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Evaluation of some metals in sediment, water and snail, from an urban flood reservoir in Benin-city, Edo state, Nigeria

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Abstract
This study was conducted to ascertain the presence of Iron (Fe), Copper (Cu), Manganese (Mn) and Nickel (Ni) in sediment, snail and water at the urban flood reservoir, Useh. Samples were collected in triplicate over a period of six months (November – April, 2023). Sediment samples were collected using a venier caliper at a depth of 10cm using Van-Veen Grab method. Snail samples were collected by randomly hand picking from the sampling site, and the water was collected using labeled water canisters of 50cl properly rinsed with deionized and site water. At the laboratory, samples were identified, prepared and digested according to standard methods. Analyses of the metals in the digest were then analyzed using the Atomic Adsorption Spectroscopy. The presence of Fe, Cu, Mn were confirmed in all the media during the period of study except for Ni that though was present in sediment and snail was only detected in April in water. The mean concentration of the metals in sediment was higher than the values in water and snail. Fe levels varied between 0.11-2.14mg/l in the snail and water, which were not significantly different ($p>0.05$) but were significantly different ($p<0.05$) in the sediment (2.24-97.73mg/l). Cu mean value of 0.43mg/l and 0.04mg/l were recorded in the sediment and snail respectively. ANOVA showed that Cu levels was only significantly different in water. The highest Ni levels observed water (0.08mg/l) and sediment (0.05), were not significantly different ($p>0.05$) in the sediment. The highest and lowest mean monthly values of 1.12mg/l Mn and 0.01mg/Mn were observed in sediment and snail respectively. Ni and Mn levels in these media showed no significant differences ($p<0.05$). Hence the free inflow of anthropogenic and other waste observed at the site if not properly managed will greatly increase the pollution level at the flood reservoir. A public awareness campaign of the implication of heavy metal accumulation in aquatic flora and fauna is therefore sacrosanct.

Key words: *Reservoir, Flood, Metals, Useh, Nigeria*

Introduction

Metal pollution in the aquatic environment has been receiving worldwide attention due to the serious health risk it poses to aquatic life and man through food intake (Asegbeloyin *et al.,* 2010). Metals are ubiquitous in the environment (Pohl *et al.*, 2011), readily dissolved in and transported by water and can be taken up by aquatic organism due to bioaccumulation and bio-magnifications in the food chain, either as such, or their metabolites thus causing concern on the animal at the top of the food chain (Odiko, 2017). Most metals are stable and persist as environmental contaminants of aquatic environments and their organisms. In the aquatic ecosystem, sediments have been commonly used as environmental indicators due to high physical-chemical stability and their chemical analysis can provide considerable information on the assessment of anthropogenic activities (Malhotra *et al*., 2014). The aquatic environment receives copious amounts of heavy metals from naturally occurring deposits, natural processes and anthropogenic activities. Heavy metals are transported dissolved in water or as an integral part of suspended sediments, with a combined action of adsorption, hydrolysis and co-precipitation, only a small part of free metal ions stay dissolved in water, and a large quantity of them get deposited in the sediment (Zubaidah *et al*., 2013).

As metals cannot be degraded, they are continuously being deposited and incorporated in water, sediment and aquatic organisms (Linnik and Zubenko, 2000, Hamed *et al.,* 2015)

Snails, water and sediments are notorious for their ability to concentrate heavy metals. They need to be screened to ensure that unnecessary high levels of toxic metals are not transferred to man through them (Igboanugo and Chiejine, 2012). At elevated levels, heavy metals can be instantly lethal, or can result in long-term health problems similar to those caused by pesticides, insecticides and herbicides (Swaroop *et al.,* 2020). Changing environmental conditions under increasing anthropogenic influences can also affect the aquatic ecosystem and might lead to drastic changes in its biological productivity.

