LEVELS OF SELECTED TOXIC HEAVY METALS (Pb, Cd, Zn, Cu and Cr) IN SOIL, SURFACE AND GROUND WATER SAMPLES FROM MIDEGA WOREDA, EASTERN HARARGHE, ETHIOPIA

MSc THESIS

TESHOME DEMILEW SHIFERAW

NOVEMBER 2017

HARAMAYA UNIVERSITY, HARAMAYA

Levels of Selected Toxic Heavy Metals (Pb, Cd, Zn, Cu and Cr) in Soil, Surface and Ground Water Samples From Midega Woreda, Eastern Hararghe, Ethiopia

A Thesis Submitted to the Department of Chemistry, Postgraduate Program Directorate

HARAMAYA UNIVERSITY

In partial Fulfillment of the Requirements for the Degree of MASTER OF SCINCE IN CHEMISTRY

Teshome Demilew Shiferaw

November 2017

Haramaya University, Haramaya

HARAMAYA UNIVERSITY

POSTGRADUATE PROGRAM DIRECTORATE

I hereby certify that I have read and evaluated this Thesis which is entitled:“**Levels of Selected Toxic Heavy Metals (Pb, Cd, Zn, Cu and Cr) in Soil, Surface and Ground Water Samples from Midega Woreda, Eastern Hararghe, Ethiopia**” prepared, under my guidance, by **Teshome Demilew Shiferaw**. I recommend it be submitted as fulfilling the thesis requirements.

Endale Teju (PhD)	____________________	____________________
Major Advisor	Signature	Date
Abebaw Adgo (PhD)	____________________	____________________
Co-Advisor	Signature	Date

As a member of the Board of Examiners of the MSc Thesis Open Defense Examination, I certify that I have read and evaluated the thesis prepared by **Teshome Demilew**, and examined the candidate. I recommend that the thesis be accepted as fulfilling the Thesis requirements for the Degree of **Master of Science in Chemistry.**

____________________	____________________	____________________
Name of Chairman	Signature	Date
____________________	____________________	____________________
Name of Internal Examiner	Signature	Date
____________________	____________________	____________________
Name of External Examiner	Signature	Date

DEDICATION

I dedicate this MSc Thesis manuscript to my beloved mother W/ro Mazengia Alamraw, who helped me to cope up with all those challenges that I have faced since my childhood and nursing me with affection for the success of my life and shaped me to be the person I am today.

STATEMENT OF THE AUTHOR

By my signature bellow, I declare and affirm that this thesis is my own work. I have followed all ethical and technical principles of scholarship in the preparation, data collection, data analysis and compliation of this Thesis. Any scholary matter that is included in this Thesis has been given recognition through citation.

This thesis is submitted in partial fulfillment of the requirements for MSc degree at the HARAMAYA UNIVERSITY and is deposited at the University Library to be made available to borrowers under the rules of the Library. I declare that this thesis is not submitted to any other institution anywhere for the award of academic degree, diploma or certificate.

Brief quotations from this thesis are allowable without special permission provided that accurate and complete acknowledgement of source is made. Requests for permission for extended quotation from or reproduction of this manuscript in whole or in part may be granted by the Head of the Department or Director of the Postgraduate Program Directorate when in his or her judgment the proposed use of the material is in the interests of scholarship. In all other instances, however, permission must be obtained from the author of the Thesis.

Name: Teshome Demilew Signature: ________________

Date: November 2017

Department: Chemistry

BIOGRAPHICAL SKETCH OF THE AUTHOR

The author was born in Weast Gojjam Zone, on October 25, 1982 E.C, from his mother **Mazengia Alamraw Yilma** and his father **Demilew Shiferaw Belay**. He attended his elementary education at Daba Elementary School and his junior secondary education at Anjenie Secondary School. Then he completed his secondary and preparatory education at Dembecha Senior Secondary and Preparatory School in 2000 E.C. After completion of his secondary education, he joined Addis Ababa University colleges of Natural sciences, Departments of Chemistry in September 2001 E.C and graduated with Bachelor of Science degree in Chemistry in July 2003 E.C. Soon after gratuation, he joined Haramaya University for Postgraduate Diploma in Teaching (PGDT) and he has worked as a secondary school teacher in Somali Region, at Kelafo Secondary and Preparatory School for three years. In 2006, he joined postgraduate program directorate of Haramaya University to pursue his Msc Degree in Chemistry. Currently he is working in Harar SOS Childrens Village, Ethiopia, since September 2008 E.C.

ACKNOWLEDGEMENTS

I would like to express my special heartfelt thanks to my thesis advisor, Dr. Endale Teju for his endless constructive comments, moral supports, continuous advice, attractive approach and professional guidance towards the realization of this work. His unreserved investment of his expertise and time in this thesis contributed to my successful completion.

In parallel my special heart full thanks also goes to my co-advisor Dr. Abebaw Adgo for his valuable comments during the thesis work especially in directing the study area.

I would like to express my deepest appreciation and thanks to Haramaya University and Department of Chemistry for providing instrument with full laboratory facility and Ministry of Education for financial support.

Once more, I am extremely grateful to my mother and father, sisters and brothers for their understanding. I should not forget my lovely friend Mahder Temesgen for her support and understanding.

Last but not least, my special thanks goes to all individuals namely Kassie Desalegn, Fituma Diriba,Teklu Eshetu, Yimeslal Atnafu, Yohanes Muche, Getabalew Shifera, Seid Hassen and Nigussie Misganu for their support and encouragement.

