Pertanika J. Sci. & Technol. 27 (4): 2201 - 2220 (2019)

SCIENCE & TECHNOLOGY

Journal homepage: http://www.pertanika.upm.edu.my/

Elemental Concentration in Three Different Fish Species Captured from Oluwa River, Okitipupa, Ondo State, Nigeria

Thompson Faraday Ediagbonya* and Ramond Babatunde Adesokan

Department of Chemical Sciences, Faculty of Science, Ondo State University of Science and Technology, Okitipupa, Nigeria

ABSTRACT

There has been a rapid turnaround from meat consumption to fish consumption in Nigeria over the last few years. As at 2013, the rate of fish consumption in Nigeria has risen to 2.6 million tonnes with a per capita consumption of 13.5 kg. Heavy metals bio-accumulate in fishes especially when the water body is polluted. Hence, humans are at risk of being affected by these metals via the consumption of contaminated fish, fish products and other aquatic foods captured from a contaminated river for this reason, there is need to monitor the level of heavy metal concentration in water bodies where they are caught. Analyses were done on fourteen (14) elements (Fe, Ni, Cr ,Cu , Mn, As, Zn,Ca, Ti, Se,Rb,K, Sr, Co) in three different fish species were analysed using Energy Dispersive X-ray florescence (EDXRF). The result showed that the mean values of Cr, Mn, Fe, Ni, Cu, Zn and As were all Higher than the recommended FAO/WHO standards. Generally, metal concentration in the gills is higher than that of the muscles for each species except Zn, Se and Fe in which is higher in the muscle for Tilapia fish and Fe, K and Rb which is higher in the muscle for Catfish. The target hazard quotient (THQ) of each metal through consumption of fishes from Oluwa river for both adults and children increased in the following order: Fe < Ni < Cr < Cu < Mn < As.

Keywords: Element, hazard index, target hazard quotient, X-Ray fluorescence

ARTICLE INFO

Article history:
Received: 10 December 2018
Accepted: 25 June 2019
Published: 21 October 2019

E-mail addresses:
tf.ediagbonya@gmail.com/tf.ediagbonya@osustech.edu.ng (Thompson Faraday Ediagbonya)
adesokan@gmail.com (Ramond Babatunde Adesokan)
* Corresponding author

ISSN: 0128-7680
e-ISSN: 2231-8526

INTRODUCTION

Elements can be grouped as metal, non-metal or metalloid or essential based on their properties. When a metal is heavy, it has relatively high density, essential, it is harmless, metallic, conduct heat, toxic and it has larger amounts or certain form (Fergusson, 1990). Heavy metals are those metallic elements with relative atomic masses higher than iron (Duffus, 2002). Elements enter the water body either naturally or through anthropogenic means. They are inevitably a natural constituent of the human environment. In riverine areas, metal pollution sources from direct atmospheric deposition, geologic weathering or through industrial and agricultural waste discharge (Dawson & Macklin, 1998; Kakulu et al., 1987). Water bodies are one of the receiving ends for pollutants, most especially heavy metals. These metals are deposited in the sediments of the benthic layer of the river or exist as ions in water. These metals are then taken in by aquatic organisms such as planktons, fishes and other invertebrates where they bio-accumulate and are transferred through the food chain to man, where it biomagnifies from one tropic level to another (Edward et al., 2013; Oti-Wilberforce et al., 2016). There are four routes through which metals can find their way into the body of fishes and they are; penetration through the skin, through the gills via respiration, through the sediments which they feed on, and through the intake of water (Odeemelam et al., 1999).

There has been a rapid turnaround from meat consumption to fish consumption in Nigeria over the last few years. As at 2013, the rate of fish consumption in Nigeria has risen to 2.6 million tonnes with a per capita consumption of 13.5 kg (Maureen, 2013). This is because fishes are a richer source of protein and in addition to that, it also provides omega-3 fatty acid which is known to prevent heart problem (Narain & Nunes, 2007). However, pollution of rivers by metallic elements is a great threat to consumer fishery products (Terra et al., 2008). This is because despite its nutritional value, consumption of fish contaminated with heavy metals is very hazardous to the human consumers. It has been reported that prolonged consumption of unsafe concentrations of heavy metals through foodstuff may lead to the chronic accumulations of the metals in the kidney and liver of humans causing disturbance in of numerous biochemical processes, leading to cardiovascular, nervous, kidney and bone diseases (Jarup, 2003; Trichopoulos, 1997), as heavy metals bio accumulate. Hence, humans are at risk of being affected by these metals via the consumption of contaminated fish, fish products and other aquatic foods captured from a contaminated river (Aderinola et al., 2009), for this reason, there is need to monitor the level of heavy metal concentration in water bodies where they are caught from so that for contaminated sites, the potential damage in the exposed biota can be determined so as to elucidate and solve many of the challenges in ecotoxicology, and for undisturbed sites or sites with moderate level of contamination, they can be kept under check (Awadesh, 2004).

These metallic elements can be categorised as essential e.g copper zinc, and selenium. semi-essential e.g nickel, vanadium and cobalt, and potentially toxic metals e.g aluminium, arsenic, lead, cadmium, antimony, and mercury (Szentmihalyi & Then, 2007). Even though some of these metals are essential but they can also be detrimental in highly concentrated amounts (Tüzen, 2003).

Okitipupa, the area chose (Oluwa River) for this study is a very important region with respect to the aquatic environment. Though they have no major industries but due to the fact that it is a small and developing town, they lack adequate refuse and sewage management. These waste products including effluents from minor industries most especially palm oil mills are being discharged directly into their water bodies. These pollutants may contain heavy metals that can endanger both aquatic and human life. Therefore, as a town with over 230,000 occupants according to 2006 census and a high rate of aquatic food consumption especially fishes from rivers, there is a need to find out and know the risks involved in consuming the fishes captured from this water body.

The objective of this study is to determine the elements present in the gills and muscles of three fish's species captured from Oluwa River in Okitipupa using Energy Dispersive X-ray florescence (EDXRF), compare their values with World Health Organisation (WHO) standard and to determine the target hazard quotient (THQ) and hazard index associated with consuming fishes from Oluwa River.

MATERIALS AND METHOD

The selected fish samples were from Oluwa River located in Okitipupa, Ondo state.

Oluwa River

Oluwa River is one of the major rivers in Okitipupa, Ondo state, Nigeria. Its geographical co-ordinates are latitude 4^{o}45'13.43" and longitude 6^{o}38'45.94". Aside fishes brought from neighbouring communities like Igbokoda, Igbonla, Mahin, Araromi, it is the major Source of fishes consumed in Okitipupa. Major activities in the river include fishing, transportation and sand mining. Some fish species that inhabit the river include Carps, Nile perch, Catfish, Snake head, and Tilapia.Oluwa River is linked to Irele and Igbokoda hence it serves as transport routes to these places. Transportation medium is usually by boats. Figure 1 shows the map of Oluwa River and the three locations in which the fishes were captured

Sampling

Twelve commercial fish species were caught using nets, four each for different species of fish namely; *Tilapia zilli, Heterobranchus bidorsalis and Cyprinus carpio* which were freshly harvested from the river were bought from the fishermen at the river side at about 11am and taken immediately to the laboratory for processing.

