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Distribution of Trace Metals in Two Commercially Important Fish Species *(Tilapia Zilli and Oreochromis Niloticus)* Sediment and Water from Lake Gudbahri, Eastern Tigray of Northern Ethiopia

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Abstract- Distribution of trace metals (Zn, Cu and Cr) in water; bottom sediment and two fish species *(Tilapia zilli* and *Oreochromis Niloticus)* collected from Lake Gudbahri were analyzed using Varian AA240FS Atomic Absorption Spectrophotometry in order to ascertain their suitability for consumption and other domestic uses. Results indicated that *Tilapia zilli* contained the highest concentration of Zn (84%) of the detected heavy metals, followed by Cu (15%), while Cr (1%) was the lowest value. Similarly, *Nile Tilapia* contained the highest concentration of Zn (77%), followed by Cu (21%). Bioaccumulation factors of *Nile Tilapia* were Cu (409), Zn (110), Cr (57) and *Tilapia zilli* showed 345.5, 112 and 28.6 for Cu, Zn and Cr respectively. The distribution of heavy metals in sediment and water samples were in the order of magnitude as by Zn>Cr>Cu and Zn>Cu>Cr respectively whereas the order of heavy metals concentration in fish samples were found to decrease in sequence as Zn>Cu>Cr. The levels of the heavy metals concentration were compared with permissible limit values provided by WHO, FEPA and various national and international agencies. These levels of heavy metals accumulated in the two fish species might be due to the increase in agricultural influx waters, domestic wastes and some anthropogenic activities.

Keywords: Heavy metals, *Tilapia zilli*, *Oreochromis Niloticus*, Bioaccumulation factor, % Bioavailability, Lake Gudbahri

I. INTRODUCTION

Water pollution has become a global problem. Contamination of aquatic ecosystems with Heavy Metal (HMs) has long been recognized as a serious pollution problem. When fish are exposed to elevated levels of metals in a polluted aquatic ecosystem, they tend to take these metals up from their direct environment [1]. Metal contamination may have deleterious effects on the ecological balance of the recipient environment and diversity of aquatic organisms [2].

During the last decades the rapid economic development of Africa has led to an increase in environmental pollution [3-5]. Heavy metals released into the environment find their way into aquatic systems as a result of Agricultural practices – for instance, the use of fertilizers and pesticides for the control of pests in the cultivation of coffee, cotton, tea and sugarcane and other activities such as mining and industry as well as growth of the human population have increased the discharge of waste effluents into lakes and rivers rendering it environmentally unstable. Consequently, aquatic organisms may be exposed to elevated levels of heavy metals due to their wide use for anthropogenic purposes [6].

Heavy metals are non-biodegradable and once discharged into water bodies, they can either be adsorbed on sediment particles or accumulated in aquatic organisms. Fish may absorb dissolved elements and heavy metals from surrounding water and food, which may accumulate in various tissues in significant amounts [7] and are eliciting toxicological effects at critical targets. Also, fish may accumulate significant concentrations of metals even in waters in which those metals are below the limit of detection in routine water samples [8], therefore, fish might prove a better material for detecting metals contaminating the freshwater ecosystems. Various studies were conducted on the levels of heavy metals in different water bodies [9-14].

Toxic heavy metal can cause dermatological diseases, skin cancer and internal cancers (liver, kidney, lung and bladder), cardiovascular disease, diabetes, and anemia, as well as reproductive, developmental, immunological and neurological affects in the human body. It is also possible that environmental toxicants may increase the susceptibility of aquatic animals to various diseases by interfering with the normal functioning of their immune, reproductive and developmental processes [15]. Long exposure to water pollutants even in very low concentrations have been reported to induce morphological, histological and biochemical alterations in the tissues which may critically influence fish quality.

Total bioaccumulated metal concentration in any organism that is a net accumulator of the metal is informative about metal bioavailability summed across exposure routes. However, there is typically no one universal metal concentration that is indicative of toxicity, especially across species, largely because of interspecies differences in detoxification [16]. The level of bioaccumulation of heavy metals can be determined through calculation of the bioaccumulation factors. Bioaccumulation factor of heavy metals is defined as the ratio between the concentrations of heavy metals in the body of the organism with the concentration of heavy metals in the environment where the species was settled [17]. The present study was carried out to investigate the bioaccumulation of heavy metals (Cr, Cu and Zn) in *Tilapia zilli* and *Oreochromis* N*iloticus*.

