Original Research Article

EVALUATION OF ESSENTIAL ELEMENTS AND HEAVY METALS IN SARDINE FISH FROM KIVUKONI, KUNDUCHI AND BAGAMOYO FISH MARKETS IN TANZANIA

ABSTRACT

This study has assessed the concentrations of the essential elements Ca, Cu, Fe, Se and Zn as well as the toxic heavy metals Al, As, Cd, Cr, Ni and Pb in samples of sardine fish collected from Kivukoni, Kunduchi and Bagamoyo fish markets. The collected fish samples were oven dried, grinded to fine powder and compressed to pellets. The pellets obtained were analyzed for both essential elements and toxic heavy metals using Energy Dispersive X- rays Fluorescence Spectroscopy (EDXRF). The mean concentrations of the analyzed elements were compared to the maximum tolerable levels (MTLs) set by international organizations. The mean concentrations of Ca, Se, Zn, As, Cr, and Cd were higher than their MTLs while, the mean concentrations of Cu and Ni were lower than their MTLs for samples from all fish markets. The mean concentrations of Al and Fe were higher than their MTLs for samples from Kunduchi and Bagamoyo fish markets. The mean concentrations of Pb were below the detection limit (0.50) µg/g for the spectrometer used in this study. The MTLs for Ca, Fe, Cu, Se, Zn, Al, Cr, Ni, As, and Cd were 130,000 ; 200 ; 30 ; 40 ; 0.75 ; 100 ; 0.15 ; 2.00 ; 0.50 ; 0.50 ; and 2.00 µg/g respectively, according to FAO/WHO 2002, WHO 1983, COMA 1998, CFS2009, WHO1985, COT 2003 and CODEX 2005..

Keywords: Aquatic Environments, Energy Dispersive X-rays Fluorescence (EDXR), Sardine Fish, Kivukoni, Kunduchi and Bagamoyo fish markets

1. INTRODUCTION

Seafood’s could be a good source of the essential elements for many African communities especially the coast communities. Contamination of the seafood’s and the general aquatic environments by heavy metals is the problem of major concern worldwide [1]. All metallic elements with an atomic number greater than that calcium (40.04) are referred as heavy metals [2]. These include arsenic (As), Cadmium (Cd), Lead (Pb) and Mercury (Hg) which are also of major concern because; they are extremely toxic even at low concentrations [3]. The above elements are brought into the aquatic environments as a result of the natural activities such as seafloor and bedrock dredging, volcanic eruptions, soil erosion and weathering as well as anthropogenic activities such as agriculture, municipal wastewater discharges, mining, incinerations, domestic discharges and industrial discharges [4]. It is reported that, more than 80% of the world's waste water and more than 95% of the least developed countries wastewater are released into the aquatic environments untreated. The wastewaters ultimately end up in the oceans and seas, thereby, introducing different contaminants into the aquatic environments as suggested by Hellawell 1986 and Machiwa 2010 [5,6].

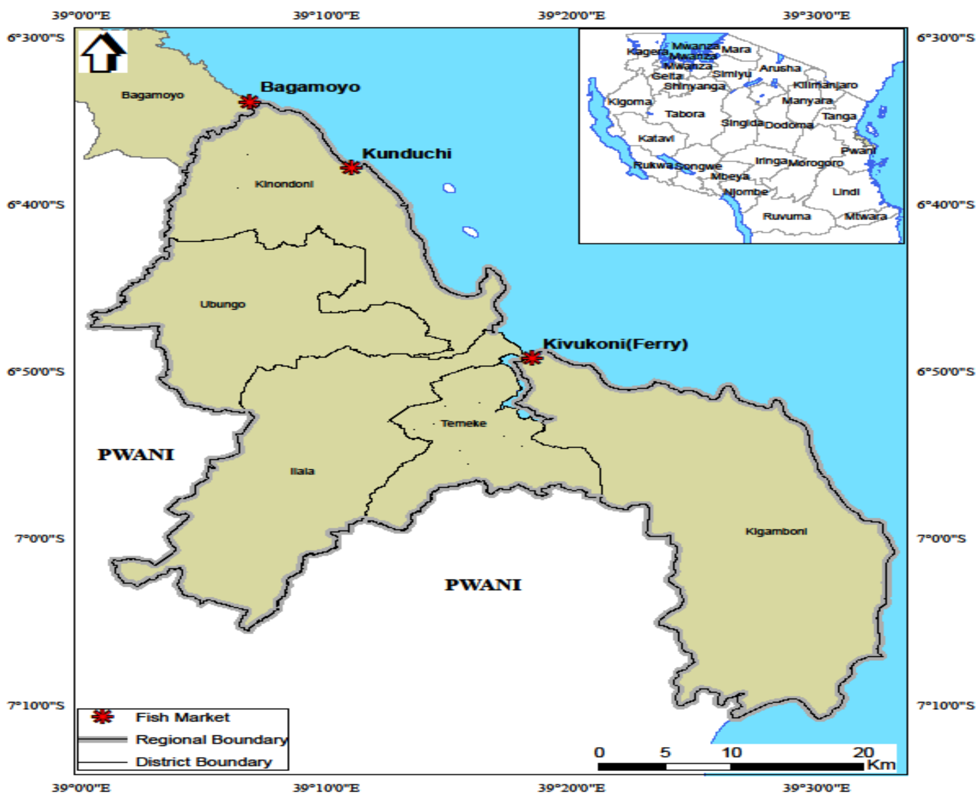
Heavy metals which enter the aquatic environments are taken up by fish through the food chain via fish consuming small plankton, as well as through non-food sources such as underwater sediment and undergo bioaccumulation In the fish body, the metal is transported through the blood stream and either stored, transformed or eliminated in the liver, kidney, the gills, intestine and other organs [7,8]. Since fish are consumed by human beings, heavy metals are eventually consumed by human beings and other organisms at the top of the food chain [1]. heavy metals therefore pose a potential threat to the health of humans and other organisms at the top of the food chain [7]. Heavy metals pollutions can trigger a wide array of health problems such as infertility, miscarriages, cancer, damages to the vital organs such as kidney, brain, central and peripheral nervous system leading to an ultimate death Druibe 2007 and Jarup 2003 [2,3].

