ADDIS ABABA UNIVERSITY

COLLEGE OF NATURAL AND COMPUTATIONAL SCIENCES

DEPARTMENT OF CHEMISTRY

Determination of Selected Heavy Metals in Little Akaki Waste Water by using Graphite Furnace Atomic Absorption Spectroscopy (GFAAS)

By

Gashaw Melese

Advisor: Dr. Merid Tessema

June 2021

Addis Ababa

ADDIS ABABA UNIVERSITY

COLLEGE OF NATURAL AND COMPUTATIONAL SCIENCES

DEPARTMENT OF CHEMISTRY

Determination of Selected Heavy Metals in Little Akaki Waste Water by using Graphite Furnace Atomic Absorption Spectroscopy (GFAAS)

By

Gashaw Melese

Advisor: Dr. Merid Tessema

A Thesis Submitted to Addis Ababa University Department of Chemistry in Partial Fulfillment of the requirements for the Degree of Master of Science in Chemistry

June 2021

Addis Ababa

Declaration

I, the undersigned, declare that this research study is my original work under the supervision of my advisor Dr. Merid Tessema in the College of Natural and Computational Sciences, Department of Chemistry, Addis Ababa University and it has not been submitted in this or any other university. All sources of ideas and materials used for the project work are honestly acknowledged.

Name: Gashaw Melese

Signature _____

This thesis has been submitted for examination with my approval as university advisor.

Advisor's Name _____

Signature _____

Place and date of submission: Addis Ababa University, Department of Chemistry, June 2021

ADDIS ABABA UNIVERSITY

DEPARTMENT OF CHEMISTRY

Determination of Selected Heavy Metals in Little Akaki Waste Water by using Graphite Furnace Atomic Absorption Spectroscopy (GFAAS)

By: Gashaw Melese

Department of Chemistry

Approved by	Signature	Date
Dr. Merid Tessema (Advisor)	_____	_____
Prof. Negussie Megersa (Examiner)	_____	_____
Dr. Negussie Negash (Examiner)	_____	_____

ACKNOWLEDGEMENTS

First and foremost, I would like to praise the *Almighty God* and his mother *St. Mary* for bestowing up on me health, strength, patience and protection throughout my study period.

I would like to express my special gratitude and thanks to my advisor, Dr. Merid Tessema for his unreserved cooperation, suggestions, supervisions and remarks, appreciable encouragement, fatherly consultation and taking his time to read and correct my research paper.

I am grateful to my family especially to my wife Mantegbosh Yihun and my son Haileyesus Gashaw for their unreserved encouragement, love and patience.

I would like to extend my gratitude to Ato Faik Awal and Mekdes Girma water quality experts, for their genuine cooperation during digestion and metal determination by atomic absorption spectroscopy.

I am grateful to Yehualawork Teshome who helped in collecting samples in the sampling areas.

I would like to thank the Ethiopian Construction, Design and Supervision Works Corporation for its financial support.

I would like to thank the Department of Chemistry, Addis Ababa University for providing the opportunity for this study.

Table of Contents

Contents **Page**

List of Tables

Contents **Page**

List of Figures

Content **Page**

Abbreviations

AAEPA	American Academy of Estate Planning Attorneys
AAS	Atomic Absorption Spectrometry
AAWSA	Addis Ababa Water and Sewerage Authority
APHA	American Public Health Association
ATP	Adenosine Triphosphate
BDL	Below Detection Limit
CRM	Certified Reference Material
CVAA	Cold Vapor and Hydride Generation Atomic Absorption
EPA	Environmental Protection Agency
ETAAS	Electro Thermal Atomic Absorption Spectroscopy
EU	European Union
GFAAS	Graphite Furnace Atomic Absorption Spectroscopy
HGAA	Hydride Generation Atomic Absorption Spectroscopy
MCL	Maximum Contamination Level
MDL	Method Detection Limit
NEMA	National Environmental Management Authority
PMT	Photo Multiplier Tube
PVC	Polyvinyl Chloride
SD	Standard Deviation
US	United States
US EPA	United States Environmental Protection Agency
WHO	World Health Organization

Abstract

In this study, river water samples taken from three different locations along the course of the Little Akaki and Entoto River in Addis Ababa were analyzed to determine potentially toxic trace element concentrations. The mean concentrations of toxic heavy metals in Little Akaki and Entoto River in (μg/L); for Zn **(**124 ± 2.2, 108 ± 1.3**)**, Cr **(**3.51 ± 0.05, 0.74 ± 0.13**)**, Cu **(**10.3 ± 1.1, 10.1 ± 0.27**)** , Pb **(**15.7 ± 0.76, 3.42 ± 0.07**)**, Co **(**13.3 ± 0.34, 3.32 ± 0.11**)** , Cd **(**5.41 ± 0.21 , 0.435 ± 0.049**)**, As **(**5.58 ± 0.32 , 1.20 ± 0.043**)**, and Hg **(**0.0564 ± 0.0123, BDL**),** respectively. A strong positive correlation was observed between several of the trace elements indicating common sources. The concentrations of Cd, Co and Pb in Little Akaki River exceeded the permissible limits of the Ethiopian, European Community and WHO for drinking water quality guidelines. The pollution of the river water is increasing alarmingly and poses serious threat to human health. Many of the concentrations were higher than previously reported. It is, thus, necessary to take serious and essential measures from the concerned bodies. Adoption of adequate measures to remove the heavy metal load from the industrial waste water and upgrading of sewage treatment plants are suggested to avoid further deterioration of the river water quality.

Keywords: River water, Potential toxic heavy metals, Heavy metal contamination, Drinking water standards

1. Introduction

1.1. Background

Heavy metals are naturally occurring elements that have a high atomic weight and a density at least five times higher than that of water. Their multiple industrial, domestic, agricultural, medical, and technological applications have led to their wide distribution in the environment, raising concerns over their potential effects on human health and the environment **[1]**. Metals are introduced in aquatic systems as a result of the weathering of soils and rocks, from volcanic eruptions, and from a variety of human activities involving the mining, processing, or use of metals and/or substances that contain metal pollutants. There are different types of sources of pollutants: point sources (localized pollution), where pollutants come from single, identifiable sources. The second type of pollutant sources are nonpoint sources, where pollutants come from dispersed (and often difficult to identify) sources. There are only a few examples of localized metal pollution, like the natural weathering of ore bodies and the little metal particles coming from coal-burning power plants via smokestacks in air, water and soils around the factory **[2]**.

An enormous increase in pollution due to discharge of effluents from industrial units into rivers and lakes is a matter of great concern in developing countries. Developed and developing countries are suffering from different form of water pollution. It is desirable to produce little waste but developing countries with lack of technical knowhow, weak implementation of environmental policies and with limited financial resources are still facing problems **[3].**

Heavy metals are both extremely toxic and found everywhere in natural environments. Heavy metals can cause severe health effects. The most common heavy metal pollutants are arsenic, cadmium, chromium, copper, lead and mercury. Their toxicity depends on several factors

including the dose, route of exposure, and chemical species, as well as the age, gender, genetics, and nutritional status of exposed individuals **[4].** Because of their high degree of toxicity, arsenic, cadmium, chromium, lead, and mercury rank among the priority metals that are of public health significance. These include reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death **[5].** An important method to determine heavy metals in industrial effluents include a liquid sample analysis by atomic absorption analysis of the liquid effluent. Atomic absorption spectrometry (AAS) is a very common and reliable technique for detecting metals and metalloids in environmental samples **[6].**

Addis Ababa city with approximately 5 million population hosts large numbers of industries whose wastewaters are discharged into small river network, most often untreated. Factories, commercial, public and domestic utilities in Addis Ababa release untreated wastes into any receiving environment found nearby. To date there have been limited studies and knowledge dealing with the concentrations of potentially toxic elements in the Little Akaki River. Studies of some fresh water bodies in Ethiopia found out that the concentration of Cr, Mn, Co, Ni, Ag, Hg and Pb were generally elevated because of the disposal of domestic and factory wastes **[7].** Studies on the Little Akaki River related the elevated levels of Cr, Cd, Co, Cu, Ni, Pb, Zn and Mn to mainly industrial activities and disposal of domestic and municipal wastes **[8].** The concentrations of metals determined in vegetables grown in soils irrigated with Little Akaki River water in Addis Ababa and the result indicated that Cd, Co, Cu, Mn, and Ni in most water samples used for irrigation were higher than the guideline limits **[9]**. The present study aimed to determine the present water quality status of Little Akaki River and Entoto Kidanmihret water with respect to potential toxic trace elements namely Co, Cr, Cd, Cu, As, Pb, and Hg and to evaluate how these trace elements are distributed in different areas of Little Akaki river. For this

purpose, water samples collected from 3 different sites were analyzed for trace elements using GFAAS. The findings of this study will provide baseline information about water quality for stakeholders and the concerned authorities for further work and intervention.

1.2 Statement of the problem

Water basins like rivers, ponds especially Akaki River are polluted with toxic heavy metals that come from untreated urban, agricultural and industrial effluents. This may result in bio-accumulation of heavy metals in humans using water directly and eating agricultural products. Since, Akaki River passes through populated residential areas, towns, industrial and agricultural sites. Heavy metal contamination has become a very serious issue to public health since they are non-biodegradable and highly toxic. Heavy metal accumulation gives rise to toxic concentrations in the body, while some elements (e.g., Arsenic, cadmium, chromium) act as carcinogens and others (e.g., mercury, copper and lead) are associated with developmental abnormalities in children **[10].** The analysis of heavy metals that include lead, zinc, copper, cobalt, cadmium, chromium, arsenic and mercury is therefore justified to provide precautionary use of water, as well as provide a basis to aware government authorities such as National Environmental Management Authority (NEMA) towards management of discharge pollutant wastes into the river.

1.3 Objectives

1.3.1 General Objective

To study the level of toxic heavy metals in Little Akaki River and its impact on irrigated farms.

1.3.2 Specific objectives

I. To determine the levels of heavy metals (Pb, Zn, Cu, Co, Cd, Cr, As, and Hg) in water from Little Akaki river and Entoto Kidanmihret as a control by using GFAAS.

II. Compare the results of this study with those reported in the literature.

1.4 Scope of the study

This study focused on the determination of toxic heavy metals (Pb, Zn, Cu, Co, Cd, Cr, As, and Hg) in waste water samples taken from Little Akaki River and Entoto water as a control by using graphite furnace atomic absorption (GFAAS). Estimation of the reliability of the test experiment was made by conducting triplicate analyses and average tests were reported to provide adequate information on the distribution of heavy metals in Little Akaki River.

