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DETERMINATION OF HEAVY METALS CONCENTRATION IN WATER, FISH SPECIES AND HUMAN URINE ASSOCIATED WITH CHRONIC KIDNEY DISEASE IN GASHUA, YOBE STATE, NIGERIA

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ABSTRACT Recently, chronic kidney disease (CKD) is considered to be a major health challenge to people living in developing countries especially to inhabitant of Gashua Town, Yobe State, Nigeria. In this region, several people are suffering from this multifaceted disease. Thus, this study evaluates the concentration of some heavy metals such as Arsenic (As), Cadmium (Cd), Copper (Cu), Chromium (Cr) and Lead (Pb) in river water samples, fish species and human urine (from hospital CKD and non-CKD patients to serve as control). Heavy Metals Concentrations were analysed using Atomic Absorption Spectroscopy during dry and wet seasons. The results show that the mean concentration for river water measured varied in the two seasons. While As was not detected in both seasons, high concentrations of Cd (0.012 ± 0.008) µg g^{-1} and Pb (0.070 ± 0.009) µg g^{-1} compared to NAFDAC permissible limits were detected in the water samples during dry season at all sites. Similarly, high concentration of Cd (0.076 ± 0.034) µg g^{-1}, Cr (0.055 ± 0.005) µg g^{-1}, and Pb (0.092 ± 0.02) µg g^{-1} were reported for some sites during the wet season. The highest bioaccumulations factor of metals (Cr) was observed in the livers of Bagrus Dogmac fish (54.23), catfish (51.65), and Tilapia fish (49.33) respectively, whereas the lowest factors for Cu (3.064) and Pb (5.176) were obtained in the gill of Bagrus Dogmac fish. A strong positive correlation was observed for the specific fish organ and the water sample. Heavy metals concentration in the urine samples for the patients already diagnosed with kidney related diseases shows the presence of As (0.032 ± 0.011 µg mL^{-1}) and Cu (0.224 ± 0.037 µg mL^{-1}) which were higher compared with other metals analysed in male urine samples. A similar trend was observed for the female urine samples, where higher concentrations of Cu (0.202 ± 0.042 µg mL^{-1}) and Cr (0.017 ± 0.007 µg mL^{-1}) were recorded. However, there was insignificant trace of heavy metal concentration in urine samples obtained from healthy persons. It is noteworthy that, the concentrations of metals detected in the samples were neither NAFDAC nor WHO/FAO compliant.

Keywords: Water; Fish; Human Urine; Chronic kidney disease; Heavy Metal

Introduction

The gradual loss of kidney function over time which may results to kidney failure is known as chronic kidney disease (CKD) (Gilbert and Weiner, 2013). CKD is a global health problem that requires urgent intervention due to its devastating effect on human health which is responsible for several deaths especially in the study area. A study by Bamgboye (2013) revealed that 10 out of every 100 people in developing society could have CKD, while in some parts, one out of every five people may possibly have CKD at some point in life. The prevalence rate of CKD in Nigeria is between 8% and 45%, depending on the area and population that was studied (Alebiosu and Ayodele, 2005). For instance, according to official reports from University of Maiduguri Teaching Hospital, out of every 100 patients that were diagnosed in the hospital having CKD, 20 of them are observed to be from Bade community in Gashua Town. However, the cause is still unknown, but the main culprit is suspected to be environmental resulting from heavy metal or toxin in food or water (Salamatu *et al.*, 2019). Contamination of water and fish with heavy metals is a global environmental health issue of concern which occurs mainly due to natural and anthropogenic activities (Wilson, 2007).

Uptake and accumulation of heavy metal occurs mainly from water and food. The effect of assimilation in different organisms might be affected by many factors such as salinity, temperature, season and interacting agents. The presence of heavy metal environ could results in uptake and accumulation of the elements in fish body. Rivers are also home to those fish species.
Most heavy metals are determined to have some toxic effect on human health, with both acute and chronic causes. Since these metals are poisonous to

kidney tissue, high concentrations in the kidney cortex are of great concern to health experts. However, kidney biopsies in human body system are readily available because of the risks associated with it. Interestingly, the current understanding on the relationship between heavy metal concentrations and the kidney are as a results of autopsy studies (Bahemann *et al.,* 1988). Therefore, this study aimed to evaluate the concentration of heavy metals in patient's urine suffering from CKD in relation to water and fish species in Gashua, Yobe State, Nigeria. Hence, the resultant heavy metal ions concentrations were compared with the World Health Organizations (WHO) and National Agency for Food and Drug Administration and Control (NAFDAC) standards for permissible limits.

