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Article

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, cadmium, copper and lead were determined in gills and muscles of catfish (*Clarias garipienus*) obtained from Dukku River in Kebbi State of Nigeria using atomic absorption spectrophotometer. 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 Pd > 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 analyzed. Hence, it could be concluded that the fish (catfish) in Dukku River was polluted with Pb.

Keywords: heavy metals; catfish; cadmium; lead; river.

1. 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 1000 kg of normal soil contains 200 g chromium, 80 g nickel, 16 g lead, 0.5 g mercury and 0.2 g 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 and 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, and 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^o and 13^1N and longitudes 30^o and 60^1W. 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 the fish from the River and to compare the levels of these metals in the two organs of the fish species.

2. Materials and Methods

2.1. 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).

2.2. 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).

2.3. Preparation of Reagents

2.3.1. Cd stock and standard working solution

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

2.3.2. Pb stock and standard working solution

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

2.3.3. Cr stock and standard working solution

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

2.3.4. Cu stock and standard working solution

The 3.7980 g of copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$) was dissolved in 250 mL of deionized water and the resulting solution was diluted with more deionized water to the mark of 1 L volumetric flask to obtain 1000 ppm stock solution. The working solutions were prepared by transferring 0.05, 0.1, 0.15, 0.2 and 0.25 mL of stock solution into a 50 mL volumetric flask separately and diluted to the mark with deionized water.

2.4. 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 labeled according to their species. The entire sample (gills and muscles) were separately dried in a laboratory oven at 175 ^oC for 3 h (Nwani et al., 2010). The samples were digested according to nitric acid-hydrogen peroxide (HNO_3/H_2O_2) wet digestion method. The samples were prepared by taking 1.0 g of each of the oven dried sample in a beaker, followed by the addition of 30 cm^3 of freshly prepared 1:1 (v/v) HNO_3 and H_2O_2. 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 ^oC for 30 min. The contents were then transferred into 50 cm^3 volumetric flask and diluted with deionized water to the mark.

2.5. Preparation of Blank Solution

The blank solution was prepared by adding all the reagents used into 50 mL volumetric flask and diluted to the mark with deionized water.

2.6. Preparation of Calibration Standard Solutions

The 10 mL each of standard reference solutions (1000 mg/L) for Cd^{2+}, Cr^{3+}, Pb^{2+} and Cu^{2+} were pipette into 250 mL volumetric flask separately and diluted to volume with distilled water. The 100 mg/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).

2.7. Atomic Absorption Analysis of Samples

The digested samples were analyzed for heavy metals using atomic absorption spectrophotometer.

3. Results and Discussion

Table 1 presents the concentrations (as mean ± standard deviation) of the heavy metals analyzed 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 Figs. 1-4.

Table 1. The mean concentration of heavy metals in catfish (*Clarias garipienus*) samples

Sample (Catfish)	Metals (µg/g)			
	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

The results of the analysis indicated that the mean concentration of Cd in the examined tissues is 0.133±0.089 µg/g in the gills and 0.117±0.028 µg/g in the muscles as shown in Table 1. These values were lower than the reported levels indicated according to FAO and WHO maximum limits (Table 2). The highest concentration of Cd was measured in gills. The mean concentration of Cd (0.133±0.089 µg/g in the gills and 0.117±0.028 µg/gin the muscles) in the present study is similar to that obtained by Nwani et al. (2010), in which the mean concentration of Cd was 0.152±0.041 µg/g in the gills and 0.125±0.038 µg/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 350 mg (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 µg/g in the gills and 9.000±3.225 µg/g in the muscles as shown in Table 1. These values were higher than the maximum limits values reported by FAO and WHO (Table 2). 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 was7.667±2.032 µg/g in the gills and 9.000±3.225 µg/g in the muscles, which was differed from Nwani et al. (2010) with the mean concentration of 4.432±3.032 µg/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.

