

Assessment of Metals Concentration in Water, Sediment and Macrophyte Plant Collected from Lake Hawassa, Ethiopia

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Abstract

This study was aimed to assess the concentration of metals (Hg, Cr, Zn Cd and Pb) in water, sediment, and *S. corymbosus* macrophyte plant samples collected from six different sites (S_1 to S_6) of Lake Hawassa. The results revealed that there was significant difference ($p < 0.05$) in metals concentration among different sampling sites as well as within the site. Generally, significantly higher values ($p < 0.05$) of metals concentration were recorded at sites S_2 , S_4 and S_5 , which received industrial effluents, urban wastes and agrochemicals respectively. and were the most contaminated sites. The concentration of metals both in sediment and macrophyte plant followed similar pattern, viz., $Zn > Cr > Pb > Cd > Hg$, while the concentration of metals in water followed the order of $Zn > Pb > Cr > Cd > Hg$. High to very high correlations were recorded within some metal pairs and with some physico-chemical parameters. - Although metals concentration in water and sediment of the lake are generally in non-polluted to moderately polluted range according to international standards based on numerical sediment quality guidelines (SQGs), almost all values at different sampling sites along the shoreline are much higher than the reference site as well as the background metals concentration of the lake. This is a clear indication that Lake Hawassa is exposed to different pollutants from all directions and the problem can easily go out of hand unless a special attention to be properly monitored for better protection of the lake and the surrounding catchment areas is given. as different human activities are increasing around the lake. Therefore, strategies to control point and non-point sources of all over the shorelines should be developed for better protection of the lake as well as the surrounding catchment areas.

Keywords: Lake Hawassa; metals; water; sediment; aquatic macrophyte; SQGs

Introduction

The problems of metal pollution are currently increasing in many Ethiopian Rift Valley Lakes. It is mainly associated with expansion of industrial activities and intensification of agricultural activities. Due to fast growing industries in and around Hawassa city, Lake Hawassa is one of the most exposing lakes to different sources of pollutant [1,2]. Under some environmental conditions, those pollutants including metals could accumulate and get biomagnified through food chain to toxic levels and eventually results in ecological damage [3]. The major factors to increase concentration of pollutants in Lake Hawassa include the Hawassa Textile Factory, Tabor Ceramic Products Share Company, Hawassa Millennium Soft Drink, City Municipality Abattoir, Hawassa ETAB Soap Factory, Flour Factories, Hawassa Referral Hospital and Floriculture Farms. Some of them dispose their solid and liquid wastes directly in to the lake or to shallow (Cheleleka) swamp, which is directly connected to the lake through Tikur Wuha River. Despite of intensive and extensive works that have been done on Lake Hawassa with regard to bacterioplankton [4], phytoplankton [5], zooplanktons [6], and fish [7], little information is documented about metal concentrations related to sediment, water and macrophytes of this lake. In addition, there is limited information on the potential mobility and simulation uptake of important metals form contaminated environments. Therefore, it is necessary to determine the concentration of metals in aquatic macrophytes, as well as in the growing media: water and sediment [8]. Consequently, information pertaining the state of metals in contaminated aquatic systems and their potential risk to aquatic organisms and other terrestrial organisms including human is of paramount importance to formulate and implement sound environment system in metal affected aquatic systems. Therefore, the main objective of this study was to assess the concentration level of selected metals in the water, sediment and aquatic macrophytes of Lake Hawassa.

Materials and Methods

Description of study area and sampling sites

Lake Hawassa is found in the middle of a series of rift valley lakes and located at $6^{\circ}33' - 7^{\circ}33'N$ latitude and $38^{\circ}22' - 39^{\circ}29'E$ longitude in the southern part of Ethiopia at a distance of 275 km south of Addis Ababa. The lake has one known small tributary namely, Tikur Wuha River that fed the lake from the northeast direction. There is no any known outflow from the lake. Different vegetation types that extend to the lake offshore cover the littoral area of the lake. The lake is also known for commercial fisheries, as it is inhabited by different fish species such as Tilapia, African catfish and Barbus sp. [6,7]. Based on the potential exposure of the lake to different source of agro-industrial and other source of pollutants, six representative sampling sites: (Site-1 (S_1): Asama Ber, Site-2 (S_2) Tikur Wuha, Site-3 (S_3) Green Wood, Site-4 (S_4) Amora Gedel, Site-5 (S_5) Bete Mengist and Site-6 (S_6) Kuyuwata: reference site) were selected (Figure 1).

Water, sediment and macrophyte sampling

Water samples were collected from six selected sites from different locations of each site of the lake at about 10 cm depth of the water

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column (Figure 1). To remove metal contaminants, the sampling plastic bottles were washed with 10% HNO₃ and were rinsed thoroughly with distilled water. Soon after collection, all the samples were acidified by adding a few drops of 10% HNO₃. Similarly, sediment samples were collected from different locations of each site using Ekman grab and were placed in polyethylene bags. The macrophyte plant samples were also collected from different location of each site for all study sites. The plant samples were washed with lake water and then with 5% EDTA solution and were rinsed with distilled water before placed in plastic bags. Later, all the samples were packed and labeled carefully and then placed at 4°C [9,10]. Finally, the samples were transported to Ethiopian Environmental Protection Authority EPA laboratory in Addis Ababa for analysis.