2 Materials and Methods

2.1. Instruments and Apparatus

All equipment and instruments used in this research were calibrated before conducting the experiments. All glassware used were thoroughly washed with detergents and tap water and then rinsed with deionized water. Suspected contaminants wares were cleaned with 10% concentrated Nitric acid (HNO_3) and metal surfaces rinsed with deionised water. The digestion tubes were soaked with 1% (w/v) potassium dichromate in 98% (v/v) H_2SO_4.

2.2 Samples Collection

Water samples were collected from three stations across the stretch of river Gashua in February, 2019 (dry season) and five stations of the river in August, 2019 (wet season) according to Yuguda *et al.* (2020). Fish samples (Bagrus Dogmac, Cat and Tilapia) were collected from the same river using a procedure described by Uba *et al.* (2019). For human urine, 40 samples were collected from 20 CKD patients and 20 healthy persons. The healthy person's urine were used as control. The samples were collected in a sandoz sterile vials at General Hospital Gashua in the Department of Chemical Pathology after obtaining approval from the research and ethics committee of the General Hospital (Ethical clearance, 2013) and with the assistance of health personnel at the hospital.

Samples Preparation

Water, fish and urine samples were digested following procedure of Akan *et al.* (2014) with little modification. For the water sample, 100 ml was transferred into a beaker and 5ml of concentrated HNO_3 was added and then heated. The content evaporated down to about 20ml and then 5ml of HNO_3 was added to the beaker covered with a watch glass. The heating process continued by adding small amount of HNO_3 until the solution turned light coloured and clear.

For the three species of the fish collected, only gills and liver organs were dried in an electric oven at 100-105 ^{0}C until a constant weight was achieved. The organs (samples) were grounded into powder using mortar and pestle. About 0.5g of the sample was weighed and then transferred into polyethylene tubes, and 10ml of nitric acid was added to the sample placed on a hot plate until a clear solution was obtained. The solution was allowed to cool before filtering. The product was washed with 10ml nitric acid and transferred into a 25ml volumetric flask (Uba *et al.,* 2019).

For the human urine, 100ml of each sample was evaporated in a hot plate to 20 ml. The resulting solution were frozen, lyophilized and stored in a refrigerator. The lyophilized sample of urine was allowed to stand at room temperature for 24 hours and then restored with 20cm^3 distilled water. A 5cm^3 of concentrated HNO_3 was added to the 20cm^3 restored urine solution and evaporated to 10cm^{3}on a water bath. The resulting solution was allowed to cool before further addition of an equal mole of HNO_3 and $HCLO_4$, and transferred to a fume chamber. The solution was heated on a hot plate and the heating process proceeded until the appearance of a dense and white fume and a clear product achieved. After cooling, 5ml of water was added and the product was boiled for 10 minute to discard free chloride and oxide of nitrogen. The resulting solution was then filtered through acidified washed Whatmann 540 filter paper into 100cm^3 volumetric flask and fill up with distilled water to the mark.

All standard solutions and chemicals used for this research were of analytical grade and obtained from Merck (Darmstadt, Germany). The determination of heavy metals in the water, fish and human urine samples was carried out using an Atomic Absorption Spectrophotometer ; AAS (PC-controlled double-beam Buck Scientific Model 210VGP) in accordance with American Public Health Association (APHA, 1999) standards. The heavy metals considered were; Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), and Lead (Pb).

Bioaccumulation Factor (BAF)

The BAF is the ratio between the accumulated concentration of a given pollutant in any organ and their dissolved concentrations in water (Authman and Abbas, 2007). The BAF for the active metal accumulation in fish from that of river water will be estimated using equation 1.

$$BAF = \frac{Concentration\ of\ metal\ in\ fish\ tissues\ (\frac{mg}{L})}{Concentration\ of\ metals\ in\ river\ water\ (\frac{mg}{L})} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

BAF is the ratio of metal concentration (C) in fish to its concentration in river water samples.

2.5 Statistical Analysis

The analysis of variance (ANOVA) was used to examine the level of metal ion concentrations in water, fish organs and human urine samples. A p-value < 0.05 was considered to be statistically significant. Correlation analysis was also carried out to determine the relationship between concentrations of metal ions in the samples. The concentrations of the heavy metals was expressed in µg mL^{-1} for water and human urine samples; and µg g^{-1} for the fish organs samples.

Results and Discussion

Levels of Heavy Metals in Water Sample

The results of heavy metal concentration in Gashua River water samples for dry and wet seasons are presented in Table 1.

