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Evaluating The Level Of Concentration Of Some Heavy Metals In Tilapia Fish Tissues In Dutsin-Ma, Katsina State Using Neutron Activation Analysis

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ABSTRACT

This study is aimed at finding out the level of concentration of some heavy metals in Tilapia fish tissues in order to offer useful and meaningful recommendations for taking some workable measures in ensuring peaceful wellbeing of the fishes themselves and the human beings who consume them. It involves the determination and analysis of some samples of Tilapia fishes collected from Zobe Dam in Dutsin-ma Local Government Area, Katsina state, Nigeria using Neutron Activation Analysis in the energy research center, Ahmadu Bello University, Zaria, Nigeria. Heavy metals such like Cr, Hg, Zn and Fe Fe, were analyzed in different tissues like Gill, Flesh, Bone and Skin of the Tilapia Fishes obtained from the Dam, so also the concentration levels of the heavy metals in the fish tissues were determined and evaluated. The evaluation shows that Fe, Zn, Cr, and Hg have concentration level as $1152 \pm 70\ \mu g g$, $126 \pm 7\ \mu g g^{-1}$, $4.3 \pm 0.28\ \mu g g^{-1}$, and $0.04 \pm 0.008\ \mu g g^{-1}$ respectively, which indicate that Fe has the highest concentration level and Hg with the lowest concentration level The research therefore concludes that the concentration level of some heavy metals especially Fe in tilapia fish tissues in Zobe Dam are above the respective recommended maximum limits and as a result of this investigation, it is recommended that all the necessary measures be taken to prevent random discharge of polluted substance into the water surface, so also regular health checking should be carried out on the level of heavy metals concentration among the consumers

Keywords: heavy metals, Tilapia fish, concentration level

INTRODUCTION

The accumulation of the toxic metals hazardous level in aquatic environment has become a problem of increasing concern. Excessive population of surface water could lead to health hazard in man in either through drinking of water or consumption of fish or water edible organisms. The increasing importance of fish as source of protein and the interest in understanding the accumulation of heavy metals at the tropic level of food chain, extend the focus toward fish.

Pollutant enters fish through five main routes: via food or nonfood particles, gills, oral consumption of water and the skin. On absorption, the pollution is carried in the blood stream to either a store point or to the liver transformation and or store. Pollutants transformed in the liver may be store here or excreted in

bile or transport to other excretory organs such as: gills or kidney for elimination or store in fat, which is extra repatic tissue. The concentration of any pollutant in any given tissue therefore is dependent on its rate of absorption and the dynamic processes associated with its elimination by the fish (1).

Fish

Fish is a diverse group of animal that live and breathe in water. All fish are vertebrates with gills for breathing. Most fish have fins for swimming, scale for protection, and a stream lined body for moving easily through the water.

Heavy Metals Pollution in Water

Water pollution has many sources and characteristics, human and other living organisms produced bodily wastes which entered rivers, lakes, oceans, and other surfaces water; industries is creating new chemicals each year, all eventually find their way to water. In high concentration these wastes results in bacterial contamination. Inorganic industrial wastes are much trickier to control and potentially more hazardous industries discharges a variety of toxic compound and heavy metals, and wastes water from industrial process may also be too hot or too low in dissolved oxygen to support life.

Sources of Hazardous Waste

The following are the source of the hazardous waste:

i. Agricultural Waste
ii.House Hold Waste
iii.Medical Waste
iv.Industrial Waste

i. Agricultural waste

Industries are not alone in the generation of hazardous waste. Agricultural products also produce such waste as pesticides and house hold waste, herbicides and the materials used in their application.

ii. House Hold Waste

House hold waste of hazardous waste includes: toxic paints, flammable solvents, toxic batteries, pesticides, drugs and mercury from broken fever thermometers.

iii. Medical Waste

Pharmacies discharges out dated and UN used drugs, testing laboratories dispose of chemical waste. Medicine also use of significant amounts of radioactive isotopes for diagnosis and treatment, and these substances most are tracked and disposed carefully.

