

Instrumental Neutron Activation Technique in Characterization of Elements in Organs of Some Fish Species Harvested from Zobe Dam, Katsina State

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ABSTRACT

Instrumental neutron activation technique has shown to be a reliable tool for its non-destructive, multi-elemental capability for analysis in various matrices. This technique has been applied to investigate the concentration of chemical elements in organs of *Oreochromis niloticus* and *Clarias gariepinus* fish varieties harvested from Zobe Dam, Katsina State, Nigeria in order to determine the essential elements and toxic elements that may pose health risk to humans when consumed. Twenty-one (21) elements, namely Mg, Al, Cl, Ca, Cr, V, Cu, I, Mn, Na, K, As, Br, La, Sm, Sc, Fe, Co, Zn, Rb, and Ba, were detected. These elements could be categorized into three main groups; the essential elements, Fe, Cu, Al, Zn, Cr, Mg, Ca, Cl, I, Mn, Na, K, and Co; non-essential elements, Ba, Rb, V, La, Sc, and Sm; and possibly toxic elements, As and Br. The dietary intake of some essential and toxic elements was estimated for tissue of the studied fishes by considering WHO/FAO tolerable daily intake of adults (TDI/70 kg). Although, the results of our analysis showed most of the concentrations of the detected elements exceeded the maximum guidelines set, however, the results of the estimated dietary intake show that the concentrations of all the identified elements in tissue of both fish species including the potential toxic elements (As and Br) 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.

Keywords: *Oreochromis niloticus*, *Clarias gariepinus*, Toxic elements, Essential elements, Dietary intake, Instrumental Neutron Activation Analysis

INTRODUCTION

There is an increase in consumption of fish as a source of protein, lipids, vitamins, minerals and a very important component of human diet due to its high nutritive value and significance in improving human health. 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. Hartl (2013) pointed 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. The accumulation of certain metals, in particular heavy metals in aquatic environment is of increasing concern due to the food chain safety issues, potential health risks and its detrimental effects on fish consumption (McLaughlin *et al.*, 1999). Although the trace elements in fish are very important for the health of fish and human consumption, however excessive levels of trace elements in fish cause health hazards to humans that feed upon them (McLaughlin, 2001; Uchida *et al.*, 2007; Rana *et al.*, 2009). Toxic elements pollution of the environment, even at low levels and their resulting long-term cumulative health effects are among the leading health concerns all over the world. Most of

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these elements are characterized by being accumulated in tissues and lead to poisoning of fish. They are extremely dangerous for the health of fish. As such fish are used as bio-indicators playing an important role in monitoring elements and toxic elements pollution (Authman, 2015).

It has been reported that prolonged consumption of unsafe concentration of elements which especially accumulate in organs of fish, such as internal organs, 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. Hence, it is important to investigate the elemental composition and concentration 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 implication of some of the toxic elements to human. We have adopted instrumental neutron activation analysis (INAA) techniques to determine and evaluate the composition, the extent 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. It is obvious that, no research work had been carried-out on the trace elements composition and concentration levels on these fish species from Zobe Dam, Katsina state using this analytical technique based on the literatures available to us. It has been shown that, this analytical technique adopted for the study is quite reliable and comprehensive enough for multi-elemental study of fish samples.

Neutron activation analysis (NAA), particularly, instrumental neutron activation analysis (INAA) is a very precise technique mainly used to determine trace concentrations of elements in samples and/or to acquire information on the spatial distribution of a neutron field via neutron activation detectors (Majerle, 2006). This technique is based upon the conversion of stable nuclei to other, mostly radioactive nuclei via nuclear reactions, and measurement of the reaction products. The use of the INAA (relative) method for the calculation of the concentration of each element in the sample irradiated with reactor thermal neutron reduces the NAA equation to the simplest form (IAEA, 1990):

$$\frac{w}{w_{st}} = \frac{N_s D_{st}}{N_{st} D} = \frac{N_s e^{-\lambda t_d(st)}}{N_{st} e^{-\lambda t_d}} \quad (1)$$

Where; N_s = net photo peak area of radionuclide of interest in sample, N_{st} = net photo peak area of radionuclide of interest in standard, W = weight of element in sample irradiated, W_{st} = weight of the element in standard irradiated, $D = e^{-\lambda t_d}$ = decay factor for sample, $D_{st} = e^{-\lambda t_d(st)}$ = decay factor for standard, t_d = decay time for sample, $t_d(st)$ = decay time for standard, λ = decay constant for radionuclide of interest

The concentration of the unknown element in the sample denoted by C_s is given by

$$C_s = \frac{W}{M} \quad (2)$$

Where; M = known weight of the irradiated sample containing the unknown weight of the element irradiated, W = unknown weight of the element irradiated.

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 (Isah, 2009). Before Dam establishment, the settlers had a history of blacksmithing and agrarian farming activities. The Dam has an average storage capacity of 170 million m³ and about 8137 hectares of land for irrigation. It covers an estimated surface area of 39.6 km². The annual rainfall is estimated to be about 817 mm per year. Dam irrigation area is located between 12°23'18''N of northern latitude and 7°28'29''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 450 m and 490 m 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.