Table1: Concentration of heavy metals in River water sample µg mL^{-1}

SITE	As	Cd	Cr	Cu	Pb
Dry Season					
A	0.00	0.009±0.005	0.037±0.003	0.245±0.027	0.067±0.011
B	0.00	0.012±0.008	0.044±0.012	0.144±0.012	0.070±0.009
C	0.00	0.011±0.010	0.039±0.007	0.219±0.012	0.067±0.020
Wet Season					
A	0.00	0.052±0.021	0.053±0.003	0.257±0.023	0.086±0.005
B	0.00	0.076±0.034	0.039±0.011	0.238±0.080	0.083±0.014
C	0.00	0.057±0.028	0.055±0.005	0.220±0.012	0.089±0.030
D	0.00	0.038±0.018	0.041±0.008	0.257±0.023	0.092±0.022
E	0.00	0.043±0.022	0.037±0.000	0.232±0.063	0.089±0.028
NAFDAC	**0.01**	**0.003**	**0.05**	**1.0**	**0.01**

From Table 1, high concentrations of Cd and Pb compared to NAFDAC permissible limits were detected in the water samples during dry season at all sites. For the wet season, high concentrations of Cd, Pb and Cr were detected with the exception of site B, D and E for Cr. More so, Cu concentration was within NAFDAC allowable limit; and no As concentration was detected at both seasons for all sites. The heavy metal concentrations during wet season at all sites were distributed according to the following pattern: Pb>Cd>Cr. The concentrations of Cd, Pb and Cr in the wet season might be attributed to agricultural activities around the river resulting from organic fertilizer. These results are similar to other studies that found higher concentrations of Cd, Pb and Cr in water bodies exceeding recommended concentrations (Davies *et al.*, 2009; Rauf *et al.*, 2009; Vicente Martorell *et al.*, 2009).

Seasonal Variation of Heavy Metals in River Water

The seasonal variation of concentrations of As, Cd, Cr, Cu, and Pb in the water sample are shown in Figure 1. A paired samples *t*-test was done to determine if there was a significant difference in heavy metal concentration in the water sample collected during the rainy and the dry seasons. This result shows that As concentrations were not detected in both seasons, and there was a significant difference in heavy metal concentrations between the two seasons except for Cr .The concentration of Cu in river water was low during the dry season (0.144 ± 0.012) µg mL^{-1} and high in the rainy season (0.257 ± 0.023) µg mL^{-1}. Similarly, Pb concentration were low (0.067 ± 0.011) to (0.070 ± 0.009) µg mL^{-1} for all the sampling sites during the dry season while the in wet season its concentration increased from (0.083 ± 0.014) µg mL^{-1} to (0.092 ± 0.022) µg mL^{-1}. It is highly possible that the water inflow from various rivers that feed the Gashua River could increase metals concentration. Cd and Cr increased from the February, to the August, period in the river, i.e. rainy and the dry season. A variety of factors, such as water levels dropped from August to February, could lead to increase in the concentration of Cd and Cr in the Gashua River. These results were similar to a study done by Weber *et al.* (2013) in a subtropical Brazilian river.

The t-test values for Cd (0.018), Pb (0.005), Cr (0.800) µg mL^{-1}, and Cu (0.389) µg mL^{-1}are less than the t-test critical value (3.182, 3.182, 2.776, and 12.706) µg mL^{-1} for Cd, Pb, Cr and Cu respectively at $p \leq 0.05$ and 95% confidence level. This suggests that seasonal variation has no significant influence on the levels of heavy metals (Cr and Cu) found in the river. Also, the correlation values of the metals in dry and wet seasons showed a positive correlation in the levels of Cd and Cu and a negative correlation for Cr and Pb with respect to the seasons' (Table 2).

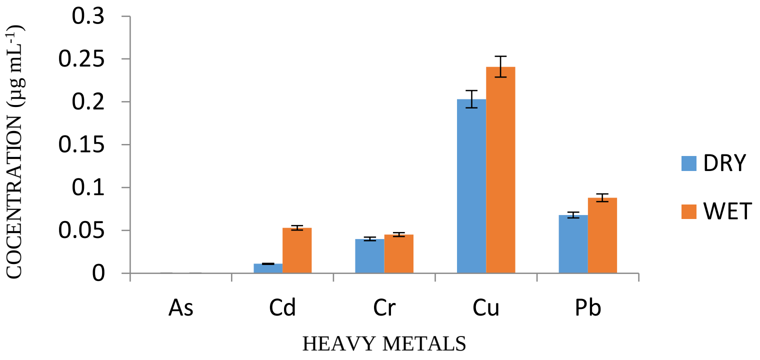

Figure 1: Seasonal Variation of Water

Table 2: Water and Human Urine Correlations

Elements	As	Cd	Cr	Cu	Pb
Seasonal Variation of Water	0.0000	0.9903	-0.9477	0.2378	-0.8947
Human Urine	0.4773	-0.1469	-0.3588	0.7289	0.1287

Distribution of Heavy Metal Concentration in Fish Parts

Results of heavy metal concentration (µg g^{-1}) analysis in the gills and livers of Bagrus Dogmac, Cat and Tilapia fish are presented in Table 3.

