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Determination of Some Selected Heavy Metals in Fish and Water Samples from a Section of Migori River

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Abstract
Samples of Tilapia (Oreochromis niloticus) and African catfish (Clarias gariepinus) were collected from a section of Migori River. The moisture content of freeze-dried body of the fish collected from four sites ranged between 62.6% and 86.6% (m/m). An optimal procedure required 12 mL mixture of HNO_3, $HClO_4$, and H_2O_2 (3:2:1, respectively) to mineralize powdered samples in open refluxed digestion vessels: 0.5 g of the fish body. The concentrations of 3 toxic elements Cd, Pb and Hg) in the body of the fish was determined by atomic absorption spectrophotometer. The concentrations varied, respectively; Cd = 0.4 - 1.85, Pb = 0.05 - 0.5 and Hg = 0.07 - 0.096 in mg of element/kg of fish. The concentration of those three heavy metals in water samples was also determined similarly and varied, respectively, as (mg of element/L of water sample); Cd = 0.06 - 0.66, Pb = 0.28 - 0.36 and Hg = 0.5 - 0.74. Application of the statistical t-test on heavy metal elements data has shown that there was a significant difference between the mean concentrations of Hg in water samples. There is no significant difference between fish as well as water sample from the river.
Keywords: Tilapia Fish, African Cat Fish, Clarias Gariepinus, Oreochromis Niloticus, Toxic Metals, Water Pollution, Migori river.

1. Introduction

Elements are the basic building blocks of all chemical compounds, and human exposure to them occurs both from natural and anthropogenic sources. Many elements are considered nutrients and are essential for the proper functioning of the body. These are generally divided between macrominerals such as calcium, magnesium, potassium, sodium and zinc, and trace minerals including selenium, iodine, boron and molybdenum.

Conversely, there are a number of elements that are toxic to the human body, interfere with its functioning and undermine health—such as mercury, lead, cadmium, aluminum, and arsenic. These toxic metals have no known physiological functions. They can be toxic to organ systems and may disrupt the balance of essential nutrients. Toxic metals and essential element status can be assessed in urine, blood, feces and hair (Djedjibegovic *et al*., 2012).

Some metals are toxic when they form poisonous soluble compounds. Certain metals have no biological role, i.e. are not essential minerals, or are toxic when in a certain form. In the case of lead, any measurable amount may have negative health effects. Not all heavy metals are particularly toxic, and some are essential, such as iron. The definition may also include trace elements when considered in abnormally high, toxic doses. An option for treatment of metal poisoning may be chelation therapy, which is a technique which involves the administration of chelation agents to remove metals from the body.

Generally, increased exposure to heavy metals in the environment increases risk of developing cancer (Jain *et al*., 2012).

In natural aquatic ecosystems, metals occur in low concentrations, normally at the nanogram to microgram per liter level. In recent times, however, the occurrence of metal contaminants especially the heavy metals in excess of natural loads has become a problem. This situation has arisen as a result of the rapid growth of population, increased urbanization, and expansion of industrial activities, exploration and exploitation of natural resources, extension of irrigation and other modern agricultural practices (FAO, 1992). Slow flowing rivers are more sensitive to pollution inputs. Even under natural conditions, such rivers undergo eutrophication, an aging process that slowly fills in the rivers with sediment and organic matter. The eutrophication process alters basic river characteristics such as depth, biological productivity, oxygen levels, and water clarity. In small amounts, trace elements are normal constituents of fresh water organisms but at higher concentrations, they exert ranges of toxic effects that are metabolic, physiologic, behavioral and economical in nature (Glover and Aust, 1979). The toxic actions of trace elements occur due to bioaccumulation and biomagnifications of the elements in tissues of living organisms (Yu *et al*., 2012; Kaim *et al*., 1994).

Toxic elements, like chemical toxins, are ubiquitous in your environment (Berzas *et al*., 2003). Depending on where you live and where your foods (including herbs, fish and meat) come from, your toxic element exposures can vary widely (Burger and Gochfeld, 2005). In addition, agriculture practices (fungicides, herbicides, pesticides, etc.), consumer products, and medicines increase your exposures to toxic elements. Because of their deliberate uses for decades, toxic elements are now in the air, water, and soil. As such, we are continually exposed to a variety of toxic elements to some degree.

The heavy metal concentration in tissues reflects past exposure via water and/or food and it can

demonstrate the current situation of the animals before toxicity affects the ecological balance of populations in the aquatic environment (Houserová et al., 2007; Forstner and Wittmann, 1983). Since water is the basis for all organisms and ecosystems, protection of aquatic resources is essential in protecting the entire ecosystem. Despite the growing influences from natural and anthropogenic origins, there exists a general belief that presumes absence of permanent alteration or contamination of Migori River. However, rivers such as this are heavily loaded with contaminants of natural and anthropogenic origin such as discharges from factories and domestic sources (Gebremariam and Desta, 2002).

