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Analysis of Selected Metals in Edible Fish and Bottom Sediment from Lake Hawassa, Ethiopia

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ABSTRACT

Sediment and fish (nile Tilapia, *Oreochromis niloticus*) were collected from six sites of Lake Hawassa namely; Tikur Wuha, Amora Gedel, Dorie Bafana, Central part of the lake, the opposite side of Amora Gedel and Referral Hospital sites. Concentration of heavy metals was analyzed quantitatively using Flame Atomic Absorption Spectrophotometer and Chemometric methods. The maximum and minimum mean levels (mg/kg dry mass) in different lake sediment sites were Cu (51.38-17.64), Mn (348.51-140.63), Cd (12.8764-403), Pb (30.05-6.72), Ni (26.73-8.43), Zn (367.84-147.49), Cr (14.15-5.34), Co (27.19-9.59), Mg (3859.86-1872.43), Na (4913.72-2903.043), Ca (5526.74 - 3608.71), K (4229.69-2255.57) and that of fish muscle were Cu (13.833-5.666), Mn (11.972-9.722), Zn (21.110-12.055), Ca (574-482), Mg (512-437), Na (771-681), K (903-785). The result shows that the metal concentration in sediment samples is in order of Ca > Na > K > Mg > Zn > Mn > Cu > Pb > Co > Ni > Cr > Cd. The detectable metals in Tilapia fish muscle were in order of K > Na > Ca > Mg > Zn > Mn > Cu. In all the samples, concentrations of metals in sediment samples were higher than those of fish samples.

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Introduction

The current concern with regards to environmental quality is focused on water because of its importance in maintaining the human health and health of the ecosystem. The pollution of surface water by trace metals is a worldwide problem and the situation is aggravated by the ability of these metals to accumulate in the sediments and food chain (fish and vegetables) [1]. Metals in aquatic environment may be of natural origin from rocks and soil or from human activities, e.g. industry, urban and agricultural discharge, mine runoff, solid waste disposal, and atmospheric deposition [2,3].Trace metal concentrations in aquatic ecosystems are usually monitored by measuring their concentrations in water, sediments and biota [4], which generally exist in low levels in water and attain considerable concentrations in sediments and biota. These trace metals including the essential and non-essential elements have a particular significance in ecotoxicology, since they are highly persistent and all have the potential to be toxic to living organisms.

The distribution of metals within sediments and their surrounding water is dynamic. Sediment solids can hold up more metal than an equivalent volume of water. The exact proportion of a chemical held by sediment relative to water is a function of a metal's chemistry as well as the chemistry of the sediment solid and the surrounding environment. Because of their large capacity to "hold" metals, sediments have been characterized as "sinks". Sediments can serve as temporary sinks from which some of the metal can enter ecological and human food webs through several routes, primarily through accumulation in benthic organisms. These organisms include those that fully or partially live in the sediments (e.g. tubificids, chironomids, and trichopteran larvae) or those that feed from the sediment bed. Some organisms obtain their chemical dose from both pelagic and benthic routes (e.g. lake white fish, walleye) but because of

Tele: E-mail addresses: nsbabusk@gmail.com high chemical concentrations in sediments, the benthic route can be the dominant route of uptake [5-7].

The Rift Valley Lakes of Ethiopia cover an area of 3,250 Km² representing 37 percent of 8,800 km² of the total area of inland waters. These lakes are very productive and contain indigenous populations of edible fish. These include Nile tilapia (Oreochromis niloticus), the African big barb (Labeobarbus intermedius) and the African sharp tooth catfish (Clarias gariepinus) [8, 9]. Lake Hawassa is located 275 Km south of Addis Ababa, capital of Ethiopia and Lake Hawassa is one of Ethiopian Rift Valley Lakes which is affected by industrial effluents and increasing anthropogenic influences in their catchments, making them ideal study sites. Previous studies on industrial effluents to the lake Hawassa revealed that heavy metals Cd, Hg, Cr, Pb and as are present [10]. This study analyzed the current concentrations of selected metals (K, Na, Mg, Ca, Zn, Mn, Pb, Co, Ni, Cd, Cu, and Cr) in edible fish (Nile Tilapia, Oreochromis niloticus) and sediment samples present in Lake Hawassa.

