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Bioaccumulation of Heavy Metals in Fish (*Tilapia zilli*) and Bullfrog (*Pyxicephalus edulis*) from River Challawa Kano State Nigeria

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Abstract
Contaminants in the form of heavy metals, such as cadmium, chromium, copper, lead, iron and zinc were evaluated in sample of fish (*Tilapia Zilli*) and African bullfrog (*Pyxicephalus Edulis*) from different sampling stations A (upstream) and B (downstream) of Challawa river, located in Kumbotso local government area of Kano state, Nigeria. Surface water and effluent discharged into the river from industries were also analyzed for these heavy metals analysis using a atomic absorption spectrophotometer. Results obtained indicate that the concentration of these metals in each sample species increased in this order Fe>Cu>Zn>Cr>Pb>Cd. Iron (Fe) was the highest recorded heavy metal concentration in all samples analyzed while cadmium (Cd) manifested the lowest concentration. Heavy metals concentration determined from surface water in the upstream and downstream (sampling points) is found to increase in the following order Fe>Zn>Cr>Cd>Cu>Pb. The concentration of copper, cadmium, chromium and iron from *T. Zilli* and *P.edulis* from sampling point B exceeded the limits stipulated by W.H.O/F.A.O and F.E.P.A while lead and zinc were within the limits set by these regulatory bodies except in for zinc which was above the limit in *P.edulis*. Heavy metals concentration was within the limits for both samples in sampling point A except for chromium and iron, which were above the maximum permissible limits. The surface water and effluents samples were generally above the standard set by federal ministry of environment of Nigeria. The bioaccumulation factor obtained from the result show that copper had the highest bioaccumulation factor (B.A.F.) in *T.zilli* and *P.edulis* from all sampling stations, while cadmium had the lowest B.A.F. The observed level of heavy metals shows that Challawa is contaminated with heavy metals which source can obviously attributed to the effluent being discharged to the river from Challawa industrial estate.-These heavy metals may be toxic to the aquatic animals (as seen from the observed level in both *T.zilli* and *P.edulis*) and also to humans when these species are consumed.

1. Introduction

Escalating environmental contamination of the environment by toxic substances is of growing concern in Nigeria and worldwide (Ezemonye and Enuneku, 2005). Contaminant of freshwater bodies with a wide variety of pollutants has been a matter of great concern over the last decades, not only because of threat to public water supplies, but also the

damage caused to aquatic lifeand ecosystem (Canli et al, 1998).

Heavy metals are normal constituents of the aquatic environment that occurs as a result of pollution principally due to discharge of untreated waste into the river by many industries (Kucuksegin et al, 2006). The metal which has a relatively high density and toxic at low quantity is referred to as "heavy metal" e.g. arsenic(As), lead(Pb), mercury(Hg), cadmium(Cd), chromium(Cr), thallium(Tl) e.t.c. some "trace metals" are also referred to as heavy metals e.g. copper(Cu), selenium(Se), zinc(Zn), iron(Fe) (Gupta, 2013). Some essentials element/metals e.g. iron (Fe) may also be toxic when in large quantity, sometimes the action of essentials metals can be changed by the toxic metals, resulting into toxicity by interfering with the metabolic process (Pandey and Madhuri,2014).The accumulation of heavy metals in tissues is mainly dependent upon the water concentration of metals and exposure period, while environmental factors such as salinity, pH, hardness and temperature play significant roles in metal accumulation. Contaminants in freshwater ecosystems are of mounting concern today, it include a diversity of substances ranging from agrochemicals to pharmaceutical, aquatic animals are often exposed to repeated influx of these pollutants in varying concentration (Mayuri, 2002).

In the case of fish and amphibians, these contaminants enter their bodies via oral pathways as result of consumption of contaminated plants and animals or due to absorption through their skin (Mayuri., 2002). The bioaccumulation of toxic metals can occur in the body and food chain, so toxic metals generally exhibit chronic toxicity; tannery industry has added pollutants to the aquatic environment, tannery wastewater continue to cause hazardous effects on the aquatic organisms as they also have endocrine disruption effect (Praveenas et al., 2013).

Severe toxicity and bioaccumulation of several heavy metals are also related to aquaculture, by aquaculture the quality of fishes will be deteriorated, resulting into detrimental health of fish eating population (Pandey and Madhuri, 2014). Heavy metals such as As, Cd, Cu, Cr, Fe, Pb, Mn, Hg, Ni, Zn, Sn etc. are very important pollutants which causes severe toxicity to fish and amphibians. Many fish may be the bioindicator of environmental pollution also (Gohil and Mankodi, 2013).

