ISSN: 2347-5129
IJFAS 2014; 1(6): 82-86

www.fisheriesjournal.com
Received: 24-05-2014
Accepted: 12-06-2014

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Distribution of heavy metals in tissues and organs of tuna

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Abstract
The occurrence of heavy metals (Copper, Zinc, Cadmium, Lead and Manganese) in fresh edible tissue and organs of three species of Tuna were assessed to determine the concentrations, distribution patterns and affinities of metals to organs and tissues. The fish samples were obtained from fish landing sites in Tema, Ghana, West Africa. Metal concentrations in the samples were determined by the Atomic Absorption Spectrometer after nitric acid digestion. From the results, the edible tissues had the lowest concentrations of metals. The concentrations of metals such as Cu, Mn and Zn which are micronutrients were generally higher than the non-essential ones (Cd and Pb) in all the species analysed. Cadmium was found to largely accumulate in the liver, whiles Mn was found to be higher in the bones. Variations observed in metal accumulation patterns were attributed to varying characteristics and possible affinities of the metals to particular organs.

Keywords: Tuna, heavy metals, fish, pollution, contamination, aquatic environment, metal accumulation.

1. Introduction
Heavy metals enter the aquatic environment from both natural and anthropogenic sources. The anthropogenic sources include; mining and industrial effluents, domestic discharges, leachates from waste dumps, inputs from agricultural activities and atmospheric sources especially burning of fossil fuels. Incineration of wastes and industrial emissions are, however, the main sources of heavy metal pollution [1]. Heavy metals are highly persistent and tend to accumulate in the environment and in aquatic organisms such as fish. Increased reports of environmental contamination by heavy metals [1, 2] thus place fish and the other aquatic resources at risk of heavy metal contamination [3]. Although some heavy metals such as zinc, copper, manganese and iron are essential micronutrients required for the growth and well-being of living organisms, including man, other such as lead and cadmium are not essential and their mere presence could be detrimental to the health of the organism. The essential metals can, however, also become toxic when certain threshold levels are exceeded. The negative effects of nonessential heavy metals on man include the displacement of essential elements or inhibition of enzyme reactions leading to a disruption of physiological activities [4].
The extent to which metals accumulate in aquatic organisms vary and depend on many factors such as, water temperature, salinity, age, size, and feeding habits [5]. Tunas are high up the food chain and are recognised as predators able to concentrate large amounts of metals [6] because they ingest all the metals that their prey has taken in. They are integral to the diets of millions and they form the basis of important commercial and recreational fisheries throughout tropical and temperate waters of the world.
A number of studies [3, 7, 8, 9] have looked at the concentrations of heavy metals in edible tissues of tuna but these largely in the processed canned fish. The study looked at the levels of heavy metals in the fresh tissues of tuna, their distribution patterns in edible muscle tissues and organs (skin, gills, liver, heart and bone) of the fish; as well as assessing possible affinities of metals for particular organs. The metals analysed were cadmium (Cd), lead (Pb), copper (Cu), zinc (Zn), and manganese (Mn).

2. Methods
2.1 Samples collection handling and storage
Three tuna fish species from the Scombridae family, namely Frigate tuna (*Auxis thazard*), Atlantic little tuna (*Euthynnus alletteratus*) and Skipjack tuna (*Katsuwonus pelamis*), obtained

from local fishermen at landing sites in Tema in the Greater Accra Region of Ghana, West Africa (Fig 1) were used for the study.
The fish, after purchase, were placed in polythene bags and transported to the laboratory in ice-packed thermo-insulated boxes. In the laboratory, the samples were rinsed with distilled water, separated into specie groups, placed in clean plastic bags and stored in a deep freezer at -20 °C until ready for analysis.

