Capabilities of Energy Dispersive X-Ray Fluorescence Techniques in Elemental Profiling of Fish from Zobe Dam, Katsina State - Nigeria

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Abstract- This study tried to investigate the concentration of chemical elements in organs of Oreochromis niloticus and Clarias gariepinus from Zobe Dam, using Energy Dispersive X-ray Fluorescence (ED-XRF) techniques. The main goal of the study is to investigate the elemental composition, the extent of the concentrations of the identified elements in organs of the two fish species, as well as to assess the health implications that the identified toxic elements may pose to human via consumption of the fishes. Twenty six (26) elements (Fe, Cu, Zn, Al, Mg, Na, S, P, Ca, K, Mn, Cr, Cl, Br, Pb, Ni, V, Bi, Si, Nb, Ta, Mo, Rb, Sr, Sn, and W) were identified. They include the essential elements; (Fe, Cu, Al, Mg, Ca, Na, S, P, Mn, Cr, Zn, I, Cl, and Mo), the non-essential elements (Bi, V, Si, Nb, Ta, Rb, Sr, Sn, and W), and the potential toxic elements (Br, Pb, and Ni). The dietary intake of some essential and toxic elements was estimated for tissue by considering WHO/FAO tolerable daily intake of adults (TDI/70kg). Other organs were neglected according to the consumption pattern of the population in the study area. Although, our findings showed most of the concentration levels of the detected elements exceeded the recommended guidelines set by some authorities, but, results of the estimated dietary intake showed that, the concentrations of all the detected elements in tissue of both fish species including the potential toxic elements (Br, Pb, and Ni) are well below the toxicological reference values provided by the WHO/FAO and were found within the nutritional threshold. Therefore, consumption of tissue of the studied fish species is considered safe.

Indexed Terms- Clarias Gariepinus, Dietary Intake, EDXRF, Essential Elements, Oreochromis Niloticus, Toxic Elements

I. INTRODUCTION

Fish and fishery products play an important role in food and nutritional security around the world [1]. Foods from the aquatic environment are a complete and unique source of both macro and micronutrients required in a healthy diet [2]. Strong evidence underlines how consumption of fish and in particular oily fish lowers the risk of Coronary Heart Diseases (CHD) mortality [3]-[4]. Fish is relatively cheaper and readily available, therefore making quality protein available to the poor people in most developing countries of the world including Nigeria [5]. However, fish as an aquatic organism exposed to various elements, some of which are highly essential to human health and in contrast some elements are toxicants presenting a serious health threat to human when consumed. Primarily because of a higher concentration of some toxic metals, marine organisms have been subjected to extensive studies compared to terrestrial organisms [6]. Fishes are widely used to evaluate the health of aquatic ecosystems, hence act as bioindicators [7]. There are many water bodies which lie in vicinity of population have been polluted by effluents released by industries, factories, power stations, domestic waste etc. which besides disturbing the quality of water and also degrade the protein source in the form of fish food and limits their use [8]-[9]- [10]- [11]- [12]. Hartl [13] remarks that "metals, of natural or anthropogenic origin, are ubiquitous in the environment and therefore understanding their behavior and interaction with aquatic organisms, particularly fishes, as a major source of protein for human consumption, is of a great socioeconomic importance. It has been reported that prolonged consumption of unsafe concentration of elements which especially accumulate in organs of fish, such as internal organs, liver, kidneys and spleen, may lead to the chronic accumulations of the toxic elements in the kidney and liver of human, causing disruption of numerous biochemical processes, leading to cardiovascular, nervous, kidneys and bone diseases.

The aim of this study is to assess the elemental composition and level of concentrations of the trace elements in various organs of some fish species from Zobe Dam, Katsina State, Nigeria, so as to evaluate the contribution of these elements to total dietary intakes, and evaluate the health implications of some of the possibly toxic elements to human. We have employed energy dispersive x-ray fluorescence (ED-XRF) techniques to determine and evaluate the composition, the level of the concentrations, and the possible health implications of some elements in organs of the two fish species (*Oreochromis niloticus* and *Clarias gariepinus*) from Zobe Dam, Katsina state.

II. MATERIALS AND METHODS

- Study Area

Zobe Dam was established in July, 1977. It is located in the southern part of Dutsin-Ma in Katsina State of Nigeria [14]. Before it was established, the settlers had a history of blacksmithing and agrarian farming activities. The Dam has an average storage capacity of 170 million m^3 and about 8137 hectares of land for irrigation. It covers an estimated surface area of 39.6km^2. The annual rainfall is estimated to be about 817mm per year. Dam irrigation area is located between 12º23’18’’N of northern latitude and 7º28’29’’E of eastern longitude. In the east, the area is delimited by Kuki and Sayaya, in the north by Dan Makubiri and Safana, and in the south by Danmusa and Makera. The area lies between 450m and 490m above Mean Sea Level (MSL). The inhabitants are predominantly Hausa and Fulani by tribe and their main occupation is farming and animal rearing. The population and activities in the local government area have increased few years back mostly due to the establishment of the new Federal University at Dutsin-ma.

