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Concentrations of heavy metals in selected fish species from Dadin Kowa Dam, Gombe state, Nigeria

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Abstract
The study was designed to investigate the concentrations of heavy metals in selected fish species and water from Dadin kowa Dam, Gombe State. The liver, gills and muscles of five commercially important fish species (*Clarias gariepinus*, *Oreochromis niloticus*, *Alestes nurse*, *Bagrus bayad* and *Synodontis schall*) and water from Difa, Dadin kowa and Gwani sampling stations of the Dam were collected during both dry (November, December, January and February) and wet (June, July, August and September) seasons. Copper, Lead, Chromium, Cobalt, Nickel, Cadmium, Manganese and Magnesium were analysed using atomic absorption spectrophotometer (Bulk scientific, model 205). The results reveal that Lead was below detectable limits in all the fish species. Meanwhile, the highest concentration of Cr (0.19±0.08mg/kg) and Mg (77.1±0.19mg/kg) were found in the gills of Synodontis schall and that of Co (0.45±0.07mg/kg), Cd (0.05±0.01mg/kg), Ni (0.33±0.03mg/kg) and Mn (2.27±0.24mg/kg) were found in Alestes nurse. There were no significant differences in the concentration of Co, Cd, and Mg among the organs of Oreochromis niloticus. The concentrations of these metals in the water showed that Mg has the highest concentration of 96.060±0.45mg/L while Pb has the least concentration of 0.030±0.01mg/L. the concentrations of Cu, Cr, Co, Ni, Cd and Mn were 0.121±0.02mg/l, 0.948±0.21mg/L, 0.184±0.04mg/L, 0.208±0.05mg/L, 0.110±0.04mg/L and 1.249±0.14mg/L respectively. The concentrations of heavy metals in the water were below the maximum permissible limits of SON, NAFDAC and WHO except Ni and Mn. Likewise, the concentrations of these heavy metals in the various fish organs were within the maximum permissible limits set by WHO and FAO.

Keywords: pollution, health hazard, bio-concentration, toxic

1. Introduction
Fish is widely acceptable in the global menu due to its taste, reduced cholesterol level and tenderness of its flesh [1]. It also receives a high level of concern because of its potential source of protein and some essential nutrients needed by humans [2]. However, pollution of the aquatic ecosystems with heavy metals has become a global concern due to the indestructible properties and adverse effects to aquatic organisms and humans alike [3]. "Heavy metals" is a general term, which applies to the group of metals and metalloids with atomic density greater than 4 g/cm^3, or 5 times or more, greater than water [4]. Among all environmental contaminants, heavy metals are of particular interest, due to their toxic effects and ability to bio-accumulate in aquatic organisms [5].

Water runoff from Ashaka, Kwadon, Zambuk, Gombe and the surrounding towns and villages tends to pick up pollutants from roadways, farmlands, mechanic workshops containing lead-acid batteries, parking lots, corrosive roofs and other materials. These pollutants include petroleum products, pesticides, fertilizers, heavy metals, trash as well as paints, colouring dyes, poisonous chemicals, detergents, cosmetic products, vehicular emissions and industrial by-products. These and many other contaminants and waste product contribute high levels of synthetic organic compounds and heavy metals which subsequently find their way into the Dadin kowa Dam. However, the incorporation of these heavy metals by aquatic organisms into their body systems during feeding may remain for a very long time and these can pass on in the food chain. Fishes, being major components of most aquatic habitats can act as bio-indicators of heavy metals in the environments, and can be used to evaluate the health of such aquatic ecosystems [6]. The study aimed at assessing the concentrations of some heavy metals in commercially important fish species from Dadin kowa Dam, Gombe State so as to establish a baseline data on the current pollution status of the Dam.

2. Materials and Methods

2.1 Study area

Dadin Kowa Dam is located 5km North of Dadin Kowa village (Along Gombe-Biu road, about 37km from Gombe town) in Yamaltu/Deba local Government Area of Gombe State. It is situated at latitude $10^{0}18'0''N$ and longitude $11^{0}30'0''E$ of the equator. The Dam was constructed in 1987 for the primary aim of providing water for Gongola plantation and domestic purposes. It was derived from River Gongola and has a surface area of $300Km^2$ [7].