Materials and methods

Study area

Lake Hawassa is a medium sized lake in the Ethiopian rift valley, with a total drainage basin of 1250 km. The Lake has an area of 88 km², the mean depth is 11m and maximum depth is 22 m. The mean annual rainfall is around 1154 mm [11].The lake is located in the vicinity of the growing city Hawassa and most of the factories operating within the catchments of Lake has liquid discharges directly or indirectly. Additionally, wastewaters from urban areas, agricultural fields and referral hospital were released or washed up by runoff and reach the lake [11, 12]. Six sampling sites in the lake were selected by considering the relative sources of pollution. Each selected sampling site has been received different types of pollutants from different sources of pollution.



Figure 1. Map of Lake Hawassa with sampling sites after editing [13]

Sites were selected based on the dominant sources of pollution to the lake (see Fig.1). Site one (S1) is near the entry of the Tikur Wuha River. This is an area where the river inputs are high to the lake. Factories release their effluent into the river and then the river finally discharges their input into Lake Hawassa. Site two (S2) is a site close to the fish market, Amora Gedel. Site three (S3) is located on the side of a referral Hospital. This is an area where the lake is directly receiving the effluent of the Hospital as well as urban runoff. Site four (S4) is located after the local village that is found near to Lake Hawassa known as Dorie Bafana, commonly used for recreational purpose and it does not have point source of pollution but there may be nonpoint source of pollution from the agricultural land and soil of the area. Site five (S5) is located opposite side of Amora Gedel which is located near the lake Hawassa. Site six (S6) is located around the central part of the sampling point of the lake.

Sample collection and preparation

Sampling sites were chosen based on proximity to expected anthropogenic emission sources. Additional site away from potential emission sources were selected from the lake and thus, presumably less polluted were sampled (Fig. 1). Fish and sediment samples were taken at all sampling sites. The sampling took place in the month of May and June 2014.

Fish sampling and Transportation

Fish samples of Nile Tilapia (*Oreochromis niloticus*), seven to nine average-sized $(23.8\pm5.1\text{cm})$ were collected from Lake Hawassa at different sites (Fig.1). The muscle samples were removed from each fish using surgical blade, forceps and scissors. The muscle samples were quickly wrapped with aluminum foil and labeled with sample title, date, name of the studied area and ID number. After that the samples were quickly wrapped with plastic bags and placed into a deep freeze. The muscle samples were then digested for further analysis after one day of storage in a deep freeze.

Fish samples pre-Treatments

In order to obtain a representative sample, composites were prepared by taking the edible tissues of the fish samples at each sampling site. The fish samples were oven dried at 105 ⁰C until they reached a constant weight [13]. Each dried sample was then ground into a fine powder using porcelain mortar with pestle and analytical mill. Thereafter all powdered tissues were kept in desiccators prior to further chemical analysis.

Sediments Sampling and Transportation

According to Composite sampling technique [14], surface sediments were collected from the same sampling locations (Fig.1), a total of about 300 g of sediments were taken at several spots from the bottom of the lake 0-10 cm depth using Eckman dredge Grab Sampler. After the sediments were transferred to polyethylene plastic bags shortly the samples were stored frozen in icebox until they were transported to the laboratory.

Sediment Samples Pre-Treatments

For sediment sample preparation, each composite sample was, homogenized properly. Then, samples were dried in an oven at 90 °C for 3 days. A drying step is usually required because most concentrations of contaminants in sediments are reported on a dry-weight basis. After drying, the sediments were disaggregated and grounded in an agate mortar using a pestle and analytical mill then, sieved using a 0.5 mm sieve. The dried sediments were stored in pre-cleaned and dried plastic bags.

Instruments, Apparatus and Chemicals

Closed microwave digester (Buck Scientific, Model BMS 1: USA) was used for the digestion of fish and sediment samples. All the fish and sediment samples were weighed on a digital analytical balance (ADAM[®], Model AFP-110L, England) with 120 g loading capacity and \pm 0.0001 precision. Flame atomic absorption spectroscopy (Buck Scientific, Model 210VGP AAS, USA) equipped with deuterium background corrector and airacetylene flame atomizer was used for determination of the selected metals (Mg, K, Ca, Na, Cr, Co, Mn, Ni, Cu, Zn, Pb and Cd) in fish and sediment samples. Drying oven (Digit heat, J. P. Selecta, Spain) was used for drying the samples placed on porcelain crucibles.

Analytical reagents concentrated 68% HNO₃ (Spectrosol®, BDH, England), 37% HCl (Aldrich, A.C.S. Reagent, Germany) and 30% H_2O_2 (Spectrosol®, BDH, England) were used. A lanthanum solution was used in the determination of Ca and Mg during the analysis of fish, and sediment samples to avoid interference (for releasing calcium and magnesium from their phosphates or sulphates). Stock standard solutions (Buck Scientific purographics calibration standards, USA) containing 1000 mg/L of the metals Mg, K, Ca, Na, Cr, Mn, Ni, Cu, Zn, Pd, Co and Cd from which 10 mg/L of intermediate standard obtained were used for preparation of calibration standards of each metal.

