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Determination of Heavy Metals in the Black-Chin Tilapia from the Sakumo Lagoon, Ghana

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Abstract: Samples of the Black-chin Tilapia were analyzed for the concentration of heavy metals (Arsenic, cadmium, chromium, copper, iron, mercury, nickel and zinc) using atomic absorption spectrophotometry and instrumental neutron activation analysis. The sequence of order of the heavy metals measured in the fish samples observed from the Sakumo lagoon was as follows: Fe > Cu > Mn> V> Hg > Cd, respectively. The results showed elevated levels of iron, copper and managanese in all the fish samples although mercury and cadmium were available in relatively low concentration in the most of the fish samples. Fe, Mn, and Zn concentration in fish were greater than WHO/FAO certified values. Hazard index < 1 suggests unlikely adverse health effects whereas HI ≥ 1 suggests the probability of adverse health effects. Although the heavy metals analysed in Blackchin Tilapia did not pose any immediate health risk to humans but due to the bio-accumulation and magnification of these heavy metals in humans, it is essential to safeguard levels of the metals in the environment.

Key words: Assessment, bioaccumulation, hazard, index, instrumental, spectrophotometry

INTRODUCTION

The Black-chin Tilapia, *Sarotherodon melanotheron* belongs to the family Cichlidae and class Actinopterygii. In its native range, the Black-chin Tilapia is found only in freshwater lagoon or slightly salty water along the coast of West Africa (Pullin and Lowe-McConnell, 1982). The Sakumo Ramsar Site lies between Accra and Tema Township in the Greater Accra region of Ghana. Economic activities identified along the lagoon include; fishing, farming, industrial development and recreation (Koranteng, 2002). Urban development is within a few meters of the eastern margin of the lagoon. Fish yield from the lagoon is estimated to be about 114 tonnes with a maximum potential of 120 tonnes annually (Ahulu, 2008). The wetland is a habitat for several species of long distance migratory birds using the East Atlantic Flyway.

Heavy metals, nutrients, and other chemical contaminants are transported in water bodies, dissolved or associated to sediment particles. It is known that the dissolved divalent ionic form of trace metals is toxic to the biota, while the adsorbed or particulate fraction is considered biologically unavailable (Allen *et al.*, 1993). Some heavy metals such as zinc and copper are important in small quantities for biological processes in aquatic plants and animals and occur naturally in many river systems. However, when they are discharged in large quantities from sewage or agricultural runoff, they can be extremely harmful. Since pollution and water quality degradation interfere with vital and legitimate uses of wetlands at any scale, the chemical evaluation of surface water and biota in the wetland will provide an understanding into the interaction of water and aquatic organisms within the environment and contribute to better resource management. Also, because biological communities integrate the environmental effects of water chemistry, biological assessment acts as a useful alternative in assessing the ecological quality of the aquatic ecosystem (Jafari and Gunale, 2006). Managing Wetlands and its water quality issues would require a catchment-based approach as land uses have effects on the quality of most water resources (Meybeck *et al.*, 1989).

The wetland and its catchment have become home to a number of companies. Food, chemical and textile beverage industries have sprung up in this area. This include the Coca Cola Bottling Company, Ghabico, Kuhmesi Cold stores, Rush Industries, the Accra Abattoir, Textile and chemical industries such as Printex and Johnson Wax among others. The operations of these companies impact negatively on the Sakumo Wetland since their effluents and other storm water drains are discharged into streams that empty into the wetland.