ACRONYMS AND ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
ATSDR	Agency for Toxic Substance and Disease Registry
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
CSIRO	Commonwealth Science and Industry Research Organization
DO	Dissolved Oxygen
DPASV	Differential Pulse Anodic Stripping Voltammetery
EC	European Commission
FAAS	Flame Atomic Absorption Spectrometry
FAO	Food and Agriculture Organization
GFAAS	Graphite Furnas Atomic Absorption Spectroscopy
HM	Heavy Metal
JECFA	Joint Expert Committee on Food Additives
LOD	Limit of Detection
LOQ	Limit of Quantitation
MCL	Maximum Contaminant Limit
NIH	National Institute of Health
Ppb	Part-per-billion
Ppm	Part-per-million
PTE	Potential Toxic Elements
PTWI	Provisional Tolerable Weekly Intake
USA	United States of America
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

TABLE OF CONTENTS

LIST OF TABLES

Table **Page**

LIST OF FIGURE

Figure

Page

LIST OF TABLES IN THE APPENDIX

Table

Page

LIST OF FIGURES IN THE APPENDIX

Levels of Selected Toxic Heavy Metals (Pb, Cd, Zn, Cu and Cr) in Soil, Surface and Ground Water Samples From Midega Woreda, Eastern Hararghe, Ethiopia

ABSTRACT

Metal contamination in soil, surface and ground water is a major component in the determination of water quality. The concentrations of selected heavy metals (Pb(II), Cd(II), Cu(II), Zn(II) and Cr(VI)) in soil and water samples collected from Midega, Eastern Ethiopia were determined after digesting the samples using acid digestion method. The physico-chemical parameters like pH,conductivity, alkalinity and hardness of the water samples were determined using appropriate instruments. The standard solutions for the selected heavy metals were prepared from commercially available salts. Out of the five selected heavy metals cadmium and chromium were not detected in all samples. But the three metals namely lead, zinc and copper were detected by the instrument and their concentrations were found to be 0.06 – 0.28, 0.206 – 1.032 and 0.487 – 0.71 ppm in soil, respectively. In water, the concentrations of the detected metals were 0.804 – 4.131 and 0.415 – 0.507 ppm for zinc and copper, respectively. The accumulations of the detected heavy metals were in the increasing order of Pb < Cu < Zn. The results obtained were compared with guidelines for drinking water quality such as the Environmental Protection Agency (EPA) and World Health Organization (WHO) guidelines. The levels of the detected heavy metals were not beyond the maximum permissible limit.

Key words: *Acid digestion, Heavy metal, Soil, Titration, Water*

1. INTRODUCTION

Metals are elements, present in chemical compounds as positive ions or in the form of cation in solution. Metals, which have a high atomic weight and a density much greater (at least 5 times) than water are known as heavy metals. Concentration of free metal in tap water is very much helpful in understanding the role of pollutant and nutrient elements (Yilmaz *et al.*, 2009).

Heavy metals are grouped within the category of environmental toxins and the investigations of these toxic heavy metals such as Fe, Mn, Cu, Zn, Co, Ba, Ag, As, Cd, Cr, Hg, Ni, Pb, Sb and Se place special importance on environmental samples (Abollino *et al.*,2000; Novotry *et al.*, 2000). These heavy metals are much toxic and have tendency to accumulate in the body and may result in chronic damage. The natural concentration of metals in water varies depend up on the metal concentration in the soil (Opydo and Jadwiga, 1989), the underlying geologica structures, the acidity of the water, its humus content and particulate matter concentration.

Industrial and household waste discharges directly or indirectly through leakages in sewage systems into water sources causes excessive pollution in suface and underground water (Akcay *et al.,* 2003). It is possible to analyse simultaneously very low levels of several metals such as Pb, Cu, Cd, Cr and Zn using different methods like DPASV, AAS, X-ray fluorescence spectrometry and Inductive coupled plasma (Farrukh *et al.*, 2006). The excellent performance of the atomic absorption spectrometry, AAS as a precise and rapid analytical tool, allows the fast acquisition of data on samples introduced into a flame. One of the attractive characters of the AAS technique is its ease of operation (Price, 1979; Welz, 1999).

Ultimately, increasing the heavy metal content in soil also increases the uptake of heavy metals by plants depending upon the soil type, plant growth stages and plant species. These heavy metals may adversely affect soil ecology, agricultural production or product quality, ground water quality and will ultimately harm to health of living organism by food chain. These effects are closely related to the biological availability of heavy metals, which in turn are controlled by the metal ion speciation in the soil. Therefore, the determination of free metal ion concentrations in soil solution becomes important.

The free metal ion concentration not only depends on the total metal content in soils, but also on the metal species that exist in the soil. In addition, some environmental conditions e.g. pH, concentration of complexion ligands in solution and the soil colloid (Ene *et al.,* 2009).

Heavy metals enter the environment by natural and anthropogenic means. Such sources include: natural weathering of the earth's crust, mining, soil erosion, industrial discharge, urban runoff, sewage effluents, pest or disease control agents applied to plants, air pollution fallout and a number of others (Ming-Ho, 2005). Although some individuals are primarily exposed to these contaminants in the work place, for most people the main route of exposure to these toxic elements is through the diet (food and water). The contamination chain of heavy metals almost always follows a cyclic order: industry, atmosphere, soil, water, foods and human. Although toxicity and the resulting threat to human health of any contaminant are, of course, a function of concentration, it is well-known that chronic exposure to heavy metals and metalloids at relatively low levels can cause adverse effects (ATSDR, 2000, 2004, 2007, 2008; Castro and Mendez, 2008). Therefore, there has been increasing concern, mainly in the developed world, about exposures, intakes and absorption of heavy metals by humans.

Populations are increasingly demanding a cleaner environment in general, and reductions in the amounts of contaminants reaching people as a result of increasing human activities. A practical implication of this trend, in the developed countries, has been the imposition of new and more restrictive regulations (Figueroa, 2008).

Drinking water may be contaminated by different contaminants which have an impact on the health and economic status of the consumers. Contaminants such as bacteria, viruses, heavy metals, nitrates and salt have found their way into water supplies due to inadequate treatment and disposal of waste (human and livestock), industrial discharges and over use of limited water resources (Singh and Mosley, 2003). Even if no sources of anthropogenic contamination exist, natural sources are also equally potential to contribute higher levels of metals and other chemicals that can harm human health.