Table 3: Concentration of heavy metal from Liver and Gill of Bagrus Dogmac, Cat and Tilapia fish samples (µg g^{-1})

SAMPLE		**As**	**Cd**	**Cr**	**Cu**	**Pb**
Bagrus Dogmac	Liver	0.051±0.051	0.316±0.076	2.169±0.074	4.269±0.159	1.919±0.220
	Gill	0.220±0.118	0.069±0.03	0.259±0.041	0.622±0.183	0.352±0.059
Cat Fish	Liver	0.000±0.000	0.063±0.022	2.066±0.222	5.808±0.190	1.163±0.071
	Gill	0.000±0.000	0.072±0.021	0.299±0.040	2.882±0.230	0.475±0.108
Tilapia	Liver	0.00±0.000	0.14±0.017	1.973±0.183	6.018±0.400	1.096±0.153
	Gill	0.000±0.000	0.126±0.032	0.439±0.034	1.118±0.308	0.431±0.102
NAFDAC (2001)		**0.1**	**2.0**	**-**	**5.0**	**2.0**
WHO/FAO (2011)		**0.26**	**0.2**	**0.15**	**3**	**1**

Concentration of Arsenic (As) in Bagrus Dogmac, Cat and Tilapia fish

The results in Table 3 indicates the levels of As in the Bagrus Dogmac fish species were higher compared to the concentrations in other fish that were considered in the work. The mean values of As concentration in gill and liver of Bagrus Dogmac fish were (0.220 ± 0.118) and (0.051 ± 0.051) µg g-1 which were significantly different ($p<0.05$). On the other, there was no As detected in gill and liver of both Cat and Tilapia fish collected from the Gashua river. The mean concentrations in Bagrus Dogmac fish gill samples were above the NAFDAC (2001) maximum guideline limit of (0.1) µg g-1 of As for safe human consumption. It is also possible such concentration could be harmful to river fish as well. Fish gill and liver has been used widely in monitoring heavy metal contamination in aquatic systems and in assessing aquatic systems quality (Weber et al., 2013). According to Weber et al. (2013), exposed aquatic organisms that are elevated to waterborne, will absorbed and then bio accumulate with these metals through gills and liver. This can also occur when organisms take contaminated water and food. Eventually this will be transmitted to humans when consumed as diet. The contaminants are normally absorbed by the organism via the blood to the liver where it will be convert and or stored (Al- Kahtani, 2009).

Concentration of cadmium (Cd) in *Bagrus Dogmac*, Catfish and Tilapia fish

As presented in Table 3 the mean value of Cd was varied in the gills and liver of the three fish species found in Gashua River. The results of one-way ANOVA revealed that the levels of Cd in gills of

Catfish (0.072 ± 0.021) µg g^{-1} and Tilapia fish (0.126 ± 0.032) µg g^{-1} are not significantly different ($p \geq 0.05$) from that of *Bagrus Dogmac* fish (0.069 ± 0.03) µg g^{-1}. The mean Cd concentration was found at (0.316 ± 0.076) µg g^{-1} and (0.063 ± 0.022) µg g^{-1} for Bagrus *Dogmac* and Catfish respectively. Similarly, the distributions of heavy metal concentration in *Bagrus Dogmac* fish species were relatively higher than catfish and tilapia fish. The mean concentration of Cd in the present study was below the maximum permissible limit recommended by NAFDAC (2001) which is (2.0) µg g^{-1}, but higher in the *Bagrus Dogmac* fish liver which is higher than the maximum permissible limit recommended by WHO/FAO (2011). Although there are inter-species as well as locality differences, the concentrations of Cd in the present study were lower when compared to reports from literature from different study areas. The result is similar to findings of Kiflom and Tarekegn (2015), reporting Cd concentration of (0.4-1.85) µg g^{-1} above maximum permissible limit recommended by WHO.