Various studies indicate that, the accumulations of heavy metals in fish and other marine foods have been increasing steadily in the recent years [9,10,11,12]. In Egypt, concentrations of copper (Cu), Zinc (Zn), Lead (Pb) and cadmium (Cd) in fish samples collected from El – Fayoun province were found to be higher than their maximum tolerable levels (MTLs) set by WHO [13]. In Kenya, the study was conducted a study to investigate the levels of Lead (Pb), Nickel (Ni), Manganese (Mn), Zinc (Zn), Cadium (Cd) and Chromium (Cr) in the gills of the tilapia fish and water in the Athi –River by using Atomic Absorption Spectrometry[8]. The study concluded that, the levels of the mentioned heavy metals in both fish and water, were above their respective maximum tolerable levels set by WHO [8]. In Tanzania, the assessment of the concentrations of heavy metals in the fish samples collected from the downstream and upstream of the north Mara gold mining using Energy Dispersive X- rays Fluorescence (EDXRF) spectrometry [14]. The samples of catfish and lungfish from both sites had higher mean concentrations of sodium (Na), potassium (K), copper (Cu), chromium (Cr) and nickel (Ni) compared to their maximum tolerable levels (MTLs) set by FAO and WHO, 1985 [14,15]. Furthermore, a study conducted by Koleleni and Haji [16] to determine the concentrations of heavy metals in the sea port of Zanzibar, reported that, the concentrations of chromium (Cr), Lead (Pb), Nickel (Ni) and Arsenic (As) in the samples of sardine fish collected from the sea port of Zanzibar were higher than their maximum tolerable level set by WHO [15]. In the best of my knowledge, there had been no study that had assessed the concentrations of the essential and toxic elements in sardine fish harvested from the Indian Ocean and sold at Kivukoni, Kunduchi and Bagamoyo fish markets. The sardine fish are the most landed fish species globally and they could serve as a good source of micronutrients for the coast communities [12]. The aim of this study is therefore, to assess the concentrations of both the essential and toxic elements in sardine fish harvested from the Indian Ocean and sold at Kivukoni, Kunduchi and Bagamoyo fish markets. The assessment will facilitate the government and the general public with information to evaluate the quality of the sardine fish to the food value and nutritional security to avoid the risk of heavy metals pollution to the coast communities.

2. MATERIAL AND METHODS

2.1 Description of the Study Area

This study was conducted at Kinondoni and Bagamoyo districts. The Kinondoni and Bagamoyo coast line are located between latitudes and longitudes 6^{0}34`0``S, 39$^{0}$06`0``E to 6^{0}51`0``S and 39^{0}19`0`E, respectively. The selected fish markets are located alongside the Indian Ocean. Kivukoni and Bagamoyo fish markets are near to Dar es Salaam and Bagamoyo harbors respectively, while, Kunduchi fish market is near to Kunduchi Beach Hotel. This coastline has a total population of 5,463,209 inhabitants. The major economic activities along this coastline include manufacturing industries, trade, agriculture, mining, tourism, and fishing [17]. Figure **1** is a description of the study area.



Source:Cartographic unit-University of Dar es Salaam

Fig. 1 Description of the study area

2.2 Sample Collection

The samples of sardine fish were bought from the fishermen at Kivukoni, Kunduchi and Bagamoyo fish markets. The purchased fish samples were kept in containers made of non-wet table plastic materials. The containers with the fish samples were kept in a refrigerator till the preparation day. Before the containers were used, they were preconditioned by a dilute acid (ultra-pure HNO_3) and rinsed thoroughly with double distilled water. Figure **2** indicates some of the collected fish samples. The details of the sample preparation techniques are given in section 2.3.

Fig. 2 Pictures of some of the collected fish samples in a closed package

2.3 XRF Sample Preparation

The collected fish samples were washed thoroughly using clean fresh distilled water and oven dried at the temperature of 45^0C to 50^0C for 48 hours. The samples were thereafter, ground and sieved to obtain fine powders (<50 µm). For each sample, a mass of 4 g was mixed with 0.9 g of starch (binder). The mixtures of the samples and the binders were homogenized using Fritsch Pulverisette^{TM} (Industriiesstrasse, 8-55743I dar Okerstein, German) homogenizer. The homogenizer was set at speed of 120 revolutions per second for 10 minutes. After homogenization, the samples were compressed to pellets using Restsch^{TM} (Restch GmbH Retsch-Allee 1-5, 42781Haan, German) pellet presser. A force of 15 N was applied to the pellet presser to produce pellets of 32 mm outer diameter. Figure **3** indicates one of the pelletized samples produced.

Fig.3 A pelletized sample

The samples so produced were properly labeled and taken to the Spectro Xepos^{TM} (Sepetro Analytical Instruments GmbH, Boschstr. 10, 47533 Kleve, German) spectrometer for heavy metals analysis. Figure **4** indicate the picture of the Spectro Xepos^{TM} spectrometer used in this study.The capability of elemental analysis cover all those described by Tanzania Bureau of Standards [17].

Fig. 4 The picture of the Spectro Xepos™ spectrometer

2.4 Sample Elemental Analysis

Each pellet was irradiated by x-rays from the x-rays tube so as to produce the characteristic x-rays. The x-ray tube was operated at a maximum power of 50W and a maximum voltage of 50KV. A semiconductor detector (Silicon Lithium) was used to detect and measure the energy of the characteristic x-rays produced. A computer connected to the spectrometer was used to display the spectra of the intensities of the characteristic x-rays against energies of the elements in the sample. The spectrometer was calibrated weekly and set according to manufactures specifications.

Elemental composition of each pellet was computed by the X- Lab Pro™ software with Turbo quant (Tq 9232) algorithm. This software, corrected for matrix effects, interference effects and background effects on the basis of fundamental parameter method. The software converts the intensities of the characteristic x-rays into concentrations of the radiating elements according to the equation 1[18]

;

$$C_i = K_i I_i M_a \quad (1)$$

Where, C_i is the concentration of the radiating element in the sample, M_a is the matrix correction factor, K_i is the constant of proportionality and I_i is the intensity of the fluorescence radiations from element (i).

3. RESULTS AND DISCUSSION

3.1 Minimum Detection Limits (MDL)

Minimum detection limits refers to the minimum concentration of the analyzed elements that can be detected by the instrument (spectrometer). It is the lowest concentration that can be determined to be statistically significant from the analytical blank [19]. The concentration of the analyzed element in the sample is considered to be statistically significant, if the net peak intensity of its characteristic x-rays is at least thrice the standard deviation of the background noise. The minimum detection limits can be very low when the background counts are not significant and vice –versa is true.

