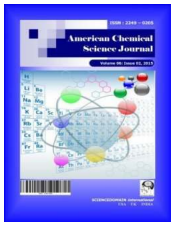

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Comparative Bioaccumulative Potential of Copper Cadmium and Lead by *Gymnarchus niloticus* and *Heterobranchus bidorsalis* in Pollution Prone Aquatic Environments of North-Western Nigeria

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Authors' contributions

This work was carried out in collaboration between all authors. Author HLM designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Authors RAS and LSB managed the analyses of the study. Author SMD managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Fishes in aquatic environment accumulate metals in their tissues many times greater than present in sediment and water. Three organs: gills, muscles, and bones were collected from *Gymnarchus niloticus* and *Heterobranchus bidorsalis* for copper (Cu), cadmium (Cd), lead (Pb) and some mineral elements analyses using atomic absorption spectrophotometry in two separate seasons (January-February) and (August-September), and from four rivers (Bunsuru, Gagare, Rima, and Goronyo) receiving chronic inputs of run-offs from illegal mining and dyeing sites. Copper (Cu) level in gills of *Gymnarchus niloticus* season I sampling of River Bunsuru river was higher

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(3.30±0.36) µg/g but not significantly ($p>0.05$) above the WHO upper limit of 3.0 µg/g in sea foods while it was lower all tissues of *Heterobranchus bidorsalis* in the two seasonal samplings with the exception of bones in season 1 sample. Copper levels in *Heterobranchus bidorsalis* of Rima River for the two seasons were above the WHO limit, particularly those of season II. Lead (Pb) concentrations in all tissues (gills (4.75±0.87) µg/g, muscles (4.68±0.67) µg/g, and bones (4.34±0.34) µg/g) of *Gymnarchus niloticus* of Goronyo Dam season II samples were high than the WHO acceptable limit. Same is the case with *Heterobranchus bidorsalis* of Goronyo Dam season II. No tissues of the two fish species bioaccumulated significant level of cadmium (Cd). In general, there was no seasonal variation or differential accumulative potentials of copper and lead (Pb) in the two fish species. The only factor responsible for high bioaccumulation may be the level of metals in sampling sites. Other essential elements: Ni, Fe, Mg, Cr, Ca, Na and K were within the WHO acceptable limits for sea foods. The chronic discharge of wastes containing the minute quantities of lead and copper may lead to bioaccumulation and biotoxicity to aquatic species and to man who is the end receptor.

Keywords: Gymnarchus niloticus; bioaccumulation; biotoxicity; toxicity.

1. INTRODUCTION

Lead (Pb) is heavy metal that is toxic at very low exposure levels with acute and chronic effects on human health. It is a multi-organ toxicant that causes neurological, cardiovascular, renal, gastrointestinal, haematological, and reproductive effects. It is released by various natural and anthropogenic sources into atmosphere, and into aquatic and terrestrial environments. Lead can move in the environment between water, air, and soil which may change the pattern of exposure. About 90% of the body burden of lead is stored in the skeleton, and major effects are manifest in three organs-systems: the haematological system, the central nervous system, and the renal system. The effect on the renal system is characterized by mild aminoaciduria, glucosuria and hyperphosphaturia [1]. Copper is an essential trace nutrient that is required in small amount (5-20) µg/g by humans. It is required in carbohydrate metabolism, in the functioning of more than 30 enzymes, formation of haemoglobin and haemocyanin (oxygen transporting pigment in shellfish). The most bioavailable and most toxic form of copper is the Cu^{2+}. Fishes and crustaceans are 10-100 times more sensitive to the toxic effects of copper than mammals. Brief exposure to copper at environmentally realistic concentrations can impair the function of olfactory neurons, and longer exposure can kill these neurons as demonstrated by [2]. Bioaccumulation of these metals depends not only on metal concentrations in the sediments but also the physiological state of the organism (e.g. season and environmental factors) and the biogeochemistry of the sediment (e.g. iron content, organic carbon content, and the oxidation–reduction condition) [3]. Lead can affect the formation of blood cells and the build-up can cause malfunctions of the liver, kidney, the circulatory system, and the movement of nerve signals. Lead and copper also build-up occurs via a steady and direct absorption from contaminated medium that holds minute but constant concentrations [4]. The incidences of metal poisoning has instigated more research effort and tougher regulatory laws in forcing lower acceptable levels of heavy metals in water bodies and in sea foods consumed by man. Biomagnificantion also plays a very important role in the problems of heavy metal pollution in food chain. There are three fundamental kinds of exposure through which metals can enter the human body. These are endemic exposure, workplace exposure, and catastrophic exposure [5]. Endemic exposure is associated with human contact with drinking water, indoor air, outdoor air, and food ingestion. The workplace exposure on the other hand is about performing specific operations and activities at workplace. Catastrophic exposure is associated with exposure to pollutants resulting from unexpected events (ecological disaster). Lead is number two on the ATSDR's Top twenty list of the most hazardous heavy metals. It accounts for most of the cases of paediatric heavy metal poisoning [6]. Lead serves no useful purpose in the human body, and its presence in the body can lead to toxic effects regardless of exposure pathway. Lead toxicity can affect every organ – system. On a molecular level, proposed mechanisms for toxicity involve fundamental biochemical processes. These include lead's ability to inhibit or mimic the actions of calcium (which can affect calcium dependent or related processes) and to interact with proteins (including those with