The lagoon serves as the major source of income for about 20-150 fishermen daily (Ahulu, 2008). Fish in the Sakumo lagoon also constitute an important source of protein for the inhabitants in and around the coastal community; there is therefore the need to ensure that fish

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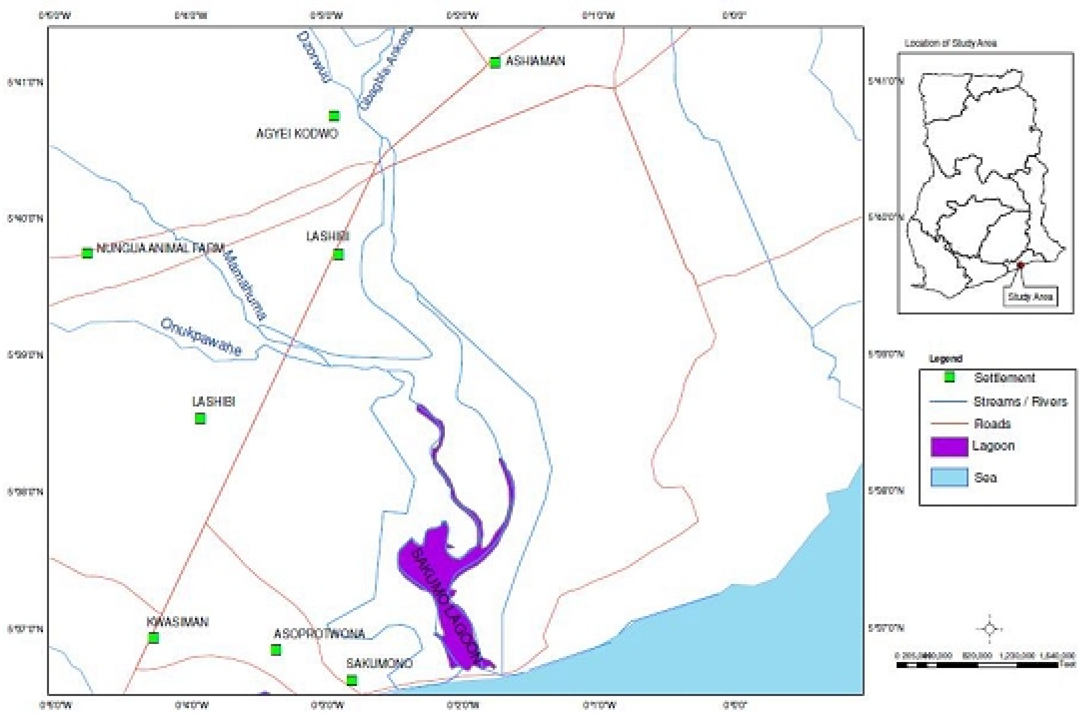

Fig. I: Map of the study area with the sampling point

products from the catchment are toxic free. It is envisage that this study will generate credible baseline data on pollution status of the fisheries from the Sakumo lagoon, the influence of human interventions and the health risk associated with contamination of the Ramsar site. The objective of the study is geared towards determining the current pollution status of the Sakumo wetland with the aim of evaluating the relevance of the Black-chin tilapia as a bio-indicator of pollution.

METHODOLOGY

Study area: The Sakumo Ramsar Site lies due east of Accra between Teshie-Nungua and Tema Township in the Greater Accra region of Ghana (Fig. 1). The Ramsar Site lies between latitude 5º35′ N to 6º40′ N and longitude 0º00′ W to 0º10′ W with an altitude of 86.9 m (286 ft) and an average elevation of 45.7 m. The effective catchment area of the Sakumo Ramsar Site is approximately 27,634 ha but the water bodies including the lagoon, reservoirs and area liable to flooding is 812 ha. the wetland is a habitat to about thirteen (13) fish species belonging to thirteen (13) genera and eight (8) families with *Sarotherodon melanotheron* also known as the Black-Chin tilapia (name for the black coloration often present under the chin) consisting of about 97% (Koranteng, 1995).

Sample collection: Fish samples were purchased from fishermen at the Sakumo lagoon in Ghana between September and November of 2009. After purchase the samples were cleaned with deionized-distilled water, weighed, measured, stored in pre-cleaned plastic bags, and kept frozen in an ice box. Twenty (20) fish samples were double bagged in separate new plastic bags, sealed and labelled accordingly.

