Levels of Some Trace Metals in Fishes Tissues, Water and Sediment at Tendaho Water Reservoir, Afar Region, Ethiopia

Wondimagegne Asefa1,2* and Tarekegn Beranu1,3
1School of Postgraduate Program, Department of Chemistry, Ambo University, Ethiopia
2Department of Chemistry, Samara University, Ethiopia
3Ethiopian Quality Control Authority, Addis Ababa, Ethiopia

Abstract

The levels of trace metals (Cd, Co, Cu, Mn, Fe, Pb, Zn, Cr and Ni) in three commercially important fish tissues and their environment of a newly constructed manmade dam, Tendaho reservoir, investigated using validated analytical method under appropriate quality control measures. The analysis result of samples after wet digestion with flame atomic absorption spectroscopy showed that excluding Zn, Mn and Co (fishes tissue>sediment>water) metals distribution in fishes tissue and their environment existed in the order of: sediment>fishes tissue>water. In fish species regardless of the type, the levels of almost all metals were higher in detoxification organs (gill and liver) than in muscle. Higher values of calculated bioconcentration factor and two-way ANOVA analysis result (P-value<0.05) also indicated that the highest level of majority metals existed in Catfish in compared to Tilapia and Barbus intermedius. The concentrations of Mn, Fe, Pb and Cr were higher than Ethiopian Environmental Protection Authority (2003) guidelines in water while the levels of all metals were below PEL guidelines of USEPA (2000) for sediment. Safety of customers from trace metal pollution hazard from fishes was indicated by low level of calculated hazard quotient and comparisons result with WHO (1989) and USFDA (1993) guideline values.

Keywords: Biococentration factor; Hazard quotient; Safety of customers; Guidelines Awash River

Introduction

Following the recent urbanization and economic developments in Africa, environmental pollution has increased [1]. This makes African aquatic environments as final sinks for trace metal pollutants originated from agricultural and industrial activities and spillage of leaded gasoline from watercrafts [2,3].

Although Ethiopia does not have the industry that flourished in developed countries and thus pollutants are not produced in large quantities, pollution due to human activities and by natural inorganic chemicals cause many changes in the aquatic environment as observed in many rift valley water bodies [4,5]. To prevent pollution disaster like Minamata disease that occurred in Japan by Hg and Cd poisoning, continuous follow up and monitoring of environmental pollutants is mandatory [6,7].

Awash River is major water sources of Tendaho reservoir. The river flows from central highlands through Ethiopia's major industrial and agro-industrial belt. Pollutants from suburb of Addis Ababa and other cities enter Awash River carrying the whole burden of all types of raw effluents from industrial and agricultural sources. The reservoir is located in very hot area with average temperature ranging from above 28.5°C where evapo-transpiration greatly exceeds mean annual rainfall that leads to the accumulation of salts on surface soil from the ground water and closeness to Ethiopia-Djibouti rides of highway also increases concentration of salt and toxic elements.

In fresh water environment trace metals are potentially accumulated in sediments and marine organisms and subsequently transferred to man through the food chain. Their concentrations in aquatic ecosystems are usually monitored by measuring their concentrations in water, sediments and biota [8]. To look into the current trace metals pollution status of the area and commercially important fishes (Tilapia, Catfish and Barbus), this study was conducted. This is important to prevent trace metal pollution disaster like Minamata disease and for better utilization of the potentially rich man-made lake.

Materials and Methods

Description of the study area

The study was conducted in Tandaho water reservoir in Afar Regional State, Ethiopia, located in the Northern part of the Ethiopian Rift Valley (Figure 1). It is situated at 11°40’786”N; 40°57’486”E about 580 km east of the capital city, Addis Ababa.

Materials and equipments

Materials and equipments used were: plastic bucket, gill nets, plastic meat chopper, plastic knives, ice box, crucibles, drying oven (DHG-9070A, India), electronic analytical balance with 0.0001 g accuracy (AA-200DS, Deriver Instrument Company), safety hood (ESCO, Singapore) and flame atomic absorption spectrophotometer (ELICO SL-194, India) equipped with deuterium background corrector and an air/acylentene flame atomizer.