Digestion of sediment and fish samples by microwave digester

For the digestion purpose each samples in triplicate of dried powdered samples (0.3 g for fish and 0.5 g for sediment in each case) were weighed and directly transferred in to DPA-60K Teflon digestion vessels followed by the addition of HNO₃ (6 mL) and H_2O_2 (2 mL) for fish sample and HNO₃ (2.5 mL) and HCl (7.5 mL) for sediment samples. Then the mixture was shaken carefully until the solid materials are dissolved. Then the vessels were placed in a fume-hood for 15 minutes for predigestion and placed inside the turntable of the microwave system and heated in the Microwave oven (BMS-1) with the optimized digestion programs as given in Table 1.

The digestion vessels were cooled to room temperature to avoid foaming and splashing. The digested cooled soil samples were forming precipitates, they were filtered with a whatman filter paper (110 mm) and were transferred to 25 mL volumetric flask and the volumes were filled with de-ionized water up to the mark with 1% lanthanum nitrate solution. The resulting clear, colorless solutions of fish were cooled to room temperature and transferred quantitatively to 25 mL volumetric flasks and to this final solution, 1% lanthanum nitrate solution was added and the solution was filled to the mark (25 mL) with deionized water. Each Fish and Sediment samples were digested in triplicate.

Instrument Operating Conditions and Calibration

In this study a total of twelve metals for each root sample were analyzed using flame atomic absorption spectrophotometer with external calibration curve after the parameters such as burner and lamp alignment, slit width and wavelength adjustment were optimized for maximum signal intensity of the instrument. For each metal, the respective hollow cathode lamp was inserted in to the atomic absorption spectrophotometer, and the solution was successively aspirated into the flame. Ten elements (Mg, Ca, Cr, Mn, Ni, Cu, Zn, Co, Cd and Pb) were analyzed by absorption mode of the instrument and two elements (K and Na) were analyzed by emission mode of the instrument. The reason for using emission mode is to avoid ionization interference. Three replicate determinations were carried out for each sample. The same analytical procedure was employed for the determination of elements in a total of ten digested blank solutions for fish and Sediment samples. The operating conditions of the instrument employed for each metal are shown in Table 2.

Calibration curves were prepared to determine the concentration of metals in fish and sediment sample solutions. For the instrument calibration an intermediate standard solutions containing 10 mg/L were prepared in 100 mL volumetric flask from the standard stock solutions (Buck Scientific purographics calibration standards, USA) that contained 1000 mg/L of each metal. Then the intermediate standards were diluted with distilled deionized water to obtain five working standards of each metal of interest for calibration purpose. A rinse blank (deionized water) was used to flush the uptake system to reduce memory interferences. Hence, the instrument was calibrated using five working standards. The correlation coefficients of the calibration curve for the entire metals were greater than or equal to 0.999 which assured the linearity of instrumental response for individual analytes.

Method Detection Limit (MDL)

Ten blank samples were digested and analyzed for both sediment and fish samples. Then the standard deviation of the ten blank samples (S_B) was calculated for each metal. Finally, the detection limits were obtained by three times of the standard deviation of the reagent blank ($3S_B$). As shown in Table 3.

Method validation

The efficiency of the optimized procedure was checked by adding known concentration of each metal in 0.3 g of fish muscle and 0.5 g of sediment sample. For spiking of fish samples, 0.05 mg/L of Zn, Cu and Mn were spiked at once in to microwave digestion vessels that containing 0.3 g fish sample. 0.03 mg/L of Ni, Cr, Co, Pb and Cd were spiked at once in another microwave digestion vessels containing the same amount of fish sample and 4.0 mg/L of Ca, Mg ,Na and K were spiked at once in the another microwave digestion vessels containing same amount of fish sample. The spiked samples were digested in the same manner and with the same reagents as described above for fish samples.

For spiking of sediment samples, 0.1 mg/L of Cu, Ni, Zn and Mn were spiked at once in to microwave digestion vessels that contain 0.5 g soil sample. 0.05 mg/L of Cd, Co, Cr and Pb were spiked at once in other microwave digestion vessels containing same amount of soil sample and 15.0 mg/L of K, Ca, Na and Mg were spiked at once in the other microwave digestion vessels containing same sample and were digested in the same manner and same reagents as described above for sediment samples. Each recovery test for both fish and sediment samples were performed in triplicates. Each sample was determined for their respective spiked metals by flame atomic absorption spectrophotometer.

