JIMMA UNIVERSITY

COLLEGE OF NATURAL SCIENCES

DEPARTMENT OF CHEMISTRY

INVESTIGATION OF THE EFFECTS OF FACTORIES EFFLUENTS ON THE LEVELS OF SELECTED HEAVY METALS ON MODJO RIVER, OROMIA REGIONAL STATE, ETHIOPIA

BY:

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NOVEMBER, 2018

JIMMA, ETHIOPIA

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A M.SC THESIS SUBMITTED TO JIMMA UNIVERSITY, SCHOOL OF GRADUATE STUDIES, COLLEGE OF NATURAL SCIENCES, DEPARTEMNT OF CHEMISTRY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTERS OF SCIENCE IN CHEMISTRY (ANALYTICAL STREAM)

NOVEMBER, 2018
JIMMA, ETHIOPIA

APPROVAL SHEET

JIMMA UNIVERSITY
COLLEGE OF NATURAL SCIENCES
DEPARTMENT OF CHEMISTRY

This is to certify that the thesis prepared by **Gemechis Tilachow Ejeta** entitled "Study on the Investigation of the effect of Factories effluent on the level of selected Heavy Metals on Modjo River, in East Shoa Zone, Oromia Regional sate, Ethiopia" and Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science in chemistry (Analytical stream) complies with the regulation of the university and meets the accepted standards with respect to originality and quality.

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ACKNOWLEDGEMENT

My heartfelt gratitude goes to my advisor Dr. Abera Gure for his unreserved support from the initiation of the proposal to defense of the thesis. I sincerely appreciate his patience, friendly approach, sincerity, and commitments to help me all the way throughout my work. I would like to extend my gratitude to my co-advisor Mr. Fuad Abduro for his valuable comments and suggestions throughout the thesis work. His valuable comments and constructive critics have improved the quality of the paper to a great extent. I appreciate all the help provided by Department of Chemistry, Jimma University, Adama Science and Technology University and Arba Minch University for their material assistance and for allowing me to use their laboratory. My thanks also go to Ato Hinsermu for sincerer approach in assisting sample preparation and running with GFAAS. My special gratitude goes to my friends Merga Amara, Megersa Leggese, Gululat Tayu, Guta Amenu, and Dagnachew Duguma for their help in sampling, data analysis and moral support. I would like to express my heartfelt thanks to my family members for their immerse support from the initial of the work until the end. I also appreciate all the contribution provided by my friends. Above all, Thanks to the almighty God for all his blessings and divine help in all my footsteps.

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ABBREVIATIONS

APHA: American Public Health Association

EEPA: Ethiopian Environmental Protection Authority

EPA: Environmental Protection Agency

ESA: Ethiopian Standard Agency

EU: European Union

GFAAS: Graphite Furnace Atomic Absorption Spectroscopy

pH: Power of hydrogen

SD: Standard deviation

USEPA: United State Environmental Protection Agency

WHO: World health organizations

ANOVA: Analysis of Variance

IMDL: Instrument manual detection limit

LOD: Limit of detection

LOQ**:** Limit of quantification

ABSTRACT

This study was aimed to investigate the effect of factories effluents on the level of selected heavy metals on Modjo River Oromia Regional State, Ethiopia. Water samples were collected from the upstream and downstream of the river water and effluent samples emanating from different factories were collected from wastewater channel in June, 2018. Six heavy metals (Cd, Cr, Pb, Cu, Co and Zn) in industrial effluents and river water were analyzed by Graphite Furnace (GFAAS) in separate experiments. The concentrations of heavy metals in the effluents were compared with corresponding heavy metal values in the water. The obtained results indicated that the concentrations of Cr and Pb in all Modjo river water samples were above maximum permissible limit set by WHO, USEPA and ESA for drinking. On other hand, the concentrations of Cr, Zn, Pb and Cu metals in industrial effluents were above the maximum permissible limit set by WHO and USEPA that effluents should contain to discharge from the factories. But Cd was found below the method detection limit for both wastewater and water samples. Results of one way ANOVA tests ($p \leq 0.05$) showed that presence of significant differences in the concentrations of heavy metals (expect for Cu) in among the various sampling stations of both factories effluents and water samples. Therefore, urgent measures needs to be taken to ameliorate the deteriorating nature of Modjo River and keep the water safe for domestic for downstream users.

***Key Words**: Industrial effluent, Wastewater, Heavy metals, Modjo river water.*

1. INTRODUCTION

River water is used for many purposes, which including drinking, irrigation, animal farming, recreations and as habitat to numerous organisms [1]. The availability of good quality water is an indispensable feature for preventing diseases and improving quality of life [2]. The contamination of river water is directly related to the water pollution. The major sources of water pollution can be classified as municipal, industrial, and agricultural and there are also other sources of water pollution like petroleum, radioactive substances and heat [3].

Increased urbanization and industrialization are to be blamed for an increased level of trace metals, especially heavy metals, in our waterways. Advanced industrialization processes have provided comforts to human beings on one hand, and on the other, it has resulted in indiscriminate release of gasses and liquids, which polluted the environment of biological system [4]. Of the various sources of pollutants industrial effluents containing heavy metals pose a threat to the ecosystem. Presence of heavy metals in effluents is a common environmental hazard since the toxic metal ions dissolved can ultimately reach the top of the food chain and becomes a risk factor for human beings [5].

Different industries directly or indirectly use various types of chemicals during processing. For instance in tannery industries various chemicals were used during soaking, tanning and post tanning process of hides and skins [6]. Besides that only about 20% large number of chemicals used in the tanning process is absorbed by leather where as the other released as wastes. Thus, the effluents discharged from tannery industries into natural water bodies could results in contamination river profile [7].

There are over ten (10) heavy metals such as cobalt (Co), lead (Pb), mercury (Hg), arsenic (As), nickel (Ni),manganese (Mn), zinc (Zn), cadmium (Cd) and chromium (Cr) that have a particular significance in ecotoxicology, since they are highly persistent [8]. The levels of metals such as Mn, Zn, and Cr are toxic beyond a certain limit, whereas Pb, Ni and Cd are toxic even in trace amounts [9]. Toxicity is realized when these heavy metal levels are higher than the recommended limit which is different for individual elements in drinking water.

Heavy metal pollution may increase the susceptibility of aquatic animals to various diseases by interfering with the normal functioning of their immune, reproductive and developmental processes [10].These heavy metals could enter into the water bodies from surround industrial discharges. Thus, investigation of the level of heavy metals in river waters which are surrounded by multiple factories, like Modjo River is crucial. Beside, the effluents discharge from numerous factories, Modjo River may also be polluted by the waste discharge from the international and the only dry port terminal hamlet of the country, which is also located in close proximity to the river. Effluents which are discharged from these factories and the dry port terminal are released through channels and/or dumped somewhere in the area could ultimately reach the Modjo river leaching and/or water runoff as well as direct discharge and thus contaminate the river. On the other hand, at the downstream the river is used for irrigation to produce fruits and vegetables for house hold consumption and local markets. It is also one of the main tributaries of Awash River, which is also widely used for irrigation purpose at the downstream.

Therefore, investigation of the effect of factories effluents on the level of selected heavy metals of Modjo River is important. Thus, this study was aimed to investigate the effect of the effluents of the factories, which are directly discharged through the channel, on the level of selected heavy metals such as Cr, Cd, Pb, Zn, Co and Cu of Modjo River. Quantitative determinations of the target metals were preformed Graphite Furnace Atomic Absorption spectrometry (GFAAS) after digesting the samples with microwave digester.

1.1. Statements of the problem

Domestic and industrial wastes that are often discharged into water bodies could lead to the raise the concentrations of potentially toxic heavy metals [11, 12]. For instance, in Nigeria industrial effluent is the major source for the contamination of dirking water [13]. River water is the primary source which can be contaminated by the effluents from industrial effluents can alter the physical, chemical and biological nature of the receiving water body [14]. Generally, increased industrial activities could lead to pollution stress on environments (water, soil, and atmosphere) and agricultural products [15].

Modjo town is located in East shoa zone Oromia regional state Ethiopia. It is available at 66 km in the east from the capital city of the country. The town is surrounded by a number of industries and also the lonesome dry port terminal of the country is also situated near the town. The existing industries and dry port terminal are discharging their waste to the surrounding area and particularly to the nearby Modjo River. Modjo River is directly and/or indirectly prone to various types of pollutions from effluents emanating from domestic and the surrounding industries. It was observed that the surrounding industries are discharging massive effluents to the river and thus, seriously polluting the water course. On the other hand, the downstream of Modjo River is being used for various purposes such as for drinking water, for fish production and for irrigation.

According to the local Modjo Woreda agriculture office (unpublished information) many farmers of the woreda uses Modjo River for cultivation of different types of crops including vegetables, fruits, and cereals such as maize and so on. Crops grown in such contaminated sites could contain high concentration of heavy metals that could harm the health of the consumers. A study conducted on the pollution levels of trace metals from Modjo tannery share company effluent into Modjo River and surrounding soils indicated that the factory effluent is highly contaminating the river water and the surrounding soils [16].This finding gives an insight to look for the impact of other factories on the contamination of the river. Therefore, in this study the impact of various factories effluents on the concentrations of selected heavy metals in the Modjo river water was investigated.

1.2.Objectives

1.2.1.General objectives

The main objective of this study was to investigate the effects of factories effluents in the concentrations of some selected heavy metals in the Modjo River water.

1.2.2. Specific objective

The specific objective of the study were:

- To determine the concentration of heavy metals (Cr, Cd, Pb, Zn, Co and Cu) in water samples collected from Modjo river.
- To determine the concentration of (Cr, Cd, Pb, Zn, Co and Cu) in various industrial effluents including (Modjo tannery Share Company, George shu tannery, Hora tannery, Hundao tannery, Friendship tannery, United vasn leather Plc Company and Farida tannery).
- To identify the factories that highly releases the selected heavy metals to the Modjo River.
- To identify whether Modjo river water could be used for drinking, irrigation, fishery and other purposes based on the international guidelines such as (WHO, EU, USEPA and EEPA).

1.3.Significance of the study

The study outcome was provides preliminary information concerning pollution status of Modjo River and the suitability of the river for drinking, irrigation and other domestic purposes based on the national and international water quality standards. Further, the findings are significant to the local communities to know about the level of industrial pollutants on the river and directly or indirectly on the agricultural products. Additionally, the results of the study serve as a source of information for further study on the river or other similar environment.

2. LITERATURE REVIEW

2.1.River water

Rivers carry water and nutrients to areas all around the earth. They play a very important part in the water cycle, acting as drainage channels for surface water. Rivers drain nearly 75% of the earth's land surface. Rivers provide excellent habitat and food for many of the earth's organisms. Many rare plants and trees grow by rivers. Ducks, voles, otters and beavers make their homes on the river banks. Reeds and other plants like bulrushes grow along the river banks. Other animals use the river for food and drink. Birds such as kingfishers eat small fish from the river. In Africa, animals such as antelopes, lions and elephants go to rivers for water to drink. Other animals such as bears catch fish from rivers. River deltas have many different species of wildlife. Insects, mammals and birds use the delta for their homes and for food. Rivers provide travel routes for exploration, commerce and recreation .Most of the rivers in the urban areas of the developing countries are the ends of effluents discharged from the industries. Rivers in urban areas in many developing countries have water quality problems because of domestic and industrial wastes are often discharged untreated into water bodies which leads to the increase in the level of potentially toxic element concentrations. African countries and Asian countries experiencing rapid industrial growth and this are making environmental conservation a difficult task [17].

2.2.Heavy metals

Heavy metals normally occurring in nature are not harmful to our environment because they are only present in very small amounts [18]. However, if the levels of these metals are higher than the recommended limits, their roles change to a negative dimension. Human beings can be exposed to heavy metal ions through direct and indirect sources like food, drinking water, exposure to industrial activities and traffic [19]. Heavy metals are pollutants discharged from industrial, domestic and agricultural wastewater into the river water system stated that heavy metals are one of the more serious pollutants in our natural environment due to their toxicity, persistence and bioaccumulation.

The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic, highly toxic or poisonous at low Concentrations .Some heavy metals such as copper (Cu), zinc (Zn), iron (Fe), chromium (Cr), manganese (Mn) and nickel (Ni) though essential to human body, are toxic at elevated levels, whereas cadmium (Cd) and lead (Pb) are non-essential

metals and are toxic even in trace amounts. Toxicity is highly aggravated by their non degradability and tendency to bio-accumulate to toxic levels [20]. Heavy metal toxicity can result in lower energy levels and damage blood composition, lungs, liver, kidneys and other vital organs, damaged or reduced mental and central nervous function or even cause cancer [20].

Most of the heavy metals are dangerous to health or to the environment. Heavy metals in industrial wastewater include lead, Chromium, Mercury, Uranium, Selenium, Zinc, Arsenic, Cadmium, Silver, Gold, and Nickel. These metals have been extensively studied and their effects on human health regularly reviewed by international bodies such as the WHO. Heavy metals cause serious health effects, including reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death. Exposure to some metals, such as mercury and lead, may also cause development of autoimmunity, in which a person's immune system attacks its own cells. Children may receive higher doses of metals from food than adults, since they consume more food for their body weight than adults. Nonessential heavy metals of particular concern because of their toxicity are cadmium, chromium, mercury, lead, arsenic, and antimony [21]. Heavy metals are released to water streams from numerous sources. Typical sources are municipal wastewater-treatment plants, manufacturing industries, mining, and rural agricultural Cultivation and fertilization. There are two major types of sources, one is industrial and another one is agriculture [22].