Currently, Ethiopia has set no guideline values on the levels of heavy metals in fish resources. The purpose of this study was to produce baseline data on the distribution of heavy metals (Cr, Cu and Zn) in water, sediment and commonly consumed fish species *Tilapia zilli* and *Oreochromis Niloticus* (Nile Tilapia*)* obtained from Lake Gudbahri. In addition, analysis of the enrichment of these heavy metals in water, sediment and fish samples was used to evaluate the magnitude, impacts and possible sources of heavy metal contamination on the Lake. The results obtained from this study would also provide information for background levels of metals in the water, sediment and fish, contributing to the effective monitoring of both environmental quality and the health of the organisms inhabiting the Lake. To the best of our knowledge, from literature survey, no work has been carried out on the level of heavy metals concentration in fish samples of the Lake and their potential impacts on human health risks and the food chain.

II. MATERIALS AND METHODS

A. Description of study area

Lake Gudbahri (figure 1) is located directly at the edge of Wukro town 47 Kms from Mekelle city near the red rock- cut church of Wukro Cherqos. The study area lies between latitudes 13 47' 31" N and longitudes 39 35' 57"E in Eastern Tigray of Northern Ethiopia at an elevation of 1930 meters above sea level.

Figure 1: Lake Gudbahri

B. Sampling

Samples of water, sediment and two most common fish species (*Tilapia zilli* and *Oreochromis* N*iloticus)* were brought directly from the study area. The sampling bag were pre-conditioned with 5% HNO_3 and later rinsed thoroughly with distilled de-ionized water. At each sampling site, the polyethylene sampling bags were rinsed at least three times before sampling was done. Water samples were taken from three different points at surface, middle and bottom of the lake using 3L Heart Valve water sampler. Homogenized water samples were collected in cleaned 2 liter polythene bags. The fishes were sampled with gill nets from the lake. Adult individuals of similar size were selected from both fish types of the lake and fish samples were taken for analysis. Sediment samples were collected from the lake using bottom sediment Grab Sampler. All samples were brought to the laboratory using portable ice box and stored in refrigerator until analysis.

C. Sample preparation

The collected fish samples were stored in a cooler packed with ice block in order to maintain the freshness and latter transported to the laboratory for dissection of the organs and washed thoroughly. The fish samples were dried for 24 hours to constant weight in an oven at 105^oC. The dried samples were pooled and milled with a mortar and pestle. They were put in dry labeled plastic containers and stored in desiccator until digestion. A standard procedure was used to digest the samples [18]. This involved digesting 10 g portion of the ground samples with 10 mL HNO_3 and 2 mL $HClO_4$ was heated on a hot plate for one hour. After complete digestion, the residue was dissolved and diluted with 0.2% HNO_3. The digest sample was stored in pre-cleaned polyethylene bottles until analysis using Atomic Absorption Spectrophotometer.

About 100 ml water sample was filtered through Nitrocellulose filter membrane of 0.45 μm pore size prior dried in 105^0C for 2 hours. The filtrated and unfiltered water samples were preserved in 2 ml concentrated nitric acid to prevent precipitation of metals and growth of algae. Dissolved metals were determined from the filtrate water samples whereas the total metals from the unfiltered water samples using nitric acid digestion. Finally 20 mL of filtered and digested samples were taken for analysis.

Sediment samples taken from the lake were air-dried, mixed and one fourth of each sample was dried in an oven at 105 ^0C for 12 hrs. The dried samples were then ground and sieved with 75 mm mesh size. A 20 g $\pm$ 0.05 g of pulverized sample was weighed into a 400 ml tall beaker. An acid mix of 50 ml HCl and 20 ml HNO_3 was slowly added to the sample while swirling, to ensure the sample is properly wetted and simmered on the hot plate for a minimum of 45 minutes at 160 ^0C, stirring with a glass rod. It was removed from the hot plate before dryness, cooled and diluted on a 200 ml volumetric flask with distilled water, shaken and poured back into the beaker and settled for 30 minutes. Finally some amount of the digested sample was taken and analyzed for trace metals.

