



## LEVELS OF HEAVY METALS IN SOME SELECTED FISH OF RIVER GONGOLA BASIN, ITS DAM AND DADINKOWA DAM, GOMBE STATE NIGERIA

\*Santuraki, A. H., Babayo, A. U., Abdu Zakari and Abdulkadir, A. G.

Department of Chemical science, Federal University of Kashere, Gombe State, Nigeria

\*Corresponding author's Email: [santurakiah65@gmail.com](mailto:santurakiah65@gmail.com)

### ABSTRACT

This study was carried out in ten (10) different locations within River Gongola, its Dam, and Dadinkowa Dam, Gombe State, Nigeria during the wet and dry season to study the water quality in terms of physicochemical properties to ascertain the levels of contaminants due to flooding and anthropogenic activities and the levels of heavy metals (Cr, Cd, Pb, and Ni) in the two species of fish (*Clarias gariepinus* and *Bagrus docmak*). A total of 200 water and 360 fish samples comprising two different species were collected in the month of March-June 2017 (Dry season) and July-October 2017 (Wet Season). The results of physicochemical properties obtained ranges between Temperature 29.0-30.0°C and 30-32.0°C, pH 5.4-7.8 and 6.0-6.9, Conductivity 93.3-161 µS/cm<sup>3</sup> and 104.9-128 µS/cm<sup>3</sup>, Dissolved oxygen 1.2-3.98 mg/l and 0.4-3.1 mg/l, Total Suspended Solids 10-860 mg/l and 13-1180 mg/l, Total Dissolved Solids 46.5-80.5 mg/l and 54.2-76.5 mg/l, Turbidity 424.7-783.5 NTU and 11.15-442.1 NTU, Phosphate 1.82-7.23 mg/l and 0.00-0.11 mg/l, and Nitrate 2.25-8.82 mg/l and 2.68-6.81 mg/l during wet and dry season respectively. The result reveals that turbidity, PO<sub>4</sub>, DO, TSS, and TDS were above the acceptable permissible limits of WHO. While the mean concentration levels of heavy metals in *Clarias gariepinus* and *Bagrus docmak* revealed that Cr was below the detectable limit while Cd ranges between 0.5-7.75 µg/g, Pb ranges between 3.9-35.6 µg/g during the wet and dry season. The mean concentrations of all the studied metals were above the permissible limit of WHO with a higher concentration during the dry season.

**Keywords:** Dadinkowa Dam, Fish, Heavy Metals, River Gongola

### INTRODUCTION

Pollution of water bodies by heavy metals has been in the public domain of recent days because human beings can be exposed to toxic metals which bioaccumulate in aquatic organisms harvested from contaminated waters (Svensson et al., 1995). In recent years, heavy metals pollution, especially in the food chain has attracted much attention (Harmanescu et al., 2011). Heavy metals are daily being leached into rivers and dams from anthropogenic sources including industrial waste both solid and liquid waste, agricultural activities by the use of agrochemical and residential activities leading to increased heavy metals and accumulation in the aquatic environment. The pollutants are distributed in the rivers water, dams and are bio-accumulated by the fishes and other aquatic animals in the water and this leads to bio-magnification of these pollutants in the food chain (Zafer et al., 2007; Bhupander et al., 2011; Ajiboye et al., 2011). Therefore, it has become of great importance to prevent agricultural and industrial contamination to water bodies (Avishai et al., 2002; UNFPA, 2003). The negative effects of heavy metals on the aquatic ecosystem are bio-accumulative behavior and their health impact on organisms (Babatunde et al., 2012). Aquatic organisms bio-accumulate heavy metals because they have membranes that are easily penetrated by heavy metals due to their lipophilicity. Hence, dietary intake of heavy metals via fish and water is a public health concern (Obiakor et al., 2014). Fish are widely consumed in many parts of the world because it has high protein content, low saturated fat and also contains omega fatty acids known to support good health (Ginsberg and Toal, 2012). Fish and other aquatic organisms can absorb and accumulate heavy metals in the body (Copat et al.,

2012) this accumulation behavior depends on various parameters such as characteristics of the species under consideration, the exposure period temperature, salinity, water pH and seasonal changes in water characteristics. River Gongola is faced with heavy metals pollution due to precipitation and urban runoff which leach these pollutants from anthropogenic sources into the water bodies like any other river across the world. The deterioration of water quality is a significant problem for the rivers due to urbanization, industrialization and trade growth along the bank of the confluence. Hence because of the toxicological importance of this edible clam, it is therefore imperative for studies to be conducted to assess the levels of heavy metals in fish muscle from some selected location within River Gongola and its dam and to verify whether or not the concentrations in the clams are within the permissible limits for human consumption in comparison to WHO guideline.

### MATERIALS AND METHODS

#### Study Area

The study area is Gombe State, which occupies part of the central position of the North-Eastern part of Nigeria located at latitude 9° 48'00"N and longitude 11° 16' 00"E with a total landmass of 20,265 km<sup>2</sup> and annual rainfall of 1550.77 mm. Gombe State has an estimated average population of 4,260,530 with the elevation of plain at 600 m above level and hills reach between 700 m and 800 m. The Gongola River is the main drainage system, running approximately north south towards the Benue river basin but with south toward the tributaries draining from west to east into Gongola River as shown in Figure 1. Dadinkowa dam is located about 5 km North of Dadinkowa village in Yamaltu Local Government Area of

Gombe State, Nigeria. The area lies at longitude  $10^{\circ} 19'19''N$  and latitude  $11^{\circ} 28'54''$ , about 37 kilometers to the eastern part of Gombe. The dam is part of River Gongola; its drainage basin is situated in North-Eastern Nigeria, with a capacity of 800

million cubic meters of water and a surface area of 300 square kilometers. Around it are villages inhabited mostly by farmers, Ashaka cement factory, and agricultural activities are performed along the river banks.