Fish condition assessments: The physical characteristics of the sampled fish species were assessed. The ratio between the fish whole body weight to body length (head to tail) was examined to identify fishes with anomalously high or low ratios. The overall health of fish species in the lagoon were assessed using the method developed by Williams (2000). A condition factor index (K) was calculated using the equation: $K = \frac{100W}{L^3}$

where, W = body weight in grams; L = body length (fork length) in cm

Sample preparation: The frozen fish samples were partially thawed on cleaned plastic sheets using scalpels with steel blades and plastic forceps. Whole taxa of a designated length range were cut into small pieces with Teflon-tipped scissors. The samples were freeze-dried for

72 h using a Christ freeze-dryer and then homogenized together in a ribbed acid-free pyrex bowl with a Biospec Products blender, Model Mi33/1281-0, Fisher Scientific, Pittsburgh, PA (Moeller *et al.*, 2001).

Neutron Activation Analysis was used to analyse the metals Ca, Cu, Mg, Mn, Na, K, V. Three replicate samples, 100 mg each of each homogenized fish were weighed into clean polyethylene foils, wrapped and heat sealed. The sub-samples were packed into a 7 mL polyethylene capsule and heat-sealed. The elemental comparator standards used in this work were made from the plasma emisssion spectroscopy standard solutions (SPEX) (Seigniory Chemical Products (SCP) Canada, Ltd.,). Standard reference material, NIST-SRM Oyster tissue was used as quality control for the INAA analyses. Three replicate samples were prepared for these reference materials in the same manner as the samples.

Sample irradiation and counting: All prepared samples and standards were irradiated using the Ghana Research Reactor-1 (GHARR-1) facility at the GHARR-1 Centre of the National Nuclear Research Institute (NNRI) of the Ghana Atomic Energy Commission (GAEC). The reactor was operated at a half-power of 15 kW and at athermal flux of 5 x 10^{11} per nc^2s. The capsules were sent into the inner the inner irradiation sites of the reactor by means of a pneumatic transfer system, operating at a pressure of 0.25 atms. The samples were analysed using irradiation schemes by optimising irradiation time (ti), decay time (td) and counting time (tc) based on the $t_{1/2}$ of respective elements. The metals Al, Ca, Cu, Mg Mn, V classified as short lived radioisotopes were analysed using ti = 2 min, td = 10 s and tc = 10 min. Cd, was classified as medium-lived and analysed using the scheme ti = 1 h, td = 24 h, tc = 2 h. The respective metals were identified using the Gamma-ray energies that were detected by a high purity Germanium (HPGe) detector and quantified using the Maestro 32 software. The quantitative analysis was done by converting the counts as area under the photopeak of the radionuclides by the comparator method.

Atomic Absorption Spectrometry was used to analyse Cd, Cr, Fe, Ni and Zn. 0.5 g of fish material, about 6 mL of 65% HNO_3 and 1 mL of 30% H_2O_2. The Teflon beakers with the bomb were closed tightly. The bomb was placed at the center of a microwave oven (ETHOS 900 Microwave Labstation) and digested for 18 min at full power. Cold vapour AAS was used in the determination of total dissolved mercury. The organomercury compounds in the sample were oxidized to inorganic mercury (II) compounds by heating with sulphuric acid, potassium permanganate and potassium persulphate. The mercury compounds were then reduced with stannous chloride in a hydroxylamine sulphate-sodium chloride solution to elemental mercury. The mercury was sparged from solution with a stream of air and passed through an absorption cell situated in the pathway of the mercury lamp (APHA, 1989).

