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Investigation of Selected Trace and Heavy Metals in Two Tropical Fish Species from the Coastal Waters of Ghana

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ABSTRACT

Cadmium (Cd), copper, (Cu), Iron (Fe), lead (Pb), and zinc (Zn) burdens were determined by atomic absorption spectrophotometry (AAS) in two tropical fish species (*Chloroscombrus chrysurus* and *Sardinella maderensis*) from the western coast of Ghana. Fish samples were collected during three designated Sampling Periods (January 2008 to March 2008 - Periods 1; September 2008 to November 2008 - Period 2; and February 2009 to March 2009 - Period 3) at three sites (Half-Assini, Aboadze and Elmina). Trace elements and heavy metal concentrations in both species followed the order Fe>Zn>Cu while Cd and Pb were below detection limits. High levels of Fe were detected in the fish samples with concentration ranges of 13.05-376.4 µg/g dw. Levels of Cu generally recorded during Period 1 were above FAO maximum recommended limits of 30 µg/g in fish while Zn burdens were below FAO recommended limit of 40 µg/g. *S. maderensis* and *C. chrysurus*, can be considered safe for human consumption with respect to Cd, Pb and Zn contaminations. However, Cu will require further monitoring to protect public health. Hazard quotients and hazard indices computed indicate that metal exposure from consumption of the two fish species will not result in any appreciable health risk. Levels of Cu and Zn recorded may however pose threats to physiological functioning of fish since levels were high enough to cause sublethal effects to fish. Metal burdens studied provide background information prior to the commercial exploitation of oil in Ghana's marine waters.

Keywords: *Chloroscombrus chrysurus; fish; heavy metals; public health; Sardinella maderensis; sublethal effects; trace elements*

1. INTRODUCTION

Analysis of trace elements and heavy metals in organisms as a means of monitoring pollution in aquatic systems has been established over the years [4, 8, 33]. Some trace metals may be very essential for the survival of living organisms due to the important physiological role they play [18]. However, beyond certain threshold levels they can be very toxic to humans and other organisms that depend on them and can result in various illnesses and eventually death [12, 25]. Heavy metals may be non-essential for biological functioning and toxic to organisms even at very minute concentrations [19].

Trace metal contamination may have devastating effects on the ecological balance of the recipient environment and a diversity of aquatic organisms [6, 17, 38]. Among aquatic species, fish and shellfish are the inhabitants that cannot escape from the detrimental effects of these pollutants [11, 13, 31]. These are therefore widely used to evaluate the health of aquatic ecosystems with respect to chemical pollution. This is because pollutants accumulate in fish and tissues of other aquatic organisms along the food chain and can be responsible for adverse effects and ultimately death of organisms in aquatic systems [3, 16].

All known metals can be harmful to organisms at a particular concentration no matter how important the metal may be [18]. For a metal to be considered as toxic, or to provoke a biological effect, it must interact with a biological structure [9]. The level at which metals can be harmful or toxic to organisms depends on their concentration [2], their physico-chemical forms which drive their bioavailability (dissolved or particulate, ionic or elemental – species) [32], the nature of the containing medium (e.g. pH) [36], and the ability of the metal to form complexes with other chemical compounds [2]. However, accumulation pattern of metal contaminants in fish is dependent on factors such as uptake and elimination rates [20].

The toxicity or availability of a metal to an organism may increase with increasing concentration of the metal in solution. Non-essential metals may however be toxic to organisms at very minute concentrations. According to Campbell [10] and Kozelke *et al.* [26], the bioavailability of a given metal better correlates with its inorganic or free metal ion concentration than its total metal concentration in solution. This is because the ionic form of a given metal is what is usually absorbed and utilized by biological systems. Heavy metals may remain in the water column or get adsorbed unto food particles, and enter the aquatic food chain by direct consumption by fish and other organisms. Nonetheless, apart from direct consumption of water and food or biota, fish may acquire these metals through non-dietary routes such as uptake through epithelia (e.g. gills, skin and digestive tracks) [7, 22].

