

The Use of Energy Dispersive X-Ray Florescence to Evaluate Some Heavy Metals as Pollutants in *Heterotis niloticus* and Sediment from Baga, Lake Chad, Nigerian Sector

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Abstract

The pollution of aquatic ecosystems by heavy metals is a major global concern, presenting significant environmental and health hazards. This research evaluated the concentrations of Cd, Cr, Cu, Pb, and Zn in *H. niloticus* and sediments from Dumba 1, Baga, Lake Chad, Nigerian Sector using energy dispersive X-ray fluorescence (EDXRF). The results indicated high concentrations of Cd, Cr, Cu, and Pb (0.45 ± 0.01 , 2.14 ± 0.03 , 14.46 ± 0.25 , and 6.38 ± 0.05 mg/kg), which are higher than the maximum acceptable limits set by World Health Organization (WHO). The findings suggest contamination of *H. niloticus* by these heavy metals (Cd, Cr, Cu, and Pb), highlighting potential health risks. Additionally, sediment analysis showed concentrations of Cd, Pb, and Zn (2.62 ± 0.1 , 120.15 ± 5.01 , and 102.67 ± 6.02 mg/kg) exceeding acceptable limits for average shale, indicating sediment contamination and possible environmental health risks to both fish and humans.

Keywords: Energy Dispersive X-ray Fluorescence, Heavy Metals, Pollution, *Heterotis niloticus*, Sediment.

Introduction

Scientists have established that heavy metals are environmental pollutants of great concern globally and that they contaminate the environments. Their presence in environments constitutes a major threat to humans around the world. This is largely because of their bioaccumulative nature, toxicity, non-biodegradable nature, and their persistent nature in the environment. (Hazrat *et al.*, 2019). Heavy metals are metallic elements that have high density greater than 5 times that of water, and they are toxic or poisonous even at low concentrations. Examples of heavy metals are cadmium (Cd), copper (Cu), chromium (Cr), iron (Fe), lead (Pb), mercury (Hg), zinc (Zn) arsenic (As). Heavy metals enter the environments and aquatic ecosystem via (1) Natural and (2) Anthropogenic sources, the natural sources are made up of weathering of rocks and soils containing heavy metals, soil erosions and volcanic eruptions, while the anthropogenic sources include the applications of phosphate fertilizers and pesticides, mining operations, wastewater effluents from industries, domestic waste, sewage sludge and surface storm runoff (Sarkar *et al.*, 2018; Srivastava *et al.*, 2018).

The anthropogenic sources give rise to larger amounts of heavy metals from agricultural practices, industrials and municipal areas are released into aquatic environments and they are transferred in the water body. Some of the heavy metals are assimilated by phytoplankton and zooplankton, while many of them are accumulated in the sediments. Heavy metals in the aquatic ecosystems are transferred from one trophic level to another via food chain (Wu *et al.*, 2014). Fishes which are at the top of trophic levels in aquatic food chain, would accumulate and biomagnified higher concentrations of heavy metals through the food chain, which can threaten the lives of fish, benthic organisms and humans (Gu *et al.*, 2018; Wang *et al.*, 2020). In aquatic environment, sediments are important and main sink for heavy metals and the standard of the sediments is seen as an important indicator of water contamination.

Fish are aquatic vertebrate animals that lives in water and breathe via gills, they are cold-blooded animals, low fat calorie, and a good source of Omega-3 fatty acids. They swim with fins, and they provide a key sources of animal proteins to humans and animals. Fish are good indicators of pollutants like heavy metals, because fishes can assimilate and accumulate heavy metals from sediments, water and food sources such as phytoplankton and zooplanktons (Sarkar *et al.*, 2018; Authman *et al.*, 2015)

Energy dispersive X-ray Florescence (EDXRF) is an important analytical tool that is use to determine environmental pollutants such as heavy metals in sediments, biological, water and geological samples. It can be used to investigate qualitative and to determine quantitative analysis. The method is a non-destructive analytical approach, conserving the sample for future analysis, and it is highly sensitive 10^{-8} g, that can be employed to measure enormous number of elements at the same time (Cesaeo and Brunetti, 2008). Very little samples preparations and very quick analysis. These heavy metals Cd, Cr, Cu, Pb, Hg, Zn and many others can be determined by EDXRF. The objectives of this research were to evaluate the concentrations of Cd, Cr, Cu, Pb and Zn in *H. niloticus* and sediments, using EDXRF, at Dumba 1 fishing community Baga, Maiduguri, Borno State and to determine the pollution level of the lake at the sampling site. Generally, EDXRF offers quick qualitative and quantitative elemental analysis for large varieties of matrices and it can be used in testing and analyzing oils, liquids, solids, metals, powder and many other substances (Rigaku EDXRF, 2024).