1.5 Significance of the study

Akaki River is among the most important investment site River in Ethiopia, and hence protecting the ecological health of the river is vital for the country. The data obtain from this research work will have multiple benefits. The data generated are expected to be usable in efforts geared towards developing system- based approaches for the protection and restoration of Akaki River. It is also important in the creation of awareness of decision makers, various stakeholders and the general public about the need for proper wastewater management and the undesirable consequences of disposal of untreated wastewater into river. The result of the study will also unravel the potential risks to public health associated with the use of polluted rivers for irrigated farms on which vegetables are cultivated. Institutions like Environmental Protection Authority,

Ministry of water, Irrigation and Power, Ministry of Agriculture, Ministry of Health, etc. and researchers will obviously benefit from the results of the present study.

2. Literature Review

2.1 Heavy Metals

The term heavy metal refers to any metallic chemical element that has relatively high density and is toxic or poisonous at low concentration. The chief heavy metals note in environmental science includes mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), lead (Pb), copper (Cu), cobalt (Co), zinc (Zn), ---?? etc. They are natural components of the earth crust. Compared to other types of water pollutants, heavy metals pollution is less visible, but their effects on the ecosystem and human beings can be intensive and very extensive. Thus, it has become a great concern in recent years because they are very harmful due to their long biological half-life and their potential to accumulate in different body parts of organism.

Arsenic

Arsenic is a metalloid. It is rarely found as a free element in the natural environment, but more commonly as a component of sulfur-containing ores in which it occurs as metal arsenide. The average abundance of As in the earth's crust is 1.8 ppm; in soils 5.5 to 13 ppm; in streams less than 2 μg/L, and in ground water generally less than 100 μg/L. It occurs naturally in sulfide minerals such as pyrite **[11]**. Arsenic is quite widely distributed in natural waters and is often associated with geological sources, but in some location's anthropogenic inputs, such as the use of arsenical insecticides and the combustion of fossil fuels, can be extremely important additional sources. Mostly through ingestion of contaminated water As_2O_3 can be absorbed through the lungs and intestines.

Arsenic is used in alloys with lead, in storage batteries, and in ammunition. Arsenic compounds are widely used in pesticides and in wood preservatives. Arsenic is nonessential for plants but is an essential trace element in several animal species. A lot of arsenic compounds are toxic and

cause acute and chronic poisoning. In aqueous environment the inorganic arsenic species arsenite (As(III)) and arsenate (As(V)) are the most abundant species **[12]**. The toxicity of arsenic depends on its chemical form. Arsenite is many times more toxic than arsenate. A known carcinogen, acute dose can be lethal causes gastrointestinal damage, severe vomiting; diarrhea. It coagulates proteins and complexes with coenzymes, inhibits production of ATP **[13].** For the protection of aquatic life, the average concentration of As^{3+} in water should not exceed 72 μg/L and the maximum should not exceed 140 μg/L. The United Nations Food and Agriculture Organization recommended maximum level for irrigation waters is 100 μg/L. The US EPA a primary drinking water standard MCL is 50 μg/L.

Cadmium

Cadmium (Cd) is a toxic non-essential transition metal that poses a health risk for both humans and animals. The average abundance of Cd in the earth's crust is 0.16 ppm; in soils 0.1 to 0.5 ppm; in streams 1 μg/L, and in ground waters from 1 to 10 μg/L. Cadmium occurs in sulfide minerals that also contain zinc, lead, or copper. Cadmium is usually associated with zinc at a ratio of about 1 part cadmium to 500 parts zinc in most rocks and soils **[14]**. Cadmium is released into the environment through various natural and anthropogenic activities such as mining, smelting, and refining. Cd exposure can be through water, air, and soil, which results in Cd toxicity. Cadmium is widely used in industrial processes, e.g. as an anticorrosive agent, a stabilizer in PVC products, a colour pigment, a neutron-absorber in nuclear power plants, and in the fabrication of nickel-cadmium batteries **[15]**. Cadmium is extremely toxic and accumulates in the kidneys and liver, with prolonged intake at low levels sometimes leading to dysfunction of the kidneys. The United Nation Food and Agriculture Organization recommended maximum level for cadmium in irrigation water is 10 μg/L. The US EPA primary drinking water standard

MCL is 10 μg/L. Long-term exposure to cadmium through air, water, soil, and food leads to cancer and organ system toxicity such as skeletal, urinary, reproductive, cardiovascular, central and peripheral nervous, and respiratory systems **[16]**.

Chromium

Chromium (Cr) is a mineral. It is called an "essential trace element" because very small amounts of chromium is necessary for human health. The average abundance of Cr in the earth's crust is 122 ppm; in soils Cr ranges from 11 to 22 ppm; in streams averages about 1 μg/L, and in ground waters generally 100 μg/L. Chromium in water occurs in the trivalent and hexavalent state and potentially quite toxic to aquatic animals and plants in the dissolved form. The 'hexavalent' form is generally more toxic than the metallic or 'trivalent' form because of its high rate of adsorption through intestinal tracts **[17]**. Being one of the commonly used metals chromium and its particulates enter the aquatic medium through effluents discharged from different industries like textiles, tanneries, electroplating workshops, ore mining, dyeing, printing-photographic and medical industries **[18]**. Chromium is used to electroplating, paints and inks, wood preservatives, textiles, refractories, metal plating and leather tanning industries **[8]**.

Chromium (VI) is dangerous for humans due to its toxicity and carcinogenic properties. The presence of hexavalent chromium in waste water is a potential hazard to aquatic animals and humans **[19]**. Cr(III) is less toxic and insoluble, while Cr(VI) is extremely toxic and highly the effluents and solid wastes from the mining, chrome-plating, leather-tanning, and dye-manufacturing industries are high in chromium concentration and identified as a major health hazard because of pollution to the environment. Inhalation is the major exposure route of the Cr(VI) toxicity in humans **[20]**.

Hexavalent chromium is known to have 100-fold more toxicity than trivalent chromium, for both acute and chronic exposures because of its high water solubility and mobility, as well as easy reduction. Chronic inhalation exposure to hexavalent chromium results in effects on the respiratory tract, with perforations and ulcerations of the septum, bronchitis, decreased pulmonary function, pneumonia, and nasal itching and soreness as reported. Chronic human exposure to high levels of hexavalent chromium by inhalation or oral exposure may produce effects on the liver, kidney, gastrointestinal, and immune systems, and possibly the blood. Dermal exposure to hexavalent chromium may cause contact dermatitis, sensitivity, and ulceration of the skin **[21]**. The United Nations Food and Agriculture Organization recommended maximum level for irrigation waters is 100 μg/L. The US EPA primary drinking water standard MCL is 0.1 mg/L for total chromium.

Cobalt

Cobalt (Co) has valences of 1, 2, and 3. The average abundance of Co in the earth's crust is 29 ppm; in soils 1.0 to 14 ppm; in streams 0.2 μg/L; and in ground waters 1 to 10 μg/L. Cobalt occurs only sparingly in ores, usually as the sulfide or the arsenide. It is widely used in alloys of various steels, in electroplating, in fertilizers, and in porcelain and glass.

Cobalt (Co) enters water bodies from effluents discharged from industries dealing with corrosion and wear-resistant alloys **[22]**.

Food and beverages are the main source of cobalt exposure. Traces of cobalt are also present in cement and various household products. In industry, the potential for exposure to cobalt is particularly important during the production of cobalt powder, the production, processing and use of hard metals, the polishing of diamonds with cobalt containing disks and the processing of cobalt alloys **[23]**. Cobalt salts are used for the preparation of enamels and pigments. Cobalt is

mainly absorbed from the pulmonary and the gastrointestinal tracts. Absorption through the skin can occur but is low. Concomitant exposure to tungsten carbide increases the pulmonary absorption rate of cobalt metal. Cobalt is not a cumulative toxin and is mainly excreted in urine and to a lesser extent via faces. Cobalt in blood and urine mainly reflects recent exposure. The two main target organs are the skin and the respiratory tract. Cobalt itself may cause allergic dermatitis, rhinitis and asthma. Inhalation of cobalt containing dust has also lead to pathologic reactions in the lung parenchyma. Concomitant exposure to cobalt and other substances such as in hard metal industry might increase the risk of lung cancer, but this requires confirmation **[24]**. The United Nations Food and Agriculture Organization recommended maximum level for irrigation waters is 100 μg/L.

Copper

Following zinc and iron, copper is the third most abundant trace element in the body. The average abundance of Cu in the earth's crust is 68 ppm; in soils 9 to 33 ppm; in streams 4 to 12 μg/L; and in ground water <0.1 mg/L. The level of copper in surface and groundwater is generally very low. High levels of copper may get into the environment through mining, farming, manufacturing operations, and municipal or industrial wastewater releases into rivers and lakes. Copper is a noble metal, like silver and gold. Useful industrial properties include high thermal and electrical conductivity, low corrosion, alloying ability, and malleability. Most of the metallic copper appears in electrical applications. Copper is a constituent of intrauterine contraceptive devices and the release of copper is necessary for their contraceptive effects. The average daily intake of copper in the US is about 1 mg Cu with the primary source being the diet. The bioavailability of copper from the diet is about 65–70% depending on a variety of factors including chemical form, interaction with other metals, and dietary components **[25]**.

Other factors that influence copper concentrations include location in the water column, season, temperature, depth, and level of dissolved oxygen. For example, concentrations of bioavailable copper may be significantly higher in the bottom waters and sediment pore waters, where organic ligands degrade much faster and dissolved copper is constantly re suspended and recycled into the aquatic system **[26]**. At low concentrations Cu ions cause headache, nausea, vomiting and diarrhea and at high concentrations it causes coronary heart diseases, chronic anemia, and gastrointestinal disorder and also leads to liver, high blood pressures and kidney and brain. If left untreated, copper toxicity can have severe health effects and even result in death **[27]**. The limit of Cu in drinking water is 2000 μg/L by EU, WHO and Ethiopian Standards.

Lead

Lead (Pb) is the most significant toxin of the heavy metals. Lead is commonly found in the environment and a potential occupational toxin, with human exposure arising from industrial activity, food, drinking water, soil, and paint sources. The average abundance of Pb in the earth's crust is 13 ppm; in soils ranges from 2.6 to 25 ppm; in streams 3 μg/L, and in ground waters generally <0.1 mg/L. Lead is obtained chiefly from galena (PbS). It is used in batteries, ammunition, solder, piping, pigments, insecticides, and alloys. The acceptable limit of lead reported by WHO, EU and Ethiopian standard in drinking water is 10 μg/L. It is used in batteries, ammunition, solder, piping, pigments, insecticides, and alloys. The distribution of anthropogenic lead in the aquatic environment is governed by atmospheric input (leaded gasoline) and input from point sources (mining areas, smelters, factories producing chemicals and goods based on lead). **[28]**.