Sample Preparation

The fish samples were washed thoroughly using distilled water and dissected with clean stainless steel instruments to separate the muscle and the gills respectively according to

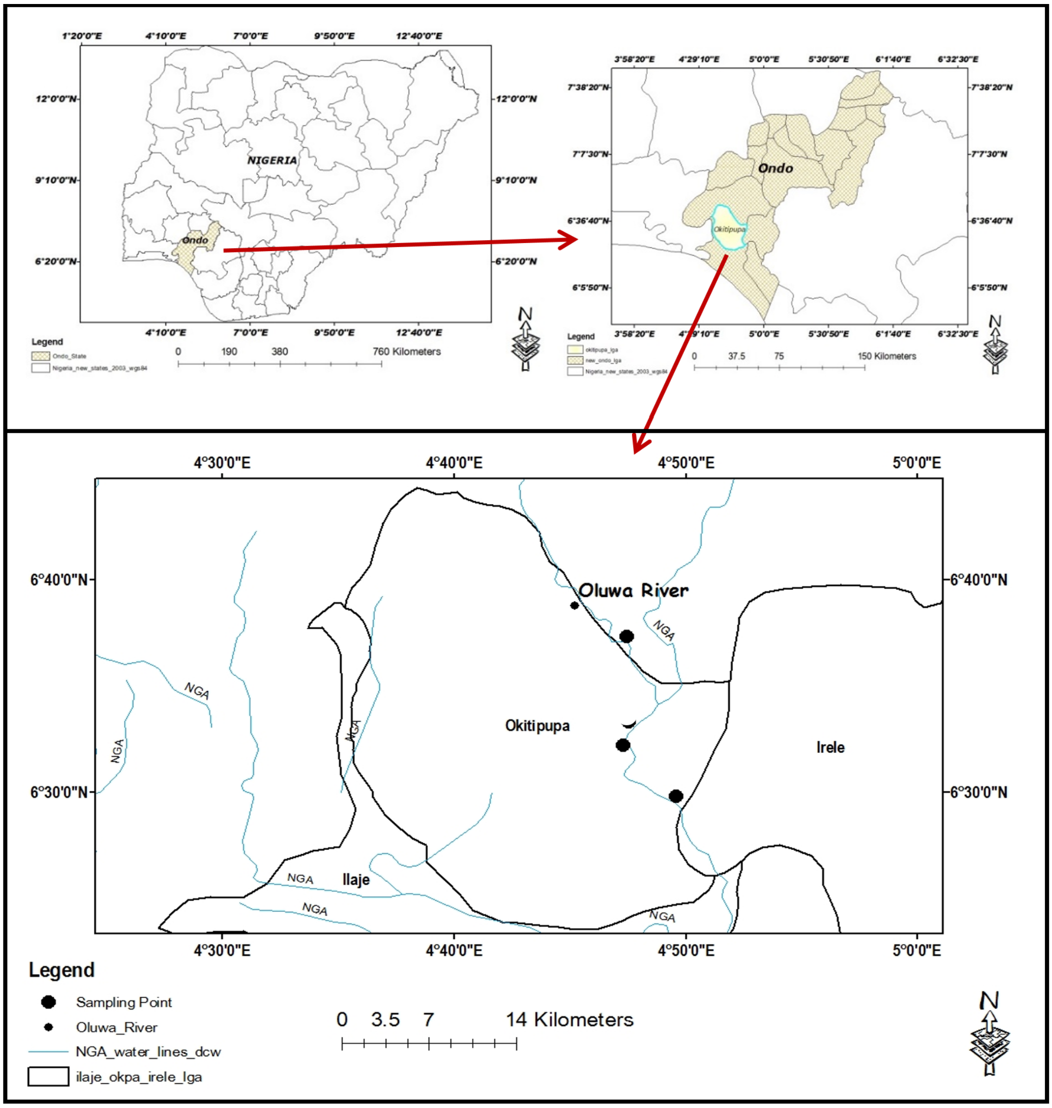

Figure 1. Shows the map of Oluwa River

FAO method (Dybem, 1993). The gills and muscles from each of the three species were rewashed thoroughly using clean water, then deionised water and kept in separate stainless steel plates. The samples were dried in an oven at 105°C until a constant weight was reached and a blender was used to reduce each dry sample to a powdered form.

Preparation and Measurement for X-Ray Fluorescence Analysis

The elemental analysis of the dried granulated fish samples was performed using the Energy Dispersive X-ray Fluorescence (EDXRF) spectrophotometer. The granulated fish sample was put in a pellet and inserted directly into the instrument. The sample was irradiated with a beam of X-rays. This primary radiation interacts with the elements in the sample to produce vacancies in the inner atomic shells, which then de-excite to produce characteristic secondary X-ray radiation. The wavelengths detected indicate which types of elements are present, and the quantity was determined from the intensity of the X-rays at each characteristic wavelength (USEPA, 1999). Each granulated fish samples was irradiated for 1000 seconds at fixed condition of 25 kV and 50 μA. The X-Ray Detector is a Model XR-100CR, high-performance thermoelectrically cooled Si-PIN photodiode, with a preamplifier. The analysis was carried out at Obafemi Awolowo University Ile-Ife.

Quality Control

Quality Assurance: Accuracy and precision were verified by using reference material (IAEA) provided by the International Atomic Agency (IAEA). Analytical results of the quality control samples indicated a satisfactory performance of heavy metal determination within the range of certified values 95–101% recovery for the metals studied.

Health Risk Assessment Parameters

Target Hazard Quotient (THQ). Potential health risk assessments based on estimated daily intake (EDI) values and target Hazard Quotient (THQ) indicated that the intakes of metals by consuming these fish species do not result in an appreciable hazard risk for the human body. To estimate the potential risk for human health derived from ingesting contaminated fish as given by FAO/WHO (2010) and the target hazard quotient (THQ) provided in the USEPA Region III Risk-based concentration table (USEPA, 2015). The target hazardous quotient (THQ) represents a complex parameter which is introduced by the US Environmental Protection Agency. It is used commonly for the assessment of the potential of non-carcinogenic risks associated with long term exposure to contaminants, such as heavy metals from food such as fish and water. Non-carcinogenic risk estimation of heavy metals consumption was determined using THQ values. THQ is a ratio of the determined dose of a pollutant to a reference level considered harmful. THQ values were determined based on the following formula (Singh et al., 2010):

$$\text{THQ} = \frac{\text{Efr} \times \text{ED} \times \text{FIR} \times C}{\text{RfDo} \times \text{B}_{\text{average wt}} \times \text{ATn} \times 10^{-3}} \quad (1)$$

where Efr is exposure frequency assumed to be 365days year^{-1}, ED is exposure duration in 70 years equivalent to an average lifetime, FIR is average daily consumption taken as 1.95×10^{-2} kg person^{-1}day^{-1}, *C* is concentration of metal in food sample in mg/kg, RfDo is reference dose in mg/kg day^{-1} which varies for different heavy metals, and ATn is average exposure time for non-carcinogens and is taken as 25550 days.

