

Bioaccumulation of Heavy Metals in African Red Snapper (*Lutjanus Agennes*) and Cassava Fish (*Pseudotolithus Senegalensis*) Caught off The Coast of Accra, Ghana

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Abstract

The level of Cu, Fe, Mn, Pb, and Zn in African red snapper (*Lutjanus agennes*) and cassava fish (*Pseudotolithus senegalensis*) caught off the coast of Accra, Ghana, were monitored from November 2011 to March 2012 using atomic absorption spectrophotometry. Over the five months period, variations occurred in the level of each of the heavy metals in each of the fish species. The heavy metals accumulated in the gills and bones more than in the muscle tissues of type of fish. The order of accumulation of the heavy metals in African red snapper in terms of magnitude were Zn>Pb>Fe>Mn>Cu in the bones, Fe>Zn>Pb>Mn>Cu in the gills and Fe>Pb>Zn>Mn>Cu in the muscle tissue. For cassava fish the order was Fe>Zn>Pb>Mn>Cu in the bones, Fe>Pb>Zn>Mn>Cu in the muscle, and Fe>Pb>Zn>Mn>Cu in the gills. In the muscle tissue, the part of fish which is normally consumed, the mean value for the various heavy metals over the five months period in the African red snapper were Cu, 0.73 mg/kg; Fe, 8.18 mg/kg; Mn, 0.66 mg/kg; Pb, 7.04 mg/kg; and Zn, 5.16 mg/kg. In cassava fish, the mean values in the muscle tissues were Cu, 0.53 mg/kg; Fe, 9.38; Mn, 0.67 mg/kg; Pb, 5.90 mg/kg; Zn, 6.18 mg/kg. The concentrations of the heavy metals found in both fish species were mostly above the safe limits recommended by WHO.

Key words: Fish, Heavy metals, accumulation, bioaccumulation, red snapper, cassava fish

1. INTRODUCTION

Fisheries is one of the most important food production sectors in Ghana, and is a vital element of the country's food production capacity. The sector comprises of artisanal, semi-industrial, industrial, inland capture fisheries, and aquaculture. It contributes about 3 % of the national Gross Domestic Product (GDP) and about 12.4 % of the agricultural GDP (MoFA, 2009). Marine fisheries produce about 90% of the annual catch landings, whilst inland fisheries produce the rest. Total marine fish production in 2009, 2010 and 2011 were 326.1, 319.6 and 327.1 metric tonnes respectively and inland fish 81.7, 93.3 and 114.4 respectively. The fish requirement for the three years were 956, 988 and 1.013 mt, but fish supply/consumption including fish imports were 518.6, 550.23 and 588.9 representing 54.2, 55.7 and 58.1 % achievement respectively and per capita consumption of 21.7, 22.3 and 23.3 kg (Fisheries Commission, 2012).

Despite the short fall in fish supply, fish remains one of the most important and cheapest source of animal protein in Ghana with a share of 13.3 % in total proteins and 57.8 % in animal proteins (Horemans 1998). In most coastal communities fish serve as the main source of protein. The fisheries sector provides employment in fishing and related activities for over 100,000 fishermen in the artisanal marine and inland fisheries (Mensah, 1994).

One issue regarding consumption of fish, which has become a matter of public health concern throughout the world, is bioaccumulation of heavy metals in fish. Heavy metals may accumulate to high toxic levels in aquatic systems and cause severe impact on aquatic organisms (Aradhna et al, 2009). Fish are liable to accumulate heavy metals under such conditions and subsequently transfer it to humans when consumed. There are two main routes for heavy metals into fish. These are exposure through fish gills or transport of dissolved contaminants in water across biological membrane/ionic membranes, and ingestion of food and sediment particles through the gut (Newarman et al., 1998; Burger et al., 2002).

Heavy metals such as iron (Fe), copper (Cu), manganese (Mn), and zinc (Zn) are classified as nutritionally essential metals, but become toxic when accumulated in the body tissues, and are not metabolized. Heavy metals such as lead (Pb), Cadmium (Cd) and mercury (Hg) are toxic even at trace levels (Dobaradaran et al, 2010). Impairments specifically related to lead toxicity in humans include abnormal size and haemoglobin content of the erythrocytes, hyperstimulation of erythropoiesis and inhibition of haem synthesis (Vonugopal & Luckey, 1975). The aquatic microflora and microfauna, which serve as food for fish species, accumulate these metals in

their living cells from the environment. The fish eat them and gradually get enriched with heavy metals through bioaccumulation. Their concentration increases into the predators and finally into humans resulting in various disease syndromes (Aradhna et al, 2009).