Some effects of toxic elements are;

- Toxic elements interfere with normal biological functions and processes throughout the mind and body. (Bose-O'Reilly *et al*., 2010).
- Increased free radical generation (highly reactive oxygen species) increasing the need for specific antioxidants.
- Toxic elements can displace and even replace essential nutritional elements through a process known as molecular mimicry.
- Eventually, toxic element accumulation may cause or contribute toward myriad health problems (Yu *et al*., 2012).

2. Methodology

2.1. Equipment and Chemicals

The equipment used was fully automated PC-controlled double-beam atomic absorption spectrometer. Three hollow cathode lamps namely Cadmium, Mercury and lead were used throughout the experiment. Other apparatus used were dissecting kit, Hooks, Rope Refluxer, Boiler, Ice box, Knives.

Chemicals

Cheemcals used were Ethanol, Perchloric acid (70% spectrosol), Formaldehyde, Hydrogen peroxide, Nitric acid (70% spectrosol)
Hydrochloric acid (HCl), Sodium Chloride (NaCl).

2.2. Study Area

This study was done on a section of Migori River just downstream of Migori town. Migori River passes through Migori town in Migori County, which is situated in Western part of Kenya. The town is 63 km south of Kisii town and 22 km north of the Tanzanian border.

2.3. Sample and Sampling

2.3.1. Fish Sampling

Fish samples were collected from four stations, 0.5 km apart, using plastic nets. The freshly collected fishes (15–30 cm long) were two types namely tilapia (Oreochromis neloticus) and African cat fish (Clarias gariepinus) washed with river water, distilled water, HNO_3 containing distilled water and was placed on plastic sheet. The collected fish were dissected using plastic knife and quickly wrapped with plastic bags. The bags were frozen in icebox until brought to laboratory. The samples were then frozen at -20^oC in deep-freezer unit until freeze-dried. The moisture contents of the samples were determined by monitoring the loss in mass of wet specimen during the freeze-drying process until constant dry mass was obtained. The freeze-dried samples of tissue from all four stations were mechanically crushed with glass rod and homogenized on their own two parts in freeze-drying flask. The dry specimen of tissue was then powdered in a blending machine.

2.3.2. Collection of Water Samples

Water sample were collected from four stations in the river downstream of town. This was performed by getting a representative sample and 50 cm depth was freshly collected in order to exclude the dust materials as well as oily liquids suspended. Finally, the freshly collected water sample was mixed together and was taken as the composite sample for digestion process.

2.4. Preparation of Stock Standard Solution for Calibration

Calibration curves were prepared for each of the metals by running a range of concentration of freshly prepared standard solution in their respective linear ranges. For the linear dynamic range, the calibration samples were prepared using appropriate dilution of the stock cadmium, mercury and lead (stock solutions of 1000 ppm for each metals) solutions in a solvent. For Cd serial concentration was prepared as follow: 0.01, 0.10, 0.20 and 0.3mL from 10ppm intermediate standard stock solutions in order to obtain the corresponding absorbance. Similarly, for Pb and Hg were prepared as follows:

0.05, 0.10, 0.20, and 0.30 and also 0.5, 1.0, 2.0 and 4.0 respectively from 10 ml of intermediate concentration.

2.5. Digestion Procedures of Fish and Water Sample

2.5.1. Digestion Procedure of Fish Sample

The collected fish sample was dried in an oven at 105 °C and the moisture content of each of the fish species was calculated. After that, it was transferred to the furnace oven and completely dried at 550 °C. The dried sample was then powdered using mortar and pistil and made ready for digestion process. 0.5 g of the powdered fish sample was placed in a 100 mL round bottom flask with ground glass joint and mineralized under reflux using a mixture of 6.0 mL nitric acid (70%, Spectrosol), 2.0 mL perchloric acid (70%, Spectrosol) and 4.0 mL hydrogen peroxide. A triplicate digestion was done for each sample and finally transferred to 25 mL volumetric flask and diluted to the final volume.

2.5.2. Digestion of Water Samples

Digestion of water took place after composite samples were prepared. First a mark in about 20 mL of the beaker was made using marker. Triplicate water samples of each station were prepared and 100 mL of each of them was measured using volumetric cylinder and was added to the previously marked beaker. Then it was boiled until the solution reached up to the mark and finally 2 mL of nitric acid was added to get clear solution.

2.6. Analysis of Heavy Metal Elements in Standard and Sample Solutions

Trace elements like Cd, Hg and Pb were analyzed from the diluted digests of fish and water samples using flame atomic absorption spectrophotometer, using aqueous calibration standards prepared from stock standard solutions of the respective elements.

