Archives of Ecotoxicology, Vol. 4, No. 2, pp. 51-58, 2022

SCICELL

ARCHIVES OF ECOTOXICOLOGY
Scientific journal

Archives of Ecotoxicology

Journal homepage: https://office.scicell.org/index.php/AE

OPEN ACCESS

Comparison of Heavy Metal Deposition in Edible Muscles of Nile Tilapia (*Oreochromis niloticus*) and Crucian Carp (*Carassius carassius*) in Lake Ziway, Ethiopia

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Article info
Received 30 March 2022
Revised 24 September 2022
Accepted 24 September 2022
Published online 05 October 2022

Regular article

Keywords:
Electrical conductivity;
Total dissolved solids;
Suspended solids;
Fish Muscles;
Heavy metals;
Physicochemical properties

Abstract

Lake Ziway is a fresh Lake playing an important role in the lives of many people in the region. These may make the Lake Ziway to receive various kinds of pollutants enriched with heavy metals through different mechanism. The purpose this study was to conducted analysis of heavy metal accumulation in the edible muscles of Nile Tilapia and Curican carp fish species which are among the most common types of fish consumed by the local people and found widespread in the lake Ziway. The water and fish samples were purposively collected from three sites in the Lake Ziway. The physicochemical properties of water samples including Temperature, pH, electrical conductivity, total dissolved solids and total suspended solids. The analysis of heavy metals including Cd, Pb, Ni, Cu, and Zn were conducted for water samples and from edible muscles of two fish species including Nile tilapia and Curician carp. Data were subjected to statistical analysis. The result of physicochemical properties of the water samples from the study sites in the Ziway Lake indicated no significance differences in temperature and pH among the three sites. However, significance differences were observed in other parameters like electrical conductivity (EC), total dissolved solids (TDS) and suspended solids (SS). Site 1 has demonstrated significantly the highest EC (1245.12±5.34 µS/cm), TDS (756.10±1.50mg/L) and SS (24.5±0.15 mg/L). The concentrations of heavy metals in water samples from Lake Ziway at site 1 (close to floriculture industry) presented significantly the highest amount of all the tested metals including Cd (2.71mg/L), Cu (4.88mg/L), Ni (8.10mg/L), Pb (6.06mg/L) and Zn (12.12mg/L). The accumulation of heavy metals in two fish species including Nile tilapia locally called 'koroso' and Curican carp locally named as 'dabe' demonstrated significance differences in the load of heavy metals between both species with Nile tilapia loaded significantly higher than Crucian carp in most of the metals assessed. Significantly the highest load of metal accumulations in fish muscles were observed at site 1 (near floriculture industry) in Nile tilapia with load of Zn (100.37), Cd (6.05), Ni (4.70), Pb (5.76) and Cu (47.54)mg/L. The comparison of heavy metal accumulation across lake sites in fish muscle samples indicated that the highest accumulations were obtained for Cu and Zn; small amounts of Cd, Ni & Pb.

1. Introduction

Fish is consumed everywhere due to its nutritional value, along with its high quality proteins, great omega-3 fatty acid content, and low saturated fat content and due to having a good level of vitamin-B **(Ozden *et al.,* 2018).** It is anticipated that fish contributes about 17% of animal protein and almost 6% of all protein consumed by human beings**.** Fresh water reservoirs play an important role in the livelihood of human populations. They are used as a source of domestic water supply, irrigation, fishery development, hydropower generation and flood control. Heavy metals in water can originate both from natural sources, industrial, agricultural and domestic activities in the drainage basin of a water system. As the metal levels in many aquatic ecosystems increase due to anthropogenic activities, they raise the concern on metal bioaccumulation through the food chain and related human health hazards **(Agah *et al.,* 2009). FAO (1992)** noted that the contamination of water supplies from both natural and anthropogenic sources has impacted on the health and economic status of populations. Human activities cause pollutants such as heavy metals, pesticides and herbicides to enter aquatic ecosystems. These anthropogenic activities continuously increase the amount of heavy metals in the environment, especially in aquatic ecosystems. Thus, heavy metal pollution is growing at an alarming rate and has become an important worldwide problem **(Malik et al., 2010).**

Heavy metals cannot be degraded but they are deposited, assimilated or incorporated in water, sediments and aquatic biota causing heavy metal pollution in water bodies **(Linnik and Zubenko, 2000).** Although Seafood is considered as a main source of high biological value protein, polyunsaturated oil and minerals such as calcium, potassium, fish form an important target for bio-magnifications of heavy metals as they are at the top of food pyramid and act as a possible transfer media to

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https://doi.org/10.36547/ae.2022.4.2.51-58

human beings **(Shady et al., 2016).** The main anthropogenic sources of heavy metals are various industrial processes, mining, foundries, and smelters, combustion of fossil fuel and gasoline, and waste incinerators. The major heavy metals of concern to EMEP are Hg, Cd and Pb, because they are the most toxic and have known serious effects on e.g. human health. Environmental exposure to high concentrations of heavy metals has been linked with e.g. various cancers and kidney damage. There are considerably more measurements data on Hg, Cd and Pb in Europe than for other metals.