Sample digestion

At EPA laboratory, all the sediment and the plant samples were digested separately using aqua-regia and dry-ash methods respectively. In aqua-regia method, 1g of sediment sample from each sample was weighed and was soaked in aqua-regia solution that contains 7.5 mL of 37% HCl and 2.5 mL of 68% HNO₃ with a ratio of 3:1. The samples were digested for two hours at 105°C and were cooled. The samples were then diluted with 20 mL of 2% nitric acid and were filtered by using 0.45 μm filter paper. Similarly, for dry-ash method, 1 g of plant sample from each sample was placed in labeled crucible glass separately. All the crucible glasses were then placed in a muffle furnace and were heated

to 450°C until the samples become a white ash. The white ash of the samples was then cooled overnight. To make solutions for all samples 5 mL of 6 mol L⁻¹ of HNO₃ was added to the white ash of the samples and then place in the fume hood. Meanwhile, step by step, 5mL of 3 mol L⁻¹ and then 1 mol L⁻¹ of HNO₃ was added to the solution. The plant samples were then heated in hot plate oven for 30 minutes. The samples were diluted with distilled water to get a total of 50 ml sample solution and were filtered using 0.45 μm filter paper [9-11]. Then, all the samples were ready for analysis.

Data analyses

In this study, some water characterization was performed for selected parameters. Total dissolved substances (TDS), temperature, concentration of dissolved oxygen (DO), hydrogen ion concentration (pH) and electrical conductivity (EC) of lake water were measured using Hydrolab meter, Model "Multi 340I/SET. Organic matter and pH of sediment samples were also analyzed at Addis Ababa EPA laboratory. Metal concentrations such as mercury (Hg), chromium (Cr), zinc (Zn), cadmium (Cd) and lead (Pb) were analyzed for all the three types of samples using Graphite Furnace Atomic Absorption Spectrometry.

Statistical analyses

Statistical analysis was carried out using SPSS Version 13 computer package. One way ANOVA t test was applied to compare the mean concentration of metals at different Sites at p ≤ 0.05. Pearson correlation coefficients were determined to examine the relationship between the levels of elements in water, sediment and aquatic macrophyte plant samples.

Results

Physico-chemical parameters from in-situ measurements

Individual characteristics of some physico-chemical parameters of the lake water and sediment samples are presented in Table 1. With a few exceptions, values recorded at S₁ to S₅ were generally higher than at S₆. Statistical analysis showed that the mean differences of the physico-chemical parameters recorded at different sampling sites of the lake water were significantly (P<0.05) different among sites. Sediment samples analysis revealed that the pH and OM values were significantly different. The total pH mean value of the sediment was generally lower than the pH value of lake water. OM in lake sediment at S₄ and S₂ were significantly higher (P<0.05) and more than threefold of the rest of the sites.

Metals concentration in water, sediments and macrophyte plant

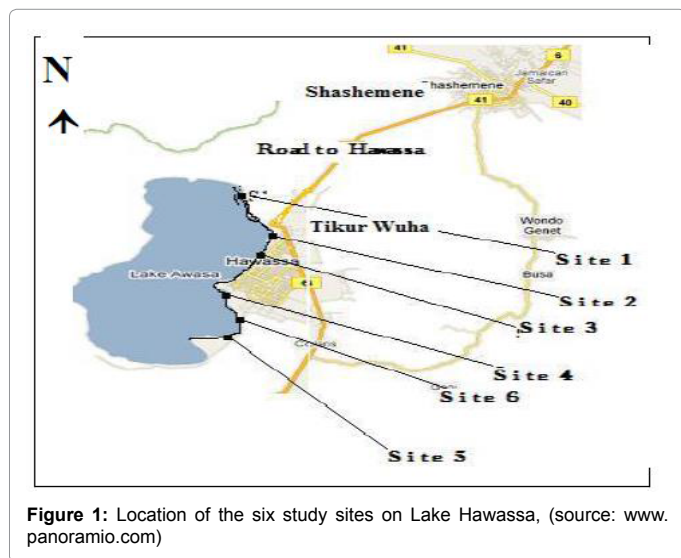


Figure 1: Location of the six study sites on Lake Hawassa, (source: www.panoramio.com)

Table 1: Mean values of different physico-chemical parameters ± standard deviation (SD) of in-situ measurement of lake water, laboratory analysis of sediment samples of Lake Hawassa and standard values for drinking water.