In Ghana aquatic systems, including the sea, are often polluted with domestic and industrial wastes, which may eventually results in accumulation of heavy metals in fish. This issue has however not received much research attention. In this study bioaccumulation of some heavy metals in two common fish species, the African red snapper and cassava fish, caught off the coast of Accra was investigated over a period of five months period.

2. Materials and Methods

2.1 Sampling

Fish samples were obtained from two landing sites, Jamestown and Ussher Fort along the coast of Accra the capital of Ghana. Accra occupies an area of 200 km² and lies between latitudes 5°-32° and latitude 0°-14° with total population of about 3.9 million. On each sampling occasion five samples each of *Lutjanus agennes* (African red snapper fish) and *Pseudotolithus senegalensis* (Cassava fish) were purchased just after landing and transported in an ice chest to the laboratory for analysis. On arrival at the laboratory, the samples were washed with demineralised water to remove all debris and other foreign particles, and prepared for analysis.

2.2 Fish sample preparation and AAS analysis

The dry ash method was used in the present study (AOAC 2005). All glassware were washed with nitric acid followed by demineralised water. The fish was dissected into muscle, gills and bones using new stainless steel knife. Each dissected part was homogenized and 4 g of bones, 5 g of muscle and 4 g of gills were weighed into platinum crucibles. The crucible and the test portion were placed in the Muffle furnace at a temperature 550 °C for 8 h until a grey ash was obtained. The crucible with grey ash was put in desiccator to cool. 5 ml of nitric acid of mass fraction not less than 65 %, having a density of approximately $\rho(\text{HNO}_3) = 1.400 \text{ mg/ml}$ was added, ensuring that all the ash came into contact with the acid and the resultant solution heated on hot plate until the ash dissolved. 10 ml of 0.1 ml/L nitric acid was added and filtered into 50 ml volumetric flask. The resultant solution was top up to the mark with 0.1 ml/L nitric acid. Blank solution was treated the same way as the sample. Flame Atomic Absorption Spectrophotometer was used to read the absorbance values at appropriate wavelength of the interested metal in the sample solution. Cathode lamps used were Cu (wavelength 324.8 nm, lamp current 1.5 mA), Fe (wavelength 248.3 nm, lamp current 7.0 mA), Mn (wavelength 279.5 nm, lamp current 3.0 mA), Pb (wavelength 217.0 nm, lamp current 3.0 mA), and Zn (wavelength 213.9 nm, lamp current 2.0 mA). Air/Acetylene gas was used for all the analysis. The metal content of the samples were derived from calibration curves made up of minimum of three standards.

3. Results and Discussion

3.1 Bioaccumulation of Cu, Fe, Mn, Pd and Zn in African red snapper and cassava fish

The moisture content and mean value for the concentration of the heavy metals, copper, iron, manganese, lead and zinc in African red snapper and cassava fish caught over a period of 5 months off the coast of Accra are presented in table 1. Each result represents the mean for 20 samples analyzed over the period of 5 months. The results show that accumulation of the various heavy metals in the fish depended upon the fish species and also on the part of fish examined.

Of the five heavy metals examined, iron, lead and zinc accumulated in heavier amounts in both types of fish than copper and manganese. Also, for both types of fish, the heavy metals accumulated in the gills and bones more than in the muscles. In African red snapper the concentration of iron was 8.18 mg/kg in the muscle, 24.28 in the gills and 21.18 in the bones. For cassava fish accumulation of iron in the muscle was 9.38, in the gills 32.80 and 29.54 mg/kg in the bones. These figures represent the heaviest concentration of any of the heavy metals found in both types of fish. Iron is required for the nutrition of fish and is essential for its metabolism (NRC, 1983; Canli & Atli, 2003), however, the amounts present in these fish far exceed safe limits recommended by WHO for fish, i.e. 0.3 mg/kg (WHO, 1985).

The levels of lead in both types of fish and also in the different parts of the fish were very excessive indeed. WHO has recommended a safe limit of 2 mg/kg for lead in fish; however, the lowest concentration found in the present analysis was 5.90 mg/kg in the muscle of cassava fish. The highest level of lead recorded was 20.14 mg/kg in the bones of African red snapper. In African red snapper, the accumulation of Pb in the gills was about 60 % more than that found in the muscle, and in the gills three times what was present in the muscle. Fish are reported to be very sensitive to Pb, with its uptake increasing with increasing concentration in the environment (Lagerwerf, 1972).

