INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS OF CONCENTRATIONS OF VANADIUM, MANGANESE, ARSENIC, MERCURY, CADMIUM AND ALUMINIUM IN MUSCLE TISSUES OF FOUR FISH SPECIES FROM THE WEIJA LAKE IN GHANA

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Abstract

The Weija Lake, formed from the Densu River, presently one of the most polluted rivers in Ghana, is a domestic source of Tilapia and Catfish. This study determined the concentration of V, Mn, As, Hg, Cd, and Al in the muscles of *Tilapia zillii*, *Clarias gariepinus*, *Sarotherodon galilea*, and *Oreochromis niloticus* from the Weija Lake using Instrumental Neutron Activation Analysis. The relationships between metal concentrations in fish muscles on one hand, and fish length and weight, condition factor (K_f), and metal concentrations in the water on the other hand were also determined. All four fish species showed negative allometric growth. K_f correlated negatively with V, Mn and Al concentrations in *T. zilli*, and positively with V, Mn and Al concentrations in *C. gariepinus, O. niloticus* and *S. galilea*. Fish lengths and weights correlated negatively with V, Mn and Al concentrations in fish, with no significant correlation with As, Hg and Cd levels. Metal concentrations in water correlated positively with concentrations in fish. The Estimated Average Daily Doses from consumption of fish from the lake were 6113µg - 33778.5µg V, 114,098.2µg - 530,371µg Al, and 34,383.6µg - 129492µg Mn respectively, and these exceeded the recommended ADIs of <1800µg V, 142.8µg Al, and 11,000µg Mn respectively. The results indicate safe levels of Arsenic, Mercury, and Cadmium, and unsafe levels of Vanadium, Aluminium and Manganese in *T. zillii, C. gariepinus, S. galilea*, and *O. niloticus* from the lake.

Keywords: Weija Lake, Fish, Metals, Pollution, Instrumental Neutron Activation Analysis

INTRODUCTION:

In many countries, cities and town especially in the developing world, water bodies are increasingly serving as receptacles of both domestic and industrial waste. In Ghana pollution of the water bodies has led to shortages of treated water across the country (GhanaWeb, 2013). The cost of treating polluted water is too expensive that it has caused the Ghana Water Company Limited (GWCL) to shut down its treatment plants in many mining areas. It is cheaper for the GWCL to drill boreholes to supply water to the affected communities. The GWCL has closed the Odaso plant on the Oda River supplying water to parts of Obuasi, the Kyebi plant on the Birim River, and the plants on the Offin River serving some parts of the Central Region (Government of Ghana Official Portal, 2014).

The Weija Lake in Ghana provides hydroelectric power and potable water supply to residents in Accra East and West. According to Dadzie, (2012) the Densu River from which the Weija Lake is formed, is presently one of the most polluted rivers in the country. The main source of pollution of the Densu is human, animal and agricultural activities (Karikari and Ansa-Asare, 2006) through the discharge of untreated solid and liquid domestic and industrial wastes, leaching of agro chemicals from large commercial farms, and the use of chemicals and rotten tree trunks for fishing (Paintsil and Abrahams, 2008).

Two major landfill sites at Oblogo and Mallam State Construction Company (SCC) in the Ga South Municipal Assembly were used as dumping sites by the Accra Municipal Authority for six and seven years respectively (AMA, 2011). During operation, the Oblogo site alone handled an average of 1,250 tonnes of solid waste daily (Osei *et al*., 2011). Leachate from the landfill sites flow down a slope into a wetland through which the Densu River passes and finally ends up in the lake (AllAfrica, 2011). At both upstream and downstream of the landfill, sites, water from the Densu River is used by the local community for domestic purposes. The Weija dam as well as the water treatment plant are located upstream of the landfill sites (Osei *et al*., 2011). Even though the two landfill sites are now decommissioned, there is continuing contamination of the River Densu by leachates from the decommissioned waste dumps (Dadzie, 2012) and this can severely damage the water quality of the lake (James, 1977). The pollution of the lake is compounded further by several agricultural, industrial and commercial activities in the Weija vicinity (Awuku - Apaw, 2011).

Currently, only four fish species, *Tilapia zillii, Clarias gariepinus, Sarotherodon galilea*, and *Oreochromis niloticus* are caught in the Weija Lake by artisanal fishermen, and these have over time shrunk in size (The Ghanaian Chronicle, 2011). The fishes which are in very high demand in Ghana (Antwi - Asare and Abbey, 2011) are main protein sources especially for Ghanaians living along the coast (Rao *et al*, 2012).

Fish species living in polluted waters tend to accumulate heavy metals in their tissues (Jezierska and Witeska, 2006) and often serve as significant indicator for assessing the impact of metal pollution in freshwater systems. The measuring of bioaccumulation of contaminants in fish tissue can be used to monitor water pollution (US EPA, 2012) and to assess the health risks associated with the consumption of the fish from these waterbodies (Lasheen *et al*, 2012). Studies by Yi and Zhang (2012) showed positive relationships between fish sizes and metal levels in *C. gariepinus* in the Yangtze River.

This study therefore determined metal (V, Mn, As, Hg, Cd, and Al) concentrations in the muscle tissue of four fish species (*T. zillii, O. niloticus, S. galilea and C. gariepinus*) from the Weija Lake in Ghana. Also, the relationships between fish size (length and weight), condition factor, bioaccumulation factor, and metal concentrations were investigated by linear regression analysis. The estimated average daily intake of the selected metals were calculated and compared to internationally recommended values of safety.

METHODOLOGY

Study area

The Weija Lake (Figure 1) is located at coordinates $5^{o}34'44.73''$N and $0^{o}21'40.94''$W in the Ga South Municipality of the Greater Accra Region of Ghana. It covers an area of about 9,000 square hectares. It was formed by damming the Densu River at Weija in 1977 to provide hydroelectric power and potable water supply to residents in Accra East and West. The lake has a depth ranging from one to seven metres.

Water samples

Water sampling and analysis were done according to APHA (2005). Water samples were collected from six points downstream on the Lake on 25th August, 2014. The researcher was transported to the sampling points in a canoe by a fishermen. Water samples were collected directly into clean acid washed Teflon bottles and transported to the laboratory, where they were prepared for Neutron Activation Analysis.