When aquatic organisms bioaccumulate metals directly or indirectly from the water column and food particles into their tissues, these are transferred to higher levels of the food chain and may pose health risks to higher organisms including humans. Fish being at a high level in the aquatic food chain in the aquatic system may accumulate a large amount of bioavailable metals.

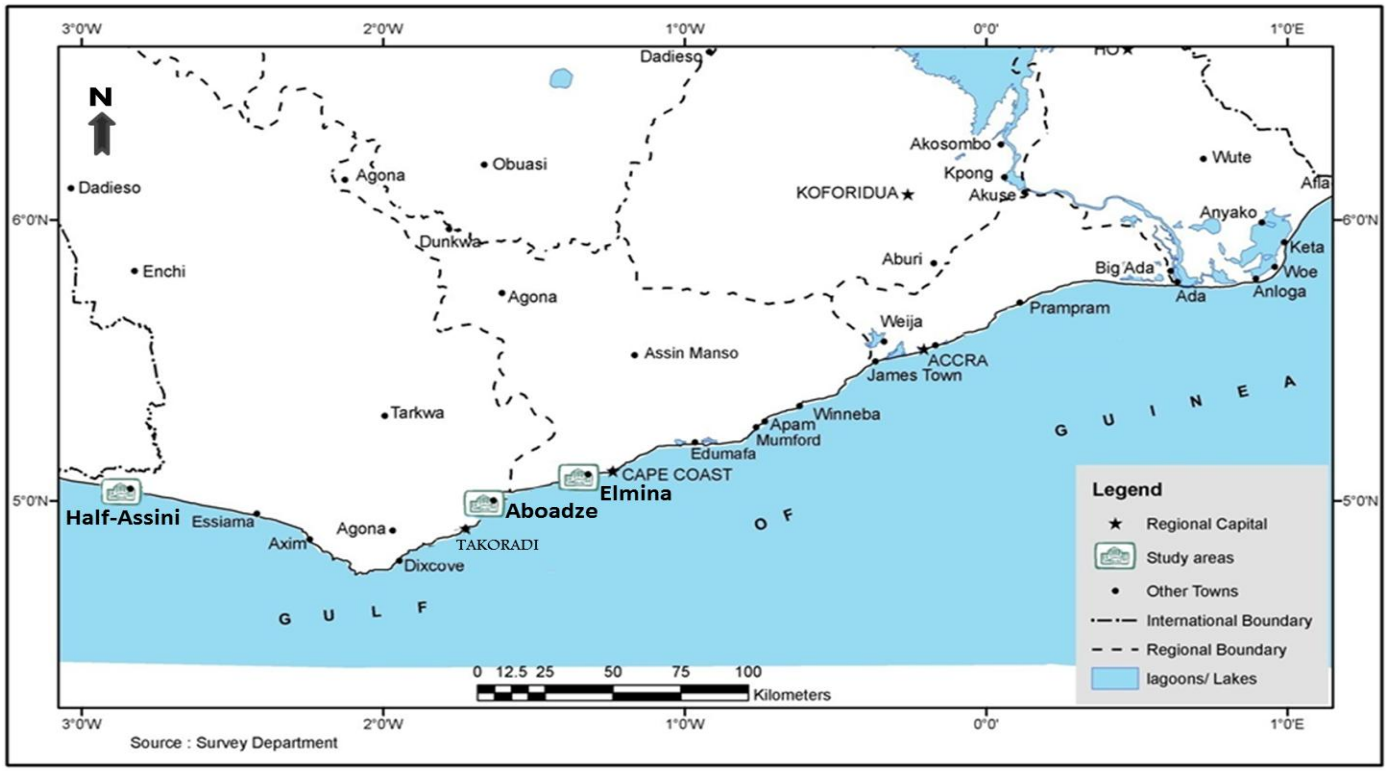


Fig. 1: Map of Study Area Showing Sampling Sites

This could pose a threat to marine mammals and seabirds that consume fish that may have bioaccumulated these metals [1]. This study assessed the levels of some trace and heavy metals accumulated in *Chloroscombrus chrysurus* (Linnaeus, 1766) and *Sardinella maderensis* (Lowe, 1838), which are commercially important fish species sampled from the western coast of Ghana and are largely depended upon by Ghanaians for their source of protein, especially the coastal inhabitants. In addition, the study also seeks to provide background information on the concentrations of these metals prior to the commercial drilling of oil in the marine environment of Ghana for monitoring purposes and to determine the impacts of the levels of these metals on the health of the selected fish species. The public health effect of consuming these fish species were also assessed using risk assessment indices. This ultimately is to protect public health as well as the fishery resource.