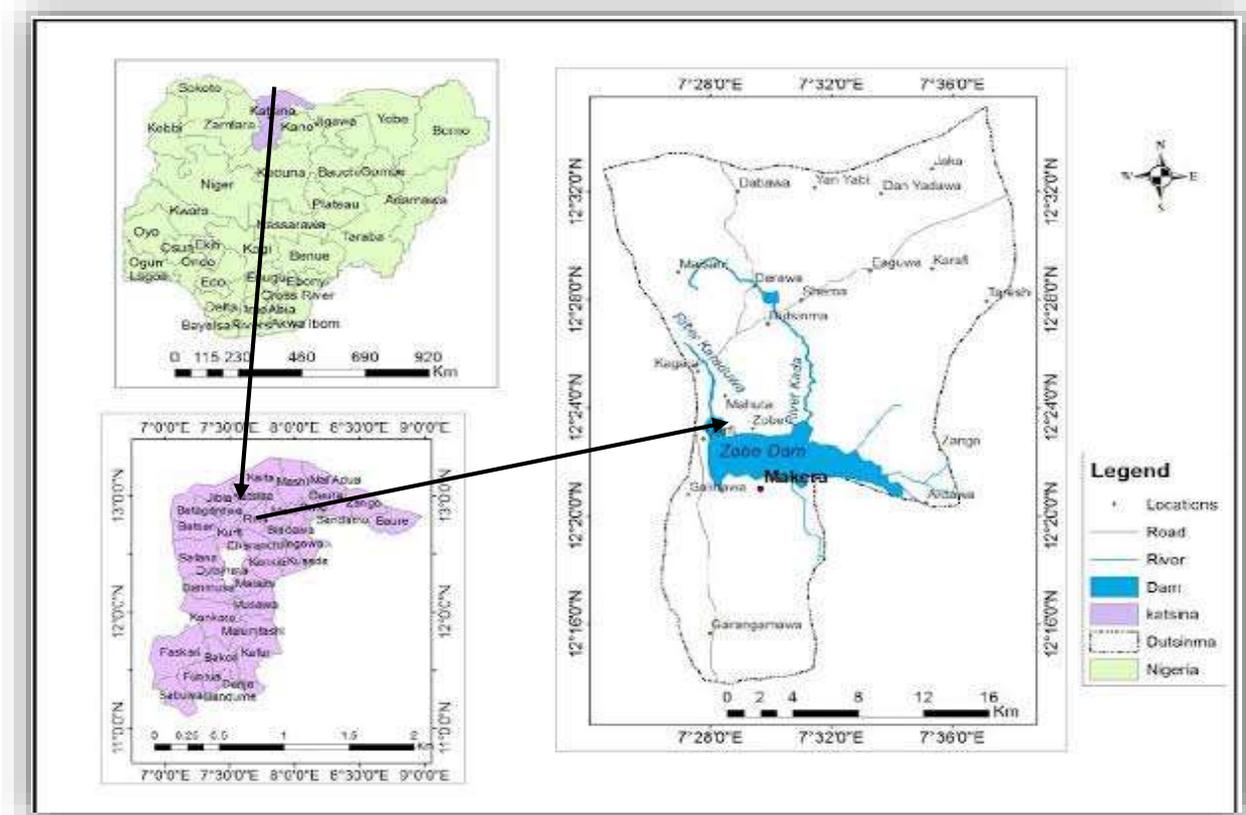


Figure 1: Dutsin-Ma Map Showing Zobe Dam (Insert: Nigeria and Katsina State)

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 air dried for some minutes and later put in an Oven at 105°C. The samples were then put on a desiccator and grinded using motor and pestle. A total of 8 samples were prepared and were taken to Center for Energy Research and Training (CERT) Zaria for analysis. Elemental analysis of the prepared samples was carried out using Instrumental Neutron Activation Analysis (INAA) Techniques. Results of the analysis were obtained from the NAA machine. For verification and quality control purpose, high grade Certified Reference Materials (CRMs) supplied by International Atomic Agency (IAEA) 452 SCALOP, (IAEA) 336 LINCHE were used as comparator standard monitors in this work. NIST 1515 and NIST 1547 were also prepared following the same procedure.

Irradiation and Measurements

Irradiation of the samples and standards was carried using NIRR-1 at Center for Energy Research and Training CERT Zaria. During the irradiation, neutrons of flux $5.0 \times 10^{11} \text{ ncm}^{-2}\text{s}^{-1}$

¹ were accessed. Using rabbit carriers, the samples and standards were sent into the reactor through a pneumatic pressure. NIRR-1 was used to irradiate the samples with a thermal neutron flux $5.0 \times 10^{11} \text{ ncm}^{-2}\text{s}^{-1}$ for 6 hours for the long irradiation. The samples were then taken to a detecting set up consisting of a high purity germanium (HPGe) detector connected to a PC based multi-channel analyzer (MCA) in a fixed sample to detector geometry. For short lived elements, the first counting was done immediately and followed by a second one 2 hours later. The samples were then allowed to decay further for the analysis of long life elements. Using the procedure for all samples, the results in Table 5 and 6 were obtained.

Quality Control and Quality Assurance

A proactive action to reduce the likelihood of errors in an analytical technique is quality assurance. It also involves quality control, which is the procedure used to check for errors after the analysis was completed. Quality assurance procedures are describe for individual steps in neutron activation analysis, namely, preparation of the test portion, selection of analytical protocol, calibration, instrument performance checks, irradiation, decay, measurement, spectrum analysis and interpretation, and internal and external quality control, as well as for ensuring the technical competence of the personnel involved. For INAA determinations, two CRMs; NIST 1515 (apple leaves) and NIST 1547 (peach leaves) were used in this study for quality control purposes.

