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Analysis of heavy metals in fish and river water of Gulbin Miyah Augie, Kebbi State, Nigeria

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ABSTRACT

In this study, the Flame Atomic Absorption Spectroscopic technique was applied to determine the concentration of Iron (Fe), Cadmium (Cd), Copper (Cu), and Lead (Pb) in fish (*Clarias gariepinus*) and river water obtained from Gulbin Miyah Augie Local Government Area, Kebbi State, Nigeria. The mean concentrations of heavy metals in fish and river water were: Cd (0.127 ppm and 0.203 ppm), Cu (1.550 ppm and 1.072 ppm), Pb (1.101 ppm and 2.497 ppm), and Iron (0.255 ppm and 0.275 ppm), respectively. The order of decreasing heavy metals concentration in fish and river water were; Cu > Pb > Fe > Cd and Pb > Cu > Fe > Cd respectively. Regarding the mean concentration of the total heavy metals concentration for each metal, it can be said that the river water sample which is (sample A) has the highest concentration of Fe, Pb, and Cd, which are below the recommended maximum limit by WHO. While the concentration of Cu is generally well high in the fish sample (*C. gariepinus*) of Gulbin Miyah (sample B) which is above the recommended maximum limit (WHO), hence it can be concluded that the fish (*C. gariepinus*) of Gulbin Miyah was polluted with Cu, this is due to the human activities around the river area, therefore the people that are around this area should be cautious.

Keywords: AAS, fish, river, WHO, metal concentration, contamination.

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INTRODUCTION

Heavy metals are members of a loosely defined subset of elements that exhibit metallic properties. It mainly includes the transition metals of some metalloids, lanthanides and actinides, mainly different definitions have been proposed, some based on density, some on atomic number or atomic weight and some on chemical properties or toxicity (Abepoju et al., 2005). Heavy metals are elements with atomic number mass between 63.546 and 200.590 and a specific gravity greater than 4 therefore at least 5 times than water. They exist in colloidal particle and dissolved phases with their occurrence in water bodies being either of natural origin (e.g. ended minerals with sediments, leaching origin, i.e. solid waste disposal, industrial or domestic affluent harbor dreading) *(*Abepoju et al., 2005).

Some of the metals are essential to sustain life, calcium, magnesium, potassium and sodium must be present for normal body function. Also, cobalt, copper, iron, chromium, zinc, cadmium, nickel, and molybdenum are needed at low levels as catalysts for enzyme activities, however excess exposure to heavy metals can result in toxicity (Marcovecchio et al., 2007).

Heavy metal can cause serious effects with varied symptoms depending on the nature of the mental ingested. They produce their toxicity by forming complexes with protein in which carboxylic acid (-COOH, amine (-NH_2), thiol (SH) groups are involved (Freije et al., 2007). These modified biological molecules lose their ability to function properly. When metal binds to these groups, they inactive important enzyme systems or affect protein structure, which is linked to the catalytic properties of enzymes. This type of toxin may also cause the formation of radicals which are dangerous chemicals that cause the oxidation of biological molecules (Marcovecchio et al., 2007).

There is an increasing concern about heavy metals contamination in indoor environments since most people spend a great extent of their time indoors. A number of students have suggested that there is a possibility that contaminated dust and water, ingested directly as a result of hand-to-mouth activity, may represent a significant pathway of environment-toxic metals in humans (Alirzaveya et al., 2006).

Rivers and lakes are very important parts of our natural heritage. They have been widely utilized by mankind over the centuries, to the extent that very few, if any, are now in a natural" condition. One of the most significant manmade changes has been the addition of chemicals, containing a lot of heavy metals, to the waters. Such inputs to water can be derived from a variety of sources, some of them are obvious and others less so. They can be varied so that the concentrations of chemicals in water are rarely constant. Contaminated sediments are significant water pollution. Water is also a vital resource for agriculture, manufacturing and other human activities. In urban areas, the careless disposal of industrial effluents and other wastes in rivers and lakes may contribute greatly, to the poor quality of river water (Chindah et al., 2004). Among environmental pollutants, metals are of particular concern due to their potential toxic effect and ability to bioaccumulate in aquatic ecosystems (Censi et al., 2006).

Heavy metals including both essential and non-essential elements have a particular significance in ecotoxicology because they are toxic to living organisms (Storelli et al., 2005). Bioaccumulation and magnification are capable of Leading to toxic levels of these metals in fish even when the exposure is low. The presence of metal pollutants in freshwater is known to disturb the delicate balance of the aquatic systems. Fishes are notorious for their ability to concentrate heavy metals in their muscles and since they play an important role in human nutrition, they need to be carefully screened to ensure that unnecessary high levels of some toxic trace metals are not being transferred to man through fish consumption (Adeniyi and Yusuf, 2007).

