

DEBRE BIRHAN UNIVERSITY

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DETERMINATION OF SOME SELECTED HEAVY METALS(Cu, Cd, Cr, Pb,and Ni)
SEDIMENT AND TILAPIA(*OREOCHROMISNILOTICUS*) FISH SPECIES FROM CHAMO
LAKE, SOUTHERN ETHIOPIA

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APPROVAL SHEET I

This is to certify that the thesis entitled “DETERMINATION OF SOME SELECTED HEAVY METALS IN SEDIMENT AND TILAPIA (*OREOCHROMISNILOTICUS*) FISH SPECIES FROM CHAMO LAKE, SOUTHERN ETHIOPIA” submitted in partial fulfillment of requirements Degree of Master Science in Chemistry, College of Natural and Computational Science, Debre Berhan University and is a faithful record of original research work carried out by Belaynesh Sema under my guidance and supervision of Alemnew Berhanu (PhD).

No part of this thesis has been submitted for any other degree or diploma.

It is further certified that the assistance and help received by him from various sources during the course of the investigation has been duly acknowledged. Therefore, I recommend that it be accepted as fulfilling the thesis requirements.

Alemnew Berhanu(Ph.D.)

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APPROVAL SHEET II

We, the undersigned members of the boarded of the examiners of the final open defense by Belaynesh Sema have read and evaluated his thesis entitled “DETERMINATION OF SELECTED HEAVY METALS(Cu, Cd, Cr, Ni, andPb) IN SEDIMENT AND TILAPIA(*OREOCHROMISNILOTICUS*) FISH SPECIES FROM CHAMO LAKE, SOUTHERN ETHIOPIA” and examined the candidates. This is, therefore, to certify that the thesis has been accepted in partial fulfillment of the requirements for the degree of Masters of Science in Chemistry.

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STATEMENT OF THE AUTHOR

I declared and affirm that the work described in this thesis is my own original work and this thesis where works of any other investigator has been properly recognized through citation. This thesis has been submitted in partial fulfillment of the requirements for MSc degree at Debre Berhan University. I also certainly declared that this thesis has neither been submitted elsewhere, nor is being currently submitted; for the award of any academic degree, diploma, or certificate.

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ABBREVIATIONS AND ACRONYM

SD- standard deviation

WHO- world health organization

FAO- Food and migration organization

AAS-Atomic absorption spectrophotometre

DWAF-Department of water and forestry

USEPA-United state environmental protection agency

SPSS- statistical package program

ANOVA- Analysis of variance

FRDD- fisher resources development department

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ABSTRACT

In the present study, some heavy metal Cd, Cu, Ni, Pb and Cr were determined in sediment and some tissue of tilapia (Oreochromis niloticus) fish from Chamo lake which is an important water source for irrigation. Heavy metal levels in sediment and fish sample were analyzed by Atomic absorption spectrophotometry (AAS). The result of the heavy metal (Cd, Cu, Cr, Pb and Ni) levels in the sediment were compared with national and international standard sediment quality guidelines as well as literature data reported of the lake. The analysis of heavy metals in sediment indicated that among the five heavy metals were present. The result showed that highest Cd concentration (6.07mg/kg) Cd was recorded. followed by Cu, Pb, Ni, Cr, and Cu. The heavy metals concentration was found to decrease sequence of Tilapia (Oreochromis niloticus) fish tissue of gill > liver > muscle. In general the heavy metals concentration in the fish tissue decreased in sequence for liver [as Cu > Cd > Cr > Ni > Pb, for gill as Cd > Cu > Ni > Cr > Pb, for muscle as Cu > Cd > Cr > Ni > Pb]. The result showed the concentration of Cd, Cu, Cr, Ni and Pb in muscle tissue of tilapia (Oreochromis niloticus) fish from lake chamo were below the value of WHO. While the concentration of Cr in muscle tissue of fish from lake chamo was higher than WHO. Therefore the muscle part of tilapia fish is safe interim of Cd, Cu, Ni, and Pb. But interim of Cr bad or may cause hazard to the fish. So that the people should not be consume the fish in this area. due to that the high intake of heavy metals in our body can cause bad impact towards health.

Key words: Heavy metals, tilapia fish, sediment

1. INTRODUCTION

1.1 Background of the study

Metals are elements, present in chemical compounds as positive ions, or in the form of cations (+ ions) in solution. Metallic elements which have high atomic weight and density much greater (at least 5 times) than water are known as heavy metals. Heavy metals are among the most serious environmental pollutants due to their high toxicity, abundance and ease of accumulation by various plant and animal organisms.

The increase in Persistent heavy metals in increase in sediments can be attributed to the contribution of effluent from wastewater treatment, plants, industries, mining, power stations and agriculture (Guevara-Riba *et al.*, 2004). Heavy metals are extremely persistent in the environment. They are non-biodegradable and non-thermo degradable and therefore readily accumulate to toxic levels (Guevara-Riba *et al.*, 2004). They are released into the environment from natural as well as anthropogenic activities.

Ethiopian Rift Valley Lakes which comprises of seven principal Lakes are an important area for commercial fisheries. The Lakes are also used for recreation, irrigation and industrial purposes (Gebremariam and Pearce, 2003). Despite the growing influences from natural and anthropogenic origins there exists a general belief that presumes the 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 (Gebremariam and Pearce, 2003; Guevara-Riba *et al.*, 2004).

Heavy metals have wide environmental dispersion with the tendency to accumulate in selected tissues of the living organisms and have the overall potential to be toxic even at relatively low levels of exposure. Heavy metals enter the fish through gills, skin, oral in food and water. In the fish's body, the metal is transported through the blood stream and either stored, transformed or eliminated in the liver, kidney or the gills (Mozaffarian and Eric, 2006; Mwangi, 2013). At high concentration, they are dangerous because they accumulate faster in living things.

The pollution of the aquatic environment with heavy metals has become worldwide problem during recent years. Because they are indestructible and most of them have toxic effects on

organism (Macfarlane and Burchett, 2000). Among environmental pollutants, metals are of particular concern, due to their potential toxic effect on the aquatic environment and ability to bio accumulate in the aquatic ecosystem (Censi et al., 2006). Heavy metal concentration in an ecosystem is usually monitored by measuring their concentrations in sediments and biota (Camusso et al., 1995), which attain considerable concentration in sediments and biota (Namminga and Wilhm, 1976). Heavy metals including both essential and non essential elements have a particular significance in ecotoxicology, since they are highly persistent and all have potential to be toxic to living organisms (Storelli et al., 2005). Studies of heavy metals in fish and sediments (Ozmen et al., 2004, Begum et al., 2005; Fernandes et al., 2008) were a major environmental focus especially during the last decade. Sediments are important sinks for various pollutants. Heavy metals also play a significant role in the remobilization of contaminants in aquatic system under favorable conditions and the interaction between water and sediment. Fish sample can be considered as one of the most significant indicators in fresh water systems for the estimation of metal pollution level (Rashed, 2001). The commercial and edible species have been widely investigated in order to check for those hazardous to human health (Begum et al., 2005). Heavy metals such as copper, chromium, and nickel are essential metals since they play an important role in biological systems, whereas cadmium and lead are non essential metals, as they are toxic. Even in trace amounts (Fernandes et al., 2008). For the normal metabolisms of the fish, the essential metals must be taken up from food or sediment (Canhand Atli, 2003). These essential metals can also produce toxic effects when the metal intake is excessively elevated (Tuzen, 2003). Of different pollutants, heavy metal pollution of aquatic environment has become a great concern in recent years because they are very harmful as a result of their non-biodegradable nature, long biological half-life and their potential to accumulate in different body parts of the organism. They can also be concentrated along the food chain, producing their toxic effect at points far removed from the source of pollution. Thus, compared to other types of aquatic pollution, heavy metals pollution is less visible, but its effects on the ecosystem and humans can be intense and very extensive (Edem et al., 2008).

The toxicity of trace metals will vary greatly between organisms in the same trace metals, and between trace metals for the same organisms. Furthermore, trace metals will not necessarily follow the same rank order of toxicities between organisms, depending on differences between uptake rate, detoxification rates and excretion rate of the different

organisms. However, the general order of toxicity of heavy metals is $Hg > Ag > Cu > Cd > Zn > Ni > Pb > Cr > Sn$ and so on (Luoma and Rainbow, 2008). Heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs (WHO, 1984)

Fish is a basic and important food for human nutrition (Abdel-Beki et al., 2011) such as fatty acid in fish that can reduce the risk of heart diseases and stroke due to their contribution in lowering the cholesterol levels in blood and also provides minerals and vitamins (Al-Busaid et al., 2011). The presence of heavy metal in fish gives impact to the human health. Besides, fish is a very suitable bioindicator of heavy metal contaminations (Karmalo *et al.*, 2007). The parts of fish that take up heavy metals from the gills, body surface, digestive tract, muscle and liver (Bashis et al., 2012). Figure 1 shows the example of edible part of fish that use for the analysis.