2. MATERIALS AND METHODS

2.1 Study Site

Fish samples were taken from the coastal waters off the western coast of Ghana, which forms part of the Gulf of Guinea Large Marine Ecosystem in West Africa. The western coast in this respect comprises two western most regional divisions along the coast of Ghana. These are the Central and Western Regions which are located within longitude 1W to longitude 3W. The fish samples were specifically taken from Elmina in the Central Region (Lat. 5.0918N and Lon. 1.3245W); at Aboadze (Lat. 4.9820N and Lon. 1.6266W); and at Half-Assini (Lat. 5.0443N and Lon. 2.8989W) in the Western Region of Ghana (Fig. 1).

2.2 Sampling and Sample Preparation

Two tropical fish species, *Sardinella maderensis* and *Chloroscombrus chrysurus*, were sampled from the coastal waters of the western coast of Ghana in 2008 and 2009 for eight months. The sampling months include January 2008 to March 2008 which is considered here as Period 1, September 2008 to November 2008 considered as Period 2, and February 2009 to March 2009 considered as Period 3. Samples were collected at the end of each month from local fishermen after landing at the beach. These fishes were caught by seine net, which is the most common gear used by artisanal fishermen in Ghana. Fish samples collected were washed with distilled water to remove adhering particles and then wrapped in aluminium foil. The samples were then placed on ice in an ice box, transferred to the laboratory and kept in a freezer (-15 °C) prior to analysis. Samples were allowed to thaw and their standard length and weight measured. They were then thoroughly rinsed with distilled water to remove any attached particles.

Whole fish samples were used for analysis with the aim of assessing the level of trace metals that basically may be transferred to consumers since these fishes are most often eaten whole. Fish samples were cut into smaller portions with a clean

plastic knife which was cleaned with acetone and distilled water. The samples were then placed in acid-washed labelled crucibles where they were lyophilized using a CHRiST Beta 1-16 freeze-drier at a temperature of 20 ^{o}C for 4 days. Lyophilized samples were then ground into fine powder with a clean acid-washed porcelain mortar and pestle to homogenize the samples.

2.3 Chemical Analysis

Aliquots of ground samples were weighed and microwave digested following Milestone Application protocol [28]. Briefly, 0.5 g of homogenized fish samples were taken into labelled acid-clean polytetraflouroethylene (PTEF) Teflon vessels (bombs) of ETHOS 900 Labstation microwave digester. Volumes of 6 ml of 65% v/v concentrated HNO_3 and 1.0 ml of 30% v/v H_2O_2 were added respectively to each vessel containing the samples in a clean fume chamber. The vessels were swirled gently to mix, loaded vertically onto a microwave carousel and the vessel cap tightly secured using an appropriate screw tool. The complete assembly was fitted into a Milestone ETOS 900 microwave Labstation and irradiated for 21 minutes using the following operation parameters; 250 W for 5 minutes, 0 W for 1 minute, 250 W for 10 minutes and 450 W for 5 minutes and then allowed for venting for 5 more minutes [28].

After digestion, the samples were cooled in water bath for 20 minutes to reduce high temperature and internal pressure built-up within the vessel, and to allow volatilized materials to re-solubilize. The digestate was quantitatively transferred into a volumetric flask and diluted to 20 ml using distilled water. Blanks were prepared similarly without fish samples. The samples were analysed with a VARIAN AA240FS Flame Atomic Absorption Spectrophotometer (FAAS) using acetylene gas as fuel and compressed air as oxidant [5, 27]. Each fish sample was analysed in triplicates. Certified reference material (CRM) of Tuna fish homogenate (IAEA-350) obtained from the International Atomic Energy Agency (IAEA) was also analysed following the same procedure as fish samples.

