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Research Article

Determination of Some Heavy Metals in Nile Tilapia (*Oreochromis niloticus*) Fish Species in the Water of Lake Hawassa: A Review

Wakessa Miheretu Bedassa*

Ethiopian Institute of Agricultural Research (EIAR), Holeta Agricultural Research Center (HARC), Natural Resource Management Process, Ethiopia

ABSTRACT

Heavy metals are of much environmental concern currently. The metals are brought into contact with the organs and tissues of the fish and consequently accumulated to a different extent in different organs and tissues of the fish. These metals are dangerous as they tend to bioaccumulate in the food chain and they can be harmful to human and animals. Nitric acid, HNO_3 (69%), and hydrogen peroxide, H_2O_2 (30%), were used for digestion. Concentration of Cu, Pb, Ni and Zn were determined in 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.

Keywords: Heavy metals; Fish; Water; Furnace atomic absorption spectrometry; Flame atomic absorption spectrometry

INTRODUCTION

Water pollution has become a global problem. Contamination of aquatic ecosystems with Heavy Metal 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]. In the recent years, world consumption of fish has increased simultaneously with the growing concern of their nutritional and therapeutic benefits. In addition to its important source of protein, fish typically have rich contents of essential minerals, vitamins and unsaturated fatty acids [3]. The American Heart Association recommended eating fish at least twice per week in order to reach the daily intake of omega-3 fatty acids [4].

During the last decades the rapid economic development of Africa has led to an increase in environmental pollution [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].

Ethiopian Rift Valley Lakes which comprises of seven principal Lakes is an important area for commercial fisheries. The Lakes are also used for recreation, irrigation and industrial purposes [7]. Despite the growing influences from natural and anthropogenic origins, there exists a general belief that presumes absence of permanent alteration or contamination of these Lakes. However, rivers that flow into some of these Lakes are heavily loaded with contaminants of natural and anthropogenic origin such as discharges from factories and domestic sources [8].

Transport of metals in fish occurs through the blood where the ions are usually bound to proteins. The metals are brought into contact with the organs and tissues of the fish and consequently accumulated to a different extent in different organs and tissues of the fish. Most heavy metals released into the environment find their way into the aquatic environment as a result of direct input, atmospheric deposition and erosion due to rainwater, therefore aquatic animals 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 they enter the environment, bioconcentration occurs in the fish tissue in the case of aquatic environment, by means of metabolic and biosorption processes [9]. These heavy metals can cause dermatological

Correspondence to: Miheretu Bedassa, Ethiopian Institute of Agricultural Research (EIAR), Holeta Agricultural Research Center (HARC), Natural Resource Management Process, Ethiopia, Tel: +2510912076660; E-mail: miheretubedassa@gmail.com; miheretu2011@yahoo.com

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diseases, skin cancer and internal cancers (liver, kidney, lung and bladder), cardiovascular disease, diabetes, and anaemia, as well as reproductive, developmental, immunological and neurological affects in the human body [10].

Lake Hawassa is a fresh closed 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. These may make the Lake Hawassa to receive various kinds of pollutants enriched with heavy metals through different mechanism [11].

The objective of this seminar is to review the level of the concentrations of the heavy metals such as copper (Cu), lead (Pb), nickel (Ni), and zinc (Zn) in water and their accumulations in the edible tissue of the Tilapia fish (*Oreochromis niloticus*) in dry season of Lake Hawassa. Other water parameters like temperature, dissolved oxygen, pH, and conductivity, total dissolved solid and suspended solid of the lake water were also determined in this study.

LITERATURE REVIEW

Heavy metals in the environment

Heavy metals are present in the environment in different forms such as in solid phase and in solution, as free ions, or absorbed to solid colloidal particles. The heavy metal concentrations in the environment are due to natural and anthropogenic source [12]. Currently, anthropogenic inputs of metals are higher than the natural input and this may pose a great threat to aquatic life in particular, and to whole ecosystems in general [13].

In natural aquatic ecosystems, heavy metals occur in low concentration. In recent times, however, the occurrence of metal contaminants in excess of natural loads has become a problem of increasing concern. Heavy metals contamination of the aquatic environment may lead to deleterious effects from localized inputs which may be acutely or chronically toxic to aquatic life within the affected area [14].

