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Assessment of Heavy Metals and Physicochemical Parameters in Fish and Water Samples in Sallari Pond, Tarauni Local Government Area, Kano State, Nigeria

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ABSTRACT

The present study was conducted to examine some physicochemical properties and heavy metal level in fish and water samples of Sallari pond, Kano State. The pH results ranged from 7.22 ±0.03 - 7.26 ±0. The conductivity results were all within the SON and WHO limits of 1000µs/cm except sample B (1233±0.00) which is above the limit. The results for turbidity ranged from (13.6 ± 0.01 - 15.00 ± 0.00) NTU, all the samples analyzed were within the SON and WHO limits of 5.0NTU. The result of the heavy metals in the water samples ranged from Zn (0.006±0.0001 - 0.011 ± 0.001) mg/l, Cd (0.00 ± 0.00 - 0.001±0.00) mg/l, Fe (0.03±0.01 - 0.16 ±0.01) mg/l, Cu (0.002 ± 0.00 - 0.0014±0.01) mg/l, Pb(0.0004±0.00 - 0.004±0.001) mg/l, Mn (0.0006±0.02 - 0.002±0.01) mg/l and Cr (0.00±0.00 - 0.002±0.001) mg/l. All the metal analyzed were within the SON and WHO limits of Zn(3.0), Cd(0.003), Fe(0.3), Cu (1.0), Pb (0.01), Mn (0.2) and Cr (0.05) mg/l respectively. The results for the fish samples ranged from Zn (27.20±0.00-545.60±0.01) mg/kg, Cd (3.20±0.01-51.20±0.03) mg/kg, Fe (30.40±0.05-6136.00±0.02) mg/kg, Cu (6.40±0.01-76.80±0.01) mg/kg, Pb (3.20±0.01-491.20±0.2) mg/kg, Mn (8.00±0.001-86.40±0.03) mg/kg and Cr (41.60±0.001-252.80±0.03) mg/kg. All the samples analyzed have their metal concentrations above FAO/WHO limits of Zn (40), Cd (0.1), Fe (100), Cu (30), Pb (0.4), Mn (1.0) and Cr(0.5)mg/kg. Also, the result for Bioconcentration Factor (BCF) shows that the entire metal studied have their BCF values above the USEPA Toxic Substance Control threshold limits of≥ 5000mg/kg, which implies that the studied metals are very bioaccumulative in the fish samples and other aquatic animals in the pond.

Keywords: Bioconcentration, FAO, Heavy Metals, Sallari pond, SON

INTRODUCTION

The day to day activities of human has continuously caused serious disturbance to the natural environment. The industrial waste water as well as domestic sewage always containing heavy metals and eventually finds their ways into nearby water bodies (Mehjbeen and Nazura, 2012). Heavy metals are trace metals that are denser than water five times or with density greater than 5g/cm^3, which means they are stable and cannot be breakdown or metabolized by body system, hence bio-accumulated (Ekpo *et al.*, 2008). The bioaccumulation and biomagnification of heavy metals in living organism explain the process and pathway in which the pollutants move from one trophical level to another (Svobodova *et al.*, 2004) Heavy metals pollution of aquatic environments always has direct consequences to aquatic organisms, man and fishes. Some heavy metals such as Zn, Fe, Mn, Cr, Cu are essentials and only become harmful when their concentration exceed acceptable limits while metals such as Pb, As, Cd, Hg are non essentials and harmful even at minute concentration (Ekweozor *et al.*, 2017). Heavy metals have been known to cause damages to the body system through the production of free radicals in key parts of the body organ such as heart, kidney, liver brain etc which caused oxidative stress which is the basis of many ailments (Castro-Gonzalez and Mendez-armenta, 2008). Higher levels of heavy metals in biota can have negative effects on the ecological health of aquatic animal species and may contribute to declines in their populations (Luo, 2014). Heavy metals are strong neurotoxins in fish species. The interaction of heavy metals with chemical stimuli in fish may interrupt the communication of fish with their environment (Baatrup, 1991). Heavy metals have been found associated with fish deformities in both natural populations and in the laboratory. Generally, such deformities have negative effects on fish populations because deformities affect their survival, growth rates, welfare, and external image. These deformities in fish can serve as excellent biomarkers of environmental heavy metal pollution (Sfakianakis, 2015). Hausawa Sallari Pond is created as a result of land excavation for the past 40years.The Pond is widely used for fishing and irrigation as well as dump site for the domestic waste water from different households. The aim of this study was to assess the physicochemical parameters in the water samples and the level of heavy metals pollution in the fish samples in the pond to know their suitability for irrigation and consumption purpose.

