Study on the Bioaccumulation of Heavy Metals in Fish Samples and Physico-Chemical Analysis of Water from Lake Hawassa, Ethiopia

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Abstract

Samples were collected from Lake Hawassa, from six selected sampling sites. The measured physico-chemical parameters in lake water ranged pH(7.70-8.69), TDS(437-495 mg/L), EC(0.729-0.825 mS/cm), DO(6.2-14.6 mg/L), Temp.(20.7-23.4 ^{0}C), Turb.(6.3-26.7 NTU), SO_4^{2-}(25-16), Cl^-(42-23), F^-(17.4-5.36), NO_3-N (2.38-11.79), PO_4^{3-}(0.81-1.55), COD(219-1216), and BOD_5(104-590) mg/L. The concentration of detected metals in water samples were in the range Cu(0.226-0.117), Mn(0.166-0.068), Zn(0.253-0.145), Mg(35.91–14.27), Ca(57.11-35.23), Na(87.49-87.49) and K(73.02-34.26) in mg/L. According to stream and potable waters standard recommendation, the maximum value of BOD_5, COD, PO_4^{3-} and F^- were above the acceptable range. The detectable metal concentration in water samples analyzed were Na>Ca>K>Mg>Zn>Cu>Mn. The concentration of Mn in the present study was above USEPA but below WHO guideline. The dendrogram figure shows that metal parameter of water samples at S1 the pollution level is higher than the other sites. All the transfer factors of water were greater than 1 in fish muscle.

Keywords: Hierarchical cluster analysis, metal, physico-chemical, transfer factor.

1. Introduction

Metals enter the aquatic environment from a variety of sources, including those naturally occurring through biogeochemical cycles (Trujillo-Cárdenas et al. 2010) and those added through anthropogenic sources, namely from industrial and domestic effluents, urban, storm water runoff, landfill leachate, and atmospheric sources (Forstner and Wittman 1981).

Continuous exposure of heavy metals to animals and humans cause hepatotoxicity and nephrotoxicity. So, periodic estimation of level of heavy metals in water is necessary (Kerketta et al. 2013).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 aquatic plants).

Lake Hawassa is one of Ethiopian Rift Valley Lake which is affected by industrial effluents and increasing anthropogenic influences in their catchments, making them ideal study sites (Gebremariam and Pearce J. 2003).The Lake has an important role for many people in the region. It is the source of commercial fishery. It serves for recreation purpose. It is influenced by human activities such as agricultural practice, deforestation, industrialization and discharging of domestic sewages (Ataro et al. 2003; Kebede and Wondimu 2004). Tikur Wuha River is the only inflow river and it carries industrial effluent and agricultural runoff from the surroundings to the lake but there is no out flow river (Ataro et al. 2003).

The fast population growth, uncontrolled urbanization and industrialization, poor sanitary situation, uncontrolled solid and liquid waste disposal, etc. caused series quality degradation of the lake water in the city. Therefore, the results obtained from this study would also provide base line information on the levels of physico-chemical parameters and heavy metals in lake, contributing to the effective monitoring of both environmental quality and the health of the organisms inhabiting Lake Hawassa.

2. Materials and Methods

2.1 Study Area

Lake Hawassa is located 275 km south of the capital Addis Ababa, with a total drainage basin of 1250 km. The Lake has an area of 88 km^2, the mean depth is 11m and maximum depth is 22 m. The mean annual rainfall is around 1154 mm(Desta et al. 2006).The lake is located in the vicinity of the growing city Hawassa and most of the factories operating within the catchments of Lake have liquid discharges directly or indirectly. Moreover, waste waters from urban areas, agricultural fields and referral hospital were released or washed up by runoff and reach the lake (Desta et al. 2006; Haile et al. 2015). The selected Six sampling site receives different types of pollutants from different sources of pollution(Fig1).