Heavy metals are of much environmental concern currently. These metals are dangerous as they tend to bioaccumulate in the food chain and they can be harmful to human and animals. Metals can be retained for long period of time after entering the environmental medium such as soil (Table 1) [15,16]. Some of these elements are required by most living organisms in small amounts and they are also referred to as micronutrients. All metals, however, can be toxic to aquatic organism where present at high levels, causing direct effects such as histological damage or a reduction in survival, growth and reproduction of the species it influences [17].

Distribution of heavy metals in the aquatic environment

Once in the aquatic environment, heavy metals are partitioned among various aquatic environmental compartments (water, suspended solids, sediments and biota). The metals in the aquatic environment may occur in dissolved particulate and complex form. The majority of metal contaminants partition onto particulate matter such as clay minerals, Fe and Mn oxides/hydroxides, carbonates, organic substances (e.g., humic acids) and biological materials (e.g., algae and bacteria) [18].

The main process governing distribution and partition are dilution, advection, dispersion, sedimentation, and adsorption/desorption. Thus speciation under the various soluble forms is regulated by the instability constants of the various complexes and by physicochemical properties of water (pH, dissolved ions, redox and temperature). However, several mechanisms indicate that heavy metals in water may be removed due to (1) adsorption onto particulate; (2) chemical transformation into insoluble form; and (3) precipitation and sedimentation. Heavy metals are taken up by both fauna and flora of the aquatic environment. This uptake could provoke an increase in the concentration of metals in an organism; if the excretion phase is slow, this can lead to the bio-accumulation phenomenon. Some heavy metals have been shown to undergo bio-magnifications through the food chain [19].

Accumulation of heavy metals in Fish

Fish are used as bio-indicator of aquatic ecosystems for estimation of heavy metal pollution and potential risk for human consumption [20]. Bio accumulation of metals in fish takes place directly, from the water by gills and indirectly from food [21]. The metals such

Table 1: Major chemical species found in natural water (Ward, 1995).

Metals	Chemical Symbol	Chemical Species
Lithium	Li	Li^+
Aluminum	Al	$Al(H_2O)_6^{3+}$ $[Al(OH)_4]^-$
Chromium	Cr	$Cr(OH)_2$ $(H_2O)_4^+$, CrO_4^{2-}
Manganese	Mn	Mn^{2+}, $MnSO_4$, $MnCl^+$
Iron	Fe	$[Fe(OH)_2]^+$, $[Fe(OH)_4]^-$
Cobalt	Co	Co^{2+}
Nickel	Ni	Ni^{2+}
Copper	Cu	Cu^{2+}, $Cu(OH)^+$, $Cu^{2+}SO_4^{2+}$, $Cu^{2+}CO_3^{2-}$
Zinc	Zn	$Zn(OH)^+$, $Zn(OH)_2$, $ZnCl^+$, $ZnCl_2$, $ZnCO_3$, Zn^{2+}
Selenium	Se	Se (IV), Se (VI)
Molybdenum	Mo	MoO_4^{2-}
Cadmium	Cd	$CdCl^+$, $CdCl_2$, $CdCl_3^-$, Cd^{2+}
Cesium	Cs	Cs^+
Mercury	Hg	$HgCl_2$, $HgCl_3^-$, $HgCl_4^{2-}$, HgOHCl, $Hg(OH)_2$
Lead	Pb	Pb^{2+}, $PbCO_3$ $PbCl^+$, $PbCl_2$, $PbCl_3^-$, $Pb(OH)^+$, $Pb(OH)_2$, $Pb(OH)_3^-$, $Pb_3(OH)_4^{2+}$, $Pb(OH)_4^{4+}$

as copper, zinc, iron, and cobalt are essential and have important biochemical functions in the organism as opposed to non-essential metals like lead, cadmium, mercury, and arsenic. The excess amount of heavy metal in the organism can be regulated by homeostasis [22].

Bioavailability of metals

The toxicity of trace pollutants to aquatic organisms is related to the bioavailable fraction of contaminants available for assimilation. Bio-availability is defined as the fraction of the total amount of a chemical substance that can be taken up by living organisms within a certain time span [23].