Moreover, gill is a modest accumulation of heavy metal even though it has low metabolic activity due to the high adsorption of metal on the gill surface of higher metals (Canali M and Atli G et al., 2003). Besides, water becomes the main source of contamination due to the high heavy metal contents in the gills (Bervoets., L., and Blus, R. 2003). While, the concentration of heavy metal in fish muscle is always low compared to the other tissues of fish (Z., Jovanov., 2001) due to their low metabolic activity (Uluturham. E and Kucuksegin. F., 2007). However, it is still important to compare muscles in order to determine the safe levels. This is because the consumption of fish muscle is the greatest mass compared to the other part of the fish (Zhuang P. and Zou B., 2013). The higher intake of heavy metal in our body can cause bad impact towards health (Ahmad, A., *et al* and Othman M *et al.*, 2010)

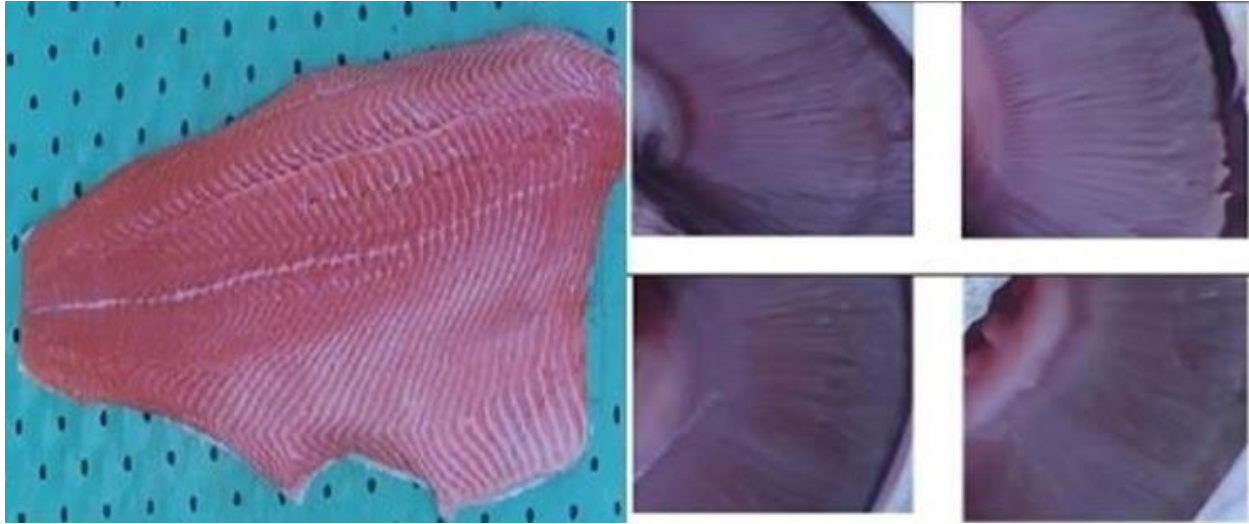


Figure 1. The edible parts of the fish's body (muscle and gill)

Source Dowlat, et al (2013);stein., et al(2007)

1.2 STATEMENT OF THE PROBLEM

Lake Chamo the research area is one of the lakes found in the Ethiopia Rift valley. It is a fresh closed lake, playing an important role in the lives of many people in the region. It is the source of the commercial fishery. The lake is influenced by human activities such as agricultural practices, deforestation and discharge of domestic sewage (AbaynehAtaro et al., 2003) solid, sediment, [fishes] and aquatic plants. Fish are used as bio indicator of aquatic eco system for estimation of heavy metal pollution and potential risk for human consumption (Agrawal et al., 2007). These may make the lake Chamo to receive different kinds of pollutant in the lake. It contains four types of fish species which are (1) Nile tilapia (*Oreochromis niloticus*) locally known as korosso, (2) Burbus (*Burbus intermedius*) locally known as Barbo, (3) Catfish (*Claris gariepinus*) locally known as ambaza and (4) Nile perch (*Lates niloticus*) locally known as nech asa (LFDP, 1997). AbaynehAtaro et al. (2003) have also stated the quantitative data on trace element in fish species from Chamo lake are scarce. The study is conducted on the edible tissue (Fillet) of Nile Tilapia fish species locally known as korosso which are the most common types of fish consumed by the local people and found widespread in the lake Chamo. Therefore, this research has been carried out to determine the level of some heavy metals in tissues of Nile tilapia (*Oreochromis niloticus*) fish species and sediment from Chamo lake. This provided an insight on the presence or absence of heavy metals in fish and sediment to ensure that levels of heavy metals whether meet agreed local or international standard requirement. In addition to this

it might also be helpful to monitor the lake quality by determining the heavy metals. To the best of our knowledge from literature survey, there is no work that has been carried out on the environmental quality of the lake and the lack of environmental regulation.

However, the consumer of this area used this fish species as commercially important, but they didn't know the effect of heavy metal within the fish body. So this study was important to take measures on the level of some heavy metals (Cd, Cu, Cr, Ni and Pb) in tilapia fish species and sediment in this lake and to inform the toxicity amount of this heavy metal in the fish.

This study is undertaken to determine the current level of the concentrations of the heavy metals such as cadmium (Cd), copper (Cu), lead (Pb), nickel (Ni), and chromium (Cr) in sediment and in the edible tissue of the Tilapia fish in Lake Chamo. As far as our knowledge, there is no previous work done on the determination of heavy metals Cd, Cu, Cr, Ni and Pb in sediment and Tilapia fish species from Chamo lake.

1.3.1 GENERAL OBJECTIVES OF THE STUDY

To determine the level of some selected heavy metals in sediment and Tilapia fish species from lake Chamo.

1.3.2 SPECIFIC OBJECTIVES

- To determine Cu, Cd, Pb, Ni, and Cr concentration in sediment and tilapia fish samples from lake Chamo.
- To compare the results with previous literature on the same fish species.
- To compare the concentration of Cu, Cd, Pb, Ni and Cr in sediments and tilapia fish species of the study area with national and international guidelines.

1.4 SIGNIFICANCE OF STUDY

The study is necessary, due to a large number of people consume tilapia fish species in this area. However, fishes are good indicators of metal contamination in aquatic system because the consumption of contaminated fish causes the effects to human health. It was also important to detect the concentration of selected metals Cu, Pb, Ni, Cr and Cd in sediment and tilapia fish species from Chamo Lake. In general, the study is important to take proper measure of heavy metals in fish and sediment in order to keep fish safe from contamination and to maintain the

aquatic ecosystem. To report the information to the other researchers because there was no literature report on selected metals such as Cu, Pb, Ni, Cr and Cd concentrations in sediment and tilapia fish species.

1.5 SCOPE AND LIMITATION OF THE STUDY

This study was focused only some selected heavy metals Cu, Pb, Ni, Cr and Cd concentration in sediment and Tilapia fish species from Lake Chamo. To compare the concentration of Cu, Cd, Cr, Pb, and Ni in sediment and tissue of Tilapia (*Oreochromis niloticus*) fish species of lake Chamo with national and international guidelines.

UNIT TWO

2 REVIEW OF LITERATURE

2.1. Environmental pollution

Environmental pollution is caused due to the discharge of substances or energy into air, water, or land that may impart acute (short-term) or chronic (long-term) detriment to the quality of life. According to Tokalioglu *et al.* (2003) and Moja., (2007), the impacts of environmental pollution is insidious and its harmful effects only become apparent after periods of exposure. For this reason environmental monitoring is recognized as being vitally important in detecting the level and types of pollutants, and their source. Furthermore this monitoring helps to take measures to mitigate the effect in those seriously polluted areas. 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 (Calamari & Naevel., 1994).

The term heavy metal is a general collection term applying to the group of metals and metalloids with an atomic density greater than 6g/cm^3 (Alloway and Ayres, 1993). Commonly the term is used to refer to elements that are associated with pollution and toxicity problems. Common urban nonpoint sources include runoff from streets or fields; such runoff contains all sorts of pollutants, from heavy metals to chemicals and sediments. Rural source of non point pollution is generally associated with agriculture, mining, or forestry (Botkin and Keller, 2007).

2.2 Heavy Metals in the Environment

The heavy metal concentrations in the environment are due to natural sources (rock weathering, soil erosion, dissolution of water soluble salts) as well as anthropogenic source such as municipal wastewater, manufacturing industries, and agricultural activities (Güven and Akýncý, 2008).

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. The heavy metals risk poses to human and animal health is provoked by their Metals can be retained

for long periods of time after entering the environmental medium such as soil (Tokalioglu, *et al.*, 2003; Moja, 2007). The natural levels of metals are normally increased through various anthropogenic processes. 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 (Weiner, 2008). 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 from localized inputs which may be acutely or chronically toxic to aquatic life within the affected area (Calamari & Naevel, 1994).

2.3 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) (Calmano *et al.*, 1993).