Recovery of metals

The validity of the analytical procedures used for sample analysis was tested by spiking experiment and calculating the recovery percent. The performance of the optimized methods was evaluated employing spiking experiments in which the concentration of the analyte is already known. The recoveries of metals in the spiked samples were obtained between 86.6% to 106.3% (muscle) and 86.0% to 107.8% (sediment). It indicates that good recoveries were obtained for the metals. Thus, the developed digestion procedures were considered reliable and were applied for the determination of selected metals in digests of muscle and sediment. All the spiked samples were digested in triplicate following the optimal digestion procedure developed for fish and sediment samples. The digested spiked samples were analyzed for their respective metals content using FAAS. Statistical analyzed

Statistical analysis

The results of different fish and sediments in six sampling site of the Hawassa Lake studied was done by using chemometric method such as Hierarchical cluster analysis (HCA) built in the statistical package Ky-plot software with bivariate comparisons. P value below 0.05 was considered as statistically significant.

Result and discussion

Results of metal concentration in hawassa lake sediment

Mean values of the trace metals detected in sediments are illustrated in Table 4. The maximum average Cu concentration (51.38±1.942 mg/Kg) was recorded at S₁ followed by S6 (38.61±0.581 mg/Kg). The minimum concentration (17.64±0.775 mg/Kg) was recorded at S5. The highest mean concentration of Mn was 348.51±3.096 mg/kg at S1and the lowest mean concentration 140.63±8.210 mg/Kg was measured at S5.The mean concentration of Cd (12.876±1.230 mg/Kg), Pb (30.05±1.068 mg/Kg), Ni (26.73±0.396 mg/Kg), Zn (367.84 ±14.28 mg/Kg), Cr (14.15±0.438 mg/Kg) and Co (27.19±2.892 mg/Kg) recorded in the lake sediment sample collected at S1 were the highest while the lowest mean concentration Cd (4.403±0.402 mg/Kg), Cr (5.34±0.427 mg/Kg), Co (9.59±2.804 mg/Kg) Pb (6.72±0.095 mg/Kg), Ni (8.43±1.065 mg/Kg), Zn (147.49±10.16 mg/Kg), and were recorded in sample obtained at S4 and S5 respectively. The mean concentration of Mg (3859.86±12.934 mg/Kg), Na (4913.72±80.733 mg/Kg), Ca (5526.74±14.515 mg/Kg), and K (4229.69±51.368 mg/Kg) recorded in the lake sediment sample collected at S1 were the highest while the lowest mean concentration Mg (1872.43±129.614 mg/Kg), Na (2903.043±62.864 mg/Kg), Ca (3608.71±16.546 mg/Kg) and K (2255.57±103.875 mg/Kg) were recorded in sample obtained at \$5,\$5,\$5 and \$4 respectively.

Results of Metals in Tilapia fish muscle

The results of the accumulation of metals in Tilapia fish muscle parameters are presented in Table 5. The maximum average concentration of Cu was recorded at S2 (13.833±0.380 mg/Kg) followed by S3 (13.194±0.628 mg/Kg). The lowest concentration of Cu was recorded at S6 (5.666±0.183 mg/Kg). The mean concentration of Mn (11.972±0.499 mg/Kg) recorded in the fish sample collected at S1 was the highest while the lowest mean concentration (9.722±0.548 mg/Kg) was recorded in sample obtained at S5. The maximum average Zn concentration (21.110±0.603 mg/Kg) was recorded at S1 followed by S3 (16.360±0.595 mg/Kg). The minimum concentration (12.055±0.715 mg/Kg) was recorded at S4.The concentrations of Pb, Cd, Ni, Cr and Co were below the detection limit at all sampling sites. The maximum average concentration of Ca was recorded at S1 (574±6.702 mg/Kg) followed by S3 (561±1.93 mg/Kg). The lowest concentration of Ca was recorded at S5 (482±0.593 mg/Kg). The highest mean concentration of Mg (512±4.081 mg/Kg), Na (771±6.180 mg/Kg) and K (903±12.025 mg/Kg) were recorded in the fish sample collected at S3, S2and S6 respectively whereas the

lowest mean concentration Mg (437 ± 3.190 mg/Kg), K (785 ± 10.635 mg/Kg) and Na (681 ± 7.503 mg/Kg) were recorded in sample obtained at S4 and S5 respectively.

