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Determination of Heavy Metals in Selected Fish Species found in Kwalkwalawa River, Dundaye. Sokoto State

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Abstract: *This work reports the concentrations of heavy metals (Zn, Cu, Pb, Cd, Fe and Ni) in the head, muscle and tail of two species of fish; Clarias gariepinus (catfish) and Oreochromis niloticus (Tilapia fish) obtained from Kwalkwalawa River along Dundaye village, Sokoto State. The analysis was done using Atomic Absorption Spectroscopy (AAS). The results of this analysis reported that there were high level of the analyzed metals (Zn; 71.60 mg/kg, Cu; 21.10 mg/kg, Pb; 24.10 mg/kg, Cd; 1.50 mg/kg, Fe; 46.60 mg/kg and Ni; 2.60 mg/kg) in Clarias gariepinus and (Zn; 58.80 mg/kg, Pb; 16.40 mg/kg, Cu; 17.40 mg/kg, Fe; 39.60 mg/kg, Cd; 1.30 mg/kg and Ni; 1.50 mg/kg) in Oreochromis niloticus sample compared to the World Health Organization (WHO) standard. Hence, the fish obtained from this river may therefore be not safe for consumption.*
Keywords: *Clarias gariepinus, Oreochromis niloticus, Kwalkwalawa River, Heavy metals.*

I. Introduction

Heavy metal is any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations (Lenntech, 2004). Examples of heavy metals include mercury, cadmium, arsenic, copper, chromium, thallium and lead. As trace elements, some heavy metals (e.g. copper, iron, zinc, manganese, cobalt and selenium) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning (Olade, 1987).

Heavy metals are important group of chemical elements, whereby food is the main route for entry into human body tissues (Olowu *et al.,* 2010). Some heavy metals irreversibly are bound to human body tissues, e.g., cadmium to kidneys and lead to bones (Kaplan *et al*., 2011).

In recent years, there have been keen concerns about the contamination of aquatic environment and the attendant consequences on human health (Kelle *et al*., 2015). The high rise in civilization and the progress of industries have led to increased emission of pollutants into the ecosystems. Some of these pollutants, which include heavy metals, are directly discharged by industrial plants and municipal sewage treatment plants; others come from polluted runoff in urban and agricultural areas (Abida *et al*., 2009).

Many dangerous chemical elements such as heavy metals, if released into aquatic environment, accumulate in the soil and sediments of water bodies. The lower aquatic organisms absorb and transfer them through the food chain to higher trophic levels, including fish (Kelle *et al*., 2015).

Fish is one of the most widely distributed organisms in the aquatic environment and considered as one of the main protein source of food for human (Rashed, 2001). Among water foods, fish are commonly consumed and hence, are a connecting link for the transfer of toxic heavy metals in human beings (Olowu et al., 2012). Heavy metals have the tendency to accumulate in various organs of fish which in turn may enter into human metabolism through consumption causing serious health hazards (Khalifa *et al*., 2010).

Fish has been recognized as an important food source for the human body. Fish provides essential fatty acids like Omega 3, proteins, vitamins, and minerals (Enkeleda *et al*., 2013). However, despite its nutritional value, consumption of fish contaminated with heavy metals brings hazard concern for the human consumers. It has been reported that prolonged consumption of unsafe concentrations of heavy metals through foodstuff may lead to the chronic accumulations of the metals in the kidney and liver of humans causing disruption of numerous biochemical processes, leading to cardiovascular, nervous, kidney and bone diseases as heavy metals bioaccumulate (Jarup, 2003).

The rate of bioaccumulation of heavy metals in aquatic organisms depends on the ability of the organisms to digest the metals and the concentration of such metal in the water body. Also, it has to do with the concentration of the heavy metal in the surrounding soil sediments as well as the feeding habits of the organism (Eneji et al., 2011).

There is increasing concern about the quality of aquatic food (e.g. fish) in several parts of the world. The determination of toxic elements in food has prompted studies on toxicological effects of heavy metals in foods (Indrajit *et al.,* 2011).