The Best common Potential Toxic Elements (PTE) listed by the United Stated Environmental Protection Agency (USEPA) are mercury (Hg), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn). Some of these PTEs are essential for the metabolic activities of living organisms. Potential toxic elements such as Cr, Cu, Ni and Zn are required by organisms at low level and become toxic at some higher levels. Non- essential elements including As, Cd and Pb are toxic and not required by organisms at any level **(Poggio et al., 2009).** Lake Ziway is one of the Rift Valley Lake of Ethiopia and it is used greatly for tourism attraction and supplies of fish for local communities. This lake serves to maintain the ecological system as habitat for various species of flora and fauna. Fish from Lake Ziway are widely caught by local people for their daily diet or to be sold. The study on heavy metal contamination in fish is vital to assess the current status of water pollution with heavy metal and threats to human health from heavy metal pollution of the Lake.

The expansion of urbanization and actually drastic increment of human population in town is major contributor in polluting globe. Just like other countries seen our environment is getting polluted in alarming rate in land and water bodies. Lake Ziway is a fresh Lake playing an important role in the lives of many people in the region. It is the source of commercial fishery. It serves for recreation purpose and also is used for drinking water supply by the communities surrounding it. It is influenced by human activities such as agricultural practice, deforestation, industrialization and discharging of domestic sewages **(Abayneh Ataro *et al.,* 2003).** These may make the Lake Ziway to receive various kinds of pollutants enriched with heavy metals through different mechanism. These different sources cause the accumulation of heavy metals in the Lake. The accumulation can be in water, suspended solid, sediment, fishes and aquatic plants. Some heavy metals may affect the growth of fish and/or are harmful to the consumer. The extent of accumulation in the fish is used as a bio-indicator for pollution of the lake water with the heavy metals. The loads of the pollutants in general and heavy metals in particular enter into the lake through different mechanism and their accumulations may vary with the seasons of the region **(Kargin, 1996).** The purpose this study was to conducted analysis of heavy metal accumulation in the edible muscles of Nile Tilapia and curican carp fish species which are among the most common types of fish consumed by the local people and found widespread in the lake Ziway.

2. Material and methods

2.1 Description of the Study Area

Lake Ziway is the largest of the northern rift valley lakes with a surface area of over 440 square kilometers which is 162 kilometer away from Addis Ababa. Lake Ziway (Figure 1), situated between 7°51′N to 8°07′N and38°4E to 38°56′ E,is located 160 km south of the capital, Addis Ababa, Ethiopia, at an altitude of 1 636 m above sea level **(Endebu and Girma, 2016)**. Lake Ziway is the second most important fishery landing site of the country **(Bekele and Hussien, 2015).** Surface area, shoreline length and total catchment area of the lake are 442 km^2, 137 km^2 and 7 380 km^2, respectively **(Lemma and Desta, 2016).** The mean and maximum depths of Lake Ziway were reported in the range of 2.5–4 m and 7–9 m, respectively **(Teklu et al., 2018).**

The differences in reported depth of the lake by several authors seem to be partly explained by the remarkable seasonal rainfall variation **(Tamire Mengistu, 2012)** of the region. The lake has two inflowing perennial rivers (Meki River and Ketar River) and drains into Lake Abjata via Bulbula River **(Ayenew, 2007).** It is one of the largest freshwater lakes found in the Ethiopian Rift Valley basin possessing high environmental, economic and social significance. For instance, the lake is known for its very high biodiversity values, fish production, tourism and irrigation for agriculture and a potable water supply for an increasing population in the catchment **(Sissay, 2003).** The climate is characterized by semiarid to sub-humid with mean annual precipitation and temperature of 650mm and 25°C, respectively **(Lijalem Zeray et al., 2006).**

