



Concentration of copper and zinc in black chin tilapia (*Sarotherodon melenotheron*) in Fosu lagoon, Cape Coast, Ghana

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ABSTRACT

The concentrations of copper and zinc in *Sarotherodon melenotheron* from the Fosu Lagoon were measured to assess the extent of contamination with these metals. The lagoon is a closed lagoon situated within the Cape Coast Municipality of Ghana. Atomic Absorption Spectrometry was employed to estimate the mean concentrations of copper and zinc within a three (3) month period from 16th September, 2005 to 2nd December, 2005. The concentration of copper was found to be in the range of 10.647mg kg⁻¹ to 26.146mg kg⁻¹ and that of zinc ranged from 4.138mg kg⁻¹ to 96.236mg kg⁻¹. The mean concentrations of copper and zinc were 19.665 mg kg⁻¹ and 38.615mg kg⁻¹ respectively. The mean concentration for copper was within the acceptable limit for human consumption whilst that for zinc exceeded the FAO's acceptable limit of 30mg kg⁻¹. The hazard index for Copper exceeded 1. There is therefore, a very high probability of severe adverse health effect on the consumption of this fish species harvested from the Fosu Lagoon especially for children of 0 – 1 year. It was moreover, observed that no correlation existed between the values obtained for copper and zinc. This is a sharp contrast to literature.

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Introduction

Black chin tilapia belongs to the family *Cichlidae* and class *Actinopterygii*. This fish species was chosen for this study due to its availability in large quantities, geographically widespread distribution, high consumption rate by man and all year availability.

The Fosu Lagoon located in the Cape Coast Municipality of Ghana has been suffering from anthropogenic activities over the past twenty years. Massive processes of urban and industrial activities are the main culprits where toxic substances especially heavy metals are released into it.

Anim et al. (2011) conducted a study to investigate the accumulation profile of heavy metals in five fish species. Concentrations of Fe, Mn, Cu, Zn, Ca, Cd, and Pb were measured in all the analysed samples. The concentration of Cu in all the samples analysed exceeded the FAO limit of 30mg/kg. Ganowick (1977) studied fish from the area of the Crozet and Kerguelen Island and obtained concentrations of copper to be 0.25 to 0.73 µg/g.

Similar reports have been obtained by other workers such as Bebbington (1977, Australia) who analysed 232 commercial fish samples for copper using Varian Techtron Atomic Absorption Spectrometer (AAS). The mean values of copper ranged from 0.1 to 2.8 µg/g. The mean value of copper in yellow fin bream was 0.50 µg/g with a range of 0.1 to 2.0

The wet weight concentrations of copper in muscle tissue have been measured taken from 12 species of teleost caught in

Cockburn sound. Copper concentration ranged from 0.04 to 5.77 µg/g (Plaskett and Potter, 1979). In 1981, Lenzio also determined the level of copper in soft tissues of four marine fishes from the Northern Tyrrhenian sea and concentrations ranged from 3.0 to 7.71 µg/g (wet weight) copper.

Copper is one of the essential trace elements for growth and normal development of microorganisms, plants and animals. Its biochemical role as an enzyme activator and constituent of respiratory pigment of many marine invertebrates are well established (Brooks and Rumsby, 1965). Copper with a positive charge of two is the chemical species that is toxic to fishes. Alkalinity is a key factor controlling copper concentrations in environmental media. Copper is extremely toxic when dissolved in water but copper highly complexes in natural waters and the stability of the complexes determines the concentration of copper species in solution. Concentrations as low as 0.5 mg/dm³ can kill trout and most tropical fishes within few hours.

Sprague (1974) has shown that juvenile Atlantic salmon markedly avoid copper solutions at concentrations as low as 9 mg/dm³ a concentration which is 20% of the incipient lethal level. Adult Atlantic salmon almost completely avoided concentrations of 90 mg/dm³ which is about two times the incipient lethal level.

Experimental evidence has also shown that there is a high mortality of eggs of plaice and herring at concentrations as low as 90 µg/dm³ and 30 µg/dm³ respectively. The lethal effects on plaice larvae was found to be about 1000 µg/dm³ in young larvae

and as low as 90 $\mu\text{g}/\text{dm}^3$ in older larvae. In herring also, the lethal concentration was found to be 1000 $\mu\text{g}/\text{dm}^3$ in young larvae and 300 $\mu\text{g}/\text{dm}^3$ in older larvae. Growth and activities of these fishes are retarded at concentrations of surrounding water between 90 and 300 $\mu\text{g}/\text{dm}^3$.

