DETERMINATION OF METALS IN SIX MARINE FISH SPECIES FROM THE WESTERN COASTAL WATERS OF GHANA USING NEUTRON ACTIVATION ANALYSIS TECHNIQUE

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Abstract
A base line study was carried out before the off-shore drilling of oil in the Western region of Ghana to assess the levels of nine (9) essential elements (Ca, Mg, K, Na, Cl, Al, V, Cu, and Mn) in the muscle of six different fishes using Neutron Activation Analysis (NAA) technique. The species; Pseudotolitus typus, Pomadasys jubelini, Sphyraena sphyraena, Chloroscombrus chrysurus, Caranyx crysos, and Scomberous tritor) were collected at landing sites from three communities in the Western Region namely, Efasu, Half-Assin and Mangyea. Metals in fish were measured on a dry weight basis.The concentrations of metals in the muscles of fish were 88.78-3593.28µg/g (Mg), 2652.64-11097.02 µg/g (Ca), 276.42-5108.14 µg/g (Na), 1432.62-26176.66 µg/g (K), 116.42-9967.66 µg/g (Cl), 1.64-8.04 µg/g (Al), n.d-1.99 µg/g (Mn), n.d-0.54 µg/g (V) and n.d-33.02 µg/g (Cu). Elements which were most abundant in all species were Ca, Mg, Na, K and Cl and this suggests their essential character to all the species. They are essential in the mechanical movement of the fish and are also necessary for neuromuscular functions. Consumption of these fish species poses no threat to human health however, there is the potential danger of metal contamination as a result of the activities of the oil exploration. Therefore a monitoring programme has to be conducted regularly to prevent such occurences.

Keywords: essential element, fish, muscle, NAA, off-shore drilling, Western Region

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1. INTRODUCTION

Fish is generally accepted as one of the healthiest and cheapest sources of protein and it has amino acid compositions that are richer in cysteine than most of the other sources of protein (Kalyoncu et al., 2011). Epidemiological studies have shown that population with a rich sea food diet have low risk of coronary heart disease, hypertension and cancer (Barrento et al., 2008). In Ghana, the marine sub-sector is the most important source of local fish production and provides more than 80% of the total fish supply (FAO, 2011). With Ghana's population currently standing a little bit over 24 million people, the per capita fish consumption averages 29.7kg per annum (FAO, 2011) but it can even be higher in coastal communities. The western coast of Ghana is noted among the locations of significant contribution of marine fish production in the country. There are different landing beaches in almost all villages and towns located along the coastal belt of the country engaged in fishing for which different types of fish are caught. The artisanal fisheries fleet account for about 70% of the total fish exploit. There are about 447 diversity of fishes in Ghana's marine waters (FAO, 2011).

In the marine environment, metals are potentially accumulated in marine organisms and sediments and finally transferred to humans through the food chain (Uluozlu et al., 2007). Inadequate amounts of essential elements (eg. Na, Mg, Cl, P, S, K, Ca, Mn, Fe, Cu, Zn, Se) leads to improper enzyme mediated metabolic functions and results in organ malfunctions, chronic diseases and death (Barrento et al., 2008).

However, essential metals could produce toxic effects when their intake is excessive (Uluozlu et al., 2007).

Although the health benefits related to essential elements in fish have been well studied from various parts of the world(Barrento et al., 2008; Tuzen, 2009;Yilmaz et al., 2010) , little attention has been focused on the elemental content of most fishes vastly consumed in the Ghanaian society.

This work was conducted in three coastal communities namely Efasu, Half-Assin and Mangyea. With the recent discovery of oil in large quantities in these areas (especially Half Assin & Efasu), several studies have been carried out mostly on the economic benefits of the exploration (Boohene& Peprah, 2011; Affam & Asamoah, 2011).

There is fear that activities involved in the exploration of oil might affect the quantity and health status of fish caught in the sea.

Fishing is one of the main sources of employment and food for the indigenes in these communities. Most common fish species caught are *Pseudotolitus typus, Pomadasys jubelini, Sphyraena sphyraena, Chloroscombrus chrysurus, Caranyx crysos, and Scomberous tritor.* There is little information on the essential element content of these fish species.