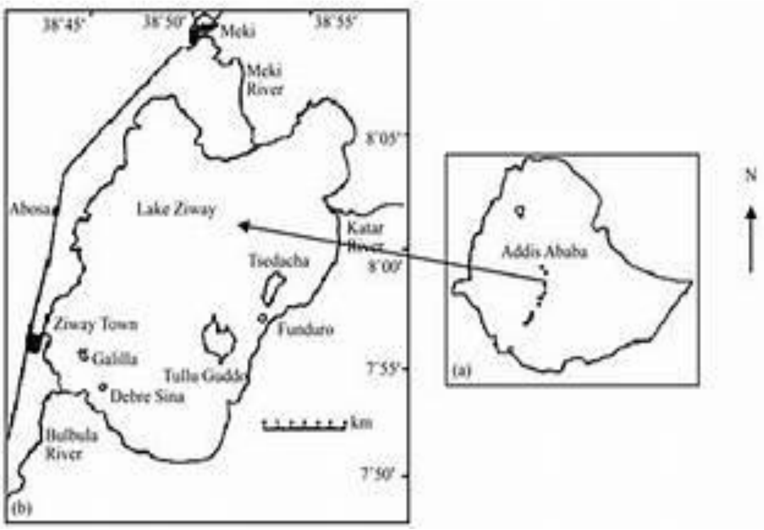

Figure 1 Map of the study area

2.2 Sampling technique

2.2.1 Sampling Site

Water and fish samples were collected for a period from 20 to 25 August, 2021. The three sampling sites were selected based on the magnitude of human influences such as the 1st site near to florifarm industry, the 2^{nd} site near frequent fishing site and the third the opposite side of the shore where human intervention is considered to be low.

2.2.2 Sample Collection and Treatment

Water samples were taken by polyethylene bottle with 250ml capacity. All sampling bottles were cleaned before use with detergents and rinsed with deionized water for the sampling purpose. The samples were acidifies with HNO_3 and transported to the laboratory for further treatment.

Two fish species including Nile tilapia and Crucian carp samples were caught and collected at each sampling site with the help of fishermen, by using plastic nets. The selected fish species were randomly collected with the help of local fishermen within the sampling stations. After collection, the samples were immediately dissected in the field using plastic knife and only the edible tissue was transferred to plastic bags and put into ice box for transportation to Analytical Chemistry Laboratory, Haramaya University.

2.2.3 Sample Preparation

The fish samples were oven dried at 105⁰C until they reached a constant weight. Each dried sample was then ground into a fine powder using electrical grinder. A 0.5g of powdered fish sample was weighted and transferred in to 50 mL volumetric flask and the mixture of 8 mL of concentrated HNO_3 (69%) and 6 mL of H_2O_2 (30%) was added. Finally, the heavy metals were analyzed using Flame Atomic Absorption Spectrophotometer (AAS).

2.3 Preparation of Stock Standard Solution for Calibration

All the chemicals use will be at analytical reagent grade. Deionized water will use for all dilutions throughout the study. Nitric acid, HNO_3 (69%), and hydrogen peroxide, H_2O_2 (30%), were used for digestion. 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. Working standards were prepare by diluting concentrated stock solution of 1000 mg/L for Cu, Ni and Zn and 1000 µg/L for Pb and Cd in de-ionized water. For Pb and Cd serial concentration was prepared as follow: 0.25, 1.0, 2.0, 3.0 and 4.0 mL from 50 ppm intermediate standard stock solutions in order to obtain the corresponding absorbance. Similarly, for Ni, Zn and Cu were prepared as follow: 0.25, 1.0, 2.0, 4.0, and 6.0mL from 50 µg/L of intermediate concentration. The matrix modifier $NH_3H_2PO_4$ and $Mg(NO_3)_2$ were used for Graphite Atomic Absorption Spectrophometery (GFAAS).

2.4 Instrumentations and Apparatus

All digestion works were carried out by using Heating Mantle (98-II-B Magnetic stirring electric sleeve). The fish samples were dried in oven and ground in mortar and pestle. The 250 mL round bottle flasks were used for digestion purpose. PG-990 Atomic Absorption Spectrometer was used for analysis of heavy metals in water and fish samples. The GF-990 graphite furnace power supply and ASC-990 programmable automatic sample loader was used for GFAAS and ASA-900 automatic sample was use for Flame Atomic Absorption Spectrophotometer (FAAS).

2.5 Determination of Physicochemical parameters of the water sample

Determination of physicochemical parameters including PH, electrical conductivity, total soluble solids, and hardness were based on standard method of APHA (2005).