II. Materials And Methods

Reagents and instruments

All reagents (HNO_3 and HCl) used were of British drug house (BDH) grades. Glass wares; beaker, measuring cylinder and volumetric flask used were washed and rinsed with deionized water before using.

Sample collection

The fish samples were collected from Kwalkwalawa River which passes through Usmanu Danfodiyo university, Sokoto. The fish samples considered are; *Clarias gariepinus* (Catfish) and *Oreochromis niloticus* (Tilapia fish). The samples were bought at the river bank after the villagers had caught them using fishing net. After collection, the fish samples were transported to the Usmanu Danfodiyo University's Chemistry laboratory for further analysis.

Methods

Preparation of aqua regia solution

Aqua regia solution, HNO_3-HCl (3:1) was prepared by adding 25ml of Conc. HCl to 75ml of Conc. HNO_3.

Preparation/digestion of fish sample

The fish samples were prepared using the method used by Ozmen et al, (2004), the part of fish sample such as heart, muscle and tail needed for the analysis were separated and oven-dried at 80°C for 48hrs. These samples were ground to powder using clean mortar and pestle. One (1) gram of each homogenized fish part was weighed into different beakers and into each beaker was added 20ml of the mixture of aqua regia solution and digested to a clear colorless solution using hot plate at 80°C. The digests were allowed to cool, filtered through Whatmann No.1 filter paper and then transferred to different 50ml volumetric flasks and filled to 25ml mark with de-ionized water and kept ready for AAS analysis. All the digested samples were taken to Energy Research Centre, Usmanu Danfodiyo University, Sokoto for AAS analysis.

III. Results And Discussion

Results

The results gotten from the atomic absorption spectroscopy (AAS) analysis of the various prepared samples are given in the table below;

Table 1: Concentration of heavy metals in fish part in (mg/kg)

S/No	SAMPLE CODE	ZINC (Zn)	LEAD (Pb)	COPPER (Cu)	IRON (Fe)	CADMIUM (Cd)	NICKEL (Ni)
1	A	85.10	25.40	31.90	76.60	2.10	4.50
2	B	65.80	18.90	17.10	32.50	1.00	1.70
3	C	63.40	17.90	15.20	30.80	1.10	1.50
4	D	74.40	20.90	25.70	5440	1.60	2.40
5	E	44.20	10.80	10.80	14.70	1.30	1..40
6	F	57.90	19.60	14.80	29.80	1.20	0.80

Key

A = The head part of *Clarias gariepinus* (Catfish)
B = The body of *Clarias gariepinus* (Catfish)
C= The tail part of *Clarias gariepinus* (Catfish)
D = The head part of *Oreochromis niloticus* (Tilapia fish)
E = The body (muscle) part of *Oreochromis niloticus* (Tilapia fish)
F = The tail part of *Oreochromis niloticus* (Tilapia fish)

Table 2: World Health Organization (WHO) recommended heavy metal levels in fish in (mg/kg)

Zn	Pb	Cu	Fe	Cd	Ni	Reference
5.000	0.010	2.250	0.300	0.010	0.100	WHO 2003

Table 3: Average concentration of heavy metals in each of the fish sample in (mg/kg)

FISH SPECIES	ZINC (Zn)	LEAD (Pb)	COPPER (Cu)	IRON (Fe)	CADMIUM (Cd)	NICKEL (Ni)
Clarias gariepinus (Catfish)	71.60	21.40	21.10	46.60	1.50	2.60
Oreochromis niloticus (Tilapia fish)	58.80	16.40	17.40	39.60	1.30	1.50

IV. Discussion

The results obtained from the Atomic Absorption Spectroscopy (AAS) analysis have shown that these heavy metals; Zn, Pb, Cu, Fe, Cd, and Ni were all present in all the two fish samples analyzed as shown in table 1. The permissible limit of the concentrations of Zn, Pb, Cu, Fe, Cd, and Ni in fishes according to World Health Organization (WHO) 2003 is presented in table 2.