These metals are toxic since they are bioaccumulation in biological organisms and in due course of time, manifest its toxicity, individual heavy metals toxicity varies depending on dose, duration of exposure, species, gender and environmental and nutritional factor (Pandey and Madhuri, 2014)

Since fish and amphibians are bioindicative of the pollution level in the aquatic habitat, this research work aims to assess the level of bioaccumulation in fish (*Tilapia Zilli*) and bullfrog (*Pyxicephalus Edulis*) of heavy metals such as Copper, Iron, Lead Zinc, Cadmium and Chromium which may be discharged into Challawa river by industries located in the study area, The physicochemical condition of the river is also considered to help explain the level of accumulation of these heavy metals.

2. Materials and Methods

2.1. Study Area

Challawa River is located in Challawa industrial estate in Kumbotso local government area of Kano state, Kano state is located in an area extending from latitude $12^0$40' and $10^0$30' and longitude $7^0$40' and $9^0$40' in the northern part of Nigeria. Challawa River is one of the receiving rivers of effluents from tanneries and textile to foods and packaging industries located in Challawa industrial estate, the effluent from the industries are connected by canal and channeled directly into river Challawa.

2.2. Sample Collection

Samples of fish (*Tilapia Zilli)* and bullfrog (*Pyxicephalus Edulis*) were collected at two sampling point/stations during the month of June 2014 were obtained with the help of a local fisherman. Samples of both species were obtained at sampling points A (upstream of the river) and sampling point/station B (downstream of the river) Surface water samples for this study were also collected, within the same period as composite sample at each sampling point.

2.3. Sample Preparation

Samples of fish (*T.zilli*) and bullfrog (*P.edulis*) were collected from sampling point A (upstream) and B (downstream) of Challawa river in Kano state – Nigeria and dried at 105^0C for 24 hours. Both samples were digested using method described by Poldoski (1980) with slight modification; after drying the samples were mashed and sieved into fine powdered. 10 grams each of the powdered samples were weighed into two separate conical flasks after which 10mls of concentrated HNO_3 and 3mls of $HClO_4$ was added, and heated a hot plate for one hour. Each sample was filtered and residue treated with 0.2%v/v HNO_3 to 20mls mark, 4mls of $HClO_4$ and 2mls of concentrated H_2SO_4 was added and the mixture heated in an aluminum block digester until white fume evolved and a clear solution obtained. The clear solution was subsequently diluted with water to the 50mls mark and stored until required for analysis.

2.4. Determinations of Heavy Metals in Fish, Bullfrog, Water and Effluent

Heavy metal analysis was carried out for the following metals; Copper, Iron, Lead Zinc, Cadmium and Chromium using Atomic absorption spectrophotometer (AAS) for samples of fish *(T zilli*) and bullfrog (*P.edulis*) at sampling point A (upstream) and B (downstream) of Challawa river in Kano state – Nigeria. Heavy metal concentration was also determined in samples of water obtained from these sampling points and also in effluent samples discharged into the river from industries in the study area.

2.5. Determination of Bioaccumulation Factor

Bioaccumulation indicates an increase in the level of a chemical/toxicant in a biological organism over time compared to the chemical/toxicant in the environment (Lenntech B.V., 2012). Bioaccumulation factor (BAF) was determined according to the formula.

BAF= Concentration of metals in sample (mg/kg.)/Concentration of metal in sediment (mg/kg)

3. Results and Discussion

Mean concentration of heavy metals analysed in sample of *T. zilli* (Mg/kg) from sampling point A (upstream) and B (downstream of the river is presented in Figures1 and 2. From figure1 it can be observed that the concentration of host heavy meals determined in this species obtained from sampling point downstream were higher than that from those from upstream of the river. For both sampling points the highest concentration (12.033mg/kg) was recorded for iron at sampling point B with cadmium having the least concentration (0.027) at sampling point A. This could be as a result of flow of most of these metals downstream of the river as reflected on the overall results in these sampling points. The recorded concentration of copper, chromium and iron can be observed to be higher than the maximum limits set by Federal Environmental Agency (FEPA-Nigeria) and Food and Agriculture Organization (FAO) Heavy metals such as lead, zinc and cadmium had concentrations below their maximum limits.