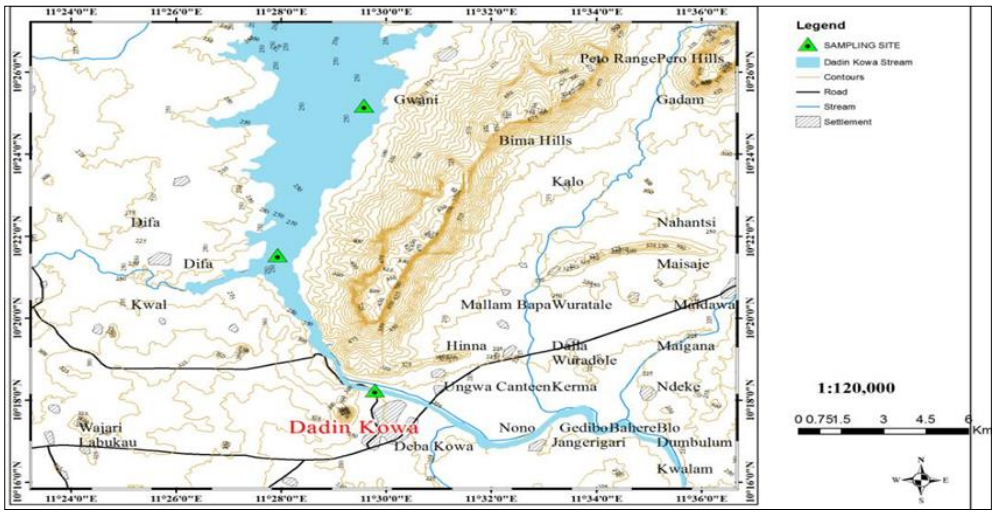

Fig 1: Map of Dadin kowa Dam, Gombe State Nigeria. Showing the sampling stations.

2.2 Collection of fish samples

Fresh fish samples of uniformly sized *Clarias gariepinus* (Burchell, 1822), *Oreochromis niloticus* (Linnaeus, 1758), *Alestes nurse* (Muller and Troschel, 1845), *Bagrus bayad* (Forsskall, 1775) and *Synodontis schall* (Bloch and Schneider, 1801) were caught during dry (November, December, January and February) and rainy (June, July, August and September) seasons from Gwani, Difa and Dadin Kowa sampling station of Dadin kowa Dam. The fish species were selected based on their abundance in the area which is widely consumed by the inhabitants. The fishes were identified using keys from [8]. The fish samples were immediately transported to Biochemistry Laboratory of Gombe State University for preparation on the same day.

2.3 Fish sample preparation

The fish samples were allowed to thaw at room temperature, and then rinsed twice with distilled water to remove dirt and impurities. The fish samples were dissected with clean stainless steel knife to remove the liver, gills and muscles separately. Organs of the five fish species were placed differently on a foil paper and put in an oven at a temperature of $105^{0}C$ for 24 hours to obtain a constant weight [9]. After oven drying, the samples were then homogenized differently using porcelain mortar and pestle. The powdered samples were then put in a sterile sample bottles and labelled.

2.4 Digestion procedure

All glass wares and sample bottles were thoroughly rinsed with deionized water and oven dried before the digestion. Powdered samples (2g of each sample) were weighed accurately with a weighing balance (Ohaus Model- AR 2130) and put into a round bottom flask. Concentrated acids of 6 ml nitric acid (HNO_3, 65%), 3 ml of hydrochloric acid (HCl, 37%) was prepared in a measuring cylinder and added to each sample and shaken. It was then placed on a hot plate to digest until a transparent or clear solution was attained. The solution was allowed to cool then filtered with whatman No.1 filter paper. The filtrate obtained was filled up to a mark of 100ml using deionized water. The solution was then transferred into a labelled sample bottle for analysis. Sample blank was also prepared using the same digestion procedure but without the fish samples in it and transferred into sample bottles for analysis.

2.5 Sample analysis

All samples were analysed in the Biochemistry laboratory of Gombe State University. An atomic absorption spectrophotometer (Bulk scientific, model 205) was used for the analysis. Calibration of the instrument was performed by first analysing two standard solutions for each metal, followed by the blank analysis before the sample analysis. Before analysing each metal, its standard solutions and blank have to be analysed first. For quality assurance, all samples were analyzed in triplicate. The metals analyzed for were Cadmium, Copper, chromium, cobalt, nickel, magnesium Lead and Manganese.

