

THE CONCENTRATIONS OF HEAVY METALS IN FISH SAMPLES FROM DUKKU RIVER IN KEBBI STATE OF NIGERIA

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Abstract:

*The concentrations of Chromium (Cr), Cadmium (Cd), Copper (Cu) and Lead (Pb) were determined in gills and muscles of Catfish (*Clarias garipienus*) obtained from Dukku River in Kebbi State of Nigeria using Atomic Absorption Spectrophotometer (A.A.S.) The mean concentration of heavy metals in gills and muscles were; Cd (0.167+ 0.029 and 0.133+ 0.058), Pb (8.433+ 4.032 and 9.570+ 3.286), Cr (0.500+ 0.259 and 0.284+ 0.076) and Cu (0.417+ 0.189 and 0.350+ 0.150) respectively. The order of decreasing heavy metal concentrations in the gills and muscles were $Pb > Cr > Cu > Cd$ and $Pb > Cu > Cr > Cd$ respectively. With the exception of Pb, gills were found to have higher concentrations of all the heavy metals analysed. Hence, it could be concluded that the fish (Catfish) in Dukku River was polluted with Pb.*

Keywords: *Heavy metals, catfish, river*

INTRODUCTION

Increasing industrialization has been accompanied throughout the world by the extraction and distribution of mineral substances from their natural deposits. Following concentration, many of these have undergone chemical changes through technical processes and finally pass, finely dispersed and in solutions, by way of effluent, sewage, dumps and dust, into the water, the earth and the air and thus into the food chain. Together with essential nutrients, plants and animals also take up small amounts of contaminant heavy metal compounds and can concentrate them. As certain heavy metals such as lead, cadmium and mercury have been recognized to be potentially toxic within specific limiting values, a considerable potential hazard exists for human nutrition (Gazza, 1990).

Not all the traces of heavy metals in plants and animals are the results of human activity. Some arise through the absorption processes of naturally occurring soil components, as has been shown for cadmium in particular. Purely theoretically, every 1000kg of normal soil contains 200g chromium, 80g nickel, 16g lead, 0.5g mercury and 0.2g cadmium (Gazza, 1990). Therefore it is not always easy to assign a definite cause for increased heavy metal content. Even foodstuffs produced in completely unpolluted areas are not entirely free of

heavy metals. The absorption of very small amounts is therefore unavoidable in principle and has always occurred.

Pollution of the environment is one of the biggest problems today. Pollution affects the health of human beings and other creatures on earth. Dilution of the purity of natural resources takes place due to environment pollution. The study of environmental pollution is quite complex since, all the different elements of nature are inter-related. If we pollute a certain section/part of the ecosystem (air, water, etc), its consequences are bound to reflect in the form of imbalance in nature. Many water-borne diseases are caused by infections which result from the intake of polluted water. Amongst the different water-borne diseases, typhoid, hepatitis, diarrhea, gastroenteritis, encephalitis, ascariasis, giardiasis and amoebiasis are the important ones. Respiratory problems, skin rashes are some of the other health problems caused by water pollution.

Begum et al (2009) reported the analysis of heavy metals in water, sediments and fish samples of Madivala Lakes of Bangalore, Karnataka, the maximum concentration of heavy metals was found in Kidney and Liver, the order of heavy metal levels in various organs is Muscle > Gills > Liver > Kidney. The order of heavy metal concentration in Muscle Pb > Cd > Ni > Cr, in Gills Pb = Cd > Ni > Cr, in Kidney Pb >> Cd > Ni > Cr and in Liver Pb > Cd > Ni > Cr. The presence of elevated levels of Pb and Cd in almost organs is a serious matter of concern and the potential for human exposure to heavy metals from eating fish caught in the lake.

The Rima River is the source of Dukku River between latitudes 10° and 13°N and longitudes 30° and 60°W. Dukku River is one of the most ancient rivers that exist under the Gwandu emirate at least in political importance. The earliest emirate and chiefs of Gwandu emirate, associated with the river in annual fishing and cultural activities in the early days up to today. It has also been used as a source of water, for obtaining food, for transport, as a defensive measure, as a source of disposing of waste. Thus, it has been noted 53% of the people surround rely on this river. It is therefore, quite imperative to conduct various researches with the view to exploring all sources of heavy metals pollution in the environment, which may lead to the discovery of the presence of heavy metals and other contaminants and equally the levels at which they occur and their possible mode of control. The River is located at northwest opposite Tarasa Mountain in Birnin Kebbi, Kebbi State. Kebbi State is an important breeding centre for cattle, sheep and goat. Dukku River is also the source of raw water for the Kebbi State treatment plant. The aim of this research was to assess the levels of heavy metals concentrations in *Clarias garipienus* fish species from Dukku River by determining the concentrations of Cd, Cr, Cu and Pb in the Gills and Muscles of *Clarias garipienus* fish from the River and to compare the levels of these metals in the two organs of the fish species.

Table 1: F.A.O. and W.H.O. recommended guideline levels of some heavy metals in fishes.