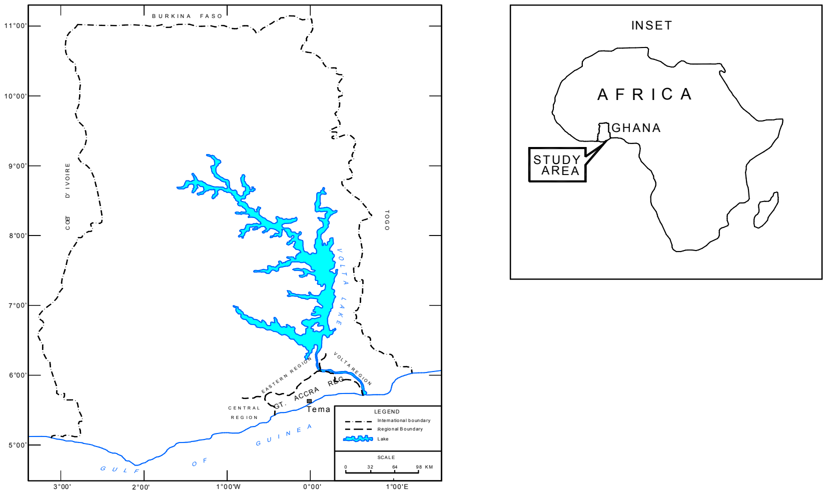

Fig 1: Map of Ghana showing the Greater Accra Region.

The number of fish samples obtained for each of the species, their sizes and the percentage dry weights are summarised in Table 1. Mean weights of the samples ranged from 603 g to 1547 g. Mean lengths ranged from 34.2 cm to 44.8 cm whilst the dry matter contents ranged from 24.4 to 30.4%.

Table 1: Types, numbers and sizes of fish obtained for analyses

Family : Species	No. of fish samples collected	Mean Weight (g)	Mean Length (cm)	Dry Weight (%)
Scombridae:				
Frigate Tuna	6	603±114	34.2±2.48	29.0±4.53
Atlantic Little Tuna	6	1002±45.9	45.0±1.41	26.9±1.60
Skipjack Tuna	7	1547±4.32	44.8±5.57	30.4±4.31

2.2 Tissue Decomposition and Analysis
Samples for digestion were taken from partially thawed specimen, which are easier to manipulate. Using plastic tweezers and plastic knives, the skin was stripped off from one side of the fish. The exposed fillet was cut and placed in a plastic vial [10]. Again, using plastic tweezers and knives as well as stainless steel scissors, other tissues - bone, liver, gill, heart and skin - were obtained from the fish by dissection and placed in plastic vials.
For solubilisation of samples, sub-samples of about 1 g of fresh weight (FW) of tissues from each sample taken out as described above, were accurately weighed into Teflon digestion crucibles and digested under pressure with 2.5 ml concentrated nitric acid (Analar grade) by slowly heating to 80 °C followed by rapid heating to 160 °C [11]. The temperature was maintained at 160 °C for 7 to 8 hours. Each sample was analysed in triplicate. Digested samples were normally clear (devoid of tissues), colourless or pale yellow in colour. These were made up to 10 ml with deionised water and analyzed for heavy metals using a UNICAM 969 Graphite Furnace Atomic Absorption Spectrometer.
The metals; cadmium, lead, copper, zinc and manganese, were determined by flame atomization [12]. For the assurance of good quality data, International Atomic Energy Agency Tuna fish flesh homogenate reference material, IAEA 436 was analyzed alongside the samples. Dry matter content of the tissues was determined by heating in an oven at 105 °C to constant weight [13]. Digestion and analysis of all the samples were completed within a week after collection.
The percentage concentrations of the metals in the various tissues were computed by simple proportion. Statistical analyses were carried out using SPSS 16 for windows. Variations in metals concentrations across the tissues and among the species were assessed using One-way ANOVA.

3. Results
In Table 2 presents a summary of the performance of the analytical methods. Quantitative recoveries were obtained for all the five heavy metals.
Results of metals concentrations in the tissues and organs of the selected tuna species are presented in Table 3.

Table 2: Performance of analytical methods: limits of detection and results for IAEA 436 Tuna powder

Metal concentration (µg/g)	Cd	Pb	Cu	Zn	Mn
Limit of detection	0.01	0.01	0.20	0.20	0.20
Certified value	0.052±0.007	0.068 ± 0.057	1.73±0.19	19.0±1.3	0.238±0.042
Measured values	0.050±0.006	0.076±0.003	2.19±0.36	18.5±2.1	0.269±0.055

The concentrations of the essential metals, Zn, Cu and Mn were generally higher than those of the non-essential metals - Cd and Pb. The essential metals, particularly Zn and Cu were relatively more evenly distributed across the different fish tissues and organs (Table 3) than the non-essential ones which accumulated in particular tissues such as the liver, bone or gills. The order of abundance of the elements in the different fish species based on concentrations in the tissues analysed were as follows:

Frigate Tuna Zn > Mn > Cu > Pb > Cd

Atlantic Little Tuna Zn > Cu > Mn > Pb > Cd

Skipjack tuna Zn > Mn > Cu > Pb > Cd

Zinc concentrations were highest in all tuna species analysed. The concentrations, which varied significantly ($p < 0.01$) from those of the other heavy metals ranged from 13.6 mg/kg to 64.7 mg/kg (fresh weight) in Frigate Tuna, 7.56 mg/kg to 87.4 mg/kg in Atlantic little Tuna and 17.8 to 80.7 mg/kg in Skipjack Tuna (Table 3). None of the concentrations, however, exceeded the recommended guideline value of 100 mg/kg (fresh weight) for edible tissue [14].