This present study was therefore undertaken to determine the levels of some major and essential elements (Ca, Mg, K, Na, Cl, V, Cu, Mn) in the muscle of six different species of marine fish (*Pseudotolitus typus, Pomadasys jubelini, Sphyraena sphyraena, Chloroscombrus chrysurus, Caranyx crysos, Scomberous tritor*) which are of economic interest in the study area.

From a public health perspective, this study will furnish consumers with better knowledge of elemental content associated to *Pseudotolitus typus, Pomadasys jubelini, Sphyraena sphyraena, Chloroscombrus chrysurus, Caranyx crysos, and Scomberous tritor*.

2. MATERIAL AND METHODS

2.1 Species sampled

In this investigation, about 10 each of 6 different species of fish were collected at three stations from the western coastal waters of the Atlantic Ocean in June 2010 by professional fishermen using their traditional methods, with nets. The sampled fishes were assigned to be sold on the market for human consumption. Species sampled were Cassava croaker (*Pseudotolithus typus),* Barracuda (*Sphyraena sphyraena),* Spotted Burro *(Pomadasys jubelini)*, *Chloroscombrus chrysurus, Caranyx crysos* and *Scomberous tritor.* Fish species were labelled, stored on ice and transported to the laboratory on ice and stored at -20C before analysis. On site, the length and weight of the fishes were measured.

2.2 Analytical procedure

Fish samples were dismembered into muscles (flesh) and weighed. Each tissue was cut into small pieces and kept frozen. The frozen samples were then freeze dried in a Christ Freeze dryer (Beta 1-16, LMC-1, Germany) at a temperature of -30C (corresponding to a vapour pressure of 0.370 mbar).

The lyophilized fish samples were homogenized by manual grinding in a ceramic mortar and stored at -20C under controlled humidity conditions until further analyses. About 200mg of each part was weighed onto well-cleaned polyethylene film. The films were wrapped and heat-sealed. Replicate samples were prepared, packed into polyethylene irradiation vials and heat-sealed. Reference tissues, oyster tissue was prepared and packed similarly as the samples and analysed for quality control purposes.

Metal concentrations were calculated µg/g dry weight.

2.3 Sample irradiation and counting

Sample irradiation and counting have been briefly described below. The samples and controls were irradiated at the Ghana Research Reactor (GHARR-1) facility at the Ghana Atomic Energy Commission, Kwabenya, operating at 15kW at a thermal flux of 5 x 10^{11} $ncm^{-2}s^{-1}$. The samples were transferred into irradiation sites through pneumatic transfer

systems at a pressure of 1.723 bars. The irradiation was categorized mainly according to the half-life of less than a few hours like ^{28}Al, ^{49}Ca, ^{38}Cl, ^{66}Cu, ^{27}Mg, ^{56}Mn, and ^{52}V, irradiation time (t_i) was 2min, decay time (t_d) of 1-10 min, and 10 min counting time (tc). For ^{42}K and ^{24}Na with half-lives of several hours, irradiated time was 1h with 24h decay and 1h counting.
The counting of the induced radioactivity was performed by a PC-based γ -ray spectrometry. It consists of an n-type HPGe detector coupled to a computer-based Multichannel Analyzer (MCA) via electronic modules. The relative efficiency of the detector is 25% and its energy resolution of 1.8keV at a γ -ray energy of 1,332 keV of ^{60}Co. For each element, a 1,000 µg/mL stock solution was prepared. The γ -ray product radionuclides were qualitatively identified by their energies emitted and the quantitative analysis was done by converting the counts as an area under the photo peak by the comparator method. Both analyses were done using the gamma-ray spectrum analyses software, ORTEC-MAESTRO-32.