Site one (S1) is near the entry of the Tikur Wuha River. This is an area where the river inputs to the lake are high. Factories release their effluent into the river and then the river finally discharges into the lake. Site two (S2) is a site close to the fish market, Amora Gedel. Site three (S3) is an area where the lake is 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 Bafano, commonly used for recreational purpose and it does not have point source of pollution but there may be nonpoint sources of pollution from the agricultural land and soil of the area. Site five (S5) is located opposite side of Amora Gedel. Site six (S6) sampling point is located around the central part of the sampling points. Water samples were taken at all sampling sites. The sampling took place in the month of May and June 2014.

2.2 Water Samples Pre-Treatments for metals

In the laboratory the contents of the bottle was treated for dissolved metals analysis according to the procedure (Clesceri et al. 1998). Finally all the samples were stored in a refrigerator at 4 ºC until analysis for maintaining the sample in a state that minimizes change in the time between collection and analysis.

2.3 Sample Preparation for physicochemical analysis

The samples were collected in one liter of polyethylene air-tight plastic and brown BOD bottles. Sample container preparation, storage and transport procedures followed the recommendations of Standard Methods for the Examination of Water and Wastewater manual (APHA 1998). Temperature of water samples were recorded on the sampling sites with Celsius thermometer.

2.4 Transfer factor

The transfer factor in fish muscle from the aquatic ecosystem, which includes water or sediments, was calculated as follows (Equation 1)(Abdel-Baki et al. 2011):

$$TF = \frac{Cmuscle}{Cse\dim ent / water} \quad (1)$$

Where: TF = Transfer Factor $[C_{Muscle}]$ = concentration of metal in fish muscle.
    $[C_{sediment\ or\ water}]$ = concentration of metal in sediment or water sample.

2.5 Measurement of water quality parameter

The pH of the sample was measured with a portable pH meter (Model HI9024, HANNA Instrument) calibrated with pH 4.0, 7.0 and 10.01 standard buffer solutions. Total dissolved solid (TDS) and conductivity were analyzed using portable digital conductivity meter (model 4200, Jenway, England instrument). It has been calibrated with 0.001 M KCl standard conductivity buffer solution to give a value of 14.7μS/m at 25ºC. Turbidity of sample was measured with portable turbidity meter (model 0839, cole-parmer) calibrated with 0.5, 10 and 20 NTU standards. Dissolved Oxygen (DO) was measured according to modified-winkler method. Biochemical Oxygen Demand (BOD) was analyzed using standard method (Delzer and McKenzie 2003).COD was determined using reactor digestion method. A photometric method was used for the determination of NH_3, NO_3^-, F^-, Cl^-, SO_4^{2-} and PO_4^{3-}. Water test tablets prescribed for Palintest® Photometer 5000 (Wagtech, Thatcham. Berkshire, UK) was used. FAAS (Buck Scientific, Model 210VGP AAS, USA) used for determination of the selected metals (Mg, K, Ca, Na, Cr, Co, Mn, Ni, Cu, Zn, Pb and Cd) in water samples.

2.6 Statistical analysis

Analysis of the results of different water samples in six sampling sites of the lake was done by using chemometric method namely Hierarchical cluster analysis(HCA) built in the statistical package Ky-plot version 2.0 software with bivariate comparisons. P value below 0.05 was considered as statistically significant.

3. Results and discussion

3.1 Concentrations of some metals in water samples

Table 1 shows the levels of some major and minor metals in water sample of the present study. These values were compared (Table 2) with reported literature values for previously measured value for Lake Hawassa and other lakes in the country (Gebrekidan et al. 2012; Nigussie et al. 2010) and with WHO (WHO 2008) and USEPA (USEPA 2008) fresh water quality guidelines for metals, mg/L.