Hazard Index (HI). The chronic hazard index (HI) is the sum of more than one hazard quotient for multiple toxicants or multiple exposure pathways; it was calculated using the equation below (USEPA, 2011):

$$HI = \Sigma THQ. \qquad (2)$$

$$HI = THQ(Ar) + THQ(Zn) + THQ(Cu) + THQ(Mn) + THQ(Ni) + THQ(Cr). \quad (3)$$

Statistical Analysis

Descriptive statistics such as mean, Standard deviation, minimum and maximum were used in mean comparison. Inferential statistical tool employed were the Pearson correlation which was used to perform the inter-relationship between the metals, while the Independent samples t-test was used to perform mean comparison between species and body parts. To explore the distribution of the physicochemical parameters, the study employed the use of Boxplot. The level of significance was set at $p<0.05$. The data analyses were carried out using the different routines in STATA version 14.

RESULTS AND DISCUSSION

Table 1 shows the mean±SD concentrations of heavy metals in Tilapia, Catfish and Carp samples. The metal with the highest concentration was calcium having its lowest value of 1115.0 mg/kg in Carp and maximum concentration value of 2650 mg/kg in Catfish. Copper had the second highest concentration having its least value of 368 mg/kg in Catfish and maximum value of 492.3 mg/kg in Carp. Zinc had the third highest concentration in the samples with a minimum value of 298.1 mg/kg and maximum value of 360.7 mg/kg in Catfish. Manganese had the fourth highest concentration with minimum value of 166.3 mg/kg in Catfish and maximum value of 244.4 mg/kg in Tilapia. Titanium had the fifth highest concentration with minimum value of 14.3 mg/kg in Catfish and maximum concentration of 25.6 mg/kg in Tilapia.

Selenium had the sixth highest concentration with minimum value 11.5 mg/kg in Carp of and maximum value of 23.8mg/kg in Tilapia. Cobalt had the seventh highest concentration with minimum value of 6.5 mg/kg in Catfish and maximum concentration of 13.1 mg/kg in Tilapia.

The level of Co detected in the fish species ranged from 6.5 – 13.1 mg/kg with the lowest concentration in Catfish and highest concentration in Tilapia. The level of Arsenic detected in the fish species ranged from 3.1 to 7.4 mg/kg, with minimum value detected in Catfish and maximum value in Tilapia. Rubidium concentration level in fish species ranged from 5.1 – 8.6 mg/kg with highest concentration in Carp and lowest level in Tilapia. Strontium level in fish species ranged from 4.1 – 9.2 mg/kg with lowest and highest concentrations in Tilapia respectively.

Table 1
Elemental concentration in Tilapia, Catfish and Carp samples collected from Oluwa River {mg/kg)

	Tilapia (n=4)			Catfish (n=4)			Carp (n=4)			FAO/WHO (1989	USFDA (1993)
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean		
K	1100	1500	1190±200	1300	1500	13700±60	2000	2000	2020±0.00	--	---
Ca	1375	2459.2	1835.68±515.15	2152	2620	2387.50±251.45	1115	1119	1117.00±2.00	--	--
Ti	17.5	25.6	20.65±3.48	14.3	20.7	17.35±3.11	14.6	14.9	14.73±0.15	---	12-13
Cr	4.1	6.40	5.10±0.96	3.1	4.4	3.87±0.50	4.4	4.9	4.67±0.25	1	-
Mn	203.7	244.40	217.61±16.46	166.3	199	181.73±16.44	215.3	215.8	215.57±0.25	1	
Fe	1200	1700	1450±0.22	1500	1700	1600±0.14	1200	1200	1240±0.01	100	--
Co	8.5	13.1	10.40±2.13	6.50	9.60	8.00±1.47	12.1	12.9	12.50±0.40	--	--
Ni	3.3	5.3	4.05±0.70	2.4	3.8	2.98±0.66	3.8	3.9	3.89±0.06	-	70-80
Cu	396.8	491.5	442.50±49.62	368	453	410±44.94	491.4	492.3	491.77±0.51	30	---
Zn	311.5	360.7	338.42±24.31	298.9	341.4	320.33±22.40	491.4	492.3	491.77±0.51	100	---
As	4.2	7.4	5.82±1.56	3.1	5.4	4.32±1.06	6.4	6.8	6.63±0.25	---	----
Se	16.0	23.8	20.58±3.34	11.5	16.6	14.07±2.60	20.4	20.9	20.67±0.25	---	---
Sr	4.1	9.2	6.57±2.53	4.4	9.1	6.58±2.16	8.1	8.5	8.27±0.21	----	---
Rb	5.1	8.2	6.53±1.44	6.4	6.9	6.60±0.20	8.1	8.6	8.33±0.25	---	----

The concentration of Nickel in the fish species ranged from 2.4-5.3 mg/kg with minimum concentration in Catfish and maximum concentration in Tilapia. The concentration of nickel in all fish species exceeded WHO permissible limit of 1.40 mg/kg hence consuming fishes from this habitat can cause larynx cancer, asthma and chronic bronchitis. The concentrations of iron and potassium in the fish species were found to be very low. Iron having a range of 1200-1700 mg/kg and potassium having a range of 1100 - 2000 mg/kg. These concentration values are very low hence they pose no significant threat to human health.

The order of concentration of heavy metals in Tilapia and Catfish was given as Ni < Cr < As < Rb < Sr < Co < Se < Ti < Mn < Zn < Cu<K< Fe < Ca respectively, while in carp as Ni <Cr < As < Rb < Sr < Co < Ti < Se< Mn < Zn < Cu< Ca <Fe<K.The concentrations of metallic elements in catfish are lower that of Tilapia and Carp fish., these could be as a result of their feeding habits as Tilipia and Carp fishes are herbivorous while the carp is Carnivorous

The concentrations of some heavy metals in all three fish species were compared with the available FAO/WHO (1989) standard. The results from the tables showed that chromium concentration was quite high when compared to previous study (Uysal et al., 2008). The health risks associated with chromium exposure includes cancer, haemolysis, renal and liver failure and damages to circulatory and nerve tissues. Manganese concentration also exceeded the FAO/WHO (1989) limit of 1.0 mg/kg. Hence, consumers are at risk of having Central nervous system disorder, liver cirrhosis and Parkinson's disease. Cobalt has no FAO/WHO (1989) limit and the health effects associated with high cobalt concentration includes asthma, pneumonia, skin rashes and wheezing (Agency for Toxic Substances and Disease Registry, 2004).The value obtained can be compared to the previous study (Uysal et al., 2008).