- Sampling and Sample Preparation

Fish species *Oreochromis niloticus* and *Clarias gariepinus* were collected directly from fishermen at their landing site at Zobe Dam in Dutsin-Ma Local Government Area of Katsina State. The fish samples were prepared at Ummaru Musa Yaradua University Central Science Laboratory. The fish organs (Tissue, Liver, gill, and Bone) were cut using dissecting kit; they were dried in three days and later put in an Oven at 50°C. The samples were then put on a desiccator and grinded using motor and pestle and the resulting powder was put in polyethylene bags. A total of 8 samples were prepared and taken to Ummaru Musa Yaradua University Central Laboratory for analysis. Elemental analysis of the prepared samples was carried out using Energy Dispersive X-ray Fluorescence (ED-XRF) Techniques. ED-XRF analysis was done using the standard method with Montana soil SRM 2710 for geological samples while IAEA – 155 Whey Powder for biological samples as a thermo fisher scientific standard reference material. 3 g of each of the samples was weighed and then poured into a sample holder and covered with cotton wool to prevent it from spraying. The bottom of the samples holder is made of polypropylene which is a thermoplastic. The sample holders containing the samples which were run in a vacuum using a vacuum pump for 10 minutes and they were inserted into the XRF Spectrometer for the elemental analysis. The method was calibrated using biological calibration. The samples were allowed to run in the XRF spectrometer each for 10 minutes after which the results were obtained.

QUALITY CONTROL

The present study uses certified reference material CRMs IAEA 155 (Whey Powder) for quality control purpose.

Table 1: Concentrations of standard reference material Whey Powder IAEA 155 used for quality control by EDXRF (in %, unless otherwise stated)

Element	Certified Values	This Work Recorded Values
Al	0.53	0.54

Br	0.39	0.37
Ca	421	434
Cl	692	667
Cr	0.59 mg/kg	0.48
Cu	0.57 mg/kg	0.64
Fe	0.62	0.58
K	417	429
Mn	0.09	0.09
Na	158	171
Ni	0.54 mg/kg	0.47
Pb	0.104 mg/kg	0.12
Zn	0.34	0.33

Table 1, shows the result of the EDXRF of Whey Powder, the certified reference material used as quality control. From the table, it is evident that the results obtained from this work are in well agreement with the certified values obtained for this sample. Thus, this analytical technique could be relied upon for accurate, precision and reproducible analysis of samples with complex matrix.

- Statistical Analysis and Inter- elemental Correlation

Concentration values obtained from the different organs of the studied fishes (*Oreochromis niloticus* and *Clarias gariepinus*) were subjected to statistical analysis using Analysis of Variance (ANOVA). The analysis of variances (ANOVA) showed statistically significant differences in mean concentrations of (S, Bi), (S, K), (Ni, Si), and (K, Ni). The level of significance was set at $P < 0.05$ or $P < 5\%$. The Pearson's correlation coefficients (r) of the element concentrations in organs of *Oreochromis niloticus* and *Clarias gariepinus* are presented in Table (2 & 3).

Table 2: Pearson's correlation coefficient (r) of elements in organs of *Oreochromis niloticus*

	Mg	*Fe*	*Cu*	*Zn*	*Al*	*Cr*	*Na*	*S*	*P*	*Ca*	*K*	*Mn*	*Ni*	*Br*	*Mo*	*Sn*	*Pb*	*Cl*	*Sr*	*V*	*Bi*	*Rb*	*Si*	*Nb*	*Ta*
Mg	1.00																								
Fe	-0.04	1.00																							
Cu	-0.09	0.68	1.00																						
Zn	-0.42	0.69	0.94	1.00																					
Al	-0.49	-0.84	-0.43	-0.28	1.00																				
Cr	-0.63	-0.01	-0.53	-0.24	0.22	1.00																			
Na	-0.21	0.34	0.92	0.87	-0.05	-0.59	1.00																		
S	0.71	0.40	-0.19	-0.35	-0.80	-0.02	-0.52	1.00																	
P	0.04	-0.98	-0.51	-0.54	0.85	-0.15	-0.14	-0.51	1.00																
Ca	-0.13	-0.97	-0.51	-0.49	0.93	-0.03	-0.13	-0.62	0.99	1.00															
K	0.65	0.64	0.12	-0.05	-0.94	-0.15	-0.25	0.95	-0.70	-0.80	1.00														
Mn	-0.53	0.72	0.87	0.98	-0.28	-0.06	0.78	-0.34	-0.61	-0.53	-0.05	1.00													
Ni	0.72	0.67	0.40	0.17	-0.95	-0.47	0.08	0.81	-0.66	-0.78	0.93	0.11	1.00												
Br	-0.58	0.77	0.80	0.94	-0.31	0.09	0.67	-0.28	-0.68	-0.59	-0.01	0.99	0.10	1.00											
Mo	-0.32	0.72	0.97	0.99	-0.35	-0.32	0.89	-0.28	-0.56	-0.52	0.03	0.96	0.26	0.92	1.00										
Sn	-0.59	-0.66	-0.10	0.04	0.94	0.07	0.28	-0.95	0.74	0.83	-1.00	0.03	-0.91	-0.03	-0.03	1.00									
Pb	-0.44	0.74	0.92	1.00	-0.33	-0.16	0.82	-0.30	-0.61	-0.55	0.00	0.99	0.19	0.97	0.99	-0.02	1.00								
Cl	-0.48	0.29	0.84	0.89	0.12	-0.35	0.96	-0.69	-0.11	-0.05	-0.44	0.84	-0.16	0.76	0.88	0.45	0.85	1.00							
Sr	-0.23	-0.96	-0.56	-0.49	0.96	0.10	-0.18	-0.63	0.96	0.99	-0.83	-0.51	-0.84	-0.55	-0.54	0.84	-0.55	-0.07	1.00						
V	-0.25	-0.95	-0.71	-0.61	0.93	0.28	-0.37	-0.52	0.91	0.95	-0.76	-0.60	-0.85	-0.61	-0.67	0.76	-0.65	-0.24	0.98	1.00					
Bi	0.82	0.31	-0.17	-0.39	-0.76	-0.18	-0.47	0.98	-0.40	-0.53	0.93	-0.41	0.83	-0.37	-0.31	-0.91	-0.35	-0.68	-0.57	-0.48	1.00				
Rb	-0.20	0.99	0.65	0.72	-0.75	0.13	0.33	0.30	-0.97	-0.93	0.53	0.77	0.54	0.83	0.73	-0.57	0.78	0.33	-0.90	-0.89	0.19	1.00			