The minimum detection limits for the analyzed elements were determined using the X-Lab Pro™ software package according to the equation 2 [19].

$$\text{MDL} = \frac{3C_i}{I_i - I_b}\sqrt{\frac{I_b}{T_b}} \quad (2)$$

Where, C_i is the concentration of the analyzed element, I_b is the intensity of the background counts, I_i is the intensity of the characteristic x-rays from the analyzed element and T_b is the time used to measure the background counts. Table **1** indicates the minimum detection limits of the spectrometer for the analyzed elements.

Table 1: The MDL (μg/g) for the analyzed elements

ATOMIC NUMBER	CHEMICAL SYMBOL	ELEMENT	MDL (μg/g)
13	Al	Aluminum	35.2
20	Ca	Calcium	6.0
24	Cr	Chromium	5.2
26	Fe	Iron	2.6
28	Ni	Nickel	1.0
29	Cu	Copper	1.4
30	Zn	Zinc	1.0
33	As	Arsenic	0.3
34	Se	Selenium	1.0
48	Cd	Cadmium	3.8
82	Pb	Lead	0.5

3.2 Mean concentrations of the essential elements for the sardine fish from Kivukoni, Kunduchi and Bagamoyo.

The statistical package for social sciences (SPSS – Version 17) software was used to compute the mean concentrations of the essential elements for samples from each fish market. Tables **2** and **3** indicate the arithmetic means and geometric means of the concentrations of the essential elements for each fish market.

Table 2 Arithmetic means of concentrations ± standard error of the mean (SEM) (μg/g) for the essential elements

ELEMENTS	FISH MARKETS		
	KIVUKONI (n = 10)	KUNDUCHI (n = 10)	BAGAMOYO (n = 10)
Calcium (Ca)	37981.9 ± 5558.2	30388.5 ± 103.9	38310.9± 103.0

Iron (Fe)	149.9 ± 0.4	211.9± 1.0	234.8 ± 0.8
Copper (Cu)	4.0 ± 0.1	2.6± 0.1	3.5 ± 0.1
Selenium (Se)	1.7 ± 0.0	2.2 ± 0.1	1.9 ± 0.0
Zinc (Zn)	159.8 ± 1.1	105.1 ± 0.6	130.9 ± 0.5

Table 3 Geometric means of the concentrations ×/÷ standard deviation (SD) (µg/g) for the essential elements

ELEMENTS	FISH MARKETS		
	KIVUKONI (n = 10)	KUNDUCHI (n = 10)	BAGAMOYO (n = 10)
Calcium (Ca)	25983.0 ×/÷ 17576.6	30405.3 ×/÷ 328.6	38282.3 ×/÷ 328.4
Iron (Fe)	149.8 ×/÷ 1.3	34.1 ×/÷ 3.3	34.1 ×/÷2.4
Copper (Cu)	4.0 ×/÷ 0.4	2.6 ×/÷ 0.2	3.4 ×/÷ 0.2
Selenium (Se)	1.7×/÷ 0.1	2.2×/÷ 0.2	2.0 ×/÷ 0.1
Zinc (Zn)	159.8 ×/÷ 3.5	105.3 ×/÷ 1.9	131.3 ×/÷ 1.5

From the tables, it can be seen that, Calcium is the highest mean concentrations for samples from all fish markets. Iron (Fe) recorded the 2nd higher mean concentrations for samples from Kunduchi and Bagamoyo fish markets while Zinc (Zn) recorded the 2nd highest mean concentration for samples from Kivukoni fish market. Copper (Cu) recorded the 3rd higher mean concentrations followed by Selenium (Se) for samples from all fish markets. It can be noted that, the mean concentrations of the essential elements were in the order; Ca > Zn > Fe > Cu > Se > (for samples from Kivukoni fish market), Ca > Fe > Zn > Cu > Se (for samples from Kunduchi fish market) and Ca > Fe > Zn > Cu > Se (for samples from Bagamoyo fish market).

It is reported that, calcium is the 5th most abundant element in the earth's crust [20]. It exists in the form of lime stones, calcite, marble, ice land spar, dolomite, stalactite, stalagmite, gypsum and phosphate in the phosphoric rocks which are soluble in water [22]. Perhaps the higher mean concentrations of calcium obtained at all sampling areas are due to the fact that, calcium compounds are highly soluble in water and therefore are easily absorbed by the aquatic organisms. Iron is the 4th most abundant element in the earth's crust. In most cases, it exists as oxides which are highly insoluble in water as given by Nazzanin et al. 2014 [21]. Concentrations of iron in water bodies due to natural activities are quite low due to its low solubility in water; however, expansions of populations, rapid urbanizations and industrialization lead to various ecological problems in the ecosystems of most water bodies. Significant speciation, concentration and bioavailability of iron in water and sediments occur as a result of the anthropogenic activities [22]. This suggests that, apart from the natural activities such as precipitation, dust, as well as weathering of rocks and soils, the higher mean concentrations of iron recorded for samples from all fish markets, may be due to industrial discharges, domestic discharges and municipal wastewater treatment plants [4].

Zinc exists naturally in rocks, soil and water and in most cases as zinc sulphide (ZnS). Most of zinc compounds are water soluble, though; the metal itself is not [23]. The high concentrations of zinc recorded for samples from all fish markets, might be due to the fact that, most of zinc compounds are water soluble and hence are easily absorbed by aquatic organisms. Also natural activities such as weathering and abrasion of rocks as well as anthropogenic activities such as corrosion of zinc galvanized ships and boats, domestic and industrial discharges are the factors which might have caused elevated levels of zinc for samples from all fish markets [23].

The mean concentrations of copper and selenium were lower compared to those of the other essential elements analyzed in this study. Selenium occurs naturally in rocks; soil and water although; it's also associated with mining of coal, phosphates, as well as refinery and combustion of fossil fuels [24]. Also agricultural drain water, sewage slugs, fly of ash from coal-fired power plants are sources of selenium into the aquatic environments [25]. Industrial sources of copper into the aquatic environments include; wood production, iron and steel production, waste incinerations, coal combustion, oil and gasoline combustion. Also agricultural runoffs and domestic use of fertilizers also contributes to raise the levels of copper in the aquatic environments [26]. Since there was no evidence of elevated levels of lead (Pb) which is more associated with fossil fuels, it implies that, the levels of copper and selenium recorded at all fish markets, are not related to refinery and combustion of fossil fuels; rather, they might be related to sewage slugs, agricultural drain water, industrial discharges, domestic discharges and natural activities [26].