Manganese concentrations were the second most abundant metal for Frigate tuna, and Skipjack tuna, but third for Atlantic little tuna, for which Cu was the second most abundant metal in the tissues. Differences in the concentrations of Mn and Cu in the Atlantic little tuna were, however, smaller when compared to that between Zn and the two elements (Mn and Cu) and statistically insignificant ($p>0.05$). Mean Pb concentrations were the second least abundant after Cd, whose concentrations in the tissues were lowest for all the fish analysed.

Although the Frigate Tuna samples were the smallest in terms of size (length and weight, Table 1), metal concentrations in the tissues were slightly higher than those of the other species but the differences were found to be insignificant ($p>0.05$).

Table 3: Concentrations of metals in tissues and organs of Tuna fish (mg/kg wet weight).

Specie	Tissue	Cd	Pb	Cu	Zn	Mn
Frigate tuna	Bone	0.07±0.2	7.01±0.9	4.96±0.9	64.7±11.7	36.3±12.5
	Liver	2.44±1.9	1.08±0.4	4.91±1.7	63.7±24.2	1.48±0.6
	Gills	0.28±0.6	2.47±0.3	2.0±0.2	34.9±6.7	4.5±1.1
	Heart	0.22±0.3	1.36±0.3	6.32±1.0	19.9±3.3	0.52±0.1
	Skin	0.24±0.2	0.92±0.4	5.29±1.6	44.6±18.4	0.93±0.3
	Fillet	<0.10	0.64±0.2	1.08±0.3	13.6±4.2	<0.20
Atlantic Little tuna	Bone	0.51±0.1	0.66±0.1	3.99±0.5	51.6±7.0	9.92±0.9
	Liver	1.17±0.4	0.23±0.1	3.92±1.2	87.4±20.2	0.80±0.1
	Gills	0.18±0.04	0.33±0.02	1.80±0.1	33.3±8.2	3.34±0.6
	Heart	<0.10	0.22±0.1	5.22±0.7	19.6±2.1	<0.20
	Skin	<0.10	0.20±0.02	1.93±0.5	56.7±15.4	<0.20
	Fillet	<0.10	0.20±0.03	0.31±0.1	7.56±2.2	<0.20
Skipjack tuna	Bone	0.35±0.5	0.76±0.1	2.28±0.7	46.1±5.7	14.7±5.7
	Liver	1.71±0.9	0.42±0.1	3.73±2.0	80.7±31.9	1.97±1.0
	Gills	0.10±0.06	0.51±0.2	1.70±0.2	72.7±33.5	5.46±1.0
	Heart	<0.10	0.30±0.2	2.52±0.4	19.5±9.9	0.78±0.4
	Skin	0.13±0.09	0.39±0.2	0.40±0.10	74.0±34.1	0.64±0.5
	Fillet	<0.10	0.32±0.1	0.60±0.2	17.8±7.3	<0.20
Permissible guide values**		**2.0**	**2.0**	**30.0**	**100.0**	**-**

** Nauen (1983)

The order of abundance of metals in the various tissues with the exception of Pb and Mn varied from one metal to the other.

Below is a summary of the general distribution of the five metals in the tissues:

Cd: Liver > Bone > Gills > Heart > Skin = Fillet

Pb: Bone > Gills > Liver > Heart > Skin > Fillet

Cu: Liver > Heart > Bone > Gills > Skin > Fillet

Zn: Liver > Bone > Skin > Gills > Heart > Fillet

Mn: Bone > Gills > Liver > Heart > Skin > Fillet

Cadmium, Cu and Zn were most abundant in the liver. The tissues with the second highest concentrations of these metals were, however, varied. For Cd and Zn, the bone had the second highest concentrations, whilst for Cu, it was varied. Lead and Mn on the other hand were most abundant in the bone and the order of abundance in the tissues followed a similar trend; with the gills having the second highest concentrations of these metals and, following in decreasing order of the metals concentration were the liver, heart, skin and fillet. Edible muscle tissues of the three species had the lowest concentrations of all the metals. Using Pearson's correlation text, significantly positive direct correlations were found between Zn and Cd ($r^2 = 0.494$, $p < 0.05$); and Mn and Pb ($r^2 = 0.877$, $p < 0.01$) concentrations in the fish tissues (Table 4).