Concentration of chromium (Cr) in *Bagrus Dogmac*, Catfish and Tilapia fish

The levels of Cr in the gills and livers of *Bagrus Dogmac*, Catfish, and Tilapia fish were analyzed by ANOVA at ($p<0.05$). However, the concentrations of Cr measured in three fish species used in this work were ranged from (2.169 ± 0.074) µg g^{-1}, (2.066 ± 0.222) µg g^{-1} and (1.973 ± 0.183) µg g^{-1} in the livers of *Bagrus Dogmac*, Catfish and Tilapia fish respectively. Although, the distributions of Cr contents were (0.259 ± 0.041) µg g^{-1}, (0.299 ± 0.040) µg g^{-1}, and (0.439 ± 0.034) µg g^{-1}in gill. This shows there was no significant difference ($p<0.05$) in Cr content among the three fish species' gill as compared to the Cr contents in the liver. A higher level of Cr was determined in the liver of the fish species, this is due to the fact that the liver is important organs for trace metal storage and decontamination in fish, where metal ions induced by trace metals takes place (Kebede *et al*., 2010). The extent of chromium concentration in the three fish species was higher than the maximum permissible limit recommended by WHO/FAO (2011) and that reported by Mulu *et al*. (2012). Therefore, the levels of chromium concentration in the present study would be detrimental to human health.

Concentration of copper (Cu) in *Bagrus Dogmac*, Catfish and Tilapia fish

As presented in Table 3, the mean value of copper concentration in gill and liver of Bagrus Dogmac fish was (0.622 ± 0.183)µg g^{-1} and (4.269 ± 0.159) µg g^{-1} while in Tilapia fish, it was (1.118 ± 0.308)µg g^{-1} and (6.018 ± 0.400) µg g^{-1}, for gill and liver respectively. In the case of Catfish, the mean values are (2.882 ± 0.230) µg g^{-1} and (5.808 ± 0.190) µg g^{-1}. The levels of Cu in liver and gill was significant for all the fish species and not significance for the liver of Catfish only at ($p<0.05$). The minimum and maximum levels of this heavy metal were recorded in the liver of tilapia fish and gill of Bagrus Dogmac respectively. According to NAFDAC (2001) established limits for Cu in fish is (5.0) µg g^{-1} for human health risk concerns, the concentrations of Cu in some these samples were above while some are very close to the maximum permissible limit. Therefore, regular consumption of fish with such amounts of Cu could lead to serious health risk. Cupper is an essential part of several enzymes and it is necessary for the synthesis of haemoglobin but can cause harm at high concentrations (Akoto *et al.*, 2014). A high accumulation of copper is seen in the liver as observed in Table 3. The relatively high content of these metals found in the liver could be because most of the heavy metals are accumulated in the liver and gill after ingestion (Kebede *et al.*, 2010).

Concentration of lead (Pb) in Bagrus Dogmac, Catfish and Tilapia fish

The mean values of Pb concentration in the gills of the three fish species were (0.352 ± 0.059) µg g^{-1},(0.475±0.108) µg g^{-1}, and (0.431 ± 0.102) µg g^{-1}, the concentrations were not significant at ($p<0.05$) for both Bagrus Dogmac and Tilapia fish but significant for Catfish. The concentrations of Pb in the liver of Bagrus Dogmac (1.919 ± 0.220)µg g^{-1}, Catfish (1.163 ± 0.071)µg g^{-1}, and Tilapia fish (1.096 ± 0.153) µg g^{-1} were significantly different at ($p<0.05$), while not significant for the Catfish liver. The concentration of Pb, which was obtained to be the highest (1.919 ± 0.220) µg g^{-1} was found in the liver of Bagrus Dogmac fish collected from Gashua River, whereas, the lowest (0.352 ± 0.059) µg g^{-1} was observed in the gill. This variation may be due to the liver is probably the target organ for acute Pb toxicity and aspect little to whole body mass accumulation, which is dominated by Pb content in the liver. The mean concentration of Pb in the present study was below the maximum permissible limit recommended by NAFDAC (2001) which is (2.0) µg g^{-1}, but higher in all the three fish liver than the maximum permissible limit recommended by WHO/FAO (2011) which is (1.0) µg g-^{1}. The pattern of metal distribution in the liver has been suggested to reflect the route of metal uptake in fish, and this process is also strongly influenced by the water chemistry (Kebede *et al.*, 2010). The concentrations of Pb in the present study were low when compared to literature reported by (Kiflom and Tarekegn,

2015) which was 3.85 µg g^{-1} from Hawassa and Ziway Lake.