Si	0.67	0.71	0.50	0.27	-0.95	-0.52	0.19	0.74	-0.68	-0.79	0.89	0.21	0.99	0.19	0.36	-0.86	0.29	-0.05	-0.86	-0.89	0.76	0.58	1.00		
Nb	0.27	0.82	0.89	0.74	-0.78	-0.57	0.67	0.27	-0.70	-0.76	0.55	0.67	0.77	0.62	0.81	-0.53	0.74	0.50	-0.82	-0.92	0.29	0.74	0.84	1.00	
Ta	-0.04	0.76	0.99	0.92	-0.53	-0.51	0.86	-0.08	-0.60	-0.61	0.23	0.86	0.49	0.80	0.96	-0.22	0.91	0.77	-0.66	-0.79	-0.07	0.72	0.59	0.93	1.00

Table 3: Pearson's correlation coefficients (r) of elements in organs of *Clarias gariepinus*

Elements	*Mg*	*Fe*	*Cu*	*Zn*	*Al*	*Mn*	*Na*	*S*	*P*	*Ca*	*K*	*Cl*	*Sr*	*Sn*	*Cr*	*Br*	*Pb*	*Ni*	*Rb*	*V*	*Bi*	*W*	*Si*	*Nb*	*Ta*
Mg	1.00																								
Fe	-0.02	1.00																							
Cu	0.06	1.00	1.00																						
Zn	0.01	1.00	1.00	1.00																					
Al	0.08	0.33	0.32	0.35	1.00																				
Mn	-0.67	0.75	0.70	0.73	0.14	1.00																			
Na	0.38	0.91	0.94	0.92	0.23	0.43	1.00																		
S	0.82	0.54	0.61	0.57	0.35	-0.14	0.82	1.00																	
P	-0.29	0.96	0.93	0.95	0.40	0.89	0.75	0.31	1.00																
Ca	-0.81	-0.56	-0.62	-0.59	-0.31	0.12	-0.83	-1.00	-0.32	1.00															
K	0.83	0.54	0.60	0.56	0.26	-0.15	0.82	0.99	0.28	-1.00	1.00														
Cl	0.05	0.95	0.95	0.96	0.59	0.65	0.87	0.61	0.93	-0.61	0.58	1.00													
Sr	-0.66	-0.62	-0.67	-0.65	-0.63	0.00	-0.79	-0.95	-0.46	0.93	-0.91	-0.76	1.00												
Sn	0.99	-0.19	-0.11	-0.16	0.05	-0.79	0.22	0.72	-0.44	-0.71	0.73	-0.10	-0.56	1.00											
Cr	-0.81	-0.11	-0.18	-0.12	0.43	0.42	-0.49	-0.68	0.18	0.70	-0.74	0.00	0.40	-0.76	1.00										
Br	0.09	0.99	0.99	1.00	0.41	0.67	0.94	0.64	0.93	-0.65	0.63	0.98	-0.73	-0.07	-0.15	1.00									
Pb	0.98	-0.21	-0.13	-0.18	-0.04	-0.79	0.21	0.69	-0.47	-0.69	0.71	-0.14	-0.51	1.00	-0.81	-0.10	1.00								
Ni	0.99	0.00	0.08	0.03	0.18	-0.66	0.39	0.84	-0.26	-0.83	0.84	0.10	-0.71	0.98	-0.76	0.12	0.97	1.00							
Rb	0.86	0.49	0.56	0.52	0.30	-0.20	0.79	1.00	0.24	-1.00	1.00	0.55	-0.92	0.76	-0.73	0.59	0.74	0.87	1.00						
V	0.37	-0.31	-0.26	-0.32	-0.90	-0.42	-0.04	0.04	-0.49	-0.07	0.13	-0.52	0.29	0.38	-0.76	-0.34	0.47	0.27	0.11	1.00					
Bi	0.99	-0.16	-0.09	-0.13	0.03	-0.77	0.24	0.73	-0.43	-0.72	0.74	-0.09	-0.57	1.00	-0.79	-0.05	1.00	0.98	0.77	0.41	1.00				
W	0.11	0.99	1.00	0.99	0.35	0.66	0.95	0.65	0.91	-0.67	0.64	0.96	-0.71	-0.06	-0.21	1.00	-0.08	0.13	0.60	-0.27	-0.03	1.00			
Nb	0.95	-0.32	-0.25	-0.29	-0.01	-0.86	0.08	0.61	-0.56	-0.60	0.63	-0.23	-0.45	0.99	-0.73	-0.21	0.99	0.94	0.66	0.43	0.99	-0.19	#DIV/0!	1.00	
Ta	0.32	0.94	0.96	0.95	0.36	0.48	0.99	0.80	0.81	-0.81	0.79	0.93	-0.83	0.16	-0.37	0.97	0.14	0.34	0.76	-0.19	0.18	0.98	#DIV/0!	0.02	1.00