Concentration, mg/kg	Heavy metals	Reference
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0.500	Cd	FAO (1983)
0.500	Pb	FAO (1983)
30.000	Cu	FAO (1983)
12 – 13. 00	Cr	USFDA(1993)

(Anderson et al., 1985, Huijuan et al., 2005, Mwita and Nkwengulila, 2008, Olaifa et al., 2010, W.H.O. 1992, 1995).

MATERIALS AND METHODS

Washing Procedure of glass wares

All glass wares were soaked overnight in 10% (v/v) nitric acid, followed by washing with 10% (v/v) hydrochloric acid and rinsed with distilled water and dried before using (Emami et al., 2004).

Sampling

Three samples of Catfish (*Clarias garipienus*) were caught using netting devices in Dukku River, Birnin Kebbi, Kebbi State, Nigeria in April, 2015. The samples were kept in plastic ice box and brought to the laboratory (San and Shrivastava, 2011).

Preparation of reagents

Cd Stock and Standard working solution

2.1032g of cadmium nitrate were dissolved in 250ml of deionised water and the resulting solution was diluted to the mark of 1 litre volumetric flask to obtain 1000ppm stock solution. The working solutions were prepared by transferring 0.1, 0.2, 0.3, 0.4 and 0.5ml of stock solution into a 50ml volumetric flask separately and diluted to the mark with deionised water.

Pb Stock and Standard working solution

1.5980g lead nitrate $Pb(NO_3)_2$ were dissolved in 100ml of deionised water and the resulting solution was diluted to the mark of 1 litre volumetric flask with deionised water to obtain 1000ppm stock solution. The working solutions were prepared by transferring 0.1, 0.2, 0.3, 0.4 and 0.5ml of stock solution into a 50ml volumetric flask separately and diluted to the mark with deionised water.

Cr Stock and Standard working solution

7.6960g of chromium nitrate ($Cr(NO_3)_3 \cdot 9H_2O$) were dissolved in 250ml of deionised water and the resulting solution was diluted with more deionised water to the mark of 1 litre volumetric flask to obtain 1000ppm stock solution. The working solutions were prepared by transferring 0.025, 0.05, 0.075, 0.1 and 0.125ml of stock solution into a 50ml volumetric flask separately and diluted to the mark with deionised water.

Cu Stock and Standard working solution

3.7980g of Copper nitrate [Cu(NO₃)₂·3H₂O] was dissolved in 250ml of deionised water and the resulting solution was diluted with more deionised water to the mark of 1 litre volumetric flask to obtain 1000ppm stock solution. The working solutions were prepared by transferring 0.05, 0.1, 0.15, 0.2 and 0.25ml of stock solution into a 50ml volumetric flask separately and diluted to the mark with deionised water.

Sample Preparation: In the laboratory, fish samples were dissected using a cleaned washed high quality corrosion resistant stainless knife to separate various organs. After dissection, all the samples were labelled according to their species. The entire sample (gills and muscles) were separately dried in a laboratory oven at 175°C for 3 hours (Nwani et al., 2010). The samples were digested according to Nitric Acid- Hydrogen Peroxide (HNO₃/H₂O₂) wet digestion method. The samples were prepared by taking 1.0g of each of the oven dried sample in a beaker, followed by the addition of 30cm³ of freshly prepared 1:1 (v/v) HNO₃ and H₂O₂. Each beaker was covered with a watch glass for about an hour to allow the initial reaction to subside. The beakers were heated on a hot plate with the temperature not exceeding 90°C for 30 minutes. The contents were then transferred into 50cm³ volumetric flask and diluted with deionised water to the mark.

Preparation of blank solution: The blank solution was prepared by adding all the reagents used into 50ml volumetric flask and diluted to the mark with deionised water.

Preparation of Calibration Standard Solutions: 10ml each of standard reference solutions (1000mg/L) for Cd²⁺, Cr³⁺, Pb²⁺ and Cu²⁺ were pipette into 250ml volumetric flask separately and diluted to volume with distilled water. 100mg/L working standards for each metal solution were prepared from the stock solutions. Calibration standards for Cd, Cr, Pb and Cu were prepared by adding appropriate volumes of standard working solutions with distilled water at 4 levels in the range between 0.5 mg/L, 1.0 mg/L, 2.0 mg/L, and 5.0 mg/L (San and Shrivastava, 2011).

Atomic Absorption Analysis of Samples: The digested samples were analysed for heavy metals using Atomic Absorption Spectrophotometer.

RESULTS AND DISCUSSION

Table 2 presents the concentrations (as mean + standard deviation) of the heavy metals analysed in the gills and muscles of *Clarias garipienus* fish species surviving in Dukku River. The levels of these metals in the gills and muscles were compared in Figure 1 - 4.

Table 2: The mean concentration of heavy metals in catfish (*Clarias garipienus*) samples (µg/g).