The water samples were shaken in their containers to obtain homogenous samples. With the aid of a micropipette, 500 µl of each water sample was transferred into a small cylindrical polyethylene vial of diameter 1.2 cm and height 2.35 cm. Each vial was heat-sealed with a soldering rod. Each vial was put into a bigger polyethylene vial of diameter 1.6 cm and height 5.5 cm (rabbit capsule). The rabbit capsule was also heat-sealed with a soldering rod for irradiation.

Figure 1. Map showing the Weija Lake, sampling area (●) and fish landing site (★)

Fish samples

Twenty four freshly caught fish samples made up of six samples each of four species of fish *Tilapia zillii* (red belly tilapia), *Clarias gariepinus* (African *C. gariepinus*), *Sarotherodon galilaea* (Tilapia galilaea), *and Oreochromis niloticus* (Nile tilapia) were purchased from fishermen at the landing site at Manhean near Galilee, a fishing community along the Weija Lake on 25th August, 2014. The samples were brought to the laboratory on crushed ice blocks in an ice box. The fish samples were washed several times with distilled and deionised water.

The total length (cm) of each sample was measured in a straight line from the tip of the snout to the tip of the longer lobe of the caudal fin, with the lobes compressed along the midline. The weight (g) of each sample was measured with an Explorer Pro weighing scale (Model EP2102C), and then stored in a deep-freezer at -20^{o}C prior to analysis.

Preparation of fish samples for Neutron Activation Analysis

Fish samples were removed from the freezer and rinsed several times with de-ionised water and allowed to thaw. Samples were gutted with a stainless steel knife and the intestines, scales, head, tail, fins and bones removed. The samples were cut into pieces and freeze dried in a freeze dryer (CHRiST LMC-1, Germany) for 72 h. Samples were then homogenized in a Waring Blender (8011ES, HGB2WTS3) to obtain dry fish powder. Two 200 mg portions of the dry fish powder were weighed as replicates for each sample and each wrapped in a transparent polyethylene film and further encapsulated in 7 ml polyethylene irradiation vials. The vials were heat-sealed for irradiation.

Neutron activation analysis (NAA)

Samples were irradiated in the Ghana Research Reactor (GHARR-1) at the Ghana Atomic Energy Commission (GAEC), operating at a power of 15 KW at a neutron thermal flux of 1 x 10^{11} ncm^{2} S^{-1}. Samples were transferred into irradiation sites via a pneumatic transfer system at a pressure of 60 psi.

Two separate irradiations were performed based on the elements of interest and on the half-life of the radionuclide. Two minutes and one hour irradiation times were used for short lived radionuclide(s) and medium lived radionuclide(s) respectively. Certified IAEA reference material (IAEA-407) for fish tissue (IAEA, 2003) was irradiated the same way as the samples and used to calibrate and validate the method.

Counting of irradiated samples

Radioactivity measurement of induced radionuclide was performed by a PC-based γ-ray spectrometry, which consisted of an N-type HpGe detector (coaxial type) coupled to a computer based multi-channel analyzer (MCA) via electronic modules. The energy resolution of the detector is 1.8keV at a γ-ray energy of 1332keV of ^{60}Co. The data acquisition and identification of γ-rays of product radionuclide were identified by their γ-ray energies via ORTEC MAESTRO-32. Quantitative analysis was done via relative comparator method. The peak area determinations, processing and concentration calculation were done by multipurpose γ-ray spectrum analysis software; winSPAN-2010 version 2.10. Nuclear data used for Al, Mn and V are shown in Table 1.

Table 1. Irradiation and counting scheme

Element	Isotopes	Half – Life	Gamma Ray Energies (keV)	Irradiation times	Counting time
Al	^{28}Al	2.24 min	1778.9	120 s	600 s
Mn	^{56}Mn	2.58 h	846.7, 1810.7, 2112	120 s	600 s
V	^{52}V	3.76 min	1434.1	120 s	600 s

However, because of the low concentrations of As, Cd and Hg, the sensitivity method was used for their quantification. This required a separate standard solution of As, Cd and Hg. The net counts under the full energy peak of both samples and standards were then integrated manually from the Ortec Maestro software.

The Length - Weight relationship

The relationship between the length and weight of fish is $W=aL^b$
Where *W* is observed fish weight,
L is observed fish length
A plot of *Log W* was made against *Log L*
a and *b* were estimated from the plot
Where *a* was the intercept and *b* the slope
Values of the exponent b was used to provide information on fish growth (Sangun *et al*, 2007).
When b = 3, increase in weight was isometric.
When b ≠ 3, increase in weight was allometric
Allometry was positive when b > 3, and negative when b < 3

Condition Factor (K_f)

The condition factor was calculated as $K_f = 100W/L^3$
Where *W* is the weight of the fish in grams, and
L is the total length of the fish in centimeters (CDFO, 2004; 1983; Tacon *et al*, 1989).

The condition factor was used to compare the condition, fatness, and well-being of the fish, based on the assumption that the heavier fish of a given length were in better condition (Froese, 2006), and for the comparison of K_f among the samples to be valid all the fish samples were collected from the same water and on the same date (Williams, 2000).

Calculation of estimated average daily intake (µg/g) of metals

Daily intake of heavy metals from fish = A × B
Where
A - Average quantity of fish consumed per individual per day
B - Average concentration of metal in studied fish species

Statistical analysis

SPSS for windows (version 16.0) and Microsoft Excel was used to perform the statistical analysis and tests. The paired t-test was used to make comparisons between any two groups. A probability value of $P < 0.05$ was considered as statistically significant.

RESULTS AND DISCUSSIONS

The concentrations (mg/kg) of Mg, V, Al and Mn obtained for IAEA reference material (IAEA-407) for fish tissue in this study agreed within the limits of experimental error with reported values (IAEA, 2003). The values obtained in this study were in most cases within 0.5 - 5% deviation of the reported values (Table 2).

This showed the accuracy and reliability of the NAA method for determining the concentrations of Mg, V, Al and Mn.