Comparison of Heavy Metal Concentration in Liver and Gill of Fish species

The comparisons of As, Cd, Cr, Cu and Pb concentrations in organs of the three fish species were shown in Figures 2A, B and C. The maximum mean accumulation of Cd, Pb and Cr are (0.316, 1.919 and 2.169) µg g^{-1} observed in liver of Bagrus Dogmac fish (Figures 2A and 2B), while 0.622 µg g^{-1} and 0.063 µg g^{-1} of Cu and Cd were found in gill of Bagrus Dogmac and liver of Catfish respectively. Figure 2C indicate high accumulation of Cu in gill of Catfish, with lower concentration of Cd and Cr content.

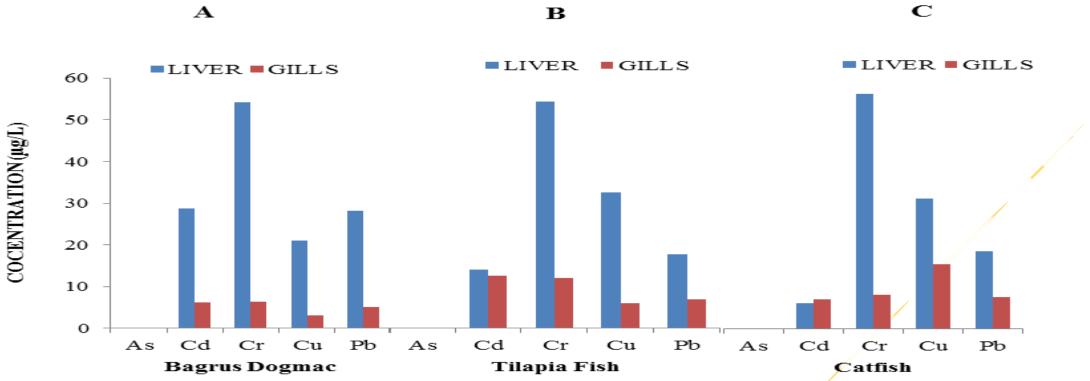

Figure 2: Comparing the Bioaccumulation Factor of Fish Liver and Gill (A: Bagrus Dogmac; B: Tilapia and C; Catfish)

Pearson's Correlation Heavy Metal in Water and Fish Sample

Table 4 shows the result of correlation coefficients between the various heavy metals in fish and water samples collected from Gashua River. The relationship between different elements content in water and fish were analyzed by Pearson's correlation coefficient. The results showed that the relationship among the elements As, Cd, Cr, Cu, and Pb were significantly correlated between the three fish species from Gashua River except for Pb in Catfish. The positive correlation among contents may be due to common sources of anthropogenic activities in the surrounding. In this case, the results showed that only Pb has a negative correlation in Catfish. Similarly, Cd, Cr, and Cu in Catfish show positive correlations at ($p<0.05$). Generally, the Pearson correlations of Cd, Cr, Cu, and Pb in Bagrus Dogmac and Tilapia fish indicated that these metals are positively correlated at ($p<0.05$).

The value of Pearson's correlation coefficient, r between +0.7 and +1.0 indicates a strong positive correlation; however, the mostly weak negative association are having a value of r between -0.7 and -0.3 as recommended by Raphael et al. (2012). These confirms that the heavy metal elements investigated in this study comes from same sources having the same topographical area and anthropogenic emission sources (Hossam *et al.*, 2017).

Table 4: Correlation of heavy metal from River Water and fish Samples

Type of Fish	Heavy Metals (Correlations)				
	As	Cd	Cr	Cu	Pb
Bagrus Dogmac	0.00	0.784537237	0.748811402	0.818762657	0.986767168
Cat	0.00	0.957425201	0.30437262	0.36022929	-0.68603000
Tilapia	0.00	0.826431398	0.901076488	0.97564200	0.141969000

Bioaccumulation Factor (BAF) from Fish to Water Sample

The BAF of each of the five heavy metals investigated for the different samples of fish parts were quantified. BAF is a major concern for environmental contamination, is the extent to which pollutants concentrate from water into aquatic organisms such as fish.