Lead is one of the highly poisonous metals that affects human soft tissues and organs, causing cancer in kidneys, lung, or brain, and acts synergistically with other carcinogens. Lead is highly

persistent in the environment, mainly due to its non-biodegradability. The toxicity of lead could result in irreversible health effects to the central nervous, hepatic, circulatory, cardiovascular, reproductive, and renal systems. Lead exposure during childhood causes adverse and permanent neurodevelopmental consequences, sometimes even with "low" blood lead levels. Symptoms are frequently silent, making lead exposure an often unrecognized and underestimated threat for pervasive neurocognitive disorders **[29]**. Although lead in bone may not cause harm to the body directly, it acts as a reservoir. Certain conditions such as osteoporosis become more prevalent as populations age. During these settings of bone loss, lead may be mobilized from bone and reenter the bloodstream **[30]**. The lead poising is a real threat to the public health, especially in the developing countries. Hematopoietic, renal, reproductive, and central nervous system are among the parts of the human body and systems that are vulnerable toward the dangers following exposure to high level of Pb **[31]**. The Food and Drug Administration regulates lead content in food and in house paints. Under the lead-copper rule, the US EPA drinking water 90th percentile action level is 15 μg/L.

Mercury

Mercury (Hg), a global pollutant produced by anthropogenic and natural means acts as a bio-cumulative toxin that severely affects our environment and human lives. Mercury exists naturally and as a man-made contaminant. The average abundance of Hg in the earth's crust is 0.09 ppm; in soils 30 to 160 ppb; in streams 0.07 μg/L, and in ground waters 0.5 to 1 μg/L. Mercury occurs free in nature, but the chief source is cinnabar (HgS). The release of processed mercury can lead to a progressive increase in the amount of atmospheric mercury, which enters the atmospheric-soil-water distribution cycles where it can remain in circulation for years **[32]**. Due to the ability to travel over long distances in the atmosphere as gaseous elemental species,

far from the point emission source, mercury is regarded as a `global pollutant'. The main pathway of contamination of the humans with mercury is the food chain, where the most toxic species, methyl mercury, bio accumulates **[33]**. During combustion mercury in coal is almost totally emitted to the atmosphere. With a huge amount of coal consumed, coal combustion is one of the main anthropogenic sources of this element in the environment. The Hg content in coals varies in different coal basins, geological ages and coal ranks **[34]**. Mercury is used in amalgams, mirror coatings, vapor lamps, paints, measuring devices (thermometers, barometers, and manometers), pharmaceuticals, pesticides, and fungicides.

Mercury is a ubiquitous environmental toxin that causes a wide range of adverse health effects in humans. Three forms of mercury (elemental, inorganic, and organic) exist, and each has its own profile of toxicity. Exposure to mercury typically occurs by inhalation or ingestion. Readily absorbed after its inhalation, mercury can be an indoor air pollutant, for example, after spills of elemental mercury in the home; however, industry emissions with resulting ambient air pollution remain the most important source of inhaled mercury. The developing fetus and young children are thought to be disproportionately affected by mercury exposure, because many aspects of development, particularly brain maturation, can be disturbed by the presence of mercury. Minimizing mercury exposure is, therefore, essential to optimal child health **[35]**. The major route of human exposure to methylmercury (MeHg) is largely through eating contaminated fish, seafood, and wildlife which have been exposed to mercury through ingestion of contaminated lower organisms. MeHg toxicity is associated with nervous system damage in adults and impaired neurological development in infants and children. Ingested mercury may undergo bioaccumulation leading to progressive increases in body burdens. Mercury has profound cellular, cardiovascular, hematological, pulmonary, renal, immunological, neurological,

endocrine, reproductive, and embryonic toxicological effects **[36]**. The recommended guideline values for Hg are 0.1, 0. 6 and 1 μg/L for drinking water as given by the EU, WHO and Ethiopian standards, respectively **[7]**.

Zinc

Zinc is a fairly abundant metal, it has been estimated that zinc represents 0.004 percent of the earth's crust and is twenty-fifth in the order of abundance. Its concentrations in surface waters vary greatly with locality; the highest concentrations of zinc have been observed in areas with acid mine drainage, but zinc enters surface waters in many other ways **[37]**.

The average abundance of Zn in the earth's crust is 76 ppm; in soils 25 to 68 ppm; in streams 20 μg/L, and in ground waters <0.1 mg/L. The solubility of zinc is controlled in natural waters by adsorption on mineral Surfaces, carbonate equilibrium, and organic complexes. Zinc is used in a number of alloys such as brass and bronze, and in batteries, fungicides, and pigments. Zinc is an essential growth element for plants and animals but at elevated levels it is toxic to some species of aquatic life. The United Nations Food and Agriculture Organization recommended level for zinc in irrigation waters is 2 mg/L. The US EPA secondary drinking water standard MCL is 5 mg/L. Concentrations above 5 mg/L can cause a bitter astringent taste and an opalescence in alkaline waters. 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 **[38]**. Zinc most commonly enters the domestic water supply from deterioration of galvanized iron and dezincification of brass. In such cases lead and cadmium also may be present because they are impurities of the zinc used in galvanizing. Zinc in water also may result from industrial waste pollution **[39]**.

People living near smelters or industries using zinc could be exposed to higher levels of zinc by drinking water, breathing air and touching soil that contains the metal. Exposure to high levels of zinc over long periods of time may cause adverse health effects. Acute and long-term exposure of Zn may lead many health disorders such as fever, vomiting, stomach cramps, diarrhea and carcinogenic. Eating large amounts of zinc for longer periods may cause anemia, nervous system disorders & damage to the pancreas **[40]**. Too little zinc in the diet also can cause adverse health effects such as loss of appetite, decreased sense of taste and smell, lowered ability to fight off infections, slow growth, and slow wound-healing and skin sores **[41]**.

2.1.1 Environmental effect of heavy metal polluted waste water effluent

Heavy metals, also known as trace metals, are one of the most persistent pollutants in wastewater. The discharge of high amounts of heavy metals into water bodies leads to several environmental and health impacts. The exposure of humans to heavy metals can occur through a variety of routes, which include inhalation as dust or fume, vaporization and ingestion through food and drink **[42]**. Some negative impacts of heavy metals to aquatic ecosystems include death of aquatic life, algal blooms, habitat destruction from sedimentation, debris, increased water flow, other short and long term toxicity from chemical contaminants. Abundant amounts of heavy metals present in soils cause reduction in quality and quantity of food preventing plants' growth, uptake of nutrients, physiological and metabolic processes. Severe effects on animals may include reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death **[43]**.

2.1.2 Adverse health effects of heavy metals

Heavy metal toxicity has proven to be a major threat and there is several health risks associated with it. The toxic effects of these metals, even though they do not have any biological role,

remain present in some or the other form harmful for the human body and its proper functioning. They sometimes act as a pseudo element of the body while at certain times they may even interfere with metabolic processes. Few metals, such as aluminum, can be removed through elimination activities, while some metals get accumulated in the body and food chain, exhibiting a chronic nature. Various public health measures have been undertaken to control, prevent and treat metal toxicity occurring at various levels, such as occupational exposure, accidents and environmental factors. Metal toxicity depends upon the absorbed dose, the route of exposure and duration of exposure, i.e. acute or chronic **[44]**. Because of their non-biodegradable composition the heavy metals are the most toxic and dangerous pollutant. The reason for these parameters' higher values can be attributed to the disposal of sewage estates, waste from metal processing industries and household refuses. Due to their presence beyond specified limits, heavy metal pollutants cause direct toxicity to both humans and other living organisms. Many of these metals are bio-accumulative, and hazardous to human health **[45]**.

2.2 Graphite Furnace Atomic Absorption Spectrophotometry

Graphite furnace atomic absorption spectroscopy (GFAAS) (also known as electro thermal atomic absorption spectroscopy (ETAAS)) is a type of spectrometry that uses a graphite-coated furnace to vaporize the sample. Flame AA can only analyse solutions, but graphite furnace can accept very small absolute quantities of solution, slurry or solid samples. GFAA spectrometry instruments have the following basic features: (1) a source of light (lamp) that emits resonance line radiation; (2) an atomization chamber (graphite tube) in which the sample is vaporized; (3) a monochromator for selecting only one of the characteristic wavelengths (visible or ultraviolet) of the element of interest; (4) a detector, generally a photomultiplier tube (light detectors that are

useful in low-intensity applications), that measures the amount of absorption; (5) a signal processor-computer system (strip chart recorder, digital display, meter, or printer).

2.2.1 Basic principles

The technique is based on the fact that free atoms absorb light at frequencies or wavelengths characteristic of the element of interest. Within certain limits, the amount of light absorbed can be linearly correlated to the concentration of analyte present. Free atoms of most elements can be produced from samples by the application of high temperatures. In GFAAS, samples are deposited in a small graphite or pyrolytic carbon coated graphite tube, which can then be heated to vaporize and atomize the analyte. The atoms absorb ultraviolet or visible light and make transitions to higher electronic energy levels. Concentration measurements are usually determined from a working curve after calibrating the instrument with standards of known concentration. The main advantages of the graphite furnace comparing to aspiration atomic absorption are the following:

(1) The detection limits for the graphite furnace fall in the ppb range for most elements.

(2) Interference problems are minimized with the development of improved instrumentation.

(3) The graphite furnace can determine most elements measurable by aspiration atomic absorption in a wide variety of matrices.

In a flameless graphite furnace system, instead of using an aspiration device, both liquid and solid samples (a few microgram or microliter sample) can be deposited directly to a graphite boat using a syringe inserted through a cavity. The graphite furnace can hold an atomized sample in the optical path for several seconds, compared with only a fraction of a second in the flame system. This results in a significantly higher sensitivity of the GFAA as compared with FAA.

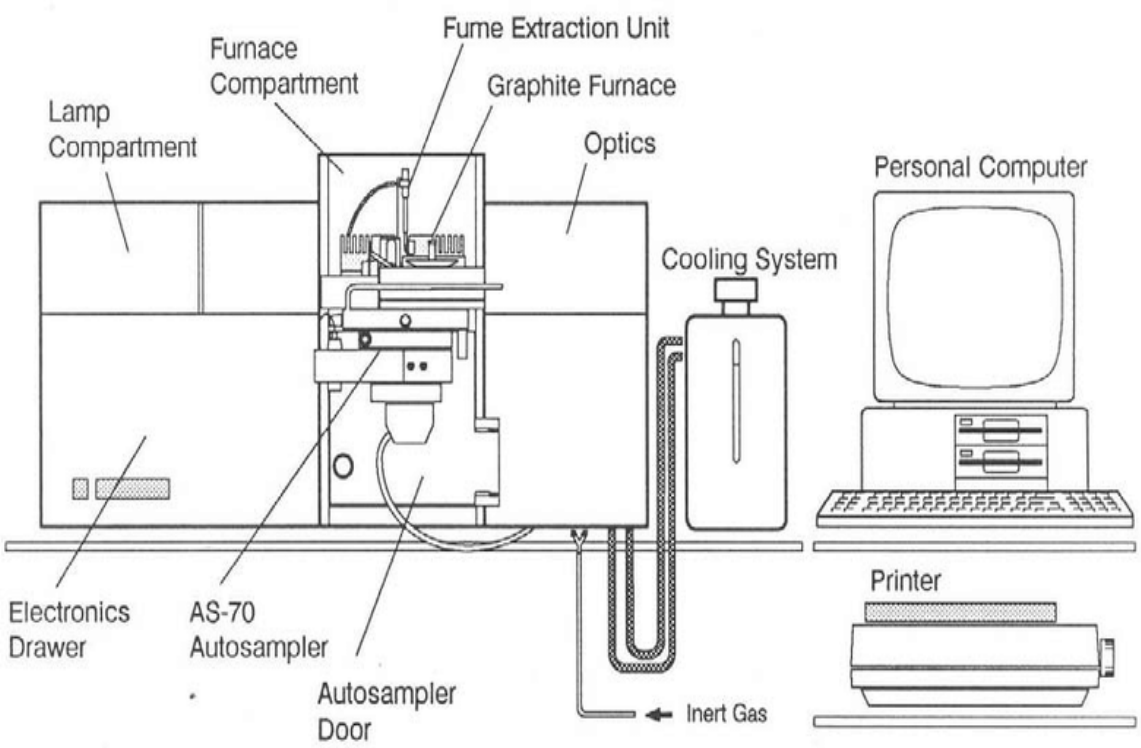

Figure 1: Schematic diagram of GFAAS

2.2.2 GFAAS Operating Conditions

The instruments used in this study include hot plate and graphite furnace atomic absorption spectrophotometer. The operating conditions for the AAS are given in the Table 1.