Table 2. Comparison of concentrations (mg/kg) of Mg, V, Al and Mn obtained in this study to reported values for IAEA reference material (IAEA-407) for fish tissue

Elements	This Work	IAEA-407	Standard Deviation	Percent deviation	95% Confidence Interval (mg kg^{-1}) for IAEA-407
Mg	2.82	2.72	0.07	3.55%	2.58 – 2.86
V	1.36	1.43	0.05	4.90%	1.34 – 1.52
Al	13.4	13.8	0.28	2.90%	12.4 – 15.2
Mn	3.73	3.52	0.15	5.63%	3.44 – 3.60

Weights and lengths of the fish species

The length of fish varied significantly among the species ($p<0.05$) with the *C. gariepinus* having the longest mean length of (31.7 ± 12.2) cm, and the *Tilapia zillii* the shortest mean length of (11.7 ± 1.4) cm (Figure 2). There were also significant differences ($p<0.05$) in the weight of the four fish species with *C. gariepinus* having the highest mean weight of (207.2 ± 27.7) g, and the Tilapia zillii the lowest mean weight of (39.2 ± 12.1) g (Figure 3). A negative allometric growth pattern was observed in all four fish species meaning that the lengths of the fish increased relatively slower compared to the weights (Shingleton, 2010) (Table 3).

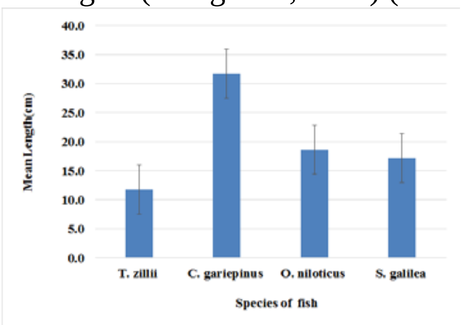

Figure 2 Mean lengths (cm) of samples of four species of fish from the Weija Lake, Ghana

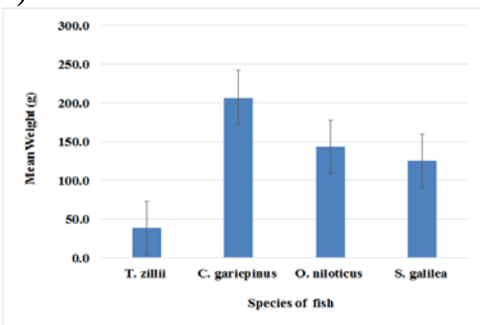

Figure 3 Mean weights (g) of samples of four species of fish from the Weija Lake, Ghana

Table 3. Relationship between the lengths and weights of four fish species from the Weija Lake, Ghana

	Slope (b) (Relative weight – length increase)	Intercept (Length across all body sizes)
Tilapia zillii	1.5202	0.0154
C. gariepinus	2.0436	0.6296
O. niloticus	2.1077	0.9933
S. galilea	1.9119	0.8459

Fishes with values of b closer to 3, or allometric coefficient (α = b/3) closer to 1, had relatively faster increase in weight compared to length. Fishes with values of b further from 3, or allometric coefficient (α = b/3) further from 1, had relatively faster increase in length compared to the weight (Sangun *et al*, 2007). In this study, all four fish species exhibited hypoallometric growth where the length increased faster relative to the weight. Nehemia, *et al.* (2012) reported negative allometric growth with b = 2.94 for *T. zilli* in fresh water ponds. In this study the relative increases in length compared to the weight for the four fish species were: *O. niloticus* (b = 2.1077; α = 0.70) > *C. gariepinus* (b = 2.0436; α = 0.68) > *S. galilea* (b = 1.9119; α = 0.64) > *T. zilli* (b = 1.5202; α = 0.51).

The four fish species had different intercepts on the Log W against Log L plot. The differences in intercepts indicate differences in the proportionate lengths of the fish, irrespective of body weight (Shingleton, 2010). Species with a higher intercept had proportionally longer length across all body sizes (Shingleton, 2010). Therefore, the order of the four fish species, with proportionally longer length across body sizes is:

O. niloticus (a = 0.9933) > *S. galilea* (a = 0.8459) > *C. gariepinus* (a = 0.6296) > *T. zilli* (a = 0.0154).

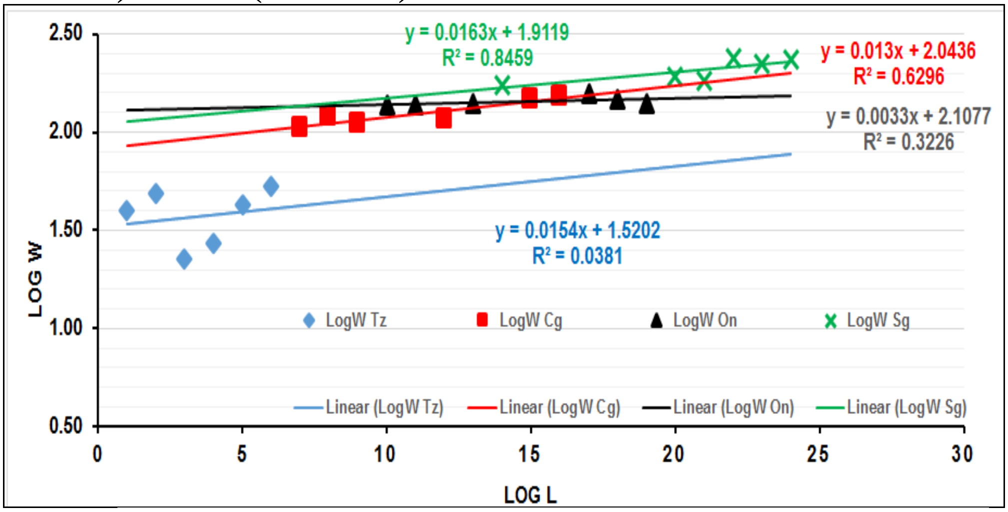

Figure 4. The Length - Weight relationship of four fish species from the Weija Lake in Ghana

The condition factor (K_f) determines the physiological condition of a fish including its reproductive capacity (CDFO, 2004). The K_f values varied considerably among individual samples of each species, with ranges of (1.61 - 4.01), (0.27 - 2.55), (1.71 - 3.08) and (2.00 - 3.13) for *T. zilli*, *C. gariepinus*, *O. niloticus* and *S. galilea* respectively (Table 4). Sakar *et al* (2013) also noted considerable variation of (0.76 - 2.95) in K_f of fish from the river Ganga, Gomti and Rapti in India. The differences in K_f among the individual samples in this study reflected differences in the degree of nourishment, sexual maturity and age of the fish (Williams, 2000).