Furthermore, the results of this study indicate that, sardine fish from Kivukoni, Kunduchi and Bagamoyo fish markets are rich in essential elements Ca, Fe, Cu, Se and Zn. This implies that, they can be used as a good source of the essential elements for the coast communities, provided that; they are prevented from being polluted by heavy metals. Calcium is essential in muscle contraction, acolyte activation, building of strong bones and teeth, blood clotting, nerve impulse transmission, heart beat regulation and fluid balance within cells [20]. Iron is essential for almost all living organisms as it takes part in a wide range of metabolic processes such as oxygen transport, deoxyribonucleic acid (DNA) synthesis and electron transport. Iron can however form free radicals, thus; its concentration in blood must be in proper levels because, excessive amounts of iron can damage the tissues [21].

Zinc is an essential mineral for normal fetal growth and development as well as milk production during lactation [27]. Zinc deficiency triggers an array of health problems in children, many of which become chronic, such as weight loss, stunted growth, weakened resistance to infections and early deaths. In fact, zinc deficiency is linked to about 116,000 child deaths every year as given by Frank et.al.2015 [11]. Selenium is a major component of many enzymes and it plays important roles in ant oxidation, reproduction, muscle function and tumors prevention [28].

The analysis of the variances of the means (Turkey HSD) indicate that, samples from Kivukoni fish market had significantly higher ($p < 0.05$) mean concentrations of Ca, Cu, and Zn when compared to samples from Kunduchi fish market while samples from Bagamoyo fish market had significantly higher ($p < 0.05$) mean concentrations of Ca and Cu when compared to samples from Kunduchi fish market. On the hand, samples from Kunduchi fish market had significantly higher ($p < 0.05$) mean concentration of Se when compared to samples from Kivukoni and Bagamoyo fish markets. Since, there are many human activities around Kivukoni and Bagamoyo fish markets compared to Kunduchi fish market, these variations suggest that, apart from natural activities, human activities plays a significant role to rise the levels of Ca, Cu and Zn among the sampling markets. Furthermore, variations of the mean concentrations of the essential elements might indicate that, sardine fish sold at the three fish markets have different feeding areas and hence different diets [28].

3.3 Mean Concentrations of the Toxic Heavy Metals for the Three Fish Markets

The statistical package for social sciences (SPSS - Version 17) software was used to compute the mean concentrations of the toxic heavy metals for samples from each fish market. Tables **4** and **5** indicate the arithmetic means and geometric means of the concentrations of the toxic heavy metals for samples from each fish market.

Table 4 Arithmetic means of concentrations ± standard error of the mean (SEM) (µg/g) for the toxic heavy metals

ELEMENTS	FISH MARKETS		
	KIVUKONI (n = 10)	KUNDUCHI (n = 10)	BAGAMOYO (n = 10)
Aluminum (Al)	52.8 ± 3.6	105.4 ± 4.5	129.3 ± 6.7
Chromium (Cr)	2.0 ± 0.2	21.7 ± 0.4	27.2 ± 1.0
Nickel (Ni)	0.9 ± 0.1	0.3± 0.0	0.8 ± 0.1
Arsenic (As)	3.8 ± 0.1	7.2 ± 0.0	5.39± 0.1
Cadmium (Cd)	0. 6 ± 0.1	2.6 ± 0.1	0.7± 0.7
Lead (Pb)	BDL	BDL	BDL

BDL for Pb = 0.50 µg/g

Table 5 Geometric means of the concentrations ×/÷ standard deviation (SD) (μg/g) for the toxic heavy metals

ELEMENTS	FISH MARKETS		
	KIVUKONI (n = 10)	KUNDUCHI (n = 10)	BAGAMOYO (n = 10)
Aluminum (Al)	51.2 ×/÷ 11.4	102.7 ×/÷ 14.3	130.0 ×/÷ 21.3
Chromium (Cr)	2.1 ×/÷ 0.4	22.0 ×/÷ 1.4	27.3 ×/÷ 3.1
Nickel (Ni)	0.9 ×/÷ 0.2	0. 3 ×/÷ 0.7	0.7×/÷ 0.3
Arsenic (As)	3.8 ×/÷ 0.6	7.2 ×/÷ 0.1	5. 3 ×/÷ 0.2
Cadmium (Cd)	0.6×/÷ 1.0	2.6 ×/÷ 0.1	0.7×/÷ 0.2
Lead (Pb)	BDL	BDL	BDL

BDL for Pb = 0.50 μg/g

From the table 5, it can be seen that, aluminum recorded the highest mean concentration followed by arsenic for samples from all sampling areas. The mean concentrations of aluminum were (52.8 ± 33.6; 105.4 ± 4.5 and 129.3 ± 6.7) μg/g for samples from Kivukoni, Kunduchi and Bagamoyo fish markets respectively. Aluminium is the third most abundant element in the earth's crust and it occurs naturally in rocks, soil and water. It is not essential for life; however, aluminium compounds are widely used in various industrial applications or consumer products such as antacids, food additives and antiperspirants [29]. Apart from natural activities in rocks and soils, the high levels of aluminium for samples from all fish markets, might be related to coagulants used in water treatment process and drugs (medicines) such as antacids or antiperspirants which are brought to the ocean by rain water, municipal wastewater treatment plants as well as industrial and domestic discharges[30].

The mean concentrations of arsenic were (3.8 ± 0.1; 7.2 ± 0.0 and 5.3 ± 0.1) μg/g for samples from Kivukoni, Kunduchi and Bagamoyo fish markets respectively. It is reported that, arsenic concentrations are normally higher in marine fish compared to fresh water fish [30]. Arsenic in fish muscles is mainly found in organic form, which is less toxic compared to inorganic arsenic [31]. Chromium recorded the 3^{rd} higher concentrations after aluminium and arsenic. The mean concentrations of chromium were (2.0 ± 0.2; 21.8 ± 0.4 and 27.2 ± 1.0) μg/g for samples from Kivukoni, Kunduchi and Bagamoyo fish markets respectively. Rarely chromium occurs naturally in the earth's crust as an element (metal), but, in most cases it occurs in compound forms or ions in water [32]. Many chromium compounds are used in painting pigments. Almost all chemical laboratories (academic, research, industry) discharge considerable amounts of chromium into the environment every day [33]. This suggests that, natural activities and industrial discharges are the main sources of chromium for samples from all fish markets as indicated by Rumpa et. al. 2011 [33].

