated with the consumption and utilization of the water and associated products from each study locations using a human model.

Hazard Quotient and Hazard index of the Consumption of Fish contaminated with Heavy metals

The Hazard Quotient (HQ) is used to assess the potential health risk from exposure to individual heavy metals, while the Hazard Index (HI) is a cumulative measure of the overall health risk from exposure to multiple heavy metals. In this study, the evaluated Hazard Quotient for all the heavy metals from both Makurdi and Ibi fish samples was found to be less than 1 for both adults and children, indicating a low risk associated with individual heavy metal exposure. However, the calculated Hazard Index (HI) for the Makurdi fish samples was greater than 1 for both adults and children, suggesting a potential health risk due to the cumulative effect of exposure to multiple heavy metals in those samples. On the other hand, the HI for Ibi fish samples was less than 1 for adults but greater than 1 for children, indicating a higher cumulative health risk for children consuming fish from the Ibi river. Comparatively, this means that children who consume fish from the Makurdi river may be more susceptible to serious non-carcinogenic health challenges due to the cumulative exposure to multiple heavy metals present in those fish samples. This observation suggests that fish samples from Makurdi are more contaminated with heavy metals compared to those from Ibi, posing a potentially higher health risk, especially for children.

Conclusions

The presence of heavy metals in water resources poses a significant threat due to their toxic properties and ability to accumulate in organisms, especially as they move up the food chain. This can disrupt the ecological balance of rivers and soils, leading to poisoning of the aquatic environment and putting populations dependent on these rivers at risk. The study conducted an analysis of heavy metal concentrations in fish samples from both the Benue River (Makurdi) and Ibi River. The results confirmed the presence of various heavy metals, including Mn, Fe, Zn, Cu, Pb, Cd, Co, Cr, As, and Hg, in these fish samples. Bioaccumulation analysis revealed that some of these heavy metals accumulate in fish at concentrations capable of causing toxicity, which can ultimately affect human health when consumed. The Hazard Index evaluation highlights the cumulative effect of these heavy metals on human health, indicating that there may be severe health implications associated with the consumption of bio accumulated fish containing these toxic substances. Overall, this study emphasizes the importance of monitoring and managing heavy metal contamination in water resources to protect both the environment and human health. Proper measures, such as regulatory actions, public awareness, and further research, are necessary to mitigate the risks posed by heavy metal contamination in aquatic ecosystems.

Recommendation

Indeed, the information from this study is crucial for establishing public policies aimed at effectively managing water contamination in Nigeria. Sensitization and awareness campaigns are vital to educate the public about the health risks associated with consuming water and aquatic resources affected by contaminants. Such awareness programs can empower people to make informed decisions about their water sources and adopt necessary precautions. Government intervention is essential to enforce regulations and prevent irregular dumping of pollutants into river bodies. Implementing and monitoring strict environmental regulations can significantly reduce the contamination of water resources and protect both aquatic life and human health. Furthermore, future research should focus on conducting risk analyses for the entire population in the affected areas. Analyzing samples from animals and humans, such as blood and urine, can provide valuable insights into the true toxicity levels and potential health impacts of heavy metal contamination in these riverine areas. This data will be invaluable for understanding the extent of the problem and designing effective mitigation strategies. In summary, a combination of informed policies, public awareness, government enforcement, and continued research is essential to address the water contamination issue and safeguard the health and well-being of the population in Nigeria's riverine areas.

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