2.3.Sources of heavy metals

Excess heavy metals in water environment occur via a wide range of process and pathways by natural and anthropogenic sources. The natural source includes wet and dry deposition of atmospheric salts, water-soil and water-rock interaction. Anthropogenic sources comprise rapid urbanization and industrialization

2.3.1. Natural Source

Occurrence of heavy metal in water by natural sources depends on the local geology, hydrogeology and geochemical characteristics of the aquifer [23]. The basic source of elements polluting the water body is by weathering of sedimentary rock like limestone, dolomite, shale, sandstone. Interaction of water with igneous rock such as granite, gabbro, nepheline syenite, basalt, and ultramafic also contributes some major elements. The specific minerals or ores that on dissolution increase the level of elements are magnetite, hematite, goethite, siderite (Fe);

calcite, cuprite, malachite, azuite (Cu); chromite (Cr); kaolinite, montmorillonite, arsenic trioxide, orpiment, arsenopyrite (As); calamine, smithsonite (Zn); pyrolusite, rhodochriste (Mn) [24-29]. As is also founds in concentrated sulfide-bearing mineral deposits, especially associated with gold mineralization; and hydrous iron oxides ores [30]. Few minor elements like Cd, Co, Mn occurs in earth crust along with other minerals [31]. Apart from this Ni, Pb and Hg get deposited into aquatic system from dry or wet fall out of atmospheric aerosols formed from wind-blondest, volcanic emissions, forest fires and vegetation [32–34].

2.3.2. Anthropogenic Source

The rapid race of industrialization and urbanization decreases the carrying capacity of water sharply. The concentration level of Hg in water increases mostly due to agricultural activities, human activities such as tillage and logging, domestic sewage discharge, atmospheric deposition from solid waste incineration, coal and oil combustion, hydrometallurgical processes (Fe, Pb and Zn) and mining activities. Surface runoff from rain or snow brings Hg contaminated soil to adjacent water systems [35, 36]. Industrial processes which are responsible for polluting water with Hg includes chlor-alkali, batteries, fluorescent lamps, thermometers, and electronic switches production. Chemical industry has been among the largest intentional polluting source of mercury in the world.

2.4.Heavy metals in the Environments

Heavy metals are present in the environment in different forms such as in solid phase and in solution, as free ions, or absorbed to solid colloidal particles. Heavy metals concentrations in the environment are due to natural sources such as rock weathering, soil erosion, and dissolution of water soluble salts as well as anthropogenic sources as municipal wastewater, manufacturing industries, and agricultural activities [37].

Heavy metals are of much environmental concern currently. These metals are dangerous as they tend to bioaccumulation in the food chain and they became harmful to human and animals. The heavy metals risk pose to human and animals health is provoked by their long term persistence in the environment. Since the beginning of human kind we have used metals for different activities, and thus heavy metals have been emitted to and deposited in the environment. Metals can be retained for long period of time after entering the environment medium such as soil and water [38].

Metals are introduced into the environment by a wide range of natural and anthropogenic sources and with anthropogenic source being either domestic or industrials. They occur naturally at levels that are considered mot to have toxic effects to living organisms. 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 [39].

In natural aquatic ecosystems, heavy metals occur in low concentration. In recent times, however, the occurrence of metal contaminants in excess of human activities loads has become a problem of increasing concern. Heavy metals contamination of the aquatic environment may lead to deleterious effects from localized input which may be acutely or chronically toxic to aquatic life within the affected areas [40]. The term heavy metal is a general collection term applying to the group of metals and metalloids with an atomic density greater than 6 g/cm^3 [41]. Commonly the term is used to refer to elements that are associated with pollution and toxicity problems. Table 1 shows that, the major metals in natural water and their chemical species according to [42].

Table 1**:** Major chemical species found in natural water

Metals	Chemical Symbol	Chemical species
Lithium	Li	Li^+
Aluminum	Al	$Al(OH)_3$, $Al(OH)_2^+$,$[Al(OH)_4]^-$
Chromium	Cr	$Cr(OH)_2(H_2O)_4$+, $CrO_4$2-
Manganese	Mn	Mn^{2+}, MnSO4, $MnCl^+$, MnO2
Iron	Fe	$[Fe(OH)_2]^+$,$[Fe(OH)_4]^-$, $Fe(OH)_3$
Cobalt	Co	Co^{2+}, $CoCO_3$
Nickel	Ni	Ni^{2+} , $NiCO_3$
Copper	Cu	Cu^{2+}, $Cu(OH)^+$, $CuSO_4$, $CuCO_3$
Zinc	Zn	$Zn(OH)_2$, $ZnCl^+$, $ZnCl_2$, Zn^{2+}
Selenium	Se	Se(IV), Se(VI), SeO_4^{2-}
Molybdenum	Mo	MoO_4^{2-}
Cadmium	Cd	CdCl+, $CdCl_2$, $CdCl_3^-$, Cd^{2+}.
Arsenic	As	$HAsO_4$
Mercury	Hg	$HgCl_2$, $HgCl_3^-$, $HgCl_4^-$,$Hg(OH)_2$
Lead	Pb	Pb^{2+} , $PbCO_3$, $PbCl_2$, $PbCl_3$, $Pb(OH)_2$

Some of these elements are required by most living organisms in small amounts and they are also referred to as micronutrients. All metals, however, can be toxic to aquatic organism where present at high levels, causing direct effects such as histological damage or a reduction in survival, growth and reproduction of the species it influences [43].

Generally, the pattern of the flow of anthropogenic sources of heavy metals in the environment is illustrated in the Figure 1 as proposed by Chalermsupanimit [44].

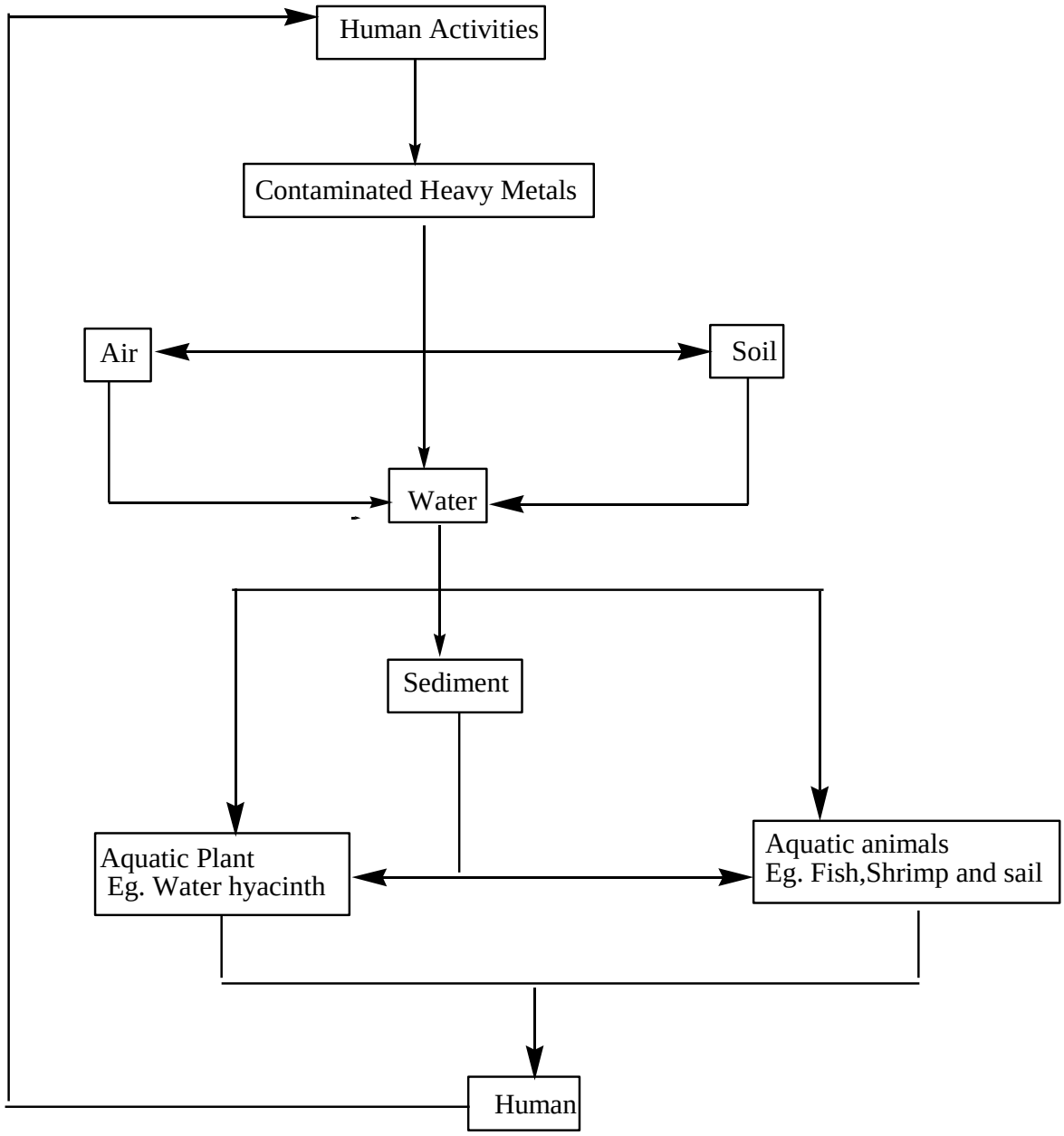

Figure 1: Anthropogenic sources of heavy metals flow in environment.

2.5. Heavy metals in Water

High heavy metals concentrations can be naturally occurring [45]. Every geologic formation contains a certain amount of heavy metal. Mine operations extract and process these metals in areas with the highest concentrations. Water in these areas may have high metal concentrations due to the combination of naturally occurring deposits and mine waste. Water samples are usually taken randomly within a contaminated areas and offsite to identify the source of contamination and the pathway it travels, into the drinkable ground water system or away from potable water sources [46]. Accurate determination of heavy metal contamination is important to identify cumulative risks to people drinking water derived from these areas [47].

2.6.Health Effect of Heavy Metals

Today heavy metals are abundant in drinking water, river water, air and soil; due to increased use of these compounds. They are present in virtually a very area of modern consumerism from construction materials to cosmetic medicines to processed foods fuel sources to agents of destruction appliances to personal care products [48]. It is very difficult for anyone to avoid exposure to any of many harmful heavy metals that are so prevalent in environment. While it does not appear that utilizes are going to neither neutralize the threat of heavy metal toxicity in communities nor decrease utilization of many commercial goods that they help produce. Users can take steps to understand this threat and put into action policies of prevention and treatment that may help to lessen the negative impacts that these agents have on human health [49].

Water, unless it is distilled, contains many natural elements. It gathers constituents from the rock and ground through different activities. Water constituents are defined as a hazard when they have potential to impair health. Heavy metal toxins contribute to variety of adverse effect. There exist over 20 different heavy metal toxins that can impact human health and each toxic will produce different behavioral physiological and cognitive changes in an exposed individual

The degree to which a system organ tissue or cell is affected by a heavy metal toxic depends on the toxin itself and the individual's degree of exposure to the toxin. These metals affect an individual in such a way that its respective accumulation within the body leads to a decline in the mental cognitive and physical health of the individual.

The body requires approximately 70 friendly trace elements which are called as heavy metals, but there are another 12 poisonous heavy metals, such as Lead, Copper, Aluminum, Arsenic, Cadmium, Nickel, Mercury etc., that act as poisonous interference to the enzymes systems and metabolism of the body. Heavy metal overload will be a detriment to the natural healing functions of the body. Some metals are naturally found in the body and are essential to human health. For example Iron which prevent anemia, and Zinc is a cofactor in over 100 enzyme reactions.

Heavy metals are trace metals that are at least five times denser than water. As such, they are stable elements that they cannot be metabolized by the body. These include: Mercury, Nickel, Lead, Arsenic, Cadmium, Aluminum, Platinum and Copper. Heavy metals are taken in to the body via drinking of water, inhalation, ingestion, and skin absorption [50]. If metals enter and accumulate in the body tissue faster than the body's detoxification pathways can dispose of tem, gradual build of these toxins will occur. High concentration exposure is not necessary to produce a slate of toxicity in the body tissues and over time can reach toxic concentration levels [51].

In general, heavy metals are systemic toxins with specific neurotoxin, nephrotoxic, fetotoxic and teratogenic effects. Heavy metals can directly influence behavior by impairing mental and neurological function, influencing neurotransmitter production and utilization, and altering numerous metabolic body processes. Systems in which toxic metal elements can induce impairment and dysfunction include the blood and cardiovascular, eliminate pathways (colon, liver, kidneys, skin), endocrine (hormonal), energy production pathways, enzymatic, gastrointestinal, immune, nervous (central and peripheral), reproductive, and urinary [52].

2.6.1.Heavy Metal Toxicity

Heavy metals in industrial wastewater include lead, Chromium, Mercury, Uranium, Selenium, Zinc, Arsenic, Cadmium, Silver, Gold, and Nickel. These metals have been extensively studied and their effects on human health regularly reviewed by international bodies such as the WHO.

Heavy metals cause serious health effects, including reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death. Exposure to some metals, such as mercury and lead, may also cause development of autoimmunity, in which a person's

immune system attacks its own cells. Children may receive higher doses of metals from food than adults, since they consume more food for their body weight than adults. Living organisms require trace amounts of some heavy metals, including cobalt, copper, iron, manganese, molybdenum, vanadium, strontium, and zinc.

Excessive levels of essential metals, however, can be detrimental to the organism. Nonessential heavy metals of particular concern because of their toxicity are cadmium, chromium, mercury, lead, arsenic, and antimony [53]. Heavy metals are released to water streams from numerous sources. Typical sources are municipal wastewater-treatment plants, manufacturing industries, mining, and rural agricultural Cultivation and fertilization. There are two major types of sources, one is industrial and another one is agriculture [54].

2.7. Heavy Metals in the study

2.7.1. Copper

Environmental contamination due to copper is caused by mining, printed circuits, metallurgical, fiber production, pipe corrosion and metal plating industries [55]. The other major industries discharging copper in their effluents are paper, pulp, petroleum refining and wood preserving. Agricultural sources such as fertilizers, fungicidal sprays and animal wastes. Also lead to water pollution due to copper. Copper may be found as a contaminant in food, especially shell fish, liver, mushrooms, nuts and chocolates. Any packaging container using copper material may contaminate the product such as food, water and others. Cu is both an essential nutrient and a drinking water contaminant. Cu in a drinking water supply usually arises from the corrosive action of water leaching Cu from Cu pipes in buildings. Staining of sanitary ware and laundry may occur at Cu concentrations above 1mg/L. At levels above 5mg/L, Cu also imparts a color and an undesirable bitter taste to water.