Cadmium recorded lower means concentrations for samples from all fish markets, compared to aluminium, arsenic and chromium. The mean concentrations of cadmium were (0.6 ± 0.0; 2.6 ± 0.1 and 0.7 ± 0.7) μg/g for Kivukoni, Kunduchi and Bagamoyo respectively. Cadmium occurs naturally in the earth's crust. It is vastly used in batteries, coating, plating and various industrial applications [34]. Cadmium from various industrial applications enters into air and binds with small particles which combine with water and soil, thereby, causing contamination of fish, animals and plants. Spills from hazardous waste sites and improper wastes disposal can cause cadmium leakages into the aquatic environments [35]. On the other hand, the mean concentrations of lead were below the detection limits of the spectrometer used in this study for samples from all fish markets. The minimum detection limit of the spectrometer was 0.50µg/g for lead. The mean concentrations of mercury were not included in this analysis due to the fact that, EDXRF is not suitable for determination of concentrations of mercury.

Analysis of the variances of the means (Turkey HSD)[28] for the toxic heavy metals indicate that, samples from Bagamoyo fish market had significantly higher ($p< 0.05$) mean concentrations of Al, As, Cd and Ni when compared to samples from Kivukoni. The samples from Kunduchi fish market had significantly higher ($p< 0.05$) mean concentration of Al, As and Cd when compared to samples from Kivukoni fish market. On the other hand, samples from Kivukoni fish market had significantly higher ($p < 0.05$) mean concentration of Ni when compared to samples from the other fish markets. Since Bagamoyo and Kunduchi fish markets are more close to human settlements compared to Kivukoni fish market, this suggests that, large percentages of the toxic heavy metals Al, As and Cd originates from domestic discharges and agricultural drain waters [28].

3.4 Correlations Analysis for the Toxic Heavy Metals

Spearman correlation tests were carried out to determine the nature, magnitude and directions of correlations among the toxic heavy metals. At Kivukoni fish market, a strong and a statistically significant correlation was recorded between arsenic and nickel ($r = 0.63$; $p = 0.05$). This correlation suggests that, arsenic and nickel originates from similar sources, probably municipal wastewater treatment plants, domestic and industrials discharges. Also, at this fish market, a moderately positive but not a statistically significant correlation was recorded between arsenic and chromium ($r = 0.37$; $p = 0.30$). This correlation suggests that, arsenic and chromium for samples from this fish market, originates from sources with weak similarities. Probably, large or less amounts of arsenic could originate from agricultural and domestic discharges while large or less amounts of chromium could originate from industrial discharges. Also some of these heavy metals might be brought to the ocean by inorganic and, or organic matters brought to the ocean by rain water and surface road run offs.

3.5 Correlations Analysis for the Essential Elements

Spearman correlation tests were carried out to determine the nature, magnitude and directions of correlations among the essential elements. At Kunduchi fish market, strong, positive but not statistically significant correlations were recorded between calcium and zinc ($r = 0.56$; $p = 0.095$) and between copper and zinc ($r = 0.59$; $p = 0.072$). At Kivukoni fish market, moderately positive but not statistically significant correlations were recorded between copper and iron ($r = 0.33$; $p = 0.33$) and between copper and zinc ($r = 0.44$; $p = 0.19$). Furthermore, at Bagamoyo fish market, moderately positive but not statistically significant correlations were recorded between calcium and selenium ($r = 0.32$; $p = 0.36$) and between calcium and zinc ($r = 0.38$; $p = 0.28$). These correlations suggests that, these essential elements do not originate from common sources, rather, they originate from diversified sources, each source contributing more or less to the levels of the essential elements. These sources could include natural activities such as seafloor and bedrock dredging, soil erosions, weathering and rocks disintegrations. Also some essential elements could be related to organic matters brought to the ocean by agricultural drain water; surface road run offs and rain water.

3.6 Comparison of the mean Concentrations of the Essential Elements to the Maximum Tolerable Levels (MTLs) Sets by International Organizations

Essential element can have adverse health effects when they exceed the required levels in the body [21,36]. The table **6** indicates the mean concentrations of the essential elements with their respective (MTLs) set by international organizations.

Table 6 Mean concentrations of the essential elements with their (MTLs) set by international organizations

FISH MARKETS	CHEMICAL SYMBOL	ATOMIC NUMBER	ELEMENT	MEAN CONC. (µg/g)	MTLs (µg/g)	REFFERENCES
KIVUKONI	Ca	20	Calcium	37,981.88	130,000	[37]
	Fe	26	Iron	149.99	200	[38]
	Cu	29	Copper	4.02	30	[39]
	Zn	30	Zinc	159.84	40	[39]
	Se	34	Selenium	1.73	0.75	[40]
KUNDUCHI	Ca	20	Calcium	303,800.50	130,000	[37]
	Fe	26	Iron	211.91	200	[38]
	Cu	29	Copper	2.57	30	[39]
	Zn	30	Zinc	105.06	40	[39]
	Se	34	Selenium	2.19	0.75	[40]
BAGAMOYO	Ca	20	Calcium	38,310.85	130,000	[37]
	Fe	26	Iron	234.78	200	[38]
	Cu	29	Copper	3.45	30	[39]
	Zn	30	Zinc	130.96	40	[39]
	Se	34	Selenium	1.96	0.75	[40]

From the table above, it can be seen that, the mean concentrations of zinc and selenium are higher than their respective (MTLs) set by various international organizations. The mean concentrations of zinc for samples from all fish markets are at least 3 times higher than the recommended MTL for zinc (40µg/g) according to FAO, [39]. The mean concentration of selenium is 2times higher than its MTL (0.75µg/g) according to COMA, [40]. On the other hand, the mean concentrations of iron for samples from Kunduchi and Bagamoyo fish markets are just above their respective MTL (200µg/g) according to FAO/WHO, [39]. The mean concentrations of iron for samples from Kivukoni fish market are just below its MTL of 200µg/g according to FAO/WHO, [38]. The implication of these findings is that, diets must be properly controlled due to the fact that, excessive amounts of essential elements can have adverse health effects.

3.7 Comparison of the mean concentrations of the toxic heavy metals to the maximum tolerable levels (MTLs) sets by international organizations

Bearing in mind a wide array of adverse health effects that can arise from heavy metals pollution, this study has compared the mean concentrations of the toxic heavy metals to MTLs set by international organizations. Table **7** shows the mean concentrations of the toxic heavy metals with their respective MTLs set by international organizations.