Table 1: GFAAS operating conditions

Operating parameters	Pb	Cu	Cr	Cd	Co	As	Hg	Zn
wavelength (nm)	283	324	357	228	240	193	253	213
Silt width (nm)	0.8	0.8	0.8	0.8	0.2	1.2	1.2	0.5
Flame type	Argon							
Photo multiplier tube (PMT)	284	225	209	326	345	339	356	318
Lamp current (mA)	2	2	4	2	5	6	2.5	2

Cold Vapor and Hydride Generation Atomic Absorption

The two atomic absorption spectrometric methods using flame and graphite furnace can measure most elements with satisfactory detection limits. There are notable exceptions to these techniques, including several elements (mercury, selenium, and arsenic) that are of environmental importance. Mercury (Hg) is a volatile metal; it does not need to be heated in a flame or furnace during spectroscopic analysis. It can be analyzed by a ‘‘cold vapor’’ atomic absorption (CVAA) technique **[46]**. Arsenic (As) and selenium (Se) are not volatile at room temperature to be analyzed by the ‘‘cold vapor’’ techniques, but they are too volatile to be analyzed by FAA or GFAA. The hydride generation atomic absorption (HGAA) technique is applicable in atomic absorption spectroscopy for the analysis of As, Se, and several other elements (Bi, Ge, Pb, Sb, Sn, Te) **[47]**.

Cold Vapor Atomic Absorption (CVAA) Spectroscopy for Hg

Free mercury (Hg) atoms can exist at room temperature and, therefore, Hg can be measured by atomic absorption without a heated sample cell. In the CVAA technique, Hg is chemically reduced to the free atomic state by reacting the sample with a strong reducing agent like stannous chloride ($SnCl_2$) or sodium borohydride ($NaBH_4$) in a closed reaction system. The volatile-free mercury is then driven from the reaction flask by bubbling air or argon through the solution. Mercury atoms are carried in the gas stream through tubing connected to an absorption cell, which is placed in the light path of the AA spectrometer. As the mercury atoms pass into the sampling cell, measured absorbance rises indicating the increasing concentration of mercury atoms in the light path. The sensitivity of the cold vapor technique is far greater than can be achieved by conventional flame AA. This improved sensitivity is achieved, first of all, through a 100% sampling efficiency **[48]**. All of the mercury in the sample solution placed in the reaction flask is chemically atomized and transported to the sample cell for measurement. The sensitivity can be further increased by using very large sample volumes. Since all of the mercury contained in the sample is released for measurement, increasing the sample volume means that more mercury atoms are available to be transported to the sample cell and measured. Although the cold vapor system is the most sensitive and reliable technique for determining very low concentrations of mercury by atomic absorption, this technique requires a specialized instrument that can be used to only analyze mercury since no other element offers the possibility of chemical reduction to a volatile-free atomic state at room temperature **[49]**.

Hydride Generation Atomic Absorption (HGAA) Spectroscopy for As and Se

Many of the main parts of the HGAA system are identical to that of FAA including a hollow cathode lamp, air–acetylene flame, and optical system. The nebulizer required in FAA is not

used in HGAA, and the only required addition is the hydride generation module. Consequently, HGAA spectrometer is available through an option for many modern FAA instruments. The most advanced systems combine automation of the sample chemistries and hydride separation using flow injection techniques with decomposition of the hydride in an electrically heated, temperature-controlled quartz cell **[50]**. Similar to the cold vapor mercury systems, samples in a hydride generation module are reacted in an external system with a reducing agent (usually $NaBH_4$).

Gaseous reaction products are then carried to a sampling cell in the light path of the AA spectrometer. Unlike the mercury technique, the gaseous reaction products are not free analyte atoms but the volatile hydrides (SeH_3 and SeH_2). These molecular species are not capable of causing atomic absorption. To dissociate the hydride gas into free atoms, the sample cell must be heated. The maximum absorption reading, or peak height, or the integrated peak area is taken as the analytical signal.

The elements determinable by hydride generation techniques can not only measure As and Se, but also measure several other metals and metalloids such as Bi, Ge, Pb, Sb, Sn, and Te. For these elements, detection limits well below the mg/L range are achievable. Like cold vapor mercury, the extremely low detection limits result from a much higher sampling efficiency. In addition, separation of the analyte element from the sample matrix by hydride generation is commonly used to eliminate matrix-related interferences **[51]**.

The major limitation to the hydride generation technique is that it is restricted primarily to several elements listed above. Results depend heavily on a variety of parameters, including the valence state of the analyte, reaction time, gas pressures, acid concentration, and cell temperature. Therefore, the success of the hydride generation technique will vary with the care

taken by the operator in attending to the required detail. The formation of the analyte hydrides is also suppressed by a number of common matrix components, leaving the technique subject to certain types of chemical interference **[52]**.

3. Experimental

3.1 Materials and Methods

Waste water samples were collected from different areas of both Akaki River and Entoto Kidanmihret in polyethylene plastic bottles. Samples were collected in good quality screw capped high density pre sterilized polypropylene bottles, each of 1 lt capacity, labeled properly and analyzed in laboratory for trace metals by atomic absorption spectrometer(AAS). High purity (Analytical grade) chemicals and double distilled water were used for preparing solutions for analysis. Preservation and analysis of water samples were based on standard methods proposed by American Public Health Association (APHA). The selected heavy metals (As, Cd, Cr, Cu, Co, Hg, Pb and Zn) were determined. The detection of trace metals in the environment is accomplished by various methods. In the present study AAS was used, which is relatively simple, versatile, accurate and free from interferences. Heavy metals readily form complexes with organic constituents; therefore, it is necessary to destroy them by digestion with strong acids. Digestion destroys the organic matter and brings metallic compounds in suspension to solution.

3.2 Description of the study area

The samples for this study were collected from Little Akaki River in the city of Addis Ababa which is located 9° 1' 48" N latitude and 38° 44' 48.24" E longitude from part of the watershed for Awash River and Entoto Kidanmihret is another sampling area located at the foot of Mount Entoto which is 2600 to 3200 meters above sea level. The selection of study area (Little Akaki River) was based on availability of highly dense factory effluents, peoples waste dumping site, sampling cost and proximity of the study area and largely used for irrigation.

Figure 2: Pollution of Little Akaki River and agricultural practice

3.3 Apparatus and Instruments

The following apparatus and instruments were used in the project work. Polyethylene bottles, refrigerators, thermometers, micro pipettes, different sized beakers, Erlenmeyer flasks, funnels, volumetric flasks, Whatman filter paper no. 42, droppers, pipettes, measuring cylinders, vinyl gloves, stirrer, analytical balance, conical flasks, hot plate and graphite furnace atomic absorption spectrophotometer (Analitikjena, Model novAA, 400 p, Germany) were used.

3.4 Chemicals and Reagents

All chemicals and reagents used in the present work were high purity of analytical grade. HNO_3 (69 %, European Union, Spain), H_2O_2 (30 %, European Union, Spain) and HCl (36%, Germany) used for digestion of samples and blank. Standard solutions were prepared form 1000 mg/l stock solution certified reference material (Zn, Co, Cr, Cd, Cu, As, Pb, and Hg) from Europe accredited lab. Tap water, distilled water, and deionized water were used for washing, rinsing, and preparation of samples.

3.5 Sample collection and preparation

Three water samples were collected from different sites of both Akaki River and Entoto Kidanmihret in polyethylene plastic bottles. Plastic bottles were washed with soap and tap water then rinsed with distilled and deionized water followed by 0.02 M HNO_3 to maintain constant pH of the samples according to the standard methods **[53].** The samples were homogenized in one plastic bottle to get a representative sample. Then the samples were sealed, transported to the laboratory and stored in a refrigerator for digestion.

3.6 Digestion of River Water

50 ml of acidified sample was measured and put in a 20% of nitric acid soaked conical flask and a 5 ml of concentrated nitric acid was added. The mixture was heated at 95 ℃ with addition of 3 ml H_2O_2 until there were no brown fumes and the volume reduced to 10 ml for one hour on hot plate. The mixture was then filtered using Whatman filter paper no. 42 in 50 ml volumetric flask and dilute to the label mark with deionized water. The samples of water were digested in triplicate then labeled and stored for awaiting analysis. For background correction three blanks were digested as pre-test samples and each analyzed for the required metal by GFAAS.

Figure 3: Digestion of river water on hot plate

3.7 Stock solution and working standards

In the metal analysis procedure, the standard containing stock solution (1000 mg/l) was obtained from Europe accredited lab. That is the stocks used to prepare the intermediate standards and working standards are certified reference material (CRM). The intermediate standards and working standards are prepared from the stock solution by serial dilution with deionized water. After the working standards were prepared the instrument was calibrated to obtain good correlation between absorbance and concentration which is used to determine the unknown concentration of the sample.

3.8 Method Performance and Method validation

Method validation is an important part of analytical chemistry to confirm that the method employed for a specific test is suitable for its intended use. As such, it is an essential requirement for any package of information submitted to regulatory agencies in support of new product marketing or clinical trial applications. Currently, there is no single source or final guideline on analytical method validation that helps analysts to perform validation in a systematic manner. Therefore, industry depends on the analyst's knowledge and experience to develop simple and efficient methods of analysis.