Sanda and Gullard (1976), Munkittrick and Dixon (1988) observed that while sucker (fish) collected from the lakes with elevated levels of copper ($13 - 15 \mu\text{g}/\text{L}$) were significantly smaller, and female suckers from contaminated lakes exhibited decrease in egg size and fecundity. Although present in trace amounts, certain aquatic organisms are able to concentrate copper in their bodies far in excess of the surrounding water. Amil and Wagh, (1988), found that Banacles (*Balanus amphitrite*) accumulated copper to $864.77 \mu\text{g}/\text{L}$ dry weight while the concentration of copper in surrounding water was only $0.002 - 0.011 \text{ mg}/\text{L}$.

The toxicity of copper is enhanced by the presence of zinc or cadmium at the same time.

Zinc is an essential element found in all human and animals and is a constituent of many enzymes. "The body of the normal human contain about 2g of zinc. All tissues and organs of the body have been found to contain this metal but the highest concentration are present in testes, hair and nails, bone and pigmented tissues of the eye. It is found as an essential constituent in an enzyme structure in the red blood cells, gastric mucosa, and renal cortex. Zinc is associated with a number of enzyme systems involved in the acceleration of carbon(iv)oxide exchange, and is taught to be involved in acid secretion by the stomach and may be involved in regulation of acid-base balance by the kidney. A true deficiency has not been shown to exist in man but the vital part it played in the body system will be noted". A zinc deficient diet in animal results in prevention of growth, loss of hair, cutaneous lesions and has adverse effect on the gonads (Hodges, 1977).

It is clear that zinc has a direct adverse effect on the very life of fish and other aquatic animals. According to (Sparks 1972), the zinc induces coagulation of the muscles in the blue gills and the function of coughing might be to free the gills of mucus

Skidmore (1970) has realised that the oxygen level in the blood leaving the gills of the rainbow trout was reduced as a result of inner zinc levels. This led him to the observation that zinc reduces the effectiveness of the gills in the transfer of oxygen.

In a study of the heavy metal pollution of Brazilian waters (H.M Fernandez) stated that in the human exposure assessment, only the possibility of metal ingestion through fish consumption was considered, since the lagoon water are not good for drinking. The calculations did not take into account antagonistic or synergistic effects among different metals. Fish consumption rate was considered to be in the order of 50g/day for the hypothetical critical population, which is quite a conservative estimate (Foran, 1990).

Thus studies are being conducted all over the world to monitor the level of trace elements in fishes. This also translates into the amount of trace elements being taken by people who depend heavily on fishes from lagoonal waters since the lagoonal waters are not safe for drinking as in the case of Fosu Lagoon.

Azevedo (1988) has conducted a preliminary assessment of the most important metals introduced by the tributary rivers to the lagoonal water bodies namely zinc, copper, chromium,

nickel and cadmium. Barcellos(1988) estimated the particulate metal fluxes transported to Jacarepagua lagoon by Paruna Creek, the most important anthropogenic heavy metal source to that system; they arrived at the values of 85,000g/day of iron, 600g/day of manganese, 400g/day of lead, 840g/day of copper, 2300g/day of zinc, 130g/day of nickel and 80g/day of chromium. Metal dynamics in the lagoonal environment was studied by Fernandez (1991). It was proposed that Jacarepagua lagoon works as a depositional environment for particulate heavy metals in a net accumulation, in a 12 hour spring tidal cycle in the order of 124g of copper, 176g of zinc 55g of lead, 84g of chromium and 26g of iron.

Particulates in aquatic environment exert considerable influence on the chemical form, dispersion and sedimentation of metals present in nature or emitted by man (Krauskopf, 1956), Turekian 1977. Hart, 1982; Ohlsen, 1982;. This applies particularly in estuaries in which fresh water containing dissolved and particulate metals is mixed with sea water, whereupon chemical and physical properties such as pH, salinity, particle concentration and turbulence undergo major changes that influence the distribution of metals between planes in the water (Bourg, 1987). This can result in increasing sedimentation as a consequence of increased adsorption of metals of settling particles (Sholkowitz, 1978, Morris, 1986) and through flocculation of colloidal particles (Boyle, 1977; Esima, 1986).