2.4 Statistical Analysis

Spearman's rho non-parametric correlation was computed to evaluate the relationship between metal concentrations in fish and their length and weight measurements. An analysis of variance (ANOVA) was also conducted to determine the difference in metal accumulation pattern in fish species and among sites. Statistical analysis was done using SPSS version 16.

2.5 Human Health Risk Assessment

The potential non-carcinogenic human health risk of consuming the selected fish species contaminated with trace metals was assessed according to the method by Jiang *et al.* [24]. This was done by calculating Hazard Quotient (HQ) for each metal in fish from each study site. The hazard quotient is the ratio of single substance exposure level over a specified time period to a reference dose (or concentration) for that substance derived from a similar exposure period [39]. The hazard index (HI), which is the sum of HQs for all contaminants, was also estimated for each sampling location and species. Per capita consumption of fish for Ghana is estimated by MOFA [29] to be 25 Kg per annum and thus the daily per capita was estimated to be 0.068 kg per day [30]. The average daily exposure to each metal for the Ghanaian population was therefore calculated according to Jiang *et al.* [24] with modifications. This is shown in the equation below:

HQ = Intake / Reference Dose (mg kg^{-1} day^{-1})

Intake (mg kg^{-1} day^{-1}) = (CF x IR x FI x EF x ED) / (BW x AT)

where, HQ = Hazard quotient (unitless);
CF = contaminant concentration in fish (mg kg^{-1});
IR = ingestion rate (kg d^{-1});
FI = fraction ingested from contaminated source (unitless);
EF = exposure frequency (d y^{-1});
ED = exposure duration (y);
BW = the body weight (kg);
AT = the averaging time (period over which exposure is averaged in days).

Hazard index (HI) was also calculated as
$HI = \sum HQ_1, HQ_2, \ldots HQ_n)$

The average body weight and exposure duration were estimated to be 60 kg and 70 years respectively [24], whiles IR, FI and EF were estimated to be 0.06849 kg d^{-1}, 100 % and 365 d y^{-1} respectively. The averaging time (period over which exposure is averaged in days) was also estimated to be 25550 days (365 days x 70 years).

3. RESULTS AND DISCUSSION

The CRM analysed indicated that results were in agreement with certified values (Table 1). For both *S. maderensis* and *C. chryusurus*, metal concentrations showed no significant relationship with fish length and weight measurements ($p>0.05$) when a Spearman's rho non-parametric correlation was applied. Spearman's rho correlations of -0.52, 0.086 and 0.14 were obtained for correlations between fish length and Fe, Cu and Zn concentrations respectively while -0.37, 0.078 and 0.20 were obtained for correlations between fish weight and Fe, Cu and Zn concentrations respectively.

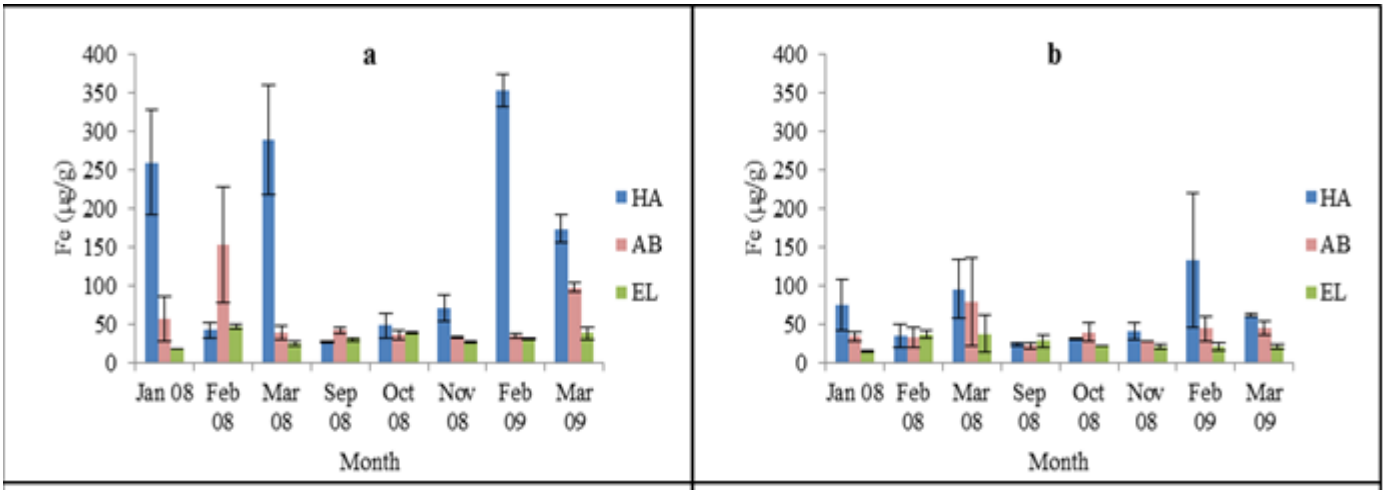
Highest concentrations of Fe in fish were recorded at Half-Assini. These high concentrations were recorded in *S. maderensis* (Fig. 2a) in the months of January 2008 (319 µg/g dw), March 2008 (337 µg/g dw), February 2009 (376 µg/g dw) and March 2009 (193 µg/g dw) during Period 1 (January 2008-March 2008) and Period 3 (February 2009-March 2009).