Heavy metals in water can be partitioned into dissolved and suspended fraction. The concentrations of five metals in water samples from six sampling sites were found to be below the instrumental detection limit. The undetectable concentrations of Cd, Pb, Ni, Co and Cr in water samples from the sampling sites might be the result of adsorption and accumulation of metals by suspendered solid and due to the low detection limit of the FAAS. The concentration of the Cu in the present study are higher than the reported values by Nigussie et al.(Nigussie et al. 2010) on Lake Hawassa and Lake Ziway and Gebrekidan et al.(Gebrekidan et al. 2012) on Lake Hashenge. They are below standard value of WHO (WHO 2008) and USEPA (USEPA 2008) fresh water quality guidelines. The concentration of Mn in the present study are higher than literature value of Nigussie et al.(Nigussie et al. 2010)on Lake Hawassa and Lake Ziway and Gebrekidan et al.(Gebrekidan et al. 2012) on Lake Hashenge. In the

present study, the level of Mn was above USEPA but lower than WHO. The value of Zn is lower than the reported value of Nigussie *et al.*(Nigussie et al. 2010) on Lake Hawassa and Lake Ziway and Gebrekidan *et al.*(Gebrekidan et al. 2012) on Lake Hashenge. Also lower than USEPA/WHO (USEPA 2008; WHO 2008) water quality guidelines. Major ions are naturally very variable in surface and ground waters due to local geological, climatic and geographical conditions.

Table 2 shows the metal concentration in water samples analyzed is in order of increasing concentration as Na > Ca > K > Mg > Zn > Cu > Mn. The observed low concentrations of the metals in water could be attributed to dilution effects. Dilution masks the local concentration effects of the low and chronic exposure of the metals in the water(Nigussie et al. 2010). Calcium is subject to the influence of geochemical precipitation reactions that generates solid-phase mineral sink for these elements in aquatic ecosystem. Under condition of elevated pH and alkalinity, Ca may precipitate from the water column as $CaCO_3$(Chapman 1996).

3.2 Hierarchical technique

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.

The results of cluster analyses and the resulting dendrogram for the analysis of metal ions in waters are shown in Fig 2, S4 and S5 are more similar and formed a pair. On the other hand, S2 and S3 also formed a separate pair based on similarities whereas S6 more close to S4 / S5. S1 far from the other sites. Therefore, at S1 the pollution level is more than the other sites.

3.3 Transfer factor (TF)

We have measured the concentrations of metals in fish tissue and sediment of the same sites and the data for calculation of transfer factor was taken from our previous report (Haile et al. 2015). Because the samples were collected and analyzed at the same time.

The transfer factor in fish muscle from sediments and water are shown in Table 3. The results showed that transfer factor of all sediment sites was less than one and the transfer factors of water were greater than those of sediments. All the transfer factor of water was greater than 1 in muscle, while all of the sediments were less than 1 in muscle.TF greater than 1 indicates bioaccumulation of metals in fish soft tissue.

3.4 The physico-chemical characteristics of Lake Hawassa

Among analyzed physico-chemical water quality parameters we report those results that are above the recommended limits for drinking, for irrigation, recreational and other common uses were BOD_5, fluoride and PO_4^{3-}.

Table 4 is compared with the European Union (EU), Ethiopia, and Russia guidelines for the maintenance of fisheries and aquatic life and also compared with WHO, EU and USA guidelines for drinking water(Chapman 1996).

The range of fluoride in this study was 17.4 ± 0.39- 5.36 ± 0.38mg/L (Table 4) with an average value of 13.31 mg/L. Fluoride was also found to be above the recommended limit of fisheries, aquatic life and drinking water standards(Chapman 1996).The Rift Valley region of Ethiopia is characterized by higher level of Lake ground water fluoride. Out of 668 wells (deep and shallow) analyzed for fluoride level in the Rift Valley region of Ethiopia, 44.5% of the wells had values above 1.5 mg/L(Tekle-Haimanot et al. 2006). According to Chapman(Chapman 1996) very high concentrations of fluoride, far exceeding the WHO guideline value of 1.5 mg/L (Table 5), are encountered in volcanic aquifers and lakes in the East African Rift system.

The five day BOD is the most widely used parameter of organic pollution applied to surface waters. BOD_5 normally gives an indication of the amount of biodegradable organic matter (Chapman 1996). Site S5 had the lowest mean value of BOD_5 (104 ± 18.06 mg/L) and site S1 had the highest mean value (590 ± 12.05 mg/L) (Table 4) were also characterized with higher levels of BOD_5 concentrations due to discharge of organic effluents by industry. All the BOD_5 values were above the ambient standard of fisheries, aquatic life and also above WHO, EU and USA guidelines for drinking water standards (Chapman 1996).