From Table 1, it could be seen that sample A (head part of Catfish) and D (the head part of Tilapia fish) showed concentration of heavy metals that were more than the rest of the samples. This was not unexpected because past works on similar research had shown that the heavy metals tend to accumulate more in the head parts than the body (muscle) and the tail part of fishes (Khalifa *et al*., 2010). For samples B (muscle part of catfish) and E (muscle part of tilapia fish), aside from Cadmium which recorded concentration that is higher in E than in B (Cd; 1.30 mg/kg in E, and 1.00 mg/kg in B), the concentration of the other analyzed metals were higher in B than in E. For instance, Zn, Pb, Cu, Fe and Ni had concentration of 65.80 mg/kg, 18.90 mg/kg, 17.10 mg/kg, 32.50 mg/kg and 1.70 mg/kg respectively in sample B while their respective concentrations were 44.20 mg/kg, 10.80 mg/kg, 10.80 mg/kg, 14.70 mg/kg and 1.40 mg/kg in Sample E. Also for sample C (tail part of catfish) and F (tail part of tilapia fish), aside from Pb and Cd which recorded concentration that were higher in F than in C (for Pb; 19.60 mg/kg in F and 17.90 mg/kg in C while for Cd; 1.20 mg/kg in F and 1.10 mg/kg in C), the concentration of the other analyzed metals were higher in C than in F. For instance, Zn, Cu, Fe and Ni had concentration of 63.90 mg/kg, 14.20 mg/kg, 30.80 mg/kg and 1.50 mg/kg in sample C respectively while their respective concentration were 57.90 mg/kg, 15.80 mg/kg, 49.80 mg/kg and 0.80 mg/kg in sample F. This was as a result of the scales found on the body of *Oreochromis niloticus* (Sample E) which was removed before the sample was treated prior to analysis. These scales were absent in *Clarias gariepinus* (Sample B). The scales have been found to help in the reduction of heavy metals accumulations on the fish body (Khalifa *et al*., 2010).
Below are a detailed discussion on the concentrations of the various metals studied, the comparison of their concentrations with (i) similar studies (ii) international organizations standards and also, the implications of these results and their health consequences on human.

Zinc

Zinc had the highest concentration of all the heavy metals analyzed in sample A (85.10 mg/kg) while the lowest concentration of Zn was recorded in sample E (44.20 mg/kg). The concentration of Zn in samples B, C, D and F were 65.80 mg/kg, 63.90 mg/kg, 74.40 mg/kg and 57.90 mg/kg respectively. The levels of Zn in samples A and D (the head parts of both fish samples; 85.10 mg/kg and 74.40 mg/kg respectively) were higher than the values; 7.68 mg/kg and 6.50 mg/kg gotten by Indrajit *et al*., (2011) in their study of heavy metals level in fish samples taken from river Yamuna (Delhi) in India. The levels of Zn in the body parts of both *Oreochromis niloticus* (sample B; 65.80 mg/kg) and *Clarias gariepinus* (sample E; 44.20 mg/kg) were higher than the results; 5.80 mg/kg and 6.49 mg/kg obtained by these scholars. Also, Zn had the concentration of 63.40 mg/kg and 57.90 mg/kg in sample C and F (the tail parts of both *Oreochromis niloticus* and *Clarias gariepinus*) respectively which are higher than the ones (6.68 mg/kg and 4.91 mg/kg) reported by Indrajit *et al.*, (2011). Table 3 showed the average heavy metals contents of each of the fishes used in this research; *Oreochromis niloticus* had an average Zn concentration of 58.80 mg/kg, and 71.60 mg/kg for *Clarias gariepinus* which were higher than the values obtained by Indrajit et al.,(2011), (6.38 mg/kg and 6.36 mg/kg). And also, higher than the permissible limit reported by WHO 2003.