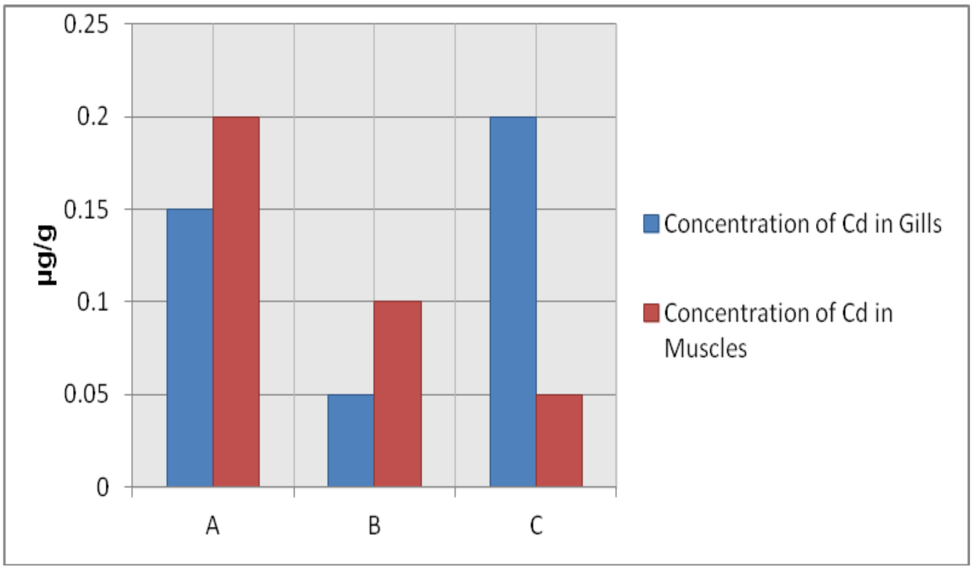

Figure 1. Distribution of Cd in fish species of Dukku River. Samples A, B and C are catfish samples of different lengths, and were 22.0, 28.5 and 30.3 cm, respectively.

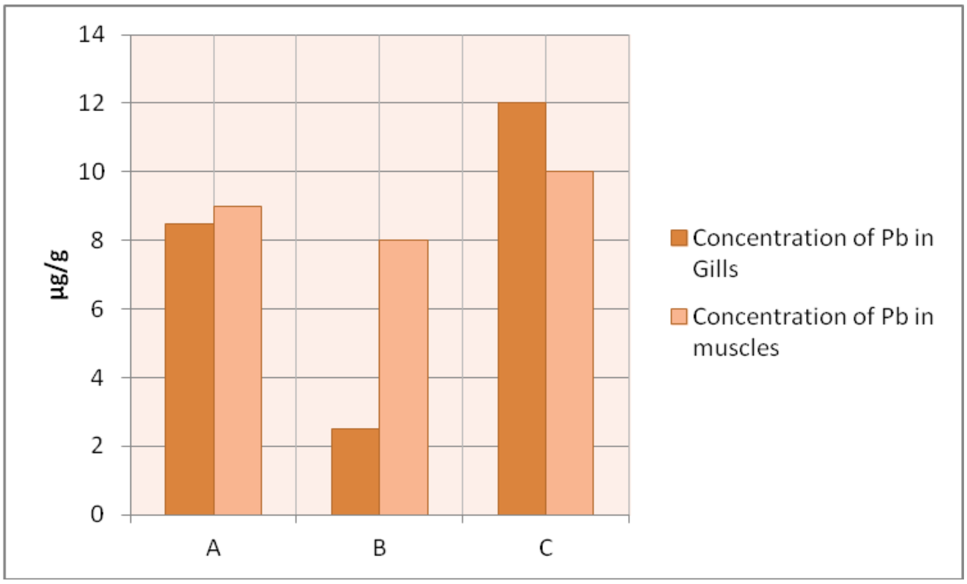

Figure 2. Distribution of Pb in fish species of Dukku River. Samples A, B and C are catfish samples of different lengths, and were 22.0, 28.5 and 30.3 cm, respectively.

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 1. The concentrations of Cr in all tissues were lower than the reported values accepted by WHO and FAO (Table 2). In all the samples, the highest concentration of Cr was measured in gills. The mean concentration of Cr was 0.517±0.249 µg/g in the gills and 0.350±0.012 µg/g in the muscles in this present study, which was differed from Nwani et al. (2010) with the mean concentration of 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).