Anthropogenic activities continuously increase the amount of heavy metals in the environment, especially in aquatic ecosystems. Pollution of heavy metals in aquatic systems is growing at an alarming rate and has become an important worldwide problem (Malik et al., 2010). Increase in population, urbanization, industrialization and agriculture Practices have further aggravated the situation (Giguere et al., 2004; Gupta et al., 2009).

As heavy metals cannot be degraded, they are deposited, assimilated, or incorporated in water, sediment, and aquatic animals (Linnik and Zubenko, 2000) thus, causing heavy metal pollution in water bodies (Malik et al., 2010). Therefore, heavy metals can be bioaccumulated and biomagnified via the food chain and finally assimilated by human consumers resulting in health risks (Agah et al., 2009). As a consequence, fish are often used as indicators of heavy metals contamination in the aquatic ecosystem because they occupy high tropic levels and are important food sources (Blasco et al., 1998; Agah et al., 2009).

It has been observed that many people living around the Augie area are diagnosed with many symptoms that are similar to those of heavy metal pollution. Also, many activities are carried out in the rivers found in the area. Some local people often use the river water for cooking and drinking while most people do consume fish caught in that river. Metal contamination of water bodies can lead to metal contamination of fish found in the water. Hence this is a serious problem in society.

Many studies have been conducted on heavy metal analysis on water bodies and fish in rivers around areas in Kebbi State, but that of the Augie area is limited or not done. Hence, the need for this study is to investigate the safety of the fish found in the river of Augie local government of the Kebbi State. The main purpose of this study is to determine the concentration of some selected heavy metals present in selected fish and river water of Gulbin Miyah Augie (Section of River Rima), Augie town, Kebbi State.

MATERIALS AND METHODS

Water sample collection and preservation

The samples were collected in a clean polyethylene bottle for the analysis because glass bottles absorb metals and therefore will cause inaccuracy in analysis. Composite samples were collected as much as possible instead of just grab samples or a single purchase. After the completion of the sampling task, preservation of the collected water samples is necessary to obtain good results. Therefore, sample preservation can be achieved by making a slurry of ice and water for cooling at 4°C to minimize the potential for volatilization or biodegradation between sampling and analysis (Blasco et al., 1998). According to Binning and Baird (2001), ‘‘some metal ions like aluminum, cadmium, chromium, copper, iron, lead, manganese, silver and zinc are subject to lose by adsorption on, or ion exchange with the walls of glass containers. Therefore, ultra-pure nitric acid is necessary to add to the sample for metal ions preservation. Besides this, acidification of the collected water sample is essential below pH 2.0 to minimize the precipitation and adsorption on container walls’’. Hence, Acidification with (1+1) nitric acid to pH 2 or less was used to stabilize the metal content. Approximately 3 ml of (1+1) nitric acid per liter of the sample was sufficient for acidification (Agah et al., 2009).

Water sample preparation for AAS analysis

Sample preparation involving the digestion of water samples for metal ion analysis by atomic absorption spectrophotometer can be achieved by adopting the standard method (Nwani et al., 2010): 50 ml of well-mixed, acid-preserved sample is measured into a beaker. 5 ml conc. HNO_3 and a few glass beads were added. It was then slowly boiled and evaporated on a hot plate up to 10 to 20 ml. Conc. HNO_3 (about 3 ml) was added until the completion of digestion (The sample was not allowed to dry). The beaker was washed down with deionized water (3 times). It was then filtered and poured in a 100 ml volumetric flask and made up to 100 ml, mixed thoroughly.

Figure 1. Gulbin Miyah River of Augie.

Fish sample collection and preservation

The method by San and Shrivastava (2011) was adopted. The selected freshwater fish which is (*Clarias gariepinus*) of Gulbin Miyah River, a section of River Rima Sokoto at Augie district, Kebbi State, were caught by the local fisherman using a gill net of various sizes. The fish samples were ice-packed and transported to the Chemistry Research laboratory at Kebbi State University, Aliero.

Fish sample preparation for AAS analysis

In the laboratory, fish samples were dissected using a cleaned washed quality corrosion-resistant stainless knife. The entire sample was separately dried in a laboratory oven at 175°C for 3 h (Nwani et al., 2010). The samples were digested using nitric acid- hydrogen peroxide (HNO_3/H_2O_2) wet digestion method. The samples were prepared by taking 1.0 g of powdered oven-dried sample in a beaker, followed by the addition of 30 cm^3 of freshly prepared 1:1 (v/v) HNO_3 and H_2O_2. The beaker was covered with a watch glass for about an hour to allow the initial reaction to subside. The beakers were heated on a hot plate with a temperature not exceeding 90°C for 30 min. The contents were then transferred into a 50 cm^3 volumetric flask and diluted with deionized water to the mark.