Chemicals and reagents

Chemicals and reagents, concentrated hydrochloric acid, concentrated perchloric acid, concentrated nitric acid and hydrogen...
peroxide purchased from UNI Chem Qualikems, India. Standard solutions and spiked standard solutions were prepared from 1000 ppm stock solutions of Pb (Pura tronic Afa Aesan Johnso Mathey Company, Germany), Ni, Cd (both Aldrich-Germany), Fe (PS Pank Scientific limited, UK), Zn, Cu (both Fluka, Switzerland), Mn and Co (both Win Lab-UK).

Preparation of sampling equipments

All sampling materials, samples holders and fish dissecting materials were washed with metal free Liquinox detergent, rinsed with distilled water, soaked with 20% (v/v) nitric acid for two days, re-rinsed with deionized water and air dried. These cleaned and dried materials were used to collect the required samples.

Convenient site selection for sampling at reservoir

Twelve stations were selected around all parts of the reservoir for water and sediment sampling and at the same time fishes were collected around water and sediment sampling sites. Again at three equidistant sites field blanks were kept (Figure 1).

Water sampling and transportation

Around twelve liters of water sample were collected at selected sites by using jug and bottles into a bucket. Thoroughly mixing collected sample three liters of composite water sample was filtered by 0.45 μm filter paper and acidified by HNO₃ to pH<2 in polyethylene bottle. The acidified sample in polyethylene bottles was kept in ice box and sample holding ice box was transported to the laboratory.

Sediment sampling and transportation

As reservoir has rapids and falls, following [9,10] sediment sampling and analysis methods around ten kilograms of sediment was collected from beneath an aqueous layer. From collected samples stones, gravels, plant materials and shells were removed. After thoroughly homogenizing the remaining sample by cone formation around 3.0 kg of composite sample was transferred to pre-cleaned polyethylene plastic bag. Keeping the plastic bag in ice box the sample was transported to laboratory.

Fish sampling and transportation

To get around 200 g composite fish tissue from each species in accordance with [11] method of fish sampling and analysis, Ten Tilapias (Oreochromis niloticus), fifteen Barbus (Barbus intermedius) and eight Catfishes (Clarias gariepinus), were caught with gillnets in Winter season. The collected fish samples were dissected with plastic knives on plastic meat chopper carefully. The composite samples of each fish muscles, gills and livers were transferred to labeled plastic bags and the plastic bags and their contents were kept in ice box and transported to laboratory.

Sample preparation

For fish sample preparation optimized procedure adopted by Kebede and Wondimu was used. In digestion procedure 1.0 g muscle or 0.5 g gill/liver was placed in 125 mL beaker and by 6 mL HNO₃ and 2 mL HClO₃ were added and the mixture was heated at 180°C for 90 minutes in watch glass closed beaker. After 115 min of digestion colorless digestate and its respective washing was transferred to 25 mL volumetric flask and diluted to the mark by deionized water for FAAS analysis.

Water sample was digested by optimized procedure [12]. In the procedure 100 mL aliquot of representative water sample was placed in 150 mL beaker and 3 mL of HNO₃ was added then digestion continued in watch glass closed beaker for 1 hour at 120°C; after 5 min cooling extra 3 mL HNO₃ was added and digestion continued for 40 min at 180°C again after another 5 min cooling by adding 10 mL 1:1 HCl to dissolve silicates from resulting digestate digestion continued for 20 min at 240°C. After 130 min beaker walls and watch glasses were washed with deionized water and the resulting washings were filtered to remove silicates and other insoluble materials that could clog the nebulizer. Finally the filtrate was transferred to 100 mL volumetric flask and diluted to the mark by deionized water for AAS analysis.

Optimizing the procedure adopted by Tolla digestion of sediment was carried out. In working procedure 0.5 g sieved grains of sediment sample was placed in 100 mL Erlenmeyer flask and 6 mL HNO₃ and 2 mL HClO₃ was added. The resulting mixture was heated for 105 min at 180°C. After 5 min of cooling 3 mL H₂O₂ was added and heating continued for 10 min at 240°C. The digestate produced by the procedure was dissolved in 10 mL 30% HNO₃ and filtered using 0.45 μm Whatman filter paper to remove silicate residue. Then, the filtrate was diluted to 50 mL by 3% HNO₃ in volumetric flask for FAAS analysis.

