EVALUATIONS OF HEAVY METALS IN FISH FROM LAKE GERIYO YOLA, NIGERIA USING X – RAY FLUORESCENCE TECHNIQUE

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ABSTRACT
The evaluation of Cr. Cu, Mn, Fe, Ni, Zn,As and Pb concentrations in *Clarias gariepinas* and *Oreochromis niloticus* from Lake Geriyo Yola,Adamawa, Nigeria using X – ray fluorescence (XRF) technique is discussed. The analytical samples are irradiated with high energy electrons of ^{109}Cd to produce fluorescent X-rays was produced which passes to the Silicon-lithium detector through Mo target as a source of monochromatic X-rays. The spectrum of energy generated on the detector was processed by a Multi- Channel Analyzer to obtain analytical data. The intensity of the fluorescent X-rays on the detector is proportional to the concentration of the individual element of interest in the sample. This method can identify up to 30 or more elements at the same time. The results showed varying levels of heavy metals in the fishes. The concentrations of Cr, Mn, Cu, and Ni in the fishes were much higher than WHO and PEPA maximum permissible limits, while the concentrations of Zn and Pb were lower than the standards. The results suggest that the lake is polluted with Cr, Mn, Cu and Ni and the consumption of fishes of the lake is life threatening to man.

INTRODUCTION
The existence of heavy metals in the aquatic environments has become a problem of much concern worldwide. Heavy metals can accumulate in the tissues and organs of fishes to a hazardous level without visible signs (Forstner *and Wittmann* 1981). The commonest sources of heavy metals contamination may arise from industrial and municipal wastes normal geological weathering of rocks, soil erosions, agrochemical leaching, atmospheric deposition, petroleum exploration or due to population increase, urbanization and exploitation of natural resources (Forstner *and Wittmann* 1981) The heavy metals of concern include cadmium, chromium, copper, arsenic, nickel, iron, zinc, mercury and manganese. Iron, zinc, copper, nickel and magnesium are essential metals and are less toxic than non-essential metals (Batley, 1993) Cadmium, chromium, copper, nickel, lead and zinc exhibit aquatic toxicity when present above recommended standard. They contaminate water, plants, aquatic life and man, through bioaccumulation. Heavy metals form one of the major contributors to the pollution of natural aquatic ecosystems (Sanders, 1997)

X-Ray fluorescence (XRF) is the emission of characteristic fluorescent X-rays from an analytical samples that has been excited by bombarding with high-energy elections. The technique is used for chemical and elemental analysis. It is fast, precise and non-destructive in nature. It can identify up to 30 or more elements at the same time by measuring characteristic fluorescence (Beckhoff *et al,* 2006). This study was carried out to evaluate heavy metal levels in fishes from Lake Geriyo to determine their suitability for public consumption, using (XRF) technique.

MATERIALS AND METHODS
This study was carried out in Lake Gerito Yola Adamawa State, Nigeria a natural lake which is located at the outskirts of Jimeta metropolis on the North-West region (longitude 12^0 25′E and between latitude 9^0 8′N and 9^0 17′E). The lake has been subjected to intense irrigation and pollution load coming up stream of River Benue during the rainy season to the lake is a major factor for high heavy metal levels in the lake and fishes (U.B.R.B.D.A. 1985).

Sample Collection
Samples for analysis included *C.gariepinus* and *O.niloticus* from Lake Geriyo. Ten Samples for each species of *C. gariepinus* and *O. niloticus* were bought directly from the fishermen at the bank of the lake. They were thereafter stored in a plastic cooler with ice flakes. The modified version of Emission – Transmission (E-T) method (Kump, 1996, Angeyo *et al,* 1998 and Funtua, 1999) was used. First, *O niloticus* was descaled and the two species of fish were oven dried to constant weight at 105^0C. The dried samples were ground to powder, sieved to grain size of less than 125μm and quartered to give representative sample weight. 0.5g of the powdered fish samples was weighed and three drops of organic binder were added to each and were pressed with 10 tons hydraulic press to form pellet of each fish samples. Three replicate of pellets of each fish sample were prepared.