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MATERIALS AND METHODS

In the preparation of reagents, all the glassware used were thoroughly washed and rinsed several times with distilled water and oven dried. The chemicals used were of analytical grade.

Study Area

Hausawa Sallari Pond is located in Gyadi gyadi Kano State, Nigeria. It is situated closed to Waje and southwest of Nassarawa Local government in Kano Metropolis. It has a geographical coordinate of latitude 11°58'8"N and longitude 8°32'45"E (Nwagbara, 2015). Figure 1 and 2 shows the Map of the studied areas.

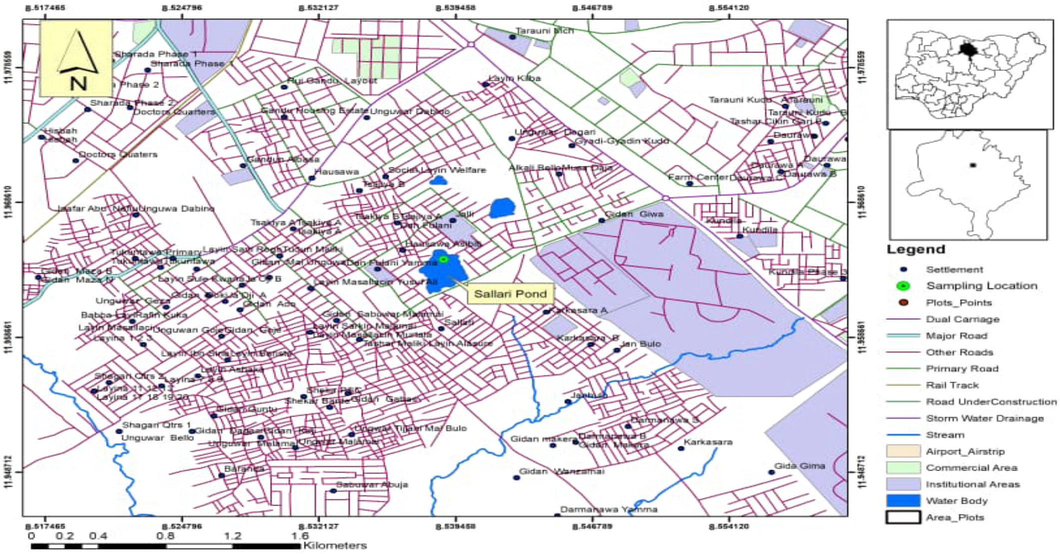

Figure 1: Map of Kano State Showing the Study Area.

Figure 2: Polluted Sallari Pond

Collection of Water Samples

Water samples were collected from five different locations of the lake. Five (5) litres were collected from each location into clean container and transferred to the laboratory and refrigerated at 4ºC for preservation (Jimoh and Sholadoye, 2013).

Collection of Fish Samples

Four (4) Samples of fish were collected from each zones and immediately kept in a pre-cleaned polythene bags, sealed and stored in an ice box and transferred to the laboratory for further analysis (Javed and Usmani, 2011).

Table 1: Water samples description and coding

Code	**Description**
A	North end of the lake
B	West end of the lake
C	South end of the lake
D	East end of the lake
E	Middle of the lake

Fish Samples Identification

The fish samples were submitted for identification at Biological Science Department of Nigeria Police Academy, Wudil, Kano State.

Table 2: Fish Samples Identification and Coding

Code	Fish Species	Description
G	*Oreochromis niloticus* (Tilapia Fish)	North end of the lake
H	*Oreochromis niloticus* (Tilapia Fish)	West end of the lake
I	*Oreochromis niloticus* (Tilapia Fish)	South end of the lake
J	*Oreochromis niloticus* (Tilapia Fish)	East end of the lake
K	*Oreochromis niloticus* (Tilapia Fish)	Middle of the lake

Pretreatment of Fish Samples

The fresh fish samples were oven dried at 60°C and ground into fine powder using pestle and mortar and sieved through 2 mm mesh sieve and stored in a clean and labeled plastic container for further analysis.