Preparation of blank solution

The blank solution was prepared by adding all the reagents used into a 50 ml volumetric flask and diluted to the mark with deionized water.

Heavy metals determination

The digested samples were taken to the Central Research Laboratory at Kebbi State University of Science and Technology, Aliero, for AAS determination of heavy metals including Cadmium (Cd), Lead (Pd), Iron (Fe), and Copper (Cu).

Analytical procedures

In Atomic Absorption Analysis, the absorption of light uses an instrument called Atomic Absorption Spectrophotometer (AAS). In this process, a flame system is generally employed to dissociate elements from their chemical bonds. The atoms absorb light at characteristic wavelength chemical bonds. The atoms absorb light at characteristic wavelength when present in their ground state. A mixture of air and acetylene produces a flame that is of a sufficiently high temperature to ensure the presence of free atoms of most elements. The use of nitrous oxide in place of air results in a higher temperature and this is necessary for the estimation of certain elements. The narrow spectral line of the sample necessitates the use of a line source as well as a high-resolution monochrometer. This helps to prevent interference from adjacent spectral lines of other species on the sample matrix. AAS in conjugation with flame atomizer will be used to determine specific metals in a liquid sample, the availability of a spectrometer equipped with a lamp turret will facilitate the measurement of multiple metals in a sample.

After the digestion has been completed, the AAS machine was used to determine the present and concentration in the sample containing the metals analyzed is aspirated into air-acetylene flame causing evaporation of the solvent and vaporization of free metal atoms this method is called atomization, a line source (hallow cathode lamp) operating in the UV-visible spectra region is used to cause electronic excitation of the metal and the absorbance is measured with a conventional UV-visible dispersive spectrometer with photomultiplier detector.

Figure 2. An atomic absorption spectrophotometer instrument in the laboratory.

RESULTS AND DISCUSSION

Table 1 shows the mean results of essential and toxic heavy metals analysis of Fe, Cu, Cd, and Pb in the river water of Gulbin Miyah which is labeled as (sample A) and fish sample (*C. gariepinus*) which is labeled as (sample B). The analyzed concentrations of heavy metals in sample A were in order Pb > Cu > Fe > Cd respectively, while the analyzed concentrations of heavy metals in sample B were in order Cu > Pb > Fe > Cd respectively. Thus the river water of Gulbim Miyah (sample A) has a high concentration of Pb, Cd, and Fe, while a high concentration of Cu, was observed in the fish sample which is labeled as (sample B). These concentrations are also represented in Figure 3.

Table 1. The mean concentration of Pb, Fe, Cu, and Cd in the samples.

Heavy metals	Sample A (Mean concentration in pp m)	Sample B (Mean concentration in ppm)
Pb	2.497 ± 0.0044	1.101 ± 0.0009
Fe	0.275 ± 0.0075	0.255 ± 0.0036
Cu	1.072 ± 0.0035	1.550 ± 0.0097
Cd	0.203 ± 0.0039	0.127 ± 0.0061

Sample A: Digested River Water sample, Sample B: Digested Fish samples

In Table 2, standard limits for the heavy metals in ppm are given by WHO. The obtained values for the samples were compared with the WHO maximum permissible limits for these metals. By comparison, it was observed that the Cu concentration in sample B is above the standard limit while sample A has the highest concentration of Fe, Pb, and Cd, which were below the recommended maximum limit by WHO.

Table 2. Maximum permissible limit (MPL) of Heavy Metals in the samples by the World Health Organization (WHO).

Metals	ppm
Fe	300
Cu	0.5
Cd	0.3
Pb	5

Source: Bazargani-Gilani and Pajohi-Alamoti (2017).