With regards to zinc, accumulations of the heavy metal in the bones of both types of fish were three times that

found in the muscles. The concentration of zinc in the gills of African red snapper was even higher, 22.08 mg/kg, but in cassava fish was lower than found in its bones. Zinc is a nutritional requirement for aquatic animal growth and essential for metabolism (NRC, 1993; Canli & Atli, 2003). However, accumulation of zinc in fish leads to the destruction of the epithelium of their gills causing hypoxia, growth retardation and mortality (Jones et al., 2001; Plachy, 2003). The acceptable range of zinc in fish according to WHO (1985) is within the range of 10-75 mg/kg. Accumulation of zinc in the two types of fish caught off the coast of Accra did, therefore, not constitute a public health hazard.

In the present work, copper and manganese were found to be present in low concentrations in African red snapper and cassava fish caught in Accra. Concentration of Cu in muscle, gills and bones of African red snapper ranged from 0.73 to 1.03 and from 0.53 to 1.19 mg/kg in cassava fish. These values were well within the acceptable safe levels of 3.0 mg/kg recommended by WHO (1985). According to Beyer et al. (2000) Cu at sub-lethal concentration in fish decreases survival growth, productivity and mainly accumulates in gills and liver. Bioaccumulation of copper in fish can decrease oxygen consumption. Diseases suspected to be caused by excessive ingestion of copper are arthritis and scleroderma (Simon, 1977). In several fish species obtained from different parts of the world, concentration of copper ranges between 0.5 to 28 mg/kg (Brungs et al., 1973).

The mean values of the concentrations of manganese found in the three different parts of the fish were very close for African red snapper and cassava fish. The values ranged from 0.66 mg/kg in the muscle of African red snapper to 4.55 mg/kg in the bones of cassava fish (Table 1). According to USEPA (1975) manganese is relatively nontoxic to aquatic biota and is seldom a problem in fresh waters.

Statistical analysis of the data in Table 1 shows that bioaccumulation of Cu, Fe, Mn and Zn in the gills of African red snapper were not significantly different from their accumulation in the bones of the fish at the 95 % confidence level. Also in cassava fish accumulation of Cu, Fe and Zn were not significantly different in the two tissues concerned. Bioaccumulation of all the heavy metals in the gills and bones were, however, significantly different from the accumulation in the muscles for both fish species. Lower concentrations of the heavy metals were found in the muscle tissues. Accumulation of Mn in cassava fish and Pb in both African red snapper and cassava fish were significantly different in all three tissues.

In comparing bioaccumulation of the heavy metals in the same tissue of the two fish species Table 1 shows that there was no significant difference between bioaccumulation of Fe, Mn, Pb and Zn in the muscles of either fish. With respect bioaccumulation of the heavy metals in the gills, it was only zinc which accumulated in significantly different amounts in the two fish species. In the bones also only iron and manganese accumulated in different amounts in the two types of fish.

3.2 Variations in the level of the heavy metals in the fish species over 5 months

Tables 2 and 3 show the variations in the concentration of the heavy metals in the three different parts of the two types of fish caught at monthly interval over the 5 months period. Each figure represents the mean and standard deviation for four of the same species of fish obtained from the landing sites on the same day. The results show considerable variations in the concentrations of each of the heavy metals on monthly basis, even in the same part of the fish. In the African red snapper, *Lutjanus agennes*, the smallest variation in the level of any heavy metal was 141 % in the concentration of Cu in the bones. Similarly the highest difference recorded was 347 % in the concentration of Zn in the muscle. In cassava fish, *Pseudotolithus senegalensis*, the lowest variation was 141 % in the concentration of Zn in the gills and the highest 404 % in the concentration of Manganese in the bones.

According to Eggleton and Thomas (2004) changes in the physico-chemical parameters of water such as pH, temperature, hardness of water, dissolved oxygen, presence of chelating materials, salinity, rainfall, climate changes etc. all affect the presence of heavy metals in the aquatic environment. For example decrease in water levels in a water body (which may not be very applicable in this case) results in an increase in the concentration of metals. These metals exert sub-lethal effect on aquatic organisms and predators, and adversely influence their reproduction and behavior (Beyer et al. 2000). Metals are generally precipitated at alkaline pH in the form of insoluble oxides and carbonates. It has been proven that lethality increases as oxygen concentration decreases. Increase in temperature also increases toxicity due to depletion in dissolved oxygen causing rise in respiration rate in organisms, leading to rapid assimilation of waste (Bonga & Lock 2003). Variations would therefore be expected to occur in the level of the heavy metals in the marine environment of the fish examined in this work over the course of the five months. This and factors affecting the absorption capacity of the various tissues of the fish would account for the variations observed in the bioaccumulation of the heavy metals in the fish.