Table 7 Mean concentrations of the toxic heavy metals with their (MTLs) set by international organizations

FISH MARKETS	CHEMICAL SYMBOL	ATOMIC NUMBER	ELEMENT	MEAN CONC. (µg/g)	MTLs (µg/g)	REFFERENCES
KIVUKONI	Al	13	Aluminum	52.75	100	[41]
	Cr	24	Chromium	2.09	0.15	[15]
	Ni	28	Nickel	0.90	2.00	[42]
	As	33	Arsenic	3.79	0.50	[36]
	Cd	48	Cadmium	0.58	0.5	[36]
	Pb	82	Lead	BDL	2.00	[43]
KUNDUCHI	Al	13	Aluminium	105.37	100	[41]
	Cr	24	Chromium	21.71	0.15	[15]
	Ni	28	Nickel	0.27	2.00	[42]
	As	33	Arsenic	7.22	0.50	[36]
	Cd	48	Cadmium	2.64	0.50	[36]
	Pb	82	Lead	BDL	2.00	[43]
BAGAMOYO	Al	13	Aluminium	129.33	100	[41]
	Cr	24	Chromium	27.15	0.15	[15]
	Ni	28	Nickel	0.84	2.00	[42]
	As	33	Arsenic	5.29	0.50	[36]
	Cd	48	Cadmium	0.70	0.50	[36]
	Pb	82	Lead	BDL	2.00	[43]

BDL for Pb = 0.50 µg/g

From the table 7, one can see that, the mean concentrations of arsenic and cadmium are higher than their respective MTL of (0.50µg/g) according to [37] for samples from all fish markets. The mean concentrations of arsenic are more at least 7times greater than their respective MTL for samples from all fish markets. The mean concentrations of cadmium are 5times greater than their MTL for samples from Kunduchi fish market and are just above their MTL for samples from Kivukoni and Bagamoyo fish markets. The mean concentrations of aluminium for samples from Kunduchi and Bagamoyo fish markets are just above their MTL, while, the mean concentration of aluminium for samples from Kivukoni fish market are below their MTL of (100µg/g) according to [41]. Inorganic arsenic is very toxic even in low concentrations. At higher concentrations it can cause infertility, heart disruptions, brain damage and ultimate death. Actually inorganic arsenic is classified as a human carcinogen [3]. Aluminium is a toxic heavy metal with no beneficial effects in the human body. When ingested, it stays in the body with a biological half life of 50 years. Furthermore, cadmium is classified as a human carcinogen [18,34]. When ingested, cadmium is efficiently retained in the kidney and liver with a biological half life of 30 years [18].

These findings suggest that, a further detailed research is needed to determine the factors which caused elevated levels of arsenic; cadmium and aluminium for samples from these fish markets and how to prevent pollutions of the sea foods by heavy metals in order avoid the adverse health effects to consumers of sea foods.

3.8 Comparison of the mean concentrations of the analyzed elements from different parts of the world

The mean concentrations of the elements analyzed in this study were compared to the mean concentrations of the same elements in samples of sardine fish collected from the different parts of the world. Table **8** shows the summary of this comparison.

Table 8 Comparisons of the mean concentrations (mg/kg) of the analyzed elements from different parts of the world

SAMPLING AREA	ANALYZED ELEMENTS											REFFERENCE
	Al	Ca	Cr	Fe	Ni	Cu	Zn	As	Se	Cd	Pb	
KIVUKONI	52.75	37,981.88	2.01	149.99	0.92	4.02	159.84	3.79	1.73	0.58	BDL	This study
KUNDUCHI	105.37	3038.45	21.71	211.71	0.27	2.57	105.06	7.20	2.19	2.64	BDL	This study
BAGAMOYO	129.33	3831.85	27.15	234.78	0.84	3.45	130.96	5.29	1.96	0.70	BDL	This study
ZANZIBAR PORT	-	-	22.30	311.90	86.80	6.6	-	-	-	BDL	1.70	[19]
ABUJA	-	-	-	3.99	-	0.311	1.89	-	-	-	BDL	[44]

FUKUSHIMA	-	-	0.60	-	0.1	9.6	130	7.5	6.6	0.01	-	[31]
EGYPT	-	-	0.22	-	-	-	2.37	-	-	0.048	-	[45]
TURKEY	-	-	22.16	-	-	23.27	-	-	0.01	-	0.20	[46]

BDL for Pb = 0.50 µg/g

As for the toxic heavy metals, it can be seen from the above table that, the mean concentrations of cadmium (Cd) for samples from Kivukoni, Kunduchi and Bagamoyo fish markets are higher than the values reported in the literatures reviewed in this study. Furthermore, samples from Bagamoyo fish market had higher mean concentration of chromium (Cr) compared to the values reported in different literatures reviewed in this study. In general, the comparisons of the mean concentrations of the toxic heavy metals were in the order;

Cr: Bagamoyo > Zanzibar port > Kunduchi > Kivukoni > Fukushima > Egypt [16,19,29,44,45]
As: Fukushima > Kunduchi > Bagamoyo > Kivukoni [16,19]
Ni: Zanzibar port > Kivukoni > Bagamoyo > Kunduchi > Fukushima [16,19,29]
Cd: Kunduchi > Bagamoyo > Kivukoni > (Turkey and Fukushima) > Egypt [29,44,45]

The toxic heavy metal (Pb) have not been involved in this comparison because, its concentrations were below the detection limits of the spectrometer used in this study. On the other hand, the mean concentrations of aluminium (Al) were not reported in the literatures reviewed in this study.

As for the essential elements, it can be seen from the table above that, samples from Kivukoni fish market had higher mean concentrations of zinc compared to the values reported in the literatures reviewed in this study. Generally, the mean concentrations of the essential elements were in the order:

Fe: Zanzibar port > Bagamoyo > Kunduchi > Kivukoni > Abuja > Turkey[16,19,44,45]
Zn: Kivukoni > Bagamoyo > Fukushima > Kunduchi > Turkey > Egypt > Abuja [44,45,46]

Se: Fukushima > Kunduchi > Bagamoyo > Kivukoni [29]

The essential element (Ca) was not reported in the literatures reviewed in this study and hence was not covered in this comparison.

4. CONCLUSION

This study has assessed the concentrations of the essential elements (Ca, Cu, Fe, Se and Zn) as well as the toxic heavy metals (Al, As, Cd, Cr, Ni and Pb) in samples of sardine fish collected from Kivukoni, Kunduchi and Bagamoyo fish markets. The mean concentrations of the analyzed elements were compared to their respective maximum tolerable levels (MTLs) set by international organizations. The mean concentrations of the essential elements (Ca and Cu) were found to be lower than their respective MTLs while the mean concentrations of Zn were higher than their MTLs for samples from all fish markets. The mean concentrations of Fe and Se were higher than their respective MTLs for samples from Kunduchi and Bagamoyo fish markets. The respective MTLs for these essential elements were; 130,000 µg/g (for Ca), 200 µg/g (for Fe), 30 µg/g (for Cu), 0.75 µg/g (for Se), and 40 µg/g (for Zn) according to FAO/WHO [38], WHO [15] , COMA [40] and FAO/WHO [37]

Zinc (Zn) and Selenium (Se) occurs naturally in rocks, soil and water due to natural activities such as weathering and abrasion of rocks [23,35]. Most zinc compounds are soluble in water, though, the metal itself is not [23]. The elevated levels of zinc recorded for samples from all fish markets may be due to the fact that, most of zinc compounds are soluble in water and hence, are easily ingested by marine organisms. Also elevated levels of zinc may be associated to anthropogenic activities such as corrosions of zinc galvanized ships and boats, painting of ships and boats, improper damping of zinc containing compounds such as fertilizers and batteries as well as domestic and industrial discharges.