Quality control measures

Samples were prepared after verifying the methods were applicable for their intended purposes. Determined analytical methods validation criteria were: method detection limit almost less than 0.01 μg/g (fish and sediment sample) and μg/mL for water sample; matrix dependent accuracy (%R = 84.18-102.52) and precision (RPD = 1.02-13.85); repeatability with RSD below 5% and within lab reproducibility was also with RSD was all below 10% for all samples of each metal. This is an indication of practical utility of the method for trace metal analysis [12-14].

Sample prepared by optimized and validated procedures was analyzed by constant evaluations of quality of the result generated by quality control sample analysis. To control the performance of
optimized instrumental conditions and validated analytical method throughout; analysis of instrument quality control samples (IQCS) and method quality control samples (MQCS) were done. From experimental results and based on [12,13,15] all quality control sample analysis results were acceptable. In addition absence of field sample contamination was observed from analysis results of field black which has readings below method detection limits for all metals. Therefore, analytical results generated during this study can be used for decision making.

Human and fish risk assessment analysis

The human risk assessment was indicated by calculated hazard quotient (HQ). To calculate it estimated daily intake (EDI) was calculated by taking 200 g/year of Ethiopians fish consumptions [16] and the average body weight of Ethiopian as 55 Kg using following equation:

$$EDI = \frac{Cf \times DF}{BW_{av}}$$

Where: $Cf =$ average dry weight concentration of metals in fish filet
$DF =$ Daily avenge fish consumption of Ethiopian
$BW_{av} =$ Average body weight of Ethiopian

From above calculated EDI and by reference dose (RfD) established [13] HQ was calculated using:

$$HQ = \frac{EDI}{RfD}$$

Fish risk assessment was done by calculating bioconcentration factor (BCF) from average concentration in organism tissue and concentration in water using following equation:

$$BCF = \frac{Cf}{Cm}$$

Where $Cf =$ average dry weight concentration of metals in fish filet
$Cm =$ average wet weight concentration of metals in water

Results and Discussions

Moisture content of fish

Total moisture content of fish tissue was determined by procedures [17]. The results obtained are shown in Table 1 below as percentage of moisture content.

<table>
<thead>
<tr>
<th>Fish species</th>
<th>Tissue</th>
<th>% moisture content (n =3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tilapia</td>
<td>Muscle</td>
<td>83.84 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>Gill</td>
<td>82.86 ± 0.71</td>
</tr>
<tr>
<td></td>
<td>Liver</td>
<td>78.22 ± 0.38</td>
</tr>
<tr>
<td>Barbus</td>
<td>Muscle</td>
<td>77.93 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Gill</td>
<td>71.02 ± 0.16</td>
</tr>
<tr>
<td></td>
<td>Liver</td>
<td>70.56 ± 0.96</td>
</tr>
<tr>
<td>Catfish</td>
<td>Muscle</td>
<td>70.04 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Gill</td>
<td>70.29 ± 0.29</td>
</tr>
<tr>
<td></td>
<td>Liver</td>
<td>75.25 ± 0.20</td>
</tr>
</tbody>
</table>

Table 1: Total moisture content of fish tissue (muscle, gill and liver) of each fish.