In order to demonstrate the validity of the proposed method, within and between run precision, accuracy, method detection limit (MDL) and percentage of recovery tests were carried out. Precision has been defined as the level of reproducibility of experimental results. Within-run or repeatability assesses precision during a single analytical run, whereas between-run measures precision with time and may involve different analysts, equipment, and reagents. The certified value range, also known as “standard”, is used to monitor the accuracy of the analysis and to validate the analytical method. The percentage of recovery is a crucial parameter for method validation. If the percentage of recovery is small, the sample bias affects the method significantly and can lower its validity. Accuracy refers to the closeness of a measured value to a standard or known value. Method detection limit is the minimum concentration of analyte that can be measured and reported with 99% confidence level that the analyte concentration is greater than zero **[54]**.

3.8.1 Precision

Precision is defined as 'the quality of being exact' and refers to how close two or more measurements are to each other, regardless of whether those measurements are accurate or not. The precision of an analytical procedure expresses the closeness or agreement between a replicate measurements obtained from multiple sampling of the same homogeneous sample under the prescribed conditions (repeatability or reproducibility). The common term used to measure variability is the relative standard deviation (RSD), which may also be expressed as a percentage and it is the parameter of choice for expressing precision in analytical sciences. In this study, the precision of the results were evaluated by the standard deviation and relative standard deviation of the results of six measurements for a given blank sample (i.e. three samples (n = 3) and triplicate readings for each sample) **[55].**

3.8.2 Method Validation

Matrix spiking is a technique that is used to evaluate the performance of an analytical procedure when testing a specific sample type. In other words, a matrix spike test helps answer the question "Are we getting good results when we use this method to test this sample or this type of sample?''. A "good'' matrix spike result increases our confidence in the accuracy and validity of the sample test results. A matrix spike is generated by adding a known amount (a spike) of analyte to a sample, testing the spiked sample, and determining if we have recovered the amount that we added **[56]**. For spiking water sample, 50 µL of 10 mg/l Zn, 12.5 µL of 10 mg/l Cr, 25 µL of 10 mg/l Cu, 35 µL of 10 mg/l Pb, 7.5 µL of 10 mg/l Cd, 45 µL of 10 mg/l Co, 3 µL of 10 mg/l Hg and 6 µL of 10 mg/l As standard solutions were added in the flask containing the same amount of sample as the first one.

The spiked and non-spiked samples were digested and analyzed in similar conditions. The percentage recovery of the analyte was calculated by

$$\%\text{Recovery} = \frac{[\text{Mean spiked value} - \text{Un-spiked value}]}{\text{Standard added}} \times 100$$

4. Results and Discussion

4.1 Instrument calibration

Graphite furnace atomic absorption spectrophotometer (Analitikjena, Model novAA 400 p, Germany) was used to determine metal concentrations in water sample. The qualities of the results obtained for analysis of heavy metals using GFAAS are seriously affected by calibration and standard solution preparation procedures. Calibration curves were prepared to determine the concentration of metals in the sample solution. The instruments were calibrated using a series of working standards. The stock solution, that is 1000 mg/l of each metal solution, was taken and 10 mg/l was prepared as an intermediate for preparing working standards. The working standards were prepared according to the sensitivity of each lamp in the AAS instrument. By using working standards the instrument was calibrated with good correlation coefficient. After making sure the instrument was properly calibrated, the concentration of metals in each sample was measured. Concentration of the working standards in (μg/L), calibration equation and correlation coefficient value for each of the metals for Zn **(**0.125, 0.25, 0.5, 0.75, 1,y = 0.485x + 0.017 and R^2 =0.9992 **)**, Cr **(**10, 20, 30, 40, y = 0.0147x + 0.0274 and R^2 =0.9998**)**, Cu **(**6.25, 12.5, 18.75, 25, y = 0.0107x + 0.0103 and R^2 =0.9997**)** , Pb **(**10, 20, 30, 40, 50, y = 0.007x + 0.0076 and R^2 =0.9992**)**, Co **(**5, 10, 15, 20, 25, y = 0.0088x + 0.0018 and R^2 =0.9978**)** , Cd **(**0.5, 1, 1.5, 2, 2.5, y = 0.1718x + 0.0145 and R^2 =0.9998**)**, As **(**2, 4, 8, 12, 16, y = 0.0049x + 0.0029 and R^2 =0.9999**)**, and Hg **(**5, 10, 15, 20, 25, y = 0.0131x + 0.011 and R^2 =0.9984**),** respectively.

The linear correlation graph for each metal standards are described as shown in the following figures

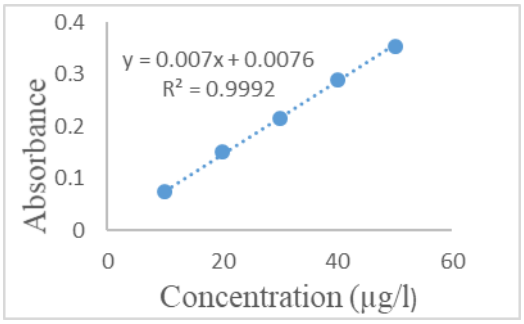

Figure 4: Calibration graph of lead

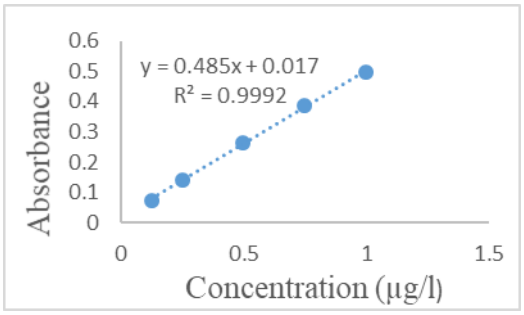

Figure 5: Calibration graph of zinc

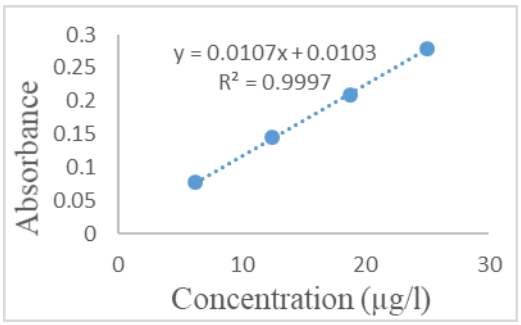

Figure 6: Calibration graph of copper

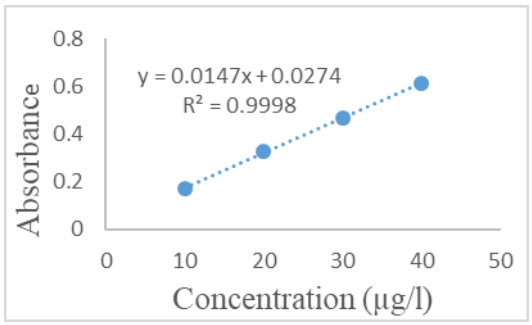

Figure 7: Calibration graph of chromium

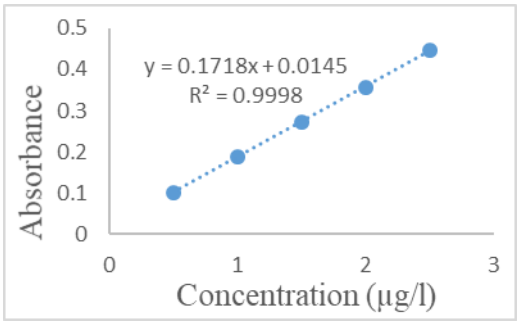

Figure 8: Calibration graph of cadmium

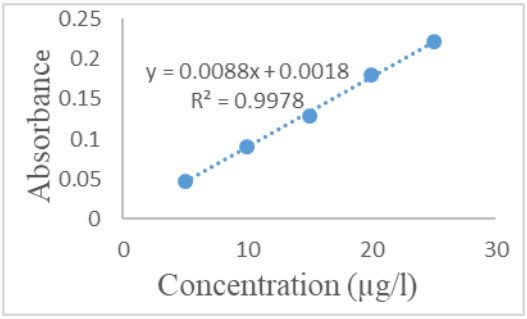

Figure 9: Calibration graph of cobalt

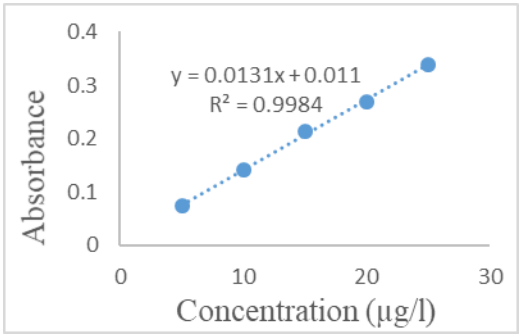

Figure 10: Calibration graph of mercury

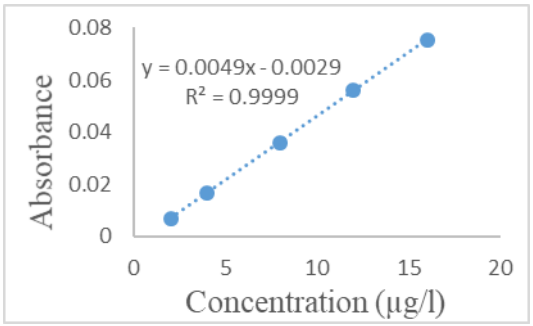

Figure 11: Calibration graph of arsenic

Table 2: Concentration of standard solution used to calibrate the instrument and their corresponding correlation coefficients for the determination of metals

Metals	Conc. of stock solution (mg/l)	Conc. of intermediate solution (mg/l)	Conc. of standard series (µg/l)	Correlation coefficient
Zn	1000	10	0.125, 0.25, 0.5, 0.75, 1	0.9992
Pb	1000	10	10, 20, 30, 40, 50	0.9992
Cu	1000	10	6.25, 12.5, 18.75, 25	0.9997
Cr	1000	10	10, 20, 30, 40	0.9998
Cd	1000	10	0.5, 1, 1.5, 2, 2.5	0.9998
Co	1000	10	5, 10, 15, 20, 25	0.9978
Hg	1000	10	5, 10, 15, 20, 25	0.9984
As	1000	10	2, 4, 8, 12, 16	0.9999

4.2 Method detection limit

Method detection limit is the minimum concentration of the analyte which can be detected at 99% confidence level. In this study method detection limit of each metal was estimated by digesting three analytical blanks for both Little Akaki and control Entoto water. Each blank solution was also determined with GFAAS as the same time and condition as with the samples. The standard deviation of the blank was determined to calculate method detection limit.

$$MDL = 3*SD$$

where, SD is standard deviation of the blank.

Table 3: Method detection limit of metals

Metal	Zn	Pb	Cu	Cr	Cd	Co	Hg	As
MDL(µg/l)	0.103	0.082	0.027	0.074	0.011	0.015	0.024	0.039

As shown in the Table 3, the MDL is low enough to detect the presence of metal at trace level in both Akaki and Entoto water.