Digestion of Fish Samples

0.5g of oven dried fish sample at 60°C were accurately weighed into 50ml pyrex beaker and digested in 15ml of solution containing conc. HNO_3 and $HClO_4$ (4;1) . the solution was filtered with Whatman filter paper (No 42), washed and transferred into 50ml volumetric flask and made up to mark with distilled water (Javed and Usmani, 2013).

Evaporation of Water Samples

4000cm^3 of each water samples were reduced to 200cm^3 by evaporation using Pyrex beaker and hot plate at 105°C. Then, 5.0cm^3 of Concentrated HNO_3 was added and further evaporated at 105°C for 5hrs. The solution was allowed to dry to about 25cm^3 and cool to room temperature. The solution was filtered into 50cm^3 standard volumetric flask and made to mark with distilled water (Abdulrahaman and Abdulhakeem, 2015).

Physicochemical parameters Measurement

The pH, Conductivity, Turbidity and TDS of the water samples were measured on the spot using Palintest Photometer 7500 Bluetooth, an Advanced Portable Water Quality Laboratory Kits. A duplicate measurement was recorded.

The COD and BOD of the water samples were determined following the procedures described by (APHA and AWWA, 2012) was calculated from equation 1.

$$COD = \frac{(A - B) \times N \times 8000}{V_s} \frac{mg}{L} \qquad (1)$$

i.e A = mL of $[Fe(NH_4)_2(SO_4)_2.6H_2O]$ in the blank. B = mL of $[Fe(NH_4)_2(SO_4)_2.6H_2O]$ in the water sample , N = normality of the titrant and Vs = the mL of sample.

The BOD_5 was calculated from equation 2.

$$BOD = \frac{DO_i - DO_f}{A} \qquad (2)$$

i.e. DO_i, DO_f and A are initial and final DO concentrations and dilution factor .

Bioconcentration Factor (BCF)

BCF, as depicted in equation 3, is used to estimate the levels of heavy metals accumulation in fish samples. It is calculated using the expression described by (Suheryanto and Ismarti, 2018).

$$BCF = \frac{C_{biota}}{C_{ambient}} \qquad (3)$$

i,e. C_{biota} = is the Concentration of the heavy metals in the fish in (mg/kg) and $C_{ambient\ medium}$ is the concentration of the heavy metals in the water sample in (mg/L).

RESULTS AND DISCUSSION

Table 3: Physicochemical parameters of the water samples

Samples	pH	Conductivity µS/cm	Turbidity (NTU)	Total Dissolved Solids (TDS)mg/L	Chemical Oxygen Demand (COD)mg/L	Biochemical Oxygen Demand (BOD) mg/L
A	7.22 ±0.03	673.30±0.006	13.6 ±0.01	301.50±0.02	41.60 ±0.03	9.80 ±0.01
B	7.23 ±0.06	1233.00±0.01	13.60 ±0.03	550.90±0.01	36.00 ±0.01	8.60 ±0.01
C	7.24 ±0.04	682.20 ±0.02	12.90 ±0.02	305.60±0.03	38.40 ±0.02	8.80 ±0.03
D	7.25 ±0.02	721.40 ±0.01	11.60 ±0.04	321.60±0.02	60.00 ±0.04	14.30 ±0.001
E	7.26 ±0.03	728.40±0.001	15.00 ±0.01	321.20±0.01	56.00 ±0.01	13.50 ±0.02
SON (2015)	**6.5 - 8.5**	**1000**	**5.0**	**500**	**30**	**6.0**
WHO (2008)	**6.5-8.5**	**1000**	**5.0**	**-**	**-**	**-**

The pH values for the water samples analyzed ranged from 7.22 to 7.26. Sample A had the least pH value while sample E had the highest value. All the samples analyzed have the pH value within SON (2015) and WHO (2008) limit of 6.5 – 8.5. High pH value usually caused by high bicarbonate concentration which can lead to blockage of irrigation system as a result of bicarbonate precipitation while low pH value can lead to corrosion problem in irrigation system. (Emmanuel *et al*, 2016). The conductivity results for the water samples analysed ranges from 673.30 to 1233 µS/cm. Sample A had the least value of 673.30 µS/cm while Sample B had the highest conductivity value of 1233 µS/cm. All the samples analysed had conductivity values within SON (2015) and WHO (2008) limits of 1000 µS/cm except Sample B. Electrical conductivity measures the dissolved ions of the solution. Water salinity is key parameters that affect crop productivity. The implication of high value of EC in water samples for irrigation is the inability of the plant to compete with ions in the soil solution for water (Bauder *et al*. 2014).

