THE DETERMINATION OF HEAVY METAL POLLUTANTS IN SOME FISH SAMPLES FROM RIVER BENUE

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Abstract

Analysis was carried out for the determination of heavy metals (zinc, cadmium, lead and platinum) in fish tissues using Atomic Absorption Spectroscopy (A.A.S.). The fish samples were purchased from Wadata market in Makurdi. *Labeo coubie* (African carp) and *Clarias species* (mudfish) were chosen and labeled F_1 aud F_2 respectively. The tissues including liver, gut, gills and muscles were digested using the method of wet decomposition to obtain sample solutions. The digest was diluted with de-ionized water and taken for heavy metal determination using A.A.S. At various wavelengths, each metal of interest was determined with the cathode lamp as light source of the particular metal. The concentration of each heavy metal was recorded in parts per million (p.p.m). Results obtained for F| from the various tissues indicate mean values of 6.76ppm for zinc, 1.41ppm for cadmium, 6.35ppm for lead and 0.45ppm for platinum. For F_2, mean values of 7.46ppm for zinc, 1.58ppm for cadmium, 6.52ppm for lead and 0.47ppm for platinum were obtained. Comparing results from both F_1 and F_2, it could be inferred that the bottom feeders F_2, accumulated slightly more of the heavy metals than the surface feeders F|. This is probably due to the accumulation of the metals in the sediments from which F_2 mostly feed as well as their physiological differences.]

Introduction

Water has many uses such as domestic, agricultural and industrial. It is also an environment for the breeding of aquatic organisms. However, the presence of certain substances at higher concentrations more than normal makes the water to be polluted.

The term pollution as applied to water is used in many senses and so cannot be defined precisely. Water becomes polluted when it contains biological, chemical or physical materials that degrade its quality for the intended use. Generally, the intended use of water determines what constitutes a pollutant. For the purpose of this study water would be regarded as polluted if it contains heavy metals or other substances that render it unsuitable for public supply or unsafe to support aquatic life as well as affect the ultimate consumers in the aquatic food web.

There is growing concern for environmental pollution particularly as it affects water. Indiscriminate discharge of domestic, agricultural and industrial waster into bodies of water, on land and into the air continues unabated. Despite regulations put in place by the Federal Environmental Protection Agency, FEPA, to control waste disposal, cases of pollution arising from waste disposal abound. However, the presence of heavy metals in water is not limited to waste discharges. It may also have geological origin.

River Benue takes its source from the Adamavva-Bamenda Highlands and travels for about 750km past Makurdi before joining River Niger at Lokoja. The Highlands is formed from the volcanic eruption of the molten magma from the earth's crust. The basement complex rock of the river is overlain by young sedimentary rock. The geology of the strata through which the water is drawn as well as the land form along its course is likely to constitute sources of pollution. However, this would depend on the nature of soluble substances it contains. Dissolved substances from rocks, peat and other natural sources would greatly affect the quality of water of River Benue.

The upper course of River Benue is dammed in Cameroun Republic. Apart from this, there is no further significant man-made development or heavy industrial development along the course of the river before Makurdi. However, there are some farmlands along the course of the river. In Makurdi, that water is clear and satisfies the water requirements of the city. Many small drains flow into the river from Gboko Road, Wurukum, North Bank and Wadata. Industries such as Benue Breweries, Nigeria Bottling Company and Burnt Bricks discharge their untreated wastes into the river rendering it unfit for use. However, due to the large size of the river, these wastes do not "change the easily observable physical properties of the river water such as colour, taste 3nd odour.