sulfhydryl, amine, phosphate and carboxyl groups [7]. One of the mechanisms underlying the neurotoxicity of lead is its ability to substitute for other polyvalent cations (Ca^{2+} and Zn^{2+}) in the molecular machinery of living organisms. In most instances, its characteristics allow it to bind with greater affinity than calcium and zinc ions to protein binding sites. These interactions allow lead to affect different biologically significant processes, including metal transport, energy metabolism, apoptosis, ionic induction, cell adhesion, protein maturation, and genetic regulation. Membrane ionic channels and signalling molecules are the most relevant molecular targets that contribute to neurotoxicity (developing central nervous system is particularly susceptible). Anaemia is a classical manifestation of lead toxicity in erythrocyte. The anaemia induced by lead toxicity is caused primarily by impairment of heme biosynthesis, but an increased rate of erythrocyte destruction may occur. Iron (Fe) is part of heme group of catalase that catalyses the degradation of H_2O_2. Nonheme iron is often found in metalloenzymes in the form of iron –sulphur clusters [8]. Metallothioneins are a class of low molecular weight proteins (about 6 000 daltons) which contain a number of cysteine residues that bind metals. Metallothioneins are synthesized in the liver and other tissues and play very important role in the toxicokinetics of cadmium as well as the mechanism of cadmium toxicity in the kidney. The cadmium combines with the newly synthesized metallothionein produced by the tubular cell and accumulate (stored) in the kidney for a long time.

Some essential ions mostly metal ions (e.g Cu^{2+}) are called activator ions and they reversibly bound and participate in the binding to substrates. Copper (Cu) is commonly found in metalloenzymes and often plays roles in catalysis. The ions of some metalloenzymes can undergo reversible oxidation and reduction by transferring electrons from a reduced substrate to an oxidized substrate. Recent research indicates that lead is associated with neurobehavioural damage at blood lead levels of 5 µg/dl and even lower. There appears to be no threshold level below which lead causes no injury to the developing human brain [9]. The joint FAO/WHO Expert Committee on Food Additives re-evaluated lead in June, 2010 and withdrew the provisional tolerable intake guideline value on the ground that it was inadequate to protect against IQ loss. Evaluation of metal toxicity have also been made by several international bodies like Centre for Disease Control (CDC), World Health Organization (WHO), Occupational Safety and Health Organization (WHO-OSHA), International Program on Chemical Safety (WHO-IPCS), International Agency for Research on Cancer (IARC).

Fresh fish samples were used as biological indicators for copper, lead and cadmium pollutant. According to Phillips [10], a biological indicator is defined as an organism which may be used to quantify relative levels of pollutant by measurement of toxicants' concentration in its tissues. Either the entire organism or a part of it or a single tissue which may sequester metals from the rest of the organism may be used. [11,12] have suggested certain characteristics that the biological organism should possess. These include: The organism should have widespread distribution in the study area, the organism should have favourable accessibility for collection, the organism should be of reasonable size, giving adequate tissues for analysis. There should also be available data on the biology of the organism, its ecological significance, and economic value, and be sedentary and thus indicative of local pollutant distribution. The fish species were chosen because of their availability throughout the year and their economic importance, and were identified at the Department of Fisheries and Forestry, Usmanu Danfodiyo University, Sokoto, Nigeria.

1.1 The Study Area

The Goronyo Dam is located near Keta village, some twenty five kilometres east of Goronyo town and ninety kilometres away from Sokoto town. The construction of the earth fill dam was completed across the Rima River in 1984, and has Gagare, Bunsuru and Maradi rivers as the main tributaries. The river Gagare comes from Kaura Namoda through Moriki to Birnin Yero. River Bunsuru on the other hand comes from Zurmi, through Bafarawa. Both rivers (Gagare and Bunsuru) have their confluence at Attalawa. Active fishing activities are taking place in the two tributaries. The dam is made up of three embankments (main dam, secondary dam and saddle dam) with a reservoir area of 200 km^2 and capacity of 942 million cubic meters at 288 meters above sea level (M.A.S.L) full storage. The dam supplies raw water for Sokoto State Water Board, stream bank (Fadama) irrigation through lifting, Wurno and Falalia irrigation schemes and fishing activities. Some of the crops grown by these schemes are rice,

cassava, vegetables and garlic. River Rima is an overflow of Goronyo Dam, active fishing activities are taking place at the study area, and the river water is also used for irrigation (Fig. 1). The study area comprises of Sokoto, Zamfara, and Katsina States in north-west, Nigeria. Effluents from artisan gold mining and dyeing sites are washed into the study sites. Preliminary investigation of water samples and sediments indicated the presence of some of the studied metals in the samples collected. Based on this, the research work proceeded to check the levels of the metals in fish tissues since the water body is their habitat and the sediment is a source of food.