In Ethiopia, the dominant source of drinking water used to supply major urban and rural communities is from wells and springs. Although there are no systematic and comprehensive water quality assessment programs in the country, there are increasing indications of water contamination problems in some parts of the country. Heavy metals normally occurring in nature are not harmful to our environment because they are only present in very small amounts (Sanayei *et al*., 2009).

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 (Ghaedi *et al*., 2005). Drinking water is one of the important sources for heavy metals for humans. Concentration of the heavy metal ions in drinking water are generally at µg/L.

So far, no sufficient study has been conducted on heavy metal contamination of soil, surface and ground water of the Oromia Region Midega Woreda.For this reason, due emphasis is given to the determination of these contaminants (heavy metals) at Midega Woreda since the risk of these contaminants are so great in humans and animals. So, this study will be conducted to determine the levels of selected contaminants as objectives of the study.

1.1. Objectives of the Study

1.1.1. General Objective

- The main objective of this research was to study the levels of some selected heavy metals in soil, ground and surface water samples of Midega Woreda by atomic absorption spectroscopy.

1.1.2. Specific Objectives

- To determine the levels of selected heavy metals in soil, ground and surface water sample from Midega Woreda by atomic absorption spectroscopy.
- To investigate some physico-chemical parameters of soil, ground and surface water samples from the study area.

2. LITERATURE REVIEW

2.1. Heavy Metals

Lead (Pb) and cadmium (Cd) are widely dispersed in the environment. These elements have no beneficial effects in humans,and there is no known homeostasis mechanism for them (Draghici *et al*., 2010; Vieira *et al*., 2011).

They are generally considered as the most toxic to humans and animals; the adverse human health effects associated with exposure to them, even at low concentrations, are diverse and include, but are not limited to neurotoxin and carcinogenic actions (ATSDR, 2000, 2004, 2007, 2008; Castro and Mendez, 2008; Jomova and Valko, 2001; Tokar *et al*., 2001).

The most common potential toxic elements listed by the United State Environmental Protection Agency (USEPA) are cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb) and zinc (Zn). Some of these PTEs are essential for the metabolic activities of living organisms. Potential toxic elements such as Cr, Cu and Zn are required by organisms at low level and become toxic at some higher levels.Non- essential elements including Cd and Pb are toxic and not required by organisms at any level (Poggio *et al*., 2009).

The toxicity of trace metals will vary greatly between organisms for the same trace metals, and between trace metals for the same organisms. Furthermore, trace metals will not necessarily follow the same rank order of toxicities between organisms, depending on differences between uptake rate, detoxification rates and excretion rate of the different organisms compared. However, the general order of toxicity of heavy metals is Hg > Ag > Cu > Cd > Zn > Ni > Pb > Cr > Sn and so on (Luoma and Rainbow, 2008). Heavy metals toxicity can result in damaged or reduced mental and central nervous function, lower energy levels and damage to blood composition, lungs, kidneys, liver, and other vital organs (WHO, 1984).

2.1.1. General Characteristics of Toxic Heavy Metals

Heavy metals are defined as those elements with a specific density at least five times the specific gravity of water. Heavy metals are not biodegradable and tend to accumulate in living o rganisms, causing various diseases and disorders (Jang *et al*., 2008). Therefore, the removal of hazardous heavy metals cation in wast water has received much attention in recent years.

Because of their dangerous tendency to bio-accumulation, there is an increase in the concentration of toxic chemical in a biological organism over time, compared to the chemical's concentration in the environment. Lee *et al. (*2010); Ouyang *et al. (*2011) and numerous researchers have been focused on synthetic of novel materials including controlled size and shape, which is important for their chemical and physical properties, On the basis of this, Heavy metals are generally present under their cationic form (Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+},Cr^{2+}etc).

2.1.1.1. Lead

Lead as a toxicologically relevant element has been brought into the environment by man in extreme amounts, despite its low geochemical mobility and has been distributed worldwide. Lead amounts in deep Ocean waters is about 0.01-0.02 µg/L, but in surface ocean waters is 0.3 µg/L (Castro and Mendez, 2008). Lead still has a number of important uses in the present day; from sheets for roofing to screens for X-rays and radioactive emissions. Like many other contaminants, lead is ubiquitous and can be found occurring as metallic lead, inorganic ions and salts (Harrison, 2001). Lead has no essential function in man. Food is one of the major sources of lead exposure; the others are air (mainly lead dust originating from petrol) and drinking water.

Plant food may be contaminated with lead through its uptake from ambient air and soil; animals may then ingest the lead contaminated vegetation. In humans, lead ingestion may arise from eating lead contaminated vegetation or animal foods. Another source of ingestion is through the use of lead-containing vessels or lead-based pottery glazes (Ming-Ho, 2005). In humans, about 20 to 50% of inhaled, and 5 to 15% of ingested inorganic lead is absorbed. In contrast, about 80% of inhaled organic lead is absorbed, and ingested organic Pb is absorbed readily. Once in the blood stream, lead is primarily distributed among blood, soft tissue, and mineralizing tissue (Ming-Ho, 2005).

The bones and teeth of adults contain more than 95% of the total body burden of lead. Children are particularly sensitive to this metal because of their more rapid growth rate and metabolism, with critical effects in the developing nervous system (ATSDR, 2007; Castro and Mendez, 2008). The Joint FAO/ World Health Organization Expert Committee on Food Additives (JECFA) established a provisional tolerable weekly intake (PTWI) for lead as 0.025

mg/kg body weight. The WHO provisional guideline of 0.01 mg/L has been adopted as the standard for drinking water (WHO, 2004a).