The comparisons of metal concentrations in fish muscle from the present study with the previous studies of the same lake as well as other lakes were compiled in Table 6. The maximum mean accumulation of copper, manganese and zinc found by Ataro et al[8] in Tilapia species collected from the same lake of this study were 1.85 mg/Kg of copper, 4.46 mg/Kg of manganese and 2.700 mg/Kg of zinc and from Lake Ziway 1.98 mg/Kg of Cu, 2.49 mg/Kg of Mn and 30.92 mg/Kg of Zn. Gebrekidan et al.[15] found the mean accumulations of Cu, Mn and Zn in Nile Tilapia fish from Lake Hashenge. Tigrav were $0.85 \pm 0.15, 1.01 \pm 0.32$ and 24.95 ± 1.80 mg/Kg, respectively. The sources of pollution in Lake Hawassa were through Tikur Wuha, agricultural activities and runoff. The accumulations of Cu, Mn and Zn in Tilapia fish from Lake Hawassa, Hashenge and Ziway were lower than the FAO/WHO [15] recommended limit (Table 6). Their accumulations were also lower than the maximum result obtained in present study except Mn (Table 6). Mn is an essential element for both animals and plants. Deficiencies of Mn result in severe skeletal and reproductive abnormalities in mammals. It is widely distributed throughout the body with little variation [16].

The effect of Mn on fish is not known, no clear relationship exists between concentrations of manganese in water and fish tissue. Redox conditions condition within a lake could alter the bioaveleblity of manganese to the fish and also, tissue metal levels may be the result of indirect uptake from food or ingested sediments, rather than that obtained directly through concentrations of dissolved metals [17].

To the best of our knowledge, no other studies about K, Mg, Na and Ca in fish from Ethiopian Rift valley Lakes were carried out, so there is a lack of available data for comparison.

The mean concentrations of the metals in surface sediments of six sampling sits were compared with literature values (Table 7).

Generally, The level of metals in Lake sediments was observed to be moderate with the highest value occurring at S1, similarly it is shown on Dendrogram (Figure 2), indicating a localized effect of the nearby factories like Hawassa Textile, Tabor Ceramics and Sisal factory which release their effluent into the river and then the river ultimately joins Lake Hawassa [8].

Our result found at site S1 is comparable to earlier works done by Nigussie et al. [18] where the authors indicated that relatively high levels of metals near this site is attributed to its close proximity to the highway from Addis Ababa to Hawassa. Highest mean concentration of Cu in the sediment of the Lake Hawassa was 51.38±1.942 mg/Kg recorded at S1 (Table 4) whereas the minimum concentration $(17.64 \pm 0.775 \text{ mg/Kg})$ was recorded at S5. Our result showed highest mean concentration of Cu in sediments of Lake Hawassa compared to earlier works of Nigussie et al. [19] which reported 37.77 ± 0.61 mg/Kg and 26.91 ± 0.76 mg/Kg for S1and Island sediment, respectively. Gebrekidan et al. [16] shown a mean concentration of Cu (56.0 mg/Kg) sediment at Lake Hashenge, Tigray, Northern Highlands of Ethiopia which is higher than the value obtained in this study. The concentration level of Mn in the present study (348.51±3.096 mg/Kg at S1 to 140.63±8.210 mg/Kg at S5) was measured which is higher than that of Nigussie et al. [18] $(197.58 \pm 0.33 \text{ to } 136.40 \pm 2.15 \text{ mg/Kg})$ Gebrekidan *et al.* [16] reported that mean concentration of Mn, 71.0+1.41 mg/Kg which is lower than the present study. The major metal concentration in sediment samples analyzed is in order of Ca > Na > K > Mg. The highest concentrations of Mn, Zn and Cu could be of natural origin. These metals easily form complexes with organic compounds because of the high formation constants of organic metal complexes, which make them rather stable in the environment. In the case of zinc, it can associate with carbonate, mainly calcium carbonate, by forming the double salt of CaCO₃.ZnCO₃ in the sediment. On the other hand, cadmium and chromium are not found in organic fraction because of low adsorption constant and liable complexion with organic matter [8].

Chemometric methods

Hierarchical technique method (HCA)

Hierarchical technique in which the elements or objects are clustered to form new representative objects, with the process being repeated at different levels to produce a tree structure, the dendrogram. In cluster analysis, search for patterns in a data set by grouping the (multivariate) observations into clusters was done. The goal is to find an optimal grouping for which the observations or objects (sites) within each cluster are similar, but the clusters are dissimilar to each other. To group the observations into clusters, many techniques begin with similarities between all pairs of observations. In many cases the similarities are based on some measure of distance.