The research group identified the level of indiscriminate effluent discharge into the study areas and projected a possible metal poisoning earlier before the outbreak of Zamfara lead poisoning. It was in Zamfara state that lead poisoning of children took place between the year 2010 and 2011. A lot of children still await urgent medical treatment, but the artisan gold miners are not relenting because according to them, it is their immediate source of legitimate earning.

2. MATERIALS AND METHODS

2.1 Specimen Collection

Fresh Five specimens of whole *Gymnarchus niloticus* and *Heteroblanchus bidorsalis* were collected from local fishermen either at the time of fishing operations or as the fishermen landed on the shores. The fishes were kept in the ice packed container for transportation to the laboratory where they were kept in the refrigerator at -4℃ till ready for dissection. The fish samples were dissected and three organs (gills, muscle, and bones) were harvested in triplicates from three specimens and used for analyses.

2.2 Tissue Digestion

Two grams (2.0) g (Wet Weight) of fresh fish tissue (gills, muscle or bone) was weighed after dissection and placed in the reflux flask. 20 ml of freshly prepared (1:1) nitric acid/hydrogen peroxide ((69-72)% and 35% purity respectively) was added.

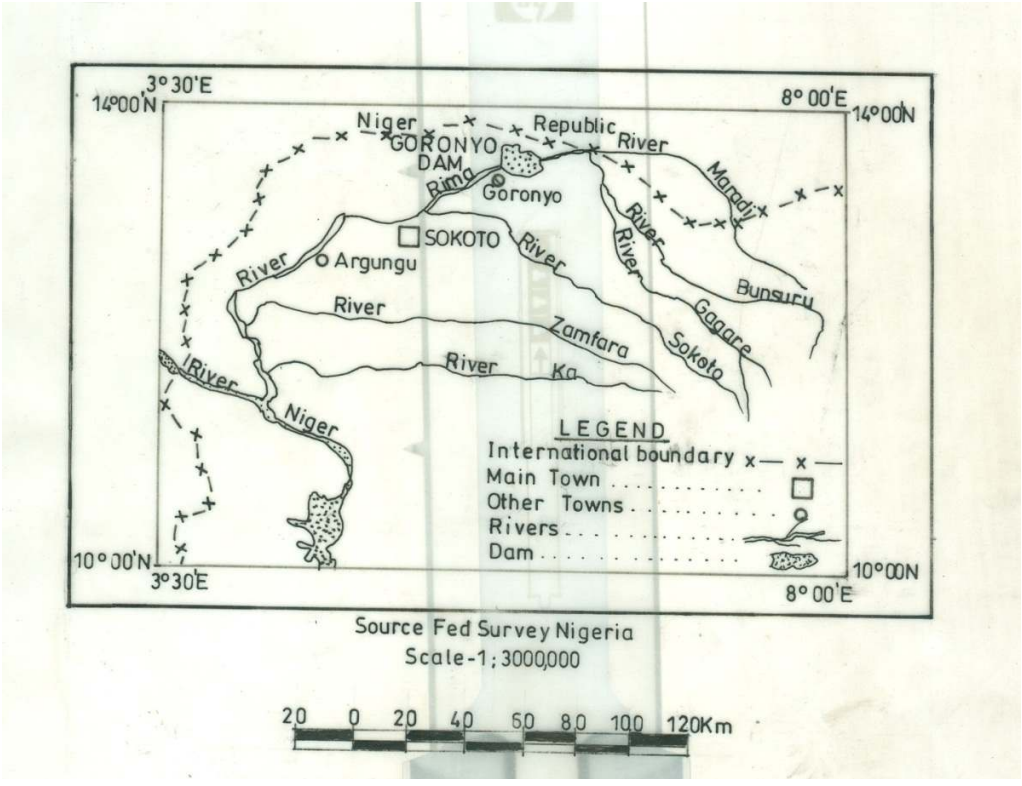

Fig. 1. The map of the study sites indicating the tributaries and the main dam

The mixture was placed in the block digestor at 360℃ for two hours till the volume was reduced to 10 ml. The digestate was allowed to cool and filtered through Whatman No. 1 filter paper and the volumes were made up to 100 ml. This procedure applied to all tissues. These digestates were further transferred to polythene bottles and stored till required for analysis [13].

2.3 Estimation of Metals

Atomic Absorption Spectrophotometer (Philips model PU 9100) was used for the estimation of Pb, Cd, Cr, Ni, Fe, Mg, Ca, Cu, Na and K as described in the Pye Unican Atomic Absorption data book (1984), and in the introduction to Atomic Absorption Spectrophotometry Scientific Analytical Equipment manual book by [14].

2.4 Statistical Analyses of Results

Statistical Product for Social Solution (SPSS) software was used to analyze all the data. Results are expressed as Mean ± Standard error mean (SEM) using one-way analysis of variance (ANOVA), followed by Turkey, Duncan and Dunnet's multiple comparison test and the values of $p<0.05$ were considered to be statistically significant.