Table 4. Condition factors (K_f) of four fish species from the Weija Lake in Ghana

	T. zillii	*C. gariepinus*	*O. niloticus*	*T. galilea*
	1.87	2.55	3.08	2.00
	2.17	1.71	2.92	2.05
	1.61	2.07	2.24	2.92
	1.79	0.29	1.71	2.21
	3.67	0.27	1.81	2.65
	4.01	0.33	1.97	3.13
Mean ± Std. Dev.	**2.52 ± 1.04**	**1.20 ± 1.03**	**2.29 ± 0.58**	**2.49 ± 0.47**

There was a weak but negative correlation between the K_f of *T. zilli* and the concentrations of V, Mn and Al (Table 5) indicating that *T. zilli* samples with higher K_f had lower concentrations of V, Mn and Al in their muscles. However, K_f for *C. gariepinus*, *O. niloticus* and *S. galilea* correlated positively and very strongly with V, Mn and Al concentrations. Fishes with higher K_f had higher concentrations of the metals in their muscles. This could be due to high intake of the metals through their feed. This agreed with similar results reported by Naz and Javed (2013) where the condition factor of *Hypophthalmichthys molitrix* correlated significantly and positively with feed intake and chronic exposure to a mixture of metals.

Table 5. Correlation between Condition Factors (K_f) and V, Mn and Al concentrations in four fish species from the Weija Lake in Ghana

	Metals		
	Va	**Mn**	**Al**
T. zillii	-0.27	-0.37	-0.36
C. gariepinus	0.90	0.90	0.97
O. niloticus	0.90	0.87	0.92
T. galilea	0.79	0.81	0.78

Table 6. Mean concentrations (µg/ml) of six metals in water from the Weija Lake

	Metals					
Sampling sites	**Va**	**Mn**	**As**	**Hg**	**Cd**	**Al**
1	<0.01	0.54 ± 0.08	0.36 ± 0.05	<0.01	0.48 ± 0.07	5.87 ± 0.34
2	<0.01	0.37 ± 0.06	<0.01	<0.01	<0.01	3.93 ± 0.16
3	<0.01	0.26 ± 0.04	0.03 ± 0.004	<0.01	0.08 ± 0.01	3.51 ± 0.23
4	0.19 ± 0.03	0.35 ± 0.05	0.65 ± 0.10	<0.01	<0.01	11.18 ± 0.25
5	0.43 ± 0.06	1.43 ± 0.21	1.25 ± 0.19	<0.01	<0.01	14.23 ± 2.13
6	0.21 ± 0.03	0.96 ± 0.14	0.03 ± 0.004	<0.01	<0.01	7.54 ± 1.13
Mean ± SD	0.14 ± 0.01	0.65 ± 0.05	0.388 ± 0.04	0.01 ± 0	0.1 ± 0.01	7.71 ± 0.41

The levels of mercury in the water samples in this study were ≤ 0.01mg/L (Table 6) and exceeded the Ghana Environmental Protection Agency’s maximum acceptable concentration of 0.005mg/L (UNEP, 2002). The high levels in the lake are from industrial effluents; waste disposal and runoff from areas where agricultural pesticides are used (Health Canada, 2012).

The levels of mercury in samples of the four fish species in this study were less than 0.001 µg/g dry weight (Tables 7, 8, 9 10). In a study by Asamoah (2012) using Cold Vapour Atomic Absorption Spectrophotometry (CVAAS) technique, Mercury concentration in the muscles of six species of fish from the Densu basin at Weija ranged from 0.001 to 0.420 µg/g wet weight. In Asamoah (2012), Mercury concentration in *Tilapia zilli ranged* from 0.022 to 0.385 µg/g wet weight with a mean of 0.155 µg/g. All the fish samples in this study showed mercury concentrations below the levels detected by Asamoah (2012).

Table 7. Mean concentrations (µg/g) of five metals in *Tilapia zilli* from the Weija Lake

	Metals					
	Va	**Mn**	**As**	**Hg**	**Cd**	**Al**
***T. zillii* 1**	468 ± 70.20	1789 ± 268	<0.001	<0.001	<0.001	1545 ± 231
	478 ± 71.22	1790 ± 268	<0.001	<0.001	<0.001	1674 ± 251
***T. zillii* 2**	419 ± 62.13	1590 ± 238	<0.001	<0.001	<0.001	1397 ± 209
	436 ± 65.12	1659 ± 248	<0.001	<0.001	<0.001	1445 ± 216
***T. zillii* 3**	564 ± 84.14	2188 ± 328	<0.001	<0.001	<0.001	1889 ± 283
	573 ± 85.13	2210 ± 331	<0.001	<0.001	<0.001	1920 ± 288
***T. zillii* 4**	524 ± 78.03	2090 ± 313	<0.001	<0.001	<0.001	1831 ± 274
	525 ± 78.01	2123 ± 318	<0.001	<0.001	<0.001	1872 ± 280
***T. zillii* 5**	446 ± 66.41	1678 ± 251	<0.001	<0.001	<0.001	1485 ± 222
	457 ± 68.11	1709 ± 256	<0.001	<0.001	<0.001	1516 ± 227
***T. zillii* 6**	513 ± 76.31	1890 ± 283	<0.001	<0.001	<0.001	1687 ± 253
	515 ± 77.12	1971 ± 295	<0.001	<0.001	<0.001	1729 ± 259
Mean ± SD	493.17 ± 1.67	1890.58 ± 82.23	0.001 ± 0	0.001 ± 0	0.001 ± 0	1665.83 ± 72.41

Table 8. Mean concentrations (µg/g) of five metals in *C. gariepinus* from the Weija Lake