4.3 Recovery test

Recovery is one of the most commonly used techniques utilized for validation of the analytical results and evaluating how far the method is acceptable for its intended purpose. The validity of the method was evaluated by spiking samples with standards of known concentrations and calculating percentage recoveries. The percentage recoveries of metals are given in Table 4. These values were within the acceptable range of 80-120% expected. So, it is indicating that the method was a good accuracy of analytical procedure.

The percentage recovery was calculated by using the following formula:

$$\%\text{Recovery} = \frac{[\text{Mean spiked value} - \text{Un-spiked value}]}{\text{Standard added}} \times 100$$

Concentrations of spiked and un-spiked samples are calculated by mean ± SD of the triplicate measurements of triplicate samples.

Table 4: Recovery values of metals for the analyzed Little Akaki water sample

Mean concentration(µg/l) ± SD				
Metals	Un-spiked samples	Spiked amount	Measured amount	Percent recovery
Zn	124 ± 2.2	5.0	129 ± 2.7	96.4 ± 4.8
Cr	3.51 ± 0.05	1.25	4.67 ± 0.05	92.8 ± 4.0
Cu	10.3 ± 1.13	2.5	12.5 ± 0.026	93.3 ± 3.7
Pb	15.7 ± 0.76	3.5	19.18 ± 0.11	101 ± 3.2
Cd	5.41 ± 0.21	0.75	6.15 ± 0.028	98.7 ± 2.7
Co	13.3 ± 0.34	4.5	17.5 ± 0.12	93.7 ± 2.7
Hg	0.0564 ± 0.0123	0.3	0.3292 ± 0.0041	90.9 ± 1.4
As	5.58 ± 0.32	0.6	6.15 ± 0.05	95.0 ± 7.9

As shown in Table 4 the percentage recovery ranged from 90.9-101%. This indicates that the method used to determine metals from river water is in the acceptable range and it is valid.

4.4 Level of Heavy Metals in Little Akaki and Entoto Kidanmihret Water

The concentration of eight metals (Zn, Cr, Cu, Pb, Cd, Co, Hg and As) in the digested water samples were analyzed by using GFAAS. Water samples were obtained from Little Akaki River and Entoto Kidanmihret. The mean ± SD level of the analyzed metals obtained were presented in Table 5.

Table 5: Mean concentration (µg/l) of heavy metals in water samples

Metals	Little Akaki river (µg/l)	Entoto Kidanmihret (µg/l)
Zn	124 ± 2.2	108 ± 1.3
Cr	3.51 ± 0.05	0.740 ± 0.133
Cu	10.3 ± 1.1	10.1 ± 0.27
Pb	15.7 ± 0.76	3.42 ± 0.07
Cd	5.41 ± 0.21	0.435 ± 0.0485
Co	13.3 ± 0.34	3.32 ± 0.11
Hg	0.0564 ± 0.0123	BDL
As	5.58 ± 0.32	1.20 ± 0.04

Among the analyzed metals Hg was below the method of detection limit (MDL) in Entoto Kidanmihret water sample. But the other analyzed heavy metals (Zn, Cr, Cu, Pb, Cd, Co and As) were detected both in Akaki and Entoto Kidanmihret water samples.

4.5 Comparison of Metals in Little Akaki with Entoto Kidanmihret Water

Metals are persistent in the environment if once released to the environment and tend to bio-accumulate in plants, organisms, and even become biomagnified in the food chain where human beings are highly exposed **[57]**. Little Akaki River is excessively used for irrigation to cultivate different grains and vegetables and even for drinking. So, if water is polluted with heavy metals, metals will be transferred to animals and humans immediately. When the metals are compared in the two water samples, all metals are present in higher amounts in Little Akaki than Entoto Kidanmihret water.

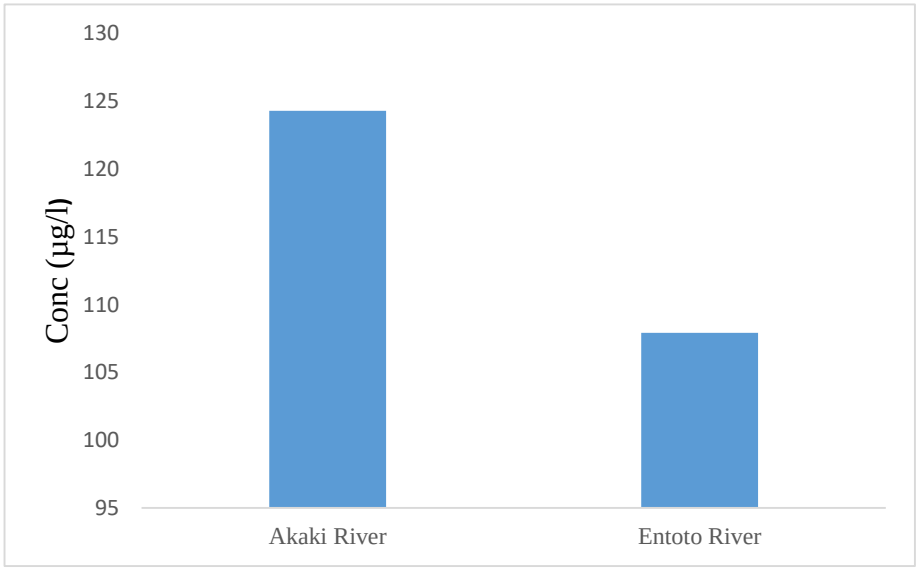

Figure 12: Concentration of Zn in Little Akaki and Entoto Kidanmihret water samples

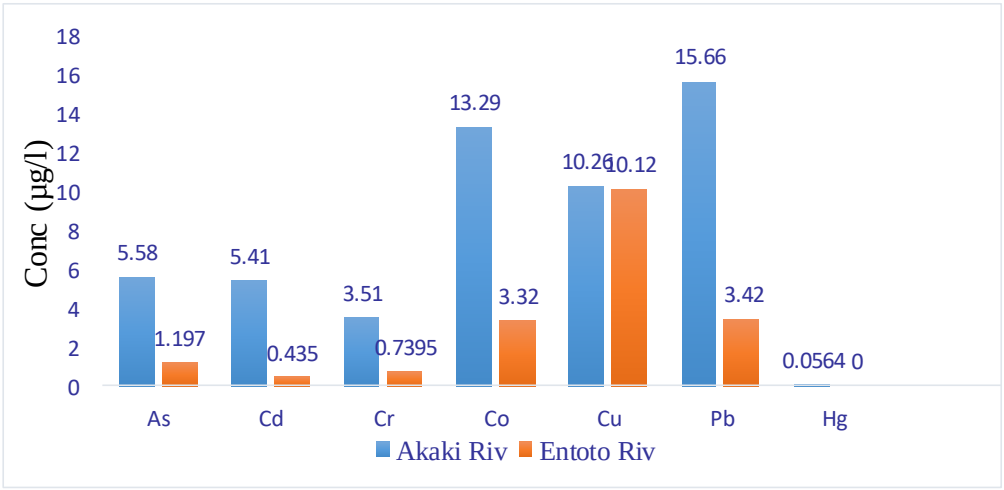

Figure 13: Concentration of (Co, Cr, Cd, Cu, As, Pb, and Hg) in Little Akaki and Entoto Kidanmihret water samples

The values of zinc obtained in this study was 124 ± 2.2 µg/l in Akaki river and 108 ± 1.3 µg/L in Entoto Kidanmihret water. WHO guideline values have been proposed for Zn in drinking water is 3000 µg/L and Ethiopian Standards have a value of 5000 µg/L for drinking water. All the values obtained in both Little Akaki river and Entoto Kidanmihret water were below this limit. The values were also lower than the international guideline values for irrigation water of 2000 µg/L. However, all were exceeded the 8 µg/L annual average threshold in SI 272 of 2009 for water with hardness values lower than or equal to 10 mg/L $CaCO_3$.

The level of lead in this study was 15.7 ± 0.76 and 3.42 ± 0.07 µg/l in Little Akaki River and Entoto Kidanmihret water, respectively. So, the amount of lead in Little Akaki River is higher than in Entoto Kidanmihret water. The acceptable limit of lead reported by WHO, EU and Ethiopian standard in drinking water is 10 µg/L. Little Akaki River was above in this limit but the value obtained in Entoto Kidanmihret water sample was below the limit. This could be due to poor environmental control, increasing industrialization and population of the city. However, the obtained values were lower than the international guideline values for irrigation water of 5000 µg/L. The mean Pb concentrations obtained in this work was also much higher than previously reported of 3.13 µg /L by **[8]**.

Cr concentrations in the analyzed water samples in Little Akaki and Entoto Kidanmihret were (3.51 ± 0.05, 0.740 ± 0.13) µg/L, respectively. The concentration of Cr in this study both in Little Akaki and Entoto Kidanmihret water samples were low when compared to the previously reported average value of 67.0 µg/L by **[8]**.

The concentration of Cu in the analyzed in Little Akaki and Entoto Kidanmihret water samples were (10.3 ± 1.1, 10.1 ± 0.27) µg/L, respectively. The desirable limit of Cu in drinking water is 2000 µg/L by EU, WHO and Ethiopian Standards. As shown in the Table 5 both Little Akaki

and Entoto Kidanmihret samples had lower Cu levels compared to the safe limit for drinking and irrigation water. However, when compared of the thresholds given in SI in 272 of 2009 both samples in Little Akaki and Entoto Kidanmihret exceeded the permissible value of 5 μg/L which applies where the water hardness measured in mg/L $CaCO_3$ is lower than or equal to 100. High level of copper may be due to presence of industrial, municipal and domestic wastes.

The concentration of Co in the analyzed water samples in Little Akaki and Entoto Kidanmihret were (13.3 ± 0.34, 3.32 ± 0.11) μg/L, respectively. No guideline value for Co in drinking water is given in the WHO, EU and Ethiopian standards. This is probably because Co is not a health concern at concentrations normally observed in drinking water. The mean concentration of Co in this study was higher when compared with the previously reported mean value of 2.62 μg/L by **[8]**. Despite this the concentrations were lower than the international guideline values for irrigation water of 50 μg/L.

The level of Cd was 5.41 ± 0.21 μg/L in Little Akaki River and 0.435 ± 0.0485 μg/L in Entoto Kidanmihret water, that is, the level of cadmium metal is higher in Little Akaki River than Entoto water.

The level of Hg determine was 0.0564 ± 0.0123 μg/L in Little Akaki river and below detection limit in Entoto Kidanmihret water, that is, the amount of Hg is higher in Little Akaki than Entoto Kidanmihret water. However, the level of Hg is below the guideline value for drinking water given in the WHO, EU and Ethiopian standards which is 1 μg/L.