Physico-chemical Parameters	Sampling sites						Drinking water Standard [12]
	S ₁	S ₂	S ₃	S ₄	S ₅	S ₆	
Lake water							
pH	7.7 ± 0.12a	9.52 ± 0.19d	9.17 ± 0.08cd	8.86 ± 0.02bc	9.14 ± 0.02cd	8.5 ± 0.06b	6.5-8.5
DO (mg L ⁻¹)	7.6 ± 0.12d	6.6 ± 0.12bc	6.2 ± 0.12ab	6.9 ± 0.05c	5.7 ± 0.17a	6.1 ± 0.15ba	4.5-7.5
Temperature (°C)	22.5 ± 0.41a	26.7 ± 0.29c	27.4 ± 0.23c	27 ± 0.29c	29 ± 0.12d	25 ± 0.12b	
TDS (mg L ⁻¹)	562 ± 1.73c	681 ± 0.58e	507 ± 2.31a	516 ± 0.58b	603 ± 1.73d	521 ± 2.31b	1000
EC (μS/cm K ₂₀)	603 ± 1.73a	895 ± 2.89f	770 ± 1.16c	785 ± 2.89d	845 ± 2.89e	642 ± 1.16b	1500
Sediment sample							
pH	6.64 ± 0.08a	8.2 ± 0.10c	7.95 ± 0.10c	7.41 ± 0.15b	8.19 ± 0.16c	7.21 ± 0.01b	
OM (%)	4.3 ± 0.09b	11.77 ± 0.26c	2.96 ± 0.15a	14.46 ± 0.26d	3.30 ± 0.02a	3.11 ± 0.01a	

*Values with different letters showed significant differences (P<0.05, ANOVA), letter "a" indicates the smallest value for a given physico-chemical parameters (DO-dissolved oxygen concentration, TDS-total dissolved substances, EC-electrical conductivity (μS/cm K₂₀ is μS/cm at 20°C), pH hydrogen ion concentration and OM-organicmatter.

The analytical results for concentrations of Hg, Cr, Zn, Cd and Pb were determined in water, sediment and plant samples collected from the six sites are presented in Tables 2-4 respectively. Among all metals in water samples, the Pb was the only metal detected at all sites, while Hg in sites S₁, S₂ and S₄, Cr in site S₂, Zn in sites S₂ and S₃ and Cd in sites S₂ and S₆. S₂ was the only site in which all the analyzed metals were detected.

Similarly, the results showed that the mean difference of metals concentration in sediment samples at all study sites were significantly different (P<0.05). Without any exception, the lowest concentrations of metals were found at S₆ (Table 2).

Similarly, the results showed that there was a significant difference (P<0.05) of most metals concentration in plant growing at different sites of the lake. The minima for the concentration of these metals were recorded at S₆ (Table 4).

Correlation matrix for intra-and inter-physico-chemical

Correlation matrix for the data was evaluated to determine the level of intra- and inter-physico-chemical correlation and the values was determined. For most parameter pairs, the results showed that there were high positive to negative correlation and even no correlation for some pairs of parameters. The results revealed that the values of

the parameters in the different samples were significantly (p<0.05) correlated. The products of the correlation coefficient [r] were evaluated as suggested in Norusis [16] as 0-0.3: No correlation; 0.3-0.5: Low correlation; 0.5-0.7: Medium correlation; 0.7-0.9: High correlation; 0.9-1.0: Very high correlation.

Discussion

Physicochemical characteristics

The present results for pH value of the water and sediment samples collected from Lake Hawassa showed a considerable variation among different study sites. The highest pH values (9.52 ± 0.19) for water sample and for sediment (8.2 ± 0.16) were recorded at S₂, while the lowest pH value for water (7.7 ± 0.12) and sediment (6.64 ± 0.08) samples were registered at S₁. Except S₁ pH values of lake water from S₂ to S₅ were above 8.5, and these values fell out of the desirable range of pH (6.5-8.5) for drinking water set by WHO, [12] indicating that there is human influences in the lake area. In all cases, the pH values of both water and sediment samples implied that the condition of the lake is alkaline. The responsible factors for the alkaline value of the pH might be agro-industrial activities found in the surrounding areas of the lake. Karpisack et al. [17] suggest that alkalinity of the lake water increases with increasing contaminants from industries and agricultural

Table 2: Mean value of metal concentration ± SD in µg L⁻¹ of lake water values in parentheses (), square brackets [] & brace {} indicate maximum permissible levels (MPL) according to international standards for drinking water¹, [12,13] international average for freshwaters² [13] background concentration of the lake water³, [1] respectively.

Sites	Chemical Parameters				
	Hg(1)[0.1]{ND}	Cr(50)[11.4]{5.7}	Zn(5000)[30]{1.6}	Cd(5)[0.017]{ND}	Pb(10)[1.7]{ND}
S ₁	0.116 ± 0.002b	ND	ND	ND	49.47 ± 0.37f*
S ₂	0.117 ± 0.006b	6.48 ± 0.31	0.219 ± 0.58b	0.094 ± 0.003a	6.111 ± 0.12d
S ₃	ND	ND	0.044 ± 0.12a	ND	9.705 ± 0.05e
S ₄	0.025 ± 0.0004a	ND	ND	ND	5.22 ± 0.028c
S ₅	ND	ND	ND	ND	4.044 ± 0.025b
S ₆	ND	ND	ND	0.1 ± 0.00b	0.79 ± 0.0001a

*Values with different letters showed significant differences (P<0.05, ANOVA), letter "a" indicates the smallest value for a given physico-chemical parameter. Values with *and bold indicate those above MPL in drinking water and the background concentration, respectively, ND= not detected

Table 3: Mean value of metal concentration ± SE in mg kg⁻¹ of dry weight of sediment samples collected from Lake Hawassa, Values in parentheses () and square bracket [] indicate maximum acceptable levels (MAL) according to international standards for soil/sediment, an non-polluted, bmoderately polluted and cheavily polluted on the basis of numerical sediment quality guidelines (SQGs) [13,14].