Although Cu can give rise to taste, it should be acceptable at the health-based guideline value of WHO [56] which 2mg/L. was The adverse health effects caused by drinking water contaminated with copper are abdominal pain, vomiting, headache, nausea, and diarrhea. Copper in large doses is dangerous to infants and people with certain metabolic disorders. On the other hand, lack of copper intake causes anemia, growth inhibition, and blood circulation problems [57].

2.7.2. Zinc

The diet is normally the principal source of Zn. Zn is an essential trace element found in virtually all food and potable water in the form of salts or organic complexes. There are several sources of elevated Zn found the water bodies including industrial discharges, sewage effluents, domestic wastes, municipal wastes, mining, as well as natural chemical weathering of geological materials [58]. Due to its remarkable resistant to atmospheric corrosion; zinc is commonly used to protect iron from rusting, in the process called galvanization. Zinc is widely used for the manufacturing of zinc white and several useful alloys such as brass, German silver, delta metal, for the preparation of gold and silver in the cyanide method, for the desilverization of lead in parks process and as an anode material in galvanic cells. Various zinc salts are used industrially in wood preservatives, catalysts, photographic paper, and accelerators for rubber vulcanization, ceramics, textiles, fertilizers pigments, steel production and batteries drinking water containing Zn at levels above 3 mg/L may not be acceptable to consumers WHO[56]. Zn in large doses causes Depression, lethargy, neurological signs and increased thirst.

2.7.3. Cadmium

Cadmium is generally classified as toxic trace element. It is found in very low concentration in most rocks, as well as in coal and petroleum and often in combination with zinc. Geologic deposits of cadmium can serve as sources to groundwater and surface water, especially when in contact with soft, acidic waters. There is no evidence indicating its essentiality to humans. Galvanized steel is plated with zinc, which is normally contains about 1% Cd. Cadmium also has specific uses in paint, photography, and nickel-cadmium batteries. Some cases of cadmium poisoning are linked to cadmium-plated food utensils. It is introduced into the environment from paint and pigments, and plastic stabilizers mining and smelting operations and industrial Operations, including electroplating, reprocessing cadmium scrap, and incineration of cadmium containing plastics. The remaining cadmium emissions are from fossil fuel use, Effluents from industries such as battery production, dye and manufacture of pigments fertilizer application, and Sewage sludge disposal [59]. Cadmium may enter drinking water as a result of corrosion of galvanized pipe. Landfill leachates are also an important source of cadmium in the environment. Cadmium that is taken into the body usually remains there. Inhaled cadmium is more hazardous than ingested cadmium. A major source of inhaled cadmium is tobacco smoke. Cd is chemically similar to Zn, an essential nutrient for plants and animals; it is readily assimilated into the food

chain. Plants absorb Cd from irrigation water. The recommended upper limit in irrigation water is 0.01 mg/L. Children are especially susceptible to lead because developing skeletal systems require high calcium levels. Lead that is stored in bone is not harmful, but if high levels of calcium are ingested later, the lead in the bone may be replaced by calcium and mobilized. Acute exposure of Cd can cause nausea, Vomiting, diarrhea, muscle cramps salivation, sensory disturbances, liver injury, convulsions, shock, and renal failure. Long-term exposure to low levels of Cd in air, food, and water leads to a build-up of Cd in the kidneys and possible kidney disease.

2.7.4. Lead

Lead is a dangerous element; it is harmful even in small amounts. Lead enters the human body in many ways. The main sources of lead contamination of the aquatic environment are the industrial discharges from smelters, paints and ceramics, through vehicular emissions, runoff from contaminated land areas, atmospheric fallout and sewage effluents. In some cases, lead is used to stabilize land pipes/plastic pipes and results in lead contamination of river water. It can be inhaled in dust from lead paints, or waste gases from leaded gasoline. It is found in trace amounts in various foods, notably fish, which are heavily subject to industrial pollution. Most of the lead we take in is removed from our bodies in urine; however, there is still risk of buildup, particularly in children, Studies on lead are numerous because of its hazardous effects.

Lead is considered the number one health threat to children, and the effects of lead poisoning can last a lifetime. Its toxicities are that damage the fetal brain, diseases of the kidneys, circulatory system, and nervous system [60].

2.7.5. Chromium

Chromium has density of 7.2g/cm^3 and is the 21st most abundant element in Earth's crust with an average concentration of 100 ppm [61]. Chromium can exist in valences of +3 and +6 with oxidation state. In Cr (III) being stable and give series of chromic compounds, like oxides (Cr_2O_3), chlorides ($CrCl_3$) and sulphates ($Cr_2 (SO_4)_3$) [61]. Chromium is used in metal alloys such as stainless steel, protective coatings of metal (electroplating), magnetic tapes, and pigments for paints, cement, paper, rubber and its soluble form is used in wood preservatives as well as additive in water to prevent corrosion in industrial and other cooling system

Hexavalent Cr is very toxic and mutagenic when inhaled and is a known human carcinogen. Breathing high levels of the element in this form can cause irritation to the lining of the nose and breathing problems such as asthma, cough, shortness of breath, or wheezing where long term exposure can cause damage to liver, kidney circulatory and nerve tissues, as well as skin irritation.

2.7.6. Cobalt

Cobalt is a compound that occurs in nature. It occurs in many different chemical forms. Pure cobalt is a steel-gray, shiny, hard metal. Cobalt used in industry is imported or obtained by recycling scrap metal that contains cobalt. It is used to make alloys (mixture of metals), colored pigments, and as a drier for paint and porcelain enamel used on steel bathroom fixtures, large appliance, any kitchen wares. Small amounts naturally occur in food. Vitamin B_{12} is a cobalt containing compound that is essential for good health. Cobalt has also been used as a treatment for anemia, as it causes red blood cell production. Some natural sources of cobalt in the environment are soil, dust, and seawater. Cobalt is also released from burning coal and oil, and from car and truck exhaust. Cobalt enters the environment from natural sources and from the burning of coal and oil. Cobalt stays in the air for a few days. Pure cobalt does not dissolve in water, but some of its compounds do. Cobalt can stay for years in water and soil. It can move from the soil to underground water.

Everyone is exposed to cobalt at low in air, water, and food. People who live near hazardous waste sites containing cobalt may be exposed to higher levels of this chemical. Food is another source of exposure to cobalt. Workers may be exposed to cobalt in industries that process it or make products containing cobalt. Acute toxicity of cobalt may be observed as effects on the lungs, including asthma, pneumonia, and wheezing that have been found in workers who breathed high levels of cobalt in the air. In the 1960, some breweries added cobalt to beer to stabilize the foam. Some people who drank large quantities of the beer experienced nausea, vomiting, and serious effects on the heart.

2.8. Methods of Selected Heavy Metal Analysis

Elements including Lead, Cobalt, Copper, Zinc, Cadmium and Chromium have been analyzed by various methods which include flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma-atomic emission

spectroscopy (ICP-AES) [62]. Atomic absorption spectrometry is commonly used because of its availability and has the advantage of being highly specific and selectivity. The technique makes use of absorption spectrometry to assess the concentration of an analyte in a sample. It requires a standard with known analyte content to establish the relation between the measured and the analyte concentrations and relies on Beer Lambert's law [63].

The sample is converted into atomic vapor by a process known as atomization. The precision and accuracy of this method depends on the atomization step and therefore a good choice of the atomization method is required. The two types of atomizers are continuous and discreet atomizers. In continuous atomizers the sample is fed into the atomizer continuously at a constant rate giving a spectral signal which is constant with time. Atomization methods that are of continuous type are flame, inductively coupled argon plasma and direct current argon plasma. With the discrete atomizers, a measured quantity of a sample is introduced as a plug of liquid or solid. The spectral signal in this case rises to a maximum and then decreases to zero. An electro thermal atomizer is one of the discrete types.

The atoms absorb radiations of characteristic wavelengths from an external source like Lead**,** Zinc, Cadmium, Cobalt**,** Copper and Chromium; absorb radiations of wavelengths of 349 nm, 370 nm 314 nm**,** 402 nm, 272 nm, 286 nm respectively from an external source which is usually a hollow cathode lamp [64].

This technique has been widely employed for elemental analysis in a number of matrices such as soils, water, nuts and wine products [20]. Figure- 2 shows a schematic diagram for the components of FAAS. The two sources of radiation are continuous source which makes use of deuterium and mercury lamps and a hollow lamp which consists of an anode made of either tungsten wire or wink and a hollow cathode made of either the element of interest or its own salt. Flame atomization method consists mainly of a fuel and oxidant. Their temperatures are determined by flow rate and ratio of oxidant and fuel while the electro thermal atomizer is basically made of carbon rods. The free atoms are vaporized from the carbon atomizer into the optical light path to a monochromator which presents a monochromatic radiation to the detector. The radiations from the monochromators are received by detectors which converts them to electrical signals. Some commonly used detectors are photocells and photo multiplier tubes.

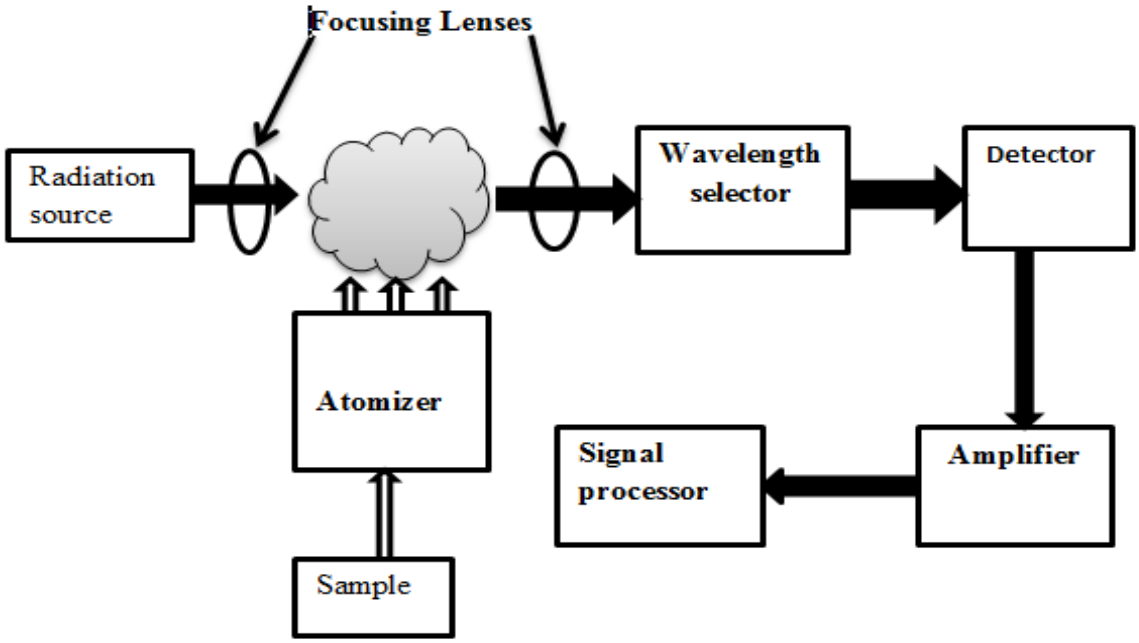

Figure 2: Schematic diagram of AAS equipment

Radiation source is the source of analytical light line for the element of interest and gives a constant and intense beam of that analytical line. The atomizer will destroy any analyte ions and break complexes to create atoms of the element of interest. Wavelength selector isolates analytical line photons passing through the flame and remove scattered light of the other wavelength from the flame. This only imposes a narrow line on the photomultiplier tube. Detector (Photomultiplier tube (PMT) determines the intensity of the analytical line exiting the monochromator. The PMT is the most commonly used detector for FAAS.

3. MATERIALS AND METHODS

3.1.Description of the Study Area

The study was conducted on Modjo River which is found in east Showa Zone, Oromia Regional State, Ethiopia. Modjo River flows in close proximity to Modjo industrial areas and the Modjo dry port terminal which is located between (latitude $08^0$20'0'' to $8^0$40'0''N and longitudes $39^0$0'0'' to $39^0$20'0''E and altitude1788 to1825 m). It is located in the east at about 66 km from capital city of the country, Addis Ababa. The Modjo River receives effluent discharges from several industries in the area including Modjo tannery Share Company, George shu tannery, Hora tannery, Hundao tannery, Friendship tannery, United vasn leather Plc Company , Farida tannery. Both sides of the downstream of the river up to its junction with Awash River is used for agricultural irrigation. It is also used for domestic activities including drinking (for human being and domestic animals), recreation (swimming), cloth as well as other utensil wishing and bathing. Figure 3 shows the map of the study area.

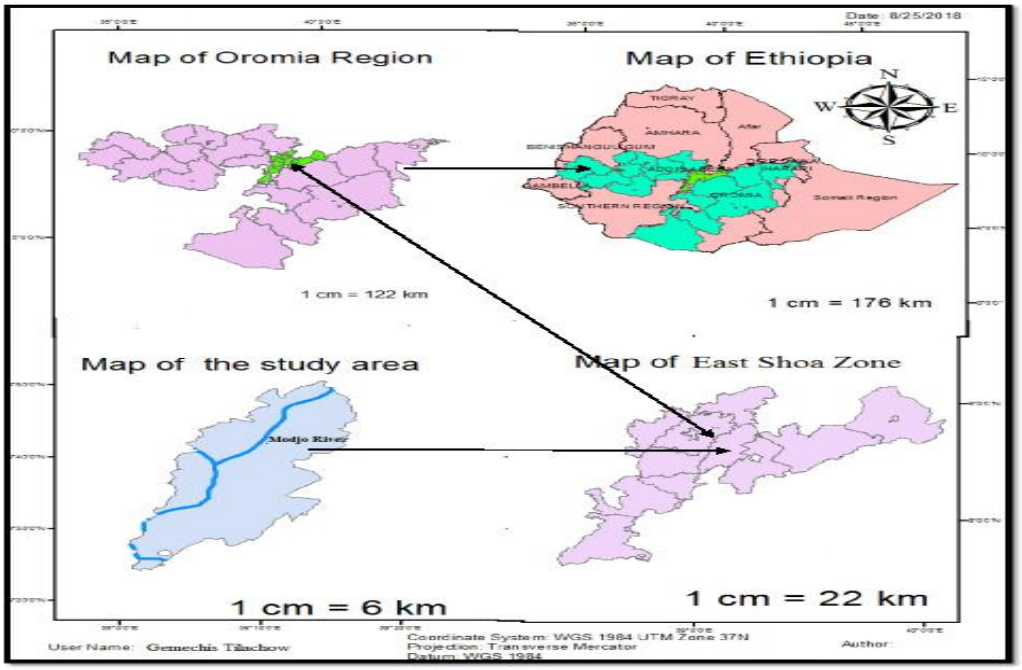

Figure 3: Map of the study area

3.2. Sampling Site

The total of 12 samples (7 samples from Modjo River and 5 effluents samples discharged from various industries) was collected to investigate the effect of various factories effluents on the level of selected heavy metals on Modjo River. Figure 4 shows Google map of the sampling point along the Modjo River and industrial effluents.