The level of As was 5.58 ± 0.32 μg/L in Little Akaki River and 1.20 ± 0.043 μg/L in Entoto Kidanmihret water, that is, the level of arsenic metal is higher in Little Akaki River than Entoto water. Therefore, all the levels of the analyzed metals (Zn, Cr, Cu, Pb, Cd, Co, Hg and As) were higher in Little Akaki river than Entoto Kidanmihret water due to large amount of contamination

by waste from industries and household discharge. As a result, Entoto Kidanmihret water is relatively suitable for irrigation and drinking purposes than Little Akaki River.

4.6 Comparison of Metals in Little Akaki and Entoto Kidanmihret Water with that Reported in the Literature and Different Guidelines

The levels of heavy metals (Zn, Cr, Cu, Pb, Cd, Co, Hg and As) in different rivers have been reported in different countries from different point of views like health problem, nutrition, for drinking, irrigation standard, etc.

Table 6: Comparison of metal concentrations with those reported in the literature (µg/l)

Country	Water type	Zn	Cr	Cu	Pb	Cd	Co	Hg	As	References
South Africa	Dzindi river	100	60	50	30	-	-	-	-	[58]
Nigeria	Ezu river	-	20-440	110-200	20-900	11-90	-	-	20-30	[59]
India	Surface water	20.8-1278	2.4-1308	2.1-535.5	6.4-2034	0.2-401	-	-		[60]
Turkey	Tigris river	37	<5	-	0.342	1.368	111	-	2.354	[61]
Ethiopia	Akaki river	8.35-77.5	1.25-485	2.1-11.55	1.15-11.35	-	0.5-8.85	-	-	[8]
Ethiopia	Akaki river	124.3	3.51	10.26	15.66	5.41	13.29	0.0564	5.58	This study
Ethiopia	Entoto Water	107.93	0.7395	10.12	3.42	0.435	3.32	-	1.197	This study

The mean level of zinc in Little Akaki River and Entoto Kidanmihret water in this study are higher than those reported in South Africa [58], Nigeria [59], India [60], Turkey [61], and Ethiopia [62].

The mean level of chromium both in Little Akaki and Entoto Kidanmihret water samples are less than the mean level of chromium those reported in South Africa [58], Nigeria [59], India [60], and Ethiopia [8].

The mean level of copper both in Little Akaki and Entoto Kidanmihret water samples are less than the mean level of copper those reported in South Africa [58], Nigeria [59], India [60], and the mean level of copper in Little Akaki River is higher than reported in the literature [8].

The mean level of Lead in this study both in Little Akaki and Entoto Kidanmihret water samples are less than those reported in South Africa [58], Nigeria [59], India [60] but higher than reported in Turkey [61] and Ethiopia [8].

The mean level of cadmium in Little Akaki River is higher than those reported in Turkey but both the mean level of cadmium in Little Akaki River and Entoto Kidanmihret water are less than those reported in South Africa [58] and Nigeria [59].

The mean level of cobalt in Little Akaki River is higher than those reported in the literature [8], and less than in Turkey [61].

The mean level of arsenic in both Little Akaki and Entoto Kidanmihret water in this study are less than reported in Nigeria [59] from literature. And the level of As in this study in Little Akaki River is higher than that of Turkey [61] reported in the literature.

The amount of mercury in this study is detected the value of 0.0564 μg/L and below detection limit in Entoto Kidanmihret water sample.

Table 7: Some guidelines for water quality (mg/l)

Standard	Zn	Cr	Cu	Pb	Cd	Co	Hg	As	References
WHO	3	0.05	2	0.015	0.003	-	0.006	0.01	[62]
EU	-	0.05	2	0.01	0.005	-	0.001	0.01	[63]
US EPA	-	0.1	1.3	0.015	0.005	0.1	0.002	0.01	[64]
Canada	5	0.05	1	0.01	0.005	-	0.001	0.01	[65]
India	5	0.05	0.05	0.05	0.01	-	0.001	0.05	[66]
New Zealand	3	-	-	0.015	0.005	1		0.01	-

The mean levels of (Zn, Cr, Cu, As and Hg) in Little Akaki river are less than all the standards in the literature WHO, EU, US, Canada and India.

The mean level of lead and cadmium obtained in this study in Little Akaki river water are higher than water quality standards of WHO, EU, US, Canada and Ethiopia, but less than Indian guidelines.

5. Conclusion and Recommendations

5.1 Conclusion

This work focused on the determination of (Zn, Cr, Cu, Pb, Cd, Co, Hg and As) concentrations in Little Akaki River and Entoto Kidanmihret water for comparative. The concentrations of (Zn, Cr, Cu, Pb, Cd, Co, Hg and As) were determined by using GFAAS technique. The results showed that the concentration of all the analyzed metals in this study (Zn, Cr, Cu, Pb, Cd, Co, Hg and As) in Little Akaki River were higher than that of Entoto Kidanmihret water. This indicates that Little Akaki River more contaminated than Entoto Kidanmihret water because, Little Akaki River found in the disposal area of different industries and household wastes from Kalti industrial site and agrochemicals applied on irrigated vegetable farms.

The level of lead, cadmium and cobalt obtained in this study were higher than all the guidelines or standards reported in the literature. This may expose to health risk for people living around the area of the river because the river is used intensively for irrigation and even for drinking purposes.

As a result, the level of heavy metals (Pb, Cd and Co) obtained from Little Akaki River are not safe enough compared with the standard level. The control water for this study was Entoto Kidanmihret water, this water was relatively free from heavy metal contamination with that of Little Akaki River and according to the guidelines reported. Therefore, Entoto Kidanmihret water is safer for irrigation and drinking purpose than Little Akaki River.

5.2 Recommendations

The time of study was very short. Since, it was difficult to address more sample sites and access large sample size from all areas of both Little Akaki River and Entoto Kidanmihret water, and to collect samples during all seasons to have more a representative sample for the study. Therefore,

it is recommended for other researchers to take more time and large number of samples to address of the limitation of this study.

Akaki River is found in the disposal area of different industries and household wastes. On the other hand, the river water is used for a variety of purposes such as irrigation, cattle drinking and domestic purposes without prior treatment.

For sustainable management of this water resource, environmental protection agencies at different levels and other concerned administrative and/or nongovernmental bodies like AAWSA, AAEPA, EPA, etc., up to the city communities who lives near to the river and far from it should take strict as well as technical measures. Enforcement of law and propagating environmental education to the community with special target to those contributors of the present degradation could be one solution. Providing treatment plant and good environmental management could be another option. Strength decentralized waste management system for already urbanized area like upgrading waste treatment plants and considers centralized waste management system for any new construction.

6. References

1. Tchounwou, P. B., Yedjou, C. G., Patlolla, A. K., & Sutton, D. J. **(2012)**. Heavy metal toxicity and the environment. *Molecular, Clinical and Environmental Toxicology, 133-164.*
2. Anastas, P. T., & Warner, J. C. **(1998)**. Principles of green chemistry. *Green Chemistry: Theory and Practice, 29-56.*
3. Panda, T. C., Mishra, S. K., & Panda, K. C. **(2002)**. Laminar diffusion of suspended particulate matter using a two-phase flow model. *International Journal for Numerical Methods in Fluids, 40(7), 841-853.*
4. Miyamura, Y., Coelho, S. G., Wolber, R., Miller, S. A., Wakamatsu, K., Zmudzka, B. Z., ... & Batzer, J. **(2007).** Regulation of human skin pigmentation and responses to ultraviolet radiation. *Pigment Cell Research, 20(1), 2-13.*
5. Huang, C., Tang, C., Feigin, A., Lesser, M., Ma, Y., Pourfar, M., & Eidelberg, D. **(2007)**. Changes in network activity with the progression of Parkinson's disease. *Brain, 130(7), 1834-1846.*
6. Korn, M. D. G. A., dos Santos, D. S. S., Welz, B., Vale, M. G. R., Teixeira, A. P., de Castro Lima, D., & Ferreira, S. L. C. **(2007)**. Atomic spectrometric methods for the determination of metals and metalloids in automotive fuels–a review. *Talanta, 73(1), 1-11*.
7. Mekonnen, K. N., Ambushe, A. A., Chandravanshi, B. S., Abshiro, M. R., & McCrindle, R. I. (**2012**). Potentially toxic elements in some fresh water bodies in Ethiopia. *Toxicological & Environmental Chemistry, 94(10), 1980-1994.*
8. Aschale, M., Sileshi, Y., Kelly-Quinn, M., & Hailu, D. (**2015)**. Potentially toxic trace element contamination of the Little Akaki River of Addis Ababa, Ethiopia. *Journal of Natural Sciences Research, 5(1), 1-13.*

9. Weldegebriel, Y., Chandravanshi, B. S., & Wondimu, T. (**2012**). Concentration levels of metals in vegetables grown in soils irrigated with river water in Addis Ababa, Ethiopia. *Ecotoxicology and Environmental Safety, 77, 57-63.*
10. Rahman, Z., & Singh, V. P. **(2019)**. The relative impact of toxic heavy metals (THMs) (arsenic (As), cadmium (Cd), chromium (Cr) (VI), mercury (Hg), and lead (Pb)) on the total environment: an overview. *Environmental Monitoring and Assessment, 191(7), 419.*
11. Jain, C. K., & Ali, I. **(2000)**. Arsenic: occurrence, toxicity and speciation techniques. *Water Research, 34(17), 4304-4312.*
12. Bissen, M., & Frimmel, F. H. **(2003)**. Arsenic—a review. Part I: occurrence, toxicity, speciation, mobility. *Acta Hydrochimica Et Hydrobiologica, 31(1), 9-18.*
13. (Matta, G., & Gjyli, L. **(2016)**. Mercury, lead and arsenic: impact on environment and human health. *Journal of Chemical and Pharmaceutical Sciences 9 (2), 718-725.*
14. *Giuseppe Genchi* 1, Maria Stefania Sinicropi 1, *, Graziantonio Lauria 1, Alessia Carocci 2, * and Alessia Catalano 2 **(2017)**. *International journal of environmental research and public health 14 (1), 74.*
15. Godt, J., Scheidig, F., Grosse-Siestrup, C., Esche, V., Brandenburg, P., Reich, A., & Groneberg, D. A. **(2006)**. The toxicity of cadmium and resulting hazards for human health. *Journal of Occupational Medicine and Toxicology, 1(1), 1-6.*
16. Rahimzadeh, M. R., Rahimzadeh, M. R., Kazemi, S., & Moghadamnia, A. A. **(2017)**. Cadmium toxicity and treatment: An update. *Caspian Journal of Internal Medicine, 8(3):135-145.*
17. Achmad, R. T., & Auerkari, E. I. **(2017)**. Effects of chromium on human body. *Annual Research & Review in Biology, 13(2), 1-8.*

18. DesMarias, T. L., & Costa, M. **(2019)**. Mechanisms of chromium-induced toxicity. *Current Opinion in Toxicology, 14, 1-7.*

19. Mukherjee, K., Saha, R., Ghosh, A., & Saha, B. **(2013)**. Chromium removal technologies. *Research on Chemical Intermediates, 39(6), 2267-2286.*

20. Coetzee, J. J., Bansal, N., & Chirwa, E. M. (2020). Chromium in environment, its toxic effect from chromite-mining and ferrochrome industries, and its possible bioremediation. *Exposure and health, 12(1), 51-62*.