Significant positive correlations were detected between some elements, e.g, Ni- Si ($r = 0.99$, $P < 0.05$), S- Bi ($r = 0.98$, $P < 0.05$). Also, negative correlations were detected between some elements, e.g, Fe- Ca ($r = -0.97$, $P < 0.05$), Fe- Sr ($r = -0.96$, $P < 0.05$), and P- Rb ($r = -0.97$, $P < 0.05$). A perfect negative correlation was noticed between K- Sn. Moreover, high positive correlations were detected between some elements, S- K, K- Ni, K- Bi, K- Si, and Cu- Nb with the values, 0.95, 0.93, 0.93, 0.89, and 0.89

respectively. Also, high negative correlations were identified between S- Sn, Ni- Sn, Fe- V, Ca- Rb, and Sr- Rb, with the values, -0.95, -0.91, -0.95, -0.93, and -0.90 respectively.

In *Clarias gariepinus*, Positive correlations were detected between some elements, e.g, S- K ($r = 0.99$, $P < 0.05$), Fe- Br ($r = 0.99$, $P < 0.05$), Cu- Br ($r = 0.99$, $P < 0.05$), Cl- Br ($r = 0.98$, $P < 0.05$), Sn- Ni ($r = 0.98$, $P < 0.05$), Pb- Ni ($r = 0.97$, < 0.05), Ni- Bi ($r = 0.98$, $P < 0.05$), Fe- W ($r = 0.99$, $P < 0.05$), Zn- W ($r = 0.99$, $P < 0.05$), Cl- W ($r = 0.96$, $P < 0.05$), Sn- Nb ($r = 0.99$, $P < 0.05$), Pb- Nb ($r = 0.99$, $P < 0.05$), Bi- Nb ($r = 0.99$, $P < 0.05$), Cu- Ta ($r = 0.96$, $P < 0.05$), Na- Ta ($r = 0.99$, $P < 0.05$), Br- Ta ($r = 0.97$, $P < 0.05$), and W- Ta ($r = 0.98$, $P < 0.05$). Also, high positive and negative correlations were identified between some elements, Cu- Na, Fe- Na, Zn- Na, Na- Br, P- Br, Na- W, Ni- Nb, Fe- Ta, and Zn- Ta with corresponding values 0.94, 0.91, 0.92, 0.94, 0.93, 0.95, 0.94, 0.94 and 0.95; and S- Sr, K- Sr, with the values -0.95 and -0.91 respectively. Accordingly, perfect positive correlations were also detected between some elements, e.g, Fe- Cu, Fe- Zn, K- Br, Sn- Pb, S- Rb, K- Rb, Sn- Bi, Pb- Bi, Cu- W, and Br- W; and a perfect negative correlation between S- Ca. The statistically significant difference between mean concentrations of some elements in organs of the studied fishes was due to the difference in affinity of metals to fish tissue, metabolic disposition of the organs, route of absorption, age of the fish and feeding habits.

III. RESULTS AND DISCUSSION

- Concentration of Elements in Organs of the Studied Fishes

Four different organs (Tissue, liver, gill, bone) of two fish species *Oreochromis niloticus* and *Clarias gariepinus* from Zobe Dam were analyzed using EDXRF Spectrometer. The results obtained from the analysis were presented in tables 4 and 5 of this work. Twenty six (26) elements (Fe, Cu, Zn, Al, Mg, Na, S, P, Ca, K, Mn, Cr, Cl, Br, Pb, Ni, V, Bi, Si, Nb, Ta, Mo, Rb, Sr, Sn, and W) were detected from the analyzed organs of the studied fishes by ED-XRF spectrometer techniques. They include the essential elements; (Fe, Cu, Al, Mg, Ca, Na, S, P, Mn, Cr, Zn, I, Cl, and Mo), the non-essential elements (Bi, V, Si, Nb, Ta, Rb, Sr, Sn, and W), and the potential toxic elements (Br, Pb, and Ni). These detected elements were of varying concentrations. This variation in concentrations may be attributed to difference in affinity of metals to fish tissue [15] metabolic disposition of the organs [16] route of absorption [17] and the age of the fish [18].