Sites	Chemical Parameters				
	Hg (0.05)	Cr (0.1-1), [<25 ^a , 25-75 ^b , > 75 ^c]	Zn (1-5), [<90 ^a , 90 -200 ^b , >200 ^c]	Cd (0.01-0.05)	Pb (0.2-2.0) [<40 ^a , 40 -60 ^b , >60 ^c]
S ₁	0.00052 ± 0.00009a	2.05 ± 0.02a	32.13 ± 06b	0.027 ± 0.0018a	0.71 ± 0.05b
S ₂	0.00068 ± 0.00003c	9.69 ± 0.18b	61.6 ± 0.35c	0.032 ± 0.009b	0.75 ± 0.009a
S ₃	0.00066 ± 0.00004a	5.69 ± 0.13e	58.89 ± 0.36c	0.021 ± 0.0005a	1.44 ± 0.03c
S ₄	0.00017 ± 0.00004b	8.10 ± 0.35d	107.5 ± 4.45e*	0.035 ± 0.0035c	1.73 ± 0.04d
S ₅	0.00054 ± 0.00003a	6.86 ± 0.1c	71.95 ± 06d	0.018 ± 0.0007a	1.32 ± 0.05c
S ₆	0.00011 ± 0.00006a	1.56 ± 0.02a	11.4 ± 0.06a	0.012 ± 0.0001a	0.56 ± 0.03a

*Values with different letters showed significant differences (P<0.05, ANOVA), letter "a" indicates the smallest value for a given physico-chemical parameter. Values with bold and * indicate those above MAL in sediment and polluted sediment[13,14].

Table 4: Mean value of metal concentration ± SD in mg kg⁻¹ of dry weight of in S. corymbosus growing around the lake, value in parentheses () is critical range of metals in plant species.

Site	Chemical parameters				
	Hg (0.00015-0.00071)	Cr (0.081-0.370)	Zn (0.1-0.4)	Cd (0.01-0.03)	Pb (0.03-0.3)
S ₁	0.00017 ± 0.000006b	8.19 ± 0.08c	21.46 ± 0.32c	0.009 ± 0.0005b	0.65 ± 0.035c
S ₂	0.00021 ± 0.00001c	12.15 ± 0.24d	17.28 ± 0.006b	0.013 ± 0.00002d	0.484 ± 0.01b
S ₃	0.00011 ± 0.000006a	8.56 ± 0.26c	22.04 ± 0.39d	0.012 ± 0.0006cd	0.67 ± 0.023cd
S ₄	0.00012 ± 0.000006a	5.98 ± 0.11b	29.4 ± 0.39e	0.01 ± 0.001bc	0.51 ± 0.012b
S ₅	0.0007 ± 0.00001d	6.25 ± 0.04b	20.92 ± 0.07d	0.0088 ± 0.0004b	0.76 ± 0.023d
S ₆	0.0001 ± 0.00000a	1.29 ± 0.03a	1.417 ± 0.04a	0.0051 ± 0.0001a	0.147 ± 0.002a

*Values with different letters showed significant differences (P<0.05), letter "a" indicates the smallest value for a given physicochemical parameters [8,15].

activities. Therefore, the higher pH levels at S_2 and S_5 could be due to the impact of Tikur Wuha River that contains different contaminants from different sources of pollutants and intensive agricultural activities respectively. Furthermore, the higher pH value for S_3 might be related to the municipal waste produced by Hawassa city that is directly or indirectly released to this site. In line with our result, Zerihun [2] reported that the pH value of Lake Hawassa and its feeders was highly alkaline particularly around the mouth of Tikur Wuha River.

The results of this study also revealed that there was a great variation in DO concentration at different locations of the lake. The highest DO concentration was recorded at S_1 , while the lowest DO concentration registered at S_5 . The reason for lower DO concentration is due to the presence of high amount of OM (11.77%) at this site, which has high oxygen-demand for bacterial decomposition [18,19]. In general, the recorded level of DO concentration in the lake water ranged between 5.7 ± 0.17 to 7.6 ± 0.12 mg L⁻¹ and fell within the range values reported by WHO [12]. Generally the DO concentration records at all selected sites were within the guideline values cited by USEPA [10] for the protection of aquatic life [for warm water biota: early life stages = 6 mg L⁻¹, other life stages = 5.5 mg L⁻¹]. The EC values were also ranged from 603 ± 1.73 to 895 ± 2.89 μ S/cm K₂₀ during the investigation period. The maximum values 895 ± 2.89 μ S/cm K₂₀ was recorded at S_2 which may be receiving the agro-industrial wastes from the surrounding environments via Tikur Wuha River as explained by Seyoum et al. [20]. In addition, the higher electrical conductivity observed at S_2 could be attributed to the relatively low DO concentration and revealed high negative correlation to each other (temp/DO: $r = -0.771$). This result is in accordance with the works of Phiri et al. [21] and Okafor [22] who reported that high EC contribute for reduction of DO concentration in the given water bodies.