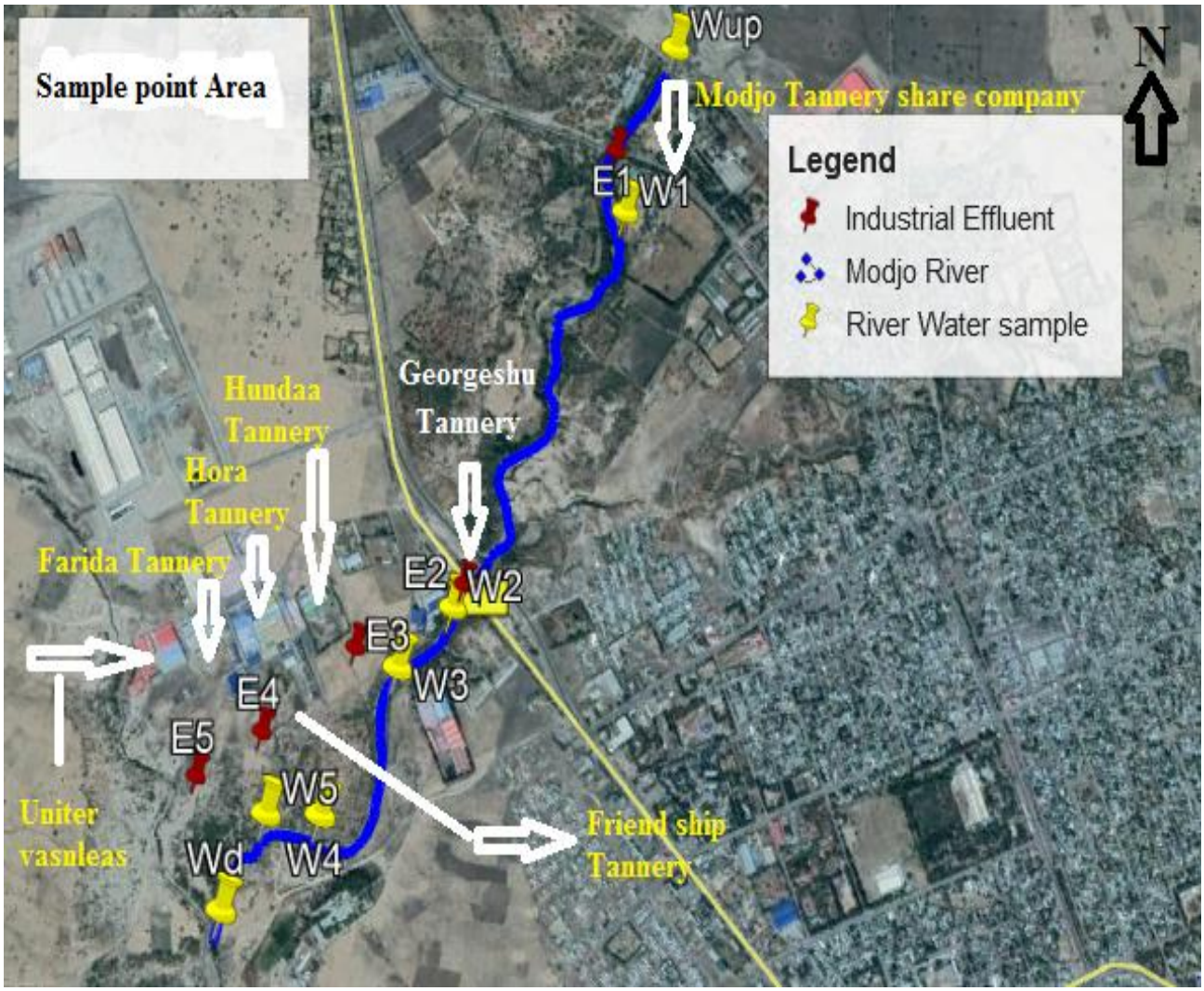

Figure 4: Google Map showing sampling point along Modjo river water and industrial effluents.

During a field reconnaissance (June, 2018), seven sampling sites (for the river water) and five sampling sites (from different factories effluents) were identified based on the bulk water location, human intervention, geographical location, water stability and effluent load of the factories.

Samples were collected based on the sampling methods reported in the literatures [65, 66]. The specific coordinate of each sampling site (taken by GPS during sampling) and other details are presented in Table 2.

One river water sample was collected from the upstream of the river, i.e., before the discharged factory effluent is joined the river. The remaining 6 samples were collected from six sampling points at the downstream of the river, approximately, at 20 m distance from the point where the factories effluent and the river water were joined. Similarly, 5 effluent samples emanating from different factories were also collected at about 20 m distance from the wastewater channel, before joining the river water. Both water and factories effulent samples were collected using 1 L plastic (poly vinyl) botles, PVC. The bottles used for sampling were cleaned with 10% HNO_3 and then, rinsed repeatedely with distilled. Prior to sampling, the bottles were also rinsed three times with the target sample (river water or the effulent discharged from the factories) [67, 68] at the time of sampling.

The samples were collected by direct immersion of the sampling bottles, to the depth of 10 - 15 cm below water surface of river or discharged effulents to exclude dust materials as well as oily liquids suspended above the surface of the water and wastewater. Immediately after collecting the samples 2 mL conc HNO_3 was added to reduce adsorption of metals on the walls of the bottles [69]. The bottles were then labelled to indicate date of sampling and sampling site and then, transported to Arba Minch University department of chemistry research laboratory Arba Minch, Ethiopia,in ice box. After arrival to the laboratory the samples ware stored in the refrigerator at 4^0 C until digestion was preforemed for the analysis. Figure 5 illustrated drainage (channel) of (a) effluent (wastewater) from one of industry in the Modjo area and (b) effulent channel where it joins the Modjo river water.

Table 2: Geographical coordinates of sampling sites and their site descriptions.

Wup	08 º 36’40’’	39 º 06’52’’	1769	Upstream river water collected from 50m distance from the first factory effluent and Modjo river bank
W1	08 º 36’23’’	39 º 06’49’’	1768	Downstream sites of river water about 20m away from the point where the Modjo tannery share company effluent joins to river.
W2	08 º 35’45’’	39 º 06’38’’	1758	Downstream sites of the river about 20m away from the point where George shu-tannery Effluent joins to river water.
W3	08 º 35’39’’	39º 06’33’’	1755	Downstream sites of the river about 20m away from the point where Hora and Hundao tannery Effluent Joins to river.
W4	08 º 35’25’’	39 º 06’28’’	1753	Downstream sites of the river about 20m away from the point where Friendship
W5	08035’25’’	39 º 06’23’’	1747	Downstream sites of the river about 20 m away from the point where effluent from United Vasn Leather Plc and Farida tannery joins to river water
Wd	08 º 35’17’’	39º 06’20’’	1743	Downstream of river water
E1	08 º36’30’’	39 º 06’47’’	1770	Effluent discharged from Modjo tanneryshare company
E2	08 º35’49’’	39 º 06’38’’	1758	Effluent discharged from George shu tannery
E3	08 º35’41’’	39 º 06’29’’	1766	Effluent discharged from Hora and Hundao tannery.
E4	08 º35’32’’	39 º06’21’’	1760	Effluent discharged from Friendship tannery.
E5	08º 35’28’’	39 º 06’15’’	1756	Effluent discharged from United Vasn Leather Plc and Farida tannery.

a) b)

Figure 5: illustrated drainage (channel) of (a) effluent (wastewater) from one of industry in the Modjo area and (b) effulent channel where it joins the Modjo river water.

3.3. Chemicals and reagents

All chemicals and reagents used were of analytical grades. HNO_3 (65.0%), HCl (37%) H_2O_2 (30.0%) from BDH Chemicals Ltd (Poole, England), were used for digestion of the samples. Stock standard solutions containing 1000 mg/L in 2% HNO_3, of each metal Pb, Cd, Cr, Cu, Zn and Co (Merck KGaA 64271 Darmstadt, German) were used. Intermediate standard solution containing 20 mg/L of each metal standard was prepared and used for preparation of series of solution of the construction of the calibration curves. Deionized water was used throughout the experiment for dilution of the standards.

3.4. Instruments and apparatus

Polyethylene plastic bottles, a portable pH-meter (Oakton, Poland), a 0.45-μm type membrane filter paper (Whatman®, No.41, England) microwave digestion (Top wave control) unit, 912A743 furnace atomic absorption spectrophotometer (GFAAS, model novAA® 400P (Analytik Jena AG, Germany) were used during the study.

3.5. Digestion Procedure of wastewater and river water samples

Both river water and wastewater samples were digested using the microwave digester. Accordingly, 15 mL the sample and the aquaregia in 1:1 ratio was added in to sample holder

(Teflon) and digestion was performed by adjusting the conditions for the microwave digestion system (Table 3).

Table 3: Microwave digestion system for river water and industrial effluents.

Temperature (^{0} C)	**Pressure (bar)**	**Time (min)**
160	20	10
180	10	15
150	10	10
50	0	5
50	0	3

After completing digestion and cooling the content was filtered using What man No 41 filter paper into a 25 mL volumetric flask. Then, remaining volume was filled up to the mark with deionized water. Blank solutions were also prepared using similarly procedure.

3.5.1. Determination of the target heavy metals

The target heavy metals including Cd, Cr, Zn, Cu, Co and Pb were determined using GFAAS. The instrument was calibrated using external calibrations by measuring the absorbance of 0.05 – 2.5 mg/L (for Cu, Zn, Cd & Co); 0.05 – 4.0 mg/L (for Pb); and 0.05 – 10 mg/L (for Cr) standard solutions at six concentration points. The calibration curves were constructed using the absorbance as a function of the concentration of the target heavy metals.

Parameters (burner and lamp alignment, slit width and wavelength adjustment) were optimized for maximum signal intensity of the instrument based on the manual of the instrument. Hallow cathode lamps for each metal operated at the manufacturers recommended conditions were used as line sources. The acetylene and air flow rates were managed to ensure suitable flame conditions. Optimal operation conditions of the instrument are presented in Table 4.

Table4: Optimal operation conditions of GFAAS.

Heavy metals	Zn	Cu	Co	Cr	Cd	Pb
Wavelength (nm)	213.9	324.8	240.7	357.9	228.8	283.3
Slit width (nm)	0.5	0.2	0.2	0.2	1.2	1.2
Lamp	HCL	HCL	HCL	HCL	HCL	HCL
Lamp current(mA)	2.0	2.5	5.0	4.0	2.0	2.0
PMT(V)	370	272	402	286	314	349
IDL (µg/L)	0.1	0.1	0.075	0.005	0.001	0.3
Gas	Acetylene	Acetylene	Acetylene	Acetylene	Acetylene	Acetylene

3.6. Analytical Method Validation

3.6.1. Evaluation of Analytical Precision and accuracy

In this study, precision (repeatability) of the obtained results were assessed in terms of standard deviations (SD) of six replicate measurements. Accuracy of the study was investigated using percent recovery (%R) obtained by spiking the river water and factories effluents samples with standard solution of known concentration [70]. The spiked and non-spiked samples were digested following the same procedure of each selected heavy metal was calculated using the equation given below:

$$R = \frac{C_s - C}{S} \times 100$$

Where: R= percent recovery

Cs = fortified sample concentration

C = sample background concentration

S = concentration equivalent of analyte added to fortify the sample

The acceptable range of %R for heavy metals analysis is between 80–120% [71].

3.7. Statistical data analysis

The obtained results were reported as mean and standard deviation. The presence or absence of significance of variations among the studied samples was statistically evaluated using t-test and one–way ANOVA ($p<0.05$) [72]

4. RESULT AND DISCUSSION

4.1. Construction of the Calibration curves

The external calibration curves were obtained using the absorbance as a function of the concentrations of the target heavy metals at six concentration points [73]. Calibration curves of each heavy metal are presented in Appendix 2. The obtained calibration curves have exhibited wide linearity ranges and good coefficient of determinations (R^2), i.e., 0.995 and better, thus, could be used for determination of heavy metals [66]. The linear ranges, R^2 and regression equations of the calibration curves are presented in Table 5.

Table 5: The linear ranges, R^2 and regression equations of the calibration curve.

Heavy metals	Linear range	Correlation coefficient(R^2)	Regression equation
Cu	0.05- 2.5	0.998	y = 0.205x + 0.004
Zn	0.05- 2.5	0.995	y = 0.651x + 0.041
Cd	0.05- 2.5	0 .997	y = 0.490 + 0.024
Co	0.05- 2.5	0.996	y = 0.058x + 0.005
Cr	0.05 -10	0.999	y = 0.078x + 0.005
Pb	0.05- 4	0.996	y = 0.023x - 0.001

4.2. Determination of method detection and quantification limits

The general accepted definition of method of detection limit (LOD) is the concentration that gives a signal three times the standard deviation of the black or background signal. The method quantification limit (LOQ) is the lowest concentration of an analyte in a sample that can be determined with acceptable precision and accuracy under the stated conditions [74]. Both LOD and LOQ of the target heavy metals were determined by digesting the six reagent blanks (aqua regia), which was used for acidifying the sample solutions. LOD and LOQ were determined as 3 and 10 times the standard deviation (SD) of the black solution (3SD and 10SD), respectively. The obtained LOD and LOQ values are presented in Table 6. The obtained LOQ of some elements were equal the maximum tolerance limits set in the international guideline, whereas for other elements the obtained LOQ values were below the fixed maximum tolerance limits, indicating the suitability of the method for the analysis of the selected heavy metals in water and similar matrices.