To assess the laboratory performance, we determined the U-score, Z-score and the relative bias (RB). These measurements were calculated according to the following equations:

$$U_{score} = \frac{|X_{Lab} - X_{Ref}|}{\sqrt{\mu_{Lab}^2 + \sigma_{Ref}^2}} \quad (3)$$

$$Z_{score} = \frac{|X_{Lab} - X_{Ref}|}{\mu_{Lab}} \quad (4)$$

$$R_{bias} = \frac{X_{Lab} - X_{Ref}}{X_{Ref}} \times 100 \quad (5)$$

where; X_{Lab} represents the laboratory results, μ_{LAB} is the standard deviation, X_{Ref} represents recommended uncertainty, and σ_{Ref} is the standard uncertainty.

The laboratory performance is evaluated as follows; satisfactory if U-score ≤ 1 , and satisfactory if Z-score is ≤ 2 , questionable for $2 < Z\text{-score} < 3$, and unsatisfactory if Z-score is ≥ 3 .

Table 1: Comparison of recorded values with the certified values in the certified reference materials of NIST 1515 (apple leaves)

Elements mg/kg	NIST 1515 Certified Values	NIST 1515 Recorded Values	U-score	Z-score	R-bias
K	1.61±0.02	1.433±1.19	0.15	8.85	10.99
Al	286±9	300.3±17.3	0.73	1.59	5
Ba	49±2	53.9±7.3	0.65	2.45	9.6
Cl	579±23	573.21±23.9	0.18	0.25	-1
Mn	54±3	57.24±7.7	0.39	1.08	6
Br	1.8	1.49±1.2	0.26	-	-17.2
La	20	27.6±5.3	1.43	-	38
Sm	3	4.38±2.09	0.66	-	46

Note: Values represent mean ± standard deviation

Table 2: Comparison of recorded values with the certified values in the certified reference materials of NIST 1547 (peach leaves)

Elements mg/kg	NIST 1547 Certified Values	NIST 1547 This work measured values	U-score	Z-score	R-bias
K	2.43±0.03	2.6487±1.6	0.14	7.3	9
Al	249±8	257±16.03	0.45	1	3.21
Ba	124±4	136.4±11.8	1	3.1	10
Cl	360±19	284.4±16.9	2.97	3.9	-21
Mn	98±3	104.86±10.24	0.64	2.3	7
Br	11	10.45±3.2	0.17	-	-5
La	9	9.36±3.1	0.12	-	4
Sm	1	1.09±1.04	0.09	-	9

Note: Values represent mean ± standard deviation

The illustrated results in Tables 1 and 2 show that, all the element concentrations are in good agreement with the certified values after using two CRMs; NIST 1515 and NIST 1547. This calculation displayed a great quality results found in this practice which could be accomplished through the statistical assessment and evaluation. The statistical parameters U-score and Relative bias calculated for all elements are acceptable only Z-score shows no satisfaction in concentrations of some elements.

Statistical Analysis and Inter-elemental Correlation

Concentration values obtained from the various organs of the studied fishes (*Oreochromis niloticus* and *Clarias gariepinus*) were equally subjected to further statistical analysis using Analysis of Variance (ANOVA) and an EXCEL spread sheet. Previous studies used ANOVA test to determine the influence that independent variables have on the dependent variables in a regression study. The analysis of variance (ANOVA) showed statistically significant differences in mean concentrations of (Al, I), (Ca, Ba), (Al, Cr), and (Mn, Ba). The level of significance was set at $P < 0.05$.

The Pearson's correlations coefficients (r) of chemical element concentrations in organs of *Oreochromis niloticus* and *Clarias gariepinus* were presented in Table 3 & 4 respectively.

A significant positive correlation was detected between some essential and potential toxic elements, for example, Al- Cr ($r = 0.97$, $P < 0.05$), Al- I ($r = 0.97$, $P < 0.05$), Ca- Ba ($r = 0.96$, $P < 0.05$), and Mn- Ba ($r = 0.99$, $P < 0.05$). Meanwhile, no negative correlation was found between chemical elements in organs of *Oreochromis niloticus*. A perfect positive correlation was noticed between I- Cr, whereas, a high positive correlation was observed between some elements in the analyzed sample, e.g., Fe- Zn, Na- As, Ca- As, Mg- Ca, and Zn- Rb with the values 0.95, 0.89, 0.86, 0.95, and 0.93 respectively. Table 4 shows the data correlation coefficients between the chemical element concentrations in various organs of *Clarias gariepinus*. In this data, no positive correlation was detected between any of the chemical elements. This shows that, there is no positive relationship between the concentrations of the chemical elements in organs of this fish species. Moreover, a negative correlation coefficient was noticed in mean concentrations of Mg- Br ($r = - 0.96$, $P < 0.05$). High negative correlations were detected between Al- As, and Mn- K with $r = - 0.89$, $- 0.95$ respectively. Also, Al shows negative correlations with Cl, V, Cu, I, and Fe. This statistically significant difference between mean concentrations of some elements in organs of the studied fishes was likely due to the difference in element concentrations, time of exposure, way of metal uptake, environmental conditions and intrinsic factors such as fish age and feeding habits.