Factors affecting metal bioavailability and bioaccessability include metal speciation and biotransformation, availability of complexing ligands (e.g., organic carbon, chloride, carbonate, sulfide, manganese and ferrous oxides), competition by other cations for membrane adsorption sites (e.g., calcium, magnesium), pH, redox, particle sorption, sediment and soil physicochemical properties and hydrology. pH affects both solubility of metal hydroxide minerals and adsorption-desorption processes. Most metal hydroxide minerals have very low solubility under pH conditions in natural water. Because hydroxide ion activity is directly related to pH, the solubility of metal hydroxide minerals increases with decreasing pH, and more dissolved metals become potentially available for incorporation in biological processes as pH decreases. Ionic metal species also are commonly the most toxic form to aquatic organisms [24].

Sources of heavy metals

Natural and anthropogenic sources of soil, water and air contaminations are widespread and variable. Heavy metals occur naturally in rocks. Mineral rock weathering and anthropogenic sources provide two of the main types of metal inputs to soil, water and air. In localized mineral zones or around volcanoes an elevated level of the elements arsenic, lead, cadmium, copper and zinc can also be found [25]. Cadmium is associated with sphalerite, and lead is found in many ores [26].

Anthropogenic activities, such as mining, industrial effluents, floriculture, application of fertilizer, pesticide, Bio solids, manures and sewage sludge application, are the main sources of heavy metal contamination in the environment [27]. This sources increases heavy metal concentrations in the soil, water and air and considered to pose possibly serious hazards in the soil-plant-animal system [28].

Copper

Sources, uses, and toxicity of Cu: Copper is one of the world's most widely used metals. The most common copper-bearing ores are sulfides, arsenates, chlorides, and carbonates [13]. It reaches aquatic systems through anthropogenic sources such as industry, mining, plating operations, usage of copper salts to control aquatic vegetation or influxes of copper containing fertilizers.

Although copper is important, it is toxic when concentrations exceed that of natural concentrations (<0.05 µmol/L) [29]. The toxicity of copper in aquatic organisms is largely attributable to Cu^{2+} that forms complexes with other ions. A reduction in water dissolved oxygen, hardness, temperature, pH, and chelating agents can increase the toxicity of copper [30].

Lead

Sources, uses, and toxicity of Pb: The major sources of lead in the environment are automobile exhaust, industrial wastewater, wastewater sludge and pesticides [31]. The global mean lead concentration in lakes and rivers is estimated to be between 1.0 µg/L to 10.0 µg/L. Lead is toxic and a major hazard to human and animals. Lead has two quite distinct toxic effects on human beings, physiological and neurological. In more severe situations neurological effects such as restlessness, hyperactivity, confusion and impairment of memory can result as well as coma and death [32].

Nickel

Sources, uses, and toxicity of Ni: Nickel is found in many ores as sulfides, arsenides, antimonide, silicates and oxides. Its average crustal concentration is about 75 mg/kg and in aquatic ecosystem, dissolved nickel concentrations are generally between 0.005 mg/L and 0.01 mg/L [33].

Nickel is an essential micro-nutrient required to produce red blood cells but it is known to be toxic at high intakes. The toxicity of Ni to aquatic life has been shown to vary significantly with organism species, pH and water hardness [34].

Zinc

Sources, uses, and toxicity of Zn: Major sources of zinc to aquatic environment include the discharge of domestic waste water, manufacturing processes involving metals and fallout atmosphere. Even though zinc is an essential trace element and help in homeostatically control in fish, but at high concentration of zinc can be toxic to fish [35].

Acute toxic zinc concentrations result in gill damage, which interferes with respiration, leading to hypoxia. Chronically toxic are generally extensive deterioration of liver, kidneys, heart, and muscle. Chronic sub-lethal zinc concentration can also delay or inhibit the growth sexual maturity and reproduction of the fish, and can also induce pathological and morphological abnormality in adult fish [36].