Table 1: Results of Analysed Certified Reference Materials (CRM) of Tuna Fish Homogenate (IAEA-350)

Elements	No. of analysis	Certified value (µg/g)	Measured value (µg/g)	Percentage recovery
Fe	3	72.1	71.4	99.4
Pb	3	0.10	0.09	90.0
Cd	3	0.020	0.027	135.0
Cu	3	2.83	2.76	97.5
Zn	3	17.4	17.3	99.0

Fe concentrations in *S. maderensis* were generally low for Aboadze but some high concentrations were recorded in February 2008 and March 2009 with mean values of 152 ± 75 µg/g dw and 98 ± 6 µg/g dw respectively. Fe concentrations recorded in *S. maderensis* at Elmina showed low and consistent levels throughout all the periods. Concentrations recorded ranged from 16.9 µg/g dw (January 2008) to 50.1 µg/g dw (February 2008). *C. chrysurus* also recorded relatively consistent low concentrations of Fe at Aboadze (18.3 – 143 µg/g dw) and Elmina (13.1 – 64.2 µg/g dw) but Half-Assini had some relatively varying levels, especially in the months of January 2008 (39.0 – 103 µg/g dw), March 2008 (64.6 – 138 µg/g dw) and February 2009 (81.8 – 234 µg/g dw) (Fig. 2b). Fe concentrations in both *S. maderensis* and *C. chrysurus* ranged from a minimum of 13.1 µg/g dw to a maximum of 376 µg/g dw with *C. chrysurus* recording lowest concentrations for fish taken from Elmina. Sampling Period 2 (September, October and November 2008) had consistently low concentrations of Fe in both *S. maderensis* and *C. chrysurus* compared to Periods 1 and 3. Fe concentrations recorded in this study were far higher than those recorded by Tay *et al.* [37] in *Sardinella eba* (Valenciennes, 1847) obtained from the Greater Accra region in 2003 and 2004. Iron deficiency is known to cause anaemia and fish is said to be a major source of iron for adults and children. The recommended dietary allowance (RDA) of Fe for 7-12 months infants and 51-70 year old adults is 11 and 8 mg/day respectively, while the upper tolerable intake level of Fe for children (1-3 years old) and adults (19-70 years old) is said to be 7 to 40 mg/day respectively [23]. The high levels of Fe recorded in the fish samples therefore make these fish species good sources of iron for human consumption.

Lead (Pb) and cadmium (Cd) concentrations were always below detection limits in both fish species taken from all the sites throughout the sampling periods. In a similar study by Tay *et al.* [37] at a different location, no Cd was detected in *S. maderensis*. Undetected levels of Pb could be a good indication of low lead pollution in the area which may be as a result of the ban on use of leaded fuels as well as proper disposal of waste substances containing lead or less use of leaded materials.