The organic particles consist mostly of living plankton, microorganisms and dead organic matter, detritus, in different stages of degradation. These biogenic particles have also been found to contribute to the sedimentation of metals in natural waters (Noriki, 1985; Sigg, 1987).

Minerals are minute amounts of metallic element that are vital for the healthy growth of teeth and bones. They also, help in such cellular activities as enzyme action, muscle contraction, nerve reaction and blood clotting. Mineral nutrients are classified as major elements and trace elements. These trace elements include chromium, copper, fluoride, iodine, iron, selenium and zinc, molybdenum, cobalt etc.

Some of these trace elements such as copper and zinc play either stimulating or inhibitory roles in living organisms depending on their level of accumulation. Hence in some instances, human health, success in agriculture and equilibrium between organisms in ecological competition are controlled by these trace elements. Trace elements (metals) are useful to living organisms, as well as harmful and the level of exertion adversely affects the ecosystem when they reach toxic levels.

Toxicity of trace elements occur when accumulated through bio amplification in organisms such that they reach levels that can no longer be tolerated.

Aquatic organisms are surrounded or bathed in a solution of dissolved metals and therefore may take up the metals directly in the dissolved form. These metals can be taken through pathways such as inhalation, ingestion, or by dermal contact.

If the above results are taken into account, it is of great importance to determine the concentration of trace elements in edible fishes present in the Fosu Lagoon. The Fosu Lagoon due to urbanization has been polluted and is still being polluted by a variety of pollutants on a daily basis.

Hence the purpose of this study is to determine the concentration of copper and zinc in *Sarotherodon melonotheron* from Fosu Lagoon.

Methodology

Sampling method

The sampling was carried out within three (3) month duration on weekly basis. The sampling was done between 16th September and 2nd December, 2005. In the field sampling, the fish was collected alive and undamaged from fishermen at the sampling site.

Sample Handling

The fish was washed with water from the lagoon and wrapped in non-coloured polyethylene bag. The fish was subsequently sent to the Chemistry Department Laboratory of University of Cape Coast for sun drying. The sampled fish were then oven dried at 150°C for three hours. After cooling, they were milled to fine powder in plastic containers and labelled with date for subsequent identification.

Preparation of Solutions

Copper Standard

A weighed amount of 0.3932g copper (ii)tetraoxosulphate (iv) pentahydrate was dissolved in a minimum volume of distilled water in a 1000ml volumetric flask and made up to the mark. From this solution, 100ml was measured into a 1000ml volumetric flask and diluted to the mark to produce a 10µg/ml standard solution.

Zinc Standard

A weighed amount of zinc(ii) tetraoxosulphate(vi) heptahydrate was dissolved in a minimum volume of distilled water in a 1000ml volumetric flask and made up to the mark. From this solution, 100ml was measured into a 1000ml volumetric flask and diluted to the mark to produce 10µg/ml standard solution.

Materials and reagents

Reagents

Concentrated trioxonitrate(v)acid (BDH 65%), concentrated tetraoxosulphate(vi)acid (BDH 98%), concentrated tetraoxochlorate (vii)acid (BDH, Analar 60%), copper(ii)tetraoxosulphate (vi)pentahydrate (BDH), zinc (ii)tetraoxosulphate (vi)heptahydrate (BDH, Analar).

Materials/ Equipment

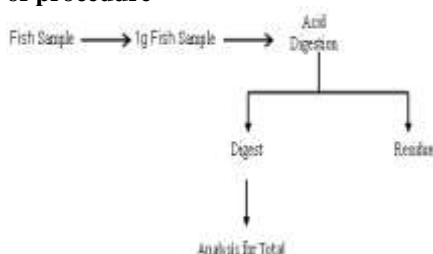
250ml volumetric flask, 25ml volumetric flask, 1000ml volumetric flask, 10ml measuring cylinder, Whatman Number 1 filter paper, hot plate.

Acid Digestion of Fish

1g of milled (ground) sample was placed in a 250ml volumetric flask, 10ml of concentrated trioxonitrate(v)acid, 2ml 60% concentrated tetraoxochlorate(vii)acid were added. Finally, 1ml of concentrated tetraoxosulphate(vi)acid was added. The flask with its contents was kept on heated mantle and digested at moderate temperature, then at high temperature.

The digest was then diluted with distilled water and filtered through a Whatman Number 1 filter paper into a 25ml volumetric flask. After thorough washing of the residue with distilled water and made to the mark. The solution was stored for subsequent analysis with Atomic Absorption Spectrometer.