Phosphate concentration ranged between 0.81 ± 0.05 mg/L(S5) and 1.55 ± 0.02mg/L (S2). The higher levels of phosphate recorded in impacted sites of S1 and S2(Table 4). Agricultural fertilizers normally contain phosphate minerals and arised from the breakdown of plant materials and animal wastes. The discharge of phosphate salts and detergents used for washing in the factory is a regular source of phosphate at the discharge point. phosphate concentrations were higher than 0.005mg /L(limit for stream waters) with rapid unwanted plant growth in rivers and lakes(Marquita 2010). In most natural surface waters, phosphorus ranges from 0.005 to 0.020 mg/L PO_4-P(Chapman 1996).

4. Conclusion

This study assessed the physico-chemical characteristics and level of heavy metal in water quality of Lake Hawassa

for multiple designated water uses like, irrigation, recreation and aquatic life.

The measured value of the detectable metal concentration in water samples analyzed is in order of Na>Ca>K>Mg>Zn>Cu>Mn. The concentrations of Mn in the present study above of USEPA but lower than WHO. All the transfer factor (TF) of water was greater than 1 in muscle. Transfer factor greater than 1 indicates bioaccumulation of metals in fish soft tissue.

Generally, the dendrogram figure shows that the high concentration of the selected and analyzed metals were observed at Tikur wuha site (S1) which might be attributed to its proximity to the highway, wastes of textile, Moha soft drink, BGI St. George Brewery, domestic and agricultural runoff.

Acknowledgement
Conflict of Interest: The authors declare that they have no conflict of interest.

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First A.

Ermias H.Mulugeta received his BSc degree (Chemistry) in 2008 and His MSc degree (Analytical Chemistry) in 2015 from Hawassa University, Hawassa, Ethiopia. He was engaged in the Analysis of Selected Metals in Edible Fish and Bottom Sediment from Lake. At present the main focus of his research was on the removal of contaminants from waste water using various biosorbents. Assessing liquid west characteristics and management practices. Determination of Dietary Toxins in Selected Wild Edible Plants: Breaking a Barrier to the Use as a Source of Food and Income. My research interest is quality test of environmental samples, method development and Natural Product Chemistry, medicinal plant extraction, fractionation, purification chemical and chromatographic test methods.

Second A.

Sisay T.Anshebo received his BSc degree (Chemistry) in 1990, His MSc degree (Analytical Chemistry) in 2000 and his Ph.D. degree (Physical Chemistry) in 2012, from Addis Ababa University, Addis Ababa, Ethiopia. Joining Chemistry Department, Hawassa Universityin 2012 he was engaged in the synthesis and characterization of inorganic nanomaterials, use of those materials for photovoltaics application and in the modification of electrochemical sensors for analysis of Environmental samples. In July, 2015 he was appointed as anAssociate Professor of Physical Chemistry. At present the main focus of his research was on the removal of contaminants from waste water using various biosorbents.
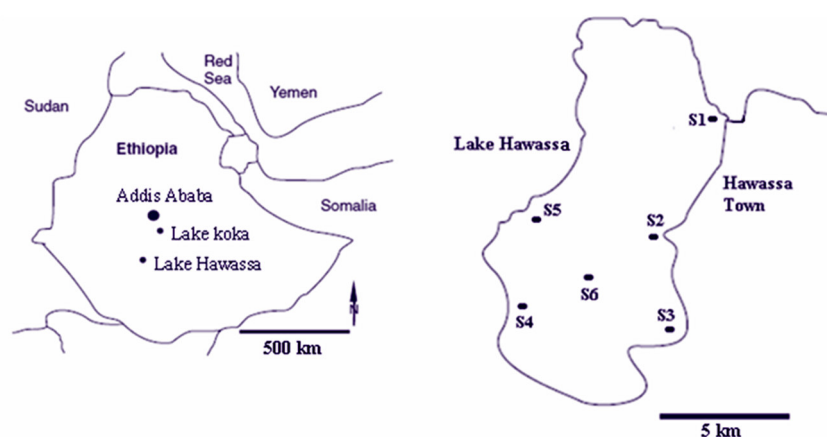