<table>
<thead>
<tr>
<th>Fish Tissue</th>
<th>EDT</th>
<th>EDTs</th>
<th>Water</th>
<th>Sediment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>0.31 ± 0.01</td>
<td>0.84 ± 0.06</td>
<td>0.41 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>3.65 ± 0.03</td>
<td>7.05 ± 0.06</td>
<td>5.28 ± 0.25</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>2.53 ± 0.03</td>
<td>4.04 ± 0.08</td>
<td>3.29 ± 0.06</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>3.82 ± 0.04</td>
<td>5.16 ± 0.23</td>
<td>7.90 ± 0.29</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>55.12 ± 1.13</td>
<td>31.52 ± 1.19</td>
<td>71.55 ± 1.38</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.73 ± 0.03</td>
<td>5.16 ± 0.12</td>
<td>3.42 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>32.29 ± 1.12</td>
<td>41.84 ± 1.16</td>
<td>53.87 ± 1.5</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0.76 ± 0.02</td>
<td>1.48 ± 0.06</td>
<td>0.83 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>2.17 ± 0.13</td>
<td>3.21 ± 0.03</td>
<td>2.73 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>0.23 ± 0.01</td>
<td>0.51 ± 0.01</td>
<td>0.32 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>3.18 ± 0.07</td>
<td>4.63 ± 0.03</td>
<td>5.15 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>2.13 ± 0.03</td>
<td>3.12 ± 0.02</td>
<td>3.54 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>4.23 ± 0.03</td>
<td>3.61 ± 0.02</td>
<td>6.28 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>24.98 ± 1.27</td>
<td>22.26 ± 1.22</td>
<td>37.96 ± 1.14</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.52 ± 0.01</td>
<td>3.34 ± 0.04</td>
<td>2.45 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>21.74 ± 1.01</td>
<td>34.56 ± 1.24</td>
<td>27.62 ± 1.01</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0.53 ± 0.01</td>
<td>1.05 ± 0.05</td>
<td>0.73 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>1.67 ± 0.12</td>
<td>1.42 ± 0.02</td>
<td>2.06 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>0.18 ± 0.01</td>
<td>0.24 ± 0.01</td>
<td>0.16 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>2.21 ± 0.04</td>
<td>4.43 ± 0.03</td>
<td>6.20 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>1.26 ± 0.02</td>
<td>2.32 ± 0.03</td>
<td>2.23 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>2.11 ± 0.01</td>
<td>4.62 ± 0.05</td>
<td>3.27 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>18.27 ± 0.24</td>
<td>15.13 ± 0.30</td>
<td>25.07 ± 1.03</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.33 ± 0.01</td>
<td>0.84 ± 0.04</td>
<td>0.41 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>12.60 ± 0.06</td>
<td>15.76 ± 0.08</td>
<td>13.58 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0.25 ± 0.02</td>
<td>0.74 ± 0.01</td>
<td>0.81 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>1.23 ± 0.04</td>
<td>2.14 ± 0.01</td>
<td>1.56 ± 0.07</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Levels of trace metals (average ± Sd, n =3, in μg/g for sediment and mg/L for water) in Tendaho reservoir sediment and water samples.
In Barbus: gill > liver > muscle for Cu, Mn, Pb, Zn and Ni; liver > gill > muscle for Co and Cr; liver > muscle > gill for Fe and gill > muscle > liver for Cd. The metal content determined in the three fish species is in the order: Catfish > Tilapia > Barbus in Cd, Co, Cu, Fe, Pb and Zn content in all tissues. Their Mn content is in order: Tilapia > Catfish > Barbus in muscle, Catfish > Barbus > Tilapia in gill, Catfish > Tilapia > Barbus in liver, Cr exist in the order: Catfish > Tilapia > Barbus in muscle and gill, Catfish > Barbus > Tilapia in liver whereas Ni exist in the order: Catfish > Tilapia > Barbus in muscle and liver and Catfish > Barbus > Tilapia in gill.

Exposure of fishes and humans with trace metals

Bioconcentration factor (BCF) calculated (Table 4) is the highest in Catfish for all metals except for Mn which maximum in Tilapia. For remaining two fishes BCF in the order: Tilapia > Barbus. BCF existence in low (<250) level indicates, each fish species excrete trace metal after ingesting or do not consume in excess from water [19].

From hazard quotient (HQ) calculated (Table 5) and according to [20,21] values found are in no hazard level (<0.1) for all metals in the three fish species. Therefore, it is an indication for absence of any hazardous consequences on consumption of the fish species. HQ (Figure 2) is highest in Catfish for all metals except Mn and the least in Barbus. Therefore, trace metals exposure from eating catfish is higher than either of the two species.

Statistical analysis

Two-way ANOVA results confirmed that there was a significance difference in levels of trace metals between fish tissues and within tissues of different fishes (P-value < 0.05). However, multiple comparison by Post Hoc test at 95% CI indicated absence of significant difference (P-value > 0.05) between Cu and Pb in gills, Cd and Pb; Cd and Cr; Co and Mn; Cu and Ni; Pb and Cr in muscles and Cd and Cr; Co and Mn; Pb and Ni in livers.