However, several mechanisms indicate that heavy metals in water may be removed due to (1) adsorption onto particulate; (2) chemical transformation into an insoluble form; (3) precipitation and (4) sedimentation (Balasubramania *et al.*, 1997). Adsorption could be the first step in the ultimate removal of metal from water. In the Adsorption could be the first step in the ultimate removal of metal from watercourse of distribution, permanent or temporary storage of metal takes place in the sediments of both freshwater and marine environments (Aksu *et al.*, 1998). Redox processes may change the properties of sediments and affect the composition of interstitial water (Vale *et al.*, 1998). Reworking of the sediments by organisms will also bring heavy metals from sediments to the surface water. 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 bioaccumulation phenomenon. Some

heavy metals have been shown to undergo biomagnifications through the food chain (Suter, 1993).

2.4 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 (Agrawal *et al.*, 2007). Bioaccumulation of metals in fish takes place directly, from the water by gills and indirectly from food (Barron, 1990). The metals such 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 essential trace metals are only used in trace amounts by the organism and usually they are found in small concentration in the environment. The excess amount of heavy metal in the organism can be regulated by homeostasis (Bryan and Hummerstone, 1973). But, if the heavy metal concentration at the source of supply such as water and food is too high, the homeostasis mechanism ceases to function and the essential heavy metal act in either an acutely or chronically toxic manner. The function of uptake and excretion in fish is determined the accumulation of metal in fish. The gills are likely sites of metal uptake from water due to their large surface area and the close proximity of the internal constituent of the body and external environment (Wepener, 1997). Dallingier *et al.*, 1987) stated that as far as fish is concerned, there are three possible ways by which metals may enter the body (i) the body surface, (ii) the gill, (iii) the alimentary tract.

2.5. Bioavailability of Metals

The toxicity of trace pollutants to aquatic organisms is related to the bioavailable fraction of contaminants available for assimilation. Bioavailability 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 (Wang *et al.*, 2002). Bioavailability and bioaccumulation of contaminants in an aquatic environment is mainly dependent on the partitioning behavior or binding strength of the contaminant to sediment. Dissolved or weakly adsorbed contaminants are more bioavailable to aquatic biota compared to more structurally complex mineral-bound contaminants which may only become bioavailable upon ingestion with food. For example, metals in the aquatic phase are the most bioavailable compared to particulate, complexed or chelated forms. Cadmium is less bioavailable in seawater than freshwater due to complexation with chloride ions and organic

binding competition with calcium and magnesium, whereas copper bioavailability increases with increasing salinity (Forstner *et al.*, 1989). 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. Weathering or aging of metals over time also can reduce their bioavailability. Hydrogen ion activity (pH) is probably the most important factor governing metal speciation, solubility from mineral surfaces, transport, and eventual bioavailability of metals in aqueous solutions. 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 of aquatic organisms (Salomons, 1995). Temperature exerts an important effect on metal speciation, because most chemical reaction rates, are highly sensitive to temperature changes (Elder, 1989). An increase of 10 0C can double biochemical reaction rates, which are often the driving force in earth surface conditions for reactions that are kinetically slow, and enhance the tendency of a system to reach equilibrium. Temperature may also affect quantities of metal uptake by an organism, because biological process rates typically double with every 100C temperature increment. Because increased temperature may affect both influx and efflux rates of metals, net bioaccumulation may or may not increase (Luoma, 1983).

In recent organic carbon-rich sediments, trapped interstitial fluids can commonly form a strongly reducing (anoxic) environment. The low redox potential in this environment can promote sulfate reduction and sulfide mineral deposition. During diagenesis, much of the non-silicate-bound fraction of potentially toxic metals such as arsenic, cadmium, copper, mercury, lead, and zinc, can be co-precipitated with pyrite, form insoluble sulfides, and become unavailable to biota. Seasonal variation in flow rates or storms that induce an influx of oxygenated water can result in rapid reaction of this anoxic sediment and thereby release significant proportions of these metals. Pyritization and/or de-pyritization of trace metals probably can be an important process in

controlling the bioavailability of many trace metals, especially in the aquatic environment (Morse, 1994).

2.6 Heavy Metals under the Study

Copper: is one of the world's most widely used metals. The most common copper-bearing ores are the sulfides, arsenates, chlorides, and carbonates (Weiner, 2008). 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 (Nussery, 1998). Copper is an essential trace element for plants, animals and even humans, and although the concentration of copper is usually low in nature, it happens in adequate quantities for growth in all aquatic environments. "It is required for bone formation, maintenance of myelin within the nervous system, synthesis of haemoglobin, component of key metalloenzymes, plus it forms an important part of cytochrome oxidase, and assorted other enzymes involved in the redox reactions in the cells of animals. It is also essential for cellular metabolism, where its concentration is well regulated, but becomes toxic at elevated levels" (Pelgomet *al.*, 1995). Although copper is important, it is toxic when concentrations exceed that of natural concentrations ($< 0.05 \mu\text{mol/L}$) (Stouthart *et al.*, 1996). The toxicity of copper in aquatic organisms is largely attributable to Cu^{2+} that forms complexes with other ions (Nussey, 1998). A reduction in water dissolved oxygen, hardness, temperature, pH, and chelating agents can increase the toxicity of copper (Nussey, 1998). Organic and inorganic substance can easily complex the cupric form of copper, which is the most common speciation of this metal, and it is then absorbed on to particulate matter. Therefore, the free ion is rarely found except in pure acidic soft water.

The chemical speciation of copper strongly depends on the pH of water (Stouthart *et al.*, 1996). Copper, in water, particulate at high pH (alkaline) and is thus not toxic, while at low pH (acidic) it is mobile, soluble and toxic (Nussey, 1998). Acute poisoning result from ingestion of excessive amount of copper salt and can lead to "nausea, vomiting, stomachache and diarrhea and may produce death. Copper fume, dusts and mist from industrial exposure affect to upper respiratory tract. At low concentration, copper can result in anemia, gastrointestinal disturbances, bone development abnormalities, and death. Copper toxic effects in fish include; change biochemistry, anatomy, physiology and behavior.

It damages the gill and head area of fish, could probably cause mucous to accumulate on the gill area” (Lewis, 1971).

Lead:is major sources in the environment are automobile exhaust, industrial wastewater, wastewater sludge and pesticides (Balbaet *al.*, 1991). The global mean lead concentration in lakes and rivers is estimated to be between 1.0 to 10.0 µg/L (Weiner, 2008). Lead enters the aquatic environment through erosion and leaching from soil, lead dust fallout, combustion of gasoline, municipal and industrial waste discharges, runoff of fallout deposit from streets and other surfaces as well as precipitation (DWAF, 1996).

Lead is toxic and a major hazard to human and animals. Lead has two quite distinct toxic effects on human beings, physiological and neurological. “The relatively immediate effects of acute lead poisoning are ill defined symptoms, which include nausea, vomiting, abdominal pains, anorexia, constipation, insomnia, anemia, irritability, mood disturbances and coordination loss. In more severe situations neurological effects such as restlessness, hyperactivity, confusion and impairment of memory can result as well as coma and death” (Ansari, *et al.* 2004).

The main targets of lead toxicity are “the hematopoietic and nervous systems. Several of the enzymes involved in the synthesis of heme are sensitive to inhibition by lead. Besides this, the nervous system is another important target for lead toxicity, especially in infants and young children where the nervous system is still developing. Even at low levels of exposure, children may show hyperactivity, decreased attention span, mental deficiencies and impaired vision. Lead damages the arterioles and capillaries resulting in cerebral edema and neuronal degradation. Another system affected by lead is the reproductive system. The exposure can cause reproductive toxicity, miscarriages and degenerated offspring” (Kocak *et al.*, 2005).

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 ecosystems, dissolved nickel concentrations are generally between 0.005 and 0.01 mg/L (Galvin, 1996).

Chemical and physical degradation of rocks and soils, atmospheric deposition of nickel-containing particulates, and discharges of industrial and municipal wastes are released nickel into ambient waters (USEPA, 1986; WHO, 1991). The main anthropogenic sources of nickel in water are primary nickel production, metallurgical processes, combustion and incineration of fossil

fuels, and chemical and catalyst production (USEPA, 1986). The atmosphere is a major conduit for nickel as particulate matter. The atmospheric loading of nickel comes from both natural sources and anthropogenic activity. Nickel particulates eventually precipitate from the atmosphere to soils and waters. Soil-nickel enters waters with surface runoff or by percolation of dissolved nickel into ground water (Weiner, 2008).

Zinc: is a very common environmental contaminant and usually outranks all other metals and commonly found in association with lead and cadmium (Finkelman, 2005). Major sources of the zinc in aquatic environment include the discharge of domestic wastewater, manufacturing processes involving metals and fallout atmosphere.