Selenium occurs naturally due to erosion of rocks containing salinities and serenades which are associated with sulphide minerals. Its abundance in the earth's crust is very low, estimated as 0.05µg/kg to 0.1µg/kg [48]. Since, the abundance of selenium in the earth's crust is very low, large percentages of selenium are brought to the ocean by glaciations, floods, agricultural drain waters, industrial discharges and domestic discharges [47].

The mean concentrations of the toxic heavy metals arsenic and cadmium for samples from all fish markets were found to be higher than their respective MTL of 0.50µg/g[36]. Arsenic in marine fish is normally in higher concentrations than in fresh water fish. Arsenic in fish is mostly found in organic form which is less toxic compared to inorganic arsenic [31]. Combinations of natural activities such as weathering, volcanic eruptions and biological activities are the main sources of arsenic into the aquatic environments [49]. Also arsenic is brought into the aquatic environments by floods, domestic and industrial sewages and from human activities such as mining, agriculture (use of arsenic based pesticides) and improper damping of arsenic based compounds [49]. Cadmium is widely used in batteries, coating, and plating [33]. Cadmium levels in the aquatic environments are raised mainly due spills from hazardous waste sites and industrial discharges [34].

The mean concentration of aluminium for samples from Kunduchi and Bagamoyo fish markets were found to be higher than its respective MTL of 100µg/g according to CFS 2009. Aluminium is the third most abundant element in the earth's crust and it occurs naturally in rocks, soil and water. Apart from natural activities, aluminium is brought into the aquatic environments by surface road run offs, domestic and industrial discharges carrying chemicals such as antacids or antiperspirants and coagulants used in water treatment processes [29]. On the other hand, the concentrations lead was found to be below the detection limits of 0.50µg/g for the spectrometer used in this study.

It can be fairly concluded that, sardine fish from Kivukoni, Kunduchi and Bagamoyo fish markets are rich in essential elements Ca, Cu, Fe, Se and Zn. The sardine fish therefore can contribute significantly to the food and nutritional security of the coast inhabitants provided that, measures are taken to prevent them from being polluted by heavy metals.

REFERENCES

1. Mbuthia JW, Ogendi GM, Moturi WN, Koskey JC and Maina GM 2014 Heavy Metals Concentrations in Tissues of Commercially Exploited Fish (Oereochromis Niloticus Baringoensis, Aethiopicus, and Clarias Gariepinus) from lake Baringo Kenya. *Journal of Enviromental Science Taxicology and Food Technology* **8:** 55 – 63

2. Duruibe JO, Ogwuegbu MOC and Egwugw JN 2007 Heavy metals pollution and human bio toxic effects. *International Journal of physical sciences* **2(5):**112-118

3. Jarup L 2003 Hazards of heavy metals contamination. British Medical Bulletin **68:** 167 - 182

4. Arif Tasleem Jan, Mudsser Azam, Kehkashan Siddiqui, Arif Ali, Inho Choi and Qazi Mohd Rizwanul Hag 2015 Heavy Metals and Human Health: Mechanistic Insight into Toxicity and Counter Defense System of Antioxidants. *Molecular Sciences* **16:** 29592 - 29630

5. Hellawell, J.M. Ed., 1986. Biological Indicators of Freshwater Pollution and Environmental management. Elsevier Applied SciencePublishers Ltd., London and New York, pp: 546.

6. Machiwa JF 2010 Coastal Marine Pollution in Dar es Salaam (Tanzania) relative to Recommended Environmental Quality Targets for Western Indian Ocean. *WIOMSA* **9:** 17 - 30

7. Al –Weher SM 2008 Levels of heavy Metals Cd, Cu, and Zn in three Fish species collected from the north Jordan Valley. *Jordan Journal of biological sciences* **1:** 4-46

8. Muiruri JM, Nyambaka HN and Nawiri MP 2013 Heavy metals in water and tilapia fish from Athi – Galana – Sabaki tributaries, Kenya. *International food research journal* **20 (2):** 891- 896

9. Falah S. Al- Fartusie, Saja N. Mohssan 2017 Essential Trace Elements and Their Vital Roles in Human Body, *Indian Journal of Advances in Chemical Sciences* **5(3):** 127 – 136

10. Haldimann M Alt A, Blank A and Blondeau 2004 Iodine contents of food groups Journal of food composition and analysis **18:** 461 – 471

11. Frank T. Wieringa, Marjoleine A. Dijkhuzen, Marion Fiorentino, Arnauld Laillou and Jacques Berger 2015 Determination of zinc status in humans: Which indicator should we use? *Nutrients* 7: 3252 - 3263

12. Moeniba Isaacs 2016 The humble sardines (small pelagic): Fish as food or fodder. Agriculture and food security **5:** 2 - 14

13. Ali M.H.H and Amaal M.A 2005 “Studies of some heavy metals in water, sediments, fish and fish farms in El- Fayoum Province, Egypt” *Egyptian Journal of Aquatic Research 31(2): 261 - 273*

14. Ntarisa AV 2013 Assessment of the Impact of North Mara Gold Mine Activities on Heavy Metals Concentrations in River Mara Fish Using EDXRF Spectrometry, Msc thesis, Physics Department, University of Dar es Salaam

15. 15 WHO (World Health Organization) 1985 “Guidelines for drinking water quality” 3 Geneva, Switzerland

16. Koleleni Y A and Haji O 2014 Determination of the Concentration of Heavy Metals in Fish From Sea Port of Zanzibar by Energy Dispersive X-ray Fluorescence (EDXRF). *Tanzania Journal of Sciences* **(40):** 80-89

17. Tanzania Bureau of Standards(TBS), 2007, Soil quality, limits for soil contaminants in habitat and agriculture, Dar es Salaam TBS:972.