Table 1: Physical data on selected fish samples

Fishes	Length (cm)	Fresh weight (g)	Dry weight (g)	Moisture content (%)	Condition of fish (K)
Fish 1	12.5	35.19	9.61	72.69	1.8
Fish 2	11.5	25.33	6.26	74.42	1.7
Fish 3	12.0	26.62	6.9	74.08	1.5
Fish 4	11.8	26.35	5.61	78.71	1.6
Fish 5	12.4	28.37	7.35	74.09	1.5
Fish 6	11.2	25.38	7.2	71.63	1.8
Fish 7	15.0	59.69	16.34	72.63	1.8
Fish 8	11.0	24.59	6.24	74.63	1.8
Fish 9	13.0	22.05	7.88	64.24	1.5
Fish 10	11.1	22.05	5.91	73.22	1.6
Fish 11	10.4	17.25	4.25	75.36	1.5
Fish 12	9.5	15.45	3.86	75.02	1.8
Fish 13	8.0	9.57	2.59	72.9	1.9
Fish 14	7.5	8.51	2.4	71.80	2.0
Fish 15	8.0	9.24	2.21	76.08	1.8
Fish 16	7.4	7.07	1.9	73.12	1.7
Fish 17	7.0	6.75	1.77	73.79	2.0
Fish 18	6.5	4.44	1.13	74.55	1.6
Fish 19	6.3	4.71	1.21	74.30	1.9
Fish 20	6.5	5.04	1.22	75.77	1.8

RESULTS AND DISCUSSION

The condition factor is an estimation of the general well being of fish and crustaceans (Jones *et al.*, 1999). It is based on the hypothesis that heavier individuals of a given length are in better condition than less weightier ones (Bagenal and Tesch, 1978). Condition factor has been used as an index of growth and feeding intensity. Most notably, fish measured with an exceptionally low weight-to-length ratio may indicate the organism is stressed, either by physical injury, disease, dietary limitations, or poor water quality. The sampled fish species recorded an average K factor of 1.7 (Table 1).

Heavy metals contamination: The mean elemental concentrations measured in the fishes during the study period are also presented in Table 2. Reported values of the various elements are the results of the total concentrations (dry weight) measured in each individual whole fish. Almost all the fish samples collected from the lagoon contained detectable amounts of the elements studied (Ca, Cd, Cu, Cr, Fe, Hg, K, Mn, Na, and V). The elements Ca, Mg, Na, K, and Fe were present in all the fish samples and at varying concentrations. It must be noted that, varying concentrations of the heavy metals were measured in the sampled fishes with some fishes reporting very high concentrations whilst other samples measured relatively lower concentrations and in some cases no concentrations of the elements.

Cadmium, chromium and mercury tended to be the least concentrated in the fish as compared to other elements measured. Concentrations of cadmium varied from <0.002 to 0.045 mg/Kg (dry wt.). The low cadmium values in the lagoon fish may be due to the high salt content of the lagoon since salt-water organisms are

Table 2: Elemental concentrations in measured fish samples, in mg/Kg unless otherwise stated