Iv. Industrial Waste

Hazardous wastes are generated by almost any industry.

MATERIALS AND METHOD

The materials used for the conduct of this research work are fresh fish tissues (gills, bones and skin), ceramic mortar and pestle polyethylene vials, air dryer, precision balance and a research reactor. As earlier stated this research is mainly on the evaluation of concentration level of some heavy metals in Tilapia fish tissue from Zobe dam, Katsina state using neutron activation analysis; the researcher at this junction is to prepare and irradiate the sample in the research reactor. A variety of small nuclear reactor has been built in many countries for use in education and training, research and production of radioactive isotopes. This reactor generally operate at power level near one mw, and they are more easily started up and short- down than larger nuclear reactors. The core partially or the fully enrich uranium-235 contained in aluminum alloy plates, immersed in a large pool of water that serves as both coolant and moderator. Materials may be place directly in our near reactor core to be irradiated with neutrons.

2.1 Sample Collection

Fresh fish sample were collected directly from fisher men at their landing site at zobe dam in Dutsin-ma Local Government Area. It's located on latitudes [12^{o} 15^{1} N] and longitudes [8^{0} 32^{1} E] (18) the dam is joined by 'Yar-gamji and katsina river which drained from katsina, mani, charanachi cities. Waste water from domestic sources; drainage and raw sewages from the cities are discharged into the rivers. Blood

and animal excreta from Katsina abattoir are discharged in to the river, this making it highly contaminated.

Sample preparation

The fresh tissue (gills, flesh bones and skin) would be dried, and be taken to preparatory lab energy research center A.B.U Zaria for grinding using ceramic mortar and pestle, the sample would be crushed in to powder, a small portion of the powdered sample would then be prepared, weighed using precision balance (METTLER AE 240) and then packed in to small 8 mil polyethylene vials. An air dryer was used to seal the vials. It was made sure that the laboratory has a weighing standard range of 0.2500g to 0.3000g so that it virtually suit all required weight measurements of the samples that would be prepared for irradiation.

The sample were then taken to a detecting set up consisting of a high purity germanium (HPGe) detector, connected to a pc- based multi-channel analyzer (M.C.A) in a fixed sample to detector geometry. For short live elements, the first counting was done immediately and followed by a second counting two hours later. The samples were then be allowed to decay further for the analysis of long life elements. Counting after 3 days referred to as first long count and is done in 30mins.

Sample Irradiation

Using rabbit carries the sample and standard would be sent in to the reactor of a pneumatic test system which uses pneumatic pressure. (NIRR-1) at A B U Zaria irradiated the samples with thermal neutron flux of $5.0x10^{11}$ ncm $^{-2}$s^{-1} for 6 hours for a long irradiation. The whole system is equipped with electronic timers which help in monitoring the exact irradiation and decay time. At the end of irradiation the vials were returned from the reactor with the help of pneumatic pressure to an ejector. It is then allowed to decay, by allowing the activity of the sample to fall down. Sample is usually handled when its activity is within the acceptable handling limit. The acceptable limit is 30µ Sv/h, which is well below the activity if several mSv/h it comes with when removed from reactor. The sample were then taken to a detecting set up consisting of a high purity germanium (HPGe) detector, connected to a pc- based multi-channel analyzer (M.C.A) in a fixed sample to detector geometry. For short live elements, the first counting was done immediately and followed by a second counting two hours later. The samples were then be allowed to decay further for the analysis of long life elements. Counting after 3 days referred to as first long count and is done in 30mins. The samples were then further cooled for another 7 days after which they were ready for second long count in a period of 1 Hours.

The NAA Method

Neutron activation analysis is a sensitive multi-element analytical technique used for both qualitative and quantitative analysis of major, minor, trace and rare elements. NAA was discovered in 1936 by Hevesy and Levi, who found that samples containing certain rare earth elements became highly radioactive after exposure to a source of neutrons.(3) This observation led to the use of induced radioactivity for the identification of elements. NAA is significantly different from other spectroscopic analytical techniques in that it is based not on electronic transitions but on nuclear transitions. To carry out an NAA analysis, the specimen is placed into a suitable irradiation facility and bombarded with neutrons. This creates artificial radioisotopes of the elements present. Following irradiation, the artificial radioisotopes decay with emission of particles or, more importantly gamma rays, which are characteristic of the element from which they were emitted.