Lead has been the intense focus of environmental health research for many decades. Lead is a highly toxic metal whose widespread use has caused extensive environmental contamination and health problems in many parts of the world. The various sources of lead (Metal plating, Wastes from battery industries, Soil wastes, exhaust from automobiles, additives in gasoline and pigment, Factory chimneys, Smelting of ores, Fertilizers and pesticides) pollution in the environment (Sharma and Dubey, 2005). Hence human exposure of lead in the general population is either due to food or drinking water (Goyer, 1990).

2.1.1.2. Cadmium

The use of cadmium by man is relatively recent and it is only with its increasing technological use in the last few decades that serious consideration has been given to cadmium as a possible contaminant. Cadmium is naturally present in the environment: inair, soils, sediments and even in unpolluted seawater. Cadmium is emitted to air by mines, metal smelters and industries using cadmium compounds for alloys, batteries, pigments and in plastics, although many countries have stringent controls in place on such emissions (Harrison, 2001).

Tobacco smoke is one of the largest single source of cadmium exposure in humans. In all of its form tobacco contains appreciable amount of cadmium. The absorption of the metal from lung is much greater than the gastro-intestinal tract, smoking contributes significantly to the total body burden (Ming-Ho, 2005; Figueroa, 2008).

In general, for non-smokers and non-occupationally exposed workers, food products account for most of the human exposure burden to cadmium. In food, only inorganic cadmium salts are present. Organic cadmium compounds are very unstable. In contrast to lead and mercury ions, cadmium ions are readily absorbed by plants. They are equally distributed over the plant. Cadmium is taken up through the roots of plants to edible leaves, fruits and seeds. During the growth of grains such as wheat and rice, cadmium taken from the soil is concentrated in the core of the kernel. Cadmium also accumulates in animal milk and fatty tissues (Figueroa, 2008). Therefore, people are exposed to cadmium when consuming plant and animal based foods. Seafood, such as mollusks andcrustaceans, can be also a source of cadmium (WHO 2004b, 2006; Castro and Mendez, 2008).

The Joint FAO/WHO has recommended the PTWI as 0.007 mg/kg bw for cadmium. The EPA maximum contaminant level for cadmium in drinking water is 0.005 mg/L whereas the WHO adopted the provisional guideline of 0.003 mg/L (WHO, 2004a).

Cadmium is emitted to air by mines, metal smelters and industries using cadmium compounds for alloys, batteries, pigments and in plastics, although many countries have stringent controls in place on such emissions (Harrison, 2001).Cadmium also accumulates in animal milk and fatty tissues (Figueroa, 2008). Therefore, people are exposed to cadmium when consuming plant and animal-based foods. Seafood, such as mollusks andcrustaceans, can be also a source of cadmium (WHO 2004b; WHO 2006; Castroand Mendez, 2008).

Cadmium accumulates in the human body affect several organs like liver, kidney, lung, bones, p lacenta, brain and the central nervous system. Other damages of cadmium include reproductive and development toxicity, hepatic, hematological and immunological effects (Castro and Mendez, 2008).

2.1.1.3. Copper

Copper is one of the world's most widely used metals. The most common copper-bearing ores are sulfides, arsenates, chlorides, and carbonates (Weiner, 2008). It reaches aquatic systems through anthropogenic sources such as industry, mining, plating operations, usage of copper salts to control aquatic vegetation or influxes of copper containing fertilizers (Nussery, 1998).

The toxicity of copper in aquatic organisms is largely attributable to Cu^{2+} that forms complexes with other ions (Nussey, 1998). A reduction in water dissolved oxygen, hardness, temperature, pH, and chelating agents can increase the toxicity of copper (Nussey, 1998).

Organic and inorganic substance can easily complex the cupric form of copper, which is the most common speciation of this metal, and it is then absorbed on to particulate matter. Therefore, the free ion is rarely found except in pure acidic soft water.

The chemical speciation of copper strongly depends on the pH of water (Stouthart *et al.,* 1996). Copper in water, particulate at high pH (alkaline) and is thus not toxic, while at low pH (acidic) it is mobile, soluble and toxic (Nussey, 1998). Acute poisoning result from ingestion of excessive amount of copper salt and can lead to nausea, vomiting, stomachache and diarrhea and may produce death. Copper fume, dusts and mist from industries exposure affect to upper respiratory tract.

At low concentration, copper can result in anemia, gastrointestinal disturbances, bone develop ment abnormalities and death. Copper toxic effects in fish include; change biochemistry, anatom y, physiology and behavior. It damages the gill and head area of fish, could probably cause mucous to accumulate on the gill area (Lewis and Lewis, 1971).

2.1.1.4. Zinc

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

Even though zinc is an essential trace element and help in homeostatically control in fish but at high concentration of zinc can be toxic to fish (Counture and Rajotte, 2003). Acute toxic zinc concentrations result in gill damage, which interferes with respiration, leading to hypoxia. Chronically toxic are generally extensive deterioration of liver, kidneys, heart, and muscle. Chronic sub-lethal zinc concentration can also delay or inhibit the growth sexual maturity andreproduction of the fish, and can also induce pathological and morphological abnormality in adult fish (Somasun *et al*., 1984).

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

2.1.1.5. Chromium

Chromium is an essential nutrient for plant and animal metabolism. However, the increasing accumulation of chromium in the environment from industrial outputs has caused great concern. Chromium contaminated waste waters can originate from dyes and pigment manufacturing, wood preserving, electroplating and leather tanning. Chromium exists in (+3) and (+6) oxidation states, as all other oxidation states are not stable in aqueous solutions (Dakiky *et al.,* 2002a).

According to WHO the tolerable limit of chromium in any food staff should not exceed more than 250 µg/ day (WHO, 1996). Cr(VI) has been demonstrated to have a number of adverse effects ranging from irritation to causing cancer. Effects in humans occupationally exposed to high levels of chromium compounds, primarily Cr(VI) by inhalation, may include irritating respiratory effects, effects on stomach and blood, liver and kidney effects, and increased risk of death from lung cancer (Dakiky *et al*., 2002). Evidence from studies on experimental animals' shows that Cr(VI), especially those of low solubility, can induce lung cancer. Trivalent chromium is not considered to be carcinogenic (David *et al*., 2008).