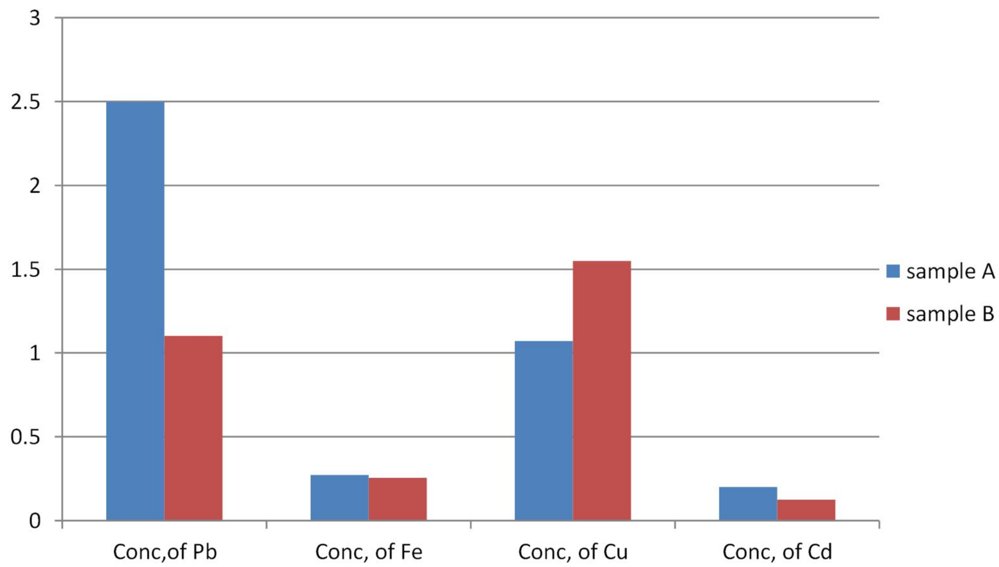

Figure 3. The mean concentration of essential and toxic heavy metals in the samples in ppm.

In the context of nutrition, a mineral is a chemical element required as an essential nutrient by organisms to perform functions necessary for life. Minerals originate in the earth and cannot be made by living organisms. Plants get minerals from the soil. Most of the minerals in a human diet come from eating plants and animals or from drinking water. As a group, *minerals* are one of the four groups of essential nutrients, the others of which are vitamins, essential fatty acids, and essential amino acids. Mineral nutrients are divided into two broad groups; major and trace elements. Major minerals represent 1 percent of body weight and are required in amounts greater than 100 mg per day, while trace minerals make up less than 0.01 percent of body weight and are essential in much smaller amounts. The five major minerals in the human body are calcium, phosphorus, potassium, sodium, and magnesium. All of the remaining elements in the human body are called "trace elements". The trace elements that have a specific biochemical function in the human body are sulfur, iron, chlorine, cobalt, copper, zinc, manganese molybdenum, iodine and selenium. Some essential metals are involved in numerous biochemical processes and adequate intake of certain essential metals relates to the prevention of deficiency diseases. Iron (Fe) deficiency anemia for instance affects one-third of the world population. On the other hand, excessive iron intake has been associated with an overall increased risk of colorectal cancer. Copper (Cu) and zinc (Zn) are essential metals that perform important biochemical functions and are necessary for maintaining health throughout life. Zn constitutes about 33 ppm of adult body weight and is essential as a constituent of many enzymes involved in a number of physiological functions, such as protein synthesis and energy metabolism. Zn deficiency, resulting from poor diet, alcoholism and malabsorption, causes dwarfism, hypogonadism and dermatitis, while the toxicity of Zn due to excessive intake may lead to electrolyte imbalance, nausea, anemia and lethargy. Heavy metals are generally defined as metals with relatively high densities, atomic weights, or atomic numbers. The criteria used, and whether metalloids are included, vary depending on the author and context. In metallurgy, for example, a heavy metal may be defined based on density, whereas in physics the distinguishing criterion might be atomic number, while a chemist would likely be more concerned with chemical behavior. More specific definitions have been published, but none of these have been widely accepted. A density of more than 5 g/cm^3 is sometimes quoted as a commonly used criterion. Some heavy metals are either essential nutrients (typically iron, cobalt and zinc), or relatively harmless (such as ruthenium, silver, and indium), but can be toxic in larger amounts or certain forms. Other heavy metals, such as cadmium, mercury, and lead, are highly poisonous. Potential sources of heavy metal poisoning include mining, tailings, industrial wastes, agricultural runoff, occupational exposure, paints and treated timber. Hence, this study indicated that no toxic Pb was found in the samples which is good news, but Cd, however, was found to be present above the MPL set by WHO. Though some of the values of Cd are slightly above the WHO limit, it generally implies that consumers of these spices should be cautious.

CONCLUSIONS

This study was carried out to provide information on the heavy metals concentration of the catfish and river water obtained from Gulbin Miyah Augie. The results can be used to evaluate the possible health risks associated with the consumption of the species that was analyzed. Regarding the mean concentration of the total heavy metals concentration for each metal, it can be said that the river water sample which is (sample A) has the highest concentration of Fe, Pb, and Cd which were below the recommended maximum limit (WHO). While the concentration of Cu was generally well high in the fish sample (*C. gariepinus*) of Gulbin Miyah (sample B) which is above the recommended maximum limit (WHO), hence it can be concluded that the fish (*C. garefinus*) of Gulbin Miyah was polluted with Cu, this is due to the human activities around the river area, therefore, the people that are around this area should be cautious. Further research should carried out in order to determine more heavy metals and fish species around the area. The people who live in this area should purchase better quality water for drinking as a precautionary measure to avoid health impacts.

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