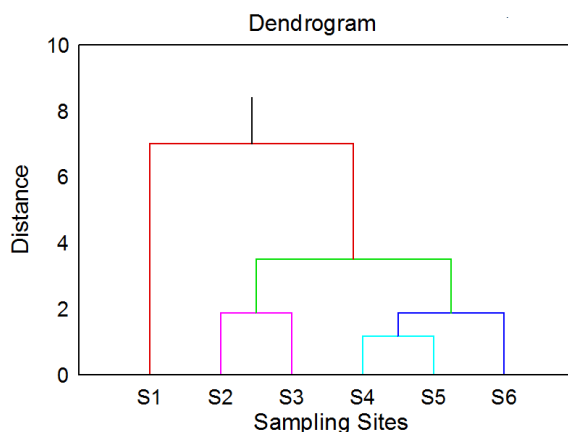Fig1: Lake Hawassa with sampling sites (Haile et al. 2015).

Fig.2: Dendrogram developed to the different water parameter in six sampling site.

Table 1: Average value of metal concentration (n=3,mg/L) in lake water samples of the six sites.

Metals	Sampling Sites
	S1	S2	S3	S4	S5	S6
Cu	0.226 ±0.019	0.1183±0.0025	0.158±0.003	0.129±0.001	0.117±0.002	0.123±0.0045
Mn	0.166±0.0046	0.094±0.002	0.136±0.003	0.068±0.001	0.075±0.002	0.084±0.003
Cd	ND	ND	ND	ND	ND	ND
Pb	ND	ND	ND	ND	ND	ND
Ni	ND	ND	ND	ND	ND	ND
Zn	0.253±0.0297	0.184±0.013	0.196±0.010	0.153±0.015	0.165±0.012	0.1446±0.010
Cr	ND	ND	ND	ND	ND	ND
Co	ND	ND	ND	ND	ND	ND
Mg	35.91±2.07	26.78±2.58	28.01±0.710	14.27±1.591	16.88±1.425	21.34±3.166
K	57.11±3.144	35.23±1.771	43.01±2.488	36.52±2.465	41.60±2.680	47.38±5.775
Na	87.49±5.179	75.26±3.360	70.83±4.654	58.07±5.454	62.84±2.115	59.40±7.426
Ca	73.02±4.915	51.89±4.483	44.48±3.835	41.43±3.073	50.90±5.512	34.26±4.222

ND = not detected

Table 2: Comparison of level of metals in water in the present study compared with other reported literature values (mg/L).

Metals	Present study Lake Hawassa	(Nigussie et al. 2010) Lake Hawassa	(Nigussie et al. 2010) Lake Ziway	(Gebrekidan et al. 2012) Lake Hashenge
Cu	0.117±0.002-0.226 ±0.019	0.03 ± 0.002-0.04± 0.002	0.03 ± 0.006-0.04 ± 0.002	0.0021±0.00007
Mn	0.068±0.001-0.166±0.004	< 0.01-0.02 ± 0.024	0.01 ± 0.001 in all	0.020 ± 0.00424
Cd	ND	< 0.005-0.007 ± 0.001	0.009 ± 0.001-0.01 ±0.001	0.0087 ±0.0032
Pb	ND	< 0.10-0.18 ± 0.01	0.11 ± 0.006-0.11 ± 0.013	0.0033 ±0.00071
Ni	ND	< 0.04-0.07 ± 0.006	< 0.04	0.0023 ± 0.0014
Zn	0.145±0.010-0.253±0.029	0.46 ±0.002-0.49 ± 0.002	0.46 ± 0.003-0.47 ± 0.001	0.9375 ± 0.0035
Cr	ND	0.05 ± 0.002-0.09± 0.004	0.06 ± 0.007-0.06 ± 0.002	0.0034 ±0.00049
Co	ND	< 0.05	< 0.05-0.064 ± 0.004	0.0035 ± 0.0007
Mg	14±1.09 -35±2.04	NM	NM	NM
K	35±1.09-57±3.81	NM	NM	NM
Na	58±5.20-87±6.30	NM	NM	NM
Ca	34±4.82- 73±4.27	NM	NM	NM

ND: not detected   NM: not measured

Table 3: Transfer factors (TF) of metals in fish muscle from sediment and water samples.