2.6 Bio-concentration factor

The Bio-concentration Factor was determined using this formula:

$$Cf = \frac{C0}{Cwa}$$ [10]

Where
Cf = concentration factor
C_0 = concentration of metal in tissues
C_{wa}= concentration of metal in test water

2.7 Data analysis

Data obtained were analyzed using Statistical Package and Service Solution (SPSS version 20.0) for Windows. Means of significance were separated using Duncan multiple range test ($P<0.05$) to assess variability between species and organs.

3. Results

The heavy metal concentration in fish species obtained from

Dadin Kowa Dam is shown in Table 1. Despite the differences in the mean value, there were no significant differences in the concentration of Co, Cd, and Mg among the organs in *Oreochromis niloticus*. However, there were significant differences (P<0.05) in Ni, Cd and Mg among the organs in *Synodontis schall*. Lead was below detectable limits in all the fish species. Meanwhile, the highest concentration of Cr (0.19±0.08mg/kg) and Mg (77.1±0.19mg/kg) were found in the gills of *Synodontis schall* and that of Co (0.45±0.07mg/kg), Cd (0.05±0.01mg/kg), Ni (0.33±0.03mg/kg) and Mn (2.27±0.24mg/kg) were found in *Alestes nurse*. The lowest concentrations of Co (0.18±0.02mg/kg), Cd (0.01±0.00mg/kg) and Mn (1.12±0.05mg/kg) were found in *Synodontis schall*. The concentration pattern of heavy metals in all the organs of *S. schall* was in the order of Mg>Mn>Co>Cr>Ni>Cd>Cu>Pb. All the organs of *O. niloticus* showed the same order of Mg>Mn>Co>Ni>Cr>Cu>Cd<Pb while the muscles and gills of *C. gariepinus* had follow the order of Mg>Mn>Co>Ni>Cr>Cu>Cd>Pb.

Table 2 shows the bio-concentration factor of heavy metals in Liver, Muscles and Gills of Fish species obtained from Dadin Kowa Dam. The highest bio-concentration factor of Cu (1.06±0.40), Cd (4.40±2.12) and Mn (1.82±0.18) were found in liver of *C. gariepinus*, gills of *B. bayad* and muscle of *A. nurse* respectively. There were no significant differences in the bio-concentration factor of all the five fish species among the various organs except in the bio-concentration factor of manganese in *C. gariepinus* and *A. nurse*. The lowest value of Co (1.23±0.42) and Ni (0.80±0.31) were observed in the liver of *S. schall*. The bio-concentration factors of heavy metals in *O. niloticus* muscles and gills were in the order of Co>Mn>Ni>Cd>MgCu>Cr>Pb while that of liver, was Co>Ni>Mn>Cd>Mg>Cu>Cr>Pb. The bio-concentration pattern of the liver, muscles and gills of *C. gariepinus* were in the order of Co>Mn>Ni>Cu>Cd>mg>Cr>Pb; Cd>Co>Mn>Ni>Mg>Cu>Cr>Pb and Co>Mn>Cd>Ni>Mg>Cu>Cr>Pb respectively.

Table 3 shows the mean heavy metal concentration of water from Dadin kowa Dam. Mg has the highest concentration of 96.060±0.45mg/L while Pb has the least concentration of 0.030±0.01mg/L. the concentrations of Cu, Cr, Co, Ni, Cd and Mn were 0.121±0.02mg/l, 0.948±0.21mg/L, 0.184±0.04mg/L, 0.208±0.05mg/L, 0.110±0.04mg/L and 1.249±0.14mg/L respectively.

Table 1: Mean heavy metal concentrations (mg/kg) in fish species obtained from Dadin Kowa Dam, Gombe State.