Fish	Fish 1	Fish 2	Fish 3	Fish 4	Fish 5	Fish 6	Fish 7	Fish 8	Fish 9	Fish 10
Ca^{2+}	36529±730	65565±954	62883±930	53060±904	53065±950	53255±899	53510±750	53739±916	60785±910	63152±789
Mg^{2+}	551±127	862±189	987±155	860±175	810±168	906±189	774±172	632±168	963±191	956±194
Na^{+}	6237±169	5254±134	7110±117	5318±196	5254±144	6107±120	4950±171	5266±183	5854±191	6035±210
K^{+}	9165±265	8654±178	8230±226	7646±288	7243±214	7225±191	7572±183	8088±197	8152±256	8360±249
Fe	50.8±12.3	54.24±12.8	50.72±12.0	58.88±11.6	33.04±10.2	38.8±10.5	25.28±10.0	96.8±13.4	59.68±11.8	37.04±10.3
Cd	0.012±0.0	0.013±0.0	0.011±0.0	<0.002	<0.002	<0.002	0.034±0.02	0.002±0.0	0.013±0.0	0.012±0.01
Cr	0.72±0.5	0.72±0.4	1.28±0.5	1.12±0.5	0.56±0.3	<0.001	1.2±0.8	2.64±0.9	1.28±0.8	0.64±0.3
Cu	1.51±0.23	1.88±0.27	1.19±0.21	73.47±9.97	2.07±0.30	13.56±1.75	6.20±0.80	0.68±0.10	1.43±0.31	10.15±1.21
Hg	0.051±0.008	0.049±0.008	0.051±0.008	0.038±0.006	0.044±0.007	0.032±0.005	0.028±0.004	0.012±0.002	0.016±0.002	0.063±0.010
Mn	9.45±1.86	8.39±1.72	10.14±1.69	7.56±1.89	4.52±1.75	6.26±1.64	3.15±1.56	0.87±0.09	5.08±1.28	10.26±1.66
V	0.34±0.10	1.18±0.15	0.69±0.12	0.65±0.15	1.06±0.11	0.75±0.15	1.10±0.18	0.48±0.10	0.78±0.16	0.23±0.13
Fish	Fish 11	Fish 12	Fish 13	Fish 14	Fish 15	Fish 16	Fish 17	Fish 18	Fish 19	Fish 20
Ca^{2+}	68745±950	95443±1137	91264±110	80863±1074	77959±1087	74489±102	7507±1010	78665±103	100255±165	108676±110
Mg^{2+}	992±179	1292±22	1269±216	787±170	1028±198	1195±224	940±193	1045±245	1196±263	1297±219
Na^{+}	6913±220	7244±182	6580±163	4456±236	6421±210	6219±210	5461±140	5516±190	6870±218	7670±224
K^{+}	9040±271	12629±362	9570±272	8236±236	9150±252	9874±281	9260±249	7279±241	1357±2895	1444±3980
Fe	31.28±10.0	76.24±12.9	70.8±12.1	44.08±10.8	88.96±13.0	55.13±11.6	70.47±12.4	45.81±10.7	87.2±11	106.8±34
Cd	0.010±0.0	<0.002	0.004±0.0	0.003±0.0	0.011±0.0	0.004±0.0	0.015±0.0	0.034±0.01	0.019±0.0	0.045±0.01
Cr	<0.001	<0.001	1.2±0.9	1.04±0.9	0.72±0.4	<0.001	<0.001	<0.001	<0.001	<0.001
Cu	<0.003	0.71±0.11	12.91±1.94	<0.003	12.7±1.91	3.09±0.46	13.74±2.06	10.84±1.56	12.90±1.92	15.05±2.10
Hg	0.056±0.008	0.016±0.002	<0.001	0.015±0.003	0.028±0.004	<0.001	<0.001	<0.001	<0.001	<0.001
Mn	11.02±1.92	13.18±2.05	7.99±1.89	6.53±1.45	10.05±2.10	10.20±1.95	14.25±1.99	10.18±2.04	12.76±1.90	16.01±2.6
V	0.16±0.09	0.52±0.11	1.11±0.12	0.08±0.14	1.66±0.17	1.07±0.19	0.07±0.13	1.80±0.11	0.92±0.15	1.71±0.19

known to be more resistant to cadmium poisoning than freshwater organisms (Asagba *et al.*, 2008). The greatest sources of cadmium in humans are seafoods and meats (Reigart and Roberts, 1999).

Concentration of chromium in the fishes were relatively high (<0.001 to 2.64 mg/Kg). Chromium in surface waters is usually due to industrial emissions. The maximum permissible chromium levels for fish are1.0 mg/kg as reported by FAO (1983). The hexavalent form (6^{+}) is highly toxic and has deleterious effect on the liver and kidneys when ingested through food (Environment Canada, 1997).