	Metals					
	V	**Mn**	**As**	**Hg**	**Cd**	**Al**
***C. gariepinus* 1**	103 ± 15.13	2.76 ± 0.41	<0.001	<0.001	<0.001	10990 ± 1648
	110 ± 16.01	2.91 ± 0.44	<0.001	<0.001	<0.001	11043 ± 1656
***C. gariepinus* 2**	92 ± 13.04	2.48 ± 0.37	<0.001	<0.001	<0.001	9879 ± 1481
	93 ± 13.12	2.5 ± 0.38	<0.001	<0.001	<0.001	10780 ± 1617
***C. gariepinus* 3**	92 ± 13.04	2.34 ± 0.35	<0.001	<0.001	<0.001	8180 ± 1227
	93 ± 13.12	2.45 ± 0.38	<0.001	<0.001	<0.001	9876 ± 1481
***C. gariepinus* 4**	85 ± 12.03	2.21 ± 0.33	<0.001	<0.001	<0.001	1108 ± 166
	87 ± 13.03	2.3 ± 0.35	<0.001	<0.001	<0.001	1156 ± 173
***C. gariepinus* 5**	81 ± 12.04	2.2 ± 0.33	<0.001	<0.001	<0.001	1090 ± 163
	84 ± 12.21	2 ± 0.30	<0.001	<0.001	<0.001	978 ± 146.03
***C. gariepinus* 6**	75 ± 11.32	1.97 ± 0.30	<0.001	<0.001	<0.001	908 ± 136.22
	76 ± 11.02	1.99 ± 0.30	<0.001	<0.001	<0.001	881 ± 132
Mean ± SD	89.25 ± 3.75	2.34 ± 0.1	0.001 ± 0	0.001 ± 0	0.001 ± 0	5572.42 ± 312.99

Table 9. Mean concentrations (µg/g) of five metals in *O. niloticus* from the Weija Lake

	Metals					
	Va	**Mn**	**As**	**Hg**	**Cd**	**Al**
***O. niloticus* 1**	2.485 ± 0.37	18.97 ± 2.85	<0.001	<0.001	<0.001	15901 ± 2385
	2.647 ± 0.40	23.29 ± 3.49	<0.001	<0.001	<0.001	14907 ± 2236
***O. niloticus* 2**	1.852 ± 0.28	17.24 ± 2.59	<0.001	<0.001	<0.001	13875 ± 2081
	1.852 ± 0.32	17.24 ± 2.59	<0.001	<0.001	<0.001	13990 ± 2098
***O. niloticus* 3**	1.1 ± 0.17	10.96 ± 1.64	<0.001	<0.001	<0.001	11998 ± 1799
	1.305 ± 0.21	11.61 ± 1.74	<0.001	<0.001	<0.001	12536 ± 1880
***O. niloticus* 4**	0.7488 ± 0.11	8.131 ± 1.22	<0.001	<0.001	<0.001	1756 ± 263
	0.8514 ± 0.13	10.42 ± 1.56	<0.001	<0.001	<0.001	1803 ± 270
***O. niloticus* 5**	0.3167 ± 0.05	6.333 ± 0.95	<0.001	<0.001	<0.001	1564 ± 234
	0.7379 ± 0.11	6.598 ± 0.99	<0.001	<0.001	<0.001	1690 ± 253
***O. niloticus* 6**	<0.01	1.722 ± 0.26	<0.001	<0.001	<0.001	1398 ± 209
	<0.01	1.02 ± 0.15	<0.001	<0.001	<0.001	1503 ± 225
Mean ± SD	1.16 ± 0.06	11.13 ± 0.56	0.001 ± 0	0.001 ± 0	0.001 ± 0	7743.42 ± 429.36

The detection of mercury by the NAA technique used in this study is more highly precise and sensitive than the CVAAS technique (Sharma and Davis, 1979). Dadzie, (2012) reported 0.014 µg/ml of mercury in leachate at the point of entry into the lake. Mercury concentrations in fish from this study were below 0.5 µg/g. according to Driscoll *et al* (2013), fish muscle tissue with Hg concentrations of ≥0.5 µg g^{-1} compromises fish reproduction, embryonic development, and biochemical process, and damage cells and tissues.

Table 10. Mean concentrations (µg/g) of five metals in *S. galilea* from the Weija Lake

	Metals					
	Va	**Mn**	**As**	**Hg**	**Cd**	**Al**
T. galilea 1	0.4146 ± 0.11	440 ± 66.23	<0.001	<0.001	<0.001	6837 ± 1025
	0.8541 ± 0.13	452 ± 67.23	<0.001	<0.001	<0.001	6862 ± 1029
***T. galilea* 2**	0.8856 ± 0.13	473 ± 70.03	<0.001	<0.001	<0.001	6937 ± 1040
	1.026 ± 0.15	479 ± 74.33	<0.001	<0.001	<0.001	6951 ± 1042
***T. galilea* 3**	1.043 ± 0.16	491 ± 73.03	<0.001	<0.001	<0.001	7168 ± 1075
	1.198 ± 0.18	491 ± 73.03	<0.001	<0.001	<0.001	7385 ± 1107
***T. galilea* 4**	1.249 ± 0.19	500 ± 75.13	<0.001	<0.001	<0.001	7492 ± 1123
	1.281 ± 0.23	501 ± 75.11	<0.001	<0.001	<0.001	7548 ± 1132
***T. galilea* 5**	1.421 ± 0.21	516 ± 77.31	<0.001	<0.001	<0.001	7641 ± 1146
	1.967 ± 0.32	517 ± 77.12	<0.001	<0.001	<0.001	8735 ± 1310
***T. galilea* 6**	2.052 ± 0.21	581 ± 87.03	<0.001	<0.001	<0.001	8831 ± 1324
	2.544 ± 0.38	583 ± 87.14	<0.001	<0.001	<0.001	9036 ± 1355
Mean ± SD	1.33 ± 0.06	502 ± 21.79	0.001 ± 0	0.001 ± 0	0.001 ± 0	7618.58 ± 331.44

The results of this study agrees with that of Asamoah (2012) that consumption of fish from the Weija Lake does not pose a significant mercury hazard to the public. A study by the U.S. Geological Survey found mercury in every freshwater fish from nearly 300 streams. About a quarter of the fish contained mercury levels above the US EPA safe level of 0.3 ppm (Savard, 2009). The levels of Mercury in the fish in this study show that the pollution of the Weija Lake by mercury is insignificant.

A study by Dadzie (2012) showed mean concentration of cadmium in leachate discharged into the Weija Lake to be 0.025 µg/ml but not at the point of entry of the leachate into the lake. Timub and Ananga (2013) detected cadmium in the muscles of *C. gariepinus* and Tilapia from the Weija Lake at concentrations of 0.808 µg/g and 0.129 µg/g respectively using AAS. In this study the mean concentration of cadmium in the water samples from the lake was 0.10 **–** 0.48 µg/ml (Table 6) and the levels in the muscles of the fish species in this study was ≤0.001 µg/g (Table 7, 8, 9, and 10). This agreed with Jezierska and Witeska (2006) that cadmium and mercury are accumulated by fish in amounts below 1.0 µg/g d.w. Cadmium is released to the environment in wastewater, and from fertilizers and air pollution. Food is the main source of daily exposure to cadmium (WHO, 2011).