Species	Organs	Cu	Pb	Cr	Co	Ni	Cd	Mn	Mg
Oreochromis	Liver	0.03±0.00^{a}	ND	0.06±0.01^{a}	0.42±0.02	0.25±0.01^{b}	0.01±0.00	1.84±0.02^{c}	55.8±0.07
Niloticus	Muscle	0.04±0.00^{a}	ND	0.07±0.00^{a}	0.37±0.04	0.15±0.02^{a}	0.01±0.00	1.71±0.02^{b}	56.7±0.10
	Gills	0.06±0.01^{b}	ND	0.10±0.01^{b}	0.44±0.03	0.20±0.01^{c}	0.01±0.00	1.61±0.04^{a}	59.7±0.12
Clarias	Liver	0.11±0.02^{b}	ND	0.04±0.00	0.23±0.03	0.18±0.01	0.02±0.00	1.46±0.09^{a}	57.9±0.05
Gariepinus	Muscles	0.03±0.01^{a}	ND	0.04±0.00	0.23±0.02	0.14±0.01	0.03±0.01	1.42±0.19^{a}	60.0±0.02
	Gills	0.04±0.00^{a}	ND	0.05±0.02	0.26±0.03	0.17±0.02	0.01±0.00	1.96±0.08^{b}	60.3±0.08
Bagrus	Liver	0.04±0.01^{b}	ND	0.07±0.02	0.30±0.03	0.20±0.02^{b}	0.03±0.01	1.50±0.06	60.3±0.11
Bayad	Muscles	0.01±0.00^{a}	ND	0.04±0.00	0.27±0.03	0.15±0.01^{a}	0.03±0.01	1.65±0.16	67.8±0.14
	Gills	0.03±0.01^{ab}	ND	0.06±0.00	0.33±0.03	0.18±0.02^{ab}	0.03±0.01	1.68±0.08	72.6±0.13
Synodontis	Liver	0.01±0.01	ND	0.17±0.08	0.18±0.02	0.12±0.02^{a}	0.01±0.00^{a}	1.26±0.12^{ab}	76.5±0.22
Schall	Muscles	0.01±0.00	ND	0.18±0.08	0.19±0.02	0.17±0.01^{b}	0.03±0.01^{ab}	1.12±0.05^{a}	72.9±0.17
	Gills	0.02±0.01	ND	0.19±0.08	0.2033	0.18±0.01^{b}	0.04±0.01^{b}	1.48±0.11^{b}	77.1±0.19
Alestes	Liver	ND	ND	ND	0.40±0.05	0.33±0.03^{b}	0.05±0.01^{b}	1.35±0.06^{a}	66.0±0.16^{b}
Nurse	Muscles	ND	ND	ND	0.45±0.07	0.20±0.05^{a}	0.01±0.00^{a}	2.27±0.24^{b}	49.8±0.10^{a}
	Gills	0.01±0.00^{b}	ND	0.04±0.00^{b}	0.36±0.03	0.15±0.01^{a}	0.02±0.00^{a}	1.87±0.11^{b}	60.9±0.03^{b}

Key: Mean in the same column with different superscript differ significantly (P<0.05); ND= Not Detected

Table 2: Bio-concentration factor of heavy metals in liver, muscles and gills from fish species in Dadin Kowa Dam.

Species	Parts	Cu	Pb	Cr	Co	Ni	Cd	Mn	Mg
Oreochromis	Liver	0.28±0.03	ND	0.04±0.01	2.73±0.70	1.60±0.54	0.68±0.32	1.50±0.17	0.59±0.07
Niloticus	Muscle	0.41±0.06	ND	0.05±0.02	2.41±0.64	0.99±0.30	0.68±0.32	1.39±0.14	0.59±0.05
	Gills	0.58±0.17	ND	0.08±0.00	2.85±0.78	1.30±0.49	0.68±0.32	1.31±0.15	0.62±0.05
Clarias	Liver	1.06±0.40	ND	0.02±0.02	1.34±0.29	1.07±0.26	1.01±0.57	1.19±0.12^{a}	0.61±0.03
Gariepinus	Muscles	0.27±0.06	ND	0.01±0.01	1.33±0.15	0.88±0.23	1.38±0.85	1.13±0.12^{a}	0.63±0.03
	Gills	0.29±0.04	ND	0.02±0.01	1.59±0.29	0.99±0.20	1.02±0.56	1.58±0.10^{b}	0.63±0.04
Bagrus	Liver	0.14±0.07	ND	0.06±0.03	1.87±0.09	1.27±0.38	2.40±1.81	1.24±0.03	0.86±0.18
Bayad	Muscles	0.11±0.02	ND	0.03±0.02	2.19±0.27	1.26±0.39	1.40±0.83	1.00±0.12	0.76±0.07
	Gills	0.27±0.12	ND	0.02±0.01	2.24±0.32	2.12±0.69	4.40±2.12	0.97±0.18	0.85±0.10
Synodontis	Liver	0.17±0.16	ND	0.16±0.16	1.23±0.42	0.80±0.31	0.69±0.31	1.41±0.41	0.79±0.07
Schall	Muscles	0.10±0.08	ND	0.18±0.16	1.32±0.52	1.09±0.36	1.71±1.17	1.38±0.39	0.75±0.06
	Gills	0.23±0.20	ND	0.18±0.16	1.42±0.55	1.12±0.33	2.72±1.40	1.57±0.32	0.80±0.04
Alestes	Liver	0.04±0.04	ND	ND	2.59±0.69	2.07±0.64	3.70±2.31	1.09±0.08^{a}	0.69±0.09
Nurse	Muscles	ND	ND	0.01±0.01	2.47±0.20	1.29±0.40	0.68±0.32	1.82±0.18^{b}	0.52±0.03
	Gills	0.02±0.02	ND	0.01±0.01	2.38±0.75	0.93±0.29	1.34±0.64	1.52±0.14^{ab}	0.64±0.03