Comparisons of results

Metals levels comparisons of present study with related works in Kubanni Reservoir and Aladja River of Nigeria indicate that except zinc and manganese all metals levels were lower in Tendaho Reservoir water (Table 6). Kubanni Reservoir has higher levels of all metals whereas Aladja River has higher levels of all compared metals excluding zinc and manganese as compared to study area. The Ethiopian Environment Protection Agency (EEPA) guide lines value comparisons with present study also revealed that the levels of manganese, iron, lead and chromium were higher and levels of copper and zinc lower in the study area as compared to safe guideline for aquatic organisms. This indicates that the presence of either natural or anthropogenic sources of manganese, iron, lead and chromium in the study area may affect aquatic organisms.

Metals level of present study in sediment compared with related works in Kowsar Reservoir and Aladja River of Nigeria indicated that all metals levels were higher in Kowsar Reservoir whereas levels of Cd, Fe, Pb, Zn and Ni were lower in Aladja River as compared to Tendaho Reservoir water (Table 7). Aladja River has higher levels of manganese and chromium as compared to Tendaho Reservoir. The USEPA (2000) PEL guide lines value as compared with present study showed that all metal levels were below guide line in study area as compared to safe guide line for aquatic organisms. This indicated that amount of trace metals present around sediments of the reservoir pose no problem to aquatic organisms.

Fishes tissue metal levels comparisons with related work (Table 8). For Tilapia fish comparison with Asasa Tikurwuha and Aladja River of Nigeria indicate that all metals level excluding Co were higher in Tilapia of Tikurwuha whereas Aladja River has lower levels of all metals as compared to Tilapia from Tendaho Reservoir. Trace metals level in Catfish muscle of present study comparison with Aladja River of Nigeria indicates that levels of Pb, Cr and Ni were higher in Aladja River whereas levels of Cd, Mn and Zn were higher in Tendaho Reservoir Catfish muscle. Comparison of the present study with the permissible limits set by WHO (1989) guideline showed that the levels of Cd, Cu, Fe, Pb, Zn and Cr were below the acceptable limits. However, Mn and Ni level was slightly higher than the permissible limit but the existence of these metals in acceptable limits according to the USFDA (1993) was shown in [22].

Conclusions

The analysis result with validated analytical method with acceptable accuracy, precision and quality control measures showed that excepting Zn, Mn and Co (fish > sediment > water) in metals distribution comparison of fishes with their environment exist in the order: sediment > fish tissue > water. This indicates that excluded metals taken by fishes more for their physiological functions as compared to other metals from their environment.
Regardless of the type of fish species, the levels of almost all metals were higher in detoxification organs (gill and liver) than muscle. This indicates that the rate of detoxification of trace metals from fishes body is higher than the rate of accumulation in their muscle. This is also in very good agreement with calculated low BCF and two-way ANOVA analysis results (P-value < 0.05). Among fish species, the highest levels of major metals existed in Catfish as observed from two-way ANOVA analysis result (P-value < 0.05) and the highest calculated BCF compared to other fish species. This may be due to carnivores feeding habit of the fish as seen during dissection, low sequestering tendency (higher BCF) of trace metals and more susceptibility of this species for trace metal pollutant compared to Tilapia and Barbus intremidus.

Comparison of results with related works indicated that the majority of trace metals from fish muscle and their environment of this study were lower than the others indicating that the area is not polluted by trace metal pollutants as much as those compared. On the other hand comparison results with guide lines showed that for water sample Mn, Fe, Pb and Cr were higher in the study area than [23-26]. This clearly indicates the presence of either natural or anthropogenic sources of Mn, Fe, Pb and Cr to the water body which may affect aquatic organisms.

Regarding customers’ safety, absence of any trace metals hazardous exposure was observed. This was guaranteed by a low calculated HQ values and all metals were below the WHO (1989) and [26-39] guidelines safety limits. Although in this study there is no trace metal exposure of water, sediments, biota and fish consumers, due to rapid urbanization, industrialization and high degree of exposure of reservoir for aquatic pollutants needs continuous follow up and monitoring to avoid unexpected events like minamata disease.

References

Table 6: Comparison of trace metals levels in water of present study with related works and guide line standards for the safety of fish food consumers (all in μg/g, dry weight).

Table 7: Comparison of trace metals levels in sediment of present study with related works and guide line standards for protection of benthic organisms (all in μg/g, dry weight).

Table 8: Comparison of trace metal levels in fish muscle of present study with related works and guide line standards for the safety of fish food consumers (all in μg/g, dry weight).