2.5.1 PH measurement

For measurement of the PH first the electrodes were calibrated with two standard buffer solutions of pH. The electrodes were immersed into the sample of water (whose pH is to be determined) and wait up to one minute for steady reading. The reading was observed after the indicated value becomes constant.

2.5.2 Electrical conductivity

Is a measure of ability of an aqueous solution carrying an electric currents. This ability depends on the presence of ions and on the temperature of measurement. The conductance of a solution (G) is defined as the reciprocal of resistance, and is directly proportional to the electrode surface area, *A*, cm2, and inversely proportional to the distance between the electrodes, *L*, cm. The constant of proportionality, *k*, such that:

$$G = K\left(\frac{A}{L}\right)$$

The units of *k* are 1/ohm-cm or mho per centimeter. Conductivity is customarily reported in micromhos per centimeter (µmho/cm). In the International System of Units (SI) the reciprocal of the ohm is the siemens (S) and conductivity is reported as millisiemens per meter (mS/m); 1 mS/m = 10 µmhos/cm and 1 µS/cm = 1 µmho/cm.

2.5.3 Determinations of Total solids (TS), Total Dissolved Solids (TDS) and suspended solids (SS)

Clean beaker (150mL) was kept at 103°C in an oven for 1 hour and weighed (Wa). A 100 ml of water sample was added into a beaker (without filtering for determination of TS), but filtered through a double layered filter paper (for determining TDS) into a beaker. Then, the beaker containing filtered water sample was kept in an oven maintained at 103°C for 24hours. After 24 hours, when whole of the water has evaporated, and the beaker was cooled and weighted (Wb). The total solids (TS), Total dissolved solids (TDS) and suspended solids (SS) was obtained as follows:

$$\text{TS in water (mg/L)} = \frac{(\text{Wb}-\text{Wa})\text{x}1000}{\text{sample volume}}$$

$$\text{TDS in water (mg/L)} = \frac{(\text{Wb}-\text{Wa})\text{x}1000}{\text{sample volume}}$$

Total solid (TS) = Suspended Solids + Total dissolved Solids (TDS)

The theoretical relations between TDS and EC was also checked TDS (mg/L) = 0.6 EC (µS/cm)

2.6 Preparation of Samples

The water samples were filtered through Whitman 541 filter paper immediately after the samples have been transported to the laboratory. The filtered samples were acidified with HNO_3 and were kept at 4°C prior to analysis. In order to obtain a representative sample, composites were prepared by taking the edible tissues (fillet) of the three fish samples at each sampling site. The fish samples were oven dried at 105°C until they reached a constant weight. Each dried sample was then ground into a fine powder using porcelain mortar and pestle, and thereafter all powdered tissues were kept in desiccators prior to further chemical analysis

2.7 Digestion of fish samples

The powdered fish samples were thoroughly homogenize before subjecting them to digestion and digested using concentrated nitric acid and hydrogen peroxide (1:1) v/v according to FAO methods. 1.0 g of dried and powdered fish samples were weighed and transfered into 250 mL round bottled flask and the mixture of 10mL of concentrated HNO_3 (65%) and 10 mL of H_2O_2 (30%) were add. The flasks were covered with a watch glass and left aside until the initial vigorous reactions occur. Then, the samples were heated on a Heating Mantle to 130°C until dissolution inside a fume hood to reduce the volume to 3-4 mL. The mixture was left at room temperature to cool, after which it was diluted with 20mL of distilled water and filtered. The filtrate was kept and analyzed for heavy metals (Cd, Ni, Cu, Pb, Zn,) using Atomic Absorption Spectrophotometer (AAS).

2.8 Analysis of Heavy metals

Concentration of Cu, Cd Pb, Ni and Zn were determined in both water and fish samples. The analyses of metals in water and fish samples were carried out by both; furnace atomic absorption spectrometry and flame atomic absorption spectrometry. The

PG-990 Atomic Absorption Spectrophotometer equipped with a graphite furnace and ASC- 990 autosampler for GFAAS and ASC-900 autosampler for flame was used for determinations. The operating conditions for Cu, Cd, Pb, Ni and Zn analysis by FAAS and/or GFAAS were indicated in Table 1. Calibration of the instrument was carried out with range of standard solution. After calibration, the samples were aspirated into the AAS instrument according to standard method (APHP, 1998). The samples were analysed in duplicates, and the blank determinations in duplicates were also run in the same manner during the analysis.