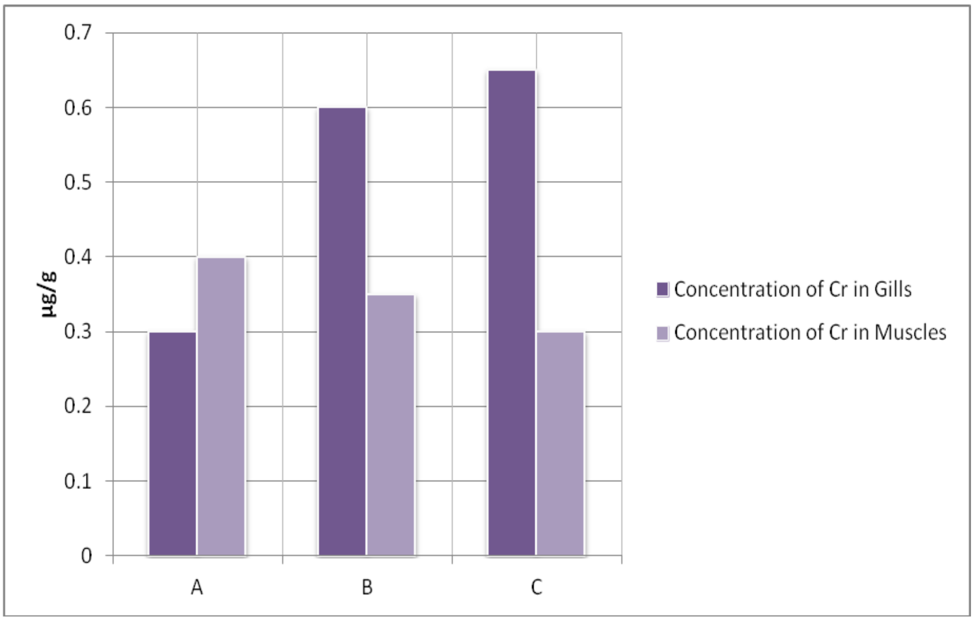

Figure 3. Distribution of Cr in fish species of Dukku River. Samples A, B and C are catfish samples of different lengths, and were 22.0, 28.5 and 30.3 cm, respectively.

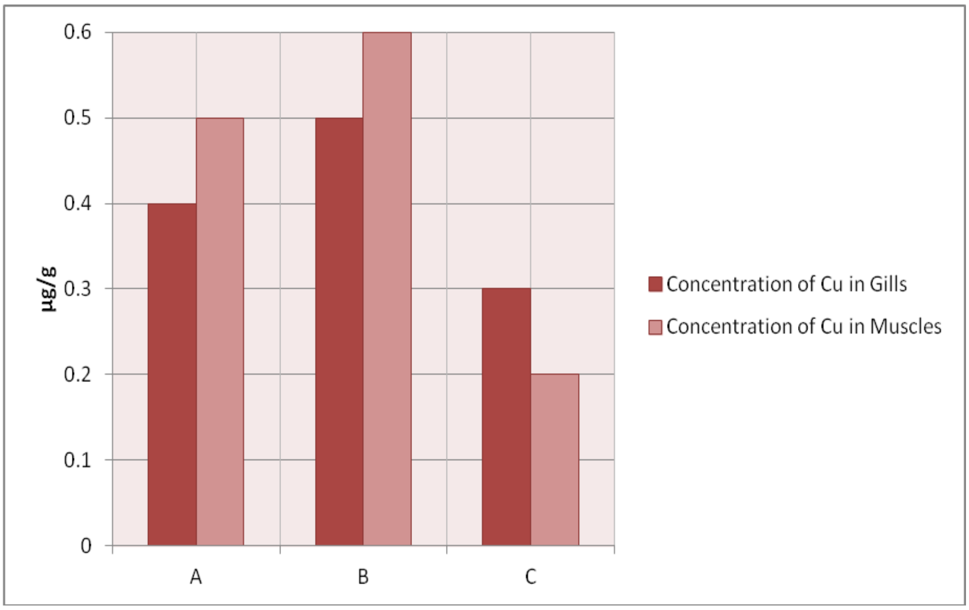

Figure 4. Distribution of Cu in fish species of Dukku River. Samples A, B and C are catfish samples of different lengths, and were 22.0, 28.5 and 30.3 cm, respectively.

Table 1. FAO and WHO recommended guideline levels of some heavy metals in fishes

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

Sources: Anderson et al., 1985; Huijuan et al., 2005; Mwita and Nkwengulila, 2008; Olaifa et al., 2010; WHO, 1992, 1995.

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 1. These values are less than the reported values by FAO and WHO (Table 2). The highest concentration of Cu was measured in gills. The mean concentration of Cu was 0.400±0.289 μg/g in the gills and 0.433±0.120 μg/g in the muscles in this study, which was differed from Nwani et al. (2010) with the mean concentrations of 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).

4. Conclusions

The results of this work were used to evaluate the possible health risk associated with the consumption of the fish species that were analyzed from Dukku River. Regarding the mean concentration of the heavy metals for each metal, it can be said that the concentrations of Pb in all the fish samples were above the recommended maximum limits of WHO and FAO. The concentrations of Cd, Cr and Cu are generally well below the recommended maximum limits of 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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