The concentration of Nickel fell below the limit set by USFDA (1993) limit of 70-80 mg/kg. Nickel is known to cause larynx cancer, asthma and chronic bronchitis (Sivaperumal et al., 2007). The concentration of copper was also found to exceed the FAO/WHO (1989) limit of 30 mg/kg. Copper is an essential element in the human body but at high concentrations, teratogenicity (Gwozdzinski, 1995) and chromosomal aberrations (Bhunya & Pati, 1987).

Zinc also exceeded the FAO/WHO (1989) limit of 100 mg/kg and is likely to cause zinc toxicosis which in turn causes diarrhoea, bloody urine, liver and kidney failure and anaemia in consumers (Duruibe et al., 2007). Arsenic concentrations in all samples were also higher than the FAO/WHO (1989) limit of 1.4 mg/kg. Large oral doses of Arsenic can result in death. Lower levels of inorganic arsenic cause irritation stomach and intestines, with symptoms such as stomach ache, nausea, vomiting, and diarrhoea. It can also cause abnormal heart rhythm, blood vessel damage and impaired nerve function (Agency for Toxic Substances and Disease Registry, 2007).

Table 2 shows the mean comparison of the level of toxic metals in Gills and Muscle of Tilapia fish. The mean concentration of K in Gills was 1330±200; which was higher than the mean in muscle 1060±0.00. The difference was not statistically significant (p>0.05). The difference between the mean Ca in Gills (2294.36±179.66) and the mean in Table 2

Muscle (1377.00±2.65) was statistically significantly (p<0.05) higher in the gills than the muscles of Tilapia fish. The amount of Cr in the Gills (5.93±.45) was significantly (p<0.05) higher than the muscles (4.27±0.15). The level of Ni in the Gills (4.53±0.67) was higher than that of the muscle (3.57±0.31), the difference in mean was not statistically significant (p>0.05). The amount of Fe in the gills of Tilapia fish (1260±50) was significantly lower (p<0.05) than the level of Fe in the muscle (1650±50). The Concentration of Zn in the Gills (316.40±4.80) was significantly (p<0.05) lower than the concentration in the muscle (360.43±0.25). Se level in the gills (17.76±1.53) was significantly lower than the level of Se in the muscle (23.50±0.30).

Table 3 shows the mean comparison of level of toxic metals in Gills and Muscle of Catfish. The mean concentration of K in Gills was 1.32±0.00; which was lower than the mean in muscle 1.43±0.02. The difference is statistically significant (p<0.05). The difference between the mean Ca in Gills (2617.00±4.36) and the mean in Muscle (2158.00±6.00) was statistically significantly (p<0.05) higher in the gills than the muscles of Tilapia fish. The amount of Cr in the Gills (4.27±.0.15) was significantly (p<0.05) higher than the muscles (3.47±0.35). The level of Ni in the Gills (3.57±0.25) was higher than that of the muscle (3.47±0.35), the difference in mean was statistically significant (p<0.05). The amount of Fe

Table 2
Mean comparison for Tilapia fish and with previous study

Parameter	Gills (n=4)	Muscles(n=4)	t	p	Uyal et al., 2009	
					Gills	Muscles
K	1330±200	1060±0.00	24018	0,0730		
Ca	2294.36±179.66	1377.00±2.65	8.843	0.001		
Ti	23.60±2.05	17.70±0.20	4.957	0.008		
Cr	5.93±0.45	4.27±0.15	6.063	0.004	0.39	<DL
Mn	230.91±12.06	204.30±0.56	3.817	0.019	20.70-20700	0.48-480
Fe	1260±50	1650±50	-9.131	0.001	130.60-1718.4	18.44-242.6
Co	12.27±0.97	8.54±0.03	6.643	0.003	0.54-108	<DL
Ni	4.53±0.67	3.57±0.31	2.286	0.084	1.51-503.3	1.51-503.3
Cu	487.73±4.02	397.27±0.50	38.673	0.000	16.07	Yildirim et al. 2009
Zn	316.40±4.80	360.43±0.25	-15.857	0.000	166.75-7579.5	30.06-1366.3
As	7.23±0.15	4.40±0.20	19.500	0.000		
Se	17.67±1.53	23.50±0.30	-6.490	0.003		
Sr	8.87±0.31	4.27±0.15	23.326	0.000		
Rb	7.83±0.35	5.23±0.12	12.182	0.000		

in the gills of Catfish (1.47±0.01) was significantly lower ($p<0.05$) than the level of Fe in the muscle (1.72±0.01). The Concentration of Zn in the Gills (340.77±0.85) was significantly ($p<0.05$) higher than the concentration in the muscle (369.67±2.08). Se level in the gills (16.43±0.15) was significantly higher than the level of Se in the muscle (11.70±0.20). There was no significant difference ($p>0.05$) in the level of Rb in Gills (6.53±0.15) and the muscle (6.67±0.25), although the amount of Rb in the Muscle was higher than the mean concentration in the Gills.

Tables 3 and 4 indicate that on the average, heavy metal concentration in the gills was higher than in muscles for all three species but for few exceptions. This result agreed with the results of previous experiments by (Akpanyung et al., 2014; Etesin & Benson, 2007). The mean concentration of K, Ca, Ti, Cr, Mn, Co, Ni, Cu, As, Sr, Rb in the gills of Tilapia were all higher than the mean concentration in the muscles while the few exceptions were Fe, Zn and Se which were higher in the muscle than in the gills.

Also, the mean concentration of Fe, Ca, Ti, Cr, Mn, Co, Ni, Cu, As, Sr, Rb in the gills of Catfish were all higher than the mean concentration in the muscles while the few exceptions were K, Zn and Se which were higher in the muscle than in the gills. This shows that Zn and Se accumulate more in the muscle than in the gills of both fish species.