3. RESULTS AND DISCUSSIONS

3.1 Element composition in the muscle tissue of each species

Two groups of elements were determined in the muscle tissues of fish samples (*Pseudotolitus typus, Pomadasys jubelini, Sphyraena sphyraena, Chloroscombrus chrysurus, Caranyx crysos, and Scomberous tritor)* as listed in Table 1. One group consists of elements which are major and present in all animal tissues (Na, K, Mg, Ca, Cl) whilst the other group is essential to life namely Cu, Mn & V.
All metal concentrations were determined on dry weight basis. Essential element content in fish samples were found to be 88.78-3593.28 µg/g for magnesium, 2652.64-11097.02 µg/g for calcium, 276.42-5108.14 µg/g for sodium, 1432.62-26176.66 µg/g for potassium, 116.42-9967.66 µg/g for chlorine, 1.64-8.04 µg/g for aluminium, n.d-1.99 µg/g for manganese, 0.038-0.54 µg/g for vanadium and n.d-33.02 µg/g for copper. According to these data, potassium had the highest concentration and followed by calcium, chlorine, sodium, magnesium, aluminium, copper, manganese and vanadium. The most abundant elements were Na, K, Ca, Mg and Cl. Concentrations of these elements varied from 88.78-26176.66µg/g.
Maximum level of sodium (5108.14 µg/g) was found in P. typus (Efasu) whilst the lowest (276.42 µg/g) in S.tritor (Half-Assin). Sodium is an essential element needed by humans to keep normal fluids balanced in the body. It plays an important role in many physiological processes: signal transduction in the human central nervous system, osmoregulation, arterial pressure maintenance and optimal salt and water balance in the body (Barrento et al., 2008).
The highest Ca & Mg concentrations were found in P.jubelini (11097.02 µg/g) from Mangyea and C.crysos (3593.28 µg/g) from Half-Assin, respectively whereas the lowest concentration of Ca was found in S.tritor (2652.64 µg/g) and the lowest concentration of Mg was found in S.sphyraena (88.78 µg/g) from Mangyea. Abundance of elements; Ca, Mg, K & Na in the muscle tissue could be attributed to the fact that they are essential in the mechanical movement of the fish and are also necessary for neuromuscular functions. The levels of Cl ranged from 116.42 µg/g in S.sphyraena to 9967.66 µg/g in P.typus. The maximum concentration of Al was found in S.tritor (8.04 µg/g) whilst the minimum concentration was found in S.sphyraena (1.64 µg/g).

Table 1 Metal concentration (μg/g dry wt.) in muscle of six different fish species sampled from the western coastal waters of Ghana

Location	Efasu	Half-Assin	Half-Assin	Mangyea	Mangyea	Mangyea
Element	P. typus	C. crysos	S. tritor	C. chrysurus	P. jubelini	S. sphyraena
Mg	2114.66±10.35	3593.28±10.56	2811.36±15.89	1683.58±12.87	3074.09±16.7	88.78±2.28
Ca	7552.34±35.97	4522.44±25.87	2652.64±35.18	3574.73±34.08	11097.02±48.61	4123.29±19.71
Na	5108.14±64.76	3287.29±56.06	276.42±14.26	3012.29±24.60	3016.36±51.92	4376.51±62.82
K	12616.08±105.44	17893.17±134.69	1432.62±33.66	13865.84±105.15	26176.66±151.66	18441.96±137.48
Cl	9967.66±105.61	5886.69±79.99	7257.4±109.5	2422.14±82.79	3172.44±80.56	116.42±13.24
Al	4.53±1.17	7.66±1.24	8.04±1.57	3.95±1.28	6.01±1.62	1.64±0.48
Mn	n.d*	n.d	1.99±0.01	n.d	n.d	n.d
V	0.54±0.02	0.52±0.02	0.52±0.02	0.33±0.01	n.d	0.038±0.002
Cu	n.d	33.02±0.72	n.d	11.34±0.61	n.d	9.29±0.18

* Not detected

Accumulation of Cu in fish species ranged from 33.02 μg/g in *C.crysos* to n.d in *(Pomadasys jubelini, S.tritor and Pseudotolitus typus)*. Levels of copper in all fish samples with the exception of C. crysos were below the toxic limit of 30 μg/g (FAO 2008). For most copper, the solubility in water is negligible, thus little copper is present in natural water. Presence of copper in surface water is due to the extensive use of pesticide sprays containing copper compounds for agricultural purposes. Copper is found in several enzymes including the cytochrome C oxidase and the superoxide dismutase and is used for biological electron transport. It is an essential element in human metabolism but can cause anemia, disorders of bone and connective tissues and liver damage at excessive levels. The toxicity of copper depends upon the hardness and pH of the water, and therefore, it is more toxic in soft water and in water with low alkalinity (Al-weher, 2008)