3. Results and Discussion

3.1. Results

3.1.1. Calibration

Calibration curves were plotted and validated with their corresponding R2 values for the determination of each metal. The values of R2 of the curves were 0.99981, 0.99985, 0.99949, for Hg, Pb, and Cd, respectively.

Table 1. Concentration of standard solutions for the determination of heavy metals

Heavy metal	Series of standards (mg/L)	R2
Cd	0.01, 0.10, 0.20, 0.30	0.99992
Pd	0.05, 0.10, 0.20, 0.30	0.99985
Hg	0.05, 1.0, 2.0, 4.0	0.99949

3.1.2. Moisture Content

The moisture content of fish tissues was determined by monitoring the weight loss of the wet tissues until constant dry mass was obtained in freeze-drying unit. The moisture content was then calculated as percent loss of the mass.

$$\text{Percent loss mass} = \frac{\text{wet mass of fish-dry mass}}{\text{Dry mass}} \times 100\ \%$$

The mass loss calculated varied from 62.6–78.4% in tilapia sample (Oreochromis neloticus), 78.7–85.3% in Africa catfish (Clarias gariepinus).

Table 2. Distribution of trace elements (mg elements/kg dry mass) in Tilapia and cat fish (mean±s.d)

Element	Site			
	1	2	3	4
Cd	1.85±0.04	1.45±0.05	0.40±0.05	0.46±0.05
Pb	0.55±0.002	3.58±0.41	1.859±0.06	3.85±0.04
Hg	0.078±0.005	0.07±0.85	0.088±0.0011	0.091±0.001

Table 3. Distribution of trace elements (mg elements/L) in water samples of Migori River (mean ± SD)

Element	
Cd	0.066±0.003
Pd	0.36±0.03
Hg	0.095±0.004

3.2. Discussion

Optimum method was selected for sample digestion from the tested procedures with preconditions producing clear and colorless solutions with minimum reagent volume, less time and digestion temperature. The method fulfilling such conditions considered to be optimum (Griepink and Tolg, 1989).

3.2.1. Distribution of Heavy Metals in Fish Species

All the three toxic elements evaluated in this study were above detection limits in the edible part of the fish species. As can be observed, the distribution of heavy metals varied as follows: Cd concentration in the four sites varies in the order: 1 > 2 > 4 > 3, while Pb concentration was accumulated in the order 4> 2 >3> 1 while the

concentration of Hg was in the order of 4 >3> 1>2 (Szkoda *et al*., 2013).

Concentration of cadmium in fish samples at the present study, as shown in table 2, was varied from 0.4-1.85 mg/Kg in the two fish species of the four sites. Lead is one of the metals of particular interest in this investigation and its concentration ranged from 0.55-3.85 mg/Kg.

Mercury is one of the most carcegonic elements found in the earth's crust. Specially, the most notorious compounds are in the forms of compounds such as monomethyl and dimethyl salt of mercury which are soluble in water. They are produced from inorganic mercury in sediment by anaerobic bacteria through the action of methyl-cobalamine and intermediate in the synthesis of methane and get into natural water (Manahan, 1989). The major anthropogenic sources of mercury are mining, agriculture and industry. There are however new, less explored routes of mercury exposure, such as its presence in cosmetics (Aranda *et al*., 2008).

4. Conclusions and Recommendation

The study determined heavy metals concentrations in edible part of two fish species (Oreochromis niloticus and Clarias gariepinus) as well as water sample of the studied section of Migori River, and evaluated bioaccumulation, food chain contamination and ecological hazard level of the toxicants. The optimum procedure selected for digestion process produced good recovery results ranged from 91.09±1.3 up to 104 ±1.37 with RSD below 10% which shows the efficiency of method used. In the heavy metal analysis cadmium, lead and mercury were studied. Both Pb and Cd concentration in both fish species as well as water samples were not significantly different at 95% confidence level. However, the concentration of Hg was significantly different. Although the concentration of mercury was higher than all the international standards that are listed the concentrations of Pb and Cd were slightly higher. The following suggestions are recommended in order to monitor and protect the ecosystem:

- Measurements of residues of heavy metals should be regularly carried out using different fish organs that have the ability to accumulate trace elements such as muscle, bone, liver, gill, kidney, scales, skin, bile, spleen and intestine should be analyzed for each element.
- Environmental concerned organizations which are governmental or nongovernmental such as Ministry of Agriculture, Health and Environmental Protection and others should take due attention on the contamination of the environment and biota with such chemicals.
- Education of the rural farmers about the use of safe pesticides and fertilizers should be encouraged.
- Replacement of chemical use by biological methods for increased crop productivity and pest and vector control should be initiated.
- Continuous and extensive studies on toxicity levels, effects and food chain transfer throughout the country should be carried out to know the burden of toxic chemicals in different areas.

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