Table 4: Concentrations of elements in various organs of *Oreochromis niloticus*

Elements mg/kg				
Essential Elements	Tissue	Liver	Gill	Bone
Mg	265	213.6	171.5	224.5
Cu	4.04	163.59	4.41	1.14
Zn	27.47	132.51	65.83	34.39
Al	584.3	618.3	714	784.2
Cr	0.41	0	1.34	0.19
Na	326	1012	440	607
S	5970	3818.5	3741.9	3195.1
P	7401	5951.7	8296	17070
Ca	4993	1576.8	24504	72972
K	13424	8274	5480	2939.7
Mn	9.16	18.85	14.11	9.26
Mo	0	7.7	2	0.09
Cl	1963	5085	3330	3504
Fe	278.7	369.1	254.5	67.56
Potential Toxic Elements				
Pb	4300	18730	10090	4050
Ni	27.2	20.4	1.5	1.2
Br	32.6	154.3	108.6	19.5
Non-Essential Elements				
Bi	1430	230	0	0
Rb	18.8	26.6	20.8	4.62
Si	1600	1400	0	0
Nb	339	642	96	62
Ta	70	384	45.6	13.6
W	288	1438	376	191
Sr	37	13.14	182.9	391.8
Sn	0	1500	2100	3100
V	3.2	0	8.61	13.9

Table 5: Concentrations of elements in various organs of *Clarias gariepinus*

Elements mg/kg				
Essential Elements	Tissue	Liver	Gill	Bone
Fe	113.4	1709.5	163.2	135.5
Cu	8.41	106.75	2.11	2.52
Zn	49.25	428.5	54.73	35.8
Al	651.2	700.7	747	517.2
Mg	260.4	210	184.4	185.3
Na	913	1659	384	526
S	5668.8	5599.4	2837.5	2364.6
P	7044	11481	8544	7917
Ca	715.7	663.7	33506	36291
K	15534	15091	4178	4073
Mn	5.63	16.19	11.65	12.02
Cr	0	0.67	1.86	0.78
Cl	2469	5354	2867	1690
Mo	38.6	5.7	0	1.9
Potential Toxic Elements				
Pb	17270	4400	1420	2710
Ni	40.9	16.3	4.8	0.9
Br	52.9	156.3	48.7	35.4
Other Elements				
Bi	7960	1870	300	450
V	16.2	12.1	9.17	17.46
Si	0	0	0	0
Nb	12310	535	107	115
Ta	160.5	446	33.7	15.2
W	496	2387	294	214
Sn	29300	5300	600	0
Rb	46.2	42.3	10.81	7.71
Sr	27.35	8.12	84.4	142.7

Copper exhibits concentrations of the range (1.14 to 163. 59 mg/kg) in Oreochromis niloticus. The highest concentration was observed in liver while the lowest in bone. Its concentration ranged (2.11 to 106.75 mg/kg) in Clarias gariepinus. The highest concentration was noticed in liver while the lowest in gill. Other studies also reported the highest concentration of Cu in liver of Oreochromis mykiss and Cyprinus carpio [24], Oreochromis niloticus [25], Tilapia nilotica [26]-[27]. Liver and kidney have Cu bioaccumulation properties with cumulative capacity much greater in liver than in kidney [28]. Cu is an essential trace metal and micronutrient for cellular metabolism in living organism on account of being a key constituent of metallic enzymes [29]. The permissible intake limit of Cu set by WHO/FAO is 30 mg/kg [23]. From this study, only liver shows Cu concentration higher than the WHO/FAO limit in both Oreochromis and gariepinus.

Zinc shows concentrations of the range (27.47 to 132.51 mg/kg) in *Oreochromis niloticus* with liver recording the highest concentration and tissue recorded the lowest concentration. Also, concentrations of the range (35.8 to 428.5 mg/kg) were identified in *Clarias gariepinus* with liver also recording the highest concentration and bone recorded the lowest concentration. Previous studies reported high concentration of Zinc in liver [21]-[22]. Zn is an essential trace metal for both animals and humans, but in excess amount, it may induce toxicity characterized by symptoms of irritability muscular stiffness and pain. The maximum guideline for Zn stipulated by WHO/FAO is 40 mg/kg [23]. This shows that Zn concentration in gill and liver of *Oreochromis niloticus* exceeded the maximum guideline set by WHO/FAO whereas tissue and bone concentrations are lower than the WHO/FAO guideline. Also Zn concentrations in all organs of *gariepinus* exceeded the maximum guideline except for bone which shows concentration lower than the WHO/FAO guideline.

Fe shows concentrations of the range (67.56 to 369.1 mg/kg) in organs of Oreochromis niloticus. The highest concentration was noticed in liver while the lowest in bone. In Clarias gariepinus, Fe concentrations were of the range (113.4 to 1709.5 mg/kg) with the highest concentration also recorded in liver and the lowest in tissue. Previous studies also recorded highest concentration of Fe in liver organ of Clarias gariepinus [19]-[20].

Manganese accumulation in *Oreochromis niloticus* was of the range (9.16 to 18.85 mg/kg). The highest accumulation was observed in liver and the lowest in tissue, whereas, in *Clarias gariepinus*, concentrations of the range (5.63 to 16.19 mg/kg) were detected with liver also accumulating the highest and tissue the lowest concentrations. Studies also reported the highest concentration of Mn in liver and gill organs of *Oreochromis mossambicus* [30], *Clarias gariepinus* [19], [31]-[27]. Mn is an essential element in virtually all living organisms for its acting as an enzyme cofactor or as a metal with catalytic activity in biological clusters [32]. In excess amount, Mn can cause toxicity. Mn toxicity mainly affects the central nervous system and can cause tremors, muscle spasms, tinnitus, hearing loss and feeling unsteady on one's feet [33]-[34]. According to NIH [35], the maximum tolerable intake of Mn is 0.16 mg/kg. Thus, the concentration of Mn in all organs of the sampled fishes exceeded the NIH guideline.

