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Assessment of heavy metal concentrations in fish, water and sediment of Koramar Wanke Dam Gusau, Zamfara State, Nigeria

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Abstract
Pollution of heavy metals in water bodies is a threat to public water supply as well as to consumers of fishery resources. This study was aimed at investigating the distribution of heavy metals in some fish species, water column and sediment of Koramar Wanke Dam. Water and sediment samples were collected from 4 different sampling stations across the dam, while fish species (*Bagrus bayad*, *Clarias gariepinus*, and *Oreochromis niloticus*,) were bought at Dabar Masunta fish landing site of the dam on monthly basis for a period of three months from August 2023 to October 2023. Heavy metals Cadmium (Cd), Copper (Cu), and Lead (Pb) were analyzed in water samples, fish samples and sediment samples the dam using Atomic Absorption Spectrophotometry (AAS). The heavy metal level ranges in fish samples examined were Cd, 0.02 mg/kg-0.04 mg/kg; Cu, 0.02 mg/kg-0.08 mg/kg; and Pb, 0.02 mg/kg-0.06 mg/kg. The result also showed the mean concentration range of 0.01-0.02 mg/l for Cd; 0.06-0.12 mg/l for Cu; and 0.03-0.11 mg/l for Pb in water samples examined. The mean concentration of detected in the sediment samples ranged from 0.08-0.29 mg/kg; 0.14-0.21 mg/kg; and 0.08-0.17 mg/kg for Cd, Cu, and Pb respectively. The results obtained show minimal concentrations of the examined heavy metals in the water body below the recommended permissible levels. However, it is advisable to continue to take adequate measures to prevent entry of sewage, toxic substances and contaminants from industrial sources and agricultural residues from pesticides and insecticides into the water body, and to conduct further study at another period.

Keywords: Fish, heavy metal toxicity, Koramar Wanke Dam, water pollution

Introduction
Intensive urbanization and increase in industrial activities have caused increasing heavy metal pollution resulting from industrial, agricultural, and geochemical wastes. Pollution of heavy metal in water bodies is a threat to public water supply and to consumers of fishery resources. These heavy metals bio-accumulate in food chain and consequently pose great risks to humans after consumption due to the persistent nature in the environment. The presence of pollutants such as metals in fish and water is known to disrupt the balance of the aquatic ecosystem and bioaccumulation and magnification is capable of leading to toxic level of these metals in fish, even when the exposure is low.

Fishes and other aquatic foods are capable of concentrating heavy metals in their muscles and for the fact that they play vital role in human nutrition, they need to be screened properly to ensure that unnecessary high levels of some organic and inorganic pollutants are not being transferred to human through consumption. Previous reports showed that industrial and domestic effluent constitute the largest sources of heavy metal which contribute to the increasing metallic pollutant in aquatic and terrestrial environment in most part of the world. Studies on bioaccumulation of pollutants in fish are important in determining different content of trace metal in fish species from bio magnifications of food chains, metabolic capability and feeding habits.

Several studies have been conducted on heavy metal contamination in freshwater ecosystems in Nigeria; However, few studies have focused on the Koramar Wanke Dam, Gusau, Zamfara State.

The dam serves the local fishermen, where fishing is as a major source of their occupation. Agricultural activities along the dam course takes place during rainy season.

Irrigation farming, bathing, washing of clothes by the dam site, are also common features of water pollution observed in Koramar Wanke dam. Large amounts of water consumed by the people in Gusau metropolis are mainly from surface waters of Koramar Wanke dam. These activities together with runoff water during the rainy season may result into deterioration of water quality in the Dam. When the impact of these activities is so extensive, the water body may largely lose its self-purification capacity.

This study, therefore, is aimed at investigating the distribution of heavy metals in some selected fish species, water column and sediments of Koramar Wanke dam in order to assess the impact of discharge into the water body from anthropogenic activities with a view to establishing their suitability for human consumption and baseline data on the current pollution status of the dam and its environment.