As indicated in Table 4, the trend of BAF for heavy metal distribution in fish samples of Bagrus Dogmac, catfish, and Tilapia fish are presented in the order of: Cr>Cd>Pb>>Cu>As (Bagrus Dogmac liver), Cr>Cu>Pb>Cd>As (Catfish liver) and Cr>Cu>Pb>Cd>As (Tilapia liver) while for the gill, Cr> Cd >Pb> Cu > As (Bagrus Dogmac gill), Cu>Cr>Pb>Cd>As (Catfish gill) and Cd>Cr>Pb>Cu>As (Tilapia gill). The highest BAF of metals concentration was observed in the Bagrus Dogmac, Catfish, and Tilapia fish liver, the values was found to be (54.23, 51.65and 49.33) for Cr, whereas the lowest was obtained as 3.064 and 5.176 in Cu and Pb of Bagrus Dogmac fish gills. This might be due to the higher mobility of these heavy metals with a natural occurrence in water and the low retention of them in the water. According to the water to fish bioaccumulation factor (BAF) calculated for tested metals and edible fish consumed by local residents, it can be concluded that the Cr followed by Cd and Pb in Bagrus Dogmac was highly accumulated among the investigated metals. While for Cat and Tilapia fish are, Cr, Cu, and Pb respectively. Higher Cr concentration in the liver may be as the liver is the target organ. This higher concentration of Cu in the gills might be since gills are the primary route for the uptake and accumulation of water born pollutants. Exposed Cu is taken up by organisms as it is an essential trace element even at low levels. It support cellular operation and is needed as a function in some metabolic enzymes (Monteiro, dos Santos, Calejo, Fontainhas-Fernandes, & Sousa, 2009). Cu and Pb are keep by organisms by means of specific binding proteins.

The low levels of Cu and Pb in the gills can be attributed to lower levels of protein that are found in gills (Papagiannis, Kagaloou, Leonardos, Petridis, & Kalfakakou, 2004). Several studies shows that low levels of Cu and Pb in the gill of different fish species have been reported by (Al-Weher, 2008; Zhang, He, Li, & Wu, 2007).

Water to fish bioaccumulation is one of the key components of human exposure to metals through the food chain. However, the higher concentrations of these heavy metals are due to irrigation, solid waste combustion, leakage of pesticides from farm to river water, and vehicular exhausted (Mulu *et al.*, 2012). Many aquatic organisms can accumulate heavy metals, as well as biomagnify these contaminants (Davies *et al.*, 2009). The pollutants can further be excreted in bile or transported to other excretory organs such as gills or liver. Thus the concentration of any pollutant in the tissue of organic organisms will depend on its rate of absorption and the dynamic processes associated with its elimination by the organism (Al-Kahtani, 2009).

Concentration of Heavy Metals in Human Urine Samples

Results of As, Cd, Cr, Cu, and Pb concentration in urine samples of CKD patients and healthy persons were presented in Figures 3 and 4 respectively. The concentrations of As (0.032 ± 0.011) µg mL^{-1} and Cu (0.224 ± 0.037) µg mL^{-1} were higher compared with other metals analysed in male urine samples. For the female urine sample, higher concentrations of Cu (0.202 ± 0.042) µg mL^{-1} and Cr (0.017 ± 0.007) µg mL^{-1} were recorded.

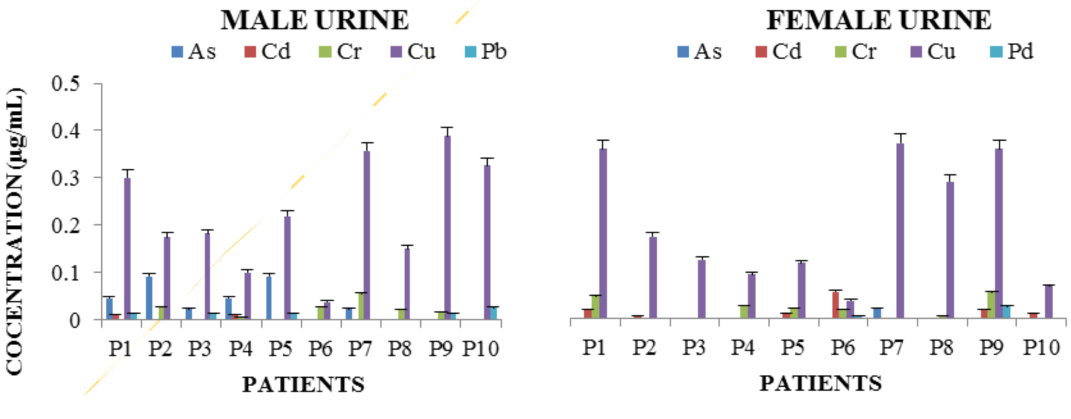

Figure 3: Heavy Metal Concentration in Urine sample (male and female)

The mean concentrations of heavy metals in the urine samples showed that As and Cd have the lowest concentration of (0.002 ± 0.002) µg mL^{-1} and (0.002 ± 0.001) µg mL^{-1} for female and male patients respectively. The mean concentrations of As, Cd, Cr, Cu, and Pb in the urine followed these orders; Cu > Cr > Cd > Pb > As and Cu >As Cr > Pb >Cd for female and male patients respectively.