For the NAA procedure to be successful, the specimen or sample must be selected carefully. In many cases small objects can be irradiated and analysed intact without the need of sampling. But, more commonly, a small sample is taken, usually by drilling in an inconspicuous place. About 50 mg (one-twentieth of a gram) is a sufficient sample, so damage to the object is minimised.(4) It is often good practice to remove two samples using two different drill bits made of different materials. This will reveal any contamination of the sample from the drill bit material itself. The sample is then encapsulated in a vial made of either high purity linear polyethylene or quartz.(5) These sample vials come in many shapes and sizes to accommodate many specimen types. The sample and a standard are then packaged and

irradiated in a suitable reactor at a constant, known neutron flux. A typical reactor used for activation uses uranium fission, providing a high neutron flux and the highest available sensitivities for most elements. The neutron flux from such a reactor is in the order of 1012 neutrons cm^{-2} s^{-1} (6). The type of neutrons generated are of relatively low kinetic energy (KE), typically less than 0.5 eV. These neutrons are termed thermal neutrons. Upon irradiation, a thermal neutron interacts with the target nucleus via a non-elastic collision, causing neutron capture. This collision forms a compound nucleus which is in an excited state. The excitation energy within the compound nucleus is formed from the binding energy of the thermal neutron with the target nucleus. This excited state is unfavourable and the compound nucleus will almost instantaneously de-excite (transmutate) into a more stable configuration through the emission of a prompt particle and one or more characteristic prompt gamma photons. In most cases, this more stable configuration yields a radioactive nucleus. The newly formed radioactive nucleus now decays by the emission of both particles and one or more characteristic delayed gamma photons. This decay process is at a much slower rate than the initial de-excitation and is dependent on the unique half-life of the radioactive nucleus. These unique half-lives are dependent upon the particular radioactive species and can range from fractions of a second to several years. Once irradiated, the sample is left for a specific decay period, then placed into a detector, which will measure the nuclear decay according to either the emitted particles, or more commonly, the emitted gamma rays.(7)

RESULTS

Results were obtained from the application of the Neutron Activation Analysis (NAA) method in the determination heavy metals concentration of four Tilapia fish tissues. The table of the results and their plotted results are given below.

Table 1: Concentration of Heavy metals in the Tilapia fish tissues in $\mu g g^{-1}$

Heavy Metal (ppm)	Flesh[FG]	Gill[FG]	Bone[FB]	Skin[FS]	Mean Metals Concentration ($\mu g g^{-1}$)
Br	20.6 ± 0.2	37 ± 0.26	16 ± 1	16.8 ± 0.1	22.6
Rb	15.3 ± 1.4	6.9 ± 1.3	9.9 ± 1.5	7.9 ± 1.3	10.0
La	BDL	2.1 ± 0.1	BDL	0.3 ± 0.04	1.2
Ba	BDL	119 ± 0.1	74 ± 16	BDL	96.5
Fe	195	1152 ± 70	530 ± 84	374 ± 45	562.75
Zn	43 ± 4	BDL	91 ± 6	126 ± 7	86.67
Cr	BDL	BDL	2.3 ± 0.3	4.33 ± 0.28	3.315
Hg	0.04 ± 0.008	BDL	BDL	BDL	0.04
Sc	0.016 ± 0.004	0.09 ± 0.01	0.03 ± 0.004	0.024 ± 0.004	0.04
Co	0.06 ± 0.01	0.47 ± 0.04	0.2 ± 0.03	0.18 ± 0.05	0.228
Se	0.4 ± 0.01	0.045 ± 0.001	BDL	0.05 ± 0.01	0.045
Th	BDL	0.12 ± 0.02	BDL	BDL	0.12

Na	3979±4	7783±16	4082±4	903±2	4186.75
K	21060±211	10310±402	9534±162	3267±49	11042.75