Biochemistry of toxicity

The poisoning effects of heavy metals are due to their interference with the normal body biochemistry in the normal metabolic processes. When ingested, in the acid medium of the stomach, they are converted to their stable oxidation states (Zn^{2+}, Pb^{2+}, Cd^{2+}, As^{2+}, As^{3+}, Hg^{2+}, Ag^{+}) and combine with the body's biomolecules such as proteins and enzymes to form strong and stable chemical bonds. The equations below show their reactions during bond formation with the sulphydryl groups (-SH) of cysteine and sulphur atoms of methionine ($-SCH_3$) [37].

MATERIALS AND METHODS

Description of study area

Lake Hawassa is a medium sized lake in the Ethiopian rift valley, with a total drainage basin of 1250 km [38]. The Lake has an area of 88 km^2, the mean depth is 11 m, and maximum depth is 22 m [39]. The mean annual rainfall is around 1154 mm, distributed throughout the eight rainy months; March to October and November to February is the dry season [39].

Collection of samples

Water samples and fish samples were collected from the three selected sites of the Lake Hawassa in December, 2010 and January, 2011 using purpose sampling techniques. Three replicate surface water samples were collected from three different points of the same station using 1L polyethylene sampling bottle during the sampling period. Bottled samples were taken to laboratory using an ice box at 4°C. Then, the three replicated samples for each site were composited for all analytical procedures conduct in the laboratory.

Three Tilapia fish species samples were caught and collected at each sampling site with the help of fishermen. After collection, the samples were immediately dissected in the field and only the edible tissue (fillet) was transferred to plastic bags and keeps in an ice box at 4°C and then transported to the laboratory.

Instrumentations and apparatus

All digestion works were carried out by using Heating Mantle (98-II-B Magnetic stirring electric sleeve). The fish samples were oven dried and grounded in mortar and pestle. The 250 mL round bottle flask was used for digestion purpose. PG-990 Atomic Absorption Spectrometer, were 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 were used for GFAAS and ASA-900 automatic sample was used for Flame Atomic Absorption Spectrophotometer (FAAS).

Reagents and standard solution

All the chemicals used were of analytical reagent grade. Deionized water was used for all dilutions throughout the study. Nitric acid, HNO_3 (69%), and hydrogen peroxide, H_2O_2 (30%), were used for digestion. Working standards were prepared by diluting concentrated stock solution of 1000 mg/L for Cu, Ni and Zn and 1000 µg/L for Cu, Pb and Ni in de-ionized water. The matrix modifier $NH_3H_2PO_4$ and $Mg(NO_3)_2$ were used for Graphite Atomic Absorption Spectrophometery (GFAAS).

Determination of physicochemical parameters

The following physico-chemical variables of water were determined *in situ* at the three sampling sites using the instruments indicated in parenthesis; temperature and dissolved oxygen (CO 411, ELMETRON), pH (Wagtech, pH meter), conductivity and total dissolved solid (Wagtech, EC/TDS). Suspended solid (SS) of the water was determined with Hack Spectrophotometer in the laboratory.

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.

Digestion of fish samples

The powdered fish samples were thoroughly homogenized before subjecting them to digestion and were digested using concentrated nitric acid and hydrogen peroxide (1:1) v/v according to FAO methods. 1 g of dried and powdered fish samples was weighted and transferred into 250 mL round bottled flask and the mixture of 10 mL of concentrated HNO_3 (65%) and 10 mL of H_2O_2 (30%) was added. The flask was 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. After that, the samples were allowed to cool, were filtered and diluted to 50 mL in volumetric flask with deionized water.

Analysis of heavy metals

Concentration of Cu, Pb, Ni and Zn were determined in 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. 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 analyzed in duplicates, and the blank determinations in duplicates were also run in the same manner during the analysis.

Recovery test

The digestion method and AAS analysis were validated by measuring the recovery of copper, lead, nickel and zinc spiked to fish samples. The known volume and concentration of standard solutions were employed on the samples in order to determine recovery. The volume of 50 µL for Cu, 1.5 mL for Pb, 1 mL for Ni and 50 µL for Zn was added to 1 g of powdered fish sample. The spiked samples were then digested in the same way as fish sample. The final volume of the digestion was diluted to 50 mL and run on AAS and metal contents determined from the calibration curve. The amount of spiked metals recovered after the digestion of spiked samples was used to calculate percentage recovery using the formula [40]:

$$\text{Percentage recovery} = \frac{\text{Con. spiked sample - Con. unspiked sample}}{\text{Con. spiked added}} \times 100$$

The recovery percentages of spiked fish sample and the results for metals under investigation (Cu, Ni, Pb and Zn) varied between 78.28% and 93.85%. The obtained results are in acceptable range which is mostly no less than 70% and no greater than 125% [41] and which revealed that the digestion method and the AAS analysis were reliable.