The above Table 5 shows the inter-relationship between toxic metals in Tilapia fish. Ca, Ti, Cr, Mn, Co, Sr and Rb had significantly positive relationship with K; while Se had significant negative relationship with K. Ti, Cr, Mn, Co, Cu, As, Sr and Rb had significant positive relationship with Ca; while Fe, Zn and Se were significantly negatively related with Ca. Cr, Mn, Co, Cu, As, Sr and Rb had significantly positive relationship with Ti,

Table 3
Mean comparison for Catfish fish

Parameter	Gills (n=4)	Muscles(n=4)	t	p
K	1320±0.00	1403±20	9.504	0.001
Ca	2617.00±4.36	2158.00±6.00	107.199	0.000
Ti	20.17±0.50	14.53±0.32	16.338	0.000
Cr	4.27±0.15	3.47±0.35	3.618	0.022
Mn	196.67±2.52	166.80±0.46	20.223	0.000
Fe	1470±10	1720±10	34.688	0.000
Co	9.33±0.25	6.67±0.15	15.689	0.000
Ni	3.57±0.25	2.39±0.03	8.035	0.001
Cu	451.67±1.15	369.7±2.08	59.664	0.000
Zn	340.77±0.85	299.90±1.25	46.843	0.000
As	5.27±0.12	3.37±0.31	10.076	0.001
Se	16.43±0.15	11.70±0.20	32.577	0.000
Sr	8.53±0.49	4.63±0.21	12.616	0.000
Rb	6.53±0.15	6.67±0.25	0.784	0.477

Table 4
Mean comparison for Carp fish

Parameter	Gills (n=4)	Muscles(n=4)	T	p
K	26300±0.42	20200±0.00	2.498	0.067
Ca	1339.33±16.17	1117.00±2.00	23.641	0.000
Ti	23.63±1.39	14.73±0.15	11.029	0.000
Cr	5.22±0.01	4.67±0.25	3.784	0.019
Mn	222.33±1.71	215.57±0.25	6.782	0.002
Fe	11300±200	12400±100	-10.165	0.001
Co	13.53±0.34	12.50±0.40	3.410	0.027
Ni	4.20±0.05	3.89±0.06	6.979	0.002
Cu	503.90±1.57	491.77±0.51	12.717	0.000
Zn	309.57±3.65	317.90±0.50	-3.918	0.017
As	7.23±0.01	6.63±0.21	4.985	0.008
Se	19.65±0.17	20.67±0.25	-5.813	0.004
Sr	11.34±0.89	8.27±0.21	-5.824	0.004
Rb	10.05±0.35	8.33±0.25	6.897	0.002

Fe, Zn, and Se had significantly negative relationship with Ti. Mn, Co, Cu, As, Sr and Rb had significantly positive relationship with Cr; while Fe, Zn, Se had significant negative relationship with Cr. Co, Cu, As, Sr and Rb had significant positive relationship with Mn, while Fe, Zn and Se had significant negative relationship with Mn. Zn, Se had significantly positive relationship with Fe, while Co, Ni, Cu, As, Sr and Rb had significant negative relationship with Fe. Ni, Cu, As, Sr and Rb had significantly positive relationship with Co; while Zn and Se had significant negative relationship with Co. Cu, As, Sr and Rb had significant positive relationship with Ni, while Zn and Se had negative significant relationship with Ni. As, Sr and Rb had significant positive relationship with Cu; while Zn and Se had significant negative relationship with Cu. Se had significant positive relationship with Zn; while As, Sr and Rb had significant negative relationship with Zn. Sr and Rb had significant positive relationship with As; while Se had negative significant relationship with As. Sr and Rb had significant negative relationship with Se. Rb had significantly positive relationship with Sr.

Table 6 shows the inter-relationship between toxic metals in Catfish. Ca, Ti, Cr, Mn, Co, Ni, Cu, As, Se and Sr had significantly negative relationship with K; while the Fe had significant positive relationship with K, except Rb which was not significantly related with K. Ti, Cr, Mn, Co, Ni, Cu, Zn, As and Sr had significant positive relationship with Ca; while Fe was significantly negatively related with Ca. Cr, Mn, Co, Ni, Cu, Zn, As and Sr had significantly positive relationship with Ti, Fe was significantly negative relationship with Ti. Mn, Co, Ni, Cu, Zn, As, Se and Sr had significantly positive relationship with Cr; while Fe had significant negative relationship with Cr. Co, Ni, Cu, Zn, As, Se and Sr had

Table 5
Inter-correlation between toxic metals in Tilapia fish

	K	Ca	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	**As**	**Se**	**Sr**	**Rb**
K	1	.890*	.951**	.921**	.971**	-.734	.915*	.587	.802	-.726	.778	-.919**	.816*	.859*
Ca	.890*	1	.986**	.991**	.958**	-.940**	.997**	.761	.985**	-.950**	.977**	-.993**	.988**	.996**
Ti	.951**	.986**	1	.989**	.985**	-.885*	.994**	.717	.945**	-.894*	.932**	-.993**	.953**	.974**
Cr	.921**	.991**	.989**	1	.976**	-.930**	.991**	.742	.963**	-.924**	.955**	-.991**	.965**	.979**
Mn	.971**	.958**	.985**	.976**	1	-.870*	.967**	.617	.907*	-.862*	.882*	-.979**	.917**	.943**
Fe	-.734	-.940**	-.885*	-.930**	-.870*	1	-.915*	-.680	-.972**	.987**	-.962**	.924**	-.968**	-.953**
Co	.915*	.997**	.994**	.991**	.967**	-.915*	1	.767	.971**	-.925**	.962**	-.992**	.975**	.988**
Ni	.587	.761	.717	.742	.617	-.680	.767	1	.755	-.679	.792	-.689	.734	.729
Cu	.802	.985**	.945**	.963**	.907*	-.972**	.971**	.755	1	-.987**	.994**	-.969**	.999**	.993**
Zn	-.726	-.950**	-.894*	-.924**	-.862*	.987**	-.925**	-.679	-.987**	1	-.979**	.935**	-.985**	-.970**
As	.778	.977**	.932**	.955**	.882*	-.962**	.962**	.792	.994**	-.979**	1	-.956**	.991**	.984**
Se	-.919**	-.993**	-.993**	-.991**	-.979**	.924**	-.992**	-.689	-.969**	.935**	-.956**	1	-.976**	-.990**
Sr	.816*	.988**	.953**	.965**	.917**	-.968**	.975**	.734	.999**	-.985**	.991**	-.976**	1	.997**
Rb	.859*	.996**	.974**	.979**	.943**	-.953**	.988**	.729	.993**	-.970**	.984**	-.990**	.997**	1