Materials and Methods

Description of the study area

Koramar Wanke dam is located at Gusau Local Government area of Zamfara State, northwestern Nigeria and lies between latitude 12.166955^0N and longitude 6.637986^0E of the equator. Koramar Wanke Dam is popular for the supply of domestic water to Gusau metropolis, fishing, washing, bathing, and irrigation activities around the catchment area of the Dam, thus make justification for the selection of the study area.

Sampling stations

Four sampling stations were selected and named as sampling station 1, 2, 3, and 4 across the Dam area.

Water sample collection

Water samples were collected at each sampling station (Station 1, 2, 3, and 4) for a period of three months. Water sampling was done by immersing sampling bottles at about 10cm below the water surface. A volume of 500 ml of water sample was collected from each sampling station.

Sediment sample collection

Sediment from each study station was collected using hand shovel into pre-cleaned polythene bag for the period of three months. All the samples were collected under the same condition in one day. The sediment samples collected were kept in polyethylene bags and preserved under a freezing condition (<-20 °C) before laboratory analysis.

Fish samples collection and identification

Three fish species (*Bagrus bayad*, *Clarias gariepinus*, and *Oreochromis niloticus*) were collected monthly for a period of three months at the Dabar Masunta fish landing site of the dam. The fishes were washed using the dam water and preserved in an ice cooler and transported to the Agric. Chemical Laboratory, Faculty of Agriculture, Usmanu Danfodiyo University Sokoto for laboratory analysis.

Heavy metal analysis in water samples

50 ml of water samples were measured into a beaker and 10 ml of concentrated nitric acid was added, the solution was placed in a hot plate and heated to digest under fume cupboard until it was evaporated halfway. The solution was allowed to cool after which it was made to 50 ml with distilled water, this was filtered with a filter paper. The filtrate was used for the determination of Copper, Lead and Cadmium using the method provided by. Atomic Absorption Spectrophotometer (Shimadzu Scientific, Model-AA6300) machine was used for the determination of heavy metals concentration in the water samples.

Heavy metal analysis in fish samples

Fish samples were dissected using sterilize dissecting tools. Two grams of muscle, liver, kidney, intestine, scales, stomach, and gills were extracted for heavy metals analysis. The samples were oven-dried at 105^0C at constant weight and grounded into powder. 10 ml of concentrated nitric acid with 2 ml of perchloric acid were then added to each sample and the mixture was heated on a hot plate at room temperature for five minutes. The samples were then made up to 50 ml using distilled water. The mixture was filtered, and the residue was analyzed for heavy metals using the Atomic Absorption Spectrophotometer (AAS) machine, using the method provided by.

Heavy metal analysis in sediment samples

All the sediment samples collected were removed from freezer, then air dried at room temperature and sieved through a 2 mm nylon sieve to remove coarse debris. The samples were then crushed into fine powder with pestle and mortar and sieved through a 0.149 mm nylon sieve. 5.0 g of each sample was weighed; 4.0 ml of perchloric acid, 125 ml of concentrated HNO_3 and 2 ml of concentrated H_2SO_4 were added. The content was mixed thoroughly and then heated on a hot plate until dense white fume appeared. It was then allowed to cool to room temperature and 40.5 ml of boiled distilled water was added, the solution was filtered completely with a wash bottle into 100 ml conical flask, and the solution was then stored for subsequent analyses. The digest was analysed for heavy metals using different wavelengths by atomic absorption spectrophotometry (AAS) method.

Data analysis

All the data collected on the concentration of Cadmium, Copper, and Lead in fish, water and sediment were subjected to statistical analysis using analysis of variance (ANOVA), and Duncan multiple range taste was used to separate the treatment means where significant differences exist (at p-value 0.05). The statistical analysis was carried out using SPSS version 23 for Windows.