The highest V (0.54μg/g) concentration was detected in P.typus but it was not detected at all in P.jubelini. The element occurs naturally in fossil fuel deposit and although it considered as a micronutrient, its role in mammals has not yet been defined. The toxicity of vanadium compounds often increases with the valency. Its toxicity is attributed to its ability to inhibit enzyme systems such as monoamine oxidase, ATPase, tyrosinase, choline esterase and cholesterol synthetase (Luckey & Venugopal, 1977). Levels of vanadium in the Western coastal waters of Ghana may increase with time as a result of the oil exploration taking place in its offshore region. This might have a detrimental effect on the health status of fish from such waters when it bioaccumulates the metal.

Manganese is the less abundant metal in all the species except C.crysos which recorded a concentration of 1.99 μg/g which was a little above the toxic limit of 1 μg/g (WHO, 1989). Manganese is an important element vital for the structure component of some enzymes and activates the actions of some enzymes (Tuzen, 2009). The metal is widely distributed with little variations in the body and does not accumulate with age (Yilmaz et al., 2010). According to FAO, 1983 there is no known carcinogenic effect of manganese. The recommended daily intake for an adult is 2-9 mg (WHO, 1994).

A number of studies have shown that muscle is a poor indicator of metal contamination (Kalyoncu et al., 2011; Pourang et al., 2003, Tepe et al., 2008) in fish. However, studies have shown that there are a number of factors that could influence the accumulation of metals in the tissues of fish and these include the size of fish (Pourang et al., 2003), season, physical and chemical status of water (Kalyoncu et al., 2011). As shown in Fig. 1, levels of vanadium are quite high in areas (especially Efasu and Half-Assin) where most of the activities of the oil exploration activities are taking place in the off-shore regions as compared to Mangyea.

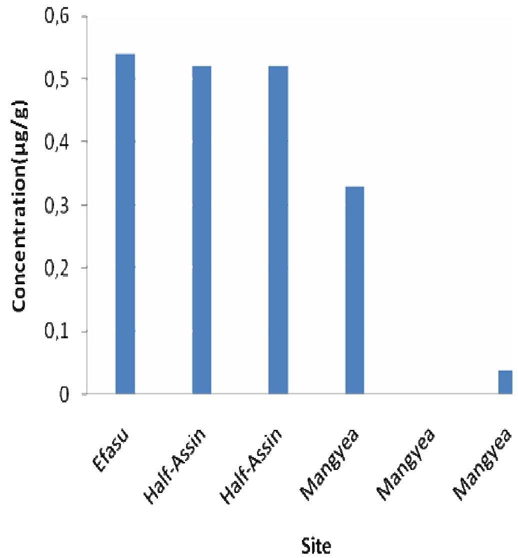

Figure 1. Levels of vanadium in fish species from Efasu, Half-Assin & Mangyea

Comparing results of metals (V, Mn & Cu) of this study with other study (Pourang et al., 2003); vanadium and copper concentrations in the fish species that were analyzed in our study recorded higher concentrations of the metals whereas Mn concentrations were low.

4. CONCLUSION

Baseline studies in the study area have shown that fish flesh is a good source of minerals. Generally, Na, K, Mg, Ca& Cl were the most abundant elements in the muscles suggesting their essential character to *Pseudotolitus typus, Pomadasys jubelini, Sphyraena sphyraena, Chloroscombrus chrysurus, Caranyx crysos* and *Scomberous tritor*. These elements are essential for human health. Differences detected between fish species likely reflect distinct availability of elements in the aquatic environment as the fishes are distributed in different regions of the Gulf of Guinea. Consumption of these fish species poses no threat to human health however for consumers who are on low sodium diet, consumption of these fish species may not be in their best interest. There may be a potential danger in the future with the onset of exploration of oil in the offshore regions of the Western coastline. Further monitoring has to be conducted.

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