Zinc is an essential element for human, animal, and certain types of plant. “The cell of living organisms contain zinc as one of the main components of various enzymes, such as carbonate anhydrase, carboxy peptidase, superoxide dismutase, lactase, dehydrogenase, phosphatase and glutamate dehydrogenase. It is also necessary for a healthy immune system, cell division and synthesis of protein and collagen, which is great for wound healing and healthy skin. However, a higher amount of it can cause anemia, pancreas damage and lower levels of high density of lipoprotein cholesterol” (Finkelman, 2005). 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 (Counture and Rajotte, 2003). Acute toxic zinc concentrations result in gill damage, which interferes with respiration, leading to hypoxia. Chronically toxic are generally an 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 (Somasundaram *et al.*, 1984).

Zinc toxicity is modified by water, chemical factors, including dissolved oxygen concentration, hardness, pH and temperature of the water (Nussey, 1998) and can also be changed through other heavy metals compounds and alkaline earth metals. High temperature tends to increase zinc toxicity, while an increase in water hardness, alkalinity and organic chelators can reduce its acute lethality and low dissolved oxygen content in water increases the toxicity of zinc (Chapman, 1978)

2.7. Relevant Studies in Ethiopia and Other African Countries

AbaynehAtaroat *al.* (2003) studied trace metals in fish from Lake Hawassa and Ziway. The results indicated the range of concentration 1.03-2.78 $\mu\text{g/g}$ in Lake Hawassa and 1.03-1.98 $\mu\text{g/g}$ in lakeZiway for Cu and 23.04 -30.92 $\mu\text{g/g}$ in Lake Hawasa and 26.29-30.92 $\mu\text{g/g}$ in Lake Ziway for Zn. Theaccumulations of Pb and Ni were below 1.66 and 0.99 in Tilapia fish of both lakes. SelamawitGeta (2010) found 1.35 Cu, 0.35 Pb and 27.13 Zn in the muscle of Tilapia fish from Lake Ziway.

The concentrations of Pb in Lake Victoria ranged from 0.04 to 0.94 mg/L and its accumulation in the muscle of fish were ranged from 3.6 to 20.3 $\mu\text{g/g}$ as studied by Tole and Jenipher (2003) and Kisamo (2003) found the concentrations of Cu, Pb and Zn in water of Lake Victoria were >0.01mg/L, 0.35- 0.36-0.63 mg/L and 0.01-5.62 mg/L and their accumulaton in the range of 2.3 -6.6 $\mu\text{g/g}$, 0.01-28.0 $\mu\text{g/g}$ and 17-179 $\mu\text{g/g}$, respectively. Sanarathne and Pathirathe (2007) estimated the accumulation of heavy metals in fish inhabiting Bolgada Lake in Sri Lanka. The result showed that the accumulation ranged from 0.8 - 9.3 $\mu\text{g/g}$ wet mass for Cu, 0.1 - 3.0 $\mu\text{g/g}$ wet mass for Pb and 5.9 - 11.5 $\mu\text{g/g}$ wet mass for Zn. Saeed and Shaker (2008) assessed the heavy metals pollution in water and sediments and their effect on Nile Tilapia (*OreochromisNiloticus*) in the northern delta Lakes in Egypt. The results indicated that the concentrations of heavy metals in water were maximum at the Lake Manzala (1.36-0.68 mg/L for Cu and 0.32-0.66 mg/L for Zn) while the minimum at Lake Edku (0.002- 0.054 mg/L) but the highest Pb concentration was at the Borollus Lake (0.11-0.31 mg/L) and the lowest Lake Edku (ND – 0.084 mg/L).The accumulations of Cu, Pb and Zn were highest in the fish of Lake Manzala (44.84 $\mu\text{g/g}$ d.w for Cu, 10.1 $\mu\text{g/g}$ d.w for Pb and 212.44 $\mu\text{g/g}$ d.w for Zn) but the lowest accumulations were recorded at Lake Borollus for Cu (1.77 $\mu\text{g/g}$ d.w.) and for Zn (9.88 $\mu\text{g/g}$ d.w.), and at Lake Edku for Pb (0.59 $\mu\text{g/g}$ d.w)

UNIT THREE

3 MATERIALS AND METHODS

3.1 Description of Study area

Lake Chamo (Amharic; Chamo Hayk) is a lake in the Southern Nations, Nationalities, and the Peoples Region of Southern Ethiopia. It is located in the main Ethiopian Rift valley lake at an elevation of 1,235 meters. It is just to the south of Lake Abaya and the city of Arbaminch, east of the Guge mountains, and west of the Amaro mountains. Lake Chamo is 26 km long and 22 km wide, with a surface area of 551 km² and a maximum depth of 10 metres. The lake climate is further characterized by a high rate of evaporation (about 2300 mm per year on average) and the precipitation average of about 600 mm. The area in the past has been affected by global climate change with a shift to a decrease in precipitation peaks and with consequent impact on the lake. Earlier studies (Amha Belay and Wood, 1982) stated that Lake Chamo has a surface area of 551 km² and a maximum depth of 16m. However, according to Seleshi Bekele (2006), the surface area of the lake declined to about 335 km². Elizabeth Kebede (1996) reported a maximum depth of 13m.

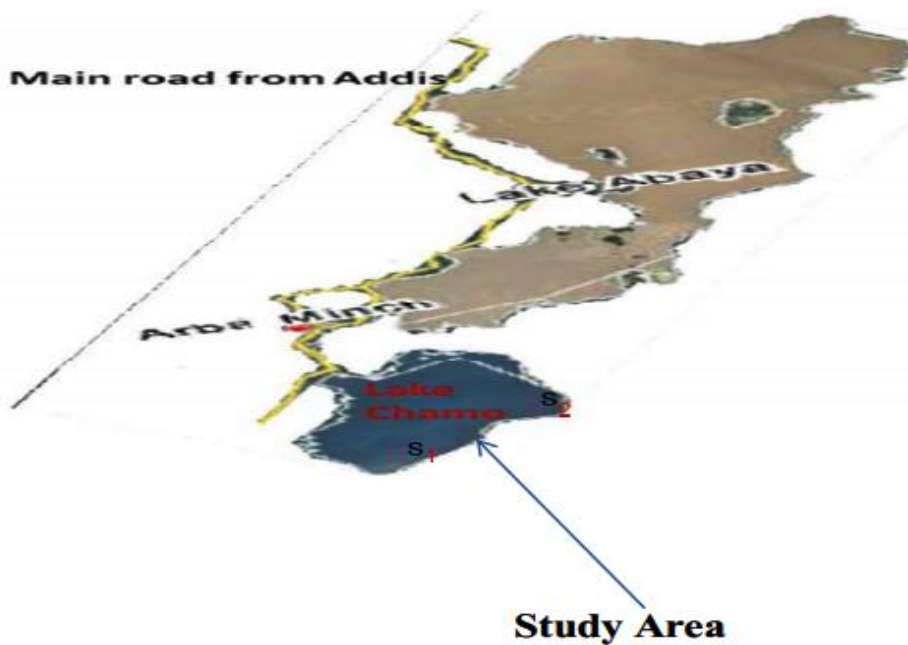


Figure 2. Map of Lake Chamo with sampling site in southern nation nationalities of people region.

3.2 Methods Using For Data Collection

3.2.1. Selection of sampling station

Two sampling sites were selected. Sampling site-1 (Figure 2) located the side of Arbaminch paradise park, which is near to Chamo lake named Chamo park 1. The site is close to highway, which sites were used during sampling period the sampling site in the Lake were selected by considering the source of pollution. Each selected sampling site has been receiving different types of pollutants from different source of pollution. Due to the sources of pollution in the lake, the may be receiving particulate pollutants related to motor vehicles.

Sampling site-2 (Figure2) located the side of Arbamich Nech sahar national park, which is located near Lake Chamo. It is commonly used for recreational purpose. The site name is Chamo park 2. It does not have point source of pollution from the agricultural land of the area.

3.2.2 Collection of sediment

Sediment samples were collected using grab sample from two sites, which are park one and park two. Then the samples were transported to the laboratory and air dried in the laboratory at room temperature. Once air dried sediment samples were powdered and packed in polyethylene bag and stored below 20C° prior to analysis.

3.2.3 Collection of fish sampl

The two tilapia fish species were caught and collected at each sampling site with the help of fishermen. The fish freshly collected fish species type, namely Nile Tilapia (*Oreochromis niloticus*) locally known as korosso. After collection, using a glove the fish to protect any contamination from the sample, then the samples were immediately dissected by plastic knife and carefully separate selected body part (gill, heart and muscle) and washed with tap water to remove dirt after that put the sample in sterile polyethylene bags and taken in an ice box. Tissue samples were placed in Aluminum foil, labeled and then frozen at -20C° in deep frozen until further pretreatment and analysis.

3.2.3 Instrumentations and Apparatus

The fish samples were oven-dried and ground in mortar and pestle. The 250 mL round bottle flask was used for digestion purpose and 50mL volumetric flask used for dilution. Atomic absorption spectrophotometer used for the analysis of heavy metals in sediment and fish sample.