Sample (Catfish)	Metals			
	Cd	Pb	Cr	Cu
Gills	0.133+ 0.089	7.667+ 2.032	0.517+0.249	0.400+0.289

Muscles 0.117+0.028 9.000+3.225 0.350+0.012 0.433+0.120

Figure 1: Distribution of Cd in fish species of Dukku River (Sample A= 22.0cm, Sample B = 28.5cm and Sample C = 30.3cm) *Samples A, B and C are Catfish Samples of different lengths

Figure 2: Distribution of Pb in fish species of Dukku River (Sample A= 22.0cm, Sample B = 28.5cm and Sample C = 30.3cm) *Samples A, B and C are Catfish Samples of different lengths

Figure 3: Distribution of Cr in fish species of Dukku River (Sample A= 22.0cm, Sample B = 28.5cm and Sample C = 30.3cm) *Samples A, B and C are Catfish Samples of different lengths

Figure 4: Distribution of Cu in fish species of Dukku River (Sample A= 22.0cm, Sample B = 28.5cm and Sample C = 30.3cm) *Samples A, B and C are Catfish Samples of different lengths

The results of the analysis indicated that the mean concentration of Cd in the examined tissues is $0.133 + 0.089 \mu\text{g/g}$ in the gills and $0.117 + 0.028 \mu\text{g/g}$ in the muscles as shown in Table 2. These values were lower than the reported levels indicated according to FAO and WHO maximum limits. The highest concentration of Cd was measured in gills. The mean concentration of Cd ($0.133 + 0.089 \mu\text{g/g}$ in the gills and $0.117 + 0.028 \mu\text{g/g}$ in the muscles) in the present study is similar to that obtained by (Nwani et al., 2010) in which the mean concentration of Cd ($0.152 + 0.041 \mu\text{g/g}$ in the gills and $0.125 + 0.038 \mu\text{g/g}$ in the muscles). The source of Cd in humans is through food consumption. Severe toxic symptoms resulting from Cd ingestion are reported between 10 to 326 mg (Anim et al., 2011). Fatal ingestion of Cd, producing shock and acute renal failure, occur from ingestions exceeding 350mg (Anim et al., 2011).

The results of the analysis indicated that the mean concentration of Pb in the examined tissues is $7.667 + 2.032 \mu\text{g/g}$ in the gills and $9.000 + 3.225 \mu\text{g/g}$ in the muscles as shown in Table 2. These values were higher than the maximum limits values reported by FAO and WHO. The high level of Pb obtained can be attributed to exhaust from trucks loading cattle, sheep and goats around the river. It can also be attributed to agricultural activities and water runoff taking place around the river from the city. In all the samples, the highest concentration of Pb was measured in muscles. The mean concentration of Pb in the present study $7.667 + 2.032 \mu\text{g/g}$ in the gills and $9.000 + 3.225 \mu\text{g/g}$ in the muscles differed from (Nwani et al., 2010) with the mean concentration of Pb $4.432 + 3.032 \mu\text{g/g}$ in the gills and

3.670+1.256 µg/g in the muscles. Pb is classified as one of the most toxic heavy metals. Pb causes renal failure and liver damage in humans.

The results of the analysis indicated that the mean concentration of Cr in the examined tissues is 0.517+0.249 µg/g in the gills and 0.350+0.012 µg/g in the muscles as shown in Table 2. The concentrations of Cr in all tissues were lower than the reported values accepted by WHO and FAO. In all the samples, the highest concentration of Cr was measured in Gills. The mean concentration of Cr 0.517+0.249 µg/g in the gills and 0.350+0.012 µg/g in the muscles in this present study differed from (Nwani et al., 2010) with the mean concentration of Cr 0.635+0.343 µg/g in the gills and 0.356+0.812 µg/g in the muscles. Deficiency of Cr results in impaired growth and disturbances in glucose, lipid and protein metabolism (Anim et al., 2011).

The results of the analysis indicated that the mean concentration of Cu in the examined tissues is 0.400+0.289 µg/g in the gills and 0.433+0.120 µg/g in the muscles as shown in Table 2. These values are less than the reported values by FAO and WHO. The highest concentration of Cu was measured in Gills. The mean concentration of Cu 0.400+0.289 µg/g in the gills and 0.433+0.120 µg/g in the muscles in this study differed from (Nwani et al., 2010) with the mean concentrations of Cu 0.212+0.010 µg/g in the gills and 0.022+0.112 µg/g in the muscles. Cu is an essential part of several enzymes and it is necessary for the synthesis of haemoglobin (Anim et al., 2011).

CONCLUSION

The results of this work were used to evaluate the possible health risk associated with the consumption of the Fish species that were analysed from Dukku River. Regarding the mean concentration of the heavy metal concentration for each metal, it can be said that the concentrations of Pb in all the fish samples were above the recommended maximum limits (WHO and FAO). The concentrations of Cd, Cr and Cu are generally well below the recommended maximum limits (WHO and FAO). The order of decreasing heavy metals in the gills and muscles were Pb > Cr > Cu > Cd > and Pb > Cu > Cr > Cd respectively, hence, it could be concluded that the Fish in Dukku River was polluted with Pb due to human activities.

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