2.2. Water and Heavy Metals

Safe and good quality drinking water is the basis for good human health. Water provides some elements, but when polluted it may become the source of undesirable substances, dangerous to human health and cause disease such as, various cancers, adverse reproductive outcomes, cardiovascular disease, teeth decay and neurological diseases. The infants and younger population are more prone to the toxic effects of heavy metals, as the rapidly developing body systems in the fetus, infants and young children are far more sensitive (Johnson and Hallberg, 2005).

Childhood exposure to some metals can result in learning difficulties, memory impairment, damage to the nervous system and behavioral problems such as aggressiveness and hyperactivity (Rajendran *et al.,* 2003). At higher doses, heavy metals can cause irreversible brain damage. Children may receive higher doses of metals from food than adults, since they consume more food for their body weight than adults. The reason for this hydrological scourge is the presence of alarming levels of heavy metal arsenic in groundwater in several villages of the globe.Toxic metals are usually present in industrial, municipal and urban runoff, which can be harmful to humans and biotic life. Increased urbanization and industrialization are to be blamed for an increased level of trace metals, especially heavy metals, in our water bodies (Dogan *et al*., 2005).

There are over 50 elements that can be classified as heavy metals, 17 of which are considered to be very toxic and relatively accessible. Characteristically, also the anions have its important role in drinking water; results also showed affecting the human health.Toxicity level depends on the type of metal, its biological role and the type of organisms that are exposed to it.Heavy metals have a marked effect on the aquatic flora and fauna which through bio-magnifications enters the food chain and ultimately affect the human beings as well (Lokhande *et al*., 2011).

Heavy metals in drinking water linked most often to human poisoning are lead, iron, cadmium copper, zinc, chromium etc. They are required by the body in small amounts but can also be toxic in large doses. They constitute one important group of environmentally hazardous substances if present.

Safe drinking water is a human birth right as much a birthright as clean air. As a matter of fact, in most of the African and Asian countries, even in relatively advanced countries such as India; safe drinking water is not easily available. Of the 6 billion people on earth, more than one billion lack accesses to safe drinking water and, about 2.5 billion do not have access to adequate sanitation services (TWAS, 2002).

Various types of water borne diseases kill on an average more than 6 million children each year i.e. about 20,000 children a day (TWAS, 2002). Water covers 70 percent of the globe's surface, but most is salt water. Freshwater covers only 3 percent of the earth's surface and much of it lies frozen in the Antarctic and Greenland polar ice.

Freshwater that is available for human consumption comes from rivers, lakes and subsurface aquifers. These sources account for only one percent of all water on the earth. Six billion people depend on this supply and a significant portion of the world's population is facing water shortages.

Some countries (31) representing 2.8 billion people, including China, India, Kenya, Ethiopia, Nigeria and Peru confront chronic water problems.With in a generation, the world's population will climb to an estimated 8 billion people. Yet, the amount of water will remain the same (Bishnoi and Arora, 2007). The challenge is as clear and compelling as pristine water cascading down a mountain stream: We must find new and equitable ways of saving, using and recycling the water that we have (Atalay *et al*., 2008).

2.2.1. **Behavior of Heavy Metals in Water**

Drinking water is exposed to different contaminants, depending on its sources.Surface water contaminations occur, when water travels over the surface of the land or through the ground.

As it travels, it dissolves naturally occurring substances and pick up the minerals resulting from the presence of animal or human activities.

While for the ground water, the contaminants come from leachate from land fills and septic systems, haphazard disposal from agricultural chemicals and household cleaning products. The contaminants inground water take more time to be cleaned because it moves slowly and isn't exposed to the natural cleansing benefits of air, sunlight and micro-organism (Nriagu and Pacyna, 1988).

Generally, the quality of drinking water is determined based on the appearance, taste, color and odor of the water. The appearance, taste, color and odor do not really tell if the water is safe to drink. Safe drinking water should also be free from hazardous compounds (Berman, 1980).

The natural concentration of metals in raw water which has not been treated or purified varies from state to state, country to country. It depends on many factors such as geological structures, the soil, the acidity of the water and the particulate matter concentration (Berman, 1980; Nriagu and Pacyna, 1988). Most metal species in natural freshwater occur in organic compounds, organic complexes or colloids. From the point of view of health, metal can be divided into two categories:

1. Metals with undesirable effect such as Iron (Fe), Manganese (Mn), Copper(Cu), Zinc (Zn), Cobalt (Co), Barium (Ba), Silver (Ag).
2. Metals with a negative toxic effect such as Arsenic (As), Cadmium (Cd),Chromium (Cr), Mercury (Hg), Nickel (Ni), Lead (Pb), Antimony (Sb), Selenium (Se).

2.3. Soil and Heavy Metals

The incidence of heavy metal contamination from both natural and anthropogenic sources has increased concern about possible health effects. Natural and anthropogenic sources of soil contamination are widespread and variable (Tahir *et al*., 2007).

Large areas of agricultural land are contaminated by heavy metals that mainly originate from former or current mining activities, industrial emissions or the application of sewage sludge. Metals exist in one of four forms in the soil: mineral, organic, sorbed (bound to soil), or dissolved.

Sorbed metals represent the third largest pool, and are generally very tightly bound to soil surfaces. Although mineral, organic, and sorbed metals are not immediately absorbed by plants, they can slowly release metals into solution (Jones, 2003).

Heavy metals naturally occur in the environment, but may also be introduced as a result of land use activities. Natural and anthropogenically introduced concentrations of metals in near-surface soil can vary significantly due to different physical and chemical processes operating within soils across geographic regions (Murray *et al.*, 2004).