3.2.4. Digestion of Sediment sample

The sediment sample was dried using air at room temperature. 1g of dried sediment was weighed and transferred into 250ml bottled flask and the mixture of 10ml nitric acid and 10ml Perchloric acid prepared in 1:1(v/v) ratio was added. The mixture was digested until a clear solution was appeared. Filter the solution in watchman filter paper in a 50mL volumetric flask and diluted in the de ionized water. After that the standard solution of Pb, Cu, Cd, Ni and Cr were prepared. Then react the sample and blank in atomic absorption spectrophotometer. From atomic absorption spectrophotometer absorbance of the sample was taken.

3.2.5. Digestion of Fish Sample

The samples were crushed using a clean mortar and pestle to produce powdered forms. 1 g of dried and powdered fish sample was weighed using an analytical balance. Each of 1 g of powdered sample was transferred into 250ml round bottle flask and the mixture of 10ml Nitric acid and 10ml hydrogen peroxide prepared in a 2:1 (v/v) ratio was added. The suspended mixture was digested for one hour, until a clear solution was obtained. Filter the solution in watchman filter paper in a 50mL volumetric flask and diluted in distilled water. After that, prepare standard solution of Pb, Cu, Cd, Ni and Cr. Then react the sample and blank in atomic absorption spectrophotometry. From atomic absorption spectrophotometry absorbance of the sample was taken

3.2.7 analysis of heavy metals

Concentration of Cu, Pb, Ni, Cr, and Cd were determined in sediment and fish samples. The analysis of heavy metals in sediment and fish samples were carried out by atomic absorption spectrophotometer and used for determination of metal concentration in the sample of fish and sediment.

3.2.6. Quality control and quality assurance

3.2.6.1 Reagents and standard solution

All chemicals were used analytical grade. Distilled water is used for dilutions throughout the study. Nitric acid, HNO_3 (69%), and hydrogen peroxide, H_2O_2 (30%), are used for digestion. Working standards were prepared by diluting concentrated stock solution of 1000 mg/L Cu, Pb, Ni, Cr and Cd in distilled water

3.2.6.2 Preparation of stock standard solution

Working standard solutions of lead (Pb), copper (Cu), chromium (Cr), nickel (Ni) and cadmium (Cd) were prepared from the stock standard solutions containing 1000 ppm of the element in 2 N nitric acid. Calibration and measurement of elements were done by using Atomic Absorption Spectrophotometer. The calibration curves were prepared for each element individually applying linear correlation by the least square method.

3.2.6.3 Calibration procedures

Calibration curves for each heavy metals were set to ensure the accuracy of an atomic absorption spectrophotometer and to confirm that the results of determination were true and reliable. The calibration of AAS was made with standard solutions. Appropriate working calibration standards were prepared by serial dilution of concentrated stock solution of 1000 mg/L for Cu, Pb, Ni, Cr, and Cd and blanks were tested into AAS and its absorbance was recorded. Calibration curves were plotted with different points for each metal standard solution using absorbance against concentrations (mg/L). After calibration using the standard solutions, the sample solutions were tested into the AAS instrument and direct reading of the metal concentrations were recorded. The concentration of standard solution that were used to calibrate atomic absorption Spectrophotometry was given in (table 1). The absorbance of each standard solution provided in appendix -1. The correlation coefficient of each metals was determined from the calibration curve, which was provided in appendix-3.

Table 1. standard concentration in (mg/L) and its absorbance of metal analyzed by AAS

Cd		Cu		Cr		Ni		Pb	
Concentration	Absorbance	Concentration	Absorbance	Concentration	Absorbance	Concentration	Absorbance	Concentration	Absorbance
0.4	0.068	0.4	1.117	0.2	0.009	0.2	0.2	0.2	0.025
0.8	0.109	0.8	0.169	0.4	0.019	0.4	0.4	0.4	0.55
1.2	0.151	1.2	0.231	0.6	0.029	0.6	0.6	0.6	0.081
1.6	0.242	1.6	0.728	0.8	0.039	0.8	0.8	0.8	0.113
2	0.302	2	0.342	1.00	0.047	1	1	1.2	0.142