Table 1 Instrumental conditions for the analysis of heavy metals using the PG-990 AAS

Element	Flame & Graphite furnace	Wave length (nm)	Lamp	Spectral band width (nm)	Lamp current (mA)	Detection limits
Cd	Argon	228.8	Cd HCL	0.8	2.0	0.03[a]
Pb	Argon	283.3	Pb HCL	0.8	2.0	1.10[a]
Zn	Air/acetylene	213.9	Zn HCL	0.5	2.0	0.01[b]
Cu	Air/Acetylene	324.8	Cu HCL	1.2	2.0	0.03[b]
Ni	Air/Acetylene	232.0	Ni HCL	0.2	3.0	0.07[b]

[a] Detection limit (±30%) in µg/L for 20µl sample aliquot
b Detection limit (±30%) in mg/L for 100mm burner and air/acetylene (C_2H_2) flame

The water samples and fish samples were analysed by GFAAS for Pb and by FAAS for Zn determinations. The fish samples for Cu and water samples for Ni were analysed by FAAS. The water samples for Cu and fish samples for Ni were analysed by GFAAS. Modifiers [Mg (NO3)2 and NH4H2PO4] were used for GFAAS to eliminate matrix interferences. The trace metal concentration in mg/kg per fish sample was then calculated using the equation as:

$$\text{Conc of the metal in mg/kg fish} = \frac{\text{AAS reading x volume of the extract}}{\text{mass of fish digested}}$$

The concentration of heavy metals in water samples were calculated from the equation of standard curve of respective standard solutions as follows.

Y=ax+b where Y= the AAS reading; x: the concentration of heavy metals (mg/L); a=the slope of the standard curve; b: is the intercept.

Thus, X(mg/L) metal concentration=$\frac{Y-b}{a}$

2.9 Data Analysis

The validity of the procedure, precision and accuracy were assured by comparing with standard of known concentration. Statistical analyses of data were carried out using SPSS 16.0 statistical package program. One-way ANOVA (Analysis of Variance) was performed for statistically significant difference in the mean value of heavy metal concentrations between the three sampling sites.

3. Results and Discussion

3.1 Physicochemical properties of the water samples from Lake Ziway

The result of physicochemical properties of the water samples from the study sites in the Ziway lake (Table 2) indicated no significance differences in temperature and pH among the three sites. However, significance differences were observed in other parameters like electrical conductivity (EC), total dissolved solids (TDS) and suspended solids (SS). Site 1 has demonstrated significantly the highest EC (1245.12±5.34 µS/cm), TDS (756.10±1.50mg/L) and SS (24.5±0.15 mg/L). There were no significance differences in EC and TDS between site 2 & 3 indicating that the human intervention in both sites are lower than the first site that has recorded the highest values of PH, EC, TDS and SS. Similar study was conducted by **Zenebe (2011)** on lake Hawasa and **Dessie et al (2019)** on Lake Hayq. The physical, chemical and biological contents of water determine the quality of water. Water quality guidelines like WHO, EU and USEPA **(UNEP, 2006)** provide basic information about water quality parameters and ecological relevant toxicology threshold values to protect specific water uses. The quality of fresh water for fish should not allow accumulation of pollutants especially heavy metals in fish to such extent that they are potentially harmful **(Alabaster and Lloyed, 1982)**.

Surface water temperature is one of the important factors affecting aquatic environments for two reasons. First, water temperature affects nearly all other water parameters and second aquatic organisms are adapted to certain temperature range. It exerts an important effect on metal speciation because most chemical reaction rates are highly sensitive to temperature change **(Prosi, 1989)**. Due to increased temperature may affect both uptake and elimination rates of metals, so net bioaccumulation may or may not increase.

The pH has an impact on solubility and bioavailability of metals in the natural water. The lower the pH indicates the higher the solubility of heavy metals, and thus increase in metal bioavailability **(Waite *et al.*, 1984)**. In this study, the Lake Ziway water was found to be slightly alkaline where pH varied from 7.59 to 9.60. The alkalinity of natural water is controlled by the concentration of hydroxide and represented by a pH greater than 7. This is usually an indication of the amount of carbonates, and bicarbonates that shift the equilibrium producing $[OH^-]$. This is happening due to the amount Carbon dioxide in water will be converted into H_2CO_3 which acidify the water to a pH of about 6. If any alkaline earth metals (sodium, calcium and magnisum, etc) are present, the carbonate and bicarbonate formed from solublisation of CO_2 will interact with alkaline earth metals increasing the alkalinity shift the pH up over 7. Other contributors to an alkaline pH include boron, phosphorous, nitrogen containing compounds and potassium **(Bellingham, 2008)**. Hence this pH values support the bioavailability of most dissolved heavy metals in Lake Ziway.