BDL: - Below Detection Limit ppm= part per million= µgg $^{-1}$

Table 2: A comparison of mean metal concentration with previous work and standard limits in µgg $^{-1}$

Heavy metals	Mean Concentration (µgg $^{-1}$) Present work	Mean Concentration (µgg $^{-1}$) Hadejia	Mean Concentration (µgg $^{-1}$) River kaduna	Mean Concentration (µgg $^{-1}$) Sokoto Rima River	Mean Concentration (µgg $^{-1}$) Standard limit (µgg $^{-1}$)	Standard Limit (µgg $^{-1}$)
Fe	562.75	-	68.7	201.50	7.90	1.00
Zn	86.67	15.83	18.1	71.80	24.14	30.0
Cr	3.315	-	92.9	-	0.41	12-13
Hg	0.04	-	-	-	-	0.1
Co	0.228	-	-	-	0.24	-
Se	0.045	-	-	-	-	0.40
K	11042.75	-	-	-	-	3500

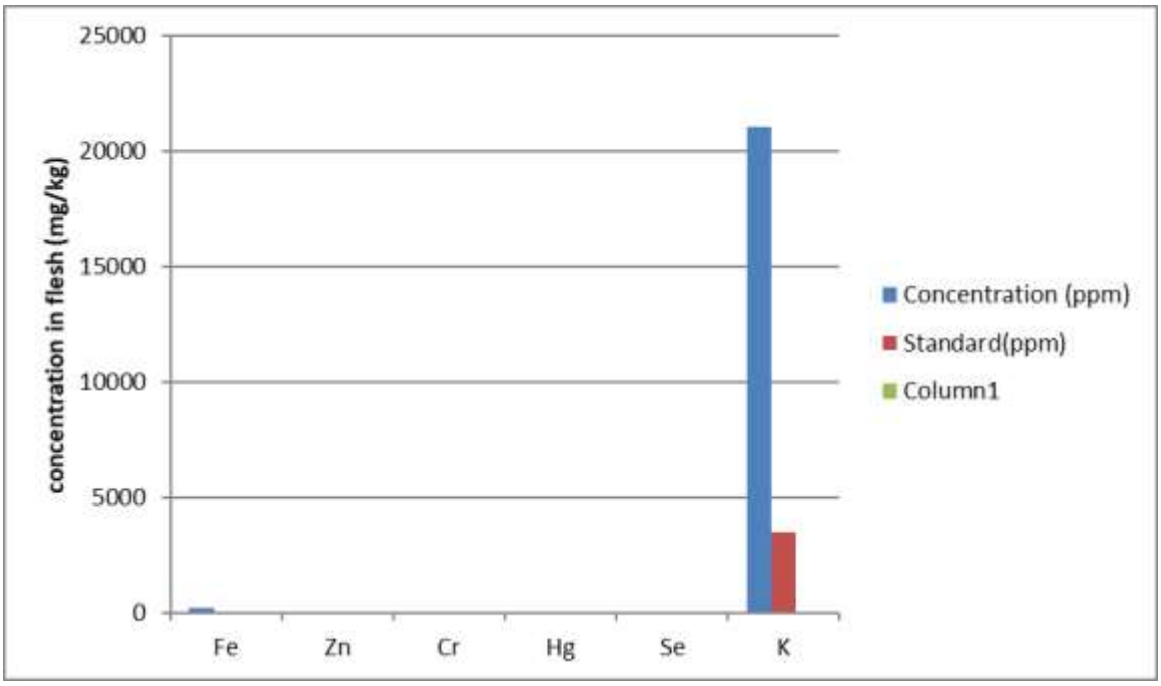

Figure 1: Concentration of Heavy Metals in the Flesh ($\mu g\, g^{-1}$)