The result for turbidity in all the analyzed samples ranged from 11.60 to 15.0NTU. Sample D had the least value of 11.60NTU while sample E had the highest value of 15NTU. The entire samples analyzed had turbidity value higher than SON (2015) and WHO (2008) limit of 5.0NTU. The high turbidity values of the present studies might be attributed to suspension of the burning and dumping of refuse practiced in the environment. Turbidity indicates the levels of materials that are suspended in water. It provides information on the scattering and absorbing properties of water caused by the presence of particle such as clay,silt,colloids and microorganism(Ojo *et al*.,2012). The total dissolves solid for the water samples analysed ranges from 301.50 mg/L to 550.90mg/L. Sample A had the least value of 301.50mg/L while Sample B had the highest value of 550.90mg/l. The entire samples analyzed were within SON (2015) limit of 500mg/L except Sample B.

Total Dissolved Solids (TDS) is a means of measuring the amount of dissolved salt in water and hence a measure of the salinity (Emmanuel *et al*, 2016). Holmes (1996) explained that a total dissolved solids value of less than 40mg/l can be used as irrigation water. From another source TDS value of less than 450mg/l can also be used as irrigation water (Ayers and Westcot, 1994). The results for Chemical Oxygen Demand (COD) in the water samples analyzed ranges from 36.0 to 60.0(mg/L). Sample B had the least value of 36.0(mg/L) while sample D had the highest value of 60.0(mg/L). The entire samples analyzed had COD values above the SON (2015) limits of 30. COD is defined as the amount of oxygen equivalents consumed in oxidizing the organic compounds of samples by strong oxidizing agents such as dichromate or permanganate. The higher the chemical oxygen demand, the higher the amount of pollution in the water sample. High values of COD in this study might be attributed to different type of domestic and industrial refuse dumped in the lake which contained strong chemical oxidants. Rubel *et al*., (2019) reported COD values ranging 80 to 1436 mg/L in their studies. High COD value was observed in one of the samples (1436 mg/L) of KB Chemicals Factory which is higher than acceptable limit of (200 mg/L).

The Biochemical Oxygen Demand (BOD) result for the water samples analyzed ranges from 8.60 to 14.30(mg/L). Sample B had the least value while Sample D had the highest BOD values. All the water samples analyzed had the BOD values above the SON (2015) limits of 6.0. Biochemical oxygen demand (BOD) is a measure of the oxygen requirement for the biochemical degradation of organic materials and the oxygen used to oxidize inorganic materials such as sulfides, ferrous ions and reduced forms of nitrogen (Rubel *et al*., 2019). As dissolved oxygen (DO) level decreases the BOD will be increased, different types of microorganism will be formed and the water sample becomes polluted.

Table 4: Metal concentration in water samples (ppm)

Samples	Zn	Cd	Fe	Cu	Pb	Mn	Cr
A	0.006±0.0001	ND	0.052±0.001	0.0014±0.01	0.0008±0.001	0.0006±0.01	0.0003±0.01
B	0.008 ±0.001	ND	0.059 ±0.01	0.002±0.002	0.0008±0.001	0.0006±0.02	0.0001±0.01
C	0.009 ±0.001	ND	0.053±0.001	0.002 ±0.01	0.0006±0.002	0.0006±0.01	0.0001±0.01
D	0.011 ± 0.001	0.001±0.001	0.16 ±0.01	0.005±0.01	0.004±0.001	0.002±0.01	0.002±0.001
E	0.011 ± 0.001	ND	0.03±0.01	0.0011±0.02	0.0004±0.001	0.0005±0.001	ND
SON (2015)	**3.0**	**0.003**	**0.3**	**1.0**	**0.01**	**0.2**	**0.05**
WHO (2008)	**3.0**	**0.003**	**0.3**	**2.0**	**0.01**	**0.2**	**0.05**

Table 5: Metal concentration in fish samples (mg/kg)