Calibration procedure

Calibration curves for each heavy metal were set to ensure the accuracy of the atomic absorption spectrophotometer and to confirm that the results of determination were true and reliable. The calibration of the PG-990 Atomic Absorption Spectrophotometer was made with standard solutions. Five working calibration standards were prepared by serial dilution of concentrated stock solution of 1000 mg/L for copper and zinc and nickel and 1000 μg/L for Cu, Pb and Ni. These solutions and blank were aspirated into AAS. A calibration curve of Absorbance Vs concentration was established for each metal and used for determination of metal concentration in the samples of fish and water.

Method Detection Limit (MDL)

Method detection limit (MDL) is defined as the minimum concentration of analytes that can be identified, measured and reported with 99% confidence that the analytes concentration is greater than zero, and is determined from analysis of a sample in a given matrix containing the analytes [42].

Method detection limit for fish samples was established using the blank reagent (mixture HNO_3 & H_2O_2) which was used to digest the fish sample. Seven replicate fish blanks were digested in the same condition as fish sample. The method detection limits for fish blanks (mixture of HNO_3 and H_2O_2 that used to digest the fish samples) were calculated according to formula: [43] (Table 2).

MDL= (S) × (t)

Where,

MDL= Method Detection Limit

S = Standard deviation of the seven replicate analysis

t = Student's value for 99% confidence level and standard deviation estimated with

n = 1 Degrees of freedom

The calculated values of MDL of the metals Cu, Pb, Ni and Zn are given in the Table 1.

Statistical analysis

Statistical analysis of data was 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 and physicochemical parameters between the three sampling sites.

RESULTS AND DISCUSSION

Physicochemical variables of water

The results of the physicochemical parameters are presented in Table 3. The minimum mean value of temperature was recorded at Tikur Wuha site (21.38°C) while the relatively maximum value was observed at Referral H. site (22.53°C). The maximum mean value of dissolved oxygen (DO) was measured at Dorie Basana site (8.43 mg/L) and minimum of 5.20 mg/L recorded at Referral H. site. The pH values of the lake water were slightly alkaline, with the lowest mean reading was recorded at Tikur Wuha site (8.64) while the relatively maximum value recorded at the Dorie Basana site (8.75) (Table 3).

The physical, chemical and biological contents of water determine the quality of water. Water quality guidelines like WHO, EU and USEPA [44] 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 (Table 4) [45].

Heavy metals concentration in water

The dissolved metal concentrations in Lake Hawassa water were measured at the three sampling sites (Tikur Wuha, Dorie Basana and Referral H) during the dry season of the area. The concentrations of dissolved zinc and nickel in Lake Hawassa were found to be below the instrumental detection limit (FAAS) in all sampling sites. But the copper concentrations ranged from undetected at Referral H. site to 0.005 mg/L at Dorie Basana and the lead concentrations also ranged from undetected at Dorie Basana and Referral H. sites to 0.003 mg/L at Tikur Wuha site. The concentrations of the metals in the three sampling sites of Lake Hawassa are presented in Table 5. When the dissolved metal concentrations in the lake water in the three sampling sites were compared with international standards, the obtained results obviously showed that the concentration of the heavy metals (Cu, Pb, Ni and Zn) in water did not exceed WHO [46], USEPA [44] and FAO [47] (Table 6).

Accumulation of metals in Tilapia fish

The FAO/WHO and EU limit of Pb in the fish muscle are 0.5 μg/g and 0.1 μg/g, respectively. The levels of Pb in the edible muscle of Tilapia fish from Gore Basana and Referral H. sites

Table 2: Method detection limit of fish samples analysis.