3. RESULTS AND DISCUSSION

According to [15], the elevation in concentration of metals in fish tissues from aquatic environment is a good indicator of man-induced pollution. Because the discharge of heavy metals into rivers by domestic and industrial activities cause their rapid association with particulates and incorporation in bottom sediments, high levels may be observed in sediment samples compared with water samples. Presence in high concentrations of metals in sediment and water means their bioavailability to fish tissues and subsequent biotoxicity. As a result of bioaccumulation, fish species can have metals in their tissues many times than present in sediment and water. This bioaccumulation can be a rich source of toxic metals to man by their replacement of the essential metals that are used as cofactors by enzymes for metabolic activities.

Only gills of *Gymnarchus niloticus* of River Bunsuru in season 1 samples had high Cu (3.30±0.36) µg/g values (Table 1) in reference to 3.0 µg/g of the WHO, 2010. Other metals (Pb and Cd), and mineral nutrients were within the WHO limits. In respect to *Heterobranchus bidorsalis*` of the same river, Cu level in the bones of season I was also high (3.48±0.15) (Table 1) while Pb and mineral elements were within the acceptable limits. The reason for this might be that muscles possibly have a mechanism of tolerating and excreting the metal burden. All metals in tissues of *Gymnarchus niloticus* of River Gagare were in the acceptable limits (Table 3). River Gagare though is a pollution prone site receiving chronic input of wastes from mining and dyeing sites but has not accumulated high enough metals for on-ward absorption by fish tissues. *Heterobranchus bidorsalis* (Table 4) had all the values of the analysed elements in the acceptable limits. Same explanation as for Table 3 can be offered for Table 4. The Cu values (3.15±0.04, 3.12±0.04, and 3.11±0.04) µg/g respectively of the three tissues (gills, muscles, and bones) of River Rima during the season II sampling were above the WHO limit of 3.0 µg/g (Table 5). As with other Tables, values of Pb and other elements are within the acceptable limits. Cu values of in all tissues of *Heterobranchus bidorsalis* in the two seasons were consistently high (Table 6). This high Cu levels may be attributed the influx of effluents from the pollution prone sites. The effluents that are discharged into the river bodies and the sediments might contain high concentrations of the toxic metals and these may be a rich source to fishes because the water body is their habitat and the sediment is a source of food. Only the season II samples of *Gymnarchus niloticus* and *Herobranchus bidorsalis* from Goronyo Dam bioaccumulated high Pb in all the three tissues (Table 7). The high level content in season II (August –September) is likely to be the result of high influx of metals from the mining and dyeing sites due to heavy rain around this period. Goronyo Dam is particularly receiving water from the three other sampling sites and supplying to the Sokoto water works and for irrigation farming in all the surrounding villages. Same is obtained for *Heterobranchus bidorsalis* (Table 8) of Goronyo Dam season II. Fishes consumed from this dam can be very rich source of Pb. Pb interferes with several enzymes in the haem pathway and decreases haem biosynthesis by decreasing aminolevulinic acid ferrochalatase activity. Pb is sulphur seeking and easily bind to $S\text{-}CH_3$ and S-H (sulphydryl groups) in enzyme protein. Such immobilized enzymes cannot function properly.

Table 1. Metal concentrations (µg/g) in *Gymnarchus niloticus* tissues of river Bunsuru

Season I	Part	Pb	Cd	Ni	Fe	Mg	Cr	Cu	Ca	Na	K
	Gills	0.88^{a}±0.31	0.32^{a}±0.10	0.37^{a}±0.08	39.75^{a}±5.78	38.61^{a}±5.25	0.30^{a}±0.07	3.30^{a}±0.36	121.28^{a}±4.20	4.48^{a}±0.54	2.69^{a}±0.35
	Muscles	0.83^{b}±0.26	0.30^{a}±0.008	0.32^{b}±0.06	38.22^{b}±6.65	36.76^{b}±4.44	0.28^{b}±0.06	2.52^{b}±0.51	111.85^{b}±4.20	4.26^{b}±0.52	2.44^{b}±0.29
	Bones	0.81^{b}±0.21	0.03^{c}±0.08	0.80^{c}±0.43	35.64^{c}±6.59	33.76^{c}±4.39	0.26^{c}±0.03	1.54^{c}±0.15	132^{c}±6.91	3.75^{c}±0.25	2.42^{b}±0.32
Season II											
	Gills	0.04^{A}±0.03	0.04^{a}+0.03	0.01^{a}±0.006	15.61^{a}±3.91	60.08^{a}±5.51	0.07^{a}+0.03	1.29^{a}±0.13	125.67^{a}±9.36	2.98^{a}±0.42	3.29^{a}±0.20
	Muscles	0.01^{A}±0.00	0.04^{a}±0.03	0.06^{b}±0.02	15.24^{b}±4.23	69.41^{b}±4.68	0.14^{b}±0.05	1.01^{b}±0.01	120.03^{b}±5.89	2.57^{b}±0.54	3.24^{a}±0.40
	Bones	0.01^{b}±0.004	0.05^{a}±0.04	0.06^{b}±0.02	19.79^{c}±2.74	60.45^{c}±5.29	0.08^{a}±0.06	1.10^{c}±0.04	138.18^{c}±9.63	3.30^{a}±0.50	3.44^{b}±0.57

Season I (January- February); Season II (August – September), a = means on the same column, with same superscripts are not significantly different (P>0.05)
b, c = means on the same column, with different superscripts differ significantly (P<0.05), The metal and mineral contents of all the samples analysed were within the WHO permissible limits.