Table 6
Inter-correlation between toxic metals in Catfish

	K	Ca	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Sr	Rb
K	1	-.977**	-.967**	-.769	-.978**	.987**	-.984**	-.943**	-.976**	-.971**	-.946**	-.987**	-.976**	.186
Ca	-.977**	1	.994**	.878*	.995**	-.998**	.992**	.970**	1.000**	.999**	.984**	.998**	.988**	-.375
Ti	-.967**	.994**	1	.856*	.979**	-.987**	.979**	.986**	.995**	.989**	.992**	.987**	.972**	-.386
Cr	-.769	.878*	.856*	1	.885*	-.857*	.849*	.811	.876*	.894*	.879*	.859*	.866*	-.619
Mn	-.978**	.995**	.979**	.885*	1	-.996**	.993**	.943**	.993**	.996**	.972**	.997**	.994**	-.333
Fe	.987**	-.998**	-.987**	-.857*	-.996**	1	-.996**	-.962**	-.997**	-.997**	-.972**	-1.000**	-.991**	.333
Co	-.984**	.992**	.979**	.849*	.993**	-.996**	1	.944**	.991**	.990**	.970**	.996**	.998**	-.340
Ni	-.943**	.970**	.986**	.811	.943**	-.962**	.944**	1	.973**	.965**	.963**	.959**	.927**	-.393
Cu	-.976**	1.000**	.995**	.876*	.993**	-.997**	.991**	.973**	1	.998**	.987**	.997**	.987**	-.374
Zn	-.971**	.999**	.989**	.894*	.996**	-.997**	.990**	.965**	.998**	1	.979**	.996**	.987**	-.385
As	-.946**	.984**	.992**	.879*	.972**	-.972**	.970**	.963**	.987**	.979**	1	.974**	.969**	-.415
Se	-.987**	.998**	.987**	.859*	.997**	-1.000**	.996**	.959**	.997**	.996**	.974**	1	.993**	-.323
Sr	-.976**	.988**	.972**	.866*	.994**	-.991**	.998**	.927**	.987**	.987**	.969**	.993**	1	-.342
Rb	.186	-.375	-.386	-.619	-.333	.333	-.340	-.393	-.374	-.385	-.415	-.323	-.342	1

significant positive relationship with Mn, while Fe had significant negative relationship with Mn. Co, Ni, Cu, Zn, As, Se and Sr had significantly negative relationship with Fe. Ni,Cu, Zn, As, Se and Sr had significantly positive relationship with Co. Cu, Zn, As, Se and Sr had significant positive relationship with Ni. Zn, As, Se and Sr had significant positive relationship with Cu. As, Se and Sr had significant positive relationship with Zn. Se and Sr had significant positive relationship with As. Sr had significant negative relationship with Se. The correlation value showed in Table 5 and 6 could be that the fishes were caught from the same source

The above Table 7 shows the inter-relationship between toxic metals in Catfish. Majority of the relationships between toxic metals in Carp were not statistically significant. Zn showed a significant positive relationship with Ca. Mn showed a significant negative relationship with Ti. Co showed a positive significant relationship with Fe. Cu showed a negative significant relationship with As. Se showed a significant negative relationship with Rb.

Figure 2 is a box plot showing the distribution of pH and EC of the water.in this study. The median pH recorded in this study is 10.34, with an Interquartile Range (IQR) of 10.2-11.16; while the median EC is 2.77×10^3, with an IQ Range of $2.39\text{-}3.16 \times 10^3$. The distribution did not show any outliers in both the pH and EC.

Figure 3 shows the hazard index of mixtures of metal intake from consumption of fishes from Oluwa river for adults and children. In children the HI value was highest in Carp (43.1451) and least in Catfish (32.8077) while for adults HI value was highest in Carp (14.9726) and least in Catfish (11.2484) as seen in Figure 3.

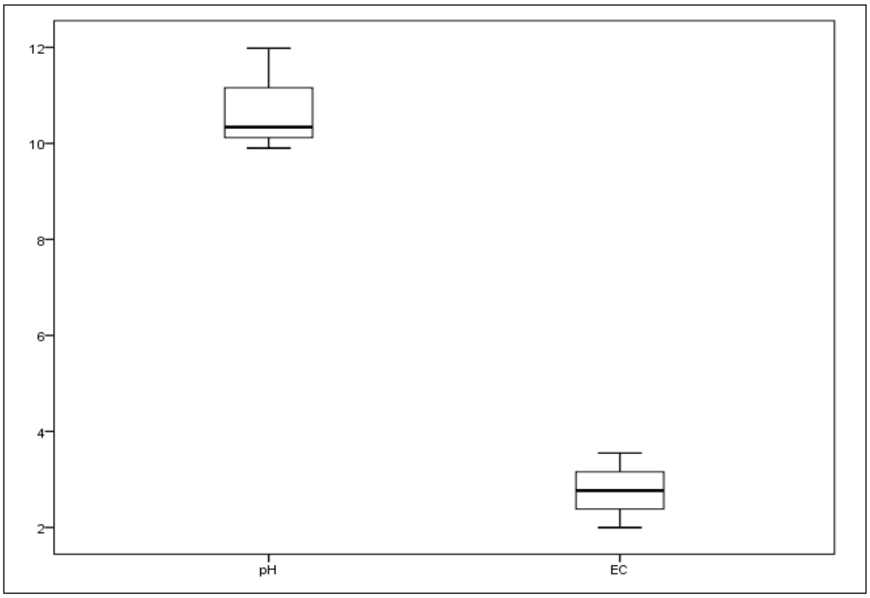

Figure 2. Box plot showing the physico-chemical characteristics of the water

Table 7
Inter-correlation between toxic metals in Carp

	K	Ca	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Sr	Rb
K	1	-.982	.929	.737	-.954	.277	.327	-.556	-.842	-.982	.839	-.434	.891	.434
Ca	-.982	1	-.982	-.596	.993	-.454	-.500	.703	.724	1.000**	-.721	.596	-.961	-.596
Ti	.929	-.982	1	.434	-.997*	.614	.655	-.825	-.581	-.982	.577	-.737	.996	.737
Cr	.737	-.596	.434	1	-.500	-.445	-.397	.151	-.985	-.596	.986	.289	.350	-.289
Mn	-.954	.993	-.997*	-.500	1	-.553	-.596	.780	.640	.993	-.636	.684	-.986	-.684
Fe	.277	-.454	.614	-.445	-.553	1	.999*	-.953	.286	-.454	-.291	-.986	.683	.986
Co	.327	-.500	.655	-.397	-.596	.999*	1	-.967	.235	-.500	-.240	-.993	.721	.993
Ni	-.556	.703	-.825	.151	.780	-.953	-.967	1	.020	.703	-.014	.990	-.873	-.990
Cu	-.842	.724	-.581	-.985	.640	.286	.235	.020	1	.724	-1.000**	-.122	-.505	.122
Zn	-.982	1.000**	-.982	-.596	.993	-.454	-.500	.703	.724	1	-.721	.596	-.961	-.596
As	.839	-.721	.577	.986	-.636	-.291	-.240	-.014	-1.000**	-.721	1	.127	.500	-.127
Se	-.434	.596	-.737	.289	.684	-.986	-.993	.990	-.122	.596	.127	1	-.795	-1.000**
Sr	.891	-.961	.996	.350	-.986	.683	.721	-.873	-.505	-.961	.500	-.795	1	.795
Rb	.434	-.596	.737	-.289	-.684	.986	.993	-.990	.122	-.596	-.127	-1.000**	.795	1