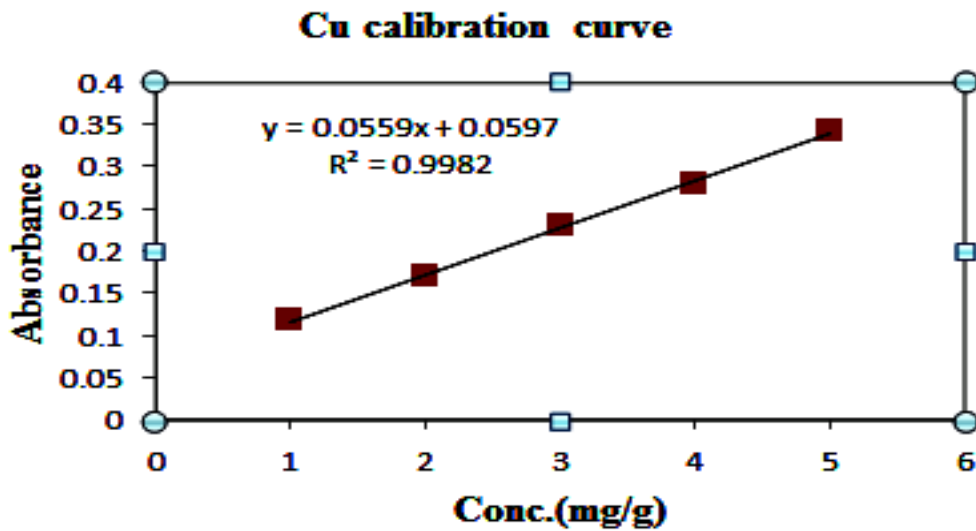


Figure 3 Calibration curve of Cu for fish and sediment

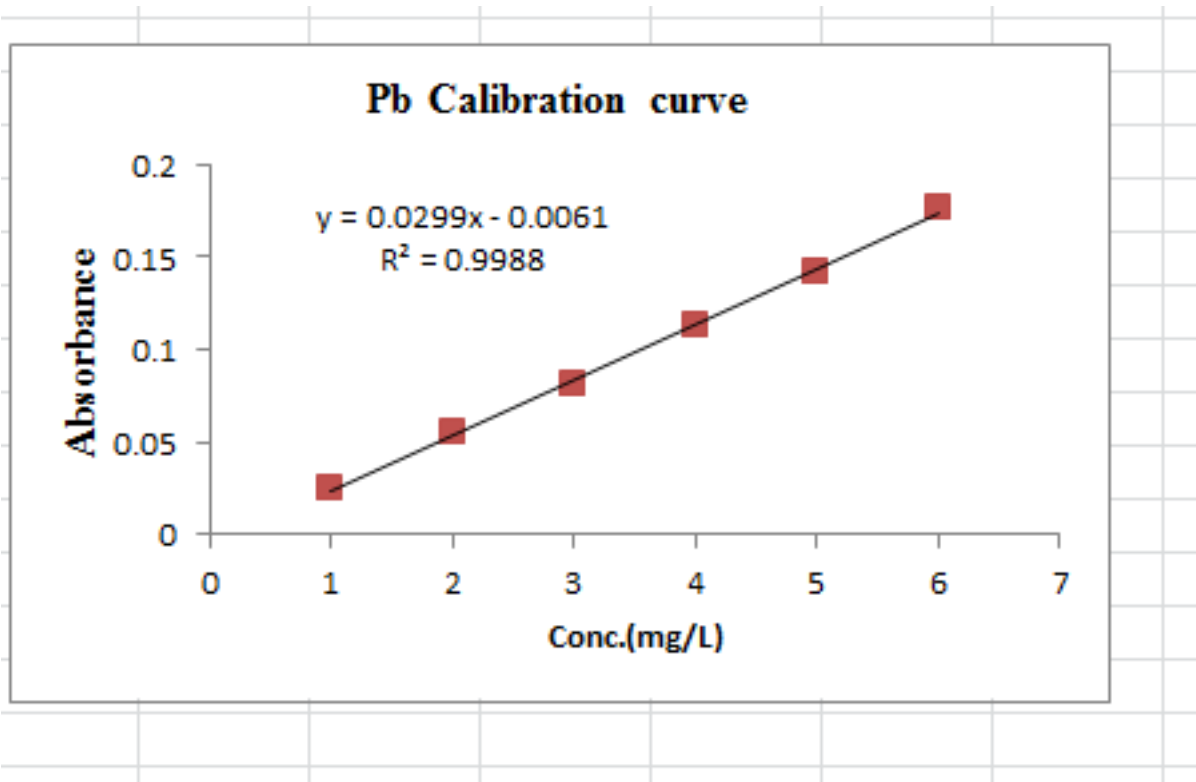


figure 4 Calibration curve of Pb for fish and sediment

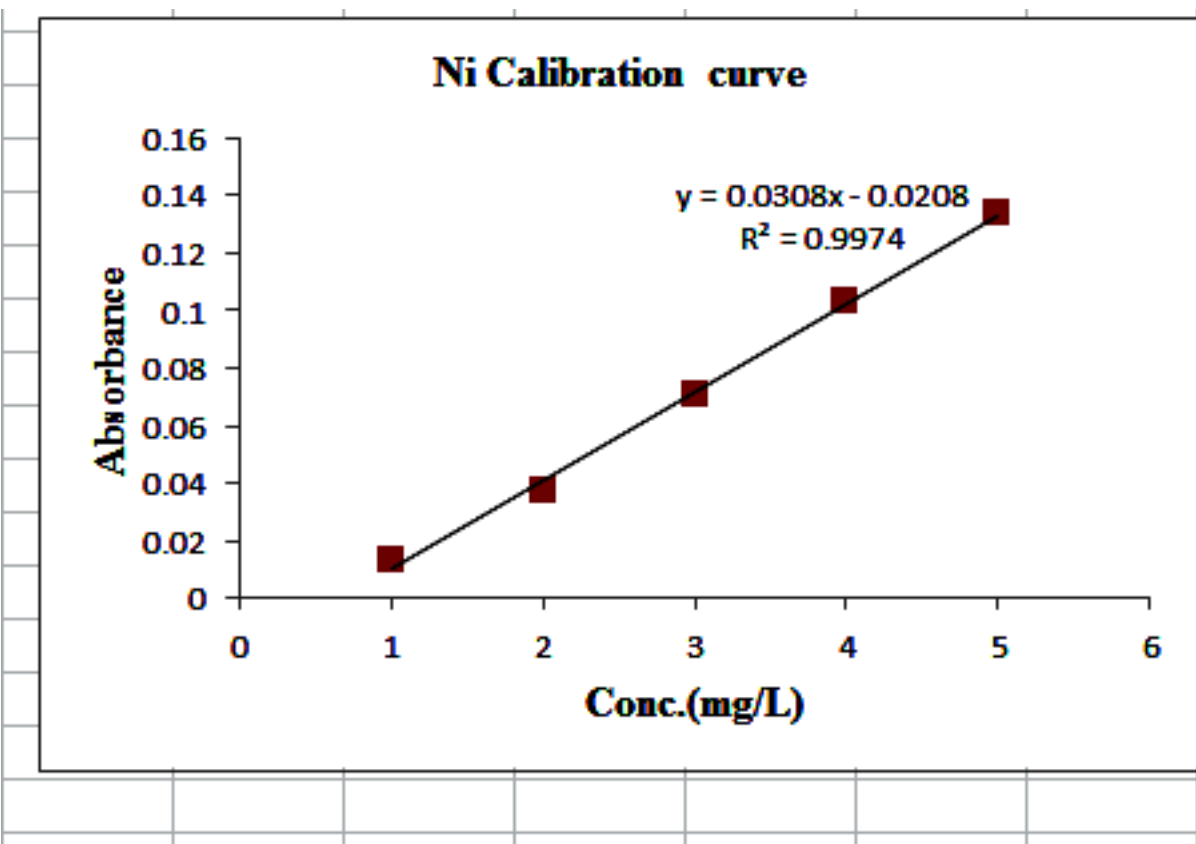


Figure 5 Calibration curve of Ni for fish and sediment

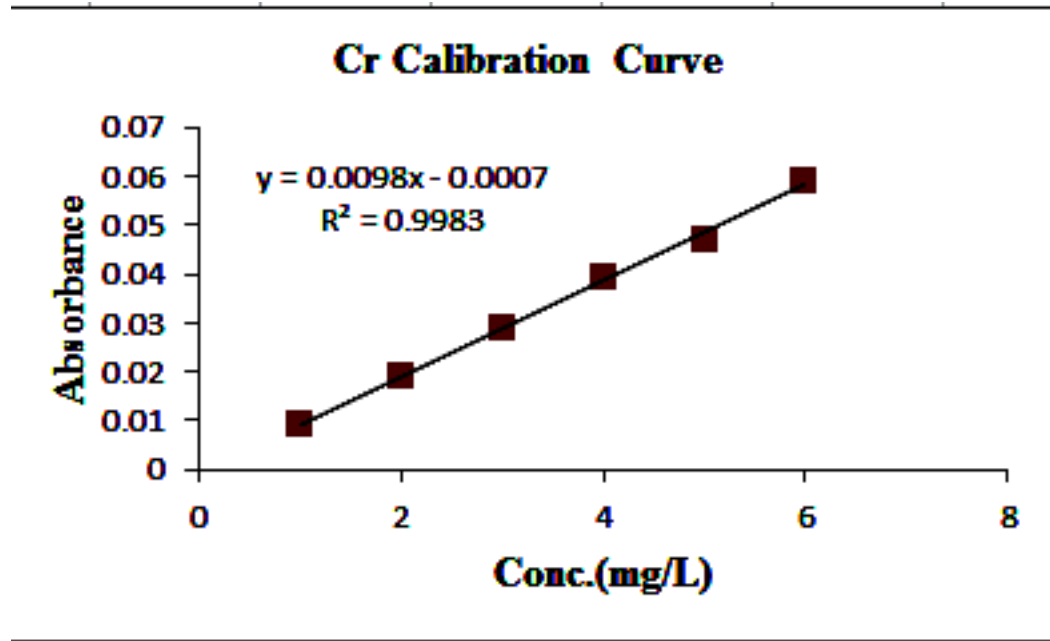


Figure 6 Calibration curve of Cr for fish and sediment

The correlation coefficient (R^2) which was obtained from the calibration curve(appendix-2) of each metal was greater than 0.99 and it was given in Table 2.

Table 2. Correlation coefficient(R^2) value for each metal.

Metal	(R^2)
Cd	0.991
Cu	0.996
Cr	0.998
Ni	0.997
Pb	0.998

.3.3. Stastical analysis

The data obtained was analyzed for mean value using MS Excell and analysis carried out using SPSS 16 version.

UNIT FOUR

4. RESULTS AND DISCUSSION

4.1 Heavy metals concentration in Chamolake sediment in two sampling sites (chamopark1 and chamopark2)

In sediment sample according to analysis results the following finding was obtained for the concentration of heavymetals. The mean concentration of Cd (6.07mg/kg) recorded in the sediment sample collected at Chamo park1(sample site -1) was highest. While the lowest mean concentration 5.14mg/kg was recorded in the sample obtained atChamo park2mple(sample site-1) table 1. The highest mean concentration of Pb(3.26mg/kg)recorded at park2 site and the lowest mean concentration of(2.683mg/kg) at park1. The concentration Pb was high in sediment ofChamopark2 (sample site-2) but low in Chamo park 1.The decreasing order of the metals concentration in sediment,was Cd>Cu>Pb>Ni>Cr.In general the result shows that the mean concentration of Cd in sediment was highest and the concentration of Cr was the lowest.

Table 3. Heavy metal concentration in Chamo lake sediment mean in mg/kg dry weight.

Heavy metals						
Sample site	Cu	Cd	Pb	Ni	Cr	
Chamopark1	4.76	6.07	2.68	2.269	2.132	
Chamopark2	4.26	5.74	3.26	2.978	2.21	

4.2. Comparison of the heavy metal concentration in the Chamo lake sediment with sediment quality guideline and otherglobal published values for deferent Literature.

The metals Concentrationobserved in the sediment samples were compared with sediment quality guideline, which our result showed in Table-2 that the mean concentration of Cd and Pb in the present study were higher than those of Avsar dam lake value reported by M.Ozturk et al.,(2008). Also the concentration of Cd was higher in the Demirkopru Dam lake reported by Ozturk et al.,2008 and lower than the lake victory reported by Kische and Machiwa et al., 2003. While the concentration of Pb, Ni, Cu and Cr at present study were lower than in lake taxom reported by Uzunogl(1999) and Pb concentration(3.265mg/kg) was lower than the Demirkopru

Dam lake value(6.5mg/kg) reported by Ozturk et al.,2008 and the lake victory(54.6) reported by Kische and Machiwa, 2003. Generally the mean concentration of Pb, Ni, Cu and Cr in Lake Chamo was found to be lower than the other studies but the Cd was higher. The concentration of Cd in sediment was maximum compared to the other study.