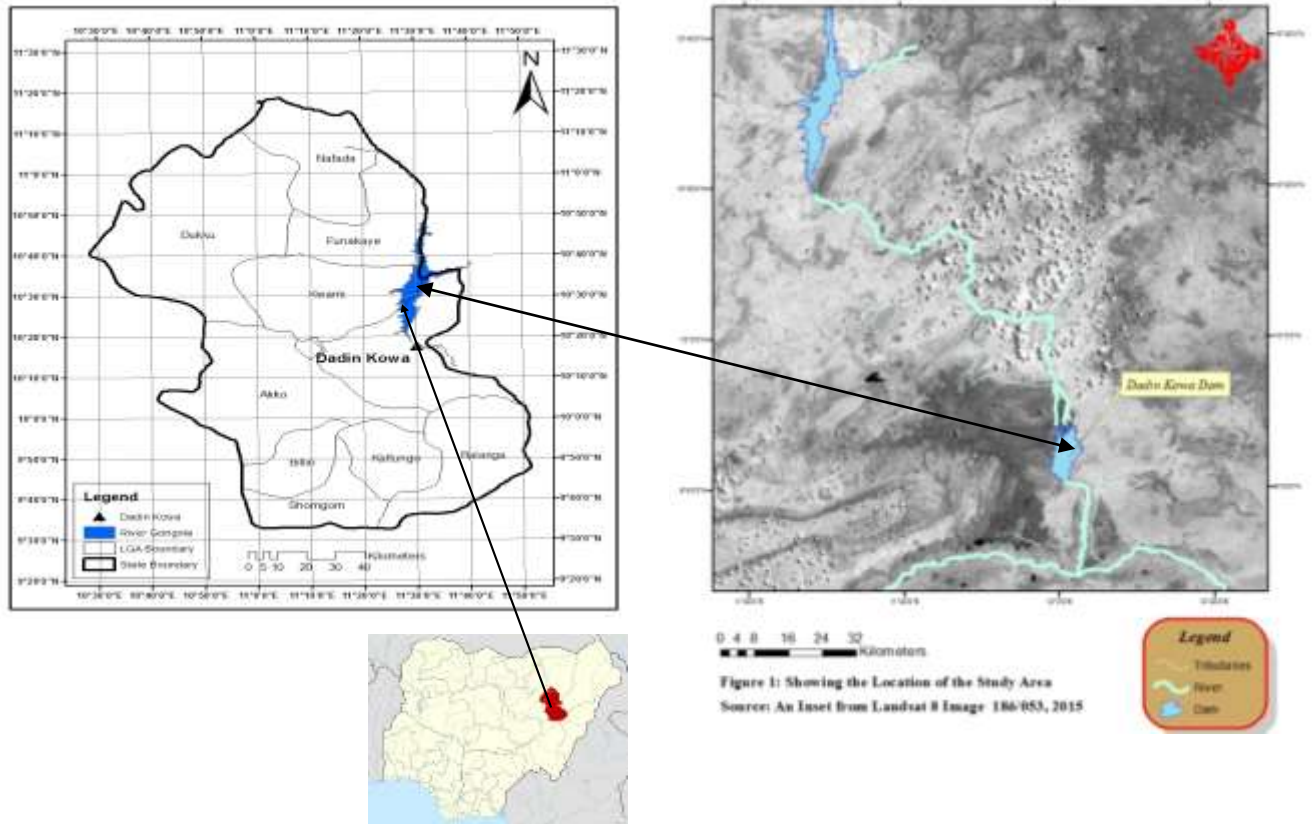


Figure 1: Map of Gombe and Nigeria showing the study area

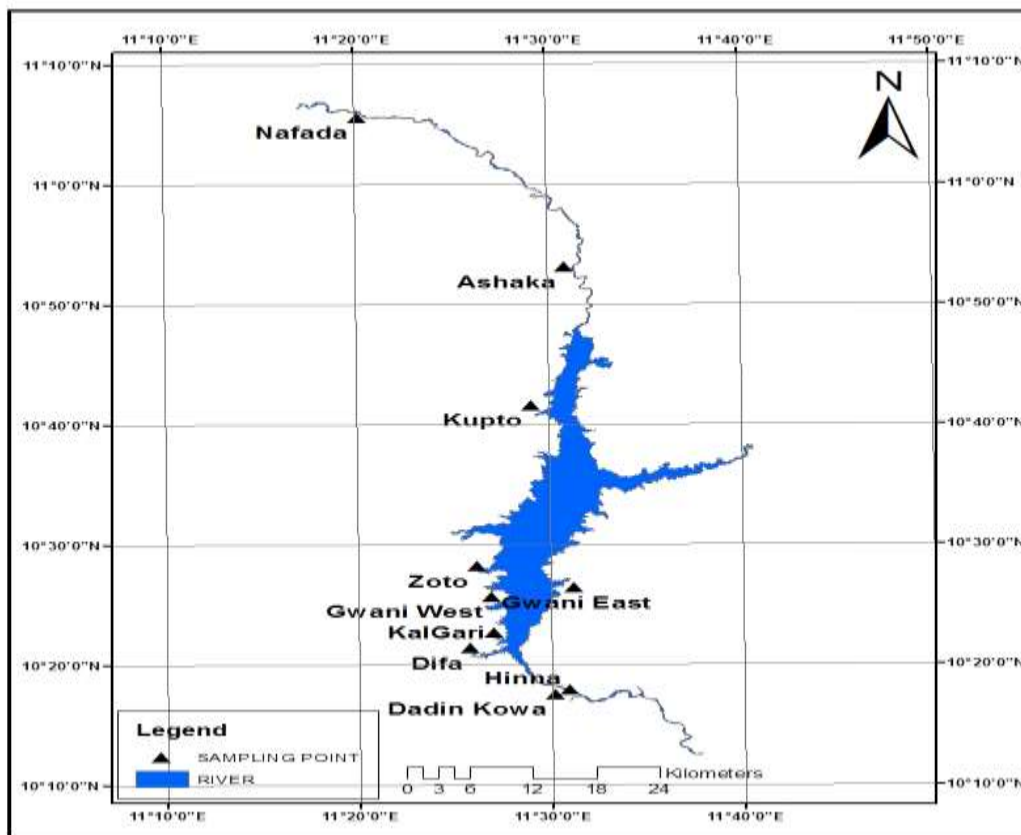


Figure 2: Map showing the sampling points

**Sample Collection**

A total of 200 water samples were collected from ten (10) different locations, comprising 10 from each location. Two samples were collected from each sampling point monthly. The sample bottle was immersed completely to a depth of about 0-2 meters; it was allowed to remain in that position until the bottle was full. Sampling was done in March - June 2017 (dry season) and July-October 2017 (wet Season) using a global positioning system to identify where samples were collected. pH, Conductivity, Temperature and Turbidity were determined immediately on the site, collected samples were transported to the chemistry laboratory, Gombe State University, Gombe State, Nigeria where analysis of TDS, TSS, DO, Alkalinity, Nitrate and Phosphate were carried out immediately.

**Table 1: Methods and instruments used for determination of physicochemical parameters in water samples**

S/No	Parameters	Units	Methods of Analysis	Instruments / Apparatus used
1.	Temperature	°C	Probe Meter	Glass bulb thermometer
2.	pH		Probe Meter	Digital JENWAY pH meter (Model 3310)
3.	Turbidity	NTU	Probe Meter	Digital JENWAY Turbidimeter (Model 3350)
4.	TDS	Mg/l	Gravimeter	Oven, Petri dish
5.	TSS	Mg/l	Gravimeter	Oven, Petri dish
6.	DO	Mg/l	Colorimeter	HANNA Dissolved oxygen meter (Model HI 9143)
7.	Conductivity	µS/cm	Colorimeter	HANNA Conductivity meter (Model HI 9143)
9.	Nitrate (NO <sub>3</sub> )	Mg/l	Uv-v spectrophotometer	JENWAY (model 6300) Spectrophotometer
10.	Phosphate (PO <sub>4</sub> <sup>3-</sup> )	Mg/l	Uv-v spectrophotometer	JENWAY (model 6300) spectrometer

A total of three hundred and sixty fish samples comprising two different species were caught randomly using gill net from River Gongola within 10 different locations for the periods of March – June 2017 as dry season and July - October 2017 as the wet season. The species for their analysis were based on the availability at both dry and wet seasons at the time of sampling. Species obtained were reflective of what was commonly for human consumption. All samples were obtained fresh on different occasions from the river and transported on an ice chest to the laboratory and kept in the freezer. The portion of edible Muscles tissue was removed from the dorsal part of each fish, homogenized and stored in a cleaned-capped glass vials and kept in the freezer in the chemistry laboratory of Gombe State University. All reagents and solvents were of analytical grade obtained from BDH Chemicals Ltd, Poole, England. All glassware and vessels used were thoroughly washed by soaking them overnight in 10% HNO<sub>3</sub> and rinsing in distilled water, they were then rinsed once with 0.5 % (v/v) K<sub>2</sub>MnO<sub>4</sub> and three times with distilled water and air-dried in the oven before use.