Table 2. Metal concentrations (µg/g) in *Heterobranchus bidorsalis* tissues of river Bunsuru

Season I	Part	Pb	Cd	Ni	Fe	Mg	Cr	Cu	Ca	Na	K
	Gills	0.45^{a}±0.08	0.18^{a}±0.02	0.22^{a}±0.06	41.78^{a}±3.45	42.04^{a}±3.49	0.19^{a}±0.02	1.66^{a}±0.08	191.67^{a}±26.70	3.53^{a}±0.66	3.31^{a}±0.39
	Muscles	0.50^{b}±0.12	0.12^{b}±0.01	0.15^{b}±0.02	32.38^{b}±2.95	44.37^{b}±2.12	0.17^{a}±0.01	1.96^{b}±0.19	197.62^{b}±20.58	3.45^{b}±0.75	2.68^{b}±0.55
	Bones	0.41^{a}±0.06	0.19^{a}±0.02	0.26^{c}±0.07	30.01^{c}±3.30	39.30^{c}±2.91	0.16^{a}±0.03	3.48^{c}±0.15	258.12^{c}±21.09	3.64^{c}±0.40	3.32^{a}±0.37
Season II											
	Gills	0.05^{a}±0.03	0.01^{a}±0.004	0.01^{a}±0.004	34.75^{a}±5.26	65.32^{a}±2.31	0.04^{a}±0.03	1.03^{a}±0.02	135.93^{a}±4.92	3.33^{a}±0.77	3.36^{a}±0.25
	Muscles	0.05^{a}±0.03	0.01^{a}±0.003	0.01^{a}±0.003	23.34^{b}±6.59	66.49^{b}±2.19	0.01^{b}±0.01	2.02^{b}±0.01	123.86^{b}±2.86	2.66^{b}±0.63	2.78^{b}±0.27
	Bones	0.10^{b}±0.03	0.01^{a}±0.02	0.01^{a}±0.003	21.76^{b}±4.06	64.96^{c}±1.99	0.05^{a}±0.03	2.03^{b}±0.02	146.13^{c}±5.80	3.54^{c}±0.73	3.41^{a}±0.42

Season I (January- February); Season II (August – September), a = means on the same column, with same superscripts are not significantly different (P>0.05)
b, c = means on the same column, with different superscripts differ significantly (P<0.05), The metal and mineral contents of all the samples analysed were within the WHO permissible limits except for Heterobranchus bidorsalis during season 1 sampling with a non-significant difference.

Table 3. Metal concentrations (µg/g) in *Gymnarchus niloticus* tissues of river Gagare

Season I	Part	Pb	Cd	Ni	Fe	Mg	Cr	Cu	Ca	Na	K
	Gills	0.15^{a}±0.02	0.05^{a}±0.01	0.18^{a}±0.02	30.50^{a}±3.88	20.88^{a}±2.69	0.30^{a}±0.09	1.14^{a}±0.01	245.65^{a}±6.91	4.00^{a}±0.54	3.50^{a}±0.44
	Muscles	0.18^{b}±0.03	0.04^{a}±0.01	0.20^{a}±0.03	27.63^{b}±2.57	19.95^{b}±2.65	0.29^{a}±0.09	2.15^{b}±0.01	232.92^{b}±7.71	3.70^{b}±0.64	3.76^{b}±0.34
	Bones	0.15^{a}±0.02	0.03^{a}±0.01	0.19^{a}±0.03	26.60^{b}±4.43	21.01^{c}±2.79	0.19^{b}±0.02	1.16^{a}±0.02	274.60^{c}±10.37	4.04^{a}±0.59	3.31^{c}±0.61
Season II											
	Gills	0.65^{a}±0.03	0.15^{a}±0.04	0.18^{a}±0.09	12.61^{a}±4.63	68.48^{a}±17.16	0.90^{a}±0.28	2.41^{a}±0.14	309.09^{a}±34.51	2.99^{a}±0.46	3.33^{a}±0.89
	Muscles	0.72^{b}±0.22	0.36^{b}±0.11	0.17^{a}±0.09	18.61^{b}±3.06	90.77^{b}±14.75	1.08^{b}±0.15	2.47^{a}±0.05	188.35^{b}±30.06	3.39^{b}±0.46	2.58^{b}±0.76
	Bones	0.82^{c}±0.30	0.17^{a}±0.07	0.15^{b}±0.11	18.66^{b}±2.48	58.57^{c}±12.41	0.39^{c}±0.21	2.70^{b}±0.11	244.79^{c}±28.41	2.97^{a}±0.60	2.91^{c}±1.12

Season I (January- February); Season II (August – September), a = means on the same column, with same superscripts are not significantly different (P>0.05), b, c = means on the same column, with different superscripts differ significantly (P<0.05), The metal and mineral contents of all the samples analysed were within the WHO permissible limits.