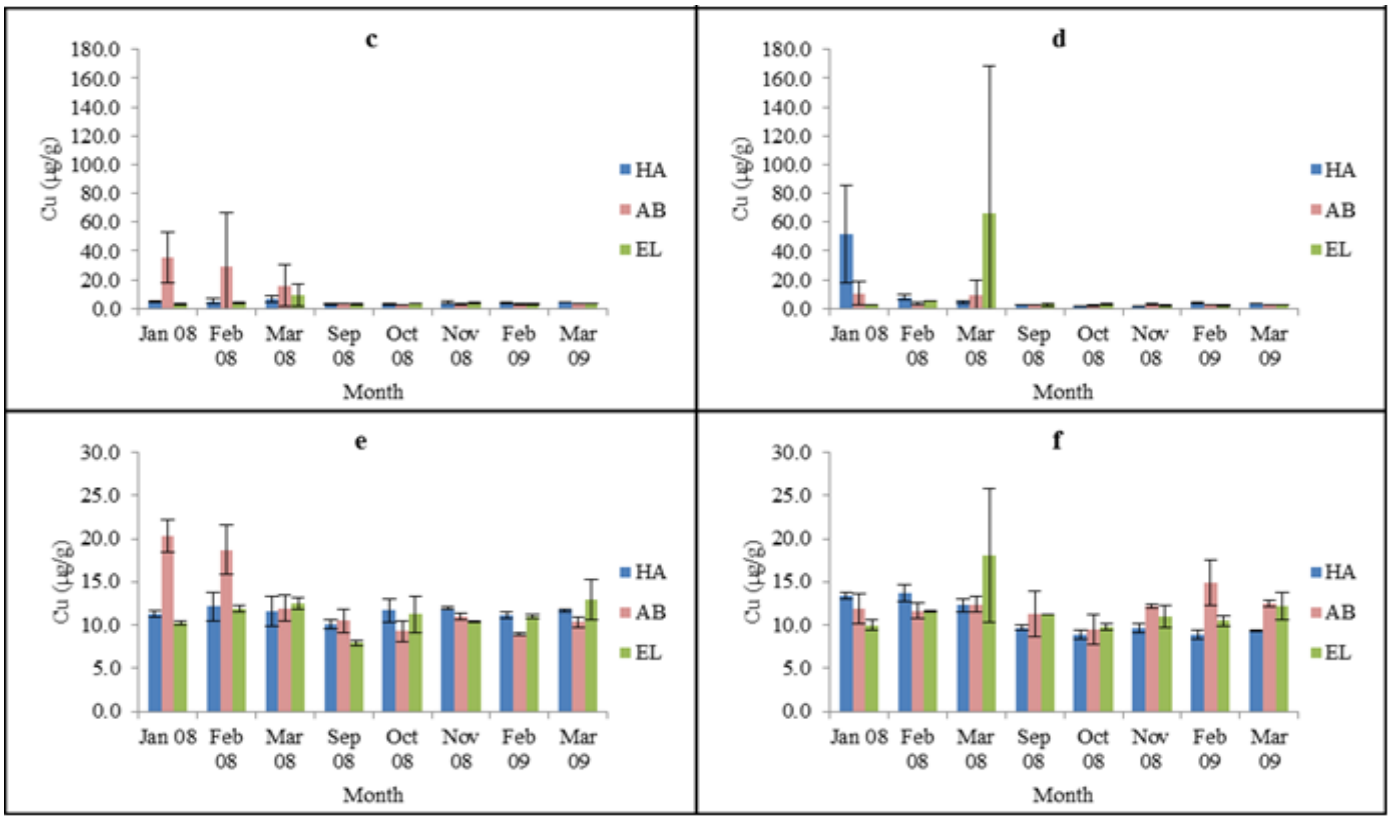


Fig. 2:Trace and heavy metal burdens (a, b= Fe; c, d = Cu; and e, f = Zn) in *S. maderensis* (a, c, and e) and *C. chrysurus* (b, d, and f) collected from study sites with error bars indicating standard deviation. HA - Half-Assini; AB - Aboadze; and EL - Elmina