#### Standard Preparation

Each metal standard solution was prepared for calibration of the instrument for each element is determined on the same day as the analyses were performed due to possible deterioration of standard with time. 1 gram of metal Cd, Pb and Ni were dissolved in HNO<sub>3</sub> solution while 2.8 gram K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (1 g of Cr) was dissolved in water and made up to 1 liter in a volumetric flask with distilled water, thus the stock solution of 1000 mg/l Cd, Cr, Ni and Pb were prepared. (Cantte, J.E 1982). Then 100 ml of 0.1, 0.25, 0.5, 0.75, 1.0 and 2.0 mg/l working standards of each metal were prepared from these stock using micropipettes of 5 ml of 2N Nitric acid

#### Validation of Proposed Develop Method

Method of validation was assessed by determining several analytical figures of merit according to the international conference on Harmonization (ICH, 1994), namely range, precision sensitivity which is expressed by determination of limit of detection (LOD) and limit of quantitation (LOQ)

#### Quality Assurance

Each sample was analyzed replicated for analytical quality control, reagent blank and sample replicates were randomly inserted in the analysis process to assess contamination and precision. Recovery studies were conducted to demonstrate the efficiency of the overall procedure using certified reference material (CRM) fish homogenate International Atomic Energy Agency (IAEA) 407, Vienna.

#### Digestion procedure

Fish muscle tissue was digested by an open tube procedure, 1 g of homogenized fish muscle was weighed into 50 ml pyrex glass test tube (26 mm \* 47mm) and 1 ml of H<sub>2</sub>O, 4ml of HNO<sub>3</sub>:HClO<sub>4</sub> (1:1) and 5 ml of H<sub>2</sub>SO<sub>4</sub> was added. The mixture was heated at a temperature of 200 °C for 30 minutes when a

colorless solution was obtained. The digest was allowed to cool to room temperature and diluted with distilled water to the 50 ml mark. The solution was then shaken thoroughly and transferred into clean capped bottles and kept in the refrigerator until the analysis.

#### Determination of Heavy Metal using AAS

Reagent blank determinations were used to correct the instrument readings. The analytical technique used for samples preparation, standard preparation and analyses of metals were determined with AAS Buck Scientific Model 205 VGP, East Norwalk, The USA. It is a standard analytical tool for metal analysis and is based on the absorption of electromagnetic radiation by atoms. The key feature is the production of free, ground state atoms from the sample, which pass through the light beam from the hollow cathode lamp. For many conditions, the absorption of radiation follows Beer's law.

Where; A = Absorbance, A<sub>s</sub> = Molar absorptivity, B = Path length and c = concentration of the absorbing species. Beer's law shows a relation between absorption and concentration of analytic so calibration of the instrument is needed. The absorption wavelengths and detection limits for Cd, Cr, Pb and Ni are 228.9 nm, 357.9 nm, 232.0 nm, and 283.3nm and 0.01 mg/l, 0.04 mg/l, 0.05 mg/l and 0.08 mg/l

#### Statistical Analysis

Pearson's product-moment Correlation matrix was done to identify the relationship among metal location/season to make the result valid obtained from multivariate analysis.

## RESULTS AND DISCUSSION

The physicochemical parameters are paramount important and influenced by natural and mammalian activities. They also depend upon the depth of the water body and the ecological condition of the ecosystem. However, both the physical and chemical parameters of collected water samples along the ten different locations during dry and wet seasons have been tested and the results were discussed and compared with WHO and other related research work. The temperature of water within all the ten different locations varies from 29-30 °C during the wet season while during the dry season temperature varies from 30-32 °C metabolic rate and reproduction activities of aquatic life are controlled by water temperature as shown in Figure below. This may have led to the scavenging of the depleted metallic element alongside nutrients from the water resulting in their ion concentration. Metabolic activity increases with a temperature rise, thus increasing the demand for oxygen by fish. However, an increase in river temperature also led to a decrease in dissolved oxygen (DO), limiting the amount of oxygen available for these aquatic organisms. With all the limited amount of DO, fishes in this system may stress. However, the temperature at p>0.05 had no significant difference along with the ten different locations during wet and dry seasons.

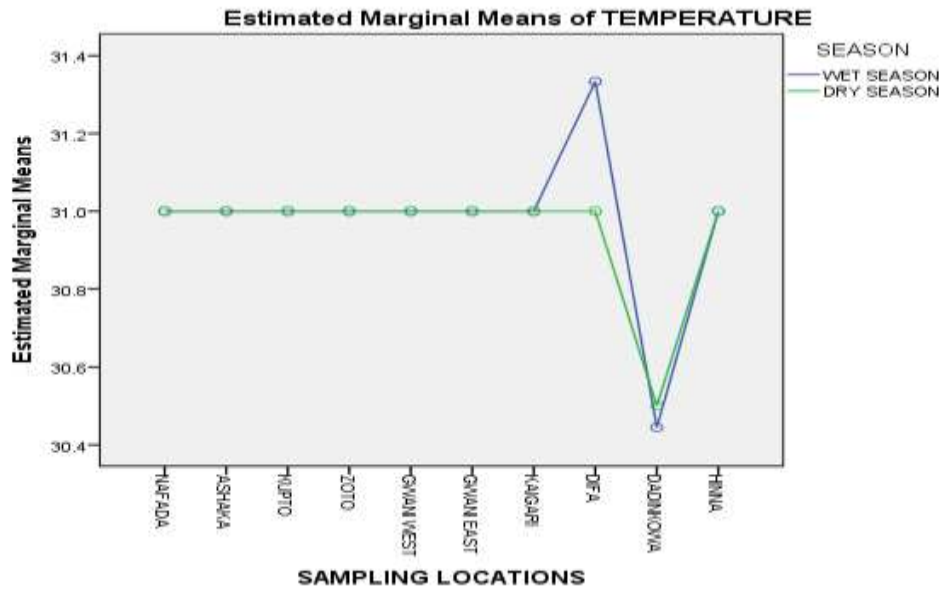


Figure 3: Recorded temperature values of the water along with different locations

pH is the measure of acidity or alkalinity of the water. It is one of the important parameters that determine the survival, physiology, metabolism and growth of aquatic pH environmental organisms (Ramana *et al.*, 2006). However, pH had the lowest mean value of 5.4 at Kalgari and the highest value of 7.8 at Dadinkowa during the dry season, while during the wet season, the lowest value of 6.0 was recorded at Zoto and the highest value of 6.9 at Hinna as shown in Figure below. Higher values of pH lead to alkalinity and this may lead to the adsorption of elements into particular matters. However, all the value obtained was within the permissible limit of 6.5-8.5 WHO 2011. Hence, pH at  $p > 0.05$  had a significant difference along with the ten different locations during wet and dry seasons.