The presence of heavy metals in water can be detrimental to human health and the aquatic ecosystem, and this is a growing problem worldwide and currently, it has reached an alarming rate (Osa-Iguehide *et al.,* 2015). Heavy metals can thus enter the food chain in the aquatic environment, and become available for accumulation in biota (Alrabie *et al*., 2019). This flood site was chosen because it is one of the largest flood sites in Benin City, Edo State. Several attempts have been made by various governments to tackle this menace; it continues to claim more streets and buildings (Vanguard, 2011). It is generally believed that there is a strong relationship between the aquatic environment and the organism in it. Long-term metals exposure by regular consumption of food and water which contain them, poses potentials health problems to animals and residents in such vicinity (Salawu *et al.,* 2014). Oyoh and Evbuomwan (2008) poor waste management causes obstruction of drainage system thereby causing flood, poor aesthetic, release of foul odour and green-house gases, obstruction of traffic flow and pollution of surface and ground water. On the other hand, Kavitha and Kumar (2013) associated the accumulation of heavy metals in the sediments and biota of receiving water bodies to rapid industrialization, urbanization, modern civilization, economic development and increase in population. Surface run-off carries these metals and their compound into water bodies, water from such water bodies and surface run-off is potentially harmful (Okoye *et al.,* 2007).

Another reason why this study needs to be carried out at this site is the aquatic life supported by this flood like the catfish (*Clarias gariepinus*) that are able to reproduce successfully, snails and other flora in the area. They are either eaten or/and also sold to the general public, thereby serving as a source of income to them. Although analysis of water, sediment and water snail has been done in some parts of Nigeria (Zira *et al*., 2021) very little work, if any, has been conducted on the assessment and analysis of metals pollution level of this flood reservoir at Useh in Edo State, that support these aquatic life. This study was therefore carried out to determine the presence and levels of four selected; metals Iron (Fe), Copper (Cu), Manganese (Mn) and Nickel (Ni) in the water, snails and sediment to enable us make inference on their levels in and around the flood reservoir with possible characterization.

Materials and Method

Description of the study area

The study was carried out at an urban flood reservoir Useh, Edo State (Figure 1). The flood reservoir is located between latitude 6.22°N and longitude 5.34°E with an elevation of 51m, and a population of about 7,920 people (Maps-streetview.com, 2021). The flooded area is made up of over five (5) streets which used to be home to more than 100 houses with a population of approximately 700 persons.

Sample Collection

Samples were collected over a period of six months (November - April). Sediment samples were collected from three selected spots using a venier caliper at a depth of 10cm below the flood water level, using a Van-Veen Grab method (Adedeji *et al*., 2018). After collection, the sediment samples were scooped into a Ziploc® bags. Snail samples were collected by hand picking randomly from the sampling site without consideration to size. The collected samples were stored in large-sized plastic cans that had been rinsed with deionized water to avoid contamination of sample. The reservoir water temperature at the time of collection was taken using a mercury-in-glass thermometer. The water was then collected using labeled water canisters of 50cl properly rinsed with deionized and site water. The canister lids were properly sealed. All samples to prevent contamination and death were immediately transported to the laboratory for identification and analysis.

Sample Preparation and digestion: Analysis of the metals was carried out at the Central Laboratory, University of Benin, Benin City, Edo State.

The snail sample was washed, dissected to separate the snail to flesh, slime and shell; the fleshy sample was then sliced into smaller sizes for quick oven drying at 105°C. Dried samples were then grinded to pulverize and homogenize the tissues after complete dryness and constant weight was observed. The homogenized snail sample (1±0.01g) was weighed into a 100ml Erlenmeyer flask for digestion, the sediment was air dried under a shaded place until constant weight was attained. This is usually done to prevent the effect of oven drying and sun drying on soils samples which alters the pH and mercury levels in samples (Zlatanovic *et al*., 2018). After which 1±0.01g of the dried sample was measured and placed in a labeled flask all according to standard methods and digest stored in 100ml volumetric flasks. The water stored in canisters already treated with dilute nitric acid, after collection and placed in labeled plastic bottles of which 10ml was measured and placed in a digestion flask for acid treatment according to standard method and digest stored in 100ml plastic reagent bottles (US EPA, 2017). The study samples were analyzed for iron, copper, manganese, and nickel from the digested samples using Atomic Absorption Spectrophotometer (AAS), equipped with solar software using air acetylene as oxidant and also with cathode lamp having ultraviolet wavelength changed at intervals for the analysis of each metal. The blanks and calibration standard solutions were also analyzed in the same way as the sample solution.