Table 6: LOD and LOQ values (in mg/L) of water samples analysis for metals

Analyte	SD	LOD	LOQ
Zn	0.0070	0.021	0.070
Cu	0.0006	0.002	0.006
Cr	0.0002	0.001	0.002
Cd	0.0003	0.001	0.003
Co	0.0005	0.002	0.005
Pb	0.0006	0.002	0.006

4.3. Recovery studies

The efficiency and accuracy of the analytical procedures are usually evaluated using %R by analyzing the digests of spiked samples [70].The obtained %R of the river water and industrial effluents samples were ranged in 82-115% and 82 -117%, respectively (Table 7). These values were within the acceptable range, i.e 80- 120% indicating good accuracy for the analysis the target heavy metals [71].

Table 7: The %R the river water & industrial effluent samples

Sites	Heavy metals				
	Pb	Zn	Cr	Co	Cu
Wup	112	102	88	92	108
W1	113	95	101	106	100
W2	94	102	106	110	115
W3	97	96	102	104	113
W4	105	103	96	112	114
W5	104	92	112	106	98
Wd	106	96	82	94	108
E1	102	105	105	97	92
E2	100	113	113	108	97
E3	95	102	100	114	99
E4	92	85	96	110	102
E5	104	108	96	112	117

4.4. Concentration of heavy metals in Modjo river water

The mean concentrations and the standard deviation of 6 replicate measurements (n = 6) (mg/L) of heavy metals in the water samples are presented in Table 8. The finding demonstrated that the concentrations of the heavy metals were varied in the river water samples collected from different sites.

Table 8: Concentrations (mean ± SD, in mg/L for n = 6) of the target heavy metals in Modjo river water sample.

Sample name	**Heavy metals**					
	Pb	Cr	Zn	Co	Cu	Cd
Wup	0.016±0.007	0.420 ± 0.027	0.737±0.020	0.023 ± 0.002	0.735±0.106	ND
W1	0.041±0.002	1.101±0.033	1.124±0.031	0.042 ± 0.004	0.890±0.042	ND
W2	0.038 ± 0.003	0.681 ±0.063	1.10±0.064	0.050 ± 0.009	0.935±0.021	ND
W3	0.044± 0.005	0.679 ± 0.012	0.941±0.055	0.055 ±0.003	0.985±0.106	ND
W4	0.074± 0.007	1.160± 0.015	0.757 ±0.026	0. 048 ± 0.005	1.030±0.002	ND
W5	0.057 ±0.003	1.169 ± 0.060	1.130±0.014	0.043 ± 0.003	0.950±0.007	ND
Wd	0.036±0.004	0.693 ± 0.035	0.820 ±0.011	0.032 ± 0.003	1.005±0.092	ND
WHO [76]	0.010	0.050	3.000	2.000	0.050	0.003
USEPA [74]	0.015	0.100	5.000	0.050	0.100	0.005
ESA[77]	0.010	0.050	5.000	2.000	0.050	0.003

As can be observed, Cd was not detected in water samples. But, the concentrations of other studied heavy metals at all sampling stations in the downstream are higher than their concentrations in the upper stream sample, indicating the impact of factories effluents on the levels of the metals in the water profile.

4.4.1. Concentration of Pb in water Samples

The average concentration value of Pb in river water varied in between 0.016 ± 0.005 - 0.074 ± 0.007 mg/L. The lowest and the largest concentration were recorded at the site of Wup and W4, respectively. The observed higher concentrations of Pb in downstream of the river water shows as the factories discharge Pb containing chemicals into the river water. The factories may discharge Pb to the river water through paints, solders, pipes, building materials, combustion of oil, gasoline etc [75]. In all water samples the concentrations of Pb water were above the maximum permissible level set in WHO [76], USEPA [74] and ESA [77] guidelines drinking water. This indicates that the Modjo river water is not suitable for drinking.

Finding of the study demonstrated water samples collected from different sites showed significant variations at ($p \leq 0.05$). This variation could possibly be attributed to the difference in the concentrations of Pb in the wastewater discharged from the factories [Table 9]. Compared to the Akaki River, which also receive massive factories effluents, Modjo river water has relatively lower concentrations of Pb in all sampling sites [78]. Generally, Pb is toxic; it damages brain, kidneys, circulatory system, and nervous system [60] and thus need monitoring.

4.4.2. Concentration of Cr in water Samples

The average concentration of Cr in river water varies from 0.420 ± 0.027-1.169 ± 0.060 mg/L. The lowest and the largest concentrations were observed at Wup and W5, respectively. The highest concentration of Cr at site W5 is because water sample was taken after effluents from two industries, United and Farida tannery industries, were joined to the river water. United and Farida tannery industries discharge their effluents through the same cannel. The obtained concentrations of Cr were higher than Wup (control sample). Because, the river water receives massive effluents, from several tannery industries which contain large amount of Cr. Cr may enter the water through industrial effluents such as Cr pigment, tannery wastes, leather manufacturing wastes and municipal sewage sludge [79].

The concentrations of Cr obtained from the river water samples were above the maximum permissible level stated by WHO [76], USEPA [74] and ESA [78] and thus, it is not appropriate for drinking. Very large amounts of Cr can cause vomiting, diarrhea and kidney failure [80].

Cr is generally more toxic at high temperatures and its compounds are known to cause cancer in humans [81]. One-way ANOVA result **(**$p \leq 0.05$**)** indicated that the Cr concentrations in the river water samples collected from different sites varied significantly. Moreover, the concentration of Cr in this study was higher than the previously reported concentration in Akaki River [78].

4.4.3. Concentration of Zn in water Samples

The average concentration value of Zn in river water varies in between 0.737 ± 0.020 - 1.130 ± 0.014 mg/L. The lowest and the largest concentration were obtained at Wup and W5 sites, respectively. The concentrations of Zn at all sites of river water were below the maximum permissible limits set by WHO [76], USEPA [74] and ESA [77]. Hence, the river water has no health effect in terms of Zn.

The One-way ANOVA result ($p \leq 0.05$) indicated that the Zn concentrations in the river water samples varied significantly. These variations may be attributed to different causes including industrial discharges, sewage effluents, agro-industries, fertilizers, domestic wastes, municipal wastes, as well as natural chemical weathering [82].

4.4.4. Concentration Cu in River water Samples

The average concentrations Cu in river water varies in between 0.735 ± 0.106 - 1.102 ± 0.120 mg/L. The lowest and the largest concentrations were obtained at Wup and W4, respectively. The largest average concentration of Cu at site W4 may be due to natural weathering of soil and discharges from industries. The concentration of Cu in river water was less than the permissible limit set by WHO [76] and ESA [77]. Therefore Cu is not supposed to be a problem for domestic use and no health problems associated with Cu for drinking and irrigation. One-way ANOVA study ($p \leq 0.05$) there is no significant variation in Cu concentrations levels in river water samples.

4.4.5. Concentration of Co in water Samples

The average result concentration value of Co in river water varies between 0.023 ± 0.002-0.055 ± 0.003 mg/L. The lowest and the largest concentration values of Co obtained were at the site of Wup and W3, respectively. The largest average concentration of Co at site W3 may be due to effluents discharged from industries dealing with corrosion and wear-resistant alloys.

Co concentration obtained from all river water sites were below permissible level stated by USEPA [74], WHO [76] and ESA [77].

Thus, Co is not a health concern at concentrations normally observed in the water. The One-way ANOVA result ($p \leq 0.05$) indicated that the concentrations of Co in the river water samples varied significantly.

4.4.6. Concentration of Cd in water Samples

The concentration of Cd in water samples of the river is very low which is below the detection limit. The WHO [76] and ESA [77] guideline for domestic water supply is 0.003 mg/L. The concentration of Cd in Modjo river water does not exceed this level; therefore Cd is not supposed to be a problem for domestic use and no health problems associated with Cd for drinking and Irrigation.

4.1. Levels of selected Heavy Metals in industrial Effluent samples

The distribution of heavy metals (Cr, Cd, Zn, Pb, Co and Cu) in industrial effluent samples from the eastern industry zone has been evaluated. Industrial effluent samples were collected at the same distances from the wastewater channel, before joining to the river water. The mean concentrations and the standard deviation of 6 replicate measurements (n = 6) (mg/L) of heavy metals in factories effluent samples are presented in Table 9. The results obtained revealed that the concentrations of the heavy metals were found to be in the order of Cr > Zn > Cu > Pb > Co. Except, Cd which was not detected, the concentration of each heavy metal in effluent samples was also higher than the maximum permissible limit set by WHO [82] and USEPA [83] which could pose a huge threat to human health and the natural environment.

Table 9: Concentrations, (mean ± SD, in mg/L for n = 6) of the target heavy metals in industrials effluent samples.

Sample name	Heavy metals					
	Pb	Cr	Co	Zn	Cu	Cd
E1	0.249±0.015	42.340±2.420	0.079±0.009	2.033±0.240	1.150±0.240	ND
E2	0.052±0.006	37.830±0.980	0.034±0.003	1.678 ± 0.04	1.032±0.101	ND
E3	0.050±0.002	60.360±2.560	0.041±0.002	2.142±0.040	0.950±0.035	ND
E4	0.230±0.004	33.600±0.930	0.081±0.012	2.120 ± 0.02	1.103±0.120	ND
E5	0.032±0.004	64.490±2.300	0.065±0.003	2.279±0.151	1.155±0.162	ND
WHO[82]	0.050	1.000	NM	0.030	0.010	0.003
USEPA[83]	0.015	1.000	NM	2.000	1.000	0.005

NM= Not mentioned ND= Not detected

4.1.1. Concentration of Pb in industrial effluent samples

The concentrations of Pb in the industrial effluent varied from 0.032 ± 0.03 - 0.249 ± 0.015 mg/L. The lowest and highest concentrations were observed at E5 and E1, respectively. The highest concentration level of Pb at site E1 may be due to high discharge through paints, solders, pipes, building material, gasoline and industrial waste [75]. Except at site E5 the mean concentration value of Lead were higher than recommended limit for industrial effluents to be discharged to water bodies for agricultural irrigation set by WHO[82]. But, according to USEPA [83] guideline at all sampling point the concentrations of Pb exceeded the recommended maximum limit for agricultural irrigation. This makes the receiving water unsuitable for human consumption and agricultural irrigation.

One-way ANOVA result ($p \leq 0.05$) indicated that the concentrations of Pb in effluent samples varied significantly. Significant difference was evident from all the sampling point, which can be attributed to the variation of the amount of effluents discharged from different industries. Pb is known to be toxic even at low levels resulting in ill-health effects. It is chronic exposure has linked to growth retardation of children [84].

4.1.2. Concentration of Cr in industrial effluent samples

The results of the study demonstrated factories effluent samples contain very high concentrations of Cr than other investigated metals. The average concentrations of Cr in the industrial effluent samples varied from 33.60 ± 0.930 - 64.49 ± 2.30 mg/L .The lowest and the highest concentrations were observed in E4 and E5, respectively. The highest concentration level of Cr at site E5 may be due to excessive waste water effluent discharged from Farida tannery and United Vasn leather plc factories through the same channel.

The One-way ANOVA result ($p \leq 0.05$) indicated that the Cr concentrations in the effluent samples varied significantly. This may be due to the fact that the amount of Cr containing compounds used for tanning might be different in different industries. Continuous discharge of Cr at even low concentration has been reported to be toxic to aquatic life and has been shown to disrupt the aquatic food chain [85]. Cr is a toxic pollutant due to its harmful effects on human health, especially in its hexavalent form [86]. Removal mechanisms must be sought for Cr levels in the effluent of industries where the metal is high in effluent.

4.1.3. Concentration of Zn in industrial effluent samples

The concentrations of Zn in the industrial effluents varied from 1.678 ± 0.04 - 2.279 ± 0.151 mg/L. The lowest and highest concentrations of Zn were observed in E2 and E5 samples, respectively. The highest concentration level of Zn at site E5 may be due to high wastes discharged from Farida tannery and United Vasn leather plc factories through the same channel). The mean concentrations of Zn in all sampling points were higher than the standard limits for industrial effluents to be discharged to water bodies for agricultural irrigation set by WHO [82]. Except at site E2, in other the concentrations of Zn were higher than the standard limit set by USEPA [83]. Zn is the least toxic and is an essential element in the human diet as it is required to maintain the proper functioning of the immune system, normal brain activity and is fundamental in the growth and development of the fetus, but a very high concentration of zinc is very toxic, hence harmful to the human body [87].

4.1.4. Concentration of Cu in industrial effluent samples

The average concentration of Cu in the industrial effluents varied from 0.950 ± 0.035 - 1.155 ± 0.101 mg/L. The lowest and highest concentrations were obtained at the site of E3 and E5,

respectively. The obtained mean concentrations of Cu were higher than recommended limit for industrial effluents to be discharged to water bodies for agricultural irrigation set by WHO [82]. Except at site E3 the obtained results were also higher than recommended level set by USEPA [83]. This could be attributed to the reason of anthropogenic activities and industrial effluent released without treatment [88]. It is important here to note that Cu is highly toxic to most fishes, invertebrates and aquatic plants and not appropriate for agricultural irrigation [89].

4.1.5. Concentration of Co in industrial effluent Samples

The average concentration of Co in the industrial effluents varied from 0.034 ± 0.003 to 0.081 ± 0.012 mg/L. The lowest and highest concentration values of Co investigated were recorded at site of E2 and E4, respectively. The maximum permissible limit of Co discharged effluents into water bodies for agricultural irrigation has not yet been set.