Results

Heavy metals concentration in fish samples

The result of heavy metals concentration in the fish samples obtained from Koramar Wanke dam is presented in Table 1. The result showed that *C. gariepinus* had a higher mean concentration of Cadmium (Cd) with a mean value of 0.04 mg/kg, than the other species examined. However, no significant difference ($p>0.05$) was observed between the treatment means. Copper (Cu) was observed to be highest in *O. niloticus* with a mean concentration of 0.08 mg/kg and significantly ($p<0.05$) differ from the mean value obtained for *B. bayad* (0.02 mg/kg), which in turn had no significant difference ($p>0.05$) with the mean concentration obtained for *C. gariepinus* (0.05 mg/kg). The highest mean concentration of Lead (Pb) was detected in *O. niloticus* with a mean value of 0.06 mg/kg and was significantly different ($p<0.05$) from Pb values obtained for the other species.

Table 1: Mean variation of heavy meatal concentrations in fish species examined from Koramar Wanke Dam.

Fish species	Heavy metals		
	Clarias gariepinus	*Bagrus bayad*	*Oreochromis niloticus*
Cadmium	0.04±0.02[a]	0.02±0.01[a]	0.03±0.01[a]
Copper	0.05±0.04[ab]	0.02±0.01[a]	0.08±0.04[b]
Lead	0.02±0.01[a]	0.02±0.01[a]	0.06±0.02[b]

Means with similar superscripts on the same row are not significantly different (p>0.05).

Heavy metal concentrations in water samples

Table 2 presents the mean variation of heavy metals in water samples examined from the different stations of Koramar Wanke Dam. The result showed that Cd concentration did not differ significantly between the sampling stations with the highest concentration (0.02 mg/l) observed in station 3, while the other stations each had a mean concentration of 0.01mg/l. Cu concentration was highest in station 4 with a mean value of 0.12 mg/l and lowest in station 1 with a mean value of 0.06 mg/l. however, no significant difference (p>0.05) was observed between the treatment means. Station 4 was observed to have highest concentration of Pb (0.11 mg/l) and differed significantly (p<0.05) with the mean concentrations obtained for the other stations with mean values of 0.05 mg/l, 0.04 mg/l, and 0.03 mg/l for stations 2, 3, and 4 respectively.

Table 2: Mean variation of heavy meatal concentrations in water samples across the stations from Koramar Wanke Dam.

Heavy metals	Sampling stations			
	Station 1	Station 2	Station 3	Station 4
Cadmium	0.01±0.01[a]	0.01±0.01[ab]	0.02±0.01[b]	0.01±0.01[ab]
Copper	0.06±0.05[a]	0.10±0.06[a]	0.07±0.12[a]	0.12±0.05[a]
Lead	0.11±0.01[b]	0.05±0.06[a]	0.04±0.02[a]	0.03±0.02[a]

Means with similar superscripts on the same row are not significantly different (p>0.05).

Heavy metal concentrations in the sediment samples

The result of heavy metal concentrations in sediment samples across the sampling stations of Koramar Wanke dam is shown in Table 3. The result showed that Cd concentration was highest in station 4 with a mean value of 0.29 mg/kg and was significantly different (p<0.05) from the concentrations obtained from the other stations. The lowest concentration was obtained in station 1 with a mean concentration of 0.08 mg/kg which is not significantly different (p>0.05) the value obtained for station 2 (0.15 mg/kg), which in turn, is not significantly different (p>0.05) from concentration obtained in station 2 (p>0.05).

Table 3: Mean variation of heavy meatal concentrations in sediment across the stations from Koramar Wanke Dam.

Heavy metals	Sampling stations			
	Station 1	Station 2	Station 3	Station 4
Cadmium	0.08±0.10[a]	0.15±0.05[ab]	0.17±0.10[b]	0.29±0.05[c]
Copper	0.21±0.13[b]	0.14±0.03[a]	0.18±0.01[ab]	0.18±0.01[ab]
Lead	0.13±0.16[a]	0.08±0.10[a]	0.12±0.10[a]	0.17±0.01[a]

Means with similar superscripts on the same row are not significantly different (p>0.05).