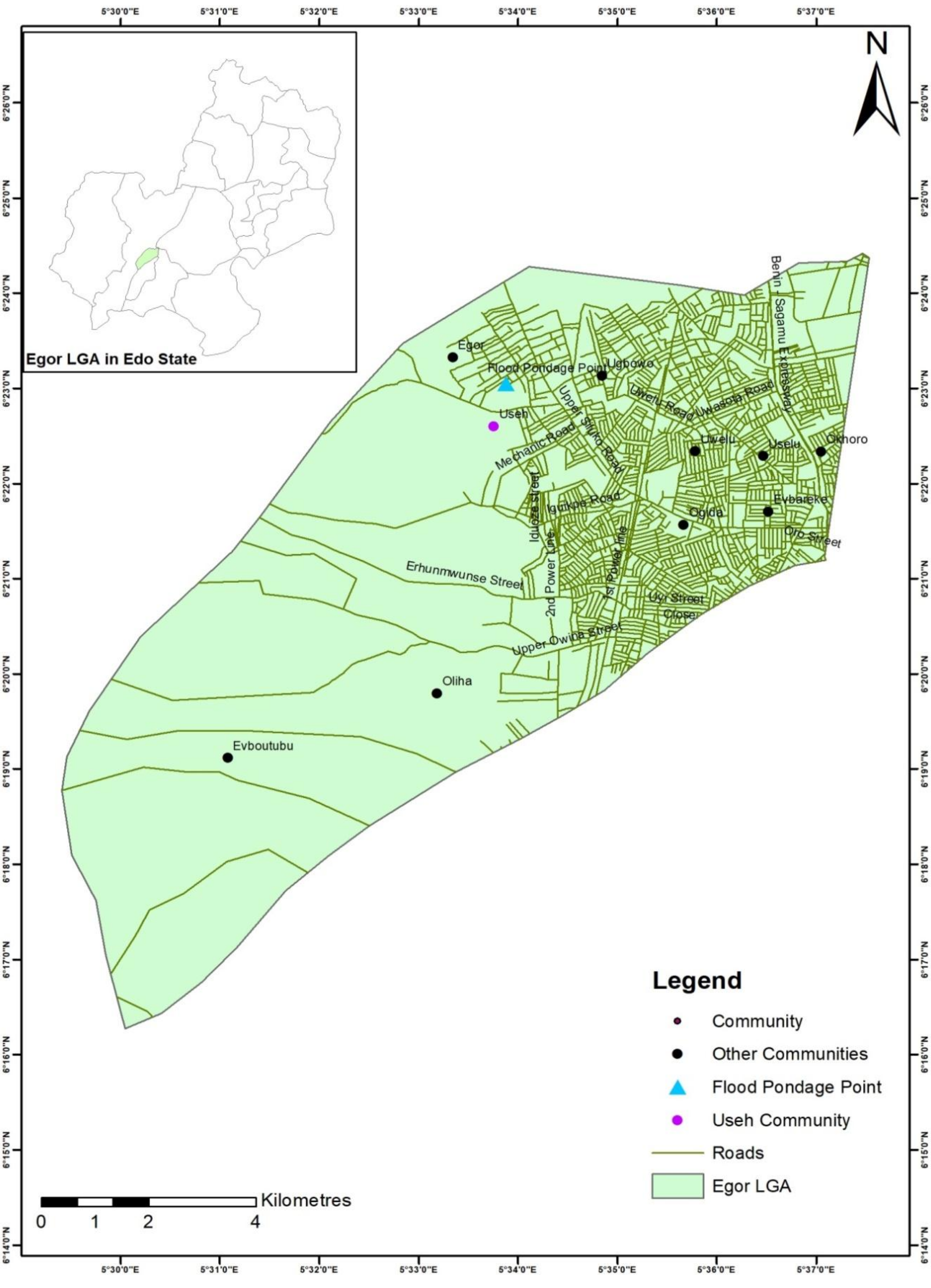

Figure 1: Map showing flood point

Statistical Analysis

Data were analyzed using one-way analysis of variance (ANOVA), this was used to test for significant difference between mean values at 5% probability level. Duncan multiple range test (DMRT) was used for the separation of means.