Similarly, TDS showed great variation and ranged from 507 ± 2.31 at S_3 to 681 ± 0.58 at S_2 mg L⁻¹. These values were far below the WHO [12] guideline value prescribed for drinking water (1000 mg L⁻¹). In general, the present results clearly indicated that there was inter-physico-chemical association with significant correlation between them in aquatic system. The results clearly indicated that OM, pH and DO concentration had significantly correlated (OM/pH: $r = 0.589$ and OM/DO: $r = -0.530$ and were consistent with the work of Kar et al. [23]. There are high correlation between most of the concentration of metals analyzed in this study and the physico-chemical parameters such as pH, temperature, EC, DO and OM.

Metals concentrations in water, sediments and *s. corymbosus* macrophyte

Metal concentrations in water

The analytical result of this study showed that the mean values of metals concentrations in lake water were significantly different among sampling sites ($P < 0.05$). Most of the metals in water samples taken from different sites were not detected. However, S_2 was the only site in which all the analyzed metals were detected. Likewise, the lead was the only metal detected at all sites and had the highest with a mean value of 0.013 ± 0.001 mg L⁻¹, while the lowest total metal concentration was Hg with a mean value of 0.00004 ± 0.000002 mg L⁻¹. This result agrees with the work of Teresa and Neff [15]. The author reported that among several metals analyzed in fresh water body, the lowest metal concentration was Hg. It was even not detected in some of the experimental sites. Moreover, our result agrees with the work of Zinabu [1] who reported that Hg and other metals were not detected in this lake. Moreover, with the exception of Pb at S_1 , all the detected metals concentrations

were below the maximum permissible levels (MPL) for drinking water [12,13]. Even though the values were below the acceptable ranges for drinking water, concentration of metals found in this study was higher than the background concentration metal level indicated by Zinabu [1]. Furthermore, with few exceptions (i.e. Zn and Cr), all the detected metal concentrations were above the international mean value of metal concentration found in freshwater [12].

Inter-site comparisons showed that the lowest Hg and Cd concentration were recorded at S_5 , while the highest concentrations of Zn, Cr and Pb were detected. The existence of two or more metals in a given location might be due to the chemical affinity between them [24]. In accordance with our result pairs of Zn/Cd ($r = 0.597$) had medium positive correlation implying that they have similar sources or phenomenon [23]. Moreover, higher metal concentration at those sites might be related to the higher correlation between those metals and physico-chemical parameters (e.g. pairs of Hg/DO, Hg/TDS, Cr/OM, Zn/Tem, Zn/TDS, Zn/OM, Cd/pH). The higher values of those physico-chemical parameters contribute for higher concentration of metals as suggested by Igbinosa and Okoh [18] and Okafor and Opuene [22]. This implies that there are potential sources of pollutant to the lake from various directions particularly from the northern side of the lake. Therefore, agro industrial activities around S_1 and S_2 might be the sources of pollutant as compare to other sites.

Metals concentrations in sediment

The analysis of metals in sediment is used for detection of pollutants that may be either absent or in low concentrations in the water column [25,26]. The concentration of metals from the overlying water to the sediment is dependent on a number of external environmental factors such as pH, EC, the ionic strength of the compound, anthropogenic input, the type and concentration of organic and inorganic ligands and the available surface area for adsorption caused by variation in grain size distribution [27].

Determination of metal elements in lake sediment during drought period revealed that all the analyzed heavy metals were present. In view of the concentration, levels of those studied metals, the highest values were for Zn and Cr at all sites. This may be attributed to the fact that Zn and Cr are the most abundant elements in the earth's crust as studied on Nile sediment [28]. The concentration levels of Hg, Cd and Pb were low as compared to Zn and Cr. They were found above the background concentration of the same lake [1] with a descending order of Zn > Cr > Pb > Cd > Hg. The above sequence agrees with the findings of Siegel et al. [29] and Ramdan [30] in Lake Manzala, Egypt.

Metals concentrations of Zn, Cr, Cr and Pb from Lake Hawassa sediment as compared to the probable-effects-level (PEL) guidelines for toxic biological effects established and sediment-quality guidelines by USEPA [31], the present results revealed that metals concentration of sediment showed higher than the level of those elements set by the guidelines. Moreover, metals concentrations in the sediment including mercury exceeded the maximum acceptable levels cited by Frances [13]. However, according to MacDonald et al. [14] and Harikumar et al. [32] Lake Hawassa sediment was moderately polluted.

Correlation coefficient "r" is some of the most important statistical tests to evaluate the strength or weakness relationships among physico-chemical parameters as well as metal concentrations determined in this study. The results from statistical analysis revealed that water temperature, pH and EC showed strong associations among different physico-chemical parameters including heavy metal concentration.

These showed that the important role of water temperature, EC and pH in the concentration of metals in aquatic ecosystem. These results coincide with the findings of Abdo [33] on Ismailia Canal, Egypt and Abdel-Satar [28] on Manzalah Lake, Egypt.