Heavy metals in trace amounts are normal constituents of freshwater. At high concentration, heavy metals are toxic to living organisms in aquatic environment. Increased accumulation of these

metals in fish and other aquatic organisms could make than unfit for food (Annune and lyaniwure, 1993). Bio-concentration is the process whereby biological organisms absorb chemical substance from the environment over a long time resulting in the chemical concentration in the organisms that may exceed those in the environment (Frank, ct. al, 1993). For our study, the reference environment is water. It is the mineralization of these heavy metals in water to form complex salt that is absorbed and accumulated in different tissues of fish in different amounts over a certain period of time that results in the bio-magnification and food chain accumulation of heavy metals and organic chemicals.-The bio accumulation of trace metals by fish has been extensively studied (Ceareley and Coleman, 1974). In a report, Oladimeji (1986) has noted that the River Kaduna is heavily contaminated with heavy metals namely copper, chromium, iron, nickel, molybdenum, selenium, vanadium, zinc, cadmium, mercury and lead. In a related study, Nwacdozie (1998) make comparison of the accumulation of lead, mercury, cadmium, and chromium among ten species of fish in River Kaduna.

Presently no studies have been carried out and reported on the accumulation of heavy metal in fishes in River Benue within Makurdi city. This therefore aroused interest in the present study to determine the bioaccumulation of certain heavy metals namely zinc, cadmium, lead and platinum in the liver, gut, gills and muscle of two species of fish *Laheo coubie* (African carp) and *Clarias species* (mud fish).

The presence of these heavy metals in the aquatic environment is known to exert a wide range of effects on fish from metabolic and physiological to behavioral and ecological (Forstner and Witttmann, 1981). Fish is found all over the world in several aquatic environments and are consumed in various ways. This work determines the levels of zinc, cadmium, lead and platinum in liver, gut, gills and muscles of fresh fish samples sold in Wadata market, Makurdi.

Experimental

A) **Reagents and Glassware:** Concentrated Analar grade nitric acid, perchloric acid and sulphuric acid were used. Laboratory distilled water was de-ionized by passing through a mixed anion and cation exchangers. All glassware were cleaned by washing with soap solution, and rinsed with de-ionized water.

B) Collection of Fish Samples: Fresh fish samples (five each) of *Labeo conbie* and *Clarias species* were purchased from a seller in Wadata market, Makurdi. A fisherman, who happens to be the fish trader's husband, using a net, caught the fishes at various locations from River Benue within Makurdi town. The samples were taken in polythene bags to the laboratory and stored in a refrigerator under 4°C.

C) **Isolation** of **Tissues for Analysis:** The fish samples were taken to the fishery laboratory for identification and isolation of the liver, gut, gills and muscles using a sterilized dissecting set. These tissues were collected in glass dishes and taken for oven drying.

D) Preparation of Sample Tissues: The isolated fish tissues were placed in acid washed glass dish and dried in an oven at a temperature of 80°C for 48hours. The dried and brittle samples were homogenized tissue by tissue in a thoroughly washed and rinsed mortar and pestle.

E) Wet Digestion: 0.5g of the fish sample was weighed, into 250ctn3 conical flask. 20cm3 of concentrated nitric acid was added and placed on a 6 units digestion heater. It was heated for about 30minutes until when brown fumes started coming out. 20cm3 of perchloric acid was then added and allowed to digest for 2hours. The flask with its content was then cooled and de-ionized water added to dissolve the digest. The content of the flask was transferred into a 100cm3 volumetric flask and made up to the mark with more de-ionized water, ready for heavy metals determination using Atomic Absorption Spectroscopy (A.A.S.). This was done in" triplicate for each of the ten samples of fish under investigation. The fish samples were labeled. F_1A, F_1, F_1 C, F_1D, F_1E, and F_2A, F_2B, F_2C, F_2D, F_2E respectively.

Results and Discussion

Results are shown in Tables 1,2 3 and 4. Table 1 is for *Labeo conbie* and Table 2 for *Clarias species*. Table 3 shows the mean for each fish sample and Table 4 indicates the values of the-concentrations of the heavy metals under consideration in River Benue.

The result shown in Table 1 for *Labeo coubie,* samples F,A to F_1E indicates a gradation in the accumulation of the metals following the order liver > gut > gills > muscles. Results also indicate that the bioaccumulation of platinum is generally small. The bio accumulation of the heavy metals in the fish samples F_1A to F_1E is in the order zinc > lead » cadmium > platinum.