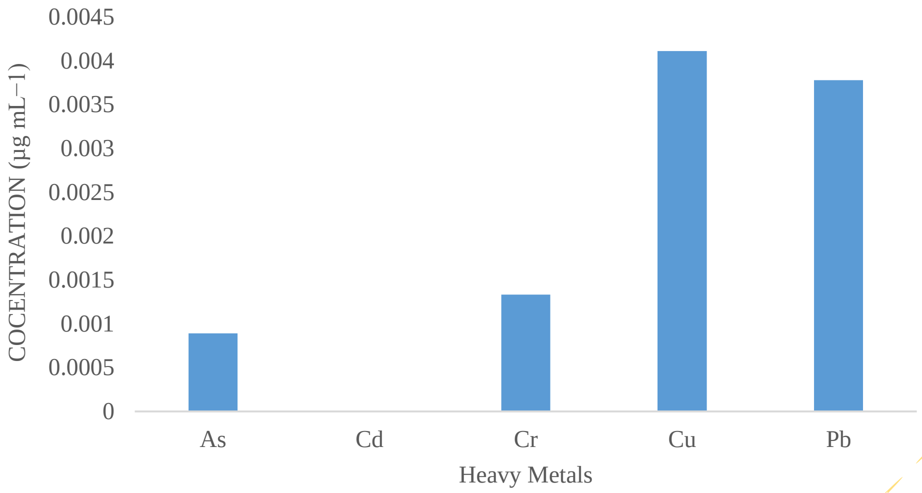

Figure 4: Concentrations of Heavy Metal from Healthy Persons (used as control)

Results of healthy persons' urine (Figure 4) indicated very small fraction in the samples of the heavy metals concentrations. More so, the metals t-test values for As (0.058), Cd (0.139), Pb (0.389), Cu (0.600) and Cr (0.754), were lower than the critical value (2.262) and (2.120) at $p \leq 0.05$ and 95% confidence level. The results showed that there is no significant influence of concentrations of heavy metals found in healthy person's samples over patient's samples. Furthermore, the results was in conformity with studies by Bartis and Ashwood (1999) and Yoo *et al.* (2000).

Conclusion

An attempt was made to determine the presence of heavy metals (As, Cd, Cr, Cu, and Pb) in river water, fish and human urine and possibly relates its impact on public health. The study of seasonal variation of As, Cd, Cr, Cu, and Pb concentration in the water was done by a paired samples t-test to determine if there was a significant difference in heavy metal concentration in the water in the seasons. This shows there was significant difference in heavy metal concentrations between the seasons for all the metals except Cr ($p< 0.05$).

The highest bio accumulations factor of metals concentration was observed as Cr in livers of Bagrus Dogmac fish, Catfish, and Tilapia fish, whereas the lowest was obtained as Cu and Pb in Bagrus Dogmac fish gill. A strong positive correlation was observed for the specific fish organ and the water sample. It is logical to say that the high concentration of metals in river water become gradually accumulated on the sediments and in due course gets transferred to fish. The order of heavy metal concentration in the different fish- Bagrus Dogmac, Catfish, and Tilapia fish were arranged in the order of: Cr>Cd>Pb>>Cu>As (Bagrus Dogmac liver), Cr>Cu>Pb>Cd>As (Catfish liver) and Cr>Cu>Pb>Cd>As (Tilapia liver) while for the gill, Cr> Cd >Pb> Cu > As (Bagrus Dogmac gill), Cu>Cr>Pb>Cd>As (Catfish gill) and Cd>Cr>Pb>Cu>As (Tilapia gill).

The concentrations of the metals in patient's urine samples were found to be higher than the maximum required levels recommended by WHO in human urine. Generally, the concentrations of metals obtained in this study were higher compared to the permissible levels of metals in urine and therefore this may be responsible for the associated diseases noticed in the patients. Finally, the concentrations of heavy metals detected in samples of the water, three fish species, and human urine were quite variable. Cd, Cr, Cu and Pb found in the samples were above the maximum permissible limits as stated by NAFDAC (2001), WHO (2008), ATSDR (2012), and WHO/FAO (2011). High concentrations of some heavy metals measured in the fish gill and liver inhabiting that Gashua Town catchment was attributed to a probable high influx of metals as a result of pollution from agricultural activities, municipal and refuge wastes runoff intrusion, thereby, increasing the potential bioavailability to the fish and also posing associated risks of affecting the quality of human health, particularly the most populous consumers in the long run. Therefore, close monitoring of heavy metal pollution and the consumption of Gashua River fishes is recommended with a view to minimizing the risk of health of the populace that depend on the river for their water and fish supply.

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