Metals	Method Detection Limit (μg/g)
Cu	1.27
Ni	0.29
Pb	1.95
Zn	1.55

Table 3: The mean (± SD) value of some physicochemical properties of Lake Hawassa water at the three sampling sites.

Physicochemical Parameters	Sampling Sites			P - value
	Tikur Wuha	Dorie Basana	Referral H.	
Temperature (°C)	21.38 ± 0.38	22.18 ± 0.62	22.53 ± 0.33	P=0.169
DO (mg/L)	6.80 ± 0.70	8.43 ± 0.68	5.20 ± 0.08	P=0.00
pH	8.64 ± 0.02	8.75 ± 0.02	8.73 ± 0.03	P=0.10
EC (μS/cm)	835.83 ± 6.03	820.50 ± 1.32	832.33 ± 0.57	P=0.00
TDS (mg/L)	501.17 ± 3.51	491.83 ± 0.76	499.00 ± 0.50	P=0.00
SS (mg/L)	17.67 ± 0.58	9.67 ± 0.58	14.67 ± 0.28	P=0.00

Table 4: Guideline values for some selected parameters.

Physicochemical properties	Fisheries and aquatic life		Drinking water		
	EU	USEPA	WHO	EU	USEPA
PH	6 – 9	6.5 – 9.0	6.5 - 9.5	6.5 – 8.5	6.5 – 8.5
EC (μS/cm)			250	250	
TDS (mg/L)			500		500
SS (mg/L)					

Table 5: Concentration of dissolved metals in Lake Hawassa water at the three sampling sites and Recommended Limit in water (in mg/L) by various organizations.

Metals	Sampling Sites					
	Tikur Wuha	Dorie Basana	Referral H.	WHO (1993)	USEPA (2006)	FAO (1985)
Cu	ND – 0.003	ND – 0.005	ND	0.2	1.5	0.2
Pb	ND- 0.003	ND	ND	0.05	0.05	
Ni	ND	ND	ND	0.02	0.1	0.2
Zn	ND	ND	ND	5	0.5	2

ND= Not Detected

Table 6: Comparison of heavy metals accumulation in Tilapia fish of Lake Hawassa with international standard (in μg/g).

Metals	Sampling Sites			
	Cu	Pb	Ni	Zn
Tikur Wuha	2.62	2.15	0.41	25.38
Dorie Basana	3.52	<1.95	0.48	25.95
Referral H.	3.17	<1.95	0.43	29.93
FAO/WHO	30	0.5		40
EU	10	0.1		
USFDA			70 - 80	

Table 7: Comparison of heavy metals in Lake Hawassa water (mg/L) with reported literature.

Location	Cu	Pb	Ni	Zn	References
L. Hawassa,Eth,	ND - 0.005	ND – 0.003	ND	ND	Present study Zebene (2011)
L. Victoria, Keny.		0.04-0.094*			Tole & Shitsama (2003)
L. Victoria, Tanza.	<0.01	0.35 - 0.63		0.01- 5.62	Kisamo (2003)
L. Qarun, Egypt	1.25 - 2.59			0.096- 0.18	Authman & Abbas (2007)
L. Borgada, (Sir Lanka)	13.2-135.5	6.5 - 7.59		58.2- 227.6	Senarathne & Pathirathe (2007)
L. Edku, Egypt	0.002-0.054	ND -0.084		0.004- 0.5	Saeed & Shaker (2008)
L. Borollus, »	0.02-0.05	0.11-0.31		0.026-0.077	“
L. Manzala, »	1.36-0.68	0.012-0.22		0.32- 0.66	“
Avsar Dam, Lake St 1, Turkey	0.01	0.01	0.004		Öztürk et al. (2009)
Avsar Dam, Lake St 2	0.01	0.005	0.006		“
USEPA (2006)	1.5	0.05	0.1	0.5	
WHO (1993)	2	0.05	0.02	5	
FAO (1985)	0.2		0.2	2	

ND=Not Detected; * = given in μg/L

were substantially lower than the maximum limit recommended by FAO/WHO and EU. But the Pb levels in muscle of Tilapia fish from Tikur Wuha site exceeded the FAO/WHO and EU limit.