4.2. Comparison of the levels of heavy metals in industrial effluents and the river water

The concentrations of heavy metals in the river water and corresponding industrial effluent samples were compared by student's t-test (at 95% confidence interval). The calculated t-values of the target metals in the industrial effluent and its corresponding sampling point from river water: in Modjo tannery Share Company (E1) and its corresponding sampling point of river water (W1); George shu tannery (E2) and W2; Hora and Hundao tannery (E3) and W3; Friendship tannery (E4) and W4; as well as United leather Plc and Farida tannery(E5) and W5 were greater than the critical t-values (Appendix 1; Table 2 – 6) in all cases. This indicates the presence of significant differences between the mean concentrations of the target heavy metals in industrial effluents discharged from the factories and the sample collected from the receiving points in the river water. The finding of the study, demonstrated that the concentrations of heavy metals were relatively higher in effluents than in the corresponding river water. The lower concentration of the metal in the receiving water might be due to dilution and adsorption of the metal by sediments and organic matters present in the river water [90].

4.3. Comparison of the levels of heavy metals in the upper and river water

The statistical t-test revealed that the concentrations of the heavy metals in the upper stream, before receiving any factory effluent (Wup) and in the downstream (after receiving effluents from various factories) Wd were significantly different (Appendix 1, Table 1). As demonstrated in Table 8 and Table 9, the concentrations of all the heavy metals in the downstream water sample were higher than their concentrations in the upper stream water. The high concentrations of the heavy metals in the downstream river water sample indicate the contributions of the industrial effluents on the levels of the heavy metals to the river water. Thus, based on this finding the industries are highly polluting the river water by releasing untreated and/or partially treated effluents to the river water.

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

In this study, the impact of industrial effluents on the levels of selected heavy metals on Modjo River was investigated. The observed finding showed that the concentrations of heavy metals in the river water samples were influenced by the discharged effluent from the factories. Except for Cd, all the studied effluent samples contain much higher concentrations of the target heavy metals than the receiving river water. The lower levels of the heavy metals in water samples could be attributed to dilution effect and/or adsorption to the sediment and suspended organic matters.

The Modjo river water was considerably contaminated by heavy metals like Cr and Pb and their observed concentrations were above the maximum permissible limits set by WHO, USEPA and ESA and thus, it is not suitable for drinking. The observed results demonstrated that, all the factories effluent samples contain high levels of the heavy metals, which exceed the maximum permissible limits that factories discharge to the surrounding environment set by WHO and USEPA. This indicates that the factories may not treat their effluents before discharging to the environment.

The sample of the effluent collected at E5 and the corresponding water sample W5 contain relatively higher concentrations of the heavy metals. This could be attributed to the combined effluent discharge from two factories, United leather Plc and Farida tannery factories. The higher level of metals observed at W5 also attributed to the effluents of the two factories. Analysis of one-way ANOVA also showed the existence of significant differences in both industrial effluent and river water except Cu in the river water sample.

The results of student t-test (at 95% confidence interval) also showed the presence of significant differences between industrial effluent sampled before joining the water and the corresponding river water sampled after receiving the industrial effluent. In addition, the levels of all the heavy metal measured in the downstream of the river were higher than the levels in upstream site which was used as the control. This indicated that the release of untreated wastewater from various industries influenced the quality of the receiving river water. Therefore, this will create a problem for downstream users as they use it for domestic, agricultural and recreational purposes.

5.2. Recommendations

In general massive industrial effluents emanating from various tannery and leather industries in Modjo area are influencing the quality of the receiving Modjo river water quality in terms of heavy metal contents and the surrounding environment. Therefore, based on this finding the following recommendations are forwarded from the researcher:

- It is recommended that the factories should treatment their effluent before disposing, to minimize the adverse impact on the receiving water body and surrounding.
- Further study should be conducted on the impact of industrial effluents on the river water and the surrounding growing crop and vegetation.
- The concerned government and non-government offices should force the factories owners to treat their waste discharge before releasing to the environment.

REFERENCES

1. Mahmoud, A.S.; Emmanuel,E.; Joseph.; L. W. Bobby,J.S. Chemical Evaluation of Drinking Water from Egypt. *Journal of Food Composition Analysis*. **2001**, *14*, 127-152.
2. Oluduro, A.O.; Adewoye, B.I. Efficiency of moringa Oleifera Sead extracts on the micro flora of surface and ground water. *Journal of plant Science*. **2007**, *6*, 453-438.
3. Botkin, D. B.; Keller, E. D. Environmental Science. Earth as a living planet 7th ed., John Wiley and son Inc. New York, USA. **2008**.
4. Lone, M. I.; Saleem, S.; Mahmood, T.; Saifullah, K.; Hussain, G. Heavy metal contents of vegetable irrigated by sewage/tube well water. *International Journal of Agriculture and Biology***. 2003**, *5*,533-535.
5. Baby, S. P. Effect of tannery effluent on water profile, plant growth and human health, PhD thesis. Avinashilingam Deemed University for Women, Coimbatore. **2010**.
6. Akan, J. C.; Abdulrahman, F. I.; Ayodele, J. T.; Ogugbuaja, V.G. Impact of tannery and textile effluent on the chemical characteristics of Challawa River, Kano state, Nigeria. *Electronic Journal of Environmental Agriculture and Food chemistry*. **2009**, *8*, 1008-1032.
7. Tariq, S.R.; Shah, M. H.; Shaheen, N.; Khalique, A.; Manzoor, S.; Jaffar, M. Multivariate analysis of trace metal levels in tannery effluents in relation river water. A case study from Peshawar, Pakistan. *Journal of Environmental Management*. **2006**, *79*,20-2
8. Storelli, M.M.; Storelli, A.; D'ddabbo, R.; Marano, C.; Bruno, R.; Marcotrigiano, G.O. Trace elements in loggerhead turtles (*Carettacaretta*) from the eastern Mediterranean Sea, Overview and evaluation. *Environmental Pollution*. **2005**, *135***,**163-170
9. Fernandes, C.; Fontaínhas, F.A.; Cabral, D.; Salgado, M. A. Heavy metals in water, sediment and tissues of Liza Saliens from Esmoriz–Paramos lagoon, Portugal. *Environmental Monitory Assessment*. **2008**,*136***,** 267-275
10. Censi, P.; Spoto, S.E.; Saiano, F.; Sprovieri, M.; Mazzola, S.; Nardone, G.; Geronimo, S.I.; Punturo, R.; Ottonello, D. Heavy metals in coastal water systems. A case study from the northwestern Gulf of Thailand. *Chemosphere*. **2006**, *64*, 1167-1176.
11. Water for Pharmaceutical Use. In Quality Assurance of Pharmaceuticals Compendium of Guidelines and Related Materials 2nd Updated Edition. WHO, Geneva, Switzerland. **2007**.

12. McCurry, J.; Fay, R. Hydrogen, Oxygen and Water. In: McCurry Fay Chemistry, K.*P.* Hamann 4th Edition., Pearson Education New Jersey and USA: **2004**.
13. Songoyin, A.Y. Characteristic of control of industrial effluents generated pollution. *Environmental management and health*. **1995**, *6*, 16-18.
14. Songoyin, A.Y. Ground water and surface water pollution by open Refuse DUMP in Ibadan, Nigeria. *Environmental management and health* .**1991**, *3*, 24-31.
15. Ajayi, S.O.; Osibanji, O. Pollution studies on Nigerian river water quality of some Nigerian rivers. *Environmental pollution series*. **198**1, *2*, 87-95
16. Reda, H.A. Pollution levels of trace metals from Modjo tannery share company effluent in the surrounding river water and soil. *College of natural science, Arba Minch, Ethiopia*. **2015**,*3*,56-60
17. Agarwal. Assessment of pollution by Physicochemical Water Parameters Using Regression Analysis: A Case Study of Gagan River at Moradabad- India, *Advances in Applied Science and Research.* **2011***, 2,* 185 -189.
18. Sanayei, Y.; Ismail, N.; Talebi, S.M. Determination of heavy metals in Zayandeh rood, *Isfahan-Iran. Science*. **2009,** *6*, 1209-1214.
19. Ghaedi, M.; Fathi, M. R.; Marahel, F .; Ahmadi, F. Simultaneous preconcentration and determination of copper, nickel, cobalt and lead ions content by flame atomic absorption spectrometry. *Freshens on Environmental Bulletin.* **2005**, *14*, 1158-1165.
20. Tüzen, M. Determination of heavy metals in water samples of the Mid DamLake Black Sea by graphite furnace atomic absorption spectrometry. *Food Chemistry*. **2003**, *80,* 19-123
21. Weiner, E. Environmental Chemistry and Practical Guide for Environmental Professionals 2nd Edition, *Boca Raton*, Florida: USA. **2008,** 170-187.
22. Erica, R.; McKenzie, Peter, G.; Green, Thomas, M. Young. "Metals Associated with storm water-relevant brake and tire samples". *Science Totton Environment* .**2009***, 407*, 5855–5860
23. Wang, S.; Mulligan, N. "Occurrence of arsenic contamination in Canada: Sources, behavior and distribution", *Science of the Total Environment*, August. **2006**, *366*,701– 721.
24. Wedepohl, K. H. "The composition of the continental crust", Geochim. *Cosmochim Acta*, April. **1995**, 329–344
25. Camacho, J.R.; Armienta, M.A. "Natural chromium contamination of groundwater at Leon Valley Mexico", *Journal of Geochemical Exploration*, April. **2000**, *68*,167–181.

26. Ball, J.W.; Izbick, J.A. "Occurrence of hexavalent chromium in ground water in the western Mojave Desert, California", *Applied Geochemistry*, July. **2004**, *19*,1123–1135
27. Viers, J., Olivia, P.; Nonell, A.; Gelabert, A.; Sonke, J.E.; Freydier, R.,;Gainville, R. Dupre, B. "Evidence of Zn isotopic fractionation in a soil–plant system of a pristine tropical watershed (Nsimi, Cameroon)". *Chemical Geology*, April .**2007**, *239*, 124–137.
28. Borrok, D.M.; Nimick, D.A.; Wanty, R.B.; Ridley, W.I. "Isotopic variations of dissolved copper and zinc in stream waters affected by historical mining", *Geochimica Cosmochimica*, January. **2004.**
29. Huffmeyer, N.; Klasmeier, J.; Matthies, M. "Geo-referenced modeling of zinc concentrations in the Ruhr river basin (Germany) using the model GREAT-ER", *Science of the total environment*, March. **2009,** *407*, 2296-2305
30. Nordstrom, D.K. "Worldwide Occurrences of Arsenic in Ground Water", *Science Compass*, June. **2002**, *296*, 2143-2145.
31. Jarup, L. "Hazards of heavy metal contamination". *British Medical Bulletin*, December. **2014**, *6*,167-182.
32. Hsu, S.C.; Wong, G.T.F.; Gong, G.C.; Shiah, F.K.; Huang, Y.T.; Kao, S.J.; Tsai, F.; Lung, S.C.C.; Lin, F.J.; Lin, I.I.; Hung, C.C.; Tseng, C.M. "Sources, solubility, and dry deposition of aerosol trace elements over the East China Sea", *Marine Chemistry*, June. **2010,** *120*, 116–127.
33. Kang, J.; Choi, M.S.; Yi, H.I.; Song, Y.H.; Lee, D.; Cho, J.H. "A five-year observation of atmospheric metals on Ulleung Island in the East/Japan Sea: Temporal variability and source identification", *Atmospheric Environment*, August .**2011**, *24*, 4252-4262.
34. Yang, R.; Zhang, A.; Wang, S. "The distribution of dissolved lead in the coastal waters of the East China Sea", August, *Marine Pollution Bulletin*. **2014** , *85*, 700–709
35. Kowalski, A.; Siepak, M.; Boszke, L. "Mercury Contamination of Surface and Ground Waters of Poznań, Poland", *Polish Journal of Environmental Study*, January. **2014**, *16* , 67-7
36. Wang, Q.; Kim, D.; Dionysiou, D.D.; Sorial, G.A.; Timberlake, D. "Sources and remediation for mercury contamination in aquatic systems literature review". *Environmental Pollution, September*. **2004**, *131*,323-336.
37. Guven, D.; Akyncy,G. Heavy metals partitioning in the sediments of Izmir Inner Bay. *Journal Environmental Science-China*. **2008**,*20*,413-418.

38. Tokalioglu,S.; Kartal,S.;Birol,G. Application of a Three-stage Sequential Extraction Procedure for the determination of Extractable Metal Contents in Highway soils. *Journal of Chemistry* .**2003,** *27*,333-346.
39. Weiner, E.R. Application of Environmental Aquatic Chemistry. Taylor and Francis, LLC.USA. **2008**
40. Calamari, D.; Navel, H. Review of pollution on African aquatic environment. *CICEA technical paper*. **1994**,*25*,37-38.
41. Alloway, B.J.; Ayres, D.C. Chemical principle of Environmental pollution. Blackie Academic and Professional. London, England. **1993.**
42. Ward, N.I. Trace elements, Environmental Analytical chemistry. Fifield, F.W and Haines, P.J. Blackie Academic and professional. London, UK. **1995**
43. Heath, A.G. Water pollution and Fish Physiology. CRS Press, Baco Raton. **1987**
44. Chalermsupanimit, S. Accumulation of heavy metals in water, sediment and aquatic plant in Snakeskin Gourami Fish Raising Pond at Amphawa District. Samut. Songkhram Provision. M.Sc. Thesis. Faculty of Graduate Studies. Mahido University, Bangkok, Thailand.**2006.**
45. Sanayei,Y.; Ismail,N.; Talebi,S.M. Determination of heavy metals in Zayandeh rood, Isfahan-Iran. *World Applied Sciences journal*. **2009**, *6,1209*-1214
46. Hanaa, M.; Eweida, A.; Farag, A. Heavy metal in drinking water and their Environmental impact on human health. International Conference on Environmental Hazards Mitigations, Cairo University, Egypt. **2000.**
47. Rajkovic,M.B.;Lacnjevac,C.M.;Ralev,N.R.;Stojanovic,M.D.;Toskovic,D.V.;Pantelic,G.K. Identification of heavy metals and Radioactive in drinking water by indirect analysis method based on scale tests. *Journal of Water Research Sensors*. **2008**, *8,* 2188-2207.
48. Bachmat,Y. Ground water contamination and control, Marcel Dekker, Inc, New York.USA.**1994**.
49. Back, W.; Hanshaw, B.B. Advance in hydro science. In Blakes.S. (Ed).Chemical geohydrology Academic press, New York, USA.1965, 49.
50. Schafer, S.G.; Froth, W.O. The interaction between cadmium and iron; a review of the literature. *Trace Elements in Medicine*. **1985,***4*,158-162
51. Singh, A.K.; Rawat, D.S.Toxicity of industrial waste water to the aquatic plant. Lemna minor L. *Journal of Environmental Biology*.**1985**, *31*, 44-48.