The Target Hazard Quotient (THQ) of each metal through consumption of fishes from Oluwa river for both adults and children increased in the following order: Fe < Ni < Cr < Cu <Mn< As. The maximum value of THQ was seen in carp (17.96 and 6.16) for adults and children in As (Figures 4 and 5). The THQ values of other fish species varied from Cu (2.86-3.42), Cr (0.72-0.95), As (4.01-6.16), Ni (0.041-0.056), Fe (0.0005–0.006), and Mn (3.61−4.33), respectively, for adults and also for children ranged from Cu (8.43-9.9), Cr (2.09-2.76), As (11.7-17.9), Ni (0.12-0.16), Fe (0.0014-0.0017), and Mn (10.5-12.6), respectively. The THQ of Cu, As and Mn were all less than 1 in all species for adults while for children, all metals except Ni and Fe had their THQ greater than 1 for all the fish species.

The THQ values for Cr, Ni and Fe for adults and that of Ni and Fe for children were below one in all three fish species. Hence, the intake of these metals by consuming these fishes is not likely to cause any appreciable health risk. While in the case of Cu, As and Mn in adults and Cu, As, Mn and Cr in children, the THQ for all three fish species exceeded the limit of one as shown in Figure 5. This indicates that there is potential health risks associated with the intake of these metals through consumption of these fishes. Copat et

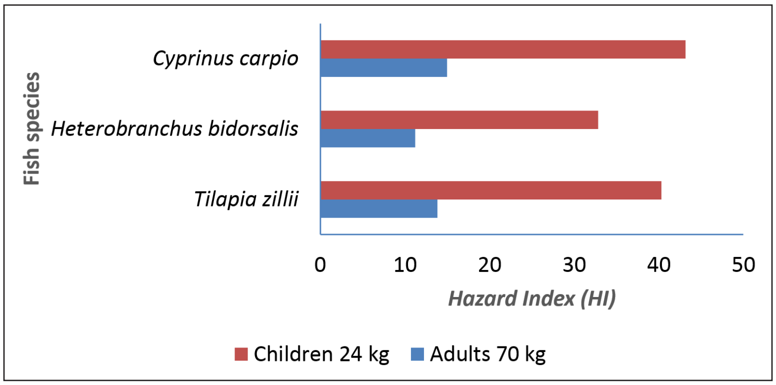

Figure 4. Target hazard quotient (THQ) in children exposed to fishes from Oluwa River

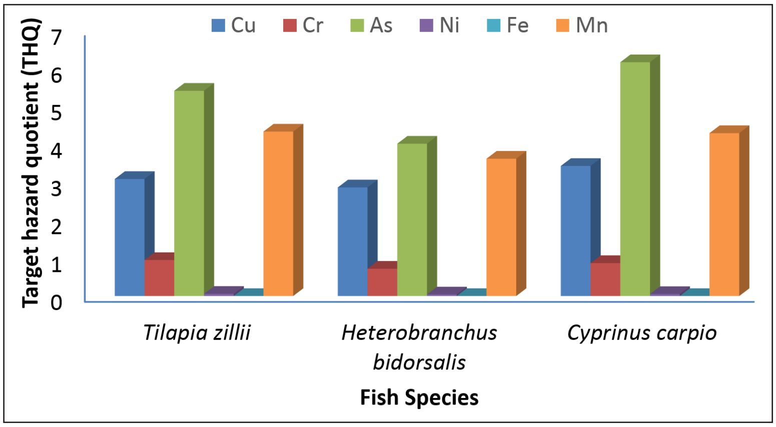

Figure 5. Target hazard quotient (THQ) adults exposed to fishes from Oluwa River

al. (2013) and Yabanli and Alparslan (2015) reported that the THQ values for Cr, Mn, Ni, V, Cu and Zn were below 1 .The values of THQ in Cr and Cu were in agreement with the values reported by previous studies (Copat et al., 2013; Yabanli & Alparslan, 2015). The THQ value has been recognized as one of the reasonable parameters for the risk assessment of metals associated with the consumption of contaminated fish (Li et al., 2013).

CONCLUSION

The concentrations of Zn, Fe, Mn and Cu in the fish samples from Oluwa River were higher than the FAO/WHO limit. The concentrations of metallic elements in Tilapia and Carp fishes were higher than the elemental concentrations in Cart fish except in Ca, Ti and Fe. These differences in metallic concentrations could be as a result of feeding habits of the fishes. Tilapia and Carp fishes are herbivorous in feeding while cart fish is carnivorous. The THQ of Cu, As and Mn were all less than 1 in all species for adults while for children, all metals except Ni and Fe had their THQ greater than 1 for all the fish species.The HI value in children was highest in Carp and least in Catfish while for adults HI value was highest in Carp and least in Catfish. The result of this study could also establish a baseline for future studies of heavy metal pollution.

RECOMMENDATION

There is a need for further extensive study and particularly the accumulation of heavy metals in humans.Point sources of heavy metals in the waters especially run-offs from small scale industries, farmland and indiscriminate dumping of waste in the water body should be closely monitored & proper treatment before disposal into water bodies should be enforced. Continuous monitoring of this water body should be done in order to ensure that the measures put in place to reduce the heavy metals concentrations in the fishes in Oluwa River, Okitipupa is reduced. Level of Heavy metal concentration in water bodies in the neighboring environments of Okitipupa should also be accessed for health and safety reasons.

ACKNOWLEDGEMENT

We appreciate the Dean Faculty of Science and the Head of Department Chemical Science for their logistic support and prayers which have really been vital in the success of this work. We also appreciate the fishermen for their immeasurable support.

REFERENCES

Aderinola, O. J., Clarke, E. O., Olarinmoye, O. M., Kusemiju, V., & Amatekhai, M. A. (2009). Heavy metals in surface water, sediments, fish and Periwinkles of lagos lagoon*. American-Eurasian Journal of Agricultural and Environmental Sciences, 5*(5), 609-617.

Agency for Toxic Substances and Disease Registry. (2004). *Toxicological Profile for Cobalt*. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.

Agency for Toxic Substances and Disease Registry. (2007). Toxicological Profile for Arsenic. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.

Akpanyung, E. O., Akanemesang, U., Akpakpan, E. I., & Anodoze, N. (2014). Levels of heavy metals in fish obtained from two fishing sites in Akwa Ibom State, Nigeria. *African Journal of Environmental Science and Technology, 8*(7), 416-421.