In the present study, Cromium concentrations were of the range (0.19 to 1.34 mg/kg). The highest level was detected in gill while the lowest was noticed in bone. In *Clarias gariepinus*, concentrations of the range (0.67 to 1.86 mg/kg) were detected, where the highest concentration was also observed in gill while, the lowest in liver. Cr concentration was not detected in liver and tissue of *Oreochromis niloticus* and *Clarias gariepinus* respectively. Cr is an essential nutrient metal necessary for metabolism of carbohydrate [36]. Fish accumulate Cr by ingestion or by the gill uptake track and accumulation in fish tissues mainly liver occurs at higher concentrations than those found in the environment [37]. Cr often accumulates in aquatic life adding the danger of eating fish that may have been exposed to high level of Cr. The maximum guideline of Cr intake set by EFSA is 0.3 mg/kg [38]. Cr concentration in tissue and gill of *Oreochromis niloticus* exceeded the maximum guideline while bone shows concentration lower than the EFSA's maximum guideline. Cr concentrations in all organs of *Clarias gariepinus* exceeded the maximum guideline.

Chlorine exhibits significant concentrations in all organs of *Oreochromis niloticus* and *Clarias gariepinus*. Cl concentrations of the range (1963 to 5085 mg/kg) were detected in *Oreochromis niloticus* with the highest concentration observed in liver and the lowest in tissue. In *Clarias gariepinus*, Cl concentrations were of the range (1690 to 5354 mg/kg), liver was noticed with the highest concentration and bone recorded the lowest concentration. Chlorine is essential to life, it is mostly present in cell fluid as a negative ion to balance the positive (mainly potassium) ions [39]. According to IOM [40], the tolerable upper intake of chlorine is 51.1 mg/kg. This shows that, the concentration of Cl in organs of the studied fishes were not within IOM limit. Phosphorus (P) exhibits concentrations of the range (5951.7 to 17070 mg/kg) in organs of both fishes. The highest level was noticed in bone of *Oreochromis niloticus* while the lowest was observed in liver of the *Oreochromis niloticus*. Phosphorus is a mineral that naturally occur in many foods and also available as a supplement. It plays multiple roles in the body and it is a key element of bones, teeth, and cell membranes [41]. Some studies postulated that, increased dietary phosphorus intake increases risks for cardiovascular disease [42].

Molybdenum is considered as an essential trace element as it enters in a cofactor (molybdopterin) of certain enzymes that catalyse redox reactions [43]. Mo shows concentrations of the range (0.09 to 38.6 mg/kg) in organs of both studied species. The highest value was observed in tissue of *Clarias gariepinus*, whereas, the lowest value was observed in bone of *Oreochromis niloticus*.

Calcium shows concentrations of the range (1576.8 to 72972 mg/kg) in *Oreochromis niloticus*. The highest accumulation was observed in bone while the lowest accumulation was noticed in liver. In *Clarias gariepinus*, Ca concentrations of the range (663.7 to 36291 mg/kg) were detected with the highest concentration detected in bone and the lowest in liver. The maximum guideline for Ca intake stipulated by IOM is 35.7 mg/kg [40]. Thus, Ca concentrations in all organs of the species from Zobe Dam exceeded the IOM limit. Calcium is important for bone health, our bodies need calcium to build and maintain strong bones. Also our hearts, muscles and nerves need calcium to function properly. However, high level of calcium in the blood and urine can cause poor muscle tone, poor kidney function, law phosphate levels, constipation, nausea, weight loss, and a high risk of death from heart disease [44]. Some research suggests that, high calcium intakes might increase the risk of heart disease and prostate cancer [44].

Sulfur (S) accumulation was significant in all organs of the sampled fishes. The concentrations of the range (2364.6 to 5970 mg/kg) were detected from organs of the two fishes. The highest concentration was observed in tissue of *Oreochromis niloticus* while the lowest concentration was noticed in bone of *Clarias gariepinus*. Sulfur is an element that exists in nature and can be found in soil, plants, foods, and water [45]. Sulfur is essential for humans, animals, and plants. When it enters our body it can be incorporated into tissue like skin and cartilage. It is also found in some proteins and vitamins [46].

Ca concentration in organs of the sampled fishes was followed by Potassium (K) in the present study. The concentration of K in organs of *Oreochromis niloticus* ranged between (2939.7 to 13424 mg/kg). The highest concentration was recorded in tissue while the lowest was recorded in bone. In *Clarias gariepinus*, K concentration of the range (4073 to 15534 mg/kg) was observed with tissue also recording the highest concentration and bone recorded the lowest concentration. Potassium is an essential mineral that is needed by all tissues in the body. Deficiency of K causes hypokalemia. However, despite its health benefit, excessive intake of K can lead to adverse kidney disease. According to WHO guideline, the maximum intake of K is 50.1 mg/kg [47]. The concentration of K in all organs of the sampled fishes exceeded the maximum guideline of WHO.