52. Talebi, S.M. Determination of Lead associated with air-borne particulate matter by flame atomic absorption and wave-length dispersive X-ray fluorescence spectroscopy. *Journal of Environmental Analytical chemistry*.**1998**, *72*, 1-9.
53. Weiner, E. Environmental Chemistry and a Practical Guide for Environmental Professionals 2 Editions. Boca Raton, Florida: USA. **2008,** 170-187.
54. Erica, R.; Peter, G.; Green Thomas, M. "Metals Associated with storm water-relevant brake and tire samples". *Science of Totten Environmental* .**2009**, *407*, 5855–5860
55. Beliles, R. P. The lesser metals, in: F.W. Oehme (Ed.), Toxicity of Heavy Metals in the Environmental; Marcel Dekke, New York: **1979**, 383.
56. Guidelines for Drinking Water Quality, 4th ed. WHO, Geneva, Switzerland. **2011**
57. National Primary Drinking Water Regulation. USEPA, United States Environmental Protection Agency.**1999**.
58. Boxall, A.B.; Comber, S.D.; Conrad, A.U.; How croft; J.d, Zaman N. Inputs, Monitoring and Fate Modeling of Antifouling Biocides in UK Estuaries. *British pollution Bulletin.* **2000**, *40*, 898-905.
59. Nassef, M.; Hannigan, R.; EL Sayed, K. A.; Tahawy, M.; S. El. Determination of some heavy metals in the environment of Sadat industrial city. Proceeding of the 2nd Environmental Physics Conference, Cairo University, Egypt. **2006,** 145-152.
60. Salem, H.M.; Eweida, E. A.; Faraz, A. Heavy metals in drinking water and their environmental impact on human heal Cairo University. Egypt, September. **2000**, 542-556
61. Emsley, J. Manganese. Nature's Building Blocks. Guide to the Elements, Oxford, UK: Oxford University Press. **2001**, 249-25.
62. Bingol, D.; Akcay, M. Determination of trace elements in fly ash samples by AAS after applying different digestion procedure. *Journal of Quantitative Specectroscopic Research*. *0* **2005**,*101*, 146-150.
63. Skoog, D.A.; West, D.M.; Holler, F.J.; Crouch, S.R. Fundamentals of Analytical Chemistry 8th Ed., Publisher, David Harries. **2005**, 720-723.
64. Eser, K.; Asuman, D.; Saraymen, R.; Engin, K. 2004. Comparative quantitative analysis of zinc, magnesium and copper content in the scalp hair of healthy people and breast cancer patients. *Journal of Trace Elements in Experimental Medicine*.**2004**, *17:* 175-180.

65. Anog,R.; Andrade,G.B.; Miasco,R.B.; Ortiz, M.F. Water quality and diversity of macro invertebrates species in river Of Cebu city, philppines. *Philoscientist*. **2010,***47,*27-45.
66. Standard Methods for the Examination of Water and Waste water 20th Edition., APHA, American Water Works Association and Water Environment Federation, Washington, D.C.USA:**1999**.
67. Manoj, K. B.; Kumar, P.; Padhy, K. Characterization of metals in water and sediments of Subarnarekha River along the projects' sites in Lower Basin, India. *Universal Journal of Environmental Research Technology*. **2012**,*2,* 402-410
68. Tareq, S.M.; Rahman, M.S.; Rikta, S.Y.; Islam S.M.N.; Sultana, M.S. Seasonal variation in water quality of the Ganges and Brahmaputra River, Bangladesh. *Environmental Bulletin*. **2013**, *2*, 71-82.
69. Standard methods for the examination of Water and wastewater. APHA, Washington DC, USA**. 1998**.
70. Deribachew, B.; Made, M.; Nigussie, D.; Taddesse, A.M. Selected heavy metals in some vegetables produced through wastewater irrigation and their toxicological implications in Eastern Ethiopia. *African Journal Food Nutrition and Development*. **2015**, *15,* 10013-10032.
71. Theodore, D. M. Method .Determinations of trace elements in drinking water by axially viewed inductively coupled plasma-atomic emission spectrometry. *USA Environmental Protection Agency Cincinnati*. **2005,** *45268*, 1-36.
72. Zar, J.H. Biostatistical Analysis. Printice –Hall, Englewood Cliffs. *Nutritional of Journal*. **2001**.
73. Duan, T. Determination of ultra-trace concentration of elements in high purity tellurium by inductively coupled plasma spectrometry after iron (III) hydroxide co precipitation. *Spectrochim Acta B.* **2003**, *58*, 1679-1685.
74. Drinking water standards and health advisories. USEPA, Office of water, US Environmental protection Agency, Washington D.C, USA. **2008.**
75. N'diaye, A. D.; Dhaouadi, M. B.; Kory, M. O.; Kankou, A.O. "Water Quality Assessment of Senegal River in Mauritania by Turbidity and Chemical Parameters Analysis during Rainy Season. *Issues in Biological Sciences and Pharmaceutical Research*. **2013**. *1*, 016-021.
76. WHO Guidelines for drinking water quality. WHO, Geneva. **2008**.

77. Ethiopian Water Technology Centre. Butajira – Ziway Areas Development Study on Water Quality. Ministry of water resources, Water technology centre. ESA, Ethiopia. **2008**
78. Melaku, S.; Wondimu, T.; Dams, R.; Moens, L. Simultaneous Determination of Trace Elements in Tinishu Akaki River Water Sample, Ethiopia, by ICP-MS. *Canadian Journal of Analytical Science and Spectroscopy*. **2004,** *49*, 374-384.
79. Rahman, M. M.; Fikria, A.F.; Kamaruzzaman, B.Y.; Wan Nik, W.B. Distribution of trace metals in pore water along Terengganu beach. *Australian Journal of Basic and Applied Sciences*. **2012**, *6*, 213 – 217.
80. Abdul R. M.; Mutnuri, L.; Dattatreya, P. J.; Mohan, D. A. Assessment of Drinking Water Quality Using ICP-MS and Microbiological Methods in the Bholakpur Area, Hyderabad, India. *Environmental Monitoring and Assessment*. **2012**,*184*, 1581–92.
81. Center of Ecological Sciences, IISc Environmental hand-Book-Documentation on Monitoring and Evaluating Environmental Impacts, Compendium of Environmental standards, Indian Institute of Science, Bangalore [online] available. http://wgbis.ces.iisc.ernet.in/eregy/HC270799/HDL/ENV/START.HTM. **2001**
82. WHO Guidelines for the Safe use of wastewater, excreta and grey water. WHO ,Geneva.**2006**
83. Risk-based concentration table. USEPA, United State Environmental Protection Agency, Washington, DC, USA.**2010**
84. Muiruri, M.J. Determination of concentration of selected heavy metals in Tilapia fish, sediments and water from Mbagathi and Ruiru Athi river tributaries, Kenya. MSc thesis, Kenyatta University, Kenya. **2012**, *6*, 114-126.
85. Baby, S. P. Effect of tannery effluent on water and soil profile, plant growth and human health, PhD thesis. Avinashilingam Deemed University for Women, *Coimbatore*. **2010**, *43*, 1-7.
86. Abagale, F.K.; Sarpong, D.A.; Ojediran, J.O.; Osei-Agyemang, R.; Shaibu, A.G. ; Birteeb, P.T. Heavy metal concentration in wastewater from car washing bays used for agriculture in the Tamale Metropolis, Ghana. *International Journal of Current Research*. **2013**, *5*, 1571-1576.

87. Helen, L.E.; Othman, O.C. 2014. Levels of selected heavy metals in soil, tomatoes and selected vegetables from Lushoto district-Tanzania. *International Journal of Environmental Monitoring and Analysis*. **2014**, *2*, 313
88. Merret, S. Industrial effluent policy: Economic instruments and Environmental regulation. *Water policy*. **2000**, *2*, 201-211.
89. Moore, J.W.; Ramamoorthy, S. Heavy Metals in natural waters. Applied monitorin and Impact Assessment. Springer-Verlad, New York. **1984**, 28-246.
90. Tang, A.; Liu, R.; Ling, M.; Wang, J. Distribution characteristics and controlling factors of soluble heavy metals in the yellow River Estuary and Adjacent Sea. Procedia. *Environmental Science*. **2010**, *2*, 1193-1198.

APPENDIXES

Appendix-1: Statistical t-test

Table 1: Mean standard deviation, number 6 replicate measurements and experimental t- values of the selected heavy metals in upper stream and down steam Modjo river water.

Metals	River	n	Mean	SD	t-exp.	t-crit.
Cr	Wup	6	0.420	0.027	14.96	2.23
	Wd		0.690	0.035		
Zn	Wup	6	0.737	0.020	8.91	2.23
	Wd		0.820	0.011		
Cu	Wup	6	0.735	0.016	7.10	2.23
	Wd		1.005	0.092		
Pb	Wup	6	0.016	0.007	6.10	2.23
	Wd		0.036	0.004		
Co	Wup	6	0.023	0.002	6.12	2.23
	Wd		0.032	0.003		

SD= standard deviation, t-exp = Experimental value of t, t-crit = Critical value of t

*** The mean difference is significant at the 0.05 level**

Table 2: Industrial effluent discharged from Modjo tannery Share Company (E1) and sampling point of river water (W1)

Metals	Sites	n	Mean	SD	t-exp	t-crit
Cr	E1	6	42.34	2.42	41.74	2.23
	W1		1.101	0.033		
Zn	E1	6	2.033	0.240	9.20	2.23
	W1		1.124	0.031		
Cu	E1	6	1.150	0.240	2.61	2.23
	W1		0.890	0.042		
Pb	E1	6	0.249	0.015	33.67	2.23
	W1		0.041	0.002		
Co	E1		0.079	0.009	9.20	2.23
	W1	6	0.042	0.004		

***The mean difference is significant at the 0.05 level**

Table 3: Industrial effluent discharged from George shu tannery (E2) and sampling point of river Water (W2)

Metals	**Sites**	**n**	**Mean**	**SD**	**t-exp.**	**t-crit.**
Cr	E2	6	37.83	0.980	92.66	2.23
	W2		0.681	0.063		
Zn	E2	6	1.678	0.040	18.76	2.23
	W2		1.10	0.064		
Cu	E2	6	1.032	0.101	1.95	2.23
	W2		0.95	0.021		
Pb	E2	6	0.052	0.006	5.11	2.23
	W2		0.038	0.003		
Co	E2		0.055	0.009	5.42	2.23
	W2	6	0.034	0.003		

*** The mean difference is significant at the 0.05 level**

Table 4: Industrial effluent discharged from Hora and Hundao tannery (E3) and sampling point of river water (W3)

Metals	Sites	n	Mean	SD	t-exp	t-crit
Cr	E3	6	60.36	2.56	57.10	2.23
	W3		0.679	0.012		
Zn	E3	6	2.142	0.040	43.26	2.23
	W3		0.941	0.055		
Cu	E3	6	0.950	0.035	1.77	2.23
	W3		0.985	0.106		
Pb	E3	6	0.055	0.002		2.23
	W3		0.044	0.005	5.00	
Co	E3		0.044	0.002		2.23
	W3	6	0.036	0.003	5.43	

***The mean difference is significant at the 0.05 level**

Table 5: Industrial effluent discharged from Friendship tannery (E4) and sampling point of river water (W4)

Metals	Sites	n	Mean	SD	t-exp	t-crit
Cr	E4	6	33.60	0.930	85.18	2.23
	W4		1.169	0.069		
Zn	E4	6	2.120	0.020	78.1	2.23
	W4		0.757	0.026		
Cu	E4	6	1.030	0.002	14.50	2.23
	W4		1.102	0.012		
Pb	E4	6	0.230	0.004	47.40	2.23
	W4		0.074	0.007		
Co	E4		0.081	0.012	7.53	2.23
	W4	6	0.043	0.003		

***The mean difference is significant at the 0.05 level**

Table 6: Industrial effluent discharged from united leather Plc and Farida tannery (E5) and sampling point of river water (W5)

Metals	Sites	n	Mean	SD	t-exp	t-crit
Cr	E5	6	64.49	2.30	67.44	2.23
	W5		1.160	0.015		
Zn	E5	6	2.279	0.151	18.56	2.23
	W5		1.130	0.014		
Cu	E5	6	1.155	0.101	4.96	2.23
	W5		0.950	0.007		
Pb	E5	6	0.057	0.004	12.25	2.23
	W5		0.032	0.003		
Co	E5		0.065	0.003	12.70	2.23
	W5	6	0.043	0.003		

*** The mean difference is significant at the 0.05 level**

Table 7: One way ANOVA analysis for between and within Groups of water samples.