Determination of Heavy metals in fish by Energy Dispersive X- ray Fluorescence (EDXRF)

The modified version of Emission Transmission (E-T) (Kump. 1996, Angeyo *et al* 1998 and Funtua (1999) method was used. The pellet of each fish sample was put into X –ray fluorescence spectrophotometer sample holder and it was bombarded with high energy electrons of ^{109}Cd (22.1kv). Fluorescent X –rays was produced which passes to the silicon lithium detector, through *Mo* target as a source of monochromatic X –rays. The spectrum of energy generated from the detector was processed by a Multi – Channel Analyzer (MCA) to obtain analytical data. The intensity of the fluorescent x-rays on the detector is proportional to the concentration of the individual element of interest in the sample.

RESULTS AND DISCUSSION

Table 1 represents the mean concentrations of heavy metals in the two species of fish from Lake Geriyo in mg/kg dry weight. The two fish species *C. gariepinus* and *O. niloticus* generally accumulated different levels of heavy metals. In *C.gariepinus*, metal levels varied with significant differences. Fe metal was highest (19.0±3.46 mg/kg dry wt), followed by Cr (13.26±0.46 mg/kg dry wt), Zn (12.26±0.23 mg/kg dry wt), Cu (10.60±0.40 mg/kg dry wt), while the least metal accumulated was Pb (0.76±0.14 mg/kg dry wt). The order of heavy metals that were accumulated *C.gariepinus* is Fe>Cr>Zn>Cu>Pb. In *O. niloticus*, Fe (45.02±3.83mg/kg dry wt) was mostly accumulated followed by Cr (15.20±0.8 mg/kg dry wt), while Mn, Ni, Zn and As 6.7±0.01 mg/kg, 2.3±0.02 mg/kg, 1.52±0.47 mg/kg and 1.02±0.02 mg/kg dry wt were accumulated in the order above. The difference in the levels of heavy metal accumulated in the two fish species might be a result of their difference in many factors such as feeding habits, habitats, sizes, metabolic rate and physiology,(Canli et al,1998). Heavy metals uptake occurs mainly from water, food and sediment(Canli et al,1998). The high concentrations of Cr, Cu and As in the fishes of the lake could be attributed to chemicals made from salts of arsenic, chromium and copper in mixed soluble formation (as copper-chrome-arsenate preservative) being used to prevent fungi and pest attack which provide a potential source of chemical spills and drainage within the catchments area of the lake (Forstner *and Wittmann 1981).*

Table 1 Mean concentration of Heavy Metals in two species of fish from Lake Geriyo in (mg/kg, dry weight) and set standard. WHO (1985) and FEPA (2003)

Metals / Fish Samples	Cr	Cu	Mn	Fe	Ni	Zn	As	Pb
C. gariepinus	13.26± 0.46	10.6.± 0.40	BDL	19± 3.46	BDL	12.26± 0.23	BDL	0.76± 0.14
O. nlioticus	15.2± 0.8	BDL	6.7± 0.01	45± 3.8	2.3± 0.02	1.52± 0.47	1.02± 0.02	BDL
WHO (1985)	0.15	3	0.5	N.S	0.6	10.75±	0.02	2.0
FEPA (2003)	0.15	1-3	0.5	N.S	0.5	75	0.1	2.0

BDL: Below detectable limits ± Standard deviation N.S : Not Specified

The high level of Fe recorded in both species of fish in the lake could be attributed to run of from rusted metallic pipes metal works and the dumping of metal scraps from metal scrap market on the bank of Lake Geriyo. Ni and Pb presence in the lake could be attributed to the fact that they are naturally found in surface waters due to weathering of minerals and soil erosions. It could also be due to phosphates fertilizers and pesticides used by the farmers within the catchments area of the lake. Mn and Zn level their presence could be due to the fact that Cr, Cu, Mn and Zn are concentrated in the sediments as well as in bacteria and seaweeds in the lake (Forstner *et al* 1981). The high levels of Cr in both fish species Cu in *C.gariepinus*, Mn, Ni and As in *O. niloticus* when compared with WHO and FEPA suggests that their consumption could pose health hazards to man (Forstner *and Wittmann*1981). The results of this findings indicated that the concentrations of heavy metals in fish can be determined by x-ray fluorescence technique, It also shows that Lake Geriyo is contaminated with heavy metals.

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