Results

The study showed that Fe, Cu, Mn and Ni were present in sediment, water and snail collected from Useh flood reservoir in Egor Local Government, Edo State, Nigeria. The monthly and general mean metal levels in these media during the period of study are as shown in Tables 1 and 2. Analysis of variance showed that iron (Fe) levels in the sediment were significantly different ($p<0.05$), except in March and April where the lowest values were observed. Fe levels in the snail varied between 0.11-2.11mg/l, analysis of variance showed that there was no significant differences except in December and April when the highest values were recorded. Fe level in water was low, except in April and December where a mean value of 0.8mg/l – 1.05mg/l was recorded. But ANOVA showed that the general mean of iron concentration in the snail and water were not significantly different ($p>0.05$) but were significantly different ($p<0.05$) from the levels in the sediment.

The highest mean value of 0.43mg/l was the highest recorded level of copper and was observed in the sediment (April). In snails, the lowest level of 0.04mg/l was reported in November and December, while the values observed during the other months were not significantly different. High mean value of 0.10mg/l in water Cu levels recorded in November and April were significantly different from the other months. ANOVA showed that Cu levels in sediment and snail were not significant difference ($p<0.05$) but were significant difference from water. Duncan multiple range tests showed that Cu was significantly different between the months in the sediment.

Table 1: Mean and Standard Deviation of Metals in Sediment, Snail and Water During the Period of Study (November to April 2023).

Metals	Media	November	December	January	February	March	April	F	P
Iron	Sediment	32.50 ± 0.71^{c}	18.40 ± 0.85^{d}	97.73 ± 1.10^{a}	56.50 ± 0.28^{b}	2.00 ± 0.00^{e}	2.24 ± 0.28^{e}	6561.630	<0.001
	Snail	0.11 ± 0.14^{c}	2.11 ± 0.01^{a}	0.82 ± 0.01^{b}	0.91 ± 0.01^{b}	1.95 ± 0.02^{a}	2.14 ± 0.03^{a}	4511.284	<0.001
	Water	0.32 ± 0.14^{b}	0.80 ± 0.14^{a}	0.36 ± 0.14^{b}	0.31 ± 0.14^{b}	0.31 ± 0.01^{b}	1.05 ± 0.13^{a}	33.549	<0.001
Copper	Sediment	0.06 ± 0.01^{b}	0.02 ± 0.01^{b}	0.23 ± 0.01^{a}	0.31 ± 0.01^{a}	0.36 ± 0.01^{a}	0.43 ± 0.01^{a}	736.644	<0.001
	Snail	0.04 ± 0.02^{b}	0.04 ± 0.01^{b}	0.22 ± 0.01^{a}	0.18 ± 0.01^{a}	0.21 ± 0.01^{a}	0.26 ± 0.00^{a}	118.926	<0.001
	Water	0.08 ± 0.00^{a}	0.03 ± 0.01^{b}	0.05 ± 0.01^{b}	0.03 ± 0.00^{b}	0.03 ± 0.01^{b}	0.10 ± 0.01^{a}	34.771	<0.001
Manganese	Sediment	0.26 ± 0.02^{b}	0.37 ± 0.01^{b}	0.83 ± 0.21^{a}	0.91 ± 0.01^{a}	0.99 ± 0.03^{a}	1.12 ± 0.01^{a}	641.739	<0.001
	Snail	0.01 ± 0.00^{a}	0.01 ± 0.00^{a}	0.02 ± 0.01^{a}	0.03 ± 0.01^{a}	0.02 ± 0.01^{a}	0.07 ± 0.00^{a}	41.481	<0.001
	Water	BDL	0.03 ± 0.01^{a}	0.03 ± 0.01^{a}	0.02 ± 0.00^{a}	0.02 ± 0.00^{a}	0.04 ± 0.01^{a}	1.417	0.350
Nickel	Sediment	0.03 ± 0.00^{a}	0.05 ± 0.01^{a}	0.06 ± 0.01^{a}	0.03 ± 0.00^{a}	0.03 ± 0.00^{a}	0.05 ± 0.01^{a}	5.200	0.034
	Snail	0.01 ± 0.00^{a}	BDL	0.02 ± 0.01^{a}	0.02 ± 0.01^{a}	0.02 ± 0.01^{a}	0.04 ± 0.01^{a}	3.344	0.109
	Water	BDL	BDL	BDL	BDL	BDL	0.08 ± 0.00		