Table 4: Correlations between metal accumulation patterns in fish tissues

	Cd	Pb	Cu	Zn	Mn
Cd	1.000				
Pb	-.060	1.000			
Cu	.377	.294	1.000		
Zn	.494*	.029	.189	1.000	
Mn	-.096	.877**	.235	.099	1.000

* Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

4. Discussion and conclusions

Variations in metal concentrations of aquatic species have been attributed to factors such as water temperature, salinity, age, size and feeding habits [5]. The similarities observed in metal concentrations in tissues and organs of the three tuna species may be attributed to these factors, considering that they dwell in similar habitat conditions and have similar feeding habits.

Lower concentrations of heavy metals observed in edible fillet and skin of the fish, compared to the organs are consistent with the findings of several other studies [15, 16, 17]. The concentrations of heavy metal in the fish samples as observed from the study followed a trend in which mean concentrations of the essential metals were generally higher than those of the non-essential metals. Of the five metals studied, Zn had the highest mean concentrations in the tissues. In a study of trace metals in canned fish [18] also found Zn concentrations to be the highest and followed in decreasing order of concentration by Fe, Mn and Cu, all of which are essential micronutrients. The abundance of Zn in the tissues may be attributed to the fact that its concentrations are regulated by physiological mechanisms in most organisms and do not necessarily relate directly with Zn concentrations in their environment [19, 20]. Copper the second most abundant metal for Atlantic Little Tuna and the third for Frigate Tuna and Skipjack Tuna is also an essential metal necessary for good health. A very high intake can, however, cause adverse health problems, such as liver and kidney damage [21]. Lead the second least accumulated metal is non-essential and is known to induce reduced cognitive development and intellectual performance in children and increased blood pressure and cardiovascular disease in adults [22].

The different patterns of metal accumulation observed in the tissues somehow confirms the fact that heavy metals do not have the same affinities for the various tissues [23]. Mineralised tissues such as bones and teeth have been found to be good markers for uptake of contaminants by living organisms from the surrounding environment and have the ability to retain Pb for long periods [24]. The liver on the other hand is an organ which is involved in the metabolic breakdown of substances and at any given time contains large quantities of metals and other substances, both toxic and non-toxic. The highest concentrations of cadmium (66.5 to 75.1%) occurred in the liver and this is quite similar to what occurs in humans where after long-term, low-level exposure about 50% to 75% cadmium can be found stored in the liver and kidney [25].

From the study, the gills did not generally accumulate large quantities of heavy metals. This trend has been found to be typical of carnivorous fishes whose metal uptake are believed to be mainly through gastrointestinal absorption, originating from the food or sediment consumed rather than the gills [27].

The highest concentrations of Pb and Mn were found in the bones, followed by the gills. This observation conformed to a study of [28] who found that the two elements tended to associate with bony organs such as (fish backbone, gills and tails). Mn is involved in the formation of bones and for Pb, in the human body, its burden is divided into 2 fractions; one firmly bound to bone and the other loosely bound to blood and soft tissues [29]. It may thus be inferred that similar processes are involved in the deposition and accumulation of metals in different tissues of fish and mammals. It may also be inferred that the presence of high heavy metal content in a particular tissue, such as bone, does not necessarily imply an equal ability to accumulate all the different metals.

In conclusion, some similarities in metal distribution patterns were observed in the tissues of the tuna species selected for the study and these were attributed to similarities in their feeding habits and habitat. The concentrations of essential metals were generally higher in the fish tissues than the non-essential metals and there seemed to be some affinities of metals to particular organs and tissues of the fish and finally the edible muscle had the lowest concentrations of metals.

5. Acknowledgement

The authors are grateful to the Water Research Institute for making funds available for the study. The authors are also grateful to Mr. Sampson Abu, a former technician of the Environmental Chemistry Laboratory of the Institute who assisted in the collection of the samples.

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