Comparison of current result with reported literature

Water: The comparison of the current study of heavy metals in water with reported literature was compiled in Table 7. Authman et al. [48] found the concentration of Cu and Zn in Lake Qarun of Egypt in the range 1.25- 2.59 mg/L and 0.0096 - 0.18 mg/L, respectively. This lake receives mainly agricultural and sewage drainage water from Fayounce province and neighboring cultivated land. The concentrations of Cu and Zn in Qarun were below the WHO [46] but Cu concentration was higher than FAO [47]. The concentrations of Cu and Zn in Lake Qarun were significantly higher than the finding of the present study (Table 7) [49-53].

Fish: The comparisons of the present study with the previous studies of the same lake as well as other lakes were compiled in Table 8. The maximum mean accumulation of copper and zinc found by

Table 8: Comparison of heavy metal accumulations (μg/g, dry mass) in fish muscle from Lake Hawassa with literature report.

Location	Cu	Pb	Ni	Zn	References
L. Hawassa, Eth.	2.62 – 3.52	<1.95-2.15	<0.29-0.48	25.38-29.93	Present study Zebene (2011)
L. Hawssa, Eth.	1.39 – 1.85	<1.66	<0.99	24.42-27.00	Abayneh et al. , (2003)
L. Ziway, Eth.	1.03 – 1.98	<1.66	<0.99	26.29-30.92	»
L. Ziway, Eth.	1.35	0.35		27.13	Selamawit Geta (2010)
L. Victoria, Ken.		3.6 - 20.3			Tole & Shitsama (2003)
L. Victoria, Tanz	2.3 – 6.6	0.01–28.0		17–179	Kisamo (2003)
L. Edku, Egypt	2.80	0.59		27.6	Saeed & Shaker (2008)
L. Borollus»	1.77	0.016		9.88	"
L. Manzala»	44.84	10.1		212.44	"
L. Borgada (Sir Lanka)	0.8-9.3*	0.1- 3.0*		5.9-11.5*	Senarathne & Pathira (2007)
Avsar Dam Lake (Turkey)	3.85*	2.14*	1.27*		Öztürk et al. (2009)
L. Köyce⃞iz (Turkey)	3..91	1.12		84.72	Yilmaz (2009)
USEPA (2006)	30	0.5		40	
WHO (1993)	10	0.1			
FAO (1985)			70 - 80		

*= given in w. m

Abayneh et al. [11] in Tilapia species collected from the same lake of this study were 1.85 μg/g of copper and 27.00 μg/g of zinc and from Lake Ziway 1.98 μg/g of Cu and 30.92 μg/g of Zn. Geta et al. [54] found the mean accumulations of Cu and Zn in Nile Tilapia fish from Lake Ziway were 1.13 μg/g and 27.13 μg/g, respectively. In 2003, the sources of pollution in Lake Hawassa were through Tikur Wuha and agricultural activities but the Referral Hospital was under construction and it did not contribute pollutants to the Lake. The accumulations of Cu and Zn in Tilapia fish from Lake Hawassa and Ziway were lower than the FAO/WHO and EU recommended limit. Their accumulations were also lower than the maximum result obtained in present study (Cu=4.80 μg/g and Zn =40.7 μg/g) [55,56].

CONCLUSION

This study revealed that the physicochemical variables such as temperature, DO, pH, TDS and SS of Lake Hawassa were below or within the range of the recommended limit of EU, WHO, USEPA. The pH of this study showed that the lake water was slightly alkaline which might have an effect on the availability of dissolved metals. In fish samples, the concentrations of Cu, Ni and Zn were detected in all sampling sites but Pb was detected only at Tikur Wuha sampling site. In the detected samples: concentration of Zn>Cu>Pb>Ni. The P-values for Cu, Ni and Zn accumulations in muscle Tilapia fish showed that there no variation throughout the lake and their accumulations are lower than the FAO/WHO (for Cu and Zn), EU (for Cu) and USFDA (for Ni) limit. Hence the consumption of this fish seems to pose no threat to human health regarding to these metals. The high accumulation of Pb in edible muscle of Nile Tilapia fish was observed only at Tikur Wuha site which exceeded the recommended limit of FAO/WHO and EU. The high concentration of Pb at Tikur Wuha site might be caused by the closeness of the site to the highway.

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