The limitations of EDXRF are:

1. Detection limits: EDXRF has limited sensitivity for light elements, helium, He, lithium, Li and trace elements
2. Energy resolutions: Peak overlap and interference can occur due to limited enery resolution.
3. Matrix effects: Interference from surrounding elements can affect accuracy.
4. Homogeneity: Inhomogeneous samples can lead to inaccurate results.

Objectives of Research

1. To determine the concentrations of heavy metals (Cd, Cr, Cu Pb and Zn) in *Heterotis niloticus* from Baga, Lake Chad, Nigerian Sector, using EDXRF.
2. To determine the concentrations of heavy metals (Cd, Cr, Cu, Pb and Zn) in Sediment from Baga, Lake Chad, Nigerian Sector using EDXRF.
3. To compare EDXRF results with international standards and guidelines in order to determine the pollution status of Bga, Lake Chad, Nigerian Sector.

Problem Statement

The pollution of heavy metal in aquatic environments, especially in Baga, Lake Chad, Nigerian Sector, poses remarkable environmental and health hazards due to heavy metals bioaccumulation by fish species and sediment. In spite of its importance, very few or limited data are found on heavy metals concentrations in *Heterotis niloticus* and sediment from Baga, Lake Chad, Nigerian Sector. Therefore, in this study, EDXRF is used to evaluate the concentrations of Cd, Cr, Cu, Pb and Zn in *Heterotis niloticus* and sediment, and to evaluate environmental and health effects.

Research Questions

1. What are the heavy metals concentrations patterns in *Heterotis niloticus* from Baa, Lake Chad, Nigerian Sector?
2. How do the heavy metals concentrations in sediment relate to the heavy metals concentrations in *Heterotis niloticus*?
3. What are the health and environmental hazards connected with heavy metals concentrations?

Significance of the Study

1. Presents the knowledge and understanding of heavy metals pollution dynamics.
2. Provides data for environmental policy and decision making body.
3. Increases knowledge on human health hazards.

Statistical Analyses:

Descriptive Statistics:

1. Mean: Average concentration of heavy metals in sediments and *Heterotis niloticus*.
2. Mean $\pm$ Standard Deviation (SD): Measure of variability in heavy metal concentrations.

Materials and Method

Study Area

The study area is Baga, the Nigerian sector of Lake Chad, based in Kukawa Local Government Area, Borno State Nigeria, West Africa. Agriculture, fishing and animals farming, intensive irrigation farming practices are carried out on the flooded plains of Lake Chad, Baga the Nigerian Sector are some of the significant economic practices of the study area.

Sample Collection

Five (5) samples of *Heterotis niloticus* weighing, 3.150 kg on average were bought from the local fishermen at Dumba 1 fishing community in Baga, Lake Chad, Nigerian Sector between the months of April 2012 to August 2012. They are kept in plastic bucket with ice flakes and they were transported to laboratory of Federal College of Freshwater Fisheries Technology Baga, Borno State for further analysis.

Fish Samples Preparations

The fish samples were washed with water and rinsed with distilled water in the laboratory, and oven-dried to constant weight at 105°C for 24 hours. The dried fish samples were manually ground to powder with agate mortar and pestle to grain size of less than 125µm. A quantity of 0.5g of the powdered fish samples were weighed and three drops of organic liquid binder polyvinylchloride (PVC) was added to it and were pressed with 10 tons' hydraulic press to form pellets of fish samples. Three replicates of pellets of fish samples were prepared (Funtuua, 1999).

Assessment of heavy metals in fish samples using energy dispersive X-Ray Fluorescence (EDXRF). The modified version of Emission Transmission (E-T) (Kump, 1996; Angeyo *et al.*, 1998 and Funtua, 1999; Jonathan *et al.*, 2020) method was used. The pellet of fish sample was put into X-ray fluorescence spectrophotometer sample holder and it was bombarded with high energy electrons of ¹⁰⁹Cd (22.1keV). fluorescent X-rays was produced which passes to the silicon lithium detector, through Mo target as a source monochromatic X-rays. The spectrum of energy generated on the detector was processed to obtain analytical data. The intensity of fluorescent x-rays on the detector would be proportional to the concentration of individual element of interest in the samples.

Sediment Samples Collection

Sediments samples for heavy metals evaluation in this research were collected from Dumba1, Baga fishing community, the Nigerian Sector of Lake Chad. The sediments samples were collected in the months of April 2013 to August 2013. A quantity of 1.0 kg of surface sediment was collected using Hand shovel or Hand trowel because the lake is shallow. A minimum of five (5) subsamples at different locations in the sampling area

(Dumba1) were collected randomly in all directions at about 10-20 cm. All the sediments samples collected were mixed together in a composite sample which was transferred into an air-tight plastic bucket and it was transported to the laboratory of Fisheries College Baga for further analysis (Keith, 1991; Jonathan *et al.*, 2016). The sediments samples were air-dried to a constant weight, it was then ground to powder with a mortar and pestle to grain size of less than 125 μ m, and was homogenized by it. A well homogenized dried sediment samples were accomplished by a cone and quartering technique. A quantity of 0.5g of the powdered sediments samples was weighed and three drops of organic liquid binders, PVC was added to it and it was pressed thereafter at 10 tons with a hydraulic press to form pellets of 19mm diameter. Three replicates of pellets of the sample were prepared. The resulting pellets were used to analyze heavy metals in the samples.