Lead

The head part of *Clarias gariepinus* (sample A) recorded the highest Pb concentration (25.40 mg/kg) of all the samples analyzed while the lowest (10.80 mg/kg) was recorded in sample E (muscl part of *Oreochromis niloticu*). 18.90 mg/kg, 17.90 mg/kg, 20.90 mg/kg and 19.60 mg/kg were the concentrations gotten from samples B, C, D and F respectively. The head parts of the fish samples (samples A and D) gave Pb concentrations; 25.40 mg/kg and 20.90 mg/kg respectively that were higher than the values; 0.75 mg/kg and 0.47 mg/kg obtained by Indrajit *et al*., (2011). Also, the muscle part concentration of Pb of 2.40 mg/kg for *Clarias gariepinus* and 0.22 mg/kg for *Oreochromis niloticus* gotten by Indrajit *et al*., (2011) was lower than the ones obtained in this study for *Clarias gariepinus* (samples B) and *Oreochromis niloticus* (sample E). For the average Pb concentration obtained in both *Clarias gariepinus* (21.40 mg/kg) and *Oreochromis niloticus* (16.40 mg/kg) were higher than the acceptable limit of 0.010 mg/kg according to WHO 2003

Copper

Sample E (tail part of *Orechromis niloticus*) showed the lowest Cu concentration with 10.80 mg/kg while the heat part of *Clarias gariepinus* (sample A) had the highest Cu concentration (31.90 mg/kg). The Cu concentration in sample B, C, D, and F were 17.10 mg/kg, 14.20 mg/kg, 25.70 mg/kg and 15.80 mg/kg respectively. Compared to Indrajit *et al*., (2011) results, the head parts of the fish samples (samples A and D) contained more Cu content than the 1.69 mg/kg and 1.50 mg/kg gotten by Indrajit and his mates. On the other hand, the body parts of both *Clarias gariepinus* (sample B; 17.10 mg/kg) and *Orechromis niloticus* (sample E; 10.80 mg/kg) had concentration higher than the values (3.68 mg/kg and 1.39 mg/kg) of Indrajit *et al*., (2011). Also, the tail parts of both catfish (sample C) and tilapia fish (sample F) showed concentrations that were higher than the values; 2.86 mg/kg and 1.43 mg/kg recorded by Indrajit *et al.*, (2011). The average Cu contents in *Clarias gariepinu* (Catfish); (21.10 mg/kg) and in Tilapia fish (17.40 mg/kg) were higher than the value (7.30 mg/kg) obtained in Odumuyiwa's study. The 2.25 mg/kg of Cu concentration recommended by WHO is well below all the concentrations showed by all the samples.

Cadmium

The Cd concentrations are generally low in all the samples. The head parts of *Clarias gariepiuns* (sample A) led the rank with 2.10 mg/kg of Cd content while the body parts of the same fish sample (sample B) had the lowest Cd content with 1.00 mg/kg. samples C, D, E and F had concentrations of 1.10 mg/kg, 1.60 mg/kg, 1.30 mg/kg and 1.20 mg/kg respectively. Comparison with the work of Indrajit *et al*., (2011) showed that the head parts of the fish samples (samples A and D) had concentrations lower than 6.10 mg/kg and 13.30 mg/kg obtained by Indrajit *et al*., (2011). The muscle part of both *Clarias gariepinus* (sample B; 1.00 mg/kg) and *Oreochromis niloticus* (sample E; 1.30 mg/kg) gave the concentration of Cd lower than 4.57 mg/kg and 3.00 mg/kg values obtained by these scholars. Also, the tail part of *Clarias gariepinus* (sample C; 1.10 mg/kg) and that of *Oreochromis niloticus* (sample F; 1.20 mg/kg) gave Cd concentrations higher than; 0.03 mg/kg and 0.02 mg/kg reported by Indrajit *et al* (2011). The average concentrations of Cd in both catfish (1.50 mg/kg) and tilapia fish (1.30 mg/kg) in table 3 were found to be higher than the 0.026 mg/kg and 0.03mg/kg recorded during Indrajit *et al.*, (2011) research. And also, higher than the WHO recommended value of 0.010 mg/kg.