Table 3: Pearson’s correlation coefficient (r) of elements in organs of *Oreochromis niloticus*

	Mg	Al	Cl	Ca	V	Cu	I	Mn	Na	K	As	Br	La	Sm	Sc	Cr	Fe	Co	Zn	Rb	Ba	
Mg	1.00																					
Al	0.26	1.00																				
Cl	-0.58	0.48	1.00																			
Ca	0.95	0.38	-0.33	1.00																		
V	0.69	0.25	-0.01	0.86	1.00																	
Cu	-0.73	-0.41	0.58	-0.56	-0.07	1.00																
I	0.03	0.97	0.61	0.15	0.05	-0.29	1.00															
Mn	0.85	0.72	-0.09	0.92	0.72	-0.65	0.53	1.00														
Na	0.84	-0.30	-0.90	0.69	0.45	-0.57	-0.50	0.41	1.00													
K	0.16	-0.64	-0.89	-0.13	-0.43	-0.39	-0.66	-0.32	0.60	1.00												
As	0.87	-0.13	-0.60	0.86	0.80	-0.36	-0.37	0.59	0.89	0.19	1.00											
Br	-0.49	0.60	0.99	-0.24	0.04	0.47	0.71	0.04	-0.86	-0.92	-0.57	1.00										
La	-0.59	-0.19	0.71	-0.35	0.17	0.96	-0.11	-0.41	-0.57	-0.62	-0.25	0.62	1.00									
Sm	-0.79	-0.59	0.42	-0.69	-0.24	0.97	-0.45	-0.81	-0.50	-0.16	-0.39	0.29	0.86	1.00								
Sc	-0.43	-0.45	-0.38	-0.68	-0.92	-0.14	-0.31	-0.66	-0.07	0.75	-0.50	-0.43	-0.41	0.09	1.00							
Cr	0.07	0.97	0.53	0.17	0.02	-0.37	1.00	0.55	-0.45	-0.59	-0.35	0.64	-0.20	-0.52	-0.25	1.00						
Fe	-0.09	0.90	0.82	0.12	0.21	0.03	0.93	0.45	-0.63	-0.89	-0.35	0.89	0.24	-0.18	-0.53	0.89	1.00					
Co	-0.66	-0.15	0.76	-0.43	0.08	0.96	-0.04	-0.45	-0.66	-0.64	-0.36	0.68	0.99	0.86	-0.35	-0.13	0.30	1.00				
Zn	0.02	0.80	0.80	0.29	0.48	0.15	0.79	0.52	-0.50	-0.97	-0.12	0.86	0.41	-0.09	-0.77	0.74	0.95	0.43	1.00			
Rb	0.00	0.55	0.77	0.30	0.63	0.39	0.52	0.41	-0.40	-0.97	0.05	0.79	0.64	0.15	-0.88	0.44	0.78	0.63	0.93	1.00		
Ba	0.89	0.62	-0.15	0.96	0.80	-0.61	0.42	0.99	0.50	-0.29	0.69	-0.03	-0.37	-0.77	-0.70	0.43	0.36	-0.42	0.47	0.41	1.00	

Table 4: Pearson’s correlation coefficients (r) of elements in organs of *Clarias gariepinus*

	Mg	Al	Cl	Ca	V	Cu	I	Mn	Na	K	As	Br	La	Sm	Sc	Cr	Fe	Co	Zn	Rb	
Mg	1.00																				
Al	-0.15	1.00																			
Cl	-0.55	-0.09	1.00																		
Ca	0.76	-0.28	-0.90	1.00																	
V	-0.33	-0.88	0.31	-0.06	1.00																
Cu	-0.57	-0.62	0.77	-0.57	0.84	1.00															
I	-0.49	-0.39	0.95	-0.76	0.56	0.91	1.00														
Mn	0.22	0.03	-0.93	0.77	-0.08	-0.56	-0.86	1.00													
Na	-0.82	0.52	0.05	-0.44	-0.09	0.03	-0.08	0.24	1.00												
K	-0.09	0.25	0.80	-0.71	-0.25	0.27	0.64	-0.95	-0.23	1.00											
As	-0.24	-0.89	0.50	-0.18	0.95	0.90	0.73	-0.35	-0.28	0.03	1.00										
Br	-0.96	0.08	0.33	-0.56	0.39	0.50	0.31	0.04	0.87	-0.18	0.23	1.00									
La	-0.36	0.93	-0.21	-0.23	-0.70	-0.54	-0.46	0.27	0.77	-0.05	-0.82	0.37	1.00								
Sm	-0.39	0.89	-0.24	-0.21	-0.65	-0.52	-0.48	0.33	0.81	-0.13	-0.79	0.42	1.00	1.00							
Sc	0.00	0.52	-0.79	0.44	-0.45	-0.71	-0.87	0.86	0.56	-0.70	-0.70	0.19	0.72	0.76	1.00						
Cr	0.16	0.50	0.50	-0.49	-0.59	-0.13	0.30	-0.75	-0.26	0.92	-0.33	-0.40	0.16	0.07	-0.44	1.00					
Fe	-0.88	-0.21	0.80	-0.81	0.60	0.88	0.82	-0.52	0.46	0.29	0.61	0.79	-0.08	-0.06	-0.44	-0.06	1.00				
Co	-0.39	0.85	-0.30	-0.14	-0.60	-0.53	-0.52	0.41	0.83	-0.22	-0.77	0.44	0.98	1.00	0.81	-0.02	-0.08	1.00			
Zn	-0.23	0.56	-0.63	0.24	-0.38	-0.57	-0.73	0.77	0.73	-0.64	-0.64	0.40	0.80	0.84	0.97	-0.44	-0.23	0.89	1.00		
Rb	0.77	0.51	-0.58	0.52	-0.85	-0.92	-0.71	0.26	-0.36	0.03	-0.79	-0.77	0.30	0.25	0.37	0.41	-0.92	0.23	0.20	1.00	

RESULTS AND DISCUSSION

Concentrations of Elements in Organs of *Oreochromis niloticus* and *Clarias gariepinus*

Four different organs (Tissue, gill, liver, bone) were analyzed from which some essential, non-essential, and possibly toxic elements are identified. The results obtained for the mentioned categories are presented in Tables 5 & 6 of this work. Twenty one (21) elements were determined which includes thirteen essential elements; Mg, Al, Cl, Ca, Fe, Cu, I, Mn, Na, K, Zn, Cr, and Co. Two possibly toxic elements; As, and Br; and six non-essential elements. The identified elements from organs of the two fish species were of varying concentrations. This variation in concentrations may be attributed to difference in affinity of metals to fish tissue (Jeziarska & Witeska, 2006), metabolic disposition of the organs (Karadede & Unlu, 2000), route of absorption (Ney & Vanhassel, 1983), and the age of the fish (Khan *et al.*, 2012). Fe concentrations in organs of the studied fishes are of the range (101.1±0 to 580.5±59.211 mg/kg).