Discussion

Mean concentration of heavy metals in fish samples

The result of this study found that Cd concentration in the studied fish samples ranged from 0.02 mg/kg – 0.04 mg/kg and this is within the acceptable limit of about 0.05 mg/kg, set by; When Cadmium is consumed at higher unacceptable limits, it affects the kidneys and causes symptoms of chronic toxicity, such as the impairment of kidney function, poor reproductive capacity, hypertension, tumours, and hepatic dysfunction.

The highest mean concentration of Pb was detected in *O. niloticus* with a mean concentration of 0.06 mg/kg, with the other species examined (*C. gariepinus* and *B. bayad*) each having significantly lower mean concentration of 0.02 mg/kg and this is within the acceptable limits for Pb concentration in fish sample set by. Pb is a non-essential element and can be toxic to humans when ingested or inhaled in high doses. Trace metals such as Pb will interfere with essential nutrients of similar characteristics such as calcium (Ca) and Zn. Pb also causes renal failure and liver damage in humans. In fish, Pb causes decrease in survival, growth, development, behaviour, and metabolism, in addition to an increase in the formation of mucus.

Mean concentration of cadmium in water and sediment across the stations

The mean concentration of Cd in the water and sediment across the stations ranged from 0.01 mg/l – 0.02 mg/l and 0.08 mg/kg – 0.29 mg/kg respectively, and this means that all the values obtained for Cd in the water and sediment during the study were below the permissible limit of 0.99 mg/kg set by. According to, Cd toxicity is characterized by chest pain and lining of lung due to excessive accumulation of watery fluids. Cadmium is a by-product of zinc and lead mining and smelting and more mobile in the aquatic environment than most of the other metals. Cadmium is similar in toxicity to lead and chromium, whereas it is less toxic than copper for plants, while it is equally toxic to invertebrates and fishes. Cadmium is added to the surface water through different sources such as paints, colours and are equally deposited on road surfaces from studded tires.

The mean concentration of Cu in water samples ranged from 0.06 mg/l – 0.12 mg/l, while that the mean concentrations ranged from 0.14 mg/kg – 0.21 mg/kg for all the sediment samples. According to, maximum permissible amount for Cu in river sediment is 31.6 mg/kg. The observed values, therefore, were found to be below the permissible limit. However, copper is very dangerous to fishes, invertebrates and other aquatic animals and plants.

Mean concentration of Pb in the water samples across the stations ranged from 0.03 mg/l-0.11 mg/l while that of the sediment was recorded to be from 0.08 mg/kg – 0.17 mg/kg across all the stations. These observed values of Pb in the present work were found to be below the permissible limit of 35.80 mg/kg set by. This means that the Pb concentration in the water and sediment in this study is safe to aquatic lives. Pb is one of the most established metals known to man and the greater part of its compound is noxious in nature. Pb is found on earth crust in an average concentration of 0.1mg/kg and binds with sulfide ores of zinc, copper and lead obtained as a by-product during processing of ores and is discharged in the surface water through building materials, pipes etc.

Conclusion

Freshwater ecosystems such as rivers, lakes, and streams are vulnerable to heavy metal pollution due to various human activities. It is very important to assess and monitor the levels of potentially toxic heavy metals in fishes, water, and sediments. The present research work was designed to assess

the concentrations of three potentially toxic heavy metals namely, Cd, Cu, and Pb in the fish, water, and sediments of Koramar Wanke Dam. However, it is evident from this study that the fish, water, and sediments in Koramar Wanke Dam were not seriously contaminated with heavy metals during the study period. Using this water for drinking, washing, and fishing may not pose any harmful effect to both humans and animals in the environment. However, it is advisable to continue to take adequate measures to prevent entry of sewage, toxic substances and contaminants from industrial sources and agricultural residues from pesticides and insecticides into the water body. Managing the quality of the water and the sediments will further make the water available for use in terms of quality to the inhabitants of this area. It is also advised that further studies be carried out on the water body in another period and on other heavy metal contaminants to assess the extent at which season play a role in the availability or otherwise of heavy metal accumulation in the water body.

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