D. Sample Analysis

All samples were analyzed at the Central Analytical Laboratory, EZANA Mining Development PLC, Mekelle, Ethiopia. Heavy metals (Cr, Cu and Zn) were determined with Varian AA240FS Fast Sequential Atomic Absorption Spectrometer, which is fully automated PC-controlled true double-beam AAS with Fast Sequential operation for fast multi-element flame AA determinations, Features 4 lamp positions and automatic lamp selection, Operated with SpectrAA base and PRO software versions, was used in this research. Values were recorded in mg/kg dry weight. Bioaccumulation Factors (BAF) between the fish tissues and the water were calculated. Data were analyzed using statistical software package SPSS and Analysis of Variance (ANOVA). Detection limits for the analyzed metals on the instrument were: Cr: 0.006 mg/Kg, Cu: 0.003 mg/Kg and Zn: 0.001 mg/Kg.

E. Bioaccumulation Factor (BAF)

The bioaccumulation factor (BAF) is the ratio between the accumulated concentration of a given pollutant in any organ and its dissolved concentration in water and it was calculated [13] using the following equation:

$$\mathrm{BAF} = \frac{\text{Concentration of HMs in dry fish muscle (mg kg}^{-1})}{\text{Concentartion of HMs in water(mgl}^{-1})}$$

F. Bioavailability

Bioavailability is defined as the degree to which heavy metals in a water-soluble form that plant and animal communities can readily uptake and assimilates [19]. Bioavailability of a contaminant to the receptor will depend upon its chemical and physical characteristics. The bioavailability of metals with respect to total metal content can be calculated as follows:

$$\%\ \text{Bioavailability} = \frac{\text{Dissolved metal concentration } (\mu\text{g l}^{-1})}{\text{Total metal concentration } (\mu\text{g l}^{-1})} \times 100$$

III. RESULT AND DISCUSSION

A. Heavy metal concentration (µg/L) in water sample from Lake Gudbahri

Heavy Metal concentrations in water samples from Lake Gudbahri are presented in Table 2. Heavy metals concentration in water sample were found to be in the following decreasing sequence: Zn (196.67±5.77) > Cu (11±9.50) > Cr (7.0±5.2). Zinc concentration (91.63 %) in water sample constituted a major portion of the total metal ions determined, while Cu and Cr concentrations were the lowest value (5.12%) and (3.27%) respectively. The average concentrations of Zn, Cr and Cu in water sample were below the permissible limits provided by WHO [20], and USEPA [21].

Table 1: HMs concentrations (µg/L) with Stdev in water and comparison with Water Quality Guidelines

Sample	Parameter	Heavy Metals		
Water		Cr	Cu	Zn
	Mean ±Stdev	7.0±5.2	11±9.50	197±5.77
	WHO (2008)	50	2000	5000
	USEPA (2011)	100	1300	5000

B. Heavy metal concentration (mg/kg) in bottom sediment from Lake Gudbahri

Table 2 shows the total extractable metals from Lake Gudbahri sediment and sediment quality guidelines of WHO and USEPA. Heavy metal concentration in sediment samples were found to be in the following decreasing order Zn (43.00) > Cr (31.33) > Cu (22.00). Zn concentration in the sediment sample constituted a major portion of the total metal ions determined (44.64%), whereas Cu concentration was the lowest (22.84%). Therefore the obtained results showed that the average values of Zn (43.00), Cr (31.33) and Cu (22.00) in sediment samples were lower than the respective reference values for USEPA [22] and ISQG [23].