Table 4. Metal concentrations (µg/g) in *Heterobranchus bidorsalis* tissues of river Gagare

Season I	Part	Pb	Cd	Ni	Fe	Mg	Cr	Cu	Ca	Na	K
	Gills	0.13^{a}±0.01	0.07^{a}±0.01	0.15^{a}±0.01	55.09^{a}±4.03	32.43^{a}±5.46	0.47^{a}±0.07	1.14^{a}±0.01	251.14^{a}±7.72	2.75^{a}±0.74	3.58^{a}±0.38
	Muscles	0.12^{a}±0.01	0.04^{b}±0.01	0.16^{a}±0.01	46.12^{b}±4.26	29.29^{b}±6.47	0.39^{b}±0.07	2.14^{b}±0.01	241.39^{b}±8.26	3.66^{b}±0.64	3.66^{b}±0.62
	Bones	0.15^{b}±0.01	0.04^{b}±0.01	0.15^{a}±0.01	47.14^{c}±4.58	31.23^{c}±4.15	0.32^{c}±0.06	1.14^{a}±0.01	188.25^{c}±28.06	3.07^{c}±0.74	3.66^{b}±0.38
Season II											
	Gills	0.22^{a}±0.07	0.17^{a}±0.07	0.19^{a}±0.10	15.39^{a}±1.77	74.61^{a}±10.95	0.84^{a}±0.29	0.57^{a}±0.23	239.68^{a}±22.46	5.06^{a}±0.85	7.84^{a}±2.12
	Muscles	0.39^{b}±0.12	0.25^{b}±0.09	0.29^{b}±0.17	14.33^{b}±2.56	65.82^{b}±10.12	0.95^{b}±0.48	1.44^{b}±0.19	219.53^{b}±17.55	5.01^{b}±0.98	5.80^{b}±1.45
	Bones	0.13^{c}±0.05	0.19^{a}±0.09	0.20^{a}±0.06	14.69^{b}±3.60	75.18^{a}±8.34	1.02^{b}±0.41	1.28^{b}±0.09	297.25^{c}±38.51	5.47^{b}±0.38	8.16^{a}±2.23

Season I (January- February); Season II (August – September), a = means on the same column, with same superscripts are not significantly different (P>0.05), b, c = means on the same column, with different superscripts differ significantly (P<0.05), The metal and mineral contents of all the samples analysed were within the WHO permissible limits.

Table 5. Metal concentrations (µg/g) in *Gymnarchus niloticus* tissues of river Rima

Season I	Part	Pb	Cd	Ni	Fe	Mg	Cr	Cu	Ca	Na	K
	Gills	0.27^{a}±0.03	0.32^{a}±0.14	0.10^{a}±0.03	54.22^{a}±11.65	23.74^{a}±5.53	0.11^{a}±0.02	3.15^{a}±0.04	159.14^{a}±10.80	4.83^{a}±1.28	3.80^{a}±0.62
	Muscles	0.34^{b}±0.05	0.29^{b}±0.10	0.10^{a}±0.03	51.16^{b}±6.89	30.67^{b}±6.47	0.10^{a}±0.02	3.12^{a}±0.04	153.45^{b}±14.36	4.97^{a}±1.11	3.73^{a}±0.71
	Bones	0.35^{b}±0.05	0.34^{a}±0.16	0.10^{a}±0.02	49.81^{c}±7.66	23.30^{a}±5.78	0.12^{a}±0.02	3.11^{a}±0.04	173.48^{c}±9.19	5.76^{b}±0.03	4.17^{b}±0.52
Season II											
	Gills	0.03^{a}±0.01	0.01^{a}±0.01	0.10^{a}±0.06	13.50^{a}±1.46	74.67^{a}±17.24	0.45^{a}±0.12	2.07^{a}±0.03	263.38^{a}±23.63	3.28^{a}±0.23	4.21^{a}±0.51
	Muscles	0.02^{a}±0.01	0.05^{b}±0.04	0.16^{b}±0.08	13.53^{a}±2.39	55.10^{b}±9.13	0.21^{b}±0.05	2.01^{a}±0.003	233.38^{b}±23.63	3.63^{a}±0.60	4.14^{a}±0.45
	Bones	0.02^{a}±0.01	0.04^{b}±0.03	0.18^{b}±0.02	13.48^{a}±2.57	70.27^{c}±16.87	0.23^{b}±0.10	2.04^{a}±0.02	249.79^{c}±28.41	3.45^{a}±0.31	3.85^{b}±0.51

Season I (January- February); Season II (August – September), a = means on the same column, with same superscripts are not significantly different (P>0.05), b, c = means on the same column, with different superscripts differ significantly (P<0.05), The metal and mineral contents of all the samples analysed were within the WHO permissible limits.