Electrical conductivity (EC) is the ability of a material to carry electrical current. In water, it is generally used as a measure of the mineral or other ionic concentration. **Michaud (1991)** defined EC as the total amount of dissolved ions in the water and is used to estimate the amount of total dissolved salts in water. Only ionizable materials contribute to conductivity. The conductivity levels of Lake Ziway ranged from 867.67 to 1245.12µs/cm which is much greater than the WHO Limit of drinking water (Table 2).

Total dissolved solid (TDS) and suspended solid (SS) are indicators for general water quality as they directly affect the aesthetic value of water by increasing turbidity. Solid suspended matter in water bodies has high surface area than the bulk sediment as a result increases the availability of toxic metals **(Ramesser and Ramjeawon, 2002)**. The density of water depends on the total dissolved solids that occur in natural water containing a complex mixture of cations and anions. TDS is an important indicator of the suitability of water for drinking, recreational, irrigation and industrial use. Total Dissolved solid (TDS) includes those materials dissolved in the water, such as, bicarbonate, sulphate, phosphate, nitrate, calcium, magnesium, sodium, organic ions, and other ions. These ions are important in sustaining aquatic life. However, high concentrations can result in damage to organism's cell **(Mitchell and Stapp, 1992)**. The range of TDS in Lake Ziway in this study ranged from 520.60 to 756.10 mg/L. The TDS values of the lake were below the WHO limit for drinking water Suspended solid (SS) can come from silt, decaying plant and animals, industrial wastes, sewage, etc. They have particular relevance for aquatic organisms that are dependent on solar radiation and those whose life forms are sensitive to deposition. High concentrations have several negative effects, such as decreasing the amount of light that can penetrate the water, thereby slowing photosynthetic processes which in turn can lower the production of dissolved oxygen; high absorption of heat from sunlight, thus increasing the temperature which can result to lower oxygen level; low visibility which will affect the fish' ability to hunt for food; clog fish' gills; prevent development of egg and larva. It can also be an indicator of higher concentration of bacteria, nutrients and pollutants in the water **(Tarazona and Munoz, 1995)**.

3.2 Analysis of heavy metals in water samples from Lake Ziway

The concentrations of heavy metals in water samples from Lake Ziway (Table 3) at site 1 (close to floriculture industry) presented significantly the highest amount of all the tested metals including Cd (2.71mg/L), Cu (4.88mg/L), Ni (8.10mg/L), Pb (6.06mg/L) and Zn (12.12mg/L). All the three sites have recorded higher load of the heavy metals above the **FAO/WHO (1989)** recommended levels with the exceptions of Zn and Cu at Site 3. Significance differences in the heavy metals load were observed among the three sites that might be due to the distance among the sample sites or the huge continuous discharge of toxic wastes from floriculture industries. Similar study was conducted by **Washe et al. (2018)** who reported that Concentration of metals in Lake ziway were 0.01±0.001, 0.06±0.001, 0.012±0.12, 0.117±0.02, and 0.05±0.01mg/L for Ni, Cr, Cu, Zn and Co respectively. Pb and Cd were below the limit of detection. Seasonal variations and flooding water subsequently lead to pollutant dilution. Even though heavy metal contents in water and sediments are below the acceptable levels, a hazardous possibility may generate depending on rapid expansion **(Kebede et al., 2012)**.

Heavy metals in water can be partitioned into dissolved and suspended fraction. It is well known that most dissolved heavy metals are present as organic complexes in natural **water (Prego and Cobelo-Garcia, 2003)**. A fraction of metals is bound to organic matters and particulate in water, which reduced the amount of metals for uptake by organism and the ability of metals to affect organism. It is known that bioavailability or toxicity of metals is directly corrected to concentration of free metals ions, which are not bounded to any matter, rather than to total concentrations **(Campbell, 1995; ATSDR, 2006)**.

Chapman (1992) stated more than 50% of the total metals present (and up to 99.9%) in water are usually adsorbed onto suspended particles. The solubility of heavy metals is predominately controlled by the water pH **(Osmond *et al.,* 1995)**, water temperature **(Iwashita and Shimamura, 2003; Papafilippaki *et al.,* 2008)** and the redox environment of the lake water **(Osmond *et al.,* 1995; Iwashita and Shimamura, 2003; Papafilippaki *et al.*, 2008)**. The behavior of metals in surface water is a function of the substrate sediment composition, the suspended solid composition and the water chemistry **(Osmond *et al.,* 1995)**.