Arsenic is found in the diet, particularly in fish and shellfish, mainly in the less toxic organic form (WHO, 2011). Arsenic is concentrated by many species of fish. Fish and meat are therefore the main sources of dietary intake (Health Canada, 2006). The mean concentration of Arsenic in the fish in this study was ≤0.001 µg/g. In Canada, arsenic levels ranging from 0.4 to 118 mg/kg have been reported in marine fish sold for human consumption (Health Canada, 2006). The mean concentration in the lake water was 0.39 ± 0.04 µg/ml (Table 6) which was higher than the 0.015 - 0.026µg/ml mean concentration detected by Dadzie (2012) in leachate discharged into the Weija Lake. Arsenic concentrations in rivers and lakes are normally below 0.01 µg/L, although individual samples may have values as high as 3.4 µg/ml.

There was no correlation between the concentration of arsenic in the water and that in the tissues of fish in this study.

Arsenic causes acute and chronic adverse health effects, including cancer. Inorganic arsenic in the pentavalent state may disrupt energy production reactions by replacing phosphate in several reactions (Hughes, 2002). In the trivalent state, inorganic and organic arsenic may react with critical Thiols in enzymes and inhibit their activity (Hughes, 2002).

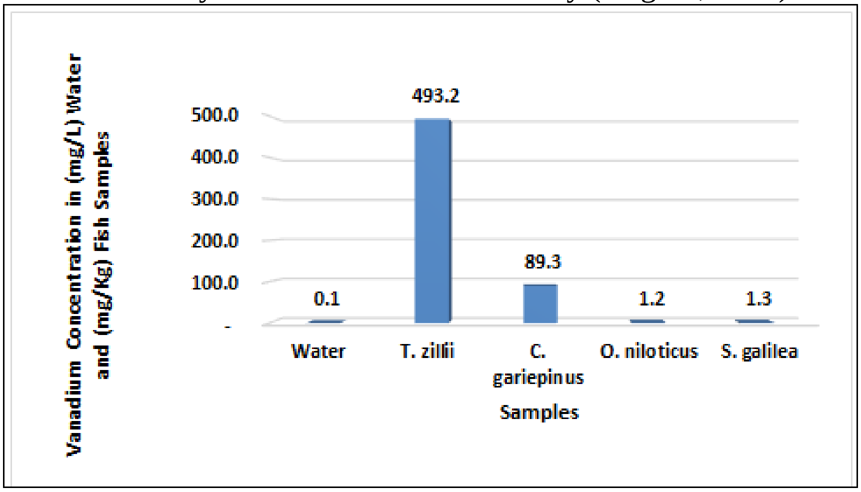

Figure 5 Mean Vanadium concentration in the water sample (µg/ml) and the four fish species (µg/g) from Weija Lake

Vanadium levels ranged between 419 – 573 µg/g, 76 – 110 µg/g, 0.01 – 2647 µg/g and 0.41 - 2.54 µg/g in *T. zilli*, *C. gariepinus*, *O. niloticus* and *S. galilea* respectively (Table2 7, 8, 9, and 10). The concentration of Vanadium in the water samples from the various sampling sites in this study ranged from 0.01 to 0.43 µg/ml (Table 6) with a mean of 0.14 ± 0.01 µg/ml. The values from this study were within the normal range of 0.04 to 0.104 µg/ml Vanadium in surface water (ATSDR, 2014b). This indicates that the amount of Vanadium in the water was mainly through the naturally release of the metal into the water from rock and soil erosion (ATSDR. 2014b).

Vanadium concentration was high in *T. zilli* (493.2 µg/g) and *C. gariepinus* (89.3 µg/g) with both fish showing very high biomagnification of the metal (Figure 5). The correlation between vanadium concentration in the water samples and that in the tissues was negative but insignificant (-0.1753) for *T. zillii*, negative and significant (-0.6892) for *C. gariepinus* and (-0.7158) for *O. niloticus*, and positive and significant (0.6761) for *T. galilaea*.

Regression analysis showed that between 3.1% - 51.2% of the vanadium in the muscles of the fish was from the lake water.

Manganese pollution of the lake could be from wastewater discharged from domestic activities, and industries such as mining and mineral processing, as well as from the combustion of fossil fuels and fuel additives (WHO, 2004). The concentration of Manganese in the Weija Lake ranged from 0.26 – 1.43 µg/ml (Table 6), with a mean of 0.65 ± 0.5 µg/ml. The amount of dissolved manganese in rivers and lakes that are free from pollution from man – made activities ranges from 0.01 to below 10 µg/ml (WHO, 2004). However, water samples taken from the surface of the unpolluted waters usually contain less than 0.02 µg/ml Mn, and this value rarely exceeds 10 µg/ml (WHO, 2004). The concentration of Mn in the Weija Lake from this study is consistent with the normal levels found in unpolluted natural waters. However, it should be noted that the water samples for this study were taken downstream of the lake. Lower concentrations of Mn tend to occur downstream of lakes that act as settling areas for sediment (WHO, 2004).