Copper burden in both *S. maderensis* and *C. chrysurus* were consistently low during Periods 2 and 3 (Fig. 2c and 2d). Concentrations ranged from 1.32 µg/g dw to 1.72 µg/g dw during these periods. Cu burdens in *S. maderensis* from Half-Assini for Period 1 ranged from 3.92 µg/g dw to 8.28 µg/g dw. Aboadze recorded the highest Cu levels in *S. maderensis* during Period 1 with high variability. Mean Cu burdens in *S. maderensis* from Aboadze for the sampling months of Period 1 were 35.7 ± 17.4 µg/g dw, 29.3 ± 37.1 µg/g dw and 15.9 ± 14.2 µg/g dw respectively. Cu in *S. maderensis* from Elmina ranged between 2.88 – 18.3 µg/g dw. Low levels of Cu in both *S. maderensis* and *C. chrysurus* (Fig. 2c and d) were recorded and consistent for Periods 2 and 3. For *S. maderensis*, relatively low Cu levels were also recorded during Period 1 for samples taken from Half-Assini and Elmina but samples from Aboadze recorded variable concentrations. However, Cu burdens in *C. chrysurus* during Period 1 was high in January and March 2008 for Half-Assini and Elmina, with concentrations of 51.9 ± 33.8 dw µg/g and 66.3 ± 102 dw µg/g respectively but with very high variability in samples taken at Elmina, resulting in very high standard deviations. These Cu concentrations were generally higher compared to previous studies [37].

Low concentrations of Cu in *C. chrysurus* ranged from 1.32 µg/g dw (Half-Assini – November 2008) to 21.0 µg/g dw (Aboadze – March 2008) whiles high concentrations ranged from 88.6 µg/g dw (Half-Assini – January 2008) to 184 µg/g dw (Elmina – March 2008). Although levels of Cu recorded in *S. maderensis* from Aboadze during the months of period 1, and *C. chrysurus* from Half-Assini in January 2008 and from Elmina in March 2008 were observed to exceed FAO maximum recommended limit of 30 ppm (30 µg/g dw) in fish [15] and may be of health concern to the consuming public. A study by Eisler [14] indicated that mammals and birds are more resistant to high copper concentrations up to levels as high as 500 µg/g than other animals, thus suggesting that the levels of copper recorded in both fish species would pose no threat to mammals including humans, except when these fishes are continually consumed in large quantities. However, these fish species may be under threat since the high concentrations recorded could cause sublethal effects on their respiration [35], osmoregulation [34], behaviour, growth and metabolism [14], and subsequently death [21], resulting in significant reduction in stocks of these commercial fish species.

The sampling periods recorded consistently low Zn burdens in the fish species except for January and February 2008 which recorded relatively high Zn levels in *S. maderensis* (Fig. 2e), and, March 2008 and February 2009 which also recorded relatively high Zn levels in *C. chrysurus* (Fig. 2f). Concentrations of Zn generally ranged from 7.64 to 21.6 µg/g dw in *S. maderensis* and from 7.64 to 26.7 µg/g dw in *C. chrysurus*. The highest concentration of Zn was recorded in *C. chrysurus* in March 2008. Zinc concentrations were again higher than those recorded in previous studies [37]. Zn burdens in samples of fish species analysed were below the FAO

maximum recommended limit of 40 µg/g in fish [15], indicating safe levels of the metal for human consumption. Again, the concentrations of Zn recorded were high enough to affect respiration of the fish species as indicated by experiment conducted by Sellers *et al.* [35] in Rainbow trouts, who found Zn concentrations of 1.43 ppm (1.43 µg/g) to produce a sharp decrease in blood oxygen and pH, which led to increased ventilatory activity.

Fish metal concentrations were in the order of Fe>Zn>Cu for the two different fish species, with the absence of Pb and Cd attributable to regulated use and disposal of these elements as well as the absence of large-scale commercial industries along the western coast. The inconsistent high levels of Cu recorded in the fish samples raises a health concern and may put consumers at risk from consumption of these fish species taken from the western coastal waters of Ghana, should the trend continue and should consumers consume large quantities of these fish species.