Samples	Zn	Cd	Fe	Cu	Pb	Mn	Cr
G	27.20±0.01	3.20 ±0.01	3219.00±0.4	76.80±0.01	491.20±0.2	86.40±0.03	252.80±0.03
H	296.0±0.03	33.60±0.02	315.20±0.03	43.20±0.2	6.40±0.03	8.00±0.001	49.60±0.01
I	262.40±0.01	51.20±0.03	6136.00±0.02	17.60±0.05	3.20±0.01	40.00±0.01	252.80±0.04
J	488.0±0.002	38.40±0.04	475.20±0.10	17.60±0.03	4.80±0.04	44.80±0.02	342.40±0.01
K	545.60±0.01	12.80±0.01	30.40±0.05	6.40±0.01	3.20±0.01	11.20±0.02	41.60±0.001
FAO/WHO 1983/ 1989	**40.0**	**0.1**	**100.0**	**30.0**	**0.4**	**1.0**	**0.5**

The concentrations of Zn in the water samples analyzed ranged from 0.006 - 0.011mg/l. Sample A had the least concentration of 0.006mg/l while sample D and E had the highest Zn concentration values of 0.011mg/l respectively. All the samples analyzed were within the SON (2015) and WHO (2008) limits of 3.0mg/l. The Zn concentration in the fish samples analyzed ranged from 27.20 to 545.6mg/kg. Sample G had the least concentration of 27.20mg/kg while sample K had the highest concentration of 545.60mg/kg. All the samples analysed for fish samples were above FAO/WHO (1989) limits of 40.0mg/kg. Zinc is important element that balances copper in the body and very essential for male reproductive activities but excess amount of it can causes body system dysfunction and can result to impairment of growth and reproduction (Nolan, 2003).

Cadmium concentrations in the analyzed water samples ranged from not detected (ND) to 0.001mg/l. Cadmium is present in only one sample (sample D) and the concentration is within the SON (2015) and WHO (2008) limits of 0.003mg/l. The concentrations in other samples might be below the detection limits of the instruments While Cadmium concentration in the fish samples analyzed ranged from 3.20 to 51.20 mg/kg. Sample G had the least concentration of 3.20mg/kg while sample I had the highest concentration of 51.20mg/kg. All the sample analysed were above the FAO/WHO (1983/1989) limits of 0.1mg/kg. Cadmium and lead have been reported not to have known function in human biochemistry or physiology but long term exposure of cadmium caused renal dysfunction, lung disease and cadmium pneumonitis (Young, 2005).

Iron concentration in the water samples analyzed ranged from 0.03 to 0.16mg/l. Sample E (0.03mg/l) had the least concentration while sample D (0.16mg/l) had the highest concentration. All the samples analyzed were within SON (2015) and WHO (2008) limits of 0.3mg/l. Likewise, Fe concentration in the fish samples analyzed ranges from 30.40 to 6136.0 mg/kg. Sample K had the least concentration of 3.40mg/kg while sample I had the highest Fe concentration of 6136.0mg/kg. All the samples analyzed had Fe concentration above the FAO/WHO (1983/1989) limits of 100.0mg/kg. Excess iron has been implicated in the pathogenesis of diabetes and its complications (Thomas *et al.,* 2003). Free iron serves as a catalyst for lipid and protein oxidation and the formation of reactive oxygen species. In addition, iron indices are correlated with obesity and insulin sensitivity. However, iron indices are strongly correlated with Hemoglobin (Hb), which represents an important risk factor for morbidity and mortality in patients with diabetes, particularly in patients with established cardiovascular disease (Beckman *et al.,* 2002).

The concentrations of copper in the water samples analysed ranged from 0.002 to 0.0014mg/l. Samples B and C had the least concentration of 0.002mg/l respectively while A had the highest concentration of 0.0014mg/l. All the samples analyzed were within the SON (2015) and WHO (2008) limits of 1.0mg/l respectively. The Cu concentrations in the fish samples analyzed ranged from 6.4 to 76.0mg/kg. Sample K had the least concentration of 6.40mg/kg while sample G had the highest concentration of 76.0mg/kg. All the samples analyzed had Cu concentration above the FAO/WHO (1983/1989) limits of 30.0 mg/kg. Cu is an essential trace element that has an important role in many physiological functions in nervous, hematological, cardiovascular, reproduction and immune systems. Moreover, Cu plays a significant role, being associated with specific proteins. The majority of the biological functions of Cu are believed to be associated with copper's role as a ligand in the active site of metalloenzymes (AbdElghany and Heba, 2015). However, an increase in Cu concentration has been linked to disorders in the structure of the arterial walls, stress, infection, and diabetes mellitus (Beshgetoor and Hambidge, 1998).