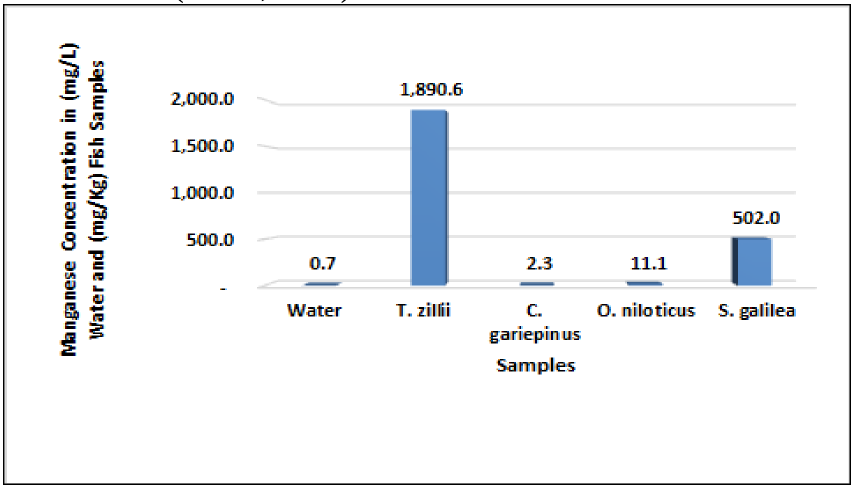

Figure 6 Mean Manganese concentration in water (µg/ml) and four species of fish (µg/g) from Weija Lake

The concentration of manganese was considerably high in *T. zilli* (Figure 6) with a mean value of 1890.6 µg/g, followed by *S. galilea* (502 µg/g), *O. niloticus* (11.1 µg/g), and *C. gariepinus* (2.3 µg/g). The concentrations of Mn in the fish indicate the biomagnification of the metal in the muscle tissues of the fish, especially in *T. zilli* and *S. galilea*. The Bioconcentration factors (BCFs) for Mn in *T. zilli* and *S. galilea* were 2908.6 and 772.3 respectively. This corroborates the report by the WHO (2004) that Manganese in water can be significantly bioconcentrated by BCFs of 35 - 930 in fish (WHO, 2004). The levels of Mn in the fish in this study could prove toxic to the fish since laboratory tests and field observations have shown that dissolved manganese concentrations of ≥0.001µg/ml can be toxic to aquatic organisms (WHO, 2004). Manganese accumulates more in the liver and gill tissue than in muscle tissue (Reimer, 1999).

The mean concentration of Aluminum in the Weija Lake was 7.7 µg/ml. Normal aluminum concentrations in surface waters is <0.1 µg/ml at pH above 5.5, where it is sparingly soluble. High amounts of Al occur in natural waters when pH is less than 5 because of the increased solubility of aluminum oxide and salts (ATSDR. 2014a). Aluminium generally does not bioaccumulate in fish because its toxicity to fish (ATSDR, 2014a). However, in this study, *O. niloticus* had very high Al concentration (7743.4 µg/g), followed by *S. galilea* (7618.6 µg/g), *C. gariepinus* (5572.4 µg/g), and *T. zilli* the least concentration (1665.8 µg/g) (Figure 7), indicating bioaccumulation of Aluminum in all four fish species. Bioaccumulation factors of Al in *T. zillii, C. gariepinus, O. niloticus and S. galilea* were 216.1, 722.8, 1,004.3, and 988.1 respectively.

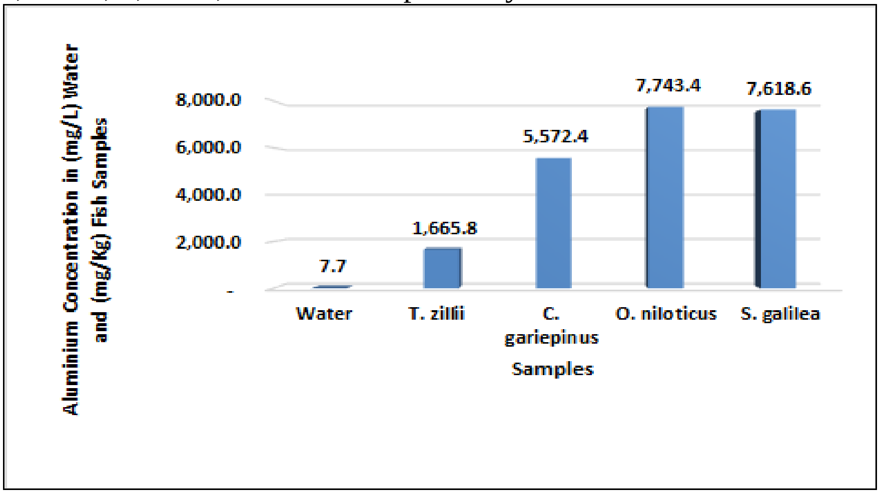

Figure 7 Mean Aluminum concentration in water (µg/ml) and four fish species (µg/g) from Weija Lake

Aluminum causes severe neurotoxic effects in adults and children with renal failure (Bishop *et al*, 1997). It alters the function of the blood-brain barrier, which regulates exchanges between the central nervous system and peripheral circulation (Banks and Kastin, 1989). There is evidence of some toxicity if it is consumed in amounts greater than 40 mg/kg/day (Piero, 2014). Aluminum has been implicated in disorders associated with chronic renal failure (AAP, 1986).

Correlation between metal concentrations to fish length

Fish length had a strong negative effect on V, Mn, and Al levels in the fish with the exception of *T. zillii* where there was a weak negative effect (Table 11). No correlation was observed between concentrations of As, Hg and Cd length of fish.

Table 11. Correlation between fish length and metals concentration in fish

	Species of fish			
	T. zilli	***C. gariepinus***	***O. niloticus***	***S. galilea***
Va	-0.56	-0.84	-0.93	-0.86
Mn	-0.49	-0.85	-0.91	-0.85
Al	-0.49	-0.99	-0.97	-0.84

Table 12. Correlation between weight of fish and concentrations of metal in the fish

	Fish			
	T. zillii	***C. gariepinus***	***O. niloticus***	***S. galilea***
V	-0.96	-0.92	-0.80	-0.85
Mn	-0.99	-0.94	-0.85	-0.84
Al	-0.99	-0.98	-0.71	-0.85

Fish weight had a very strong negative correlation with V, Mn, and Al levels in the fish. These results agree with Damodharan and Vikram, (2012) that an inverse correlation occurred between fish length and weight and Cd, Cu, Mn, Pb and Zn concentration in muscle tissues of *A. thalasinuss, L. calcarifer*, *T. mossambica* and *M. cephalus*. In this study, fish weight had no effect on As, Hg and Cd concentrations in the fish. Except in few cases in this study when the relationships were insignificant, correlation analysis showed significant negative relationships between fish length and metal concentrations, and significant negative relationships between fish weight and metal concentrations. This showed that concentrations of most metals (except for As, Hg and Cd) were inversely related to fish size (Jezierska and Witeska, 2006).

Correlation between metals concentrations in water to that in fish

The correlations between metal concentrations in water and concentrations in muscles of the four species of fish were strongly positive (Table 13).