A modified version of Emission Transmission (E-T) (Kump, 1996; Angeyo *et al.*, 1998 and Funtua, 1999) method was used to analyze heavy metals in the sediments samples. Pellets of sediment sample was put into the x-ray fluorescence spectrometer sample holder and was bombarded with ^{109}Cd as the excitation source that emits Ag-K x-rays (22.1keV) in which case all the elements with lower characteristic excitation energies were accessible for detection in the sample. Fluorescent x-rays were produced which passes to the Si (Li) detector through molybdenum (Mo) target. 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

Energy dispersive X-Rays Fluorescence (EDXRF) provides numerous advantages in determining heavy metals in sediments and fish from aquatic ecosystems: In sediments, EDXRF offers to determine many heavy metals at the same time. EDXRF offers results quickly. EDXRF is non-destructive, it preserves samples for future analysis, and it can detect trace levels of heavy metals. Minimal or simple samples preparations is required and portable EDXRF instruments allow on-site analysis. Likewise, in the ecosystems, EDXRF can be employed to monitor heavy metals pollution in ecosystem and the risk associated for human consumption and the healthy state of the ecosystems. EDXRF lowers cost-effective in analyzing samples costs as linked to conventional methods (Rigaku EDXRF, 2024).

Concentrations (mg/kg) of Heavy Metals in *H. niloticus*

The mean concentration and standard deviations of Cd, Cr, Cu, Pb and Zn in the muscle of *H. niloticus* from Dumba 1 in the vicinity of Lake Chad, Baga Nigerian Sector are presented in Table 1. The mean concentrations (mg/kg) ranged from (0.45 ± 0.01) Cd, (2.14 ± 0.03) Cr, (14.46 ± 0.25) Cu, (6.38 ± 0.05) Pb, and (64.80 ± 5.10) Zn. The lowest value is 0.45 ± 0.01 mg/kg of Cd, and the highest value is 64.80 ± 5.10 mg/kg of Zn. The concentrations of Cd, Cr, Cu and Pb (0.45 ± 0.01 , 2.14 ± 0.03 , 14.46 ± 0.25 and 6.38 ± 0.05) mg/kg were very high

when compared to the maximum permissible limit by WHO (1989) FEPA (2003). The high levels of Cd, Cr, Cu and Pb could be attributed to the activities of farmers that might have used phosphate fertilizers and pesticides that contained Cd, Cu, Pb on their farm. Cd, Cr, Cu and Pb can be found in sewage sludge and domestic wastes which may be discharged into the aquatic ecosystems, and they are accumulated in fish species (Gu *et al.*, 2018). The presence of heavy metals in the muscles of *H. niloticus* could be attributed to the food the fish consumed such as phytoplankton and zooplankton (Sarkar *et al.*, 2018). Likewise, the presence of Pb and Cu in the muscles of fish could be attributed to the accumulation of Pb by *H. niloticus* from phosphate fertilizers and pesticides improper discharges of Pb-batteries into the aquatic ecosystems where the samples were caught. It could also be due to the discharges of untreated industrial effluents, sewage and domestic wastes, other factors could be due to the assimilations of Pb from the contaminated sediments, food and water, and the high concentrations of Cd, Cr, Cu and Pb in this result could also be attributed to the large size of *H. niloticus*. The results also depicted that *H. niloticus* is contaminated with respect to Cd, Cr, Cu, and Pb because their concentrations are higher than the maximum permissible limit by WHO (1989). Zn is the only metal that did not contaminate *H. niloticus*. The result also indicated that EDXRF can be used to evaluate heavy metals concentrations in fish samples and to determine the pollution levels in fish.

The results of the present study were compared with that of Jonathan *et al.*, 2020, and the results of the present research were higher than the results of Jonathan *et al.*, 2020.