Table 2 which shows the result for *Clarias species* samples F_2A, to F_2E have relatively higher values of the bio-accumulated heavy metals in the tissues than F|A to F,E. For all the metals determined, the order is liver > gut > gills > muscles. It is also observed from the result that the bioaccumulation of the heavy metals in the fish samples F_2A to F_2E is in the same order of: zinc > lead » cadmium > platinum.

Fishes respond to the salinity or other changes in the concentration of ions in water. This necessitates the presence of osmoregulatory devices in the fishes which make them adjust to changing conditions. These heavy metals get into the body of fish through their mouth as they feed or through their gills as they respire. Osmosis plays a major role as a mechanism for the uptake of these heavy metals into the fish.

In cases where the salinity of the external medium (aquatic environment) fluctuates unduly, the fish is able to osmoregulate without breaking down. This independence of its osmotic environment is due to changes in the filtration rate of the kidney and reversal of the direction in which the salt secretory cells transfer salt (Forstner and Wittmann, 1981). This is particularly observed in salmon. More salt is made to enter the tissues in dilute environment whereas in water with more concentrated salt, the tendency is to excrete more in order to maintain a certain maximum level of the substances in the tissues.

The observed effects of heavy metals on fish include disturbances in osmoregulation (Lewis and Lewis, 1971) and respiration (Hughes, 1981), tissues damage especially in the gills (Ronald et. al; 1986), reduced energetic resources (Heath, 1984) and poor growth performance.

Heavy metals taken in through its accumulation in fish has both good and bad effects on man, that is to say, the deficiency of certain heavy metals and its presence in excess have both advantages and disadvantages in man. The presence of certain heavy metals in excess may have antagonistic effect on the metabolism of some important growth factors, for example zinc on vitamin C metabolism. In some cases, the uptake of some metals is significantly reduced as in the case of copper (Health, 1984).

It is known that little concentration of lead which get into water through waste water discharges from industrial plants and some other sources causes serious physiological effect on the human nervous system, leading to brain damage as well as poor eyesight. Lead as a pollutant in slightly high concentration destroys fishes, plankton and other aquatic animals.

Zinc is one of the most important trace elements involved in the proper functioning of over 50 enzymes in the human body. It is now believed that low zinc intake may actually contribute to the onset of anorexia (Ronald et. al; 1986). Even though lead and cadmium are known to be chronic pollutants, they are found along with other elements in the human body at the active site of the antioxidant enzymes. It has been suggested (Armac and Lassus, 1985) that some oxidase use these metals as catalyst in their active site to overcome the slow reaction of molecular oxygen.

Bio-magnification or dietary accumulation can be viewed as a two-step process. First, the chemical enters the gastrointestinal tract (GIT) in association with food. Secondly, the chemical is absorbed by the organism from the gastrointestinal tract. Bio-magnification and food chain accumulation thus could not occur unless there is an active uptake mechanism. However, if the chemical fugacity in the food is elevated from 1 to 5pa in the GIT, then passive diffusion could result in a chemical fugacity in the organism of up to Spa and bio-magnification could occur. The extent to which the fugacity in the organism is raised above that of the food and water as a result of ;the net uptake of the chemical from the GIT is dependent on the rate of chemical elimination from the organism through gills, urine excretion and metabolic transformation as well as the rate of growth.

Gastrointestinal magnification can only result in the bio-magnification in the fish -if gills elimination and metabolic transformation in the fish are small compared to gastrointestinal uptake, causing the chemical fugacity in the fish to approach that in the GIT. Growth of the organism also has a

significant effect on the extent of bio-magnification in the organism, as growth tends to reduce the chemical fugacity in the organism in a fashion similar to chemical elimination or metabolic transformation (Giesy and Wiener, 1977). Therefore, it is expected that these heavy metals will be accumulated in the fish tissues especially in the GIT more than the concentration in water.