Table 13. Relationship between metal concentrations in water and concentrations in muscles of four fish species

	Fish			
	T. zilli	***C. gariepinus***	***O. niloticus***	***S. galilea***
Correlation	0.6021	0.9966	0.9971	0.9991
Regression	36.3%	99.3%	99.4%	99.8%

This showed that metal accumulation in fish depended on the level in water (Jezierska and Witeska, 2006). Damodharan and Vikram, (2013) reported positive correlations between concentrations of selected metals in fish muscle and water attributed this to the direct accumulation of metals from the water to the fish. However the extent of correlation varied with species of fish, with *C. gariepinus* showing the least correlation (0.26) and *S. galilea* the highest (0.58). This showed that in this study metal accumulation in fish differed for the various fish species even though they lived in the same water body (Jezierska and Witeska, 2006).

From the regression analysis, metal concentrations in water accounted for only 6.6 – 37.5% of the metal concentrations in the muscles of the fish. The concentration of a metal in fish would be dependent on the level in water only if the main source of the metal in the body is from the water. However, if the main source of the metal is from the food then such a relationship may not hold (Jezierska and Witeska, 2006). The results show that the four species of fish in the Weija Lake accumulated different amounts of metals, and this may be due to their different living and feeding habits (Jezierska and Witeska, 2006).

Estimated Average Daily Dose (EADD) (µg/g) of metals in four species of fish from the Weija Lake compared to internationally recommended values of safety

The average per capita fish consumption in Ghana is 20 – 25 kg, higher than the world average of 16 kg (Global Fish Alliance, 2005). The EADD of each metal was calculated as:

Daily intake of heavy metals from fish = A × B, Where

A - Average amount of fish consumed per individual per day = 25,000g / 365 days
= 68.49g /day

B - Average concentration of metal in fish

Average concentration of Vanadium in *T. zilli* = 493.17 (µg/g)

EADD of Vanadium from *T. zilli* = 493.17 (µg V/g fish) x 68.49 (g fish/day)
= 33778.5 µg V/day

The EADD of Vanadium from *T. zilli* (33778.5 µg/day) and *C. gariepinus* (6113 µg/day) (Table 14) were above the recommended average daily intake (ADI) of <1800µg/day (IOM, 2006).

The EADD of Aluminium in *T. zilli* (114,098.2 µg), *C. gariepinus* (381,672.4 µg), *O. niloticus* (530,371 µg), and *S. galilea* (521,820.8 µg) were above the recommended ADI of 142.8 µg Al for a 70 kg individual, or weekly intake of 1000 µg/kg of Al (EFSA, 2008).

Table 14. Comparison of the Estimated Average Daily Dose (EADD) (µg/day) of metals from consumption of four fish species from the Weija Lake to recommended ADIs

	Metals					
	V	**Mn**	**As**	**Hg**	**Cd**	**Al**
T. zilli	33,778.5	129,492.0	≤0.7	≤0.7	≤0.7	114,098.2
C. gariepinus	6,113.0	160.4	≤0.7	≤0.7	≤0.7	381,672.4
O. niloticus	79.4	762.2	≤0.7	≤0.7	≤0.7	530,371.0
S. galilea	91.0	34,383.6	≤0.7	≤0.7	≤0.7	521,820.8
Recommended ADI for 70Kg adult	<1800µg IOM (2006)	11,000µg IOM (2006)	12 - 40µg (Uthus, 1994)	16µg (WHO, 2003)	70µg (WHO, 2003)	142.8µg (EFSA, 2008)

Calculations of the estimated average daily intake (µg/g) of metals are based on the estimated average per capita consumption of 25kg fish in Ghana (Global fish Alliance, 2005) and the average concentrations of metals detected in fish muscles in this study.

The EADD of Manganese in *T. zilli* (129,492 µg) and *S. galilea* (34,383.6 µg) were above the recommended ADI of Manganese for infants (0.003 – 0.6 µg), children (1.2 – 1.5µg), adults (1.8 – 2.3 µg), and pregnant and lactating mothers (2.0 – 2.6 µg) (IOM, 2006).

According to Uthus (1994), the ADI for Arsenic is 12 – 40 µg, with the Estimated Safe and Adequate Daily Dietary Intake (ESADDI) for the various age groups as: 6 kg infant, 0 – 0.5years (1.0 – 4.0 µg); 9 kg infant, 0.5 – 1years (2.0 – 5.0 µg); 13 kg children, 1 – 3 years (3.0 – 8.0 µg); 20 kg children, 4 – 6years (4.0 – 12.0 µg); 28 kg children 7 – 10years (5.0 – 16.0 µg); and 70 kg adult (12.0 – 40.0 µg). In this study the calculated EADD of Arsenic from consumption of any of the four fish species was ≤0.7 µg. This is within the ESADDI for all age groups (Uthus, 1994).

The current recommended Provisional Tolerable Weekly Intake (PTWI) of Cadmium is 7 µg/kg body weight, or 7 µg as Provisional ADI for a 70 kg adult (WHO, 2003). In this study the calculated EADD of ≤0.7 µg Cd from consumption of any of the four fish species did not exceed the PTWI for Cd.

The EADD of ≤0.7 µg Hg did not exceed the recommended PTWI of 1.6µg methylmercury/kg body weight or 16µg methylmercury as Provisional ADI for a 70 kg adult (WHO, 2003).

CONCLUSION

The levels of V, Mn, As, Hg, Cd, and Al in the Weija Lake was used to assess the extent of pollution of the lake by these metals and their levels in the muscle of four fish species (*T. zillii, O. niloticus, S. galilea and C. gariepinus*) obtained from the Lake was used to assess the safety of the fishes for human consumption.

This study showed that concentrations of metals in the muscle tissue of the fish correlated positively with the metal concentrations in the lake.

There were substantially high levels of Vanadium in *T. zilli* and *C. gariepinus*, Aluminum in *T. zilli, C. gariepinus, O. niloticus*, and *S. galilea*, and Manganese in *T. zilli* and *S. galilea*. The estimated average daily dose of Vanadium, Aluminum and Manganese obtained from consumption of the fish far exceeded the recommended ADIs for the respective metals.

The results indicate high levels of Vanadium, Aluminium and Manganese pollution of the Weija Lake. The levels of Vanadium, Aluminium and Manganese in the fish are unsafe for human consumption.

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