Figure 2 shows HCA analysis of the current study. The cluster analyses and the resulting dendrogram for the analysis of metal ions in sediments are shown (Figure 2).



Figure 2. Dendrogram developed for Ward's method applied to the different sediment parameter in six sampling site of the Hawassa Lake



Figure 3. Dendrogram developed for Ward's method applied to the different fish muscle parameter in six sampling site of the Hawassa Lake

| Table 1. The optimized dig | gestion conditions of 1 | nicrowave system for fisl | n and Sediment sample | es |
|----------------------------|-------------------------|---------------------------|-----------------------|----|
| | | | | _ |

| Fish | | | | Sediment | | | |
|-------------------------------|-------------------|-----|----|-------------------------------|-------------------|-----|----|
| Microwave digestion | Steps in settings | | | Microwave digestion | Steps in settings | | |
| programs | 1 | 2 | 3 | programs | 1 | 2 | 3 |
| Temperature (⁰ C) | 150 | 195 | 50 | Temperature (⁰ C) | 150 | 185 | 50 |
| Time (minutes) | 10 | 10 | 10 | Time (minutes) | 10 | 20 | 10 |
| Power (W) | 70 | 90 | 40 | Power (W) | 80 | 90 | 40 |

 Table 2. Instrumental operating conditions for determination of selected metals in fish and sediment sample using FAAS

 Parameters

| Elements | Wave length (nm) | Slit width (nm) | Lamp current (mA) | Energy (eV) | Instrumental detection limit (mg/L) |
|----------|------------------|-----------------|-------------------|-------------|-------------------------------------|
| Mg | 285.2 | 0.7 | 1.0 | 3.717 | 0.001 |
| K | 766.5 | 0.7 | 2.0 | | 0.010 |
| Na | 589.0 | 0.2 | 2.0 | | 0.005 |
| Ca | 422.7 | 0.7 | 2.0 | 3.912 | 0.010 |
| Cr | 357.9 | 0.7 | 2.0 | 2.712 | 0.040 |
| Ni | 341.5 | 0.2 | 7.0 | 2.624 | 0.020 |
| Cu | 324.7 | 0.7 | 1.5 | 3.938 | 0.005 |
| Zn | 213.9 | 0.7 | 2.0 | 3.237 | 0.005 |
| Mn | 279.5 | 0.7 | 3.0 | 3.913 | 0.030 |
| Pb | 283.2 | 0.7 | 2.0 | 2.874 | 0.040 |
| Cd | 228.9 | 0.7 | 2.0 | 3.214 | 0.010 |
| Со | 240.7 | 0.2 | 4.5 | 3.106 | 0.050 |

Table 3. Method detection limit (MDL) for metals of interest determined in fish muscle and sediment sample

| Metals | MDL for Fish muscle(mg/L) | MDL for sediment(mg/L) |
|--------|---------------------------|------------------------|
| Mg | 0.138 | 0.183 |
| Κ | 0.384 | 0.516 |
| Na | 0.147 | 0.163 |
| Ca | 0.116 | 0.136 |
| Cr | 0.053 | 0.065 |
| Mn | 0.070 | 0.073 |
| Ni | 0.058 | 0.071 |
| Cu | 0.047 | 0.053 |
| Zn | 0.064 | 0.078 |
| Pb | 0.066 | 0.079 |
| Cd | 0.021 | 0.022 |
| Co | 0.081 | 0.085 |

MDL = method detection limit

Table 4. Average value of two months and metal mean concentration (n=3, mg/Kg) in lake sediment samples