Table 4. Comparison of heavy metal concentration in Chamo lake sediment with sediment quality guideline(Table 5) and different literature mean (mg/kg dry weight)

Locality	Heavy metals					Reference
	Cd	Cr	Cu	Ni	Pb	
Avsardamlake	0.76±0.4	14.48±0.4	29.98	29.99	2.44	M.Ozturk 2008
Lake texom	2	30	38	17	10	Uzunog 1,999
Chamo lake site1	6.07	2.132	4.76	2.269	2.68	This study
Chamolake site2	5.52	2.21	4.26	2.97	3.265	This study
Lake victory	7.0	12.9	26.1	-	54.6	Kische andMachiwa,2003
Demirkopru dam lake	0.82	6.75	15.1	14.3	6.5	Ozturk et al.,2008

4.3 Concentration of heavy metals in tissue organ of tilapia(*Oreochromisniloticus*) fish.

Fish are one of the most indicative factors in freshwater systems and may concentrate large amount of some metals such as Cd, Cu and Pb(KalayM et.al and Canal et al., 2000). These metals accumulate differentially in fish organs and cause serious health hazards to humans(Camusso *et al.*,1995). In the present study the concentration of Cd and Cu in the tissue, organs of fish ranged from 1.27 to 5.29 and 1.75 to 4.85 (Table 5). The high concentration of Cd and Cu were recorded in the gill tissue of fish(5.29g/kg) and(4.85g/kg). While the lowest concentration of Cd in liver(1.217g/kg) and the lowest concentration of Cu in muscle(1.75g/kg).Also the highest concentration of Pb in fish muscle was found from Chamo

park 2site while the lowest concentration of Pb in fish muscle from Chamo park2 site(Table 5). This was due to the highest concentration of Cr was observed in gill and low concentration of Cr was observed in muscle.The heavy metals concentration present studywas found to decrease sequence for gill Cd> Cu>Ni> Cr>Pb, for liver Cu> Cd>Cr>Ni>Cr and for muscle Cu> Cd>Cr>Ni>Pb(Table5).

In general tabulated data in Table3 obtained the decrease sequence of heavy metal contents in fish tissue of gill>liver>muscle for two sites.

Table 5. Level of heavy metals mean, n=3 in g/kg, dry weight fish tissue of *Oreochromis niloticus*.

Sample site	Metals	Tissue		
		Liver	Gill	Muscle
Chamo park1	Cu	2.706	4.85	1.75
	Cd	1.217	5.29	1.47
	Pb	0.90	1.083	0.865
	Ni	0.957	1.382	0.88
	Cr	1.12	1.70	0.98
Chamo park2	Cu	1.955	4.33	3.118
	Cd	1.5	4.74	1.762
	Pb	0.61	1.19	0.72
	Ni	1.028	1.59	0.92
	Cr	1.09	1.9	1.122

4. 4 .Comparison of heavy metals in muscle tissue of tilapia(*Oreochromis niloticus*) fish with related reported literature and international standard value.

The level of heavy metals in the muscle of tilapia (*Oreochromis niloticus*) fish species was compared with related literature and international standard values as shown in (Table6). Therefore the comparison of the present results with related work indicated that the concentration of Ni in muscle of *Oreochromis niloticus* was comparable. But Cu and Pb were above the values reported by Abayneh Ataro et al(2003) and Selemawit Geta(2010) for the same fish species study from lake Hawssa and lake Ziway. Similarly the concentration of Cu was lower the value reported by

kisimo(2003) study from lake victory. On other hand comparison of the results with guidelines showed that the concentration of Cu, Cd, Pb and Ni in the muscle of Tilapia(*Oreochromis niloticus*) fish from Chamo lake were below the value given by WHO(1989) table 4. But the concentration of Cr in the present work was above the value given by WHO. Therefore the muscle part of the tilapia fish is safe interim of Cu, Cd, Pb and Ni. While interim of Cr may cause hazard to the fish. Therefore the high intake of Cr in our body can cause bad impact towards health(Camusso et al., 1995).

Table 6. Comparison of heavy metals in muscle tissue of Tilapia (*Oreochromis niloticus*) fish from lake Chamo with related reported literature and international standard value.

Location	Cu	Cd	Pb	Ni	Cr	Referance
Lake Chamo	1.75-3.18	1.4-1.7	0.72-0.88	0.88-0.92	0.98-1.22	Present study
Lake Hawssa	1.39-1.85	-	>1.66	>0.99	-	Abaynehataro et al(2003)
Lake Ziwaye	1.35	-	0.35	-	-	SelemawitGeta et al (2010)
Lake victory	2.3-66	-	0.01-28.0	-	-	Kismo(2003)
WHO	30	1.0	2	1	0.15	WHO(1989)

5 CONCLUSION AND RECOMMENDATIONS

5.1. CONCLUSIONS

In conclusion, some of the heavy metals (Cu, Cd, Pb, Ni and Cr) analyzed were available in measurable quantities in sediment sample and in the tissues of Tilapia (*Oreochromis niloticus*) fish samples collected from Chamopark1 and Chamopark2. The highest concentration of Cd (6.07 mg/kg) recorded in the sediment sample collected at park 1 site and the high concentration of Pb (3.26) recorded at park2 while the low concentration Cd (5.14 mg/kg) was recorded in the park2 and the low concentration of Pb (2.68 mg/kg) at park1. The metals concentration in the sediment sample of our result was decreased the sequence Cd > Cu > Pb > Ni > Cr.

The heavy metals concentration in tissue (gill, liver and muscle) of Tilapia (*Oreochromis niloticus*) fish was determined in this study. The high concentration of Cd and Cu were recorded in gill tissue of fish while the low concentration of Cd and Cu were recorded in muscle. To compare the heavy metals concentration in the muscle tissue of fish from the lake Chamo in the present study with an international standard value. The result showed the concentration of Cd, Cu, Ni and Pb in muscle tissue of Tilapia (*Oreochromis niloticus*) fish from lake Chamo were below the value. While the concentration of Cr in muscle tissue of fish from lake Chamo was above WHO (1989). Therefore the muscle part of the tilapia (*Oreochromis niloticus*) fish is safe in terms of Cd, Cu, Pb and Ni but in terms of Cr may cause hazard to the fish. So that the high intake of Cr in our body can cause bad impact towards health.

5.2. RECOMMENDATIONS

The heavy metals concentration in sediment was relatively higher and the levels in the muscle of tilapia fish. The potential source of these heavy metals to the fish in aquatic system can be identified and quantified. Hence, further research is recommended. Even though the concentration of most heavy metals in the lake from the probable source should be taken in order to keep the fish safe for consumption and to maintain the aquatic eco-system.

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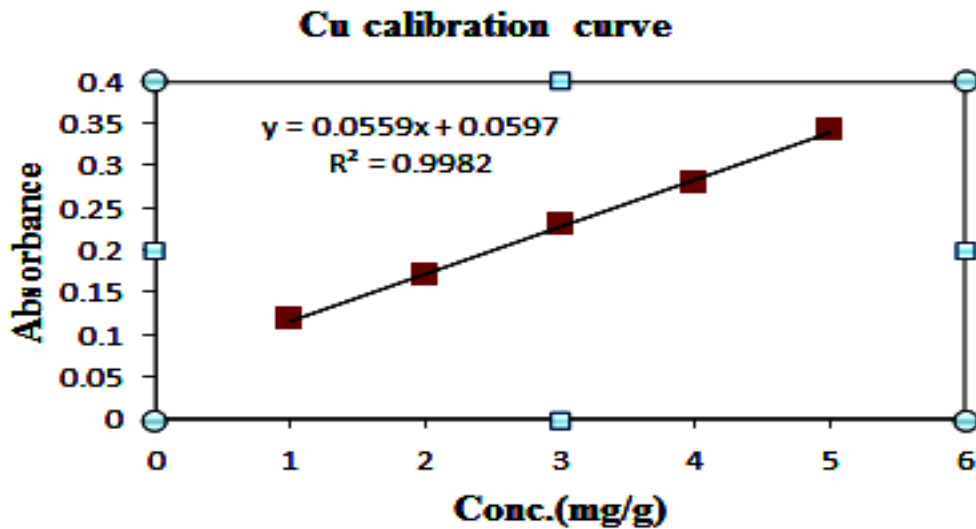
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APPENDIX:1METALS STANDARD CONCENTRATION AND THEI ABSORBANCE