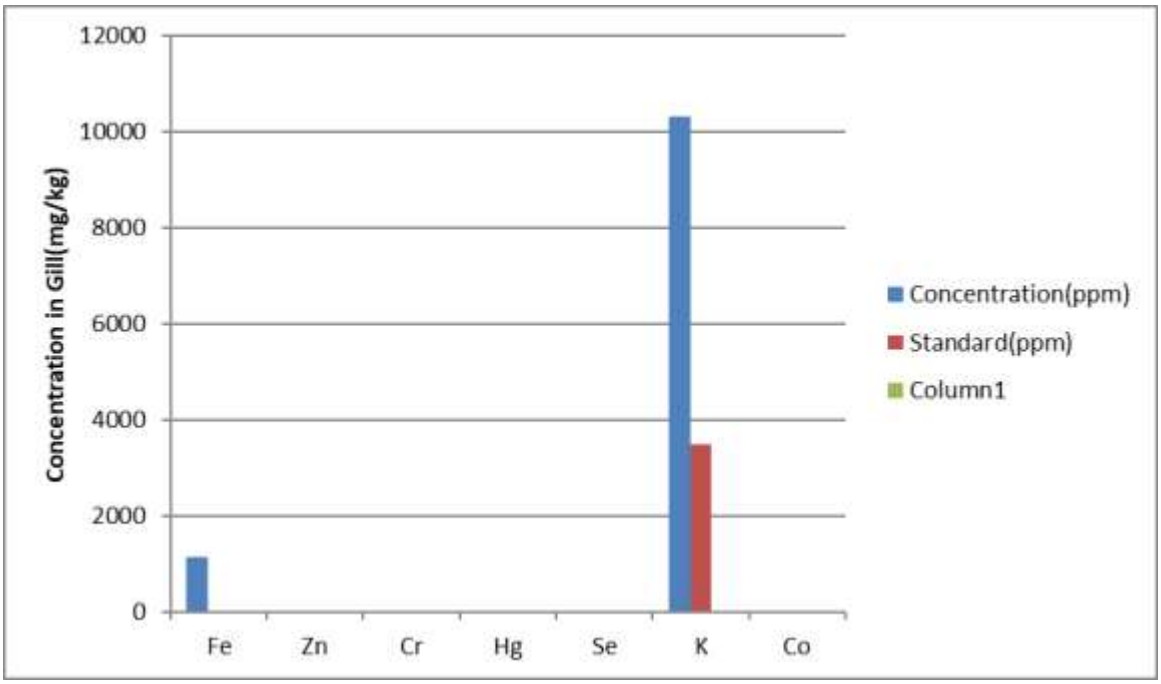

Figure 2: Concentration of Heavy metals in the Gills (μgg^{-1})