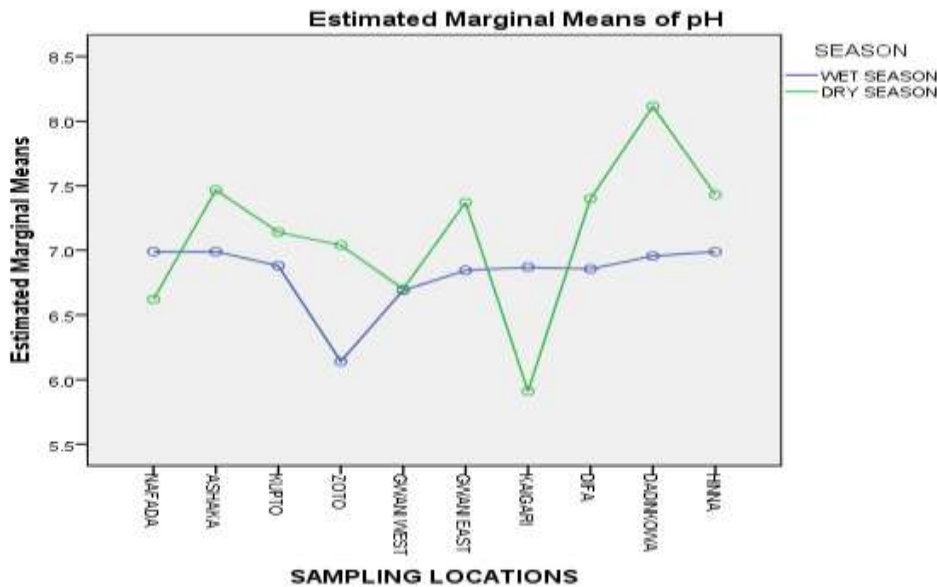


Figure 4: Recorded values of pH in the water along with the different locations

The conductivity of water is a function of the concentration of dissolved ions (Asuquo, 1999). Though conductivity is not of human or aquatic health concern because it is measured, it can serve as an indicator of other water quality problems. Increases in water conductivity indicate the sources of dissolved ions in the water bodies. However, during the dry season the lowest mean value of 104.9  $\mu S/cm^3$  was recorded at Nafada and the highest mean value of 128  $\mu S/cm^3$  at Kupto, while during the wet season, the lowest mean value of 93.3  $\mu S/cm^3$  was observed at Difa with the highest mean value 161  $\mu S/cm^3$  at Zoto obtained during dry and wet seasons as shown in Figure below were below the permissible limit of 180  $\mu S/cm^3$  WHO and USEPA 2006. This low value may be due to the dilution of water by rain during the wet season. However, at  $p > 0.05$ , conductivity had a significant difference along with the ten different locations during wet and dry seasons.

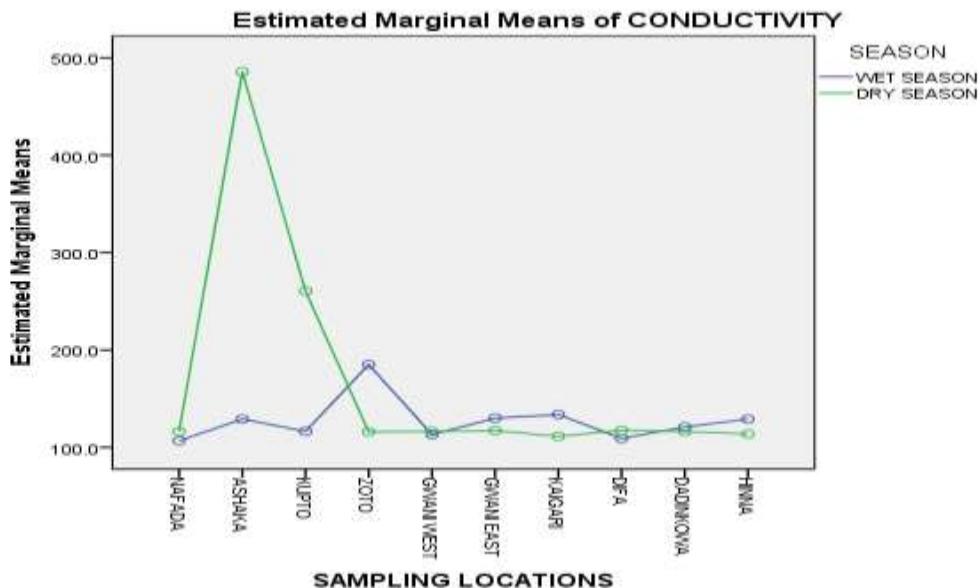


Figure 5: Recorded conductivity values of the water along with different locations

Dissolved Oxygen (DO) is an important water parameter indicating the quality of water and organic production (Wetzel and Likens, 2006). The survival of aquatic Flora and Fauna especially fish depends on dissolved oxygen in the water. Hence DO had the lowest mean value of 0.4 mg/l at Gwani East and the highest mean value of 3.1 mg/l at Ashaka & Kupto during the dry season while during the wet season the lowest mean value of 1.2 mg/l was observed at Zoto and the highest mean value of 3.98 mg/l at Nafada as shown in Figure below. All the results obtained were below the values reported by Maitera et al., 2010 and the 5.0 mg/l permissible limit of WHO 2006. This may be as a result of the high rate of microbial-mediated oxidation of contamination from runoff into the water body. However, at  $p > 0.05$ , DO had a significant difference along with the ten different locations during wet and dry seasons.



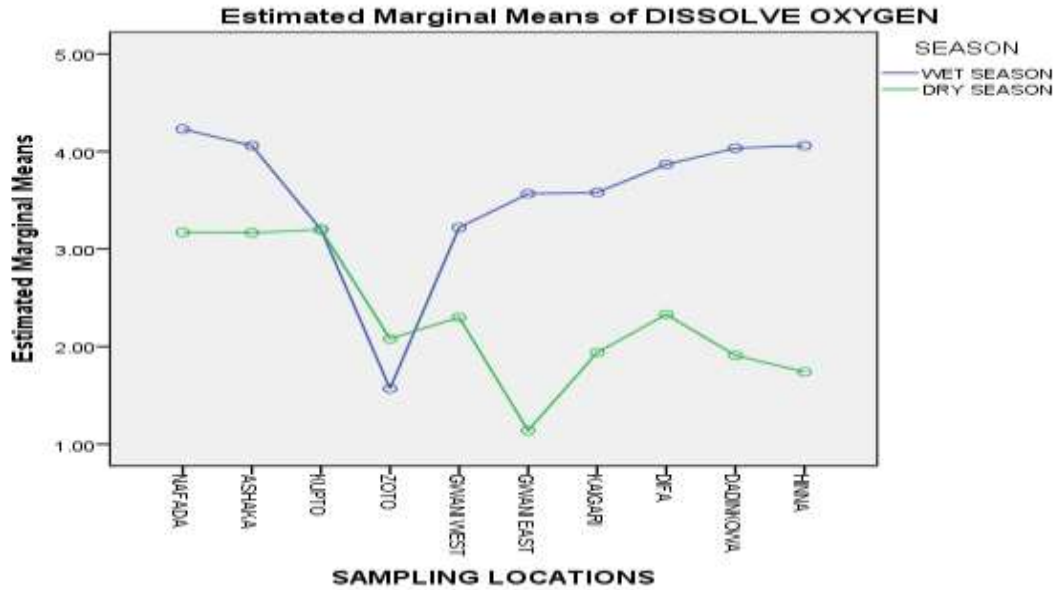


Figure 6: Recorded dissolved oxygen values of the water along with different locations

Total suspended solids (TSS) may enter the water body through run-off; that is, erosion by rainwater, upland soil erosion and land Sliding, etc. However, during the dry season, TSS had the lowest mean value of 13 mg/l at Difa and the highest mean value of 1180 mg/l at Ashaka while during the wet season TSS had the lowest recorded mean value of 10 mg/l at Gwani East, Dadinkowa and Hinna with the highest mean value of 860 mg/l at Ashaka as shown in Figure below. In the water bodies, they are present either as suspended solids which may reduce light penetration, decrease algal growth and also lead to low algal productivity and reduction in aquatic invertebrates. However, all the mean values obtained were below the permissible limit of 1000 mg/l WHO 2008 except in the dry season at Ashaka where the mean value is above 1000mg/l (1180 mg/l) which is also below the value reported by Hong et al., 2014. This could be a result of solid waste from Ashaka Cement Company. Hence, at  $p > 0.05$  TSS had a significant difference along with the ten different locations during wet and dry seasons.