Metal	S1	S2	S3	S4	S5	S6
Cu	0.153[S]	0.436[S]	0.329[S]	0.356[S]	0.147[S]	0.153[S]
	34.783[W]	116.931[W]	83.506[W]	54.472[W]	53.658[W]	46.065[W]
Mn	0.034[S]	0.043[S]	0.052[S]	0.069[S]	0.043[S]	0.034[S]
	72.120[W]	104.904[W]	83.125[W]	158.485[W]	129.628[W]	122.345[W]
Zn	0.057[S]	0.074[S]	0.075[S]	0.094[S]	0.049[S]	0.057[S]
	83.438[W]	83.483[W]	83.469[W]	78.791[W]	83.667[W]	88.167[W]
Ca	0.149[S]	0.193[S]	0.208[S]	0.257[S]	0.171[S]	0.149[S]
	15.984[W]	20.089[W]	20.028[W]	34.688[W]	28.554[W]	25.351[W]
Mg	0.092[S]	0.116[S]	0.161[S]	0.151[S]	0.133[S]	0.092[S]
	7.932[W]	13.341[W]	11.904[W]	13.746[W]	10.505[W]	9.878[W]
Na	0.139[S]	0.167[S]	0.190[S]	0.189[S]	0.173[S]	0.139[S]
	8.778[W]	10.244[W]	10.009[W]	12.760[W]	10.837[W]	12.205[W]
K	0.203[S]	0.339[S]	0.361[S]	0.300[S]	0.286[S]	0.203[S]
	11.764[W]	15.899[W]	19.424[W]	19.671[W]	15.422[W]	26.357[W]

[S] Transfer factor values are for metals in fish muscle with respect to sediment.
[W] Transfer factor values are for metals in fish muscle with respect to water.

Table 4: Average value of some physico-chemical analysis results (Mean ± SD, n = 3) of Lake Hawassa at the six sampling sites.

Parameters	Sampling Sites					
	S1	S2	S3	S4	S5	S6
pH	8.69±0.23	7.91±0.14	8.11±0.51	7.70±0.09	7.79±0.20	7.81±0.47
TDS, mg/L	495 ±4.72	471±6.08	465±2.79	437±8.35	441±5.70	467±3.05
Cond. ms/cm	0.825±0.035	0.786±0.027	0.774±0.071	0.729±0.042	0.735±0.083	0.778±0.014
DO mg/L	6.2±0.44	8.4±1.75	10.7±0.91	12.1±1.60	14.6±0.73	9.3±0.58
Temp. ^{o}C	23.4±0.95	21.1±1.84	22.6±2.59	21.4±1.28	22.9±0.71	20.7±1.02
Turb. NTU	26.7±1.36	7.8±0.71	6.3±0.59	5.3±0.82	6.1±0.48	7.8±1.06
SO_4^{2-}, mg/L	25±2.15	18±1.74	22±2.08	20±1.62	16±0.83	19±0.69
Cl^-, mg/L	42±5.62	26±2.70	35±1.51	23±3.09	28±1.92	32±2.61
F^-,mg/L	5.36±0.38	13.5±0.91	17.4±0.39	15.6±0.20	12.7±0.14	15.3±0.75
NO_3-N, mg/L	2.38±0.31	9.85±0.76	11.79±1.82	7.62±1.09	4.31±0.63	7.20±0.80
PO_4^{3-},mg/L	1.40±0.06	1.55±0.02	1.15±0.04	1.30±0.01	0.81±0.05	1.35±0.02
COD, mg/L	1216±36.72	528±27.68	705±31.84	418±21.70	219±28.95	346±19.73
BOD_5,mg/L	590±12.05	126±31.85	419±40.26	220±24.21	104±18.06	137±23.80

ND: not detected