Migration of metals in the soil is influenced by physical and chemical characteristics of each specific metal and by several environmental factors. The most significant environmental factors appear to be soil type, total organic content, redox potential, and pH (Murray *et al.*, 1999).

Although heavy metals are generally considered to be relatively immobile in most soils, their mobility in certain contaminated soils may exceed ordinary rates and pose a significant threat to water quality (Bunzl *et al.*, 2001). Organic manure, municipal waste, and some fungicides often contain fairly high concentrations of heavy metals. Soils receiving repeated applications of organic manures, fungicides, and pesticides have exhibited high concentrations of extractable heavy metals (Han *et al.*, 2000) and increased concentrations of heavy metals in runoff (Moore *et al.*, 1998). Previous studies indicate that metal constituents of surface soil directly influence the movement of metals, especially in sandy soils (Moore *et al.*, 1998; Cezary and Singh, 2001).

2.3.1. Behavior of Heavy Metals in Soil

Monitoring the endangerment of soil by heavy metals is of interest due to their influence on ground and surface water (Boukhalfa, 2007; Clemente *et al.*, 2008) and also on flora (Pandey 2008; Stobrawa and Lorenc-Plucinska, 2008), animals and humans (De Vries *et al.*, 2007). The overall behavior of heavy metals in soil is said to be governed largely by their sorption and desorption reactions with different soil constituents, especially clay components (Appel, 2002).

The chemical behavior of heavy metals in soils is controlled by a number of processes, including metal cation release from contamination source materials (e.g. fertilizer, sludge, smelter dust, ammunition, slag), cation exchange and specific adsorption onto surfaces of minerals and soil organic matter and precipitation of secondary minerals (Manceau *et al*., 2000). The relative importance of these processes depends on soil composition and pH.

In general, cation exchange reactions and complexation to organic matter are most important in acidic soils, while specific adsorption and precipitation become more important at near-neutral to alkaline pH values (Voegelin *et al*., 2003).

El-Ghawi*et al*. (2007) studied the trace metal concentrations in some Libyan soils and found that the concentrations in clay surface soil are higher than in sandy soil. The multiple regression analyses performed confirmed the importance of pH as well as other soil properties such as texture, electrical conductivity and organic matter or carbonates on the behavior of nutrients and heavy metals (Soriano-Disla *et al*., 2008). Increased anthropogenic inputs of Cu and Zn in soils have caused considerable concern relative to their effect on water contamination (Zhang *et al*., 2003). Oxidizing conditions generally increase the retention capacity of metals in soil, while reducing conditions will generally reduce the retention capacity of metals (Mclean and Bledsoe, 1992).

Filep (1998) stated that contaminants reaching the soil can be divided into two groups, namely micro pollutants and macro pollutants. Micro pollutants are natural or anthropogenic molecules, which are toxic at very low concentration. Macro-pollutants are present in the environment locally and/or temporarily to a much higher degree than normal level. The main micro-pollutants of soils are inorganic or organic compounds. Inorganic micro-pollutants are mainly the toxic and potentially toxic heavy metals (Pb, Cd, Ni, Cr, Hg, Cu, Zn etc.).

Organic micro-pollutants include pesticides and certain non-pesticide organic molecules: e.g. aliphatic solvents, monocyclic aromatics, halogenated aromatics, polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), surfactants, plastifiers.

2.4. Assessment of Exposure to Heavy Metals

The increase of industrial activities has intensified environmental pollution problems and the deterioration of several aquatic ecosystems with the accumulation of metals in biota and flora. Although trace metals at low concentrations are essential to life, at high concentrations, may become hazardous. High concentrations of trace elements are dangerous because they tend to bioaccumulation resulting in heavy metal poisoning. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking-water contamination (e.g. lead pipes), high ambient air concentrations near emission sources, or intake via the food chain (USEPA, 1995).

Many trace metals are regarded as serious pollutants of aquatic ecosystems because of their environmental persistence, toxicity and ability to be incorporated into food chains. Various metals from industrial, agricultural, domestic and urban wastes may enter river and lake waters through leaching, runoff, effluents and dry deposition. Heavy metals pollution represents a serious problem as these metals leach into ground water or soil, which is detrimental to human health.

Ground water pollution is a consequence of several activities like chemical manufacturing, painting and coating and mining. Metals exert a deleterious effect on fauna and flora of lakes and streams (USEPA, 1995; APHA, 2002).

Metals are introduced into the environment by a wide range of natural and anthropogenic sources and with anthropogenic sources being either domestic or industrials. They occur naturally at levels that are considered not 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 (Weiner, 2008).

Generally, the pattern of the flow of anthropogenic sources of heavy metals in the environment is illustrated in the figure below as proposed by (Chalermsupanimit, 2006).