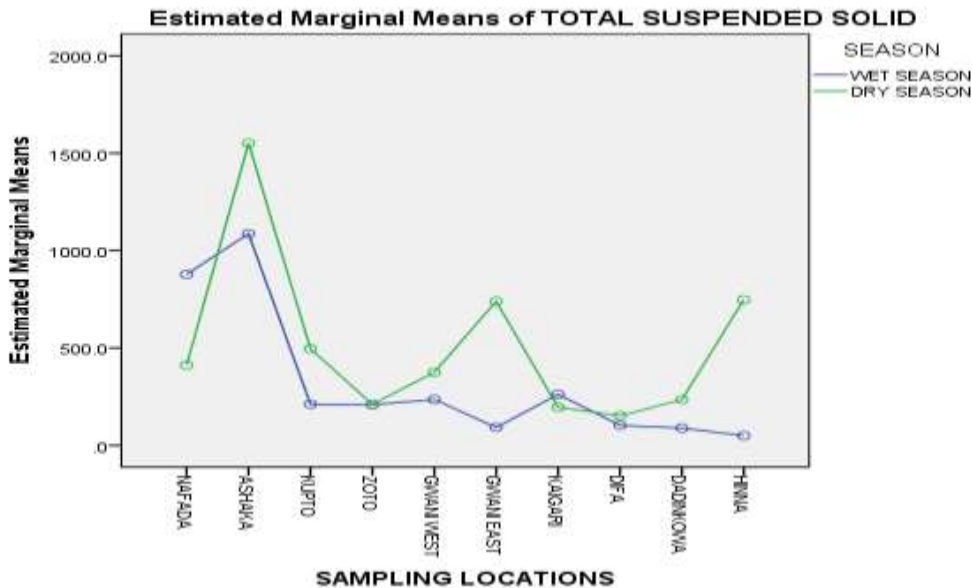


Figure 7: Recorded values of TSS in the water along with different locations

Total Dissolve Solid (TDS) water can dissolve a wide range of inorganic and organic minerals or salt such as potassium, calcium, sodium, bicarbonate, and chlorides, etc. These minerals produce an unwanted taste and diluted color in the appearance of water. TDS had the lowest value of 54.2 mg/l at Ashaka and the highest value of 76.5 mg/l at Kupto during the dry season while during wet season TDS had the lowest value of 46.5 mg/l at Difa and highest value of 80.5 mg/l at Zoto as shown in figure 1.7. However, these values were lower as compared to the values reported by Hong et al., 2014 and WHO 2002 (500 mg/l). Hence, at  $p > 0.05$ , TDS had a significant difference along with the ten different locations during wet and dry seasons.

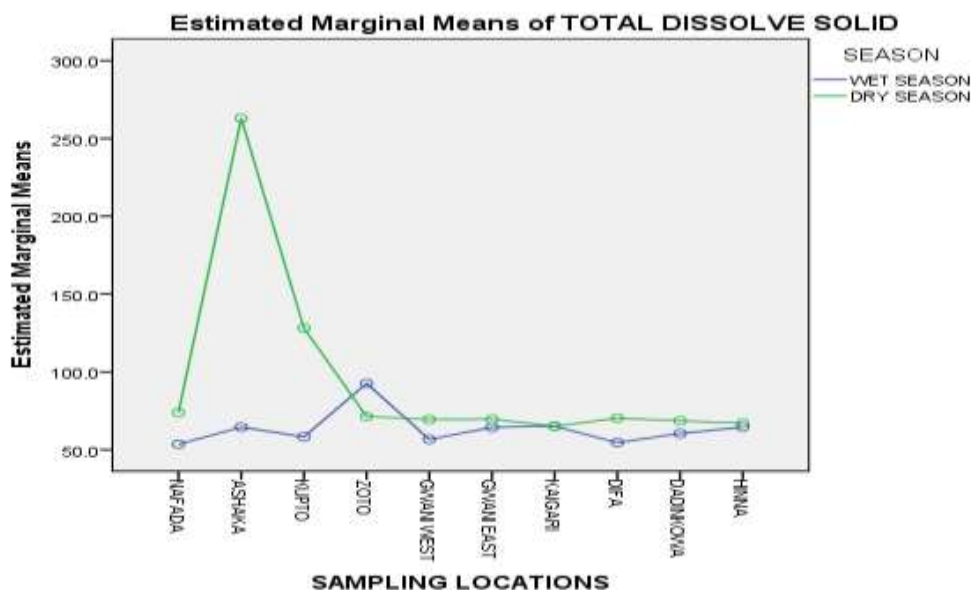


Figure 8: Recorded values of TDS in the water at different locations

Turbidity is the concentration of dissolved suspended ions or particles of soil that could deteriorate the drinking water quality. Turbidity had the lowest mean value of 11.15 NTU at Nafada and the highest mean value of 442.1 NTU at Difa during the dry season, while during the wet season, the lowest mean value of 424.7 NTU was observed at Zoto and the highest mean value of 783.5 NTU at Difa as shown in Figure below. These results were higher than the value reported by (Mohammed and Yaji, 2013) and 5.0 NTU permissible limits of WHO 2008. However, at  $p > 0.05$ , turbidity had a significant difference along with the ten different locations during wet and dry seasons.



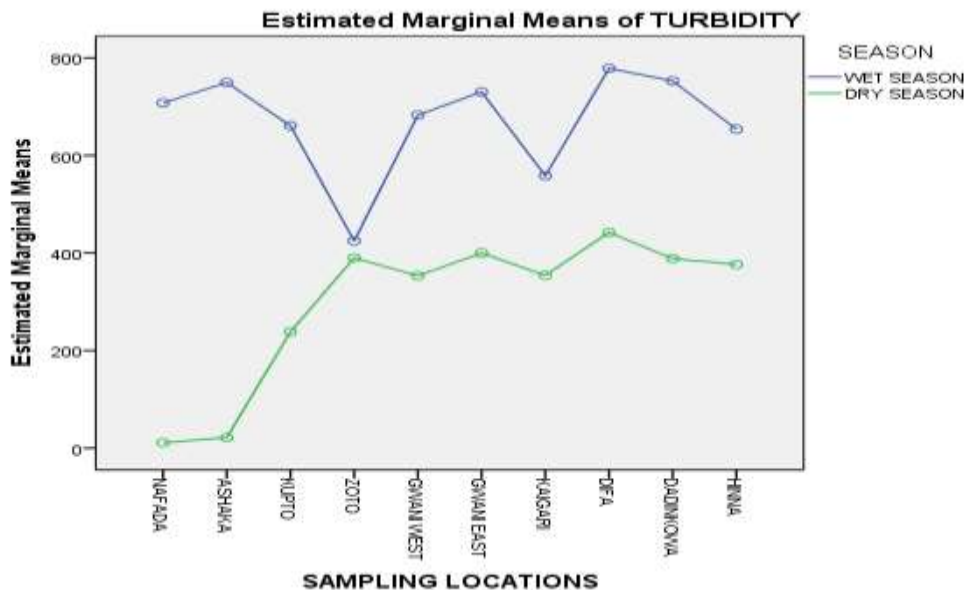


Figure 9: Recorded turbidity values of the water at different locations

Phosphate ( $PO_4^{3-}$ ); the presence of fiscal wastewater, chemical fertilizers, and detergents indicates the presence of phosphate. However, phosphate had a lowest mean concentration of 0.00 mg/l at Nafada & Gwani West and the highest mean concentration of 0.11 mg/l at Ashaka during the dry season while during the wet season lowest mean concentration 1.82 mg/l was observed at Ashaka and the highest mean concentration of 7.23 mg/l as shown in Figure below.