| Metals | Sampling Sites | | | | | | |
|--------|------------------|------------------|----------------|-----------------|----------------|----------------|--|
| | S1 | S2 | S 3 | S4 | S5 | S6 | |
| Cu | 51.38 ± 1.94 | 23.89±0.16 | 30.26±0.83 | 21.37±0.46 | 17.64±0.77 | 38.61±0.58 | |
| Mn | 348.51±3.09 | 190.04±4.21 | 261.09±0.83 | 205.45±3.25 | 140.63±8.21 | 235.25±9.61 | |
| Cd | 12.876±1.23 | 6.376±0.47 | 8.203±0.24 | 4.403±0.40 | 5.156±0.79 | 8.016±0.16 | |
| Pb | 30.05±1.06 | 11.43±0.38 | 17.33±0.75 | 8.116±0.676 | 6.72±0.09 | 21.44±1.37 | |
| Ni | 26.73±0.39 | 12.98±0.56 | 14.48±0.33 | 10.74±0.873 | 8.43±1.065 | 15.85±1.62 | |
| Zn | 367.84±14.28 | 173.34±9.09 | 219.89±21.35 | 160.09±8.61 | 147.49±10.16 | 258.79±17.84 | |
| Cr | 14.15 ± 0.43 | 7.37±0.89 | 9.23±1.23 | 5.34±0.42 | 5.65±0.62 | 5.98±0.44 | |
| Со | 27.19±2.89 | 10.88 ± 1.07 | 16.09±1.46 | 9.59 ± 2.80 | 11.90±1.68 | 14.266±0.60 | |
| Mg | 3859.86±12.93 | 2805.12±118.80 | 2903.77±82.04 | 2384.48±124.94 | 1872.43±29.61 | 3163.46±116.15 | |
| Na | 4913.72±80.73 | 3771.003±50.80 | 4410.51±97.39 | 3110.953±37.45 | 2903.043±62.80 | 3529.99±81.348 | |
| Ca | 5526.74±14.51 | 4958.55±152.36 | 4255.34±111.72 | 3893.55±56.64 | 3608.71±16.54 | 4175.22±71.96 | |
| K | 4229.69±51.36 | 3147.81±137.94 | 2546.04±100.92 | 2255.57±103.87 | 2613.78±47.39 | 3154.116±86.27 | |

Table 5. Average value of two months and metal mean concentration (n=3, mg/Kg dry weight) in Tilapia fish muscle

| samples | | | | | | | | |
|---------|-------------------|--------------|--------------|--------------|--------------|--------------|--|--|
| | Sampling Sites | | | | | | | |
| Metals | S1 | S2 | S 3 | S4 | S5 | S6 | | |
| Cu | 7.861 ± 0.176 | 13.833±0.380 | 13.194±0.628 | 7.027±0.383 | 6.278±0.407 | 5.666±0.183 | | |
| Mn | 11.972±0.499 | 9.861±0.026 | 11.305±0.725 | 10.777±1.740 | 9.722±0.548 | 10.277±0.362 | | |
| Cd | ND | ND | ND | ND | ND | ND | | |
| Pb | ND | ND | ND | ND | ND | ND | | |
| Ni | ND | ND | ND | ND | ND | ND | | |
| Zn | 21.110±0.603 | 15.361±1.07 | 16.360±0.595 | 12.055±0.715 | 13.805±1.406 | 12.749±0.630 | | |
| Cr | ND | ND | ND | ND | ND | ND | | |
| Со | ND | ND | ND | ND | ND | ND | | |
| Ca | 574±6.702 | 538±5.281 | 561±1.93 | 495±4.028 | 482±0.593 | 541±7.150 | | |
| Mg | 453±2.618 | 470±1.752 | 512±4.081 | 502±6.737 | 437±3.190 | 468±5.279 | | |
| Na | 768±8.720 | 771±6.180 | 709±4.924 | 741±10.026 | 681±7.503 | 725±6.892 | | |
| K | 859±5.361 | 825±2.830 | 864±9.693 | 815±3.106 | 785±10.635 | 903±12.025 | | |

ND = not detected

| Metals | Present study | Ataro et al. [8] | - | Gebrekidan et al. [15] | Permissible limits of FAO/WHO [16] |
|--------|---------------|------------------|------------|------------------------|------------------------------------|
| | Lake Hawassa | Lake Hawassa | Lake Ziway | Tigray, Lake Hashenge | |
| Cu | 13.833±0.380 | 1.85 | 2.78 | 0.85 ±0.15 | 30 |
| Mn | 11.972±0.499 | 4.46 | 2.49 | 1.01 ± 0.32 | 2-9 |
| Cd | ND | < 0.24 | < 0.24 | 0.58 ± 0.03 | 0.5 |
| Pb | ND | < 1.66 | < 1.66 | 1.24 ± 0.25 | 0.5 |
| Ni | ND | < 0.99 | < 0.99 | 0.41 ± 0.08 | 70-80 |
| Zn | 21.110±0.603 | 27.00 | 30.92 | 24.95 ± 1.80 | 40 |
| Cr | ND | | | 0.37 ± 0.14 | 0.15 |
| Co | ND | < 0.71 | < 0.71 | 1.61 ± 0.13 | 0.01 |
| Ca | 574±6.702 | | | | |
| Mg | 512±4.081 | | | | |
| Na | 771±6.180 | | | | |
| K | 903±12.025 | | | | |