Parameters	Method	Sum of squares	df	P- Value
Cr	Between Groups	1.633	6	.000
	With in Groups	0.015	14	
	Total	1.648	20	
Pb	Between Groups	0.123	6	.000
	With in Groups	0.0015	14	
	Total	0.125	20	
Zn	Between Groups	0.537	6	.000
	With in Groups	0.013	14	
	Total	0.550	20	
Cu	Between Groups	0.246	6	.061
	With in Groups	0.063	14	
	Total	0.309	20	
Co	Between Groups	0.0021	6	.000
	With in Groups	0.00021	14	
	Total	0.0023	20	

Table8: One way ANOVA analysis for between and within Groups of effluent samples

Parameters	Method	Sum of squares	df	P- Value
Cr	Between Groups	9351.89	6	.000
	With in Groups	54.92	14	
	Total	9406.8	20	
Pb	Between Groups	0.188	6	.000
	With in Groups	0.002	14	
	Total	0.190	20	
Zn	Between Groups	0.685	6	.001
	With in Groups	0.110	14	
	Total	0.795	20	
Cu	Between Groups	0.166	6	.123
	With in Groups	0.129	14	
	Total	0.296	20	
Co	Between Groups	0.006	6	.000
	With in Groups	0.0003	14	
	Total	0.295	20	

Appendixes II: Metallic ion standard calibration curve taken from measurement of GFAAS

Figure 1: Zinc standard calibration curve taken from measurement of GFAAS

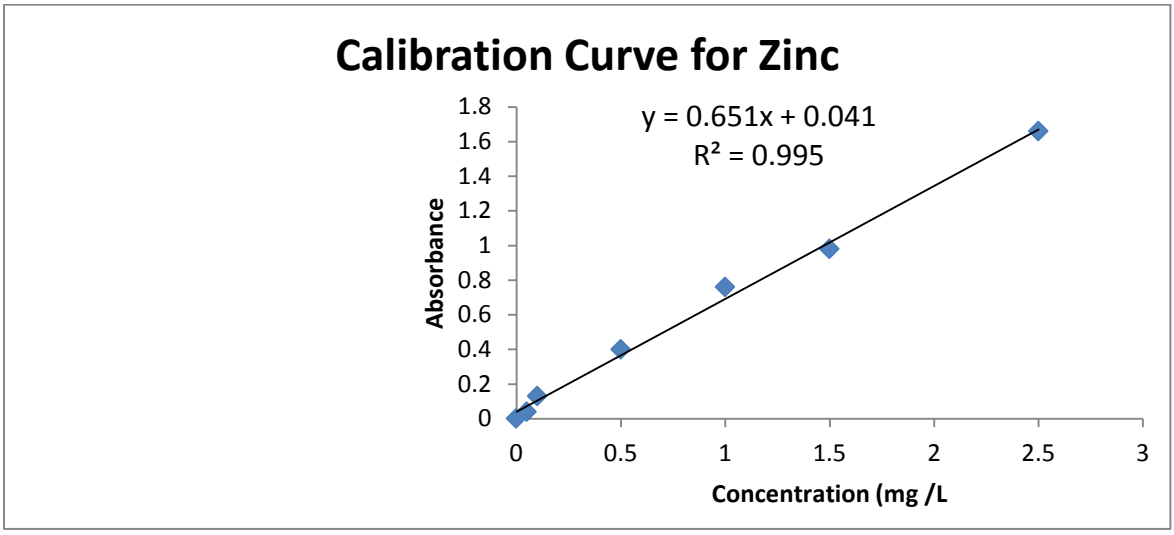

Figure 2: Chromium standard calibration curve taken from measurement of GFAAS

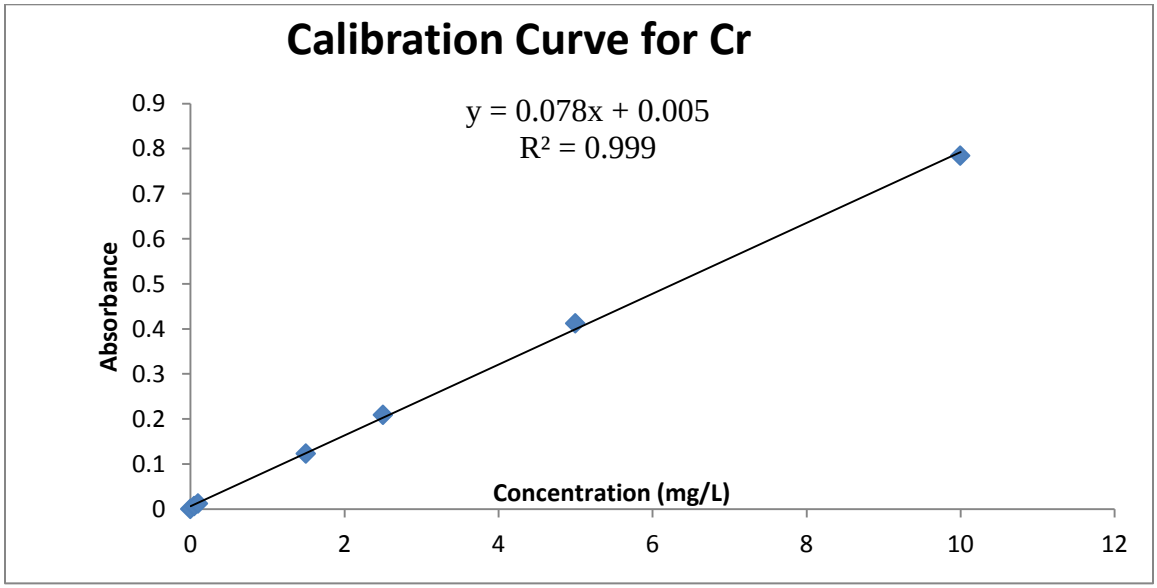

Figure 3: Cadmium standard calibration curve taken from measurement of GFAAS

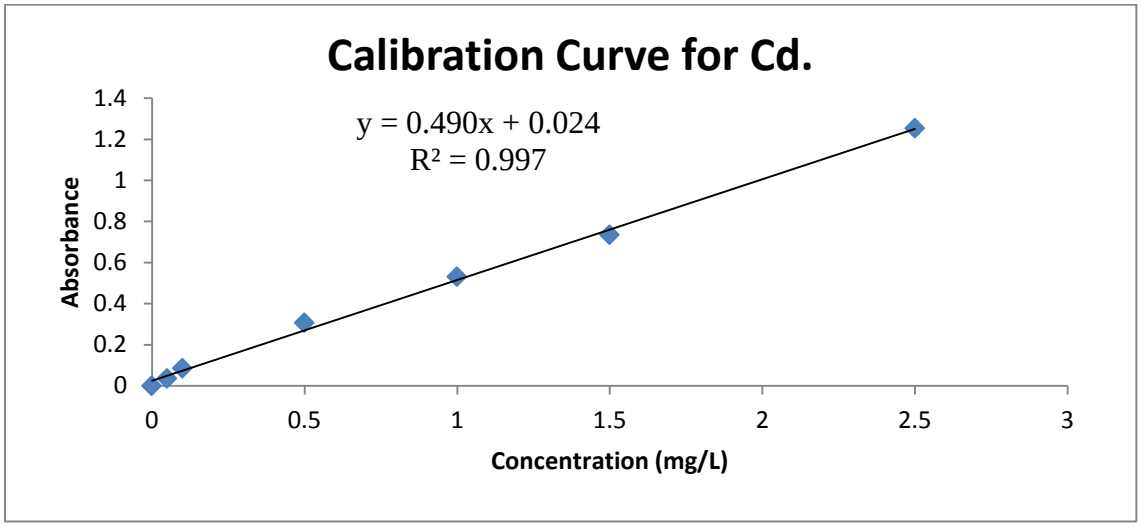

Figure 4: Cobalt standard calibration curve taken from measurement of GFAAS

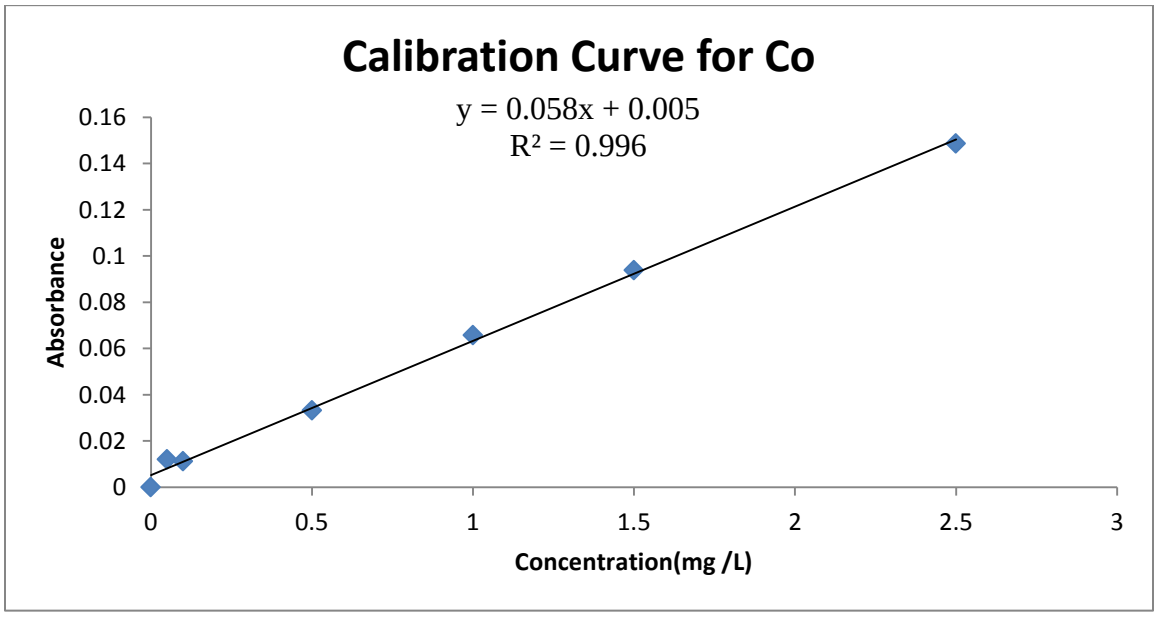

Figure 5: Lead standard calibration curve taken from measurement of GFAAS

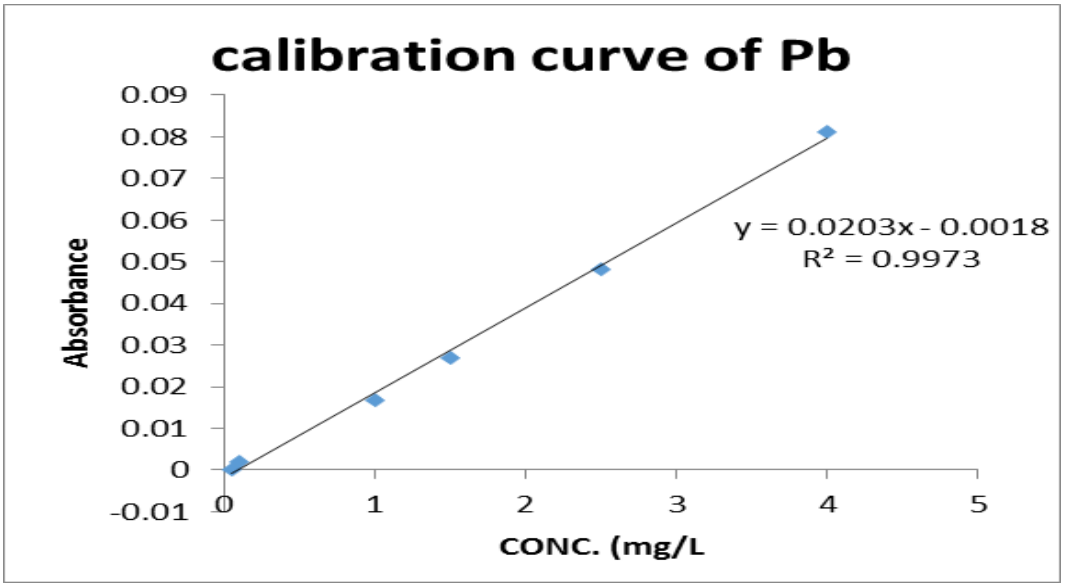

Figure 6: Copper standard calibration curve taken from measurement of GFAAS

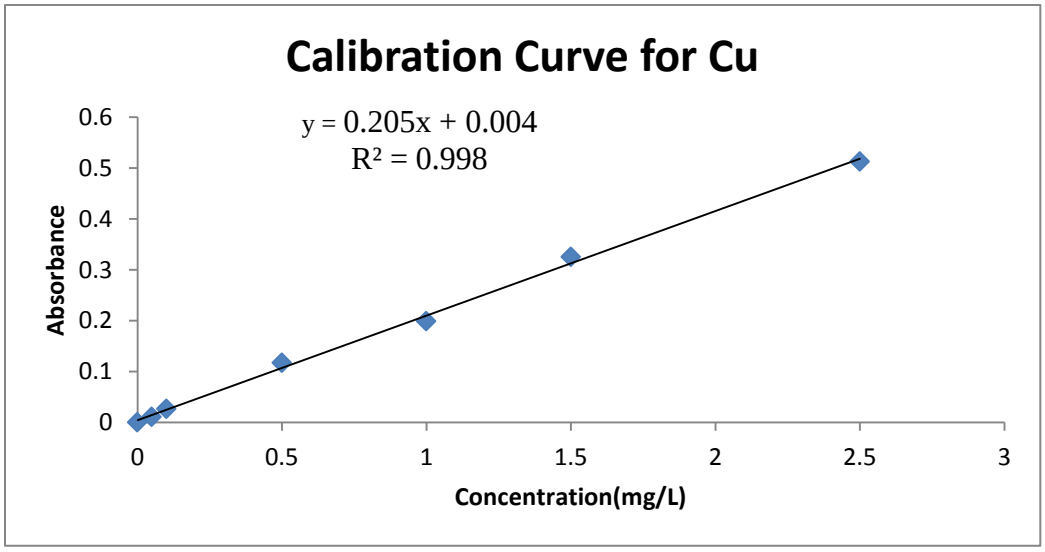

Figure 1: Industrial effluent joins to Modjo river water

Figure 2: Effluent discharged from the source

Figure 3: While Modjo river water is used for irrigation

Figure 4: Modjo river water for domestic purpose

Figure 5: Sample taken for analysis

Figure 6: Digestion process of samples

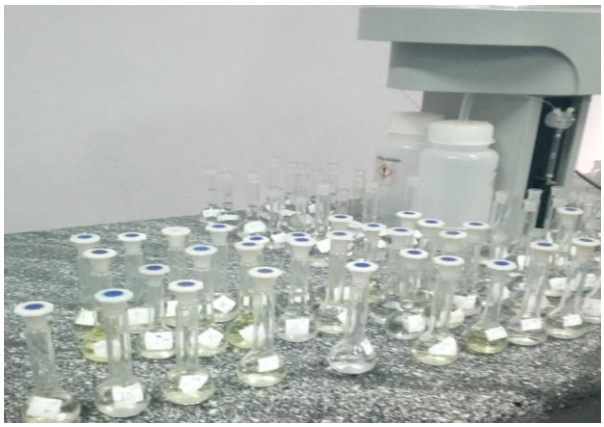

Figure 7: Chemical analysis of samples