Fish and other marine organisms are often the dominant source of mercury contamination in humans, mainly in the form of methylmercury compounds (Matthesson and Jaakkola, 1979). Concentration of mercury in the fish samples varied from <0.01 to 0.063 mg/Kg with a mean of 0.028 mg/Kg. Mercury based compounds used in chloroalkali plants, paints, thermometers and agriculture are some of the probable source of the metal in the wetland. Mercury has no known beneficial function in the human physiology. The principal health risks associated with mercury are damage to the nervous system, with such symptoms as uncontrollable shaking, muscle wasting, partial blindness, and deformities in children exposed in the womb (WHO, 1997) at levels well below WHO limits (0.05 µg/g).

Health risk estimation: Health risk estimates in this study, were calculated based on the integration of the data from heavy metals analysis and the assumed consumption rate based on US.EPA guidelines.
The following assumptions were made based:

- Hypothetical body weights of 10 Kg for children between the ages of zero and one year, 30 Kg for children between the ages of one and eleven years and 70 Kg for adults
- Maximum absorption rate of 100% and a bioavailabilty rate of 100%
- Food consumption rate of fish in Ghana given as 0.08 kg/day

Hence, for each type of contaminat (heavy metal), the estimated daily dose (ED) (mg/Kg/day) was obtained using the equation detailed in the US. EPA handbook (1989):

$$ED = \frac{Concofelement\ of\ interest \times Foodconsumption\ rate}{Bodyweight, Kg}$$

To estimate the health effects, the estimated lifetime average daily dose of each chemical was compared to its Reference Dose (RfD). The reference dose represents an estimate of a daily consumption level that is likely to be without deleterious effects in a lifetime. And the hazard index (HI) is estimated as the ratio of the estimated metal dose and the reference dose (US.EPA, 1996).

Hence, $HI = \frac{ED}{RfD}$

Where, ED = Estimated Dose and RfD = Reference Dose

Estimated health risk associated with consumption of the black-chin tilapia is presented in Table 3. Hazard index < 1 suggests unlikely adverse health effects whereas HI> 1 suggests the probability of adverse health effects. For adults, health risks estimates for chromium, copper, manganese mercury and vanadium were lowest for the general public at the highest ingestion rate (Table 3) whilst the same elements were relatively higher for children at the highest ingestion rate. Even though the

Table 3: Health risk estimates associated with heavy metals in fish

		Estimated dose (mg/Kg)			Hazard index		
Contaminant	RfD	0-1 year	1 -11 year	Adult	0-1 year	1-11 year	adult
Chromium	5.00E-03	0.0087	0.0029	0.0012	1.7	0.58	0.25
Copper	3.70E-02	0.082	0.027	0.012	2.2	0.7	0.32
Iron 8.60E-03	0.4728	0.1576	0.0675	54.98	18.32	7.85	
Manganese	4.70E-02	0.07	0.024	0.01	1.5	0.5	0.22
Mercury	5.70E-05	1.9E-05	6.5E-06	2.8E-06	0.38	0.1	0.05
Vanadium	7.00E-03	0.0065	0.0022	0.00093	0.9	0.007	0.0031

values do not pose any health hazards for the ordinary consumer, the levels are likely to be higher for families of fishmen since their meals are more fish-dependent. The use of metal-based fertilizers by farmers in the Sakumo catchment should be monitored and regulated.

CONCLUSION

The concentrations of heavy metals in the fish were quite variable and no patterns of distribution and behaviour were noted. However, high concentrations of some heavy metals measured in the fish tissues inhabiting the Sakumo lagoon were related to a high influx of metals as a result of pollution from the surrounding industries thereby increased bioavailability to the fish. The high levels also suggested that the fish were capable of concentrating the metals in their bodies from the aquatic environment. The ability of the fish samples to incorporate ethe lements into their tissue is another important factor to consider for further study. The data presented in this report indicates that the species have preference to retain some metals in their tissues than other metals. Although, no immediate health risk was estimated from consumption of the S*arotherodon melanotheron* (BlackChin tilapia), risk prevention on the consumption of fish should therefore focus on reducing the volume of heavy metals discharged from industries into the lagoon.

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