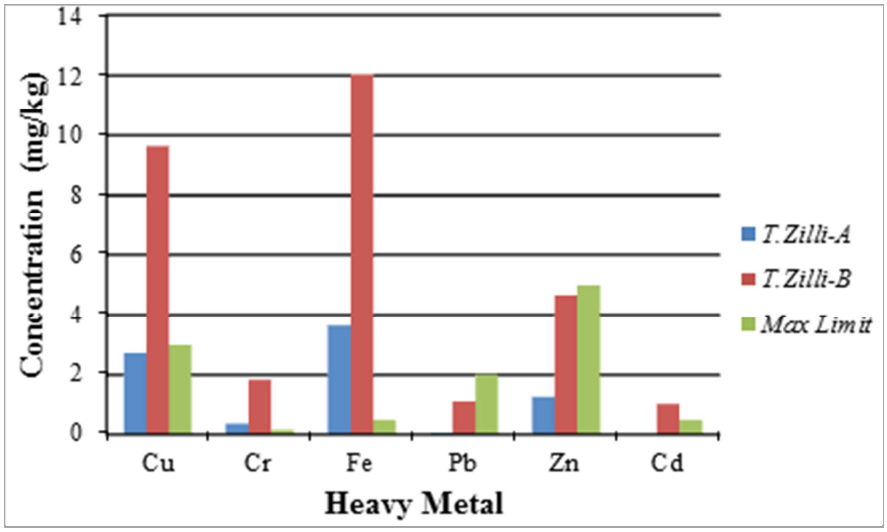

Figure 1. *Mean Concentration (mg/kg) of Heavy Metals in Tilapia Zilli Analyzed from Sampling Stations A and B.*

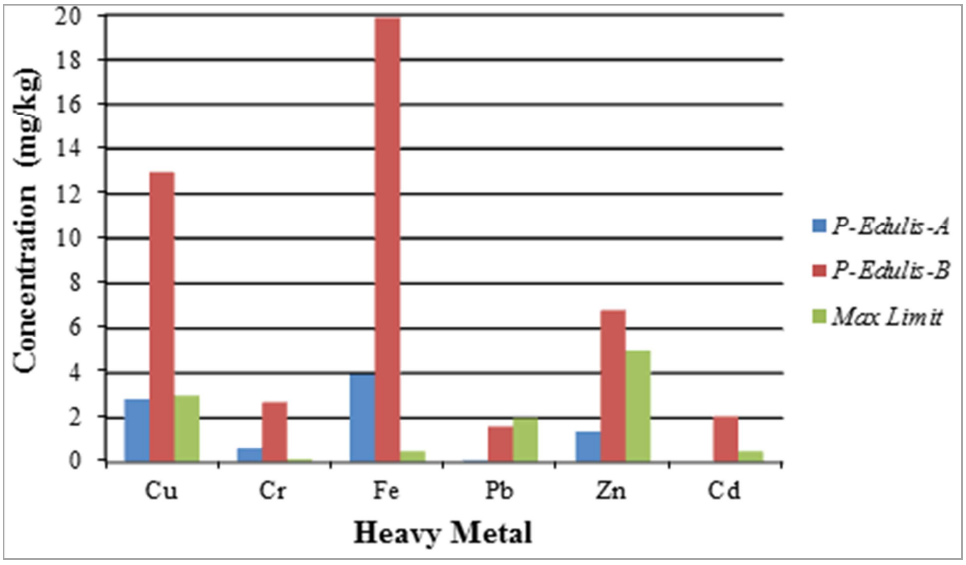

Figure 2. *Mean Concentration (mg/kg) of Heavy Metals in Pyxicephalus Edulis Analysed from Sampling Stations A and B.*

Figure 2 represents the mean concentration (mg/kg) of heavy metals analyzed in bullfrog (*P.Edulis)* from the sampling points A and B (up and downstream of the river respectively)

In the result obtained the same tend can be observed as in the result from Figure 2. In this case copper has higher concentration (19.876 mg/kg) when compared with the concentration (12.033mg/kg) of the same metal in Figure 1. This invariably means that the sample species *P.edulis* can absorb and accumulate more of the metal than *T.zilli.* For the former the concentration of all heavy metals determined from the species obtained downstream were also higher than values obtained upstream and their maximum permissible limits. This trend can also be attributed to reasons previously stated.

The mean concentration of heavy metals in sample aquatic species, water obtained from upstream of the river (Sampling point A) and effluent discharged into the river is shown on table 1. From this result, there is an observed high concentration of metals such as copper, and chromium in both species than that of these metals determined in sample of water collected from the sampling point- A. This is also an indication that *P.edulis* absorbs more easily these heavy metals in its body than *T.zilli.* However the result equally shows that both species in this sampling point absorb more of these metals than other metals determined in this study. Effluent samples analyzed recorded higher concentrations of these heavy metals than that recorded for the aquatic species at this sampling point. Worthy of note is the high concentration of heavy metals in effluent when compared with that in sample water from the river. This could be as a result of discharge of effluent containing most of these metals from industrial activities of tanneries, textile and plastic industries located in the study area.