Sodium is an essential nutrient required for maintenance of plasma volume, acid base balance, transmission of nerve impulses and normal cell function [48]. Excessive sodium intake is associated with adverse health effects, blood pressure, cardiovascular, kidney and heart diseases [49]-[50]-[51]. Deficiency of sodium causes hyponatremia. In this study, the concentrations of Na in organs of *Oreochromis niloticus* were of the range (326 to 1012 mg/kg). The highest concentration was detected in liver while the lowest in tissue. Na concentration in *Clarias gariepinus* ranged (384 to 1659 mg/kg) with the highest concentration noticed in liver and the lowest in gill. This shows that, Na concentrations in all organs of the sampled fishes are higher than the maximum guideline of 32.9 mg/kg [52].

The concentrations of Magnesium in organs of *Oreochromis niloticus* were in the range of (171.5 to 265 mg/kg). The highest concentration was detected in tissue while the lowest was detected in gill. In *Clarias gariepinus*, the concentration of Mg ranged between (184.4 to 260.4 mg/kg), where the highest concentration was also detected in tissue and the lowest in gill. According to FNB recommendations, the upper tolerable intake of Mg is 5 mg/kg [53]. This indicates that the concentrations of Mg in all organs of the studied fishes exceeded the stipulated permissible limit. Mg is an essential element that is crucial to the body's function. Deficiency of Mg causes Osteoporosis [54]. At very high doses, magnesium can be fatal [55].

Aluminium is a trivalent cation found in its ionic form in most kinds of animal and plant tissues and natural waters everywhere [56]. Exposure of aluminium in high concentration leads to several health effects such as dementia, loss of memory, damage to central nervous system and kidney, and lung problems [57]. The concentrations of Al in organs of *Oreochromis niloticus* were of the range (584.3 to 784.2 mg/kg). The highest concentration was observed in bone while the lowest was noticed in tissue. In *Clarias gariepinus*, Al concentrations of the range (517.2 to 747 mg/kg) were detected where the highest concentration was observed in gill and the lowest in bone. The observed concentrations in organs of the studied fishes exceeded the FAO/WHO maximum guideline of 1.0 mg/kg [58]. The concentrations of lead were in the range (4050 to 18730 mg/kg) in *Oreochromis niloticus*. The highest concentration was observed in liver while the lowest concentration was noticed in bone. Previous studies also reported highest concentration of lead in liver of fish [59]-[60]. In *Clarias gariepinus*, Pb concentrations were of the range (1420 to 17270 mg/kg). The highest concentration was observed in tissue while the lowest was noticed in gill. Lead deposits in various fish organs such as liver, kidneys and spleen, but also digestive tract and gills. Aquatic organisms bio accumulate lead from water and diet, although there is evidence that Pb accumulation in fish is probably originated from contaminated water rather than diet. According to ATSDR, there is no safe concentration of lead [61]. The National Research Council [62] reported that, substitution of calcium by lead resulted in toxicity of several vital enzyme systems in the central nervous system. The maximum permissible limits of lead in fish are 0.5-6.0 mg/kg [63]-[64]. Thus, the concentrations of lead in all organs of the studied fishes were not within the permissible limit.

Nickel concentrations were of the range (0.9 to 40.9 mg/kg) in the studied fishes with the highest concentration recorded in tissue of *Clarias gariepinus* and the lowest recorded in bone organ of *Oreochromis niloticus*. While Ni is an essential element at low concentration for many organisms, it is toxic at higher concentrations [65]. Exposure to nickel may lead to various adverse health effects, such as nickel allergy, contact dermatitis, and organ system toxicity. According to IOM, nickel can cause respiratory problems and is carcinogenic [66].

Bromine has sometimes been considered to be possibly essential in humans with support of only limited circumstantial evidences and no clear biological role. Br concentrations of the range (19.5 to 154.3 mg/kg) were detected in *Oreochromis niloticus*. The highest concentration was observed in liver while the lowest in bone. Meanwhile, *Clarias gariepinus* shows Br concentrations of the range (35.4 to 156.3 mg/kg) with liver and bone also recording the highest and lowest concentrations. According to JMPR [67], the maximum daily intake limit of Br is 1.0 mg/kg. Hence, concentration of Br in all selected organs of the studied fishes exceeded the maximum guideline.

Rubidium (Rb) shows significant concentrations in all organs of the sampled fishes from Zobe Dam. The concentrations of the range (4.62 to 26.6 mg/kg) were identified in *Oreochromis niloticus*. Highest concentration was observed in liver while the lowest in bone. Also, Rb concentrations of the range (7.71 to 46.2 mg/kg) were detected with tissue recording the highest concentration and bone recorded the lowest concentration. Rb requirements in humans might be rated as less than 400 ug per day [68]. This is equivalent to 0.0057 mg/kg. Thus, the concentration of Rb in all selected organs of *Oreochromis nilticus* and *Clarias gariepinus* were not within the suggested Rb requirement in humans. According to Thomas [69], rubidium has no known biological role and is nontoxic.

Vanadium (V) concentration in organs of *Oreochromis niloticus* ranged between 3.2 to 13.9 mg/kg. The highest concentration was observed in bone while the lowest was noticed in tissue. The range of Vanadium concentrations in *gariepinus* were (9.17 to 17.46 mg/kg). The highest concentration was detected in bone while the lowest in gill. Vanadium as micronutrient plays a role in carbohydrate and lipid metabolism, but can be toxic at high concentrations [70]. The maximum guideline for V is 0.5 mg/kg [71]. This shows that, V concentrations in all organs of the studied fishes exceeded the maximum guideline.