Table 5: Concentrations of element in various organs of *Oreochromis niloticus*

Elements	Bone	Gill	Liver	Tissue
Essential Elements				
Al	101±3	262±7	64.7±3.9	54.0±5.4
Cl	2791±45	7175±72	7375±74	3001±45
Ca	96430±1350	50120±1002	906±133	972±177
Fe	101.1±0	580.5±59.211	257.6±44.5648	171.5±43.0465
Cu	BDL	BDL	63.9±5.5	3.26
I	BDL	4.83±0.19	0.35	BDL
Mn	16.1±0.2	15.8±0.2	1.18±0.02	2.11±0.09
Na	3252±7	1616±5	1478±4	2317±5
K	9857±217	508±74	2672±104	17430±227
Zn	34.7±3.4	76.94.0	49.7±3.7	15.4±0.9
Co	0.39±0.07	0.87±0.09	2.93±0.14	0.29±0.07
Cr	BDL	2.66±0.66	BDL	BDL
Mg	1680±64	1238±72	800±60	1057±62
Potential Toxic Elements				
As	0.25±0.07	BDL	BDL	BDL
Br	20.1±0.2	28.1±0.2	27.0±0.2	20.0±0.2
Other Elements				
La	0.19	0.21±0.04	0.52±0.05	0.108±0.001
Rb	5.62±1.25	8.00±1.26	7.76±1.180	8.54±1.11
Ba	83.6±16.4	67.4±12.1	BDL	10.7
V	2.22±0.11	1.34±0.16	1.25±0.13	0.30±0.08
Sm	0.049±0.006	0.029±0.004	0.028±0.004	0.011±0.003
Sc	0.01	0.024±0.006	0.031±0.006	0.012

Note: BDL means; Below Detection Limit

Table 6: Concentration of elements in various organs of *Clarias gariepinus*

Element	Bone	Gill	Liver	Tissue
Mg	1563±64	821±51	786±67	1258±64
Al	67.5±2.9	151±4	61.1±6.2	155±4
Cl	2194±39	3311±50	7473±67	5835±64
Ca	73314±1173	26830±724	531±115	11520±472

Fe	188±45.12	359.6±57.536	543.6±21.2004	289.9±83.2013
Cu	BDL	BDL	40.5±5.1	BDL
I	BDL	BDL	0.24	0.1
Mn	26.5±0.3	27.8±0.1	4.97±0.01	4.45±0.14
Na	2361±5	6161±12	4050±12	3378±14
K	8532±171	8723±419	14390±245	18280±457
Zn	35.5±3.2	54.0±3.8	26.9±1.2	31.8±2.7
Co	0.23	0.70±0.12	0.21±0.02	0.42±0.06
Cr	BDL	BDL	0.40±0.09	1.89±0.48
Potential Toxic Elements				
As	0.09	BDL	0.21	BDL
Br	18.6±0.1	51.2±0.5	47.4±0.4	22.8±0.2
Other Elements				
Sc	0.028	0.053±0.008	BDL	0.015
La	BDL	0.49±0.08	BDL	0.289±0.002
Rb	8.84±1.35	6.28±1.39	1.32±0.25	9.96±1.28
Ba	BDL	BDL	BDL	BDL
Sm	BDL	0.022±0.005	BDL	0.011
V	0.61±0.08	0.37±0.08	1.03±0.14	0.075

Note: BDL means; Below Detection Limit

The highest concentration was recorded in gill of *Oreochromis niloticus* and the lowest in bone. Studies reported on *Oreochromis niloticus* and *Lates niloticus* (Mohammed, 2008, Uysal *et al.*, 2008, Javed & Usmani, 2012), also revealed the maximum accumulation of Fe in gills. Highest concentration in gills indicates that, it is an organ which always remains in direct contact with the surrounding water. However, in *Clarias gariepinus*, Fe concentrations of the range 188±45.12 to 543.6±21.2004 were detected, with liver recording the highest concentration and bone recorded the lowest. Some studies also recorded highest concentration of Fe in liver organ of *Clarias gariepinus* (Osman *et al.*, 2010) and *Tinca tinca* (Selda Tekin *et al.*, 2005).

Zinc concentrations are of the range (15.5±0.9 to 76.9±4.0 mg/kg) in organs of the studied fishes. The highest concentration was observed in gill of *Oreochromis niloticus* while the lowest concentration was noticed in tissue of the *Oreochromis niloticus*. Study on heavy elements concentrations in *Channa punctatus* was carried (Vineeta Shukla *et al.*, 2005). The result also shows a highest concentration of Zn in gills of *Channa punctatus*. These high concentrations in gills organ can be possibly subjected to fact that, gills are the main spot for Zn uptake particular in freshwater fish and as a result of large surface area that is in contact with the environmental water and the very thin membrane separating the external and internal media of the animal. The large surface area of gills in *Channa punctatus* may be a favour for metal intake (Karuppusamy, 2000). 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 (1989) is 40 mg/kg. This shows that, Zn concentration in gill and liver of *Oreochromis niloticus* exceeded the maximum guideline set by WHO/FAO whereas tissue and bone organs recorded concentrations lower than the WHO/FAO guidelines. Also Zn concentrations in all organs of *gariepinus* fall below the maximum guideline except for gill which shows concentration higher than the WHO/FAO guideline.