Iron

Fe had its lowest concentration in sample E (14.70 mg/kg) while sample A recorded the highest concentration of Fe with (76.60 mg/kg). The Fe concentration in sample B, C, D and F were 32.50 mg/kg, 30.8 mg/kg, 54.40 mg/kg and 29.80 mg/kg respectively. The concentration of sample A and D (the head parts of catfish and tilapia) were higher than the values; 20.00 mg/kg and 54.02 mg/kg gotten during Eneji *et al.*, (2011) study of bioaccumulation of heavy metals in fish (*Tilapia Zilli* and *Clarias gariepinus*) from River Benue, Nigeria. However, body part of both *Clarias gariepinus* (sample B; 32.50 mg/kg) and *Oreochromis niloticus* (sample E; 14.70 mg/kg) had concentrations lower than the values (41.3 mg/kg and 35.2 mg/kg) of Eneji *et al*., (2011). The average concentrations of Fe in both *Clarias gariepinus* (46.60 mg/kg) and *Oreochromis niloticus* (39.60 mg/kg) in table 3 were found to be higher than the 0.20 mg/kg and 0.40 mg/kg recorded during Adewumi *et al*., (2014) research. And also, higher than 0.30 mg/kg recommended by WHO 2003.

Nickel

The head part of *Clarias gariepinus* (Sample A) showed the highest concentration of Ni (4.50 mg/kg) while sample F (tail part of *Oreochromis niloticus*) with 0.80 mg/kg recorded the least concentration of Ni. Samples B, C, D and E were 1.70 mg/kg, 1.50 mg/kg, 2.40 mg/kg and 1.40 mg/kg rich in Ni respectively. Sample A (the head pat of Catfish) had the same concentration as 4.50 mg/kg gotten during Indrajit *et al.*, (2011) study for the head parts while sample D (the head of Tilapia fish) recorded value (2.40 mg/kg) higher than that of Indrajit *et al*.,(2011), (0.50 mg/kg). For the body *Clarias gariepinus* (sample B; 1.70 mg/kg) and *Oreochromis niloticus* (sample E; 1.40 mg/kg), the level of Ni obtained were higher than the ones (0.04 mg/kg and 0.30 mg/kg) obtained by same Indrajit *et al*., (2011). Also, the tail part of *Clarias gariepinus* (sample C) and *Oreochromis niloticus* (sample F) gave concentrations; 1.50 mg/kg and 0.80 mg/kg higher than 0.29 mg/kg and 0.30 mg/kg recorded by Indrajit *et al*., (2011). Table 3 showed average concentrations of Ni in *Clarias gariepinus* to be 2.60 mg/kg and and that of *Oreochromis niloticus* to be 1.50 mg/kg. These were higher than the 1.28 mg/kg and 1.40 mg/kg recorded by Adewumi *et al.*, (2014). And also higher than 0.10 mg/kg recommended by WHO 2003.

V. Conclusion And Recommendations

Conclusion

From the result obtained, it was seen that the heavy metals concentrations were all together high in the two fish samples analyzed. This study revealed that the concentration of these metals (Zn; 71.60 mg/kg , Pb; 21.40 mg/kg, Fe; 46.60 mg/kg, Cd; 1.50 mg/kg and Ni; 2.60 mg/kg) in *Clarias gariepinus* and (Zn; 58.80 mg/kg, Pb; 164 mg/kg, Fe; 39.6 mg/kg, Cd; 1.30 mg/kg and Ni; 1.50 mg/kg) in *Oreochromis niloticus* were higher than the permissible limit (Zn; 5.000 mg/kg, Pb; 0.010 mg/kg, Cu; 2.250 mg/kg, Fe; 0.300 mg/kg, Cd; 0.010 mg/kg and Ni; 0100 mg/kg) stipulated by WHO 2003.

The fishes obtained from the river may be unsafe and dangerous for consumption. This is due to especially high levels of Cd, Ni, and Pb in both fish samples. These metals are associated with various diseases for example, Cd is found to be teratogenic, carcinogenic and possibly, metagenic. Also, Pb is a poisonous metal which can damage nervous connections (especially in children) and cause blood and brain disorder. Excessive intake of lead can also cause rephropathy. Exposure to Ni causes skin irritation and ulceration.

VI. Recommendation

Based on the analysis carried out, the following recommendations are made;

1. The general public should be informed and enlightened on the health hazards involved in the consumption of fishes taken from the river.
2. The ministry of health and environment should be notified so that proper actions will be taken immediately
3. More researches should be carried out with more fish species from the river to ascertain these findings.

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