Note: Means with similar superscript along rows are not significantly different ($p > 0.05$)
BDL = Below Detection Limit

A mean value of 0.08 mg/l and 0.05mg/l Ni recorded in water in April and sediment respectively was the highest value of nickel observed during the period of study. Nickel in the sediment were not significantly different ($p>0.05$) during the period of study. In the snails, the mean value of Nickel was not significantly different, and was below detection level in December. The level of Nickel in the water sample was below detection level except in April where the highest mean value of 0.08mg/l was recorded. ANOVA showed that Nickel in the three media were not significantly different ($p>0.05$).

The highest mean monthly value of 1.12mg/l Mn in sediment was recorded in the month of April. The values of manganese in the sediment except in November and December were not significantly different. The lowest mean monthly value of 0.01mg/l was recorded in snails, and Mn though very low was also not significantly different all through the study. Mn in water was below detection level in November and was very low during the other months, thus was not significantly different during the period of study. ANOVA showed that in sediment, water and snail, manganese showed no significant differences ($p<0.05$).

Table 2: Mean Comparison of Study Metals in Sediment, Snail, Water and Some Standard Permissible Limits

Metals	**Sediment**	**Snail**	**Water**	**(NAFDAC)**	**WHO**
Fe	34.89 ± 35.27^{a}	1.34 ± 0.81^{b}	0.52 ± 0.31^{b}	0.3	1.0 – 3.0
Cu	0.23 ± 0.16^{a}	0.16 ± 0.09^{a}	0.05 ± 0.03^{b}	1.0	0.5 – 2.0
Mn	0.75 ± 0.33^{a}	0.02 ± 0.02^{b}	0.03 ± 0.01^{b}	2.0	0.1 – 0.4
Ni	0.04 ± 0.01^{a}	0.02 ± 0.0^{a}	0.08 ± 0.00^{b}	Nil	0.02

Means with similar superscript along rows are not significantly different ($p > 0.05$)

Discussion

Heavy metals are typical pollutants in urban environments and their toxicity depends also on ambient water chemistry (Arndt *et al*., 2014). Particular concern with regards to heavy metals is due to their persistence and toxicity in the aquatic ecosystem, being frequently the ultimate recipient of these heavy metal contaminants (Moore *et al.*, 2011).

Fe concentration in sediment during the period of study was 34.89mg/l which was well above the World Health Organization (W.H.O)(3mg/l) and National Agency for Food, Drugs Administration and Control (NAFDAC) (0.3mg/l) recommended limits as reported by Adefarati *et al*. (2017). The high level of iron in the sediment during the study is likely due to runoff materials washed in from the surrounding communities into the reservoir; Fe overload may be detrimental to both animals and humans (Torti and Torti, 2013). This finding agrees with a study done by Sha'ato *et al.* (2020) on the evaluation of bottom sediment qualities in Ihetutu Minefield, Ishiagu, Nigeria. The concentration of iron in snail and water during the study was within the W.H.O recommended level (3.0mg/l). Though, iron play an important role in cellular respiration, energy metabolism, DNA replication amongst others but in the presence of hydrogen peroxide if it generates large number of free radicals can become toxic in human bodies. Therefore, though iron is seen as an essential nutrient element, can also be potentially toxic (Jomova and Valko, 2011, Guo *et al*., 2021). This finding though does not align with the findings of Mahmutovic *et al.* (2018), who reported that iron concentrations in snail tissues ranged from 9.77±0.62mg/kg to 12.30±2.50mg/kg. This may not be unrelated to the fact that the Fe level of the soil in this part of the country is very high.

Copper and manganese (Mn) were within the acceptable limit in water during the period of study. Nickel (Ni) was below detection level except in the last month of analysis, a situation that may have been sparked up by effluents of certain anthropogenic source entering the flood waters. This finding agrees with the work of Javed and Usmani (2014), who assessed different metals similar to the present study and found Fe to have higher concentration than other study metals in effluent dominated rivulet water and their effect on glycogen metabolism and histology of *Mastacembelus armatus*. Fe concentration in water was highest than other metals evaluated, but still in acceptable range of WHO while Ni had a concentration above the recommended limit in the only month it was detected in water.