Strontium shows significant concentrations in organs of *Oreochromis niloticus* and *Clarias gariepinus*. Its concentrations were of the range (8.12 to 391.8 mg/kg) in organs of both species. Highest concentration was detected in bone of *Oreochromis niloticus* while the lowest organ was detected in liver of *Clarias gariepinus*. Strontium occurs naturally in earth's crust in the form of minerals such as celestiteans strontianite and for humans non-occupationally exposed major sources are drinking water and foods [72]. When Sr uptake is extremely high, it can cause disruption of bone development. The rate at which Sr is incorporated into bone is very similar to that at which calcium is incorporated [73]. Moreover, strontium enhances the synthesis of bone matrix proteins which takes place in osteoblast [74].

Silicon concentrations were only detected in tissue and liver of *Oreochromis niloticus* with tissue recording the highest concentration. Si concentration was not detected in all organs of *Clarias gariepinus*.

Tin (Sn) shows significant concentrations in organs of the sampled fishes. The concentrations in *Oreochromis niloticus* and *Clarias gariepinus* were of the range (600 to 29300 mg/kg). Highest concentration was recorded in tissue of *Clarias gariepinus* and the lowest in gill of the *gariepinus*. Sn concentration was not detected in tissue of *Oreochromis niloticus* and also it was not observed in bone of *Clarias gariepinus*. In living organisms, Sn has no established natural biological function. The low toxicity is important for the widespread use of Sn elements in foodstuffs and canned foods.

Bismuth (Bi) concentrations in both samples were of the range (230 to 7960 mg/kg). The highest concentration was detected in tissue of *Clarias gariepinus* while the lowest in liver of *Oreochromis* *niloticus*. Bi concentration was not detected in gill and bone organs of *Oreochromis niloticus.* Being a natural element, humans are exposed to bismuth primarily through diet, with background exposures estimated between 5 and 20 µg/day (0.07 and 0.29 µg/kg bw/d, assuming a body weight of 70 kg). Bi substances also have broad anti-microbial, anti-leishmanial and anti-cancer properties [75].

Tantalum (Ta) concentrations were of the range (15.5 to 446 mg/kg). The highest concentration was measured in liver of *Clarias gariepinus* and the lowest concentration was measured in bone of the *Clarias gariepinus*. Both tantalum oxide and tantalum metal have low systematic toxicity which may be due to their poor solubility. However, they are also skin, eye, and respiratory hazards.

Niobium shows significant concentrations in all organs of the sampled fishes in the present study. The concentrations were of the range (62 to 12310 mg/kg) in both samples with the highest concentration recorded in tissue of *Clarias gariepinus* while the lowest concentration was observed in bone of *Oreochromis niloticus*.

Tungsten (W) is a naturally occurring element. Exposure to very low levels of tungsten may occur by breathing air, eating food, or drinking water that contains tungsten [76]. The concentrations of tungsten in organs of the studied fishes were of the range (191 to 2387 mg/kg). The highest accumulation was noticed in liver of *Clarias gariepinus* while the lowest concentration was observed in bone of *Oreochromis niloticus*. No specific health effects have been associated with exposure to tungsten in humans [76].

- Estimation of the Dietary intake of Trace Elements

The present study attempts to provide an estimation of the dietary consumption of essential and potential toxic elements contained in various organs of both *Oreochromis niloticus* and *Clarias gariepinus*. This will provide reliable information and facts to health practitioners and scientific literatures. The detected concentrations of the essential and toxic elements in the studied samples are presented in table 6 with the stipulated daily tolerable limits. The concentration data of the studied fish organs were compared with those provided by the WHO/FAO [77]-[78]. The normal consumption values per day and per person for essential and potential toxic elements contained in organs of the studied fishes were determined assuming an intake of 10 g (dry weight) of the studied fishes ration per person. The estimation of the dietary intake was conducted only for tissue. Other organs were neglected according to the consumption practice of the population in the study area. The dietary intake estimation of the fish tissue revealed that, the concentrations of the potentially toxic elements in tissue of both studied fish species (Br, Pb, Ni) are well below the toxicological reference values provided by the WHO/FAO and were found within nutritional threshold. Therefore, consumption of tissue of the studied fishes from Zobe Dam is considered safe.

Table 6: Intake values (in mg/day) of some essential and toxic elements and tolerable daily intake of adult (TDI/70 kg) of WHO/FAO.

Elements	Ca	Cu	Fe	p	Mn	Zn	Na	K	Ni	Pb	Br	Cr
Oreochromis niloticus	49.93	0.04	2.79	74.01	0.09	0.28	3.26	134.24	0.272	43	0.326	0.0041
Clarias gariepinus	7.157	0.084	1.134	70.44	0.056	0.493	9.13	155.34	0.41	172.7	0.529	0
Males 19- 50	1000	0.9	8	700	2.3	11	1500	4700	1176	280	70	0.035

Females 19-50	1000	0.9	18	700	1.8	8	1500	4700	1176	280	70	0.025
Pregnancy 19 – 50	1000	1	27	700	2	11	1500	4700	1176	280	70	0.03
Lactation 19-50	1000	1.3	9	700	2.6	12	1500	4700	1176	280	70	0.045

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