Key: Mean in the same column with different superscript differ significantly (P<0.05); ND= Not Detected

Table 3: Heavy metal concentrations (mg/L) in water obtained from Dadin Kowa Dam, Gombe State.

Metals	Cu	Pb	Cr	Co	Ni	Cd	Mn	Mg
Conc.	0.121±0.02	0.030±0.01	0.948±0.21	0.184±0.04	0.208±0.05	0.110±0.04	1.249±0.14	96.060±0.45

4. Discussion

The highest concentrations of Ni, Cd and Mn were found in the liver of *Alestes nurse* (Table 1) which is a benthic feeder. This could be as a result of high exposure of bottom feeding fish to the sediment which contained high concentrations of these metals and it could also be as a result of the important roles performed by the liver. This is similar to Annune [11]; Demirak *et al.* [12] and Yang *et al.* [13] who reported that metals accumulate in high concentrations in the liver, because the organ has relatively higher potential for metal accumulation than the muscle. The liver is the metabolizer and major detoxifier of the body [14]. The Cd and Ni concentrations reported in this study were similar to studies of Mustafa and Guluzar [15] in the liver of *Triglacuculus* from the northeast Mediterranean Sea, Oronsaye *et al.* [16]. from Ikpoba River, Babatunde *et al.* [17]. in *H. Forskahlii* and *C. gariepinus* from downstream Ogun coastal water but higher than the study of Akpanyung *et al.* [18] in *Chrysichthys nigrodigitatus* from Ifiayong River, Akwa Ibom State.

Copper is considered to be an important part of many enzymes but occur in very low levels in food [19]. From this study, the highest concentration of Cu was found in the liver of *C. gariepinus.* This value was below the 1.0-3.0 and 3.0 mg/kg recommended limits for food fish by FEPA [20] and WHO [21] respectively; thus indicating that the fish species examined could not pose copper related hazards to consumers. The high level of Copper in the liver is due to the fact that Copper toxicity in fish is taken up directly from the water via gills and stored in the liver [22]. The concentration of Cu in this study was below the concentrations in the liver, gills and muscles of *C. gariepinus* from Kubanni River [23], *T. zilli* and *C. gariepinus* from River Benue [24], and the concentration in *T. guineensis* from Nworie River [25].

The highest concentrations of Cr and Co were found in the gills of *S. Schall* and *O. niloticus* respectively. This is because gills tissues play a very important role in interface with the environment in gas exchange, ion regulation, acid balance and waste excretion [26]. The muscles contained lesser concentrations of these heavy metals compared with the gills and the liver, this is similar with Annune [27] who reported that low accumulation of metals were found in muscle tissues of *C. gariepinus* which is considered poor in heavy metal uptake. The concentrations of Cr and Co in this study were similar with the concentration in *Parachanna obscura* from Ogba River in Benin City [28], *T. zilli* and *Schilbe mystus* from Cross River system [29]. However, it was lower than the concentrations in gills of fish found along the coastal region of Valinokkam [30], *C. gariepinus* and *H. forskahlii* as reported by Babatunde *et al.* [17] from downstream Ogun coastal water, *T. zilli* and *C. gariepinus* from River Benue [24]. In comparison to other reports on the concentrations of Mg in fish, the fish species showed lower Mg concentrations; therefore, Dadin Kowa Dam fish species are not very good sources of magnesium. Taking into account that Mg is not potentially harmful to fish and wildlife and that little is known concerning whether or not elevated levels of Mg in fish tissues are harmful to humans and others [31]. Although, the level of Mg is higher than all other metals studied, it is still safe for consumption. This is because the recommended daily intake of magnesium for adults is 220-260mg [32]. The magnesium concentrations in this study are lower than the values obtained by Adeniyi *et al.* [33], and Martinez-Valverde *et al.* [34].