Copper is an essential element if taken in minute quantities, but also has the ability to accumulate and cause irreversible harm when ingested in large amounts (Mustapha and Agunloye, 2016). The recommended standard limit for Copper in food as set by FAO is 30mg/kg (FAO, 2003). The copper level in the snail was highest in April, but the concentration in sediment and snail were within the W.H.O recommended level of 2.0mg/l and 0.4mg/l respectively. These values were however lower than the mean concentration of 5.06mg/kg recorded in *Scomber scombrus* flesh commonly consumed in Ibadan, Nigeria (Kareem *et al*., 2016) and the level of Cu reported by Nwoke *et al*. (2014) in snail tissue (10.4mg/l) during their study. In the snail, the highest concentration of metal during the period of study was recorded in Fe, followed by Cu, Mn and Ni. Although the concentration of iron of the study metals was high in the snail, it was still within the recommended levels. Nickel on the other hand was the least available, but was above the recommended levels. This finding is in agreement with the findings of Milanov *et al.* (2016) who also reported high concentration of Fe, Cu and Mn levels in the tissues of three different fish species included in human diet from Danube River.

The mean concentration of manganese (Mn) highest value of 1.12mg/l observed during this study in the snail tissue was above the W.H.O recommended level (0.4mg/l). But higher values of 6.76 ± 1.12mg/L and 8.49±1.08 mg/L respectively has previously been reported by Ebrahimi and Taherianfard (2011) and Cuadrado *et al.* (2022) while working on *Pomacea canaliculata* muscle does not agree with this present study. In this study, Nickel (Ni) was at a highest level of 0.06mg/l, in the snail sample. Nickel value recorded was higher than the W.H.O recommended limit (0.02) in sediment, although was not significant during the study. This finding is contrary to the findings of Rubio *et al.* (2019) who reported a nickel concentration of 2.04mg/l.

Manganese though a constituent of essential enzymes at levels beyond acceptable limits can become very toxic (Vieira *et al*., 2012). Mn and Ni sediment were within recommended limit, but higher than W.H.O limits in sediment. Although, Ni was not detected in water during the period of study, the only observed value that was so high may have been sparked up as a result of sudden runoffs that might have brought with it municipal solid and liquid waste, detergents, pesticides, cosmetics, organic matters, anthropogenic activities around and beyond the flood reservoir might have brought waste laden with very high iron content. As it has been reported that acidic soil render Nickel more mobile, and the soil in this community (Egor Local Government Area) is very high in Fe. Nickel-containing compounds according to Kang *et al.* (2003) has induced tumors and enhanced their growth in various experimental animals and human cell culture through varied exposure route. The amount of metals in mollusks tissue is relative to the level of ecological contamination, thus they can be used as bio indicators in evaluating and monitoring aquatic pollution (Chiara *et al*., 2013, Banace and Taheri, 2019). Snail has high accumulative capacity for metal since they feed on algae and sediment; metal uptake will therefore depend on the metal availability in the sediment and the snail's regulatory capability (Nica *et al*., 2012, Tyokumbur and Okorie, 2014).

Conclusion

The site of study which initially started as an erosion site has developed into a flood reservoir, now capable of supporting aquatic lives which are being sought after for food. The findings of this study showed that the Useh flood reservoir had higher iron (Fe) content than other metals analyzed and that most of the metals were higher in the sediment. There were significant differences observed in all metals evaluated in the sediment, snail and water but some of which were within acceptable limits as recommended by NAFDAC and WHO. The concentration of Ni was consistently above safe recommended limits in sediment, snail and water. Hence, Useh flood reservoir can be said to be presently a repository of metals that may be potentially harmful. Therefore, to manage and mitigate a foreseeable situation, there should be sensitization of the people for there is the possibility of a gradual increase in the pollution levels in this reservoir, this should be of great concern as bioaccumulation of these metals is likely in humans, animals and plants that feed on harvested snail or use the water from this reservoir.

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