The positive correlation coefficient "r" between pairs for Cr/Zn, Zn/Pb, Hg/Cr, Zn/Cd, Cr/Cd, Hg/Cd, Cd/OM, Cr/pH, Hg/TDS, Zn/EC, Pb/EC, Cr/OM, Cr/Temp, Zn/OM, Hg/OM, Cr/EC, Hg/pH, Zn/Temp and Cr/TDS represented the direct relationship between those parameters. Similarly, negative correlation coefficient "r" between elemental pairs of Hg/pH, Cd/pH and OM/DO represented the inverse relationship between those parameters which were consistent with the works of Kar et al. [23] and Nirmal et al. [24]. Generally, most of the physico-chemical parameters had higher correlation coefficient and can contribute for higher concentration of metals in aquatic ecosystems which is inconsistency with the works of Igbinosa and Okoh [18], Okafor and Opuene [22], and Kar et al. [23].

Inter-sites comparison showed that metals concentration varies from site to site so that the highest mean concentration of Zn, Cd and Pb was recorded at S_4 , whereas the highest Hg and Cr concentration was recorded at S_2 . In all cases, the lowest metal concentration was observed at reference site (S_0). The highest concentration of total metals was generally recorded at the northern sites of the lake than the southeast sites of the lake which agrees with the work of Zinabu [1] in which high concentration of metals was recorded at around Tikur Wuha River. Site variation in metal concentration in this study is probably due to variation of organic matter content, EC and pH of the different sites as mentioned by Freedman [34]. This is because variations in physico-chemical values at different sites contribute for the variation of metal concentration. In line with our results, Igbinosa and Okoh [18] and Sekabira et al. [35] reported that the concentration of metals in aquatic ecosystems are highly correlated with physico-chemical parameters as mentioned earlier by different authors. Agrochemical substances that runoff to those sites can cause variation in metal concentration. In accordance with this result, Nabizadeh et al. [36] reported that different runoff could have varieties of contaminants with different concentration and thus, contribute to increase metal concentration of the receiving water bodies.

Metal concentration in aquatic macrophyte

The analysis of metals in some macrophytes permitted to the detection of pollutants that may be either absent or in low concentrations in the water column or low concentration in sediment [17,24,37]. The accumulation of metals from the overlying water and sediment to the macrophyte plant is also dependent on a number of external environmental factors such as pH, EC, the ionic strength, anthropogenic input, the type and concentration of organic and inorganic ligands and the available surface area for adsorption caused by variation in grain size distribution [27]. In *S. corymbosus* the mean values of concentration of metals were significantly ($p < 0.05$) different among sites. In this plant, the mean value of Zn concentration was the highest, followed by Cr. This result implied that Zn and Cr were the most contaminant metals almost at all study sites. Moreover, the plant has higher uptake for those metals from the sediment in which they are growing. The lowest total metal concentration in plant samples was being Hg. The general order of metal concentration in *S. corymbosus* was Zn>Cr>Pb>Cd>Hg. This sequence agrees with the findings of Nirmal et al. [24], Siegel et al. [29], Ramdan [30] for different aquatic macrophyte plant species. The concentration of metals also varies at different studying sites. Inter-site comparison showed that the highest Hg and Pb concentration was

recorded at S_5 followed by S_2 for Hg and S_3 for Pb. The concentration of Hg at sites S_3 and S_4 had more or less similar. In case of Zn and Cd, the highest concentration was registered at sites S_4 and S_2 , respectively. Furthermore, Zn concentration at sites S_3 and S_5 was more or less similar. In all cases, the lowest metal concentration in this aquatic plant was recorded at reference site (S_0). Moreover, correlation of metals from very high to medium within metals and with physico-chemical parameters suggests that some physico-chemical parameters may contribute for high concentration of specific types of metals at a particular site. For instance, the highest metal concentrations at site S_2 are might be due to the impact of different physico-chemical parameters.

The correlation for elemental pair such as Hg/Pb, Zn/Cd and Zn/Pb in this study was consistent with the works of Kar et al. [23] and Nirmal et al. [24] and metal-physico-chemical pairs such as Cr/TDS and Zn/EC were also consistent to the work of Sekabira et al. [35]. Particularly, the correlation of Zn with Pb and Cd in this study was agreed with the work of Okafor and Opuene [22]. The result confirmed that correlations between physico-chemical parameters contribute for high or low concentration of metals in a given medium.

Comparison of metals concentration in water, sediment and macrophyte

Sediment can act as both sink and source of contaminants, whereby long-term input of contaminants can lead to sedimental concentrations that can exceed to increase concentration in water [18,38,39]. However, the process of phytoremediation is the most important biotic factor used in outlining the program of macrophytic role in purification of contaminated sediment and water of aquatic ecosystems [17]. Moreover, aquatic plants can be used as bioindicator of metal pollution in the lake since metals present in water and sediment are slowly accumulated by aquatic plants and thereby concentrated in the plant tissues. The result showed that total concentration of metals found in water was lower than those found in lake sediment and macrophyte plants. Generally, the total concentration of metals in Lake Hawassa followed the order of sediment>macrophyte>water which agrees with the work of Nirmal et al. [24]. Similarly, Lovett-Doust et al. [40] reported that the accumulation level of pollutants in aquatic ecosystems is higher in sediments than in plants if the receiving water body is exposed to different source of contaminants. The sequence of the analyzed total metal concentration found in our result is almost similar with the order of metal concentration (Fe>Mn>Zn>Ni>Cu>Pb>Cr>Cd>Hg) analyzed by Harikumar et al. [32] for different tropical aquatic plant species.