Lead concentration in the present study ranged from 0.0008 to 0.004mg/l. Samples A and B had the least concentrations of 0.0008mg/l respectively while sample D had the highest concentration of 0.04mg/l. All the samples analyzed were within the SON (2015) and WHO (2008) limits of 0.01mg/l respectively. The Pb concentration in the fish samples analyzed ranges from 3.2 to 491.0mg/kg. Samples I and K had the least concentration of 3.20mg/kg respectively while sample G had the highest concentration of 491.0mg/kg. All the samples analysed had Pb concentration above the FAO/WHO (1983/1989) limits of 0.4 mg/kg. Lead is recognized for its teratogenic effects. Lead poisoning causes dysfunction kidney, chronic damage to the central nervous system, peripheral nervous system and gastrointestinal tract (Lenntech, 2004).

The concentrations of manganes in the water samples analyzed ranged from 0.0006 to 0.002 mg/l. Samples A, B and C had the least concentrations of 0.0006mg/l each while Sample D had the highest concentration of 0.002mg/l. All the samples analyzed were within SON (2015) and WHO (2008) limits of 0.2 mg/l respectively. The Mn concentration in the fish samples analyzed ranges from 8.0 to 86.40mg/kg. Sample H had the least concentration of 8.0mg/kg while sample G had the highest concentration of 86.40mg/kg. All the samples analyzed had Mn concentration above the FAO/WHO (1983/1989) limits of 1.0 mg/kg.

Chromium concentrations in the water samples analyzed ranged from 0.0 to 0.002mg/l. Sample E had the least concentration of 0.0mg/l while sample D had the highest concentration of 0.002mg/l. All the samples analyzed were within the SON (2015) and WHO (2008) limits of 0.05mg/l respectively. The Cr concentrations in the fish samples analyzed also ranged from 41.60 to 342.40mg/kg. Sample K had the least concentration of 41.60mg/kg while sample J had the highest concentration of 342.40mg/kg. All the samples analyzed had Cr concentration above the FAO/WHO (1983/1989) limits of 0.5 mg/kg. Cr supplementation increases muscle gain and fat loss associated with exercise and improves glucose metabolism and the serum-lipid profile in patients with or without diabetes (Bahijiri and Mufti, 2002). Chromium is involved in both carbohydrate and lipid metabolism. Insufficient dietary Cr is associated with increased risk factors linked with non-insulin dependent diabetes and cardiovascular diseases (Khamaisi *et al.*, 2003).

Table 6: Bioconcentration Factor (BCF) for the fish samples (mg/kg)

Zn	Cd	Fe	Cu	Pb	Mn	Cr
35,982	27,840	28,745	14,052	77,090	44,279	375,680
Regulatory Act				Threshold limits		
Regulation (EC) No 1907/2006 (REACH)				≥ 2000 = bioaccumulative ≥ 5000 = very bioaccumulative		
US EPA Toxic Substances Control Act(TSCA)				≥ 1000 = bioaccumulative ≥ 5000 = very bioaccumulative		

The bioconcentration factors for all the metal in the present studies were shown in Table 6; Zn (35982), Cd(27840), Fe (28745), Cu (14052), Pb (77090), Mn (442790) and Cr (375680) respectively. The results show that all the metals were very bioaccumulative and biomagnified in the fish samples using threshold limits by US EPA (2016) Toxic Substance Control Act (TSCA). These results also explain the reason for high concentration of metals in all the fish samples analyzed.

CONCLUSION

The results for the physicochemical parameters analyzed in the water samples shows that only sample B have Conductivity and TDS values above WHO/SON limits. Likewise, the concentration of heavy metals in all the fish samples analyzed were above the FAO/WHO limits with very high value of bioconcentration factor (BCF) which above USEPA limits of less than 1000, but the concentrations of the metals in the water samples were within the SON/WHO limits. This implies most of the metals in the lake were bioaccummulated in the aquatic organisms and plants within the lake and its environment. Since, all metals investigated had high concentrations in the fish samples, which is one of the main sources of protein in form of fish in the environment therefore government should introduce laws which will prevent people living in the community from dumping refuses in the lake and industries that are making use of standard waste treatment plants for the treatment of their wastes before they are being discharged into water bodies. Some monitoring programs should also be introduced from time to time in order to prevent the misuse of valuable water resources, to check their water quality status, and to restore them for the welfare of society and to protect the natural environment. Since these fishes share the same local market therefore, they must be screened by food agencies such as NAFDAC before consumption.

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