4. Conclusion

African red snapper, *Lutjanus agennes*, and Cassava fish, *Pseudotolithus senegalensis*, caught off the coast of Accra present a potential risk to human health based on bioaccumulation of some heavy metals in samples

analyzed in the present work. Iron and lead pose the greatest risk as their levels far exceeded safe limits. Though zinc also accumulated in high levels, the concentrations found were still within acceptable range. Manganese and copper on the other hand accumulated in low amounts in these fish. The heavy metals accumulated more in the gills and bones than in the muscle tissues of both fish species. Wide variations also occur in the levels of the heavy metals monitored over a 5 months period.

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- Table 1. Concentration of some heavy metals in fish caught off the coast of Accra over a 5 months period

(November 2011 to March 2012).

Part of fish	Type of Fish	% Moisture	Concentration of heavy metal in mg/kg of wet weight*				
			Cu	Fe	Mn	Pb	Zn
Muscle	Red snapper	74.88	0.73 ± 0.32 ^{a1,x1#}	8.18 ± 2.99 ^{a2,x2}	0.66 ± 0.35 ^{a3,x3}	7.04 ± 2.56 ^{a4,x4}	5.16 ± 2.30 ^{a5,x5}
	Cassava fish	76.70	0.53 ± 0.20 ^{a1,xx1}	9.38 ± 4.51 ^{a2,x2}	0.67 ± 0.39 ^{a3,x3}	5.90 ± 3.00 ^{a4,x4}	6.18 ± 2.63 ^{a5,x5}
Gills	Red snapper	68.24	0.99 ± 0.33 ^{b1,y1}	24.28 ± 6.56 ^{b2,y2}	2.56 ± 1.13 ^{b3,y3}	11.24 ± 6.03 ^{b4,y4}	22.08 ± 6.60 ^{b5,y5}
	Cassava fish	73.93	1.12 ± 0.61 ^{b1,y1}	32.80 ± 18.74 ^{b2,y2}	2.46 ± 0.95 ^{b3,y3}	15.08 ± 6.65 ^{b4,y4}	16.60 ± 7.51 ^{b5,y5}
Bones	Red snapper	58.07	1.03 ± 0.38 ^{b1,z1}	21.18 ± 5.62 ^{b2,z2}	3.07 ± 1.19 ^{b3,z3}	20.14 ± 6.48 ^{b4,z4}	18.72 ± 8.11 ^{b5,z5}
	Cassava fish	64.30	1.19 ± 0.68 ^{b1,z1}	29.54 ± 15.90 ^{b2,z2}	4.55 ± 2.39 ^{b3,z3}	19.45 ± 8.52 ^{b4,z4}	18.78 ± 6.08 ^{b5,z5}

*Mean value and standard deviation for 20 determinations over the 5 months period.

#Superscripts to figures represent significant or non-significant differences at P < 0.05 where a, b, c, (for African red snapper, *Lutjanus agennes*) and a, β, γ (for cassava fish, *Pseudotolithus senegalensis*) compare heavy metals (1 = Cu, 2 = Fe, 3 = Mn, 4 = Pb, 5 = Zn) in the muscle, gills, and bones of the same fish species (i.e. in same column); and x (muscle), y (gills) and z (bones) compare heavy metal accumulation in the same part of African red snapper and cassava fish (same column).

Table 2. Variations over a period of five months in the concentration of some heavy metals in mg/kg of wet weight of muscle, gills and bones of African red snapper (*Lutjanus agennes*) caught off the coast of Accra (November 2011 to March 2012).