Copper exhibits concentrations of the range (3.26 to 63.9±5.5 mg/kg) in *Oreochromis niloticus*. The highest concentration was detected in liver of while the lowest was noticed in

tissue. Meanwhile, Cu concentration was not detected in gill and bone of *Oreochromis niloticus*, whereas in *Clarias gariepinus*, Cu concentration was only observed in liver while other organs were at BDL. Other studies also reported the highest concentration of Cu in liver of *Oreochromis mykiss* and *Cyprinus carpio* (De Boeck *et al.*, 2004), *Oreochromis niloticus* (Mohammed, 2008), and *Tilapia nilotica* (Abdel-Baki *et al.*, 2011; Javed & Usmani, 2012). Liver and kidney have Cu bioaccumulation properties with cumulative capacity much greater in liver than in kidney (Stokes, 1979). Cu is an essential trace metal and micronutrient for cellular metabolism in living organism on account of being a key constituent of metallic enzymes (Monteiro *et al.*, 2009). The permissible intake limit of Cu set by WHO/FAO (1989) is 30 mg/kg. From this study, only liver shows Cu concentration higher than the WHO/FAO limit in both *Oreochromis* and *gariepinus*.

Manganese accumulation in organs of *Oreochromis niloticus* and *Clarias gariepinus* from Zobe Dam were of the range (1.18±0.02 to 27.8±0.1 mg/kg). The highest concentration was recorded in gill of *Clarias gariepinus* and the lowest in liver of *Oreochromis niloticus*. Studies also reported the highest concentration of Mn in gill organ of *Oreochromis mossambicus* (Robinson & Avenant, 2006) and *Clarias gariepinus* (Osman *et al.*, 2010; Javed & Usmani, 2011; Javed & Usmani, 2012). 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 (Andresen *et al.*, 2018). 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 (Buchman, 2014), (Nielsen, 2012). According to NIH (2021), 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.

Chromium concentration was only observed in gill organ of *Oreochromis niloticus* while the remaining organs were at BDL. In *Clarias gariepinus*, the concentrations of Cr were observed in tissue and liver whereas it was not detected in gill and bone. Cr is an essential nutrient metal necessary for metabolism of carbohydrate (Frag *et al.*, 2006). In other studies, considerably low levels of Cr were reported in gills and liver of *Cirrhinus mrigala*, *T. mossambica*, *M. vittatus*, *C. idella*, *Epinephalus morio*, *Chanos chanos*, and *Channa striata* (Rauf *et al.*, 2009; Ambedkar and Muniyan, 2011). 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 (Ahmed *et al.*, 2013). 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 (EFSA, 2014). Cr concentrations in organs of *Oreochromis niloticus* are lower than the maximum guideline of EFSA except for gill which shows concentration higher than the EFSA's maximum guideline. In *Clarias gariepinus*, flesh and liver organs shows concentrations higher than the maximum guideline of EFSA while gill and bone concentrations fall below the stipulated guideline.

Cobalt shows concentration of the range (0.23 to 2.93±0.14 mg/kg). The highest concentration was observed in liver of *Oreochromis niloticus* while the lowest was noticed in bone of *Clarias gariepinus*. Exposure to cobalt may cause cancer (NIOSH, 2019). Co concentrations in organs of the sampled fishes corroborates with the concentrations reported from previous studies (Anim *et al.*, 2011) in *Channa Obscura*, *Hepsetus odoe*, *Tillapia zilli* inhabiting Densu River, Niger. According to FEEDAP Panel (2009a), the potential cobalt intake of consumers from food of animal origin would not exceed 14 µg/day. This is equivalent to 0.0002 mg/kgbw. Thus, the concentrations of Cobalt in organs of the studied fishes are not within the maximum tolerable limit. Generally, cobalt compounds that dissolve easily in water are more harmful than those that are hard to dissolve in water. Once cobalt enters the body, it is distributed into all tissues, but mainly into the liver, kidney and bones (ATSDR, 2004).

Arsenic (As) was the least accumulated heavy metal in organs of *Oreochromis niloticus* and *Clarias gariepinus* in the present study. Its concentration was observed only in bone of *Oreochromis* while in tissue, liver, and gill, it was untraceable. Arsenic concentration was also noticed in liver and bone of *gariepinus* while it was not detected in tissue and gill. The detected concentrations were of the range (0.09 to 0.25±0.07 mg/kg). Highest concentration was recorded in bone of *Oreochromis niloticus* while the lowest was recorded in bone of *Clarias gariepinus*. Arsenic is toxic to humans and can affect people of any age or health status (FDA, 2023). Under MFR (1985) guideline, the maximum permissible limit for As intake was set at 1.0 mg/kg. Thus, the detected As concentrations in both species are lower than the MFR maximum guideline.

Chlorine exhibits significant concentrations in all organs of *Oreochromis niloticus* and *Clarias gariepinus*. Cl concentrations of the range (2194±39 to 7473±67 mg/kg) were detected from the sampled organs. The highest concentration was detected in liver of *Clarias gariepinus* and the lowest was detected in bone of *Clarias gariepinus*. Chlorine is essential to life; it is mostly present in cell fluid as a negative ion to balance the positive (mainly potassium) ions (Emsley, 2011). According to IOM (2005), the upper tolerable intake of chlorine is 51.1 mg/kg. This shows that, the concentration of Cl in the selected organs of the two species were not within IOM limit.