With few exceptions the concentrations of metals were above the standard set for aquatic macrophytes by WHO [12] and Frances [13]. Moreover, the examined sediment can be considered slightly polluted with the analyzed metal elements, since their concentrations were out of the typical range concentrations found in soils/sediment under fresh water bodies [8,31]. This suggests that metal contents in the lake sediments are largely associated with industries, and floriculture and city sewage. According to MacDonald et al. [14] and Perin et al. [41] sediment in Hawassa Lake was moderately polluted by Zn particularly at S_4 and non-polluted by the rest of the metals at all sites. Therefore, the present study shows that bio monitoring should be taken in order to prevent further metal pollution. Generally, there are potential sources of pollutants to the lake from various directions particularly from the northern side of the lake. Agro industrial activities around S_1 and S_2 might be the most potent pollutant sources as compare to other sites. Industrial effluents and non-point pollution sources as well as changes in atmospheric precipitation can lead to local increase in

metal concentration of water. In addition, total metal concentration in aquatic ecosystem can reflect the present pollution status of these areas [42].

Conclusion and Recommendation

As compared to S_6 (reference site), all sampling sites have higher metals concentration for all the three media: water, sediment and plant samples. Although all sampling sites showed the presence of all the five metals analyzed (Zn, Cr, Pb, Cd, and Hg), the concentration in sediment and macrophyte samples at S_2 , S_4 and S_5 have higher than metals concentration at S_1 and S_3 . Metals concentration in most sites followed the order of sediment > *S. corymbosus* > water. According to international standards based on numerical sediment quality guidelines (SQGs) sediment of Lake Hawassa are generally non-polluted to moderately polluted range. All these are an early signal to take timely measure to maintain the present quality of the lake. Therefore, strategy to control point and non-point sources of all over the shorelines should be developed for better protection of the lake as well as the surrounding catchment areas.