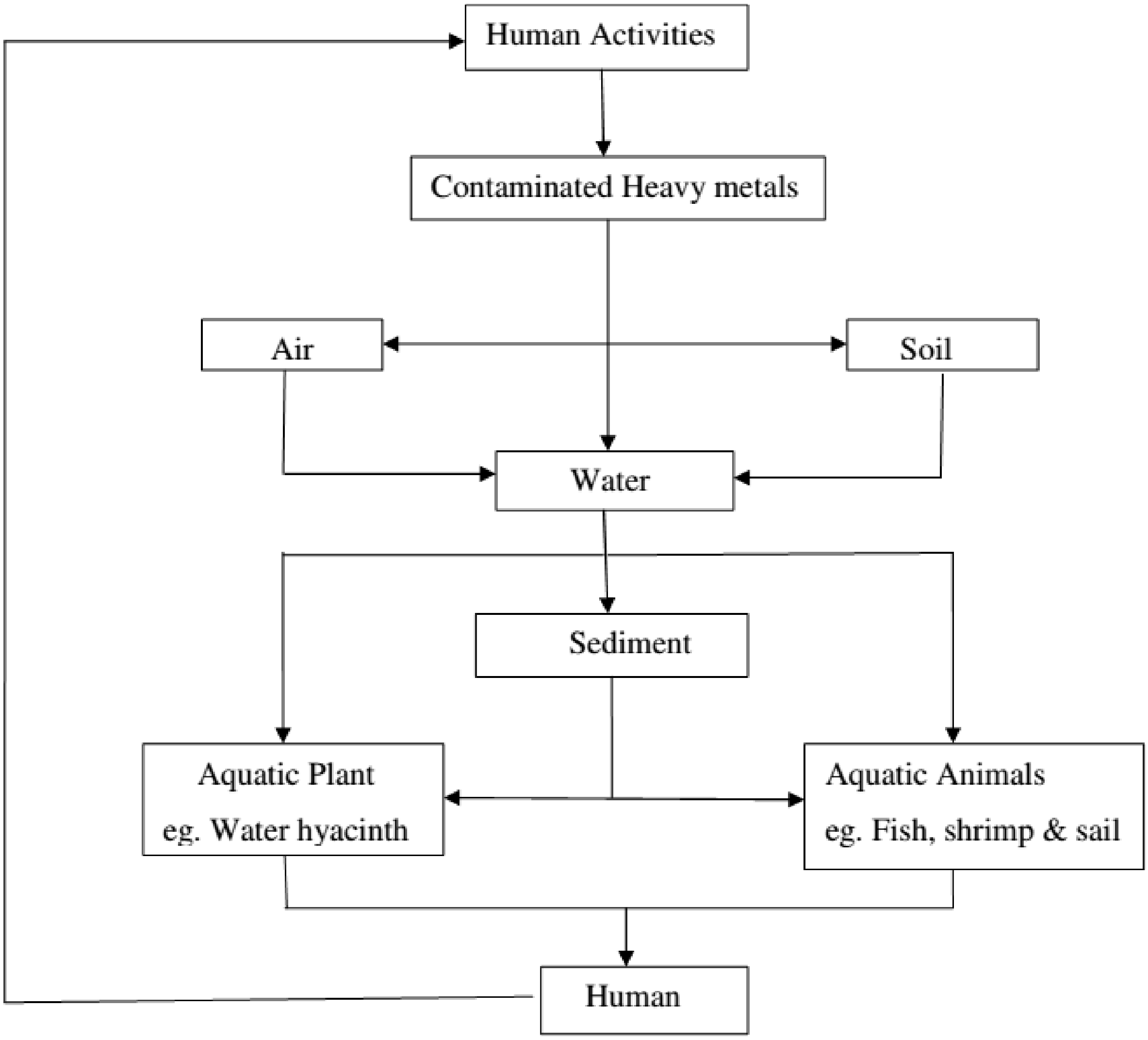

Figure 1.Anthropogenic sources of heavy metals flow in environment

Table 1. The use and health effects of some heavy metal on human being

Heavy metals	Uses	Health effects	References
Cadmium	Electroplating, fertilizers, mineral processing and battery manufacturing	Cancer, lung insufficiency disturbances in liver and kidney damage	Sharma, 1995
Chromium	Metal plating electroplating leather, mining galvanometer, dye production	Ulcer, skin irritation liver and kidney damage	Kumar *et al*., 2006
Lead	Metal plating, textile, battery manufacturer, automotive and petroleum industries	spontaneous abortion, damage nervous system, kidney and brain damage	Tunali *et al.,* 2006
Copper	Control aquatic vegetation or influxes of copper containing fertilizers	nausea, vomiting, stomachache, diarrhea and may produce death	Nussey, 1998
Zinc	Necessary for a healthy immune system, cell division and synthesis of protein	Delay or inhibit the growth, sexual maturity and reproduction of the fish	Nussey, 1998

2.5. Heavy Metal Determination by AAS

Atomic Absorption Spectrometry (AAS) is an analytical technique that measures the concentrations of elements. Atomic absorption spectroscopy can be used to analyze the concentration of over 62 different metals in a solution and is so sensitive that it can measure down to parts per billion of a gram (ug/dm^{-3}) in a sample. The technique makes use of the wave lengths of light specifically absorbed by an element (Sammut *et al.*, 2010). They correspond to the energies needed to promote electrons from one energy level to another, higher energy level.

Atomic Absorption Spectrometry (AAS) is a technique for measuring quantities of chemical elements present in environmental samples by measuring the absorbed radiation by the chemical element of interest. This is done by reading the spectra produced when the sample is excited by radiation. The atoms absorb ultraviolet or visible light and make transitions to higher energy levels. Atomic absorption methods measure the amount of energy in the form of photons of light that are absorbed by the sample (Garcia *et al.*, 2009; Sammut *et al.*, 2010).

A detector measures the wave lengths of light transmitted by the sample, and compares them to the wavelengths which originally passed through the sample. A signal processor then integrates the changes in wavelength absorbed, which appear in the readout as peaks of energy absorption at discrete wavelengths. The energy required for an electron to leave an atom is known as ionization energy and is specific to each chemical element. When an electron moves from one energy level to another within the atom, a photon is emitted with energy E. Atoms of an element emit a characteristic spectral line. Every atom has its own distinct pattern of wavelengths at which it will absorb energy, due to the unique configuration of electrons in its outer shell. This enables the qualitative analysis of a sample (Garcia *et al.*, 2009).

The concentration is calculated based on the Beer-Lambert law. Absorbance is directly proportional to the concentration of the analyte absorbed for the existing set of conditions. The concentration is usually determined from a calibration curve, obtained using standards of known concentration. However, applying the Beer-Lambert law directly in AAS is difficult due to: variations in atomization efficiency from the sample matrix, non-uniformity of concentration and path length of analyte atoms (in graphite furnace AA).