Table 1: Mean Heavy Metals Concentration (mg/kg dry wt) in the Muscle of *Heterotis niloticus* from Dumba 1 Lake Chad, Baga Nigerian Sector and Standard WHO (1989) and FEPA (2003)

Heavy Metals	<i>H. niloticus</i>	WHO (1989)	FEPA (2003)
Cd	0.45 ± 0.01	0.10	0.10
Cr	2.14 ± 0.03	0.15	0.15
Cu	14.46 ± 0.25	3.00	3.00
Pb	6.38 ± 0.05	2.00	2.00
Zn	64.80 ± 5.10	10-75	75

Value are mean ± Standard Deviation

Concentrations (mg/kg) of Heavy Metals in Sediments

The mean concentrations (mg/kg) of heavy metals in sediments from Dumba 1, Baga the Nigerian Sector of Lake Chad are presented in Table 2 as follows, Cd (2.62 ± 0.1mg/kg), Cr (66.80 ± 0.50mg/kg), Cu (19.20 ± 0.25mg/kg), Pb (120.15 ± 5.01mg/kg) and Zn (102.67 ± 6.02mg/kg). The mean concentrations were observed to be in declining order of, Pb (120.15 ± 5.01 mg/kg) > Zn (102.67 ± 6.02mg/kg) > Cr (66.80 ± 0.50mg/kg) > Cu (19.20 ± 0.25mg/kg) > Cd (2.62 ± 0.10mg/kg). Pb, Zn, and Cd possess higher concentrations than their Average

Shale (World Geochemical Background). The higher concentrations of Pb, Zn and Cd could be attributed to agricultural activities that includes the applications of phosphate fertilizers around the areas (Sarkar et al., 2018). The presence of Pb, Cd and Cr could be attributed to the agricultural discharges as well as from spill of leaded petrol from fishing boats and paints on canoes which are located in the Lake Chad, while Pb could arise from the use of tetraethyl lead used to power the canoe. The high concentrations of heavy metals in the sampling sites could be attributed to domestic wastes as well as polluted soils within the areas or that are brought from other places through storm runoffs and thereafter accumulate in the sediments. Eroded soils as well as untreated sewage and atmospheric depositions could all pollute and contaminate the sediments which have in higher concentrations of heavy metals in this research. In this study, the sediment is contaminated by Pb, Zn and Cd, while Cr and Cu have lower concentrations than their world geochemical background (Average Shale).

The present results were compared to Jonathan *et al.*, (2016) which were in agreement with each other. High concentrations of Cd, Cr and Pb (3.64 ± 0.13 mg/kg, 98.75 ± 0.25 mg/kg and 126.83 ± 10.24 mg/kg)

Table 2: Mean Heavy Metals Concentration (Mg/kg dry wt) in Sediments of Dumba 1 Baga, Lake Chad, Nigerian Sector and Average shale

Heavy Metals		*Average Scale
Cd	2.62 ± 0.10	0.30
Cr	66.80 ± 0.50	90.00
Cu	19.20 ± 0.25	45.00
Pb	120.15 ± 5.01	20.00
Zn	102.67 ± 6.02	95.00

Value are Mean $\pm$ Standard Deviation. *Turekian and Wedepohl (1961). World Geochemical Background.

Conclusion

Using EDXRF, the results of this research disclosed notable or high concentrations of Cd, Cr, Cu and Pb (0.45 ± 0.01 , 2.14 ± 0.03 , 14.46 ± 0.25 and 6.38 ± 0.05 mg/kg) in *H. niloticus* from Dumba 1, Baga, Lake Chad, Nigerian Sector. The concentrations of these heavy metals are above the maximum acceptable limits by WHO (1989), and this shows that the is contaminated by them and possibly suggesting potential environmental and health hazards. In the sediments sample, Cd, Pb and Zn concentrations (mg/kg) (2.62 ± 0.1 , 120.15 ± 5.01 and 102.67 ± 6.02) were found to be higher than the world geochemical background. The implications for the high levels of these heavy metals in fish is bioaccumulation and biomagnification in food chain can be hazardous to human health and animals. The contamination of fish and sediments may result in wider aquatic environments deterioration.

The result also indicated that EDXRF can be used to evaluate heavy metals concentrations in fish samples and to determine the pollution levels in fish.

Study Limitations

One of the glaring constraints faced in this study is the small sample size. The limited collection of sediment and fish samples poses a significant challenge, as it might fall short of capturing the full complexity and diversity of the vast Lake Chad ecosystem. Furthermore, the restrictive detection limits and energy resolution of EDXRF technology could hinder the precise analysis of certain critical elements, thus impacting the overall accuracy. Additionally, the paucity of extensive historical data stands as a significant obstacle for robust comparative analysis, leaving gaps in understanding the ecological changes over time. Compounding these issues, the processes of homogenization and drying might inadvertently alter the sample composition, potentially skewing the findings.

Recommendations

To address the pressing environmental challenges, some key recommendations are proposed:

1. The enforcement of environmental regulations to ensure sustainable use of resources.
2. The implementation of sustainable fishing practices to preserve aquatic life.
3. The regular monitoring of heavy metals in Lake Chad to prevent contamination.
4. The provision of public education on health hazards associated with fish consumption to raise awareness.
5. The advancement of further research on heavy metal bioaccumulation and its ecological effects to inform policy decisions.

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