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References

- Zinabu Gebre-Mariam (2002) The Ethiopian Rift Valley Lakes: major threats and strategies for conservation. In: *Biology of Inland Water Series*, Ethiopian Rift Valley Lakes, (Tudorancea, C and Taylor, W.D. ed.). Backhuy publishers, Leiden, The Netherlands 259-271.
- Zerihun Desta (1997) Industrial environmental management: the case of Hawassa textile factory, Ethiopia. M.Sc. thesis Wageningen Agricultural University. The Netherlands, 95.
- Walker C, Hopkin S, Sibly R, Peakall D (2006) *Principles of ecotoxicology*, CRC press: Taylor and Francis Group, LLC, London, New York.
- Zinabu Gebre-Mariam (1988) Dynamics of heterotrophic bacterioplankton in an Ethiopian rift-valley lake (Hawassa). PhD Thesis. University of Waterloo, Ontario, Canada, 180.
- Elizabeth K, Amha B (1994) Species composition and phytoplankton biomass in a tropical African lake (Lake Awassa, Ethiopia). *Hydrobiologia* 288: 13-32.
- Seyoum Mengstu, Fernando CH (1991) Seasonality and abundance of some dominant crustacean zooplankton in Lake Awassa, a tropical rift valley lake in Ethiopia. *Hydrobiologia* 226: 137-152.
- Demeke Admassu, Elias Dadebo (1997) Diet composition, length-weight relationship and condition factor of *Labeobarbus* species (Pisces: Cyprinidae) in Lake Awassa, Ethiopia. *SINET Ethiop J Sci* 20: 83-96.
- Kabata-Pendias A, Pendias H (1992) *Trace Elements in Soils and Plants*. 2nd edition. CRC Press, Boca Raton, Fla.
- USEPA (1991) *Compendium of ERT surface water and sediment sampling procedures*. Office of solid waste and emergency response directive.
- USEPA (1999) *National recommended water quality criteria-correction*-United State Environmental Protection Agency.
- Bass JAB, Blust R, Clarke RT, Corbin TA, Davison W et al. (2008) *Environmental Quality Standards for trace metals in the aquatic environment*. Environmental Agency Rio House Waterside Drive, Aztec West Almonds bury, Bristol.
- WHO (2008) *Guidelines for drinking water Quality 3rd. Ed. incorporating the first and second agenda* vol 1. World Health Organizations Geneva.
- Frances S (2008) *Impact of metal on aquatic ecosystems and human health*. Environmental and communities. British, Columbia.
- MacDonald DD, Ingersoll CG, Berger TA (2000) *Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems*. *Arch Environ Contam Toxicol* 39: 20-31.
- Teresa B, Neff J (2008) *Metals Bioavailability in the Navy's Tiered Ecological Risk Assessment Process*. Washington DC 1-15.
- Norusis MJ (1993) *SPSS for Windows Professional Statistics 61* SPSS Inc., Chicago.
- Karpiscak MM, Whiteake LR, Artiola JF, Foster KE (2001) *Nutrient and heavy metal uptake and storage in constructed wetland systems in Arizona*. *Water Sci Technol* 44: 455-462.
- Igbinoza EO, Okoh AI (2009) *Impact of discharge wastewater effluents on the physico-chemical qualities of a receiving water shade in typical rural community*. *Int J Environ Sci Tech* 6: 175-182.
- Salmasi R, Tavassoli A (2006) *Pollution of south of Tehran ground waters with heavy metals*. *Int J Environ Sci Tech* 3: 147-152.
- Seyoum Leta, Fasil Assefa, Gunnel D (2003) *Characterization of Tannary waste water and assessment of downstream pollution profiles along Mojo River in Ethiopia*. *Ethiop J Biol Sci* 2: 157-168.
- Phiri O, Mumba P, Moyo WZ (2005) *Assessment of the impact of industrial effluents on water quality of receiving rivers in urban areas of Malawi*. *Int J Environ Sci Tech* 2: 237-244.
- Okafor E, Opuene K (2006) *Correlations, partitioning and bioaccumulation of trace metals between different segments of Taylor Creek, southern Nigeria*. *Int J Environ Sci Tech* 3: 381-389.
- Kar D, Sur P, Mandal SK, Saha T, Kole RK (2008) *Assessment of heavy metal pollution in surface water*. *Int J Environ Sci Tech* 5: 119-124.
- Nirmal KJI, Soni H, Kumar RN, Bhatt I (2008) *Macrophytes in phytoremediation of heavy metal contaminated water and sediments in Parije community reserve, Gujarat, India* *J of Fisheries and Aquatic Sci* 8: 193-200.
- Binming K, Baird D (2001) *Survey of heavy metals in the sediment of the Swarkops River Estuary*. *Water Poll SA* 27: 461-466.
- Kumar SP, Edward JKP (2009) *Assessment of metal concentration in the sediment cores of Manakudy estuary, south west coastal of India*. *Indian J Mar Sci* 38: 235-248.
- Awfolu OR, Mbolekwa Z, Mtshemla V, Fatoki OS (2005) *Levels of trace metals in water and sediment from Tyume River and its effects on an irrigated farmland*. *Water Poll SA* 31: 87-94.
- Abdel-Satar AM (2008) *Chemistry of major ions, nutrient salts and heavy metals in Lake Manzalah Egypt*. *Egyptian J of Aquat Research*, 34: 130-148.
- Siegel F, Slaboda M, Stanely D (1994) *Metal pollution loading, Manzalah Lagoon, Egypt: Implications for aquaculture*. *Environ Geol* 23: 89-98.
- Ramdan AA (2003) *Heavy metal pollution and bio monitoring plants in Lake Manzala, Egypt*. *Pak J Biol Sci* 6: 1108-1117.
- USEPA (1997) *Superfund program representative sampling guidance for surface water and sediment*, Vol. 5 Washington, DC.
- Harikumar PS, Nasir UP, Mujeebu RMP (2009) *Distribution of heavy metals in the core sediments of a tropical wetland system*. *Int J Environ Sci Tech* 6: 225-232.
- Abdo MH, El-Nasharty SM (2010) *Physico-chemical evaluations and trace metals distribution in water and sediment of Ismailia Canal, Egypt*. *Nature and Sciences* 8: 198-206.
- Freedman B (1990) *Toxic elemental ecology*. Academic press.
- Sekabira K, Oryem-Origa H, Basamba TA, Mutumba G, Kakudidi E (2010) . *Int J Environ Sci Tech* 7: 759-770.
- Nabizadeh R, Mahvi A, Mardani G, Yunesian M (2005) *Study of heavy metals in urban runoff*. *Int J Environ Sci Tech* 1: 325-333.
- Flathman PE, Lanza GR (1998) *Phytoremediation: current views on an emerging green technology*. *J of Soil Cont* 7: 415-432.
- Jones R, Chambers FM, Benson-Evans K (1991) *Heavy metals (Cu and Zn) in recent sediments of Ilangrose Lake*. *Hydrobiol* 214: 149-154.
- Reza R, Singh G (2010) *Heavy metal contamination and its indexing approach for river water*. *Int J Environ Sci Tech* 7: 785-792.

39. Doust JL, Schmidt M, Doust LL (1994) Biological assessment of aquatic pollution: a review, with emphasis on plants as biomonitors. *Biol Rev Camb Philos Soc* 69: 147-186.
40. Perin G, Bonardi M, Fabris R, Simoncini B, Manente S et al. (1997) Heavy metal pollution in central Venice Lagoon bottom sediments: evaluation of the metal bioavailability by geochemical speciation procedure. *Environ Tech* 18: 593-604.
41. Haiyan W, Stuane AO (2003) Heavy metal pollution in air-water-soil-plant system of Zhuzhou City, Hunan Province, China. *Water, Air and Soil Pollution* 147: 79-107.