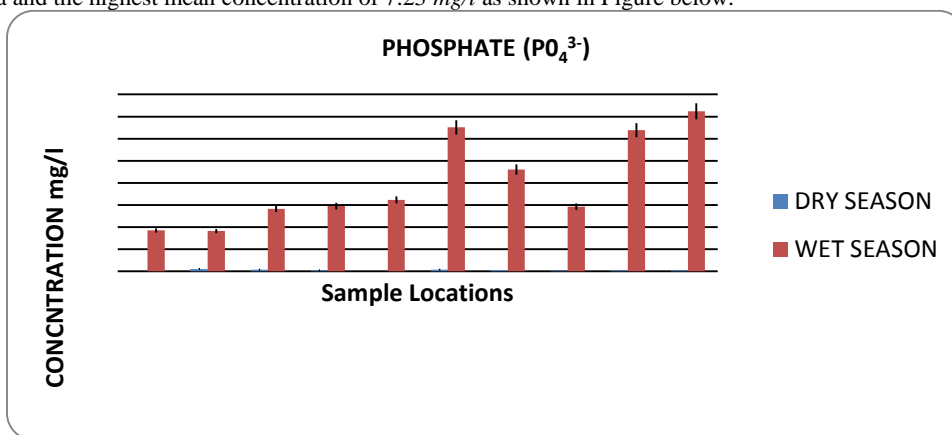


Figure 10: Showing the concentration of phosphate in water at different locations

Nitrate ( $NO_3^-$ ) are important nutrients necessary for the growth and development of algae and another aquatic plant; however, high concentration of nitrates (90 mg/l) have a toxic effect on aquatic organisms, <http://globe.pomsk.hr/prirucnik/voda.pdf> (accessed on 21<sup>st</sup> May 2017) rains, snow, fog and decomposition of organic matter are all pathways that naturally increases the content of Nitrates. The application of fertilizers in Agriculture is also one of the causes of the increase in nitrate concentration in soil and water as well as wastewater. Nitrate had the lowest mean concentration of 2.68 mg/l at Kupto and highest mean concentration of 6.81 mg/l at Gwani East and Kalgari during the dry season while during the wet season, the lowest mean concentration of 2.25 mg/l was observed at Ashaka and the highest mean concentration of 8.82 mg/l at Hinna as shown in the figure below. All results were below the permissible limit of 50.0 mg/l WHO 2012.

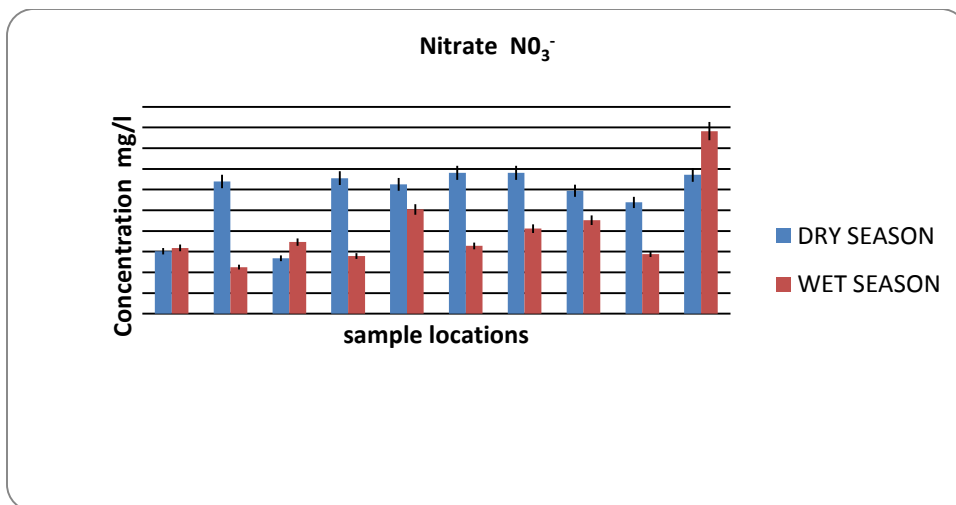


Figure 11: showing concentration of Nitrate in water along different locations

**Validation of the analytical method**

The sensitivity of the proposed method was performed by computing the limit of detection (LOD) and limit of quantitation (LOQ). The limit of detection of Cd, Cr, Ni, and Pb was found to be 0.25 ppm, 0.76 ppm, 0.07 ppm, 0.20 ppm, and the limit of quantitation of Cd, Cr, Ni, and Pb were found to be 0.77 ppm, 0.97 ppm, 0.22 ppm, 0.6 ppm and the RSD values obtained were 7.7 %, 6.2 %, 2.2 % and 6.0 % this according to Horvitz, as cited from Gonzalez and Herrador (2007), the maximum RSD value acceptable for analyte level is 16 %. While AOAC set the maximum acceptable RSD value is 11 % for the same analyte level this, therefore, reveals that the proposed method shows good precision base on RSD values obtained to be below the maximum RSD values.

To check the accuracy of the analytical method, the recovery studies were performed to confirm the lack of analyses levels due to the losses or contamination during sample preparation and matrix interferences during the measurement step (Ertas and Tezel, 2004), hence The results of the recovery of digestion method and analytical technique used for determination of Cd, Cr, Ni, and Pb, having the percentage (%) recovery of 95.± 0.33, 89± 0.94, 93 ± 0.10, 83.3± 0.83, and %RSD 0.35%, 1.06 %, 0.11 % and 1.0 % respectively. This implies that the measured results are within the acceptable range of 75% to 110. therefore the developed method was accurate for quantification.

**Table 1.2: Variety of fish species sampled and their characteristics**

Specie Name	Common Name	Feeding Habit	Length (cm)		Weight (g)	
			Wet	Dry	Wet	Dry
<i>Bagrus docmak</i>	Silve catfish (Rago Rawar)	Omnivorous	50-64	26-43	360-651	305-462
<i>Clarias gariepinus</i>	Africa catfish (Tarwada)	Canivorous	34-41	25-37	360-512	253-352

**Comparison of Heavy Metals Concentration in (µg/g) in muscles of Fish Species (*Clarias gariepinus* and *Bagrus docmak*) during wet and dry season)**

The length and weight of the studied fish species varied from 25 cm – 64 cm and 253 g – 651 g during wet and dry season respectively as shown above in Table 1.2. A continuous increase in length and weight was observed for all individuals with a significant and positive correlation ( $R^2 = 0.84$   $p < 0.001$ )

Chromium (Cr): the deficiency of Cr results in impaired growth and disturbance in glucose, lipid, and protein metabolism Calabrese et al., 1985. Cr is the biologically usable form of Cr that plays an essential role in glucose metabolism. However, Cr was below the detectable limit of instruments in all the two fish species (*Clarias gariepinus* and *Bagrus docmak*) samples around the ten different locations. Nickel (Ni) the major sources of Ni for humans is food and natural sources, as well as food processing (Nas, NRC, 1975). Increased incidence of cancer of lungs and nasal cavity caused by too much intake of Ni has been reported in many workers in Ni smelters. This, therefore, reveals that Ni has the lowest mean concentration of 15.8 µg/g in *Clarias gariepinus* at Hinna and the highest mean concentration of 96.4 µg/g in *Clarias gariepinus* at Gwani West during the wet season, while during the dry season, the lowest mean concentration of 49.1 µg/g was observed in *Clarias gariepinus* at Kupto and highest mean concentration of 145 µg/g in *Bagrus docmak* at Kalgari. These values were all above 70-80 µg/g and 0.07 µg/g of USFDA 1993, WHO 2007 and Olabanji et al., 2014. Nickel (Ni) reveals that there were no correlations in the concentration of Ni in both dry and wet seasons along with the ten different locations.