The high concentrations of Mn indicate that the Dam has a high concentration of Mn irrespective of the species. It thus suggests that all the fish species studied could pose manganese related health problems which may manifest in the form of impulsive and aggressive behaviour, in some cases euphoria and sexual stimulation [35]. On the other hand, high concentrations implies that other variables may affect the concentrations of the metal, such as the rate of uptake and excretion, chemical form of the metal, feed and feeding habit of the species [36]. The concentrations of Mn obtained in this study from the liver, muscles and gills of all the five fish species are above 0.40mg/kg as recommended by WHO [21] and FEPA [20], but lower than the concentration in *C. gariepinus* and *T. zilli* from River Benue [24]. Hence, the result obtained is similar with the findings of Obasohan [28] and Idodo-Umeh [37] in fish species from Ogba River and Olomoro water bodies respectively in Nigeria.

The non significant differences in the bio-concentrations factors of all the five fish species among the various organs except in manganese in *C. gariepinus* and *A. nurse* was because *C. gariespinus* and A. *nurse* are bottom feeders and the differences could be as a result of the mode of feeding habit and diet which serves as a major factor that determine heavy metals concentrations in fish [38]. However, the result obtained from this study is similar with the findings of Edward *et al.* [39], Orata and Birgen [38]; but were lower than the report of Syarifah *et al.* [40]

The concentrations of heavy metals in the water from this study were lower than the concentrations recorded by Aderinola *et al.* [41] in Lagos lagoon, but higher than the report by Shittu *et al.* [42], Jenyo-Oni and Oladele [43] in Lake Asejire, Maitera *et al.* [44] in River Gongola and Akaninwor *et al.* [45] in Rivers State Nigeria. The heavy metal concentration in water samples of Dadinkowa Dam when compared with National standards (National Agency for Food and Drug Administration and Control (NAFDAC), Standard Organization of Nigeria, (SON)) and International standard (World Health Organization, WHO) revealed that the concentrations of Cd, Pb, Co, Ni and Cr were higher except Cu, Mn and Mg which were lower (Table 3). This comparison becomes necessary to reveal the heavy metal pollution status of the Dam as it concerns the safe use of the water body for domestic purposes and as a healthy aquatic habitat. The increase in concentrations of these metals could be attributed to indiscriminate disposal of industrial, domestic and municipal wastes and runoffs of agricultural chemicals.

5. Conclusion

The concentrations of all the metals were below the WHO, FAO and FEPA maximum standard limit for fish food except Mn which was higher; which is an indication that the consumption of these fish species may not pose any health hazard to the consumers. The concentration pattern of heavy metals in all the organs of *S. schall* is in the order of Mg>Mn>Co>Cr>Ni>Cd>Cu>Pb. All the organs of *O. niloticus* showed the same order of Mg>Mn>Co>Ni>Cr>Cu>Cd<Pb while the muscles and gills of C. gariepinus follow the order of Mg>Mn>Co>Ni>Cr>Cu>Cd>Pb. The concentrations of Cd, Pb, Co, Ni and Cr in the water were higher than NAFDAC, SON and WHO permissible limit for human consumption while Cu, Mn and Mg were within the permissible limits. The bio-concentration factors of the fish organs indicate that the rate of uptake of metals by the studied fish through water is very low; hence the concentrations of the heavy metals might

be through the feeds they consumed.

6. Recommendation

Although, the heavy metals concentration of Dadin kowa Dam is mild for now, there is need to closely monitor the pollution status of the Dam so that it does not get out of control. Similar studies may be carried out on the bioaccumulation and magnification of these heavy metals in the Dam and to equally check contamination with other toxic metals such as Mercury, Arsenic, Tin, etc in the commercially important fish species of Dadin Kowa Dam.

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