Bromine has sometimes been considered to be possibly essential in humans with support of only limited circumstantial evidences and no clear biological role. The concentrations of Br detected in organs of *Oreochromis niloticus* and *Clarias gariepinus* were of the range (18.6±0.1 to 51.2±0.5 mg/kg). The highest concentration was detected in gill of *Clarias gariepinus* while the lowest concentration was detected in bone of the *Clarias gariepinus*. According to JMPR (1989), the maximum daily intake limit of Br is 1.0 mg/kg. Hence, concentration of Br in all sampled organs exceeded the maximum guideline.

Iodine (I) is an essential mineral found in some foods. The body needs iodine to make thyroid hormones. These hormones control the body's metabolism and many other important functions (NIH, 2022). Deficiency of iodine causes goiter (an enlarge thyroid gland). High iodine intakes can also cause thyroid gland inflammation and thyroid cancer (NIH, 2022). Iodine measures the highest concentration of 4.83±0.19 mg/kg in gill and lowest concentration of 0.35 mg/kg in liver in *Oreochromis niloticus*, while its concentration in tissue and bone were at BDL. In *Clarias gariepinus*, Iodine shows the highest concentration of 0.24 mg/kg in liver and the lowest 0.1 mg/kg in tissue. For other organs (gill and bone), I concentration was not detected. The NIH maximum guideline for Iodine intake is 0.02 mg/kg (NIH, 2022). The concentrations of Iodine in organs of the two fish species were not within the NIH limit.

Calcium concentrations in organs of the studied fishes were of the range (531±115 to 96430±1350 mg/kg). The highest accumulation was observed in bone of *Oreochromis niloticus* while the lowest was noticed in liver of *Clarias gariepinus*. The maximum guideline for Ca intake stipulated by IOM is 35.7 mg/kg (IOM, 2011). Thus, Ca concentrations in all organs of the sampled fishes 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, low phosphate levels, constipation, nausea, weight loss, and a high risk of death from heart disease (NIH, 2022). Some research suggests that, high calcium intakes might increase the risk of heart disease and prostate cancer (NIH, 2022).

Potassium concentration in organs of *Oreochromis niloticus* ranged between 508±74 to 17430±23 mg/kg. The highest concentration was recorded in tissue while the lowest was recorded in gill. In *Clarias gariepinus*, K concentration of the range 8532±17 to 18280±46 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 guidelines, the maximum tolerable intake of K is 50.1 mg/kg (WHO, 2012). The concentration of K in all organs of both species exceeded the maximum guideline set by WHO.

Sodium is an essential nutrient required for maintenance of plasma volume, acid base balance, transmission of nerve impulses and normal cell function (Widmaier, 2008). Excessive sodium intake is associated with adverse health effects, blood pressure, cardiovascular, kidney and heart diseases (Farquhar, 2014), (Kotchen, 2013), (Appel, 2011). Deficiency of sodium causes *hyponatremia*. In this study, the concentrations of Na in organs of the sampled organs were of the range (1478±4 to 6161±12 mg/kg). The highest concentration was detected in gill of *Clarias gariepinus* while the lowest was detected in liver of *Oreochromis niloticus*. This shows that, Na concentrations in all organs of the two fish species were higher than the maximum guideline of 32.9 mg/kg (Whelton et al., 2012).

Magnesium concentrations in organs of *Oreochromis niloticus* were in the range of 800±60 to 1680±64 mg/kg. The highest concentration was detected in bone organ while the lowest was detected in liver. In *Clarias gariepinus*, the concentration of Mg ranged between 786±67 to 1563±64 mg/kg, where the highest concentration was observed in bone organ and the lowest was also noticed in liver. According to FNB recommendations, the upper tolerable intake of Mg is 5 mg/kg (FNB, 1997). This indicates that the concentrations of Mg in all organs of both fish species from Zobe Dam exceeded the stipulated permissible limit. Mg is an essential element that is crucial to the body's function. Deficiency of Mg causes *Osteoporosis* (Elshal et al., 2012). At very high doses, magnesium can be fatal (Longe, 2004).

Aluminium is a trivalent cation found in its ionic form in most kinds of animal and plant tissues and natural waters everywhere (Joseph, 2015). 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 (Meenakshi, 2019). The concentrations of Al in organs of both species were of the range (54.0±54 to 262±7 mg/kg). The highest concentration was observed in gill of *Oreochromis niloticus* while the lowest was noticed in tissue of the *Oreochromis niloticus*. The detected concentrations in organs of both fish species exceeded the FAO/WHO maximum guideline of 1.0 mg/kg (FAO/WHO, 2011).

Vanadium (V) concentration in organs of *Oreochromis niloticus* ranged between 0.30±0.08 to 2.22±0.11 mg/kg. The highest concentration was observed in bone while the lowest was noticed in tissue. Other concentrations observed in liver and gill were 1.25±0.13 and 1.34±0.16 mg/kg respectively. The range of V concentrations in *Clarias gariepinus* is 0.075 to 1.03±0.14 mg/kg. The highest concentration was detected in liver while the lowest in tissue. Concentrations of 0.37±0.08 and 0.61±0.08 mg/kg were recorded in gill and bone respectively. Vanadium as micronutrient plays a role in carbohydrate and lipid metabolism, but can be toxic at high concentrations (Zenel et al., 2022). The maximum guideline for V intake is 0.5 mg/kg (WHO/FAO, 1976). This shows that, in *Oreochromis niloticus*, only tissue accumulates V concentration lower than the WHO/FAO guideline. In *Clarias gariepinus*, V concentration in tissue and gill also falls below WHO/FAO guideline, while liver and bone concentrations exceeded the stipulated limit.