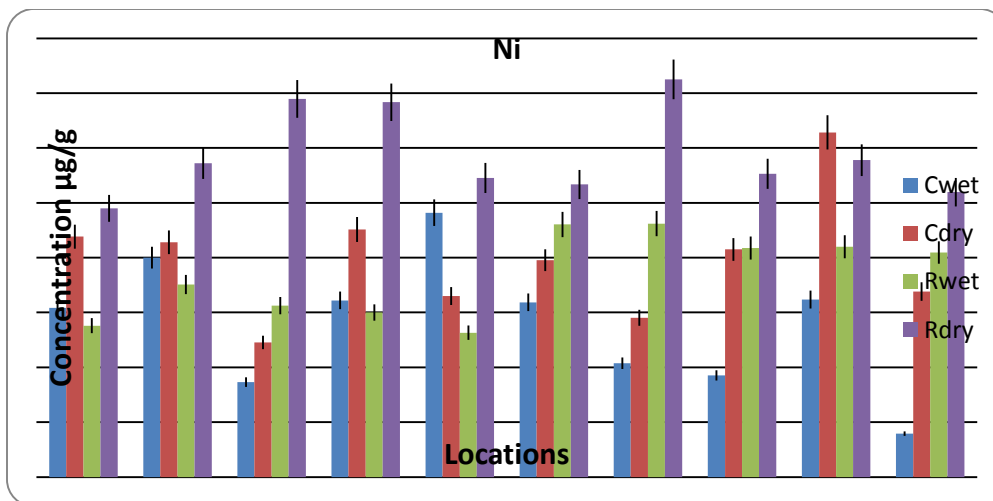


Figure 11: Showing different mean concentrations (µg/g) of Nickel (Ni) among two fish species (muscles) along with ten different locations during wet and dry seasons

Cadmium (Cd): The source of (Cd) in humans is also food consumption. Sever toxic symptoms resulting from (Cd) ingestion and reported between 10-326mg Sivapermal *et al.*, 2007, fatal ingestion of (Cd), producing shock and acute renal failure occur from ingestion exceeding 350mg/g (Nas-NRC< 1982). Cd had the lowest mean concentration of 0.5µg/g in *Clarias gariepinus* and *Bagrus docmak* at Gwani East Ashaka and Nafada respectively. The highest mean concentration of 3.3µg/g in *Clarias gariepinus* at Dadinkowa during the wet season while during the dry season, the lowest mean concentration of 2.9 µg/g was observed in *Clarias gariepinus* at Kupto and highest mean concentration of 7.75 µg/g in *Bagrus docmak* at Nafada. However, all the result obtained was above the permissible limit of 0.003 µg/g (WHO 2007) and the value reported by Ezekiel *et al.*, 2012. Cadmium (Cd) at P<0.05 (r=0.68, N=10, p=.05) the concentration of Cd in *Clarias gariepinus* and *Bagrus docmak* at dry and wet Season had a strong positive correlation, indicating that, as the concentration of Cd is increasing in *Clarias gariepinus* during the dry and wet season, so also the concentration of Cd in *Bagrus docmak* is increasing during the dry and wet season along with all the different locations.

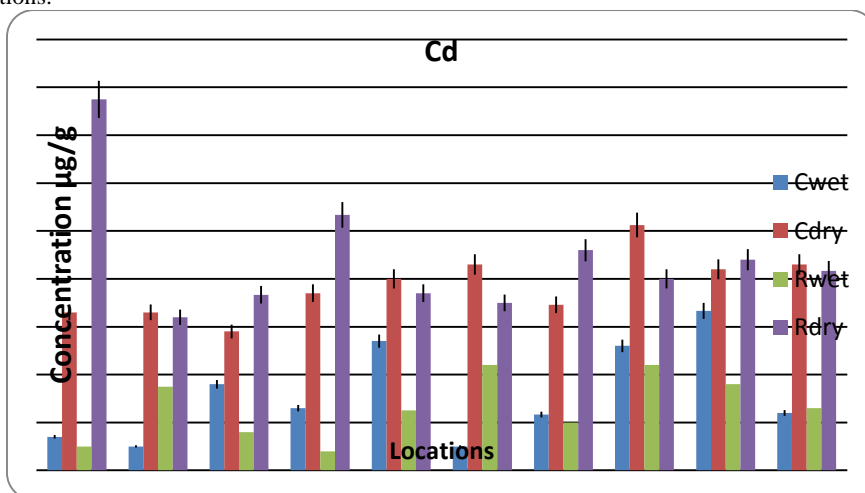


Figure 12: Showing different mean concentrations (µg/g) of Cadmium (Cd) among two fish species (muscles) along with ten different locations during wet and dry seasons

Lead (Pb) is classified as one of the most toxic heavy metals, the biological effect of sub-lethal concentrations of lead include delayed embryonic development, suppressed preproduction and inhalation of growth increased mucous formation, neurological problems, enzyme inhalation and kidney dysfunction, Kampala *et al.*, 1984. (Pb) had the lowest mean of concentration of 3.9 µg/g in *Clarias gariepinus* at Nafada and the highest concentration of 30.3 µg/g in *Bagrus docmak* at Difa during the wet season while during the dry season, the lowest mean concentration of 10.6µg/g in *Clarias gariepinus* at Hinna with a highest mean concentration of 35.6 µg/g in *Clarias gariepinus* at Kupto. These values were all above the permissible limit (5 µg/g) WHO 2006 and the value reported by Milam *et al.*, 2012. Pb at p<0.05 (r = 0.72, N =10, p = .05). The concentration of Pb in *Clarias gariepinus* and *Bagrus docmak* during dry season had a strong positive correlation, indicating that, as the concentration of Pb is increasing in *Clarias*

*gariepinus* during the dry season so also the concentration of Pb in *Bagrus docmak* is also increasing, during the dry season, while the concentration of Pb in *Bagrus docmak* during dry and wet, indicate a strong positive correlation at  $p < 0.01$ , ( $r = 0.78$  and  $N=10$   $p = .01$ ) revealing also that as the concentration of Pb in *Bagrus docmak* is increasing during the dry season so also the concentration of Pb in *Bagrus docmak* during the wet season.

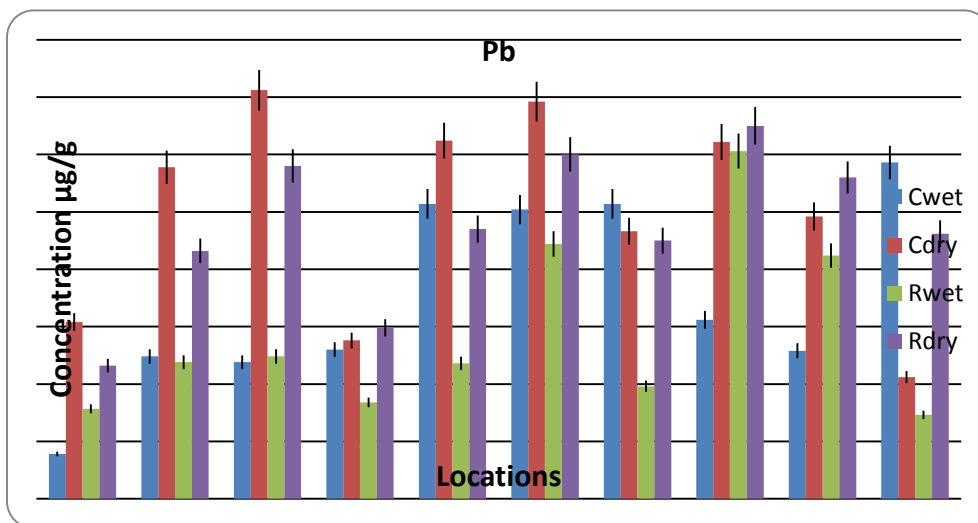


Figure 13: Showing different mean concentrations ( $\mu\text{g/g}$ ) of Lead (Pb) among two fish species (muscles) along with ten different locations during wet and dry seasons