Table 6. Metal concentrations (µg/g) in *Heterobranchus bidorsalis* in river Rima

Season I	Part	Pb	Cd	Ni	Fe	Mg	Cr	Cu	Ca	Na	K
	Gills	0.19^{a}±0.05	0.13^{a}±0.01	0.12^{a}±0.03	41.58^{a}±6.01	25.01^{a}±4.03	0.23^{a}±0.03	3.18^{a}±0.05	172.48^{a}±22.60	4.27^{a}±0.33	3.45^{a}±0.24
	Muscles	0.15^{b}±0.03	0.30^{b}±0.17	0.11^{a}±0.03	35.81^{b}±5.63	23.59^{b}±3.7	0.19^{b}±0.03	3.16^{a}±0.04	158.16^{b}±21.13	3.64^{b}±0.24	2.80^{b}±0.17
	Bones	0.16^{b}±0.09	0.15^{a}±0.02	0.12^{a}±0.03	34.90^{c}±4.66	17.89^{c}±3.38	0.24^{a}±0.03	3.17^{a}±0.03	188.25^{c}±28.06	4.28^{a}±0.27	3.33^{a}±0.21
Season II											
	Gills	0.09^{a}±0.03	0.10^{a}±0.05	0.12^{a}±0.04	13.49^{a}±2.01	56.61^{a}±6.32	0.18^{a}±0.08	4.12^{a}±0.06	166.09^{a}±11.04	3.69^{a}±0.54	4.16^{a}±0.28
	Muscles	0.15^{b}±0.06	0.08^{a}±0.06	0.14^{a}±0.03	13.51^{a}±2.40	43.22^{b}±3.4	0.12^{b}±0.06	4.05^{a}±0.02	113.87b±5.21	3.86a±0.39	3.80^{b}±0.25
	Bones	0.09^{a}±0.03	0.06^{b}±0.03	0.12^{a}±0.03	13.41^{a}±3.74	64.31^{c}±7.04	0.21^{c}±0.13	4.08^{a}±0.03	144.29^{c}±9.61	3.40^{a}±0.38	3.26^{c}±0.30

Season I (January- February); Season II (August – September), a = means on the same column, with same superscripts are not significantly different (P>0.05), b, c = means on the same column, with different superscripts differ significantly (P<0.05), The metal and mineral contents of all the samples analysed were within the WHO permissible limits except for Heterobranchus bidorsalis during season II sampling with higher increase in Cu value as much as 30 %

Table 7. Metal concentrations (µg/g) in *Gymnarchus niloticus* tissues of Goronyo dam

Season I	Part	Pb	Cd	Ni	Fe	Mg	Cr	Cu	Ca	Na	K
	Gills	0.14^{a}±0.03	0.06^{a}±0.03	0.12^{a}±0.01	41.12^{a}±3.70	27.60^{a}±2.12	0.13^{a}±0.03	1.08^{a}±0.03	131.06^{a}±3.09	22.89^{a}±2.28	12.68^{a}±0.77
	Muscles	0.12^{a}±0.03	0.08^{a}±0.02	0.12^{a}±0.003	34.7^{b}±3.19	23.58^{b}±1.63	0.13^{a}±0.03	1.10^{a}±0.02	119.13^{b}±2.45	20.15^{b}±2.25	10.83^{b}±0.43
	Bones	0.14^{a}±0.03	0.07^{a}±0.03	0.12^{a}±0.01	30.32^{c}±3.16	19.98^{c}±1.52	0.12^{a}±0.13	1.10^{a}±0.02	150.87^{c}±4.79	20.67^{c}±2.90	12.08^{c}±1.16
Season II											
	Gills	4.75^{a}±0.87	0.60^{a}±0.14	0.19^{a}±0.03	15.30^{a}±1.22	101.53^{a}±5.19	0.02^{a}±0.01	1.32^{a}±0.16	332.51^{a}±37.07	15.24^{a}±1.70	5.44^{a}±0.77
	Muscles	4.68^{a}±0.67	0.59^{a}±0.04	0.17^{a}±0.03	14.50^{b}±2.44	92.02^{b}±11.29	0.08^{b}±0.002	1.63^{b}±0.18	310.53^{b}±26.56	15.10^{a}±1.47	4.61^{b}±0.62
	Bones	4.34^{a}±0.34	0.73^{b}±0.11	0.14^{b}±0.02	16.01^{c}±3.31	96.18^{c}±4.13	0.03^{a}±0.01	1.46^{a}±0.13	327.07^{a}±20.92	15.17^{a}±1.98	5.03^{a}±0.58