Awadesh, N. J. (2004). Genotoxicological studies in aquatic organisms: an overview. *Mutation Research, 55*(2), 1-7.

Bhunya, S. P., & Pati, C. P (1987) Genotoxicity of an inorganic pesticide, copper sulphate, in a mouse in vivo test system. *Cytologia, 52*, 801-808.

Copat, C., Arena, G., Fiore, M., Ledda, C., Fallico, R., Sciacca, S., & Ferrante, M. (2013). Heavy metals concentrations in fish and shellfish from Eastern Mediterranean Sea: consumption advisories. *Food and Chemical Toxicology, 53*, 33-37.

Dawson, E. J., & Macklin, M. G. (1998). Speciation of heavy metals in floodplain and flood sediments: a reconnaissance survey of the Aire Valley, West Yorkshire, Great Britain. *Environmental Geochemistry and Health, 20*(2), 67-76.

Duffus, J. H. (2002). "Heavy metals" a meaningless term? (IUPAC Technical Report). *Pure and applied chemistry, 74*(5), 793-807.

Duruibe, J. O., Ogwuegbu, M. C., & Egwurugwu, J. N. (2007). Heavy metal pollution and human biotoxic effects. *International Journal of Physical Sciences, 2*, 112-118.

Dybem, B. (1993). Field sampling and preparation subsamples of aquatic organism for analysis metals and organochlorides, FAO. *Fishery Technology, 212*, 1-13.

Edward, J. B., Idowu, E. O., Oso, J. A., & Ibidapo, O. R. (2013). Determination of heavy metal concentration in fish samples, sediment and water from Odo-Ayo River in Ado-Ekiti, Ekiti-State, Nigeria. *International Journal of Environmental Monitoring and Analysis, 1*(1), 27-33.

Etesin, M. U., & Benson, N. U. (2007). Cadmium, copper, lead and zinc tissue levels in Bonga Shad (Ethmalosa fimbriata) and Tilapia (Tilapia guineensis) caught from Imo River, Nigeria. *American Journal of Food Technology, 2*(1), 48-54.

FAO/WHO. (1989). *National Research Council Recommended Dietary Allowances* (10th Ed.). Washington, DC: National Academy Press.

FAO/WHO. (2010). *Codex Alimentarius Commission Procedural Manual* (19th Ed.). Rome, Italy: World Health Organization and Food and Agriculture Organization of the United Nations.

Fergusson, J. E. (1990). *The Heavy Elements: Chemistry, Environmental Impact and Health Effects*. Oxford, England: Pergamon Press.

Gwozdzinski, K. (1995). Structural changes in erythrocyte components induced by copper and mercury. *Radiation Physics and Chemistry, 45*(6), 877-882.

Jarup, L. (2003). Hazards of heavy metal contamination. *British Medical Bulletin, 68*(1), 167-182.

Kakulu, S. E., Osibanjo, O., & Ajayi, S. O. (1987). Trace metal content of fish and shell fishes of the Niger-Delta area of Nigeria. *Environment International, 13*(3), 247-251.

Li, J., Huang, Z., Hu, Y., & Yang, H. (2013). Potential risk assessment of heavy metals by consuming shellfish collected from Xiamen, China. *Environmental Science and Pollution Research, 20*(5), 2937-2947.

Maureen, A. (2013). Nigeria under pressure to meet 700,000 metric tonnes fish deficit. *Punch Newspaper, Nigeria, 2*, 3-15.

Narain, N., & Nunes, M. L. (2007). *Handbook of meat, poultry and seafood quality*. Iowa, USA: Blackwell Publishing.

Odeemelam, S. A., Iwuozor, C. C., & Ozuo, J. U. (1999, May 18-20). Baseline levels of some toxic metals in selected Nigerian rivers. In *2nd National Conference of the tropical Environment Forum (TEFO)*. Calabar, Nigeria.

Oti-Wilberforce, J. O., Nworie, F., & Oti-wilberforce, R. O. (2016). Comparative assay of heavy metals in gills and muscles of common fishes in Afikpo, Ebonyi State, Nigeria. *World Applied Sciences Journal, 34*(2), 268-272.

Singh, A., Sharma, R. K., Agrawal, M., & Marshall, F. M. (2010). Risk assessment of heavy metal toxicity through contaminated vegetables from waste water irrigated area of Varanasi, India. *Tropical Ecology, 51*(2), 375-387.

Sivaperumal, P., Sankar, T., & Nair, P. V. (2007). Heavy metal concentrations in fish, shellfish and fish product from internal markets of India vis-a-vis international standards. *Food Chemistry, 102*(3), 612-620.

Szentmihalyi, K., & Then, M. (2007). Examination of microelements in medicinal plants of the Carpathian basin. *Acta Alimentaria, 36*, 231-236.

Terra, B. F., Araujo, F. G., Calza, C. F., Lopes, R. T., & Teixeira, T. P. (2008). Heavy metal in tissue of three fish species from different trophic levels in a tropical Brazilian river. *Water Air Soil Pollution, 187*, 275-284.

Trichopoulos, D., (1997). Epidermilogy of cancer. In V. T. DeVita (Ed.), *Cancer, principles and practice of oncology*. Philadelphia: Lippincott Company.

Tüzen, M. (2003). Determination of heavy metals in fish samples of the Mid Dam Lake Black Sea (Turkey) by graphite furnace atomic absorption spectrometry. *Food Chemistry,* 80, 119-123.

USFDA. (1993). *Food and drug administration, guidance document for nickel in shell fish*. Washington, DC: DHHS/PHS/FDA/CFSAN/office of seafood.

USEPA. (1999). *Particulate Matter (PM2.5) Speciation Guidance: US Environmental Protection Agency* (Final Draft). United States Environmental Protection Agency.

USEPA. (2011). *USEPA Regional Screening Level (RSL) Summary Table*. United States Environmental Protection Agency.

USEPA. (2015). *Regional ScreeningLevel (RSL) Summary Table*. United States Environmental Protection Agency.

Uysal, K., Köse, E., Bülbül, M., Dönmez, M., Erdoğan, Y., Koyun, M., ... & Özmal, F. (2008) The comparison of heavy metal accumulation ratios of some fish species in Enne Dame Lake (Kütahya/Turkey). *Environmental Monitoring and Assessment, 157*(1-4), 355-362.

Yabanli, M., & Alparslan, Y. (2015). Potential health hazard assessment interms of some heavy metals determined in demersal fishes caught in eastern Aegean Sea. *Bulletin of Environmental Contamination and Toxicology, 95*(4), 494-498.

Yildirim, Y., Gonulalan, Z., Narin, I., & Soylak, M. (2009). Evaluation of trace heavy metal levels of some fish species sold at retail in Kayseri, Turkey. *Environmental Monitoring and Assessment, 149*(1-4), 223-228.