Table 2: HMs (mg/kg dry weight) in sediment and comparison with sediment quality guidelines

Sample	Parameter	Heavy Metals		
Sediment		Cr	Cu	Zn
	Mean ± Stdev	31.33±0.58	22.00±1.00	43.00±1.00
	USEPA (2010)	43.4	31.6	121
	ISQG (2002)	37.3	35.7	123

C. Heavy metal concentration (mg/kg) in Nile Tilapia and Tilapia zilli

Concentration heavy metals in the two fish species (*Nile Tilapia and Tilapia zilli*) from Lake Gudbahri are shown in Table 3. Several studies indicated that metal bioaccumulation in fish tissues depend on a number of factors such as food habits and foraging behavior of the fish [24]; trophic status, source of a particular metal, distance of the organism from the contamination source and the presence of other ions in the environment [25]; food availability [26]; bio-magnification and/or bio-diminishing of a particular metal [27]; metal detoxifying proteins in the body of the fish [28]; temperature, transport of the metals across the membrane and the metabolic rate of the animal [29]; species, age, size of fish and exposure time [30]. Metal accumulation in the tissues of fish varied according to the rates of uptake, storage and elimination [6]. Our study also showed that accumulation of each heavy metal varied between the fish species, i.e. in Tilapia zilli were found to decrease in sequence as Zn (84%) >Cu (15%)> Cr (1%) and in Nile Tilapia Zn (77%) > Cu (21%) > Cr (2%). Results showed that the highest and lowest contents of HMs in both fish samples were related to Zn and Cr concentration, respectively. The extent of the concentration of the HMs in the two fish species were compared to the tolerable values provided by IAEA-407[31, 32], FEPA [33], FAO/WHO [34] and WHO [35].

Table 3: Mean concentration (mg/kg dry weight) with Stdev of HMs in fish species from Lake Gudbahri.

Fish species	Parameter	Heavy metals		
		Cr	**Cu**	**Zn**
Nile Tilapia	Mean± Stdev	0.004±0.005	0.060±0.024	0.217±0.234
Tilapia zilli	Mean± STDV	0.002±0.004	0.038±0.013	0.220±0.214
IAEA-407 (2003)		0.73	3.28	67.1
FEPA (2003)		0.15	1.3	75
FAO/WHO (1989)		0.15	30	40
WHO (1985)		0.15	3.0	10-75

Figure 2 shows the comparative accumulation of heavy metals in *Nile Tilapia* and *Tilapia zilli*. Zn was the highest in both species but relatively higher in *Tilapia zilli* (84%) than *Nile Tilapia* (77%) and Cr was the lowest in both species with Cr (2%) for Nile Tilapia and Cr (1%) for Tilapia zilli. Though, there are no data's on heavy metal distribution in fishes in Ethiopia, compared to literature reported [36] the concentrations of Cu and Cr were very low in both *Nile Tilapia* and *Tilapia zilli* of Lake Gudbahri than fishes from Lake Awassa and Ziway. But a high concentration of Zn was observed in Lake Gudbahri than Lake Awassa and Ziway.

Level of heavy metals in water, sediment and different fish species indicates that there is an interrelation of metal accumulation in the various components of the fish as suggested [37] fish acquires metals both directly from water and sediment and indirectly through the food chain.