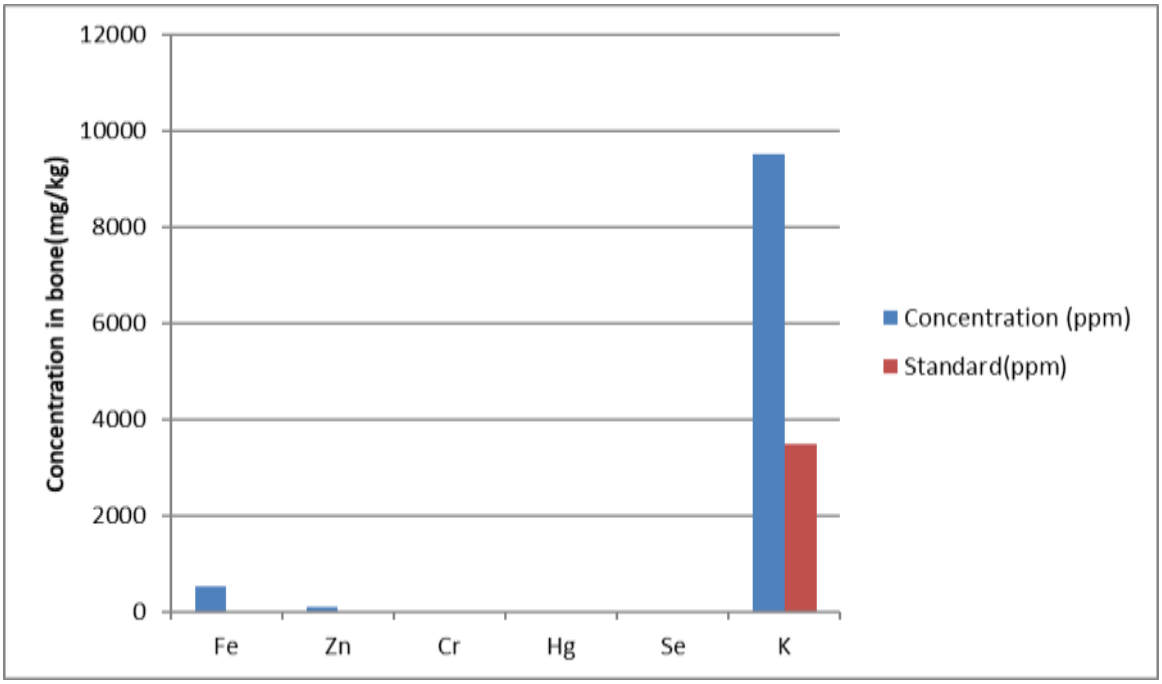

Figure 3: Concentration of heavy metals in bone (μgg^{-1})

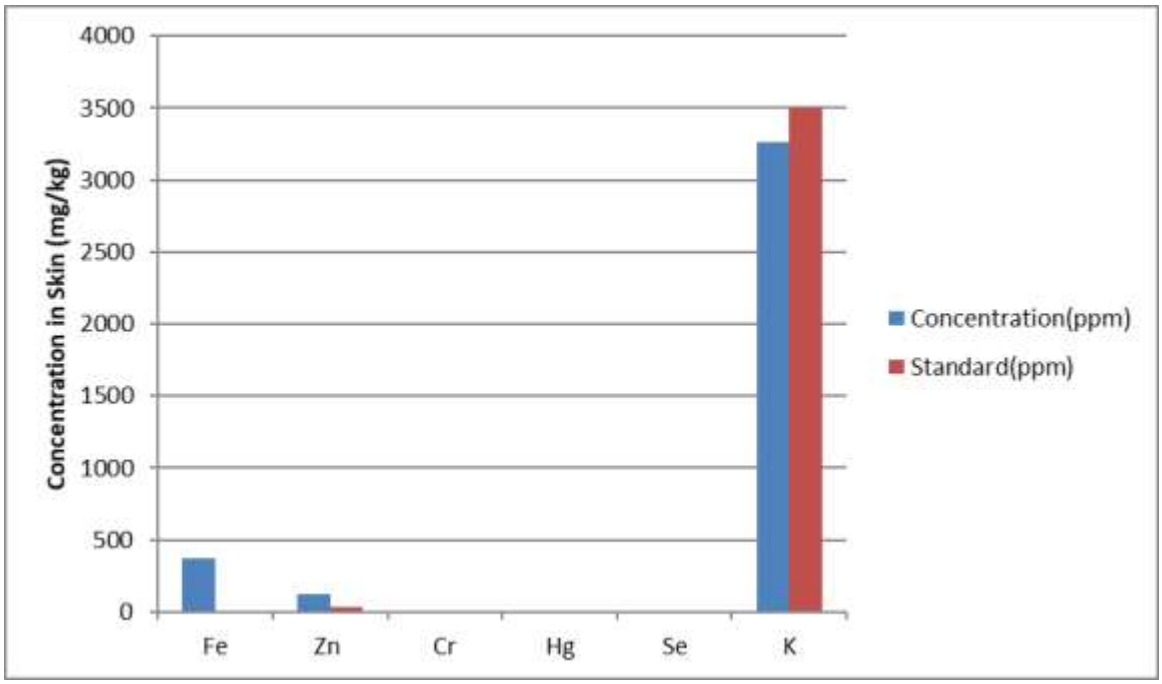

Figure 4: Concentration of H heavy Metals in the Skin (µgg^{-1})

DISCUSSION

The heavy metals such Fe, Zn, Cr, Hg, and Se were analyzed in different tissues like Gill, Flesh, Bone and Skin of the Tilapia fish obtained from Zobe Dam. The concentration of heavy metals in fish tissues were analyzed at the end of the experiment and compared with international standard limit.