Sample	Month	Cu	Fe	Mn	Pb	Zn
Muscle	November	0.51 ± 0.37	9.63 ± 2.42	0.55 ± 0.26	8.90 ± 1.03	5.34 ± 1.47
	December	0.49 ± 0.08	6.85 ± 4.18	0.67 ± 0.17	5.31 ± 1.69	2.06 ± 1.47
	January	1.09 ± 0.22	10.47 ± 1.97	1.09 ± 0.37	7.69 ± 2.08	5.69 ± 0.38
	February	0.80 ± 0.23	8.18 ± 1.98	0.66 ± 0.36	7.84 ± 3.07	7.15 ± 2.71
	March	0.74 ± 0.26	5.78 ± 2.44	0.35 ± 0.78	5.48 ± 3.26	5.55 ± 1.69
			(214%)*	(181 %)	(311 %)	(168 %)
Gills	November	0.73 ± 0.13	30.25 ± 5.70	3.59 ± 0.31	7.09 ± 6.17	24.57 ± 3.75
	December	0.84 ± 0.11	21.83 ± 4.66	2.26 ± 0.62	12.30 ± 3.06	14.50 ± 2.61
	January	1.17 ± 0.34	28.41 ± 2.57	2.39 ± 0.95	12.19 ± 4.75	22.73 ± 5.38
	February	1.15 ± 0.45	25.27 ± 3.35	3.26 ± 1.46	16.62 ± 8.58	28.55 ± 3.05
	March	1.07 ± 0.36	15.60 ± 4.47	1.30 ± 0.48	7.97 ± 2.86	19.90 ± 8.49
			(158 %)	(194 %)	(330 %)	(234 %)
Bones	November	0.87 ± 0.09	20.88 ± 5.56	4.61 ± 0.53	27.15 ± 1.56	29.49 ± 7.60
	December	0.74 ± 0.31	22.38 ± 5.14	2.94 ± 0.36	17.30 ± 6.02	11.70 ± 2.63
	January	1.23 ± 0.28	27.64 ± 2.57	3.13 ± 0.89	19.10 ± 6.99	16.93 ± 4.22
	February	1.14 ± 0.39	20.95 ± 1.93	3.30 ± 0.72	21.71 ± 5.56	19.23 ± 9.82
	March	1.20 ± 0.55	14.07 ± 2.77	1.35 ± 0.16	15.43 ± 6.05	16.26 ± 2.23
			(141 %)	(196 %)	(341 %)	(176 %)

*Figure in parenthesis represents the percentage increase between the lowest and highest concentration of the heavy metal recorded in the tissue over the five months period.

Table 3. Variations over a period of five months in the concentration of some heavy metals in mg/kg of wet weight of muscle, gills and bones of Cassava Fish (*Pseudotolithus senegalensis*) caught off the coast of Accra (November 2011 to March 2012).

Sample	Month	Cu	Fe	Mn	Pb	Zn
Muscle						
	November	0.38 ± 0.10	7.77 ± 2.63	0.97 ± 0.16	7.34 ± 3.19	2.98 ± 2.22
	December	0.43 ± 0.29	10.85 ± 2.75	0.88 ± 0.47	6.69 ± 3.58	7.10 ± 0.62
	January	0.49 ± 0.06	9.18 ± 1.56	0.87 ± 0.37	6.67 ± 4.33	4.60 ± 1.15
	February	0.63 ± 0.11	6.63 ± 0.95	0.27 ± 0.13	4.19 ± 0.50	6.54 ± 1.45
	March	0.72 ± 0.18 (190%)*	12.78 ± 8.76 (192 %)	0.39 ± 0.12 (240 %)	4.62 ± 2.16 (175 %)	9.70 ± 0.38 (325 %)
Gills						
	November	0.62 ± 0.32	18.44 ± 15.01	3.00 ± 0.22	11.35 ± 0.93	17.40 ± 1.18
	December	0.71 ± 0.08	28.13 ± 16.35	3.05 ± 0.97	18.65 ± 2.09	16.39 ± 0.99
	January	1.41 ± 0.39	25.51 ± 1.59	2.35 ± 0.73	17.60 ± 3.51	14.58 ± 5.89
	February	1.39 ± 0.65	17.96 ± 7.70	1.58 ± 0.31	6.63 ± 0.89	14.33 ± 2.12
	March	1.93 ± 0.36 (311 %)	45.86 ± 8.40 (255 %)	2.32 ± 0.48 (193 %)	21.19 ± 8.53 (311 %)	20.31 ± 16.86 (141 %)
Bones						
	November	0.66 ± 0.28	24.47 ± 6.28	5.43 ± 2.45	13.21 ± 5.11	14.60 ± 2.52
	December	0.69 ± 0.17	28.09 ± 3.86	4.25 ± 0.59	19.74 ± 6.48	19.34 ± 3.16
	January	1.20 ± 0.30	22.12 ± 4.47	3.59 ± 1.09	21.40 ± 6.18	18.83 ± 4.59
	February	1.01 ± 0.29	16.52 ± 2.07	1.88 ± 0.39	13.25 ± 1.54	15.14 ± 3.16
	March	2.38 ± 0.19 (360 %)	56.51 ± 14.64 (342 %)	7.60 ± 2.04 (404 %)	29.67 ± 10.19 (225 %)	25.98 ± 8.75 (347 %)

*Figure in parenthesis represents the percentage increase between the lowest and highest concentration of the heavy metal recorded in the tissue over the five months period.

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