21. Saha, R., Nandi, R., & Saha, B. **(2011)**. Sources and toxicity of hexavalent chromium. *Journal of Coordination Chemistry, 64(10), 1782-1806.*

22. Eichenberger, B. A., & Chen, K. Y. **(1982)**. Origin and nature of selected inorganic constituents in natural waters. *Water Analysis, 1, 1-44.*

23. Leyssens, L., Vinck, B., Van Der Straeten, C., Wuyts, F., & Maes, L. **(2017)**. Cobalt toxicity in humans—A review of the potential sources and systemic health effects. *Toxicology, 387, 43-56.*

24. Lauwerys, R., & Lison, D. **(1994)**. Health risks associated with cobalt exposure—an overview. *Science of the Total Environment, 150(1-3), 1-6.*

25. Barceloux, D. G., & Barceloux, D. **(1999)**. Copper. *Journal of toxicology: Clinical Toxicology, 37(2), 217-230.*

26. Kiaune, L., & Singhasemanon, N. **(2011)**. Pesticidal copper (I) oxide: environmental fate and aquatic toxicity. *Reviews of Environmental Contamination and Toxicology Volume, 213, 1-26.*

27. Ozdemir, S., Kilinc, E., & Oner, E. T. **(2019)**. Preconcentrations and determinations of copper, nickel and lead in baby food samples employing Coprinus silvaticus immobilized multi-walled carbon nanotube as solid phase sorbent. *Food Chemistry, 276, 174-179.*

28. Prosi, F. **(1989)**. Factors controlling biological availability and toxic effects of lead in aquatic organisms. *Science of the Total Environment, 79(2), 157-169.*

29. Naranjo, V. I., Hendricks, M., & Jones, K. S. **(2020)**. Lead toxicity in children: An unremitting public health problem. *Pediatric Neurology, 113, 51-55.*

30. Vig, E. K., & Hu, H. **(2000)**. Lead toxicity in older adults. *Journal of the American Geriatrics Society, 48(11), 1501-1506.*

31. Assi, M. A., Hezmee, M. N. M., Abd Wahid Haron, M. Y. M., & Sabri, M. A. R. **(2016)**. The detrimental effects of lead on human and animal health. *Veterinary World, 9(6), 660.*

32. Kumari, S., Jamwal, R., Mishra, N., & Singh, D. K. **(2020)**. Recent developments in environmental mercury bioremediation and its toxicity: a review. *Environmental Nanotechnology, Monitoring & Management, 13, 100283.*

33. Jitaru, P., & Adams, F. **(2004)**, December). Toxicity, sources and biogeochemical cycle of mercury. *In Journal de Physique IV (Proceedings), 121, 185-193.*

34. Zheng, L., Liu, G., & Chou, C. L. **(2007)**. The distribution, occurrence and environmental effect of mercury in Chinese coals. *Science of the Total Environment, 384(1-3), 374-383.*

35. Goldman, L. R., Shannon, M. W., & Committee on Environmental Health. **(2001)**. Technical report: mercury in the environment: implications for pediatricians. *Pediatrics, 108(1), 197-205.*

36. Rice, K. M., Walker Jr, E. M., Wu, M., Gillette, C., & Blough, E. R. **(2014)**. Environmental mercury and its toxic effects. *Journal of Preventive Medicine and Public Health, 47(2), 74.*

37. Vymazal, J. **(1985)**. Occurrence and chemistry of zinc in freshwaters—its toxicity and bioaccumulation with respect to algae: a review. Part 1: Occurrence and chemistry of zinc in freshwaters. *Acta Hydrochimica Et Hydrobiologica, 13(6), 627-654.*

38. Holt, M. S. **(2000)**. Sources of chemical contaminants and routes into the freshwater environment. *Food and Chemical Toxicology, 38, 21-27.*

39. Meher, H., Behera, P. K., & Panda, S. N. **(2018)**. Evaluation of water quality index (WQI) of pond water of paradeep area, Odisha, India. *Indian Journal of Environmental Sciences, 22(2), 76-81.*

40. Plum, L. M., Rink, L., & Haase, H. **(2010)**. The essential toxin: impact of zinc on human health. *International Journal of Environmental Research and Public Health, 7(4), 1342-1365*

41. Bhowmik, D., Chiranjib, K., & Kumar, S. **(2010)**. A potential medicinal importance of zinc in human health and chronic. *International Journal of Pharmaceutical, 1(1), 05-11.*

42. Lokhande, R. S., Singare, P. U., & Pimple, D. S. **(2011)**. Toxicity study of heavy metals pollutants in waste water effluent samples collected from Taloja industrial estate of Mumbai, India. *Resources and Environment, 1(1), 13-19.*

43. Akpor, O. B., Ohiobor, G. O., & Olaolu, D. T. **(2014)**. Heavy metal pollutants in wastewater effluents: sources, effects and remediation. *Advances in Bioscience and Bioengineering, 2(4), 37-43.*

44. Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B. B., & Beeregowda, K. N. **(2014)**. Toxicity, mechanism and health effects of some heavy metals. *Interdisciplinary Toxicology, 7(2), 60.*

45. Sahu, O. P., & Chaudhari, P. K. **(2015)**. The characteristics, effects, and treatment of wastewater in sugarcane industry. *Water Quality, Exposure and Health*, *7*(3), 435-444.

46. Mohammed, E., Mohammed, T., & Mohammed, A. **(2018)**. Optimization of instrument conditions for the analysis for mercury, arsenic, antimony and selenium by atomic absorption spectroscopy. *MethodsX, 5, 824-833.*

47. Oliveira, A. F., Svoboda, M., Musil, S., Machado, I., Vaněk, D., Matoušek, T. ... & Kratzer, J. **(2020)**. Selenium preconcentration in a gold "amalgamator" after hydride generation for atomic spectrometry. *Journal of Analytical Atomic Spectrometry, 35(10), 2132-2141*.

48. Belluzzi-Muiños, M., Dol, I., & Pistón, M. **(2017)**. A low-cost device for sample introduction and determination of mercury by Cold Vapour Atomic Absorption Spectrometry–application for irrigation water and paddy soil. *Brazilian Journal of Analytical Chemistry, 4 (14), 34 – 43.*

49. Tamiji, T., & Nezamzadeh-Ejhieh, A. **(2018)**. A comprehensive study on the kinetic aspects and experimental design for the voltammetric response of a Sn (IV)-clinoptilolite carbon paste electrode towards Hg (II). *Journal of Electroanalytical Chemistry, 829, 95-105.*

50. Haring, B. J. A., Van Delft, W., & Bom, C. M. **(1982)**. Determination of arsenic and antimony in water and soil by hydride generation and atomic absorption spectroscopy. *Fresenius' Zeitschrift für Analytical Chemistry, 310(3), 217-223.*

51. Maleki, N., Safavi, A., & Doroodmand, M. M. **(2005)**. Determination of selenium in water and soil by hydride generation atomic absorption spectrometry using solid reagents. *Talanta, 66(4), 858-862.*

52. Samanta, G., Chowdhury, T. R., Mandal, B. K., Biswas, B. K., Chowdhury, U. K., Basu, G. K., ... & Chakraborti, D. **(1999)**. Flow injection hydride generation atomic absorption spectrometry for determination of arsenic in water and biological samples from arsenic-affected districts of West Bengal, India, and Bangladesh. *Microchemical Journal, 62(1), 174-191.*

53. Bonadonna, L., Briancesco, R., Ottaviani, M., & Veschetti, E. **(2002)**. Occurrence of Cryptosporidium oocysts in sewage effluents and correlation with microbial, chemical and physical water variables. *Environmental Monitoring and Assessment, 75*(3), 241-252.

54. Shabir, G. A., John Lough, W., Arain, S. A., & Bradshaw, T. K. **(2007)**. Evaluation and application of best practice in analytical method validation. *Journal of Liquid Chromatography & Related Technologies, 30(3), 311-333.*

55. Kane, M. **(1996)**. The precision of measurements. *Applied Measurement in Education, 9(4), 355-379.*

56. Feinberg, M. **(2007)**. Validation of analytical methods based on accuracy profiles. *Journal of Chromatography A, 1158(1-2), 174-183.*

57. Arslaner, A., & Salık, M. A. **(2020)**. Some Quality Properties, Mineral and Heavy Metal Composition of Wild Fruit Traditional Marmalades. *Turkish Journal of Agriculture-Food Science and Technology, 8(3), 678-687.*

58. Edokpayi, J. N., Odiyo, J. O., & Olasoji, S. O. **(2014)**. Assessment of heavy metal contamination of Dzindi River, in Limpopo Province, South Africa. *International Journal of Natural Sciences Research, 2 (10), 185-194.*

59. Ekere Nwachukwu, R., Ihedioha Janefrances, N., Eze Ifeanyi, S., & Agbazue Vitus, E. **(2014)**. Health risk assessment in relation to heavy metals in water sources in rural regions of South East Nigeria. *International Journal of. Physical Sciences, 9(6), 109-116.*

60. Gowd, S. S., & Govil, P. K. **(2008)**. Distribution of heavy metals in surface water of Ranipet industrial area in Tamil Nadu, India. *Environmental Monitoring and Assessment, 136(1), 197-207.*

61. Varol, M., & Şen, B. **(2012)**. Assessment of nutrient and heavy metal contamination in surface water and sediments of the upper Tigris River, Turkey. *Catena, 92*, 1-10.

62. Frisbie, S. H., Mitchell, E. J., & Sarkar, B. **(2015)**. Urgent need to reevaluate the latest World Health Organization guidelines for toxic inorganic substances in drinking water. *Environmental Health, 14(1), 1-15.*

63. Moodley, K., Serrano, P. V. H., van Dijck, G., & Dumontier, M. **(2019)**. Similarity and Relevance of Court Decisions: A Computational Study on CJEU Cases. *In JURIX, 63-72.*

64. EPA, U. **(2017)**. Drinking water requirements for states and public water systems. *Environmental Science Technology, 51(22), 13450-13460.*

65. Fardous, Z., Rashid, M. H., Chowdhury, M. A. Z., Alam, M. K., Rahman, M. A., Uddin, M. A., & Bari, M. L. **(2015)**. Assessment of heavy metals, minerals, and pesticides in different branded drinking bottled water of Bangladesh and their impact on human health. *Asia-Pacific Journal of Food Safety and Security, 1(1), 27-41.*

66. Verma, P., Singh, P. K., Sinha, R. R., & Tiwari, A. K. **(2020)**. Assessment of groundwater quality status by using water quality index (WQI) and geographic information system (GIS) approaches: a case study of the Bokaro district, India. *Applied Water Science, 10(1), 1-16.*