18. Lugendo I, Mohammed NK, Mussa LM and Spyrou NM 2012 Assessment of the Lake Gendambi Salt for Trace Elements and Toxic Heavy Metals by Energy Dispersive X-rays Fluorescence Spectrometry. *Radio analytical and Nuclear Chemistry* **294(3):** 9 - 12

19. Koleleni Y I and Haji O 2016 Analysis of Heavy Metals in the Shellfish from the Neighborhoods of the Sea Port of Zanzibar. *Merit Research Journals* **4(3):** 016 - 024

20. Piste P, Sayaji D and Avinash M 2015 Calcium and its role in human body. *International Journal of research in pharmaceutical and biosciences* **4(2):** 659 – 668

21. Nazanin A, Hurrel R and Kelishadi R 2014 Review on Iron and its importance for human health. *Journal of Research in Medical Science* **19(2):** 164 - 174

22. Xing Wei and Guihua Liu 2011 Iron Biochemistry and its Environmental Impacts in Freshwater Lakes, *Fresenius Environmental Bulletin* 20: 1339 - 1345

23. Brita T. Muyssen A, Krel A. Schamphalaere C D, Colin R. Janssen C 2006 Mechanism of chronic waterborne Zn toxicity in Daphnia magna. *Aquatic Toxicology* **77:** 393 - 401

24. Hamilton SJ. 2004 Review of selenium toxicity in the aquatic food chain. *Science of the Total Environment* **326:** 1 - 31

25. Chapman PM, Adams WJ, Brook Mh, Delos CG, Luona SN, Maher WA, Ohlendorf HM, Presser TS, Shaw DP 2009 Ecological assessment of selenium in the aquatic environment : Summary of a SETAC Pellston Workshop. Pensacola FL (USA) : Society of Environmental Toxicology and Chemistry (SETAC)

26. Willis B E. and Bishop W M. 2016 Understand Fate and Effects of Copper Pesticides in Aquatic Systems. *Journal of Geosciences and Environmental Protection* **4:** 37 - 42

27. Salgueiro M J, Marcella BS, Zubillaga B, Lysionek A E, Caro R A, Weill R and Boccio J R 2002 The Role of Zinc in the Growth and Development of Children. *Nutrition* 18: 510 - 519

28. Mehdi Y, Hornick JL, Istasse L and Dufrasne I 2013 Selenium in the Environment, Metabolism and Involvement in Body Functions. *Molecules* **18:** 3292 - 3311

29. Kawahara M, Konoha K, Nagata T and Sadakane Y 2007 Aluminum and Human Health: Its intake, bioavailability and neurotoxicity. Biomedical Research of Trace Elements **18(3):** 211 - 220

30. Schaeffer R, A.K Francesconi, N. Kienzi, C. Soeroes, P.Fodor, L. Varadi, R. Raml, W. Goessler and D Kuchnelt 2006 Arsenic speciation in fresh water organisms from the Danube in Hungary. Talanta **69:** 856 - 865

31. Hayase D, Horai S, Isobe T, Miller T W, Takahashi S, Omari K and Tanabe S 2009 Monitoring Trace Elements in Coastal Waters Using Sardine as Bio indicator. *Interdisciplinary Studies on Environmental Chemistry – Environmental Research in Asia* **2:** 167 - 175

32. Krejpcio Z 2001 Essentiality of Chromium for Human Nutrition and Health *Polish Journal of Environmental Studies* **10:** 399 - 304

33. Rumpa S, Nandi R and Saha B 2011 Sources and Toxicity of Hexavalent Chromium, *Journal of coordination chemistry* **64:** 1782 – 1806

34. Sharma H, Rawal N and Mathew B B 2015 The characteristics, toxicity and effects of cadmium. *Research Gate* **2:**11 - 17

35. Olszowsk T, Bosiak I B, Gutowska I and Chlubek D 2012 Pro – inflammatory properties of cadmium, *Biochemical Polonica* **59:** 475 - 482

36. Laura M, Lather R and Hajo H 2010 The Essential Toxin: Impact of Zinc on Human Health. *International Journal of Environmental Research and Public Health* **7:** 1342 - 1365

37. FAO/WHO 2002 Human Vitamin and Mineral Requirements, *Report of joint FAO/WHO expert consultation, FAO, Rome.*

38. FAO/WHO 1983 Compilation of legal limits for hazardous substances in fish and fishery products, FAO Fishery Circular **464,** 5 - 10

39. FAO/WHO.1984 Contaminants. In Codex Alimentarius, Vol. XVII,Edition , FAO/WHO. Contaminants.Codex Alimentarius Commission, Rome;.

40. COMA 1998 Statement from the Committee on Medical Aspects of Food and Nutrition Policy on Selenium, *Food Safety Information Bulletin no.39 MAFF: DH 1998*

41. Center for food safety (CFS) 2009 Guidelines on the use of aluminum containing food, Food and Environmental Hygiene Department, The Government Logistics Department, Hong Kong

42. COT secretariat 2003 Nickel leaching from kettle elements into boiled water. Committee on toxicity of chemicals in food consumer products and environment http://www.cot. Food grades. Gov. UK, Accessed on 19 August 2017

43. Codex Alimentarius Commission 2006 Codex standard: Standard for food grade salt. CXSTAN 150 – Amend 3 – 2006. Codex Alimatarius Commission, Joint FAO/WHO Food standard Program, Rome

44. Igwemmar N.C, S.A Kolawole, S.O Odunoku 2013 Heavy Metals Concentration in Fish Species Sold in Gwagwalada Market, Abuja. *International Journal of Sciences and Research* **2(11):** 7 - 9

45. Eldin A, Morshdy MA, Hafez AEE, Darwish WS and Tharwat AE 2013 Heavy Metal Residuals in Canned Fishes in Egypt. *The Japanese Journal of Veterinary Research* **61**: 4 – 7

46. Mol S 2010 Levels of Heavy Metals in Canned Bonito Sardines and Mackerel, Produced in Turkey. *Biological Trace Elements Research* **143(2):** 74 - 82

47. Lopes G, Avila F W, Guilherme L R G 2017 Selenium behavior in the soil environment and its implication for human health. *Cienciae Agrotecnologia*. **41(6):** 605 - 615

48. Mahimairaja S, Bolan NS, Adriano DC and Robinson B 2005 Arsenic contamination and its risk management in complex environmental settings. *Advances in agronomy* **86:** 1 - 65

49. Brett R, Brent C, Nanth SB, Santiago M, Marc G, Christopher M, Monica M, Carlo VD and Georgina M 2004 Arsenic in the New Zealand, *Environment Super Soil:* **1:** 1 – 8