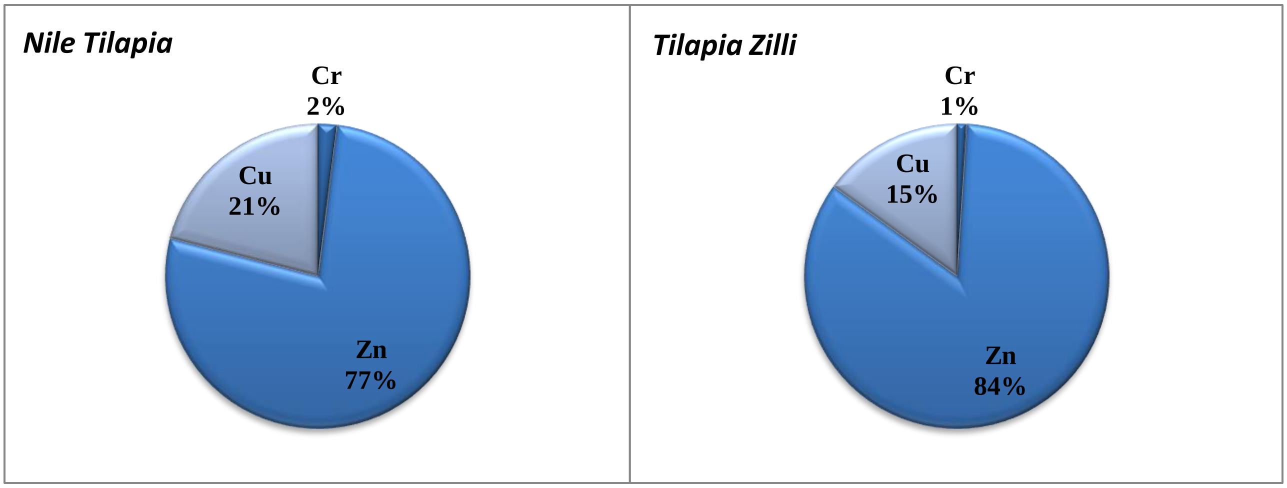

Figure 2: MHs content (%) in fish samples of *Nile Tilapia* and *Tilapia zilli* from Lake Gudbahri

Table 4 shows that the Bioaccumulation Factor (BAF) of the three HMs in the study area. The BAF of heavy metals in *Nile Tilapia* and *Tilapia zilli* was in the order of Cu (409) >Zn (110) > Cr (57) and Cu (345.5) > Zn (112) > Cr (28.6), respectively with highest BAF of Cu (409) for Nile Tilapia and (345.5) for Tilapia zilli from water. It is obvious from the data given in Table 4 that the highest bioaccumulation factors (BAF) were recorded from water while the lowest values of BAF were recorded from sediment in both species.

Table 4: Bioaccumulation (BAF) of HMs in *Nile Tilapia* and *Tilapia zilli* from Lake Gudbahri

Fish species	**Parameters**	**Heavy metals**		
		Cr	**Cu**	**Zn**
Nile Tilapia	water →fish	57	409	110
	sediment →fish	0.013	0.205	0.504
Tilapia Zilli	water →fish	28.6	345.5	112
	sediment →fish	0.006	0.172	0.52

The bioavailability of heavy metals is shown in Table 4. The dissolved metal concentration is determined via analysis of filtered water samples and the total metal concentration of unfiltered water samples. The results obtained were decreased in the sequence Cu (45.45%) > Cr (42.86%) > Zn (27.41%). The bioavailability of the heavy metals exhibited maximum and minimum values for Cu (45.45%) and Zn (27.41%) respectively. Bioavailability of the HMs depend in part on the concentration of anions and chelating ligands present in the water, pH and Redox status and the presence of absorptive sediments [38] of the lake.

Table 5: Bioavailability (%) of HMs in *Nile Tilapia* and *Tilapia zilli* from Lake Gudbahri

Sample	**Parameter**	**Heavy metals**		
		Cr	Cu	Zn
filtered	average	3	5	54
unfiltered	average	7	11	197
Bioavailability %		42.86	45.45	27.41

IV. CONCLUSION

Fish is one of the most commonly consumed diets of man therefore, it is necessary that regular biological monitoring of the water and fish for consumption should be done to ensure continuous safety of the seafood. Safe disposal of agricultural, domestic sewage and industrial effluents should be practiced and where possible, recycled to avoid these metals and other contaminants from going into the ecosystem.

It is logical to say that the high concentration of metals in river become gradually accumulated on the sediments (as a function of pH) and in due course get transferred to fish. Finally, the high level of bioaccumulation factor of Cu and Zn shows that they were good bio-indicator to monitor pollution in the lake for the two fish species. Although, we did not investigate the role of adsorption, precipitation of metal ions and influence of interference in this work these will be considered in our next work.

The results of this study revealed that consuming fish from Lake Gudbahri, Tigray, Northern, Ethiopia may not be harmful to consumers because the observed values of heavy metals were below the permissible limits issued by IAEA-407, 2003; FEPA, 2003 and WHO, 1985, for human consumption.

The values reported in this study can serve as baseline data to monitor future anthropogenic activities along the coast, information on concentrations and distribution of heavy metals in *Nile Tilapia* and *Tilapia zilli* of Lake Gudbahri, eastern Tigray, Northern highlands of Ethiopia. The study showed a need for continuous pollution assessment study of aquatic organisms in Ethiopia and recommends the country to set guideline values on the levels of toxic heavy metal contaminants in fish resources.

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