The water chemistry of the system controls the rate of adsorption and desorbtion of metals to and from sediment. Adsorption removes the metal from the water and stores the metal in the sediment and suspended solid. Desorption returns the metal to the water column, where recirculation and bioassimilation may take place. Metals may be desorbed from the sediment and suspended solid if the water experiences increases in salinity, decreases in redox potential, or decreases in pH. A lower pH increases the competition between metals and hydrogen ions for binding sites. A decrease in pH may also dissolved metals-carbonate complexes, releasing metals ions into the water column **(Osmond *et al.,* 1995)**. A decreased redox potential, as it is often seen under oxygen deficient conditions, will change the composition of metal complexes and release the metals into the overlying water **(Osmond *et al.,* 1995)**.

Even though there are significant discharges from surrounding industrial wastes into Lake Ziway, the concentration of suspended solid (SS) in the present were ranged from 12.67 mg/L to 24.50 mg/L. These concentrations of SS were enough to make the metals unavailable for an organism. This might be due to most metals being absorbed into suspended particulate matter. Several mechanisms indicated that heavy metals in water are removed due to (1) adsorption onto particulate; (2) chemical transformation in to insoluble form; and (3) precipitation and sedimentation **(Balasubramania *et al.,* 1997)**.

Table 2 Mean Physicochemical properties of water samples from Lake Ziway

Lake sites	Temperature (°C)	pH	EC (μS/cm)	TDS (mg/L)	SS (mg/L)
Site1	29.4±0.25a	9.60±0.52a	1245.12±5.34a	756.10±1.50a	24.5±0.15a
Site2	30.1±0.67a	8.36±0.20a	962.13±4.56b	577.28±2.45b	16.87±0.90b
Site3	28.7±1.2a	7.59±0.85a	867.67±3.45b	520.60±4.21b	12.67±0.24c
WHO (1993)	Nf	NF	250	500mg/L	25 mg/L (Rossi et al., 2006)

Means followed by the same letter within a column were not significantly different at 0.05 probability level based on Least Significance difference (LSD) test. Small letters: significance within a column. NF: not found.

Table 3 Heavy metal concentrations (mg/L) of water sample sites in Lake Ziway

Sites	Heavy metal concentrations (mg/L)				
	Cd	Cu	Ni	Pb	Zn
site1	2.71±0.05a	4.88±0.65a	8.10±0.16a	6.04±0.75a	12.12±0.22a
site2	2.19±0.25b	2.86±0.18b	4.25±0.15b	4.60±0.30b	8.37±0.67b
site3	1.80±0.12b	1.89±0.90c	0.15±0.20c	0.07±0.05c	1.42±0.15c
FAO/WHO(1989)	0.003	2	0.07	0.01	3

Means followed by the same letter within a column were not significantly different at 0.05 probability level based on Least Significance difference (LSD) test. Small letters: significance within a column.

Table 4 Heavy metal loads in Nile tilapia and Curican carp edible muscle samples from Lake Ziway

Lake site	Fish species	Heavy metals accumulated in fish muscle (mg/kg)				
		Zn	Cd	Ni	Pb	Cu
Site 1	Nile tilapia	100.37±0.81a	6.05±0.06a	4.70±0.07a	5.76±0.14a	47.54±0.87a
	Crucian carp	88.12±0.25b	4.55±0.40b	4.58±0.01a	4.81±0.03b	37.34±0.45b
Site 2	Nile tilapia	27.11±0.20c	4.13±0.18b	2.94±0.18b	3.34±0.24c	14.03±0.76c
	Crucian carp	14.42±0.01d	2.71±0.15c	2.06±0.19c	2.33±0.02d	9.43±0.02d
Site 3	Nile tilapia	10.71±0.12d	1.63±0.00d	1.90±0.00c	0.100±0.00e	8.63±0.36d
	Crucian carp	6.09±0.56d	1.63±0.00d	1.90±0.00c	0.100±0.00e	7.00±0.98d
FAO/WHO		75	2	0.4	2	30

Means followed by the same letter within a column were not significantly different at 0.05 probability level based on Least Significance difference (LSD) test. Small letters: significance within a column.