Barium is not considered to be an essential element for human nutrition (Schroeder, 1976). At high concentration, barium causes vasoconstriction by its direct stimulation of arterial muscle, peristalsis as a result of the violent stimulation of smooth muscles and convulsions and paralysis following stimulation of the central nervous system (Stockinger, 1981). From this study, the concentrations of Ba in *Oreochromis niloticus* were of the range (10.7 to 83.6±16.4 mg/kg). The highest concentration was observed in bone while the lowest concentration was noticed in tissue. Ba Concentration was not detected in all organs of *Clarias*

gariiepinus. The maximum guideline set for Ba is 0.21 mg/kg (WHO, 2016). The concentration of Ba in all organs of *Oreochromis niloticus* except for liver exceeded the maximum guideline.

Rubidium (Rb) shows significant concentrations in all organs of both species from Zobe Dam. The concentrations of the range (1.32 ± 0.25 to 9.96 ± 1.28 mg/kg) were detected, where the highest level was observed in tissue of *Clarias gariepinus* while the lowest was noticed in liver of the *gariiepinus*. Rb requirements in humans might be rated as less than 400 ug/day (Anke *et al.*, 2005). This is equivalent to 0.0057 mg/kg. Thus, the concentration of Rb in all selected organs of *Oreochromis niloticus* and *Clarias gariepinus* were not within the (Anke *et al.*, 2005) suggested Rb intake requirement for humans. According to Thomas (2014), rubidium has no known biological role and is nontoxic.

Lanthanum exhibits concentrations of 0.289 ± 0.002 and 0.49 ± 0.08 mg/kg in tissue and gill of *Clarias gariepinus* while La concentration was not detected in liver and bone. Lanthanum concentration in organs of *Oreochromis niloticus* ranged between 0.108 ± 0.001 to 0.52 ± 0.05 mg/kg. The highest level was recorded in liver while the lowest was observed in tissue. Other concentrations are 0.21 ± 0.04 and 0.19 mg/kg which are noticed in gill and bone respectively. La carbonate as a drug was approved for human use by USEFA and EU to reduce serum phosphate levels in chronic kidney failure (Jan, 2022).

Samarium accumulation is one of the least incidences recorded in all detected elements in the present study. The concentrations of the range (0.011 to 0.049 ± 0.006 mg/kg) were detected from the sampled organs. The highest concentration was observed in bone organ of *Oreochromis niloticus* while the lowest concentration was noticed in tissue of *Clarias gariepinus*. Tiny amounts of Samarium are found in the human body of about 50 mg (0.71 mg/kg), but it has no biological role (Emsley, 2015). Thus, Sm concentrations in all organs of the studied fishes cannot pose any health implications to human consumers.

Scandium is the least incidence recorded in all the detected elements in this study. The concentrations of the range (0.01 to 0.053 ± 0.008 mg/kg) were detected from the samples. The highest value was recorded in gill of *Clarias gariepinus* while the lowest was observed in bone of *Oreochromis niloticus*. Meanwhile, Sc was not detected in liver of *Clarias gariepinus*. Scandium has no biological role. Only trace amounts reach the food chain, so the average person's daily intake is less than 0.1 µg.

Estimation of the Dietary intake of the 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 7 with the suggested daily tolerable limits. The concentration data of the studied fish organs were compared with those provided by the WHO/FAO. 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 assumed intake estimation of the fish tissue revealed that, the concentration of the potentially toxic elements in tissue of both studied fish species (As, Br) 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 is considered safe.

Table 7: Intake values (in mg/day) of some essential and toxic elements and tolerable daily intake of adult (TDI/70 kg) of FAO (1991) WHO (1999)

Elements	Ca	Cu	Fe	I	Mn	Zn	Na	K	Cr	As	Br
Oreochromis niloticus	9.72	0.033	1.715	BDL	0.021	0.154	23.17	174.3	BDL	BDL	0.2
Clarias gariepinus	115.2	BDL	2.9	0.001	0.05	0.23	33.78	182.8	0.03	BDL	0.23
Males 19-50	1000	0.9	8	0.15	2.3	11	1500	4700	0.035	150	70
Females 19-50	1000	0.9	18	0.15	1.8	8	1500	4700	0.025	150	70
Pregnancy 19-50	1000	1	27	0.22	2	11	1500	4700	0.03	150	70
Lactation 19-50	1000	1.3	9	0.29	2.6	12	1500	4700	0.045	150	70

CONCLUSION

The present study tried to determine and evaluate the composition, the extent of the concentrations, and the possible health implications of elements in organs of two fish species (*Oreochromis niloticus* and *Clarias gariepinus*) from Zobe Dam, Katsina state which are proved to be the most consumed fishes by the people in the study area by using Instrumental Neutron Activation Analysis (INAA) techniques. Twenty one (21) elements were determined which includes thirteen essential elements; Mg, Al, Cl, Ca, Fe, Cu, I, Mn, Na, K, Zn, Cr, and Co. Two possible toxic elements; As, and Br; and six non-essential elements. An inter-elemental correlation was performed which shows a variation in correlation level between some element pairs with some elements having correlations higher than others. Moreover, it was found that, the essential and toxic elements concentrations in tissue of both fish species were considerably below the estimated daily tolerable human consumption limits set by the WHO/FAO. Finally, the outcomes of the present investigation might be used for nutritional data base.

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