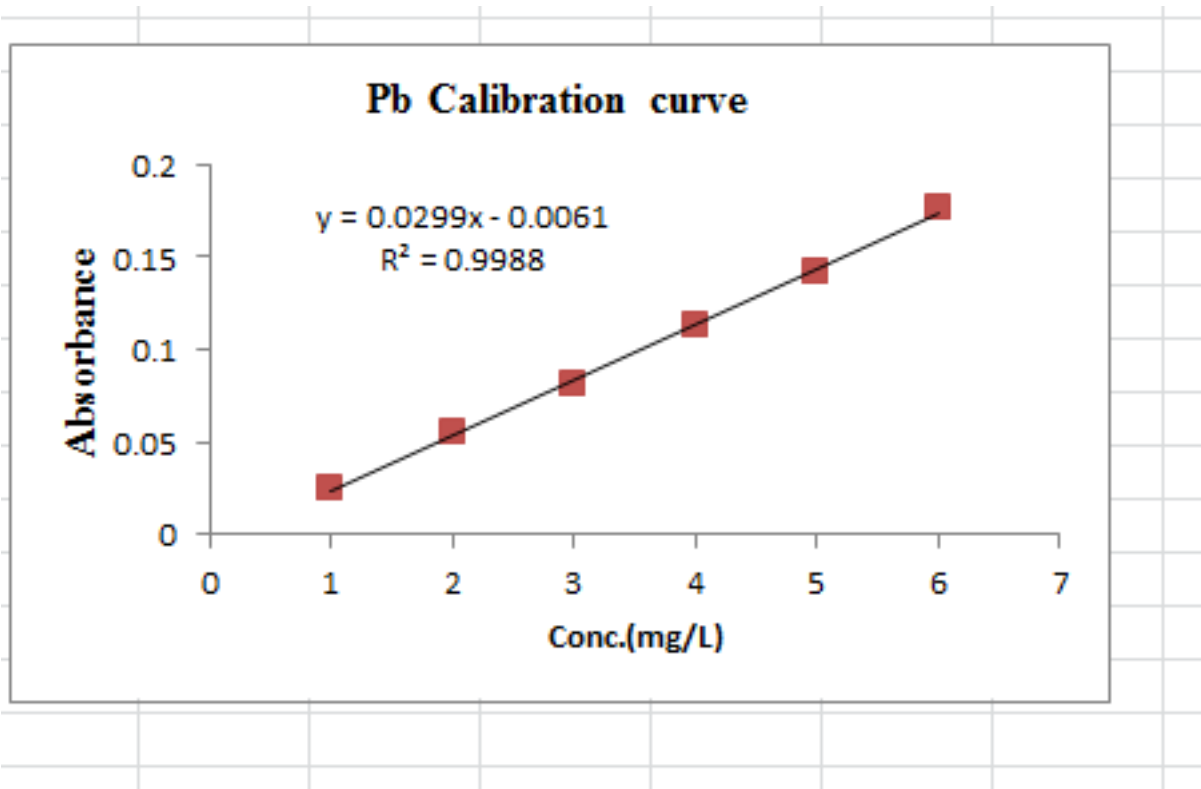
Standard concentration(in mg/L) and its absorbance of metals anlztz by AAS.

Cd		<i>Cu</i>		<i>Cr</i>		<i>Ni</i>		<i>Pb</i>	
Concentration	Absorb	Concen	Absorb	Concen	Absorb	Concen	abso	Concent	Orbanceabs
		tration	ance	tration	ance	tration	rbanc	ration	
0.4	0.068	0.4	1.117	0.2	0.009	0.2	0.013	0.2	0.025
0.8	0.109	0.8	0.169	0.4	0.019	0.4	0.037	0.4	0.55
1.2	0.151	1.2	0.231	0.6	0.029	0.6	0.071	0.6	0.081
1.6	0.242	.61	0.728	0.8	0.039	0.8	0.130	0.8	0.113
2	0.302	2	0.342	1.2	0.047	1.2	0.134	1.2	0.142

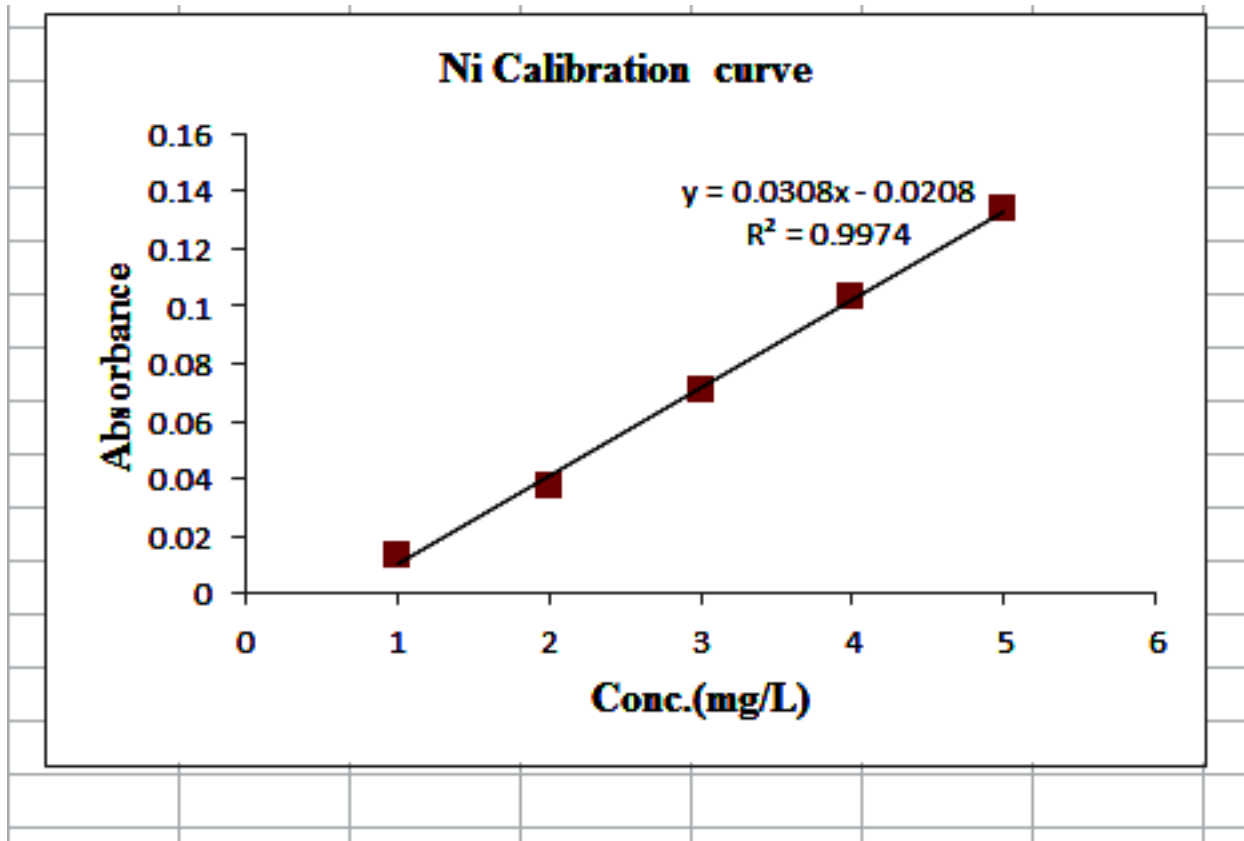
APPENDIX _2 Calibration curve Cu, Pb, Ni Cr and Cd



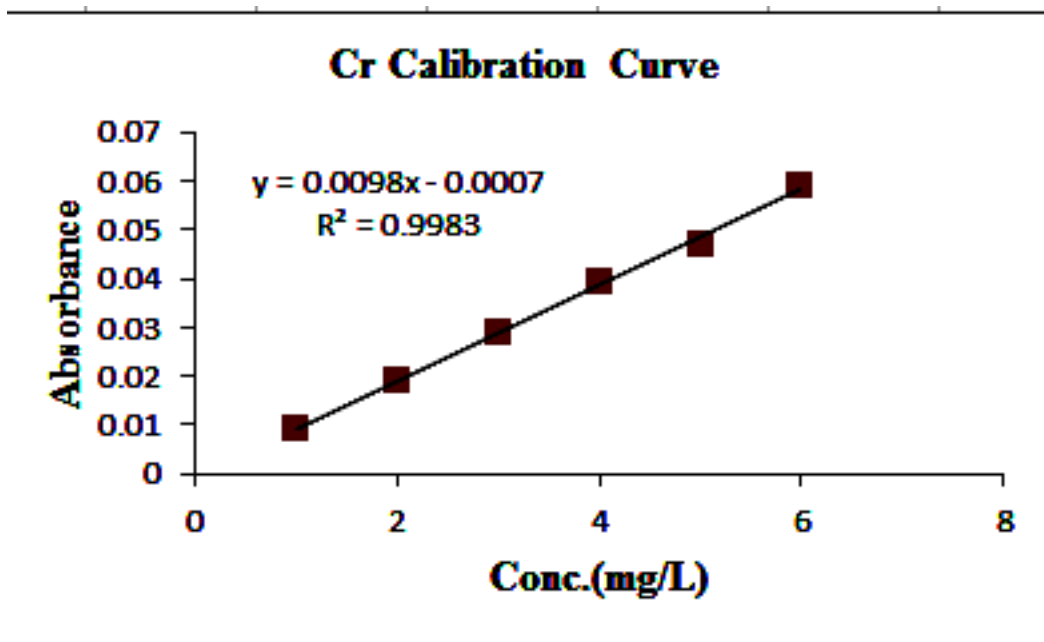
Calibration curve of Cu for fish and sediment



Calibration curve of Pb for fish and sediment



Calibration curve of Ni for fish and sediment



Calibration curve of Cr for fish and sediment

APPENDIX-3 the correlation coefficient (R^2) was obtained from the calibration curve.

Heavy metals	Correlationcoefficient(R^2)	Remark
Cu	0.996	AAS
Pb	0.998	AAS
Ni	0.997	AAS
Cr	0.998	AAS
Cr	o.991	AAS