Flow chart of procedure



Results and discussion

From the experimental data, the concentration range of Cu in fish species analysed was in the range 10.647 – 26.146 g/kg with a mean concentration of 19.665g/kg whilst the mean concentration of Zn was 38.615g/kg. These values were found to be much higher than that obtained by Dapaah(1985) and Laar et al. (2011). The concentration range was found to be between 4.138g/kg and 96.236g/kg for Zn. Comparing the values of Zn to those of Cu accumulated by the fish species, the Zn values far exceeded those of the Cu.

The highest copper concentration of 31.941g/kg was obtained for sample L and the highest zinc concentration of 96.236g/kg was obtained for sample A. The least copper and zinc concentrations are 10.647g/kg for sample A and 4.138g/kg for sample H respectively.

It can be observed that both copper and zinc concentrations in sample H were very low compared to other samples. Since the same species of fish was used and the fishes were exposed to the same conditions in the lagoon, the varying concentrations of Cu and Zn for the different samples obtained can be linked to the age and size of the various fishes obtained.

HealthRisk Estimation: Health risk estimates in this study were calculated based on the integration of the data from the metals analysis and assumed consumption rate based on US EPA guidelines.

The following assumptions were made:

Hypothetical body weights of 10kg for children between the ages of zero and one year, 30kg for children between the ages of one year and eleven years and 70kg for adults.

Maximum absorption rate of 100% and a bioavailability rate of 100%

Food consumption rate of fish in Ghana given as 0.08kg/day.

Hence, for each type of contaminant, the estimated daily dose (ED) (mg/kg/day) was obtained using the equation detailed in the US EPA handbook (1989):

ED =

$$\frac{\text{Concentration of Element of Interest} \times \text{Food Consumption Rate}}{\text{Bodyweight}}$$

To estimate the health effects, the estimated lifetime average daily dose of each chemical was compared to the 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. The hazard index (HI) is estimated as the ratio of the estimated metal dose and the reference dose (US EPA).

$$\text{Thus, HI} = \frac{\text{ED}}{\text{RfD}}$$

Where, ED = Estimated Dose

RfD = Reference Dose

Estimated health risk associated with consumption of the black-chin tilapia is presented in Table 3.2. Hazard index < 1 suggests unlikely adverse health effects whereas HI > 1 suggests the probability of adverse health effects.

The Hazard Index (HI) assessment for copper for all categories of consumers has indicated values far in excess of 1. This suggests a very high probability of severe adverse health effects on the consumption of fish especially for children of 0 – 1 year.

Conclusion

The concentration of copper and zinc has been detected to be in the range of 10.647 – 26.146 mg/kg and 4.138 – 96.236 mg/kg respectively in the fish samples. From the study, there was no correlation between copper and zinc concentration.

The mean concentration of copper and zinc are 19.665mg/kg and 38.615mg/kg respectively. The mean concentration of 19.665mg/kg falls within the maximum permissible limit set by FAO. The mean concentration of zinc however exceeded the FAO maximum limit of 30mg/kg. The fish are therefore not safe for human consumption.

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TABLE 4.1: The overall concentration of copper and zinc from the fish species for the 12 weeks

SAMPLE	METALCONCENTRATION (mg/kg)	
	Cu	Zn
Sample A	10.647	96.236
Sample B	26.146	33.364
Sample C	17.251	55.716
Sample D	18.059	15.192
Sample E	22.237	61.478
Sample F	23.450	45.167
Sample G	14.421	73.281
Sample H	12.534	4.138
Sample I	20.081	38.336
Sample J	21.833	17.426
Sample K	17.385	10.688
Sample L	31.941	12.361

TABLE 3.2: Dose estimates and Hazard Index for the various year groups

CONTAMINANT	RfD	ESTIMATED DOSE (mg/kg)			HAZARD INDEX		
		0-1 YR	1-11 YRS	ADULT	0-1 YR	1-11 YRS	ADULT
COPPER	3.70E-02	1.573	0.524	0.225	42.514	14.162	6.081

TABLE 3.3: A comparison of the mean of total concentration (mg/kg) with maximum allowable limit

METAL (TRACE ELEMENT)	MEAN OF TOTAL CONCENTRATION (mg/kg)	MAXIMUM LIMIT (mg/kg)	REFERENCE
Zn	19.665	30	FAO (1983)
Cu	38.615	30	FAO (1983)