The chemical methods used are based on matter interactions, i.e. chemical reactions. For a long period of time these methods were essentially empirical, involving, in most cases, great experimental skills. Although AAS dates to the nineteenth century, the modern form of this technique was largely developed during the 1950s by Alan Walsh and a team of Australian chemists working at the CSIRO (Common wealth Science and Industry Research Organization)

Division of Chemical Physics in Melbourne, Australia. Typically, the technique makes use of a flame to atomize the sample, but other atomizers, such as a graphite furnace, are also used (Garcia *et al*., 2009; Sammut *et al*., 2010).

Three steps are involved in turning a liquid sample into an atomic gas,these are:

1. Desolvation – the liquid solvent is evaporated, and the dry sample remains,
2. Vaporization – the solid sample vaporizes to a gas and
3. Volatilization – the compounds that compose the sample are broken into free atoms.

Baez *et al*. (2007) to measure how much of a given element is present in a sample, one must first establish a basis for comparison using known quantities of that element to produce a calibration curve.

To generate this curve, a specific wavelength is selected, and the detector is set to measure only the energy transmitted at that wavelength. As the concentration of the target atom in the sample increases, the absorption will also increase proportionally. A series of samples containing known concentrations of the compound of interest are analyzed, and the corresponding absorbance, which is the inverse percentage of light transmitted, is recorded. The measured absorption at each concentration is then plotted, so that a straight line can then be drawn between the resulting points. From this line, the concentration of the substance under investigation is extrapolated from the substance's absorbance. The use of special light sources and the selection of specific wavelengths allow for the quantitative determination of individual components in a multi-element mixture (Garcia *et al*., 2009; Sammut *et al*., 2010).

2.6. Physico- Chemical Parameters of Water and Soil Sample

It is very essential and important to test the water before it is used for drinking, domestic, agricultural or industrial purpose. Water must be tested with different physic-chemical parameters. Selection of parameters for testing of water is solely depends upon for what purpose we going to use that water and what extent we need its quality and purity. Water does content different types of floating, dissolved, suspended and microbiological as well as bacteriological impurities.

Some physical test should be performed for testing of its physical appearance such as temperature, color, odor, pH, turbidity, TDS etc., while chemical tests should be perform for its

BOD, COD, dissolved oxygen, alkalinity, hardness and other characters. Different technique that used to measure physico-chemical parameters are given bellow in table 2.

Table 2. Different analytical water quality parameters with their analytical technique

No.	Parameter	Technique used
1	Electrical conductivity	Conductivity meter
2	pH	pH meter
3	Total Hardness	Titration
4	Alkalinity	Acid – Base titration

For obtaining more and more quality and purity water, it should be tested for its trace metal, heavy metal contents and organic i.e. pesticide residue. It is obvious that drinking water should pass these entire tests and it should content required amount of mineral level. Only in the developed countries all these criteria's are strictly monitored. Due to very low concentration of heavy metal and organic pesticide impurities present in water it need highly sophisticated analytical instruments and well trained manpower. The following different physic chemical parameters are tested regularly for monitoring quality of water (Patil *et al*., 2012). Table 3 show the source and health effects of physico-chemical parameters.

Table 3. Different analytical water quality parameters used for testing of quality of water and their source of occurrence and potential health effects with USEPA guidelines

No.	Parameter	Source of occurrence	Potential health effect
1	Electrical conductivity	Due to different dissolved solids	Conductivity due to ionizable ions. High conductivity increases corrosive nature of water.
2	Ph	pH is changed due to different dissolved gases and solids.	Affects mucous membrane; bitter taste; corrosion
3	Total Hardness	Presence of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions in a water supply	Poor lathering with soap; deterioration of the quality of clothes; scale forming
4	Total alkalinity	Due to dissolved gases	Embrittlment of boiler steel.

3. MATERIALS AND METHODS

3.1. Study Area

The study sites are located at the Eastern part of Ethiopia, Eastern Hararghe Zone particularly Midega Woreda. The experiment including sample preparation, sample digestion, physico-chemical parameter determination (pH, hardness, alkalinity and electrical conductivity) were conducted in the inorganic laboratory, Department of Chemistry, Haramaya University. Analyses of water and soil samples were carried out by using atomic absorption spectroscopic technique at Haramaya University Central Laboratory.

3.2. Instruments and Apparatus

Equipment and apparatus used during the experiment include: Atomic absorption spectrometer (Buck scientific model 210 VGP AAS, USA), pH meter (pH-ion level 2, Germany), analytical balance (Mttlertoleadop, model AG 204, Switzerland), hot plate, plastic bottles, conductivity meter, volumetric flasks, measuring cylinder (Duran, Germany), pipettes (Pyrex. USA), beakers, zip plastic bag and safety goggles. Theequipments and instruments used in this study were calibrated to check their status before and in the middle of the experiments to remove contaminations.

3.3. Reagents and Chemicals

Reagents and chemicals used during the laboratory session were all analytical grade; Nitric acid (69-72% conc. HNO_3, India), Hydrochloric acid (92% conc. HCl, Germany), Sulphuric acid (98% conc. H_2SO_4, India), potassium dichromate (99% $K_2Cr_2O_7$, BDH chemicals Ltd, England), Hydrogen Peroxide (30% H_2O_2), lead nitrate (99% Pb(NO3)2, Sigma-Aldrich England), Cadmium nitrate (99% $Cd(NO_3)_2.4H_2O$, Sigma-Aldrich, England), zinc sulphate ($ZnSO_4.7\ H_2O$) copper chloride ($CuCl_2.\ 2H_2O$), EDTA, calcium carbonate, potassium chloride, phenolphthalein and deionised water.

3.4. Standard Solution Preparation Methods

Standard solutions (1000 mg/L) of each metal ion was prepared by dissolving calculated amounts of each metal salt in 100 mL round bottom flask and diluted to the mark with deionised water