C wet and C dry = *Clarias gariepinus* and R wet and R dry = *Bagrus docmak*

## CONCLUSION

The general desire to protect water bodies has led to an expansion of research into their water quality requirement in terms of their physicochemical parameter such as pH, Temperature, Turbidity, conductivity, TDS, TSS, DO,  $\text{PO}_4^{3-}$  and  $\text{NO}_3$ . The mean value/ concentration of the physicochemical parameter of River Gongola and its Dam, in Gombe North-East part of Nigeria along ten different locations were monitored for the period of Feb-June 2017 for Dry season and July-November 2017 for Wet season the results reveals that turbidity,  $\text{PO}_4^{3-}$  DO, TSS, and TDS were above the acceptable permissible limits of WHO and USEPA due flooding and anthropogenic activities such as application of fertilizer, organic pesticides, herbicide, insecticides and industrial discharges along the River banks. The analytical method developed by evaluation of sensitivity, precision and accuracy shows the acceptable result which can successfully use for determination of heavy metals. The results reveal that both species of fish (*Clarias gariepinus* and *Bagrus docmak*) indicate that the mean concentration of heavy metals of the study was significantly different for Wet and Dry season and significant the same among the locations. Therefore both the fish species accumulate high heavy metal concentrations which exceeded the permissible limits of FAO/WHO guidelines, due to anthropogenic activities such as Agricultural activities and industrial effluent discharges into the River taking place along the bank of the and Dam however this indicates that the two fish are not fully safe for human consumption and people should be very conscious about the fish around River Gongola and its Dam in Gombe North-Eastern part of Nigeria. However, it was observed that *Bagrus docmak* accumulate more heavy metal concentration as compared to *Clarias gariepinus* this could be

as a result of feeding habit and metabolism activities of the fish species.

## Acknowledgment

Authors are indeed TETFUND – Nigeria for funding the research, the Management of Federal University of Kashere for the administrative and moral support. The staff of Department of Chemical Sciences, Federal University of Kashere are indispensable colleagues.

## Conflict of Interest

The authors wish to report no conflict of interest

## REFERENCES

- Ajiboye OO, Yakubu AF, Adams TE. (2011). A review of polycyclic aromatic hydrocarbons and heavy metal contamination of fish from fish farms. *J. Appl. Sci. Environ Manag.* 15(1):235–8.
- Avishai N, Rabin OWHZ C, Moiseeva E, And Rinkeveh B. (2002). Genotoxicity of the Kishon River, Israel: The Application of an in vitro cellular assay. *Mutation Res.* 518:21–37.
- Babatunde Am, Waid Oyebajo A, Adeolu AA. (2012). Bioaccumulation of Heavy Metals in fish (*Hydrocynus forskahlii* (*Hydrocygariepinus*)) organs in Downstream Ogun Coastal Water, Nigeria *Transa J Sci Technol* 2 (5): 119-33
- Bhupander K, Mukherjee DP, Sanjey K, Mishra M, Prakash D, Kingh SK, (2011). Bioaccumulation of heavy metals in muscle tissue of fishes from selected aquaculture ponds in East Kolkata wetlands. *Ann Biol Res.* 2(5):125–34.

- Copat C, Bella F, Castaing M, Fallico R, Sciacca S, Ferrante M, (2012) Heavy metals concentration in fish from Sicily (Mediterranean sea) and evaluation of possible health risks to consumers *Bull Environ Contain-Toxicol*; 88 (1): 78-83.
- Ezekeil, O. A., Benedict, O. O. and Fidelis, B. A. (2012). Heavy metal profile of water, sediment and freshwater catfish, *Chrysichthyes nigrodigitatus* (Siluriformes: Bagridae) of Cross River, Nigeria. *International Journal of Tropical Biology: Vol. 60(3), pp. 1289-1301*.
- FAO/WHO, (2004) "Summary of Evaluations Performed by the Joint FAO/WHO Expert Committee on Food Additives (JECFA 956-2003)", ILSI Press International Life Sciences Institute.
- Ginsberg GL, Toal BF (2012) Quantitative approach for Incorporating Methylmercury risk and omega-3 fatty acid benefit in development species-specific fish consumption *Bull Environ Contain Toxicol* 88 (1): 78-83.
- Harmanescu M, Alda LM, Bordean DM, Gogoasa I, Gergen I. (2011) Heavy Metals Health risk assessment for population via consumption of the country, Romania *Chent* 5: 64.
- International Conference on Harmonisation (ICH), 1994. Validation of Analytical Procedures: Text and Methodology. Downloaded from: [http://www.ich.org/fileadmin/public/web\\_site/ICH\\_Products/Guidelines/Quality/Q2\\_RI\\_Guideline.pdf](http://www.ich.org/fileadmin/public/web_site/ICH_Products/Guidelines/Quality/Q2_RI_Guideline.pdf), 19/04/2011
- Maitera O. N., Barminas J.J. and Magili (2011) Determination of Heavy Metal Level in Water and Sediments of River Gongola in Adamawa State, Nigeria. *Journal of Emerging Trends in Engineering and Applied Science (JETEAS)* 2 (5): 891-896.
- Maitera, O. N., Barnabas, J.T. and Shinggu, D. Y. (2010). An evaluation of the physical parameters of river Gongola in Adamawa state, Nigeria. *Journal of Physical Science and Innovations*. Vol. 2, pp.56-63.
- Milam C, Maina HM, Onyia LU, Ozoemena PE (2012) Heavy metal pollution in benthic fishes from Kiri Dam in Guyuk local government area of Adamawa State, Nigeria. *African Journal of Biotechnology* 11: 11755-11759.
- NAS-NRC (1982). National Academy of Sciences-National Research Council. *Drinking-Water and Health*. Vol. 4. Washington DC: National Academic Press, p: 299.
- Obiakor MO, Okonkwo JC, Ezeonyejiaku CD, Okonkwo CN. (2014). Polycyclic aromatic hydrocarbons (PAHs) in freshwater media: factorial effects and human dietary exposure risk assessment. *Resource Environ*. 4(6):247-59.
- Olabanji, I. O. and Oluyemi, E. A. (2014). Preliminary Assessment of Heavy Metal Pollution of Opa Reservoir, Ile-Ife, Southwest Nigeria using *Mormyrus rume* and *Tilapia zillii*. *Ife Journal of Science*: Vol. 16, pp. 35-43.
- Ramana, S., Biswas, A. K., Ajay and Subba, R. A. (2008). Tolerance and bioaccumulation of Cadmium and Lead by the gladiolus. *National Acad. Sci. Lett*. Vol. 31: pp. 327-332.
- Svensson BG, Nilsson A, Jansson E, Schütz A, Åkesson B, Hagmar L. (1995). Fish consumption and exposure to persistent organochlorine compounds, mercury, selenium and methylamines among Swedish fisherman. *Scand J Work Environ Health*. ;21:96105.
- UNFPA (United Nations Population Fund). (2003). *Global Population and water access and Sustainability, Population and Development Strategies Series*. New York, NY 10017.
- USFDA, "Food and Drug Administration, Guidance Document for Chromium in Shellfish," DHHS/PHS/FDA/ CFSAN/Office of Seafood, Washington DC, 1993.
- Voegborlo R. B. and A. A. Adimado, "A simple wet classical digestion technique for the determination of total mercury in fish tissue by cold vapor atomic absorption spectrometry in the low technology environment," *Food Chemistry*, Vol. 123, pp. 1142-1147, 2012.
- Who Guidelines for Drinking-Water Quality, 4<sup>th</sup> ed; World Health Organization; Geneva, Switzerland, 2012
- World Health Organisation (WHO) (2006). *Guideline for Drinking Water Quality, First Addendum to the Third Edition*. Vol. 1: Recommendations, pp. 491-493.
- World Health Organization (WHO) (2008) *Guidelines for drinking-water quality (electronic resource): incorporating 1st and 2nd addenda*. 3rd eds. Recommendations. Geneva 1: 515.
- World Health Organization (WHO) (2011) *Guidelines for drinking-water quality*. 4th eds. World Health Organization
- Zafer A, Guler E, Sedat V, Murat O. (2007) Heavy metal accumulation in water sediments and fishes of Nallihan bird paradise, Turkey. *J Environ Biol*. 28(2):545-9.