The concentration of Fe ranged between 195 $\pm 47\ to\ 1152 \pm 70 \pm \mu g g^{-1}$. The highest concentration of $1152 \pm 70\ \mu g g^{-1}$ was recorded in the gill, with the lowest $195 \pm 47 \mu g g^{-1}$ been recorded in the flesh. The concentration Fe in all the tissues exceeded the WHO guideline of $1.00\ \mu g g^{-1}$ (8) as shown in figure 1, 2, 3 and 4.

Zn has the highest concentration of $126 \pm 7\ \mu g g^{-1}$ in the skin while the lowest concentration, $43 \pm 4\ \mu g g^{-1}$ was measured in the flesh. The FAO maximum guideline for Zn is $30 \mu g g^{-1}$ (FAO, 1983). Thus the concentration of Zinc in the fish tissues exceeded FAO limits, except in the gill which is below detection limit as shown in fig. 3. Also the mean of the total concentration of Zinc in all the fish tissues, 86.67 $\mu g g^{-1}$ was not within the FAO limits. Zn is an essential trace metal for both animals and humans. At concentration up to $40\ \mu g g^{-1}$, it may induce toxicity, characterized by symptoms of irritability muscular stiffness and pain.

Cr is an essential trace element and it plays an important role in glucose metabolism. The concentration of Cr in the tissues was in the range of $2.3 \pm 0.3\ to\ 4.3 \pm 0.28\ \mu g g^{-1}$ as shown in the figure 1, 2, 3 and 4.4. The concentration of Cr in all the fish tissues is lower than the maximum limits of 12-13 $\mu g g^{-1}$ stipulated by the USFDA (1993a). However long term exposure can cause kidney and liver damage.

The maximum Hg level permitted is 0.1$\mu g g^{-1}$ for WHO. Generally, mercury levels in analyzed fish tissues were found to be below detection limit except in flesh 0.04$\pm 0.008\ \mu g g^{-1}$ which is also below the permitted level. In humans, Hg is toxic to the developing fetus. Hg is a known human toxicant and the primary sources of Hg contamination in man are through eating fish (4). When consumed it first passes to the liver, kidneys and the brain. In the case of chronic consumption, first cause tiredness, loss of appetide and weight loss, followed by kidney failure.

CONCLUSION

The result shows the evaluation of some heavy metals ie Zn, Hg, Fe Cr in that, indication shows tha the concentration of Fe $(195 \pm 47\ to\ 1152 \pm 70\ \mu g g^{-1})$ and Zn $(43 \pm 4\ to\ 126 \pm 7 \mu g g^{-1})$ were above the respective recommended maximum limits, while Cr $(2.3 \pm 0.3\ to 4.33 \pm 0.28\ \mu g g^{-1})$ and Co ($0.04 \pm 0.01\ to\ 0.47 \pm 0.04\ \mu g g^{-1}$)were below the standard limits. The result further indicated that tissues like Gills and flesh are very good bio-indicator of heavy metals concentration. Consequently, very stern and workable measures on heavy metals concentration in Zobe Dam is recommended in view of the possible risk to the health of consumers.

RECOMMENDATION

It is therefore recommended that:

i. Regular health checking should be carried out on the level of heavy metals among the consumers
ii. The random discharge of sewage, agricultural waste and industrial effluent in to the river should be regulated by government.
iii. Regular checking of heavy metal concentration in the fish obtained from Zobe Dam.
iv. Our industries should introduce recycling process that is to save or collect used or waste material for reprocessing into useful product.
v. Waste should first be under physical, chemical or biological treatment in order to reduce its hazardous effect. For example, sodium hydroxide has been used to treat acid waste. Some newer plants now treat hydrofluoric acid waste with lime, producing relatively harmless calcium fluoride. Sulfuric acid wastes, if not recycled can be treated with ammonium sulfate to a fertilizer.

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