Conclusion

Results of this research indicate a general low level of pollution of River Benue with these heavy metals with the resultant low level of bioaccumulation in the fish samples. So far, no cases of fish poisoning have been reported in Makurdi and its environs arising from heavy metals pollution of the water. However, there is need to educate the people on the effects of unchecked domestic, industrial and agricultural waste discharges on aquatic flora and fauna and on the ultimate consumer which is man.

Table 1; Results of Analysis *of Labeo Collbie* (African Carp) (Surface Feeder) F,A to F_1E

Sample	Zn	Cd	Pb	Pt
F,A				
Liver	7.93	1.52	7.11	0.56
Gut	7.55	1.46	6.90	0.45
Gills	7.00	1.26	6.23	0.36
Muscles	5.23	1.15	5.10	0.30
F,B				
Liver	7.98	1.63	7.42	0.58
Gut	7.11	1.48	7.02	0.47
Gills	6.16	1.30	6.03	0.40
Muscles	5.35	1.17	5.28	0.34
F,C				
Liver	7.90	1.72	7.01	0.60
Gut	7.02	1.49	6.70	0.50
Gills	6.50	1.33	6.40	0.44
Muscles	5.46	1.18	5.22	0.35
F,D				
Liver	7.75	1.93	6.61	0.55
Gut	6.96	1.50	6.63	0.46
Gills	6.36	1.35	6.28	0.42
Muscles	5.68	1.20	5.51	0.32
F,E				
Liver	7.91	1.65	6.98	0.62
Gut	7.03	1.38	6.60	0.49
Gills	6.44	1.25	6.25	0.41
Muscles	5.83	1.15	5.42	0.30

Table 2: Results of Analysis of *Clarias species* (Mud Fish) (Bottom Feeders) F_2A to F_2E (in ppm)

Sample	Zn	Cd	Pb	Pt
	8.72	2.19	6.97	0.59
F_2A Liver	7.63	1.52	6.72	0.45
Gut Gills	6.63	1.67	6.12	0.34
Muscles	6.05	1.18	5.59	0.30
F_2B	8.67	2.25	7.03	0.61
Liver Gut	7.65	2.04	6.48	0.52
Gills	6.78	1.47	6.10	0.44
Muscles	6.04	1.20	5.68	0.32

F_2C	8.76	1.82	7.66	0.60
Liver Gut	7.70	1.50	7.09	0.54
Gills	7.18	1.32	6.25	0.46
Muscles	6.40	1.21	5.65	0.34

F_2D				
Liver	8.78	1.74	7.48	0.65
Gut	8.00	1.42	7.06	0.56
Gills	7.20	1.35	6.30	0.43
Muscles	6.45	1.18	J L 5 9	
F_2E				
Liver	8.80	2.15	7.44	0.64
Gut	7.91	1.92	7.00	0.50
Gills	7.40	1.60	6.55	0.45
Muscles	6.38	1.25	5.70	0.31

Table 3: Mean Values (in ppm) for the Accumulation of Heavy Metals in the Fish Samples (Summary of Tables 1 and 2)

Sample	Zn	Cd	Pb	Pt
F,A	6.93	1.35	6.34	0.42
F,B	6.65	1.40	6.44	0.45
FiC	6.72	1.43	6.33	0.47
F,D	6.69	1.50	6.33	0.44
F,E	6.80	1.36	6.31	0.64
F_2A	7.26	1.54	6.35	0.42
F_2B	7.29	1.74	6.32	0.47
F_2C	7.51	1.45	6.66	0.49
F_2D	7.61	1.42	6.61	0.50
F_3E	7.62	1.73	6.67	0.48

Table 4: Results of Determination of Heavy Metals Concentration (ppm) in Water Samples

Sample	Zu	Cd	Pb	Pt
Water	3.85	1.05	3.05	0.30

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