Season I (January- February); Season II (August – September), a = means on the same column, with same superscripts are not significantly different (P>0.05), b, c = means on the same column, with different superscripts differ significantly (P<0.05), Lead (Pb) in gills, muscles and bones of season II were found to have been bioaccumulated to as much as 60 % above the WHO permissible limit of 2.0 µg/g. Other metals and mineral elements were within the permissible limits

Table 8. Metal concentrations (µg/g) in *Heterobranchus bidorsalis* in Goronyo dam

Season I	Part	Pb	Cd	Ni	Fe	Mg	Cr	Cu	Ca	Na	K
	Gills	0.08^{a}±0.04	0.03^{a}±0.02	0.07^{a}±0.03	28.03^{a}±3.82	16.93^{a}±1.24	0.11^{a}±0.04	1.14^{a}±0.05	119.64^{a}±5.41	15.30^{a}±1.46	13.59^{a}±1.32
	Muscles	0.07^{a}±0.04	0.03^{a}±0.02	0.07^{a}±0.03	25.15^{b}±3.18	17.04^{a}±1.36	0.10^{a}±0.04	1.21^{a}±0.11	114.00^{b}±4.75	16.88^{b}±1.64	16.06^{b}±0.93
	Bones	0.08^{a}±0.04	0.04^{a}±0.03	0.08^{a}±0.03	17.85^{c}±2.12	15.65^{c}±1.13	0.11^{a}±0.04	1.14^{a}±0.04	147.97^{c}±4.25	14.45^{c}±1.21	13.24^{a}±1.10
Season II											
	Gills	4.02^{a}±0.78	0.64^{a}±0.08	0.19^{a}±0.07	14.74^{a}±1.34	80.48^{a}±10.10	0.07^{a}±0.03	1.01^{a}±0.004	122.14^{a}±11.57	5.03^{a}±0.20	5.14^{a}±0.31
	Muscles	5.27^{b}±0.51	0.54^{b}±0.03	0.14^{b}±0.06	15.12^{b}±2.27	80.23^{a}±7.03	0.13^{b}±0.06	1.12^{a}±0.06	246.51^{b}±16.16	5.08^{a}±0.65	5.31^{a}±1.10
	Bones	5.23^{b}±0.88	0.46^{c}±0.06	0.15^{b}±0.10	14.78^{a}±3.29	83.21^{b}±7.90	0.09^{a}±0.06	2.06^{b}±0.03	262.59^{c}±6.15	4.78^{b}±0.68	5.02^{a}±0.76

Season I (January- February); Season II (August – September), a = means on the same column, with same superscripts are not significantly different (P>0.05), b, c = means on the same column, with different superscripts differ significantly (P<0.05), Gills, muscles and bones in season II were found to have bioaccumulated to as much as 50 %, 60 % and 60 % respectively of Pb above the WHO permissible limit of 2.0 µg/g. Other metals and mineral elements were within the permissible limits.

Since Pb plays no role in enzyme activities, chronic discharge of effluents containing wastes to aquatic environment will lead to bioaccumulation over time. [16] views bioaccumulation as a result of the competing rate of a chemical uptake and elimination. Thus, bioaccumulation may likely occur in the fishes with continuous discharge of effluents from dyeing and gold mining activities. And as with Pb, Cd is also sulphur-seeking. It binds to S-CH_3 and S-H groups in enzymes proteins. Cd^{2+} and Zn^{2+} are similar in their chemical properties including size. Due to these similarities, Cd can replace Zn in many biological systems, in particular, sulphur ligands. Cd can bind up to ten times more strongly than Zn in biological systems. Cd can also replace Mg and Ca in biological systems, although these replacements are rare [17]. It has been observed that Cd-Containing enzymes do not perform the same function as Zn-containing enzymes. Presence of Cd in tissues when bound to metallothioneins allows it to be transported to the blood by the erythrocyte or bound to large muscular weight proteins [18].

In general, differential levels of metals in different tissues may be attributed to some biological factors: Nature of the body covering with respect to penetrability, availability of right type of enzymes and optimal physicochemical conditions, excretory capacity and the rate of elimination of by-products of metabolism, availability of body size and the sensitivity of the site of action, age and life cycle stage as well as ecology with particular reference to location [19]. Nickel (Ni) is essential for enzyme activities, particularly in urease and dehydrogenase activities, absence of which retards growth or cause the death of the living organism. Ni is highly tolerable by organisms except the divalent state Ni^{2+}. Ni has not been found to be in high availability in all tissues and from all the locations during the two seasonal sampling. The Ni^{2+} when above the recommended limit binds strongly to the gills rendering it less functional. Fishes however, have developed mechanisms to control and regulate their nickel burdens.

5. CONCLUSION

Gills muscles and bones of *Heterobranchus bidorsalis* in season II have high affinity for copper (Cu) absorption when compared to *Gymnarchus niloticus* of the same river and season. On the other hand, Goronyo Dam season II samples had high lead (Pb) concentrations when compared to season I samples of the same river. The high Pb content has lead to low Cu levels in all the tissues. This is because Pb binds with greater affinity to enzymes than Cu.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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