Table 6. Comparison of level of metals in Nile Tilapia (O. niloticus) muscle of present study with other reported literature values and fishes dietary standards guidelines (mg/Kg dry weight)

ND = not detected; -- = not measured

Table 7. Comparison of level of metals in sediment of present study with other reported literature values (mg/Kg)

| Metals | Present study | Nigussie et al.[19] | | Gebrekidan <i>et al</i> . [16] |
|--------|-------------------------------------------|--------------------------------------------|----------------------------------------------|--------------------------------|
| | Lake Hawassa | Lake Hawassa | Lake Ziway | Tigray, Lake Hashenge |
| Cu | $17.64 \pm 0.775 - 51.38 \pm 1.942$ | $26.91 \pm 0.76 37.77 \pm 0.61$ | $33.98 \pm 0.78\text{-}78.49 \pm 0.60$ | 56.0±0.00 |
| Mn | 140.63±8.210-348.51±3.096 | $105.88 \pm 1.12 \text{-} 197.58 \pm 0.33$ | $170.79 \pm 1.11 117.38 \pm 0.90$ | 71.0±1.41 |
| Cd | $4.40 \pm 0.402 - 12.87 \pm 1.230$ | $3.19 \pm 0.09 \text{-} 9.18 \pm 0.09$ | $8.75 \pm 0.07 \text{ - } 10.51 \pm 0.13$ | 208.0±8.49 |
| Pb | $6.72 \pm 0.095 - 30.05 \pm 1.068$ | $8.49 \pm 0.89 \text{-}20.18 \pm 0.83$ | $8.55 \pm 0.56 \ \text{-}\ 20.18 \pm 0.83$ | 3.0 ± 0.00 |
| Ni | 8.43±1.065 -26.73±0.396 | $8.09 \pm 0.83 20.16 \pm 1.07$ | $15.17 \pm 0.62 24.00 \pm 1.05$ | 39423.5±773.87 |
| Zn | 147.49±10.16-367.84±14.28 | $107.48 \pm 0.33 \text{-} 130.82 \pm 0.24$ | $111.12 \pm 0.62 \text{ - } 173.82 \pm 0.39$ | 1129.0±5.66 |
| Cr | $5.34 \pm 0.427 - 14.15 \pm 0.438$ | $4.14 \pm 0.41 8.66 \pm 0.41$ | $4.67 \pm 0.50 7.52 \pm 0.30$ | 86.5±3.54 |
| Со | 9.59±2.804-27.19±2.892 | $13.39 \pm 1.13 - 37.72 \pm 1.34$ | 9.42 ± 0.70 - 31.11 ± 1.51 | 34.0±0.00 |
| Mg | $1872.43 \pm 29.614 - 3859.86 \pm 12.934$ | | | |
| Na | 2903.04±62.864-4913.72±80.733 | | | |
| Ca | 3608.71±16.546-5526.74±14.515 | | | |
| K | 2255.57±103.875-4229.69±51.368 | | | |

-- = not measured

The dendrogram showed that S4 and S5 are more similar and formed a pair. On the other hand, S3 and S6 also formed a separate pair based on similarities whereas S3 was more close to S3/S6 than S4/S5. S1 was far from the other sampling sites. Therefore, at S1 the pollution level higher than the other sites. Similarly Figure 3 shows the dendrogram developed for the analysis of metal ions in fish muscles six sampling sits which showed that S4 with S6 and S2 with S3 were more similar to each other than the other two sits (S1 and S5). Their pair was closer to S1 than S5. Therefore, the similarity may presumably show the movement of the fish in the lake.

Conclusion

Lake Hawassa is one of tourist attraction sites in the country for large number of national and international visitors. However, sufficient attention has not been given for the protection of water quality and biodiversity in and around the lake. The result showed that the metal concentration in sediment samples analyzed is in order of Ca > Na > K > Mg > Zn > Mn > Cu > Pb> Co > Ni > Cr > Cd. Metals analyzed in fish muscle samples from six sampling sites were found to be below the instrumental detection limit and hence are safe for human consumption. The undetectable concentrations of Cd, Pb, Ni, Co and Cr in fish muscle samples from the six sampling sites might be attributed to the detection limit of the FAAS. The measured value of the detectable metal concentration in Tilapia fish muscle samples analyzed is in order of K > Na > Ca > Mg > Zn > Mn > Cu. In all the samples, concentrations of metals in sediment samples were higher than those of fish samples. However, concentrations of metals in fish samples were below the safety limit. Generally, dendrogram figure shows that the high concentration of sediment parameters was observed at Tikur wuha site (S1). Acknowledgement

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