A one way analysis of variance (ANOVA) conducted to determine differences among metal accumulation patterns for Fe, Cu and Zn in the fish species from the sampling locations showed no significant difference ($p>0.05$) in the accumulation patterns of Cu and Zn in the two species among the three sites. However, significant differences ($p<0.05$) were recorded for Fe concentrations between the two fish species as well as among the three sampling sites (Table 2). This implies that Fe accumulation pattern is not similar in the two fish species while accumulation of Cu and Zn may be similar. This may probably be due to the difference in depuration rates of Fe in the two fish species.

3.1 Human Health Risk Assessment

For each sampling location, hazard quotient was calculated as a function of ingestion rate and concentration of the metals in the fish species. Non-carcinogenic effect was estimated using reference dose values (RfD) for Fe, Cu and Zn. Results of hazard quotients and hazard indices are presented in Table 3 with their corresponding RfDs. Hazard ratios and hazard indices calculated for the three metals (Fe, Cu and Zn) were all below 1 (Table 3), which is an indication of a low non-carcinogenic effect on human health for all the three metals. This means that the exposure of these metals to the human population from the consumption of *S. maderensis* and *C. chrysurus* will not result in any appreciable health risks that may be associated with the metals. This confirms the fact that the fish species analysed are relatively safe for public consumption with respect to the Cd, Cu, Fe and Pb concentrations.

4. CONCLUSION

Iron (Fe) was recorded in high concentrations in the two fish species sampled, indicating that *C. chrysurus* and *S. maderensis* from the study locations can be very good sources of Fe in human diet. Levels of Cu recorded in some circumstances were higher than the FAO recommended limits for human consumption. Pb and Cd contamination may not pose any health risk to the consuming population in all the samples analysed since they were below detection limits. Even though low hazard quotients and hazard indices were recorded for the fish species, indicating that metal exposure from the consumption of these fish species may not result in any appreciable health risk, relatively high levels of Cu recorded may be of public health concern and need to be consistently monitored to protect public health. In addition to Cu, Zn levels in the two fish species were high enough to cause physiological dysfunctions in these fishes and may threaten their survival, leading to decline in their abundance and commercial availability. We recommend that further studies be conducted on the distribution of metals in the tissues of these fish species for the purpose of monitoring in order to protect human health.

Table 2: ANOVA for Metal Concentrations between Species and among Sites

Comparison	Element	Groups	Sum of Squares	df	Mean Square	F	Sig.
Species	Fe	Between Groups	416.82	1	416.82	4.316	0.043
		Within Groups	4 442.639	46	96.579		
		Total	4 859.459	47			
	Cu	Between Groups	0.522	1	0.522	0.156	0.694
		Within Groups	153.308	46	3.333		
		Total	153.829	47			
	Zn	Between Groups	0.008	1	0.008	0.067	0.797
		Within Groups	5.410	46	0.118		
		Total	5.418	47			
Site	Fe	Between Groups	1 156.610	2	578.305	7.028	0.002
		Within Groups	3 702.848	45	82.286		
		Total	4 859.459	47			
	Cu	Between Groups	0.234	2	0.117	0.034	0.966
		Within Groups	153.596	45	3.413		
		Total	153.829	47			
	Zn	Between Groups	0.277	2	0.138	1.211	0.307
		Within Groups	5.141	45	0.114		
		Total	5.418	47			

Table 3: Estimated Hazard Quotient and Hazard Index for Fe, Cu and Zn at Half-Assini, Aboadze and Elmina

		HQs			HIs
Fish species	**Station**	**Fe**	**Cu**	**Zn**	**(HQ_{Fe} + HQ_{Cu} + HQ_{Zn})**
C. chrysurus	**Half-Assini**	0.195	0.552	0.041	0.788
	Aboadze	0.128	0.250	0.014	0.392
	Elmina	0.079	0.616	0.013	0.708
S. maderensis	**Half-Assini**	0.501	0.247	0.013	0.761
	Aboadze	0.194	0.684	0.014	0.893
	Elmina	0.101	0.236	0.013	0.349
Reference dose (RfD – mg/kg/day)		0.360[a]	0.020[b]	0.300[b]	

[a] Source: USEPA (2006)

[b] Source: Mishra (2007)

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