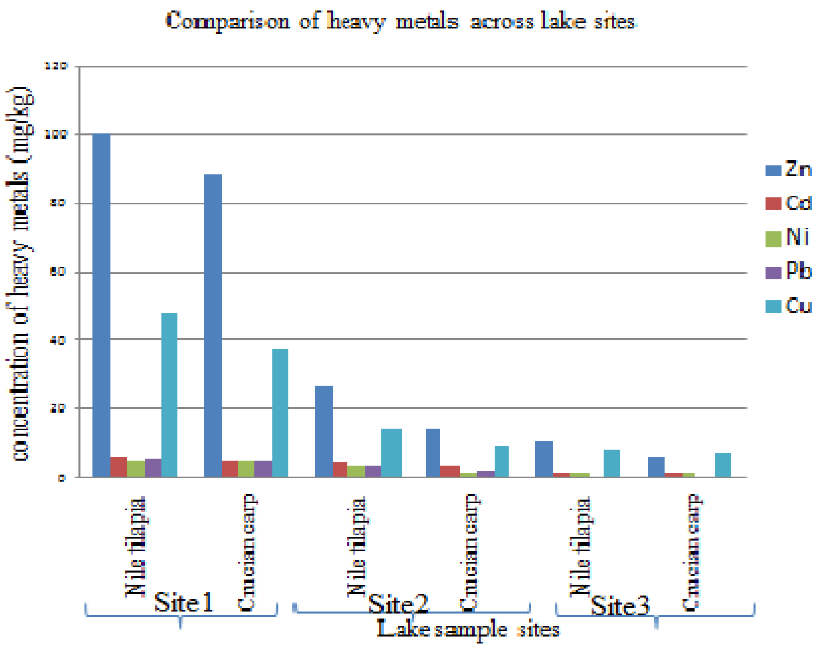

Figure 2 Comparison of heavy metal accumulation in fish muscles across sites

3.3 Determination of heavy metal load in fish muscles

The accumulation of heavy metals in two fish species including Nile tilapia locally called 'koroso' and Curican carp locally named as 'dabe ' (Table 4) demonstrated significance differences in the load of heavy metals between both species with Nile tilapia loaded significantly higher than Crucian carp in most of the metals assessed. Significantly the highest load of metal accumulations in fish muscles were observed at site 1 (near floriculture industry) in Nile tilapia with load of Zn(100.37), Cd (6.05), Ni(4.70), Pb (5.76) and Cu (47.54)mg/L with all loads being above WHO recommended levels as in Table 3. Similar study was conducted by **Zenebe (2011)** who reported the mean accumulations of Cu and Zn in the edible muscle of Nile Tilapia collected from Lake Hawassa ranged from 2.62- 3.52 µg/g and 25.38 – 29.93 µg/g dry weight, respectively. The levels of Cu and Zn in the muscle were not significantly different (P = 0.612 for Cu and P = 0.683 for Zn) among the three sampling sites of Lake Hawassa.

Fish are important aquatic organism that are used as bio-indicators of aquatic ecosystems for estimation of heavy metal pollution and risk potential for human consumption **(Agarwal *et al.,* 2007)**. Bioaccumulation of metals in fishes takes place directly, from the water by gills and indirectly from food **(Barron, 1990)**. Bioaccumulation of metal by an organism is the consequences of the interactions between physiological factor (growth, weight loss, absorption and accumulation), chemical factors (metal concentration, speciation and bioavailability) and environmental factors (temperature, pH, water hardness, conductivity, salinity and food concentration **(Casas and Bacher, 2006)**.

Copper and zinc are essential elements and are regulated by physiological mechanisms in most organisms. However, they show toxic effects when organisms are exposed to levels higher than normally required **(Biney *et al.*, 1994)**. Nickel is also an essential micronutrient required to red blood cells. It is known to be toxic at high intakes. The long term exposure can cause decrease in body weight, heart and liver damage and skin irritation. The toxicity of Ni to aquatic life has been shown to vary significantly with organism species, pH and water hardness **(Birge and Black, 1980)**.

The comparison of heavy metal accumulation across lake sites (Fig. 2) in fish muscle samples indicated that the highest accumulations were obtained for Cu and Zn; small amounts of Cd, Ni & Pb.

4. Conclusion

Even though there are significant discharges from surrounding industrial wastes into Lake Ziway, the concentration of suspended solid (SS) in the present were ranged from 12.67 mg/L to 24.50 mg/L. These concentrations of SS were enough to make the metals unavailable for an organism. This might be due to most metals being absorbed into suspended particulate matter. Due to bio-accumulation and bio-magnification of these metals in the body of the fish, the concentration of fish samples was higher than that of the water concentration. There is a need for continuous monitoring of the heavy metal concentrations in Lake Hayq, since the lake are serving as place of tourism and source of water for irrigation and fish for the local inhabitants.

Conflict of Interest

The authors report no conflicts of interest. The authors are responsible for the content of the paper.

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