Table 1. *Concentration (mg/kg) of Heavy Metals in Both Aquatic Species under Investigation Sampled from Upstream of the River (Sampling Point A).*

Heavy metal	T.Zilli-A	Water-A	P-Edulis-A	Effluent
Cu	2.734	2.55	2.836	3.443
Cr	0.348	0.093	0.652	7.425
Fe	3.647	4.334	3.937	32.667
Pb	0.063	0.561	0.098	3.698
Zn	1.274	2.356	1.421	18.379
Cd	0.011	Nd	0.015	0.027

Table 2 reflects the mean concentration of heavy metals in sample aquatic species, water obtained from downstream of the river (Sampling point B) and effluent discharged into the river) The highest heavy metal concentration of 19.876 and 12.033mg/kg of iron in *P.edulis* and *T.zilli* respectively at this sampling point- B. Except for the concentration of copper in both species, other heavy metals determined have values below their concentrations in water samples collected at the sampling point downstream and also that of effluent samples. This is also an indication of increased accumulation of the metal (copper) in the bodies of the species especially *P.edulis* which is observed to have very significant concentration

The overall result indicate that the level of cadmium, iron and copper was higher than the stipulated benchmark by W.H.O/F.A.O (1985) and F.E.P.A (2003) in *T. zilli* and *P.edulis* samples while zinc and lead were within the limits except in *P.edulis* found in sampling point 2 had zinc values higher than the set limit. Generally, the level of heavy metals in the two samples species increased in the following order: Fe>Cu>Zn>Cr>Pb>Cd.,

Table 2. *Concentration (mg/kg) of Heavy Metals in Both Aquatic Species under Investigation Sampled from Downstream of the River (Sampling Point B).*

Heavy metal	T.Zilli-B	Water-B	P-Edulis-B	Effluent
Cu	9.633	3.112	12.966	3.443
Cr	1.845	5.906	2.081	7.425
Fe	12.033	25.422	19.876	32.667
Pb	1.132	2.207	1.636	3.698
Zn	4.663	10.824	6.834	18.379
Cd	1.044	4.568	2.081	0.027

Bioaccumulation factor of heavy metals in the aquatic *T.zilli and P.edulis* obtained from sampling points A and B of the river is presented in table 3. Metals bioaccumulation was observed to be low in the samples of *T.zilli* and *P.edulis* with copper having the highest and cadmium having the least, aquatic organisms living in contaminated water tend to accumulate heavy metals in their organs and tissues, various metals accumulate in different amount.(Jizierska and Witesta,2001). Generally the higher the level of heavy metals in the environment, the more it may be taken and accumulated by aquatic animals (Moissenko et al, 1995). While both species had an bioaccumulation factor for copper in the ranges from 1-4 the bioaccumulation factor for other metals analyzed were below 1. This trend simply shows that the tissues of these organisms have higher affinity for certain heavy metal in this case copper than other metals,\. Despite the fact that some of the metals had higher concentration in water, their accumulation in the tissues of the fish and bullfrog was lower. Various metals are accumulated in aquatic organism body in different amount, these difference results from different affinity of metals to their tissues, different uptake and deposition, excretion rate etc. (Jizierska and Witesta, 2001). Metal distribution in various organs is also time related, accumulation of metals in organs of fish and amphibians is a function of uptake and elimination rate, the effect of time on metal distribution within the organism is a complex issue because of the different affinity of various metals to the tissues of various aquatic organisms. (Jizierska and Witesta, 2001).

Table 3. *Bioaccumulation Factor of Heavy Metals in Both Tilapia Zilli and Pyxicephalus Edulis Obtained from Sampling Point A and B.*

Species/Sampling point	Copper	Iron	Lead	Zinc	Cadmium	Chromium
T. zilli (station A)	3.091	0.473	0.513	0.43	0.229	0.312
P.edulis (station A)	4.166	0.782	0.741	0.631	0.456	0.461
T.zilli (station B)	1.072	0.841	0.112	0.542	0.027	0.375
P.edulis (station B)	1.112	0.908	0.175	0.603	0.048	0.703

4. Conclusion

The levels of Cr, Cd, Fe, Pb, Cu and Zn in *Tilapia zilli* and *Pyxicephalus edulis* sampled from sampling point B located downstream of River Challawa were higher than that in both species obtained from upstream of the river and are also above the maximum permissible limit prescribed by FAO/WHO (1985) and FEPA (2003) for fishes and fish product. Also the level of these heavy metals in the surface water samples from all sampling point were above the limit set by the limit set by the Federal Ministry of Environment of Nigeria (2011) with few exceptions.

The bioaccumulation factors of the heavy metals in *T.zilli* and *P.edulis* could help in elaborating the nature of pollution of the river, although the level of heavy metals is high above set benchmark, the level of accumulation of these heavy metals in the fish and bullfrog sample is low, as a results of the decreased affinity of organs of the sample species to the heavy metals under investigation. River Challawa has been polluted by heavy metals which obvious source is the effluent from surrounding industries being discharged into it. Toxicity of the heavy metals is likely to increase in the long run on these aquatic organism and its human consumers. Continuous monitoring of contamination in River Challawa as well as proper effluent treatment is necessary to prevent further deterioration of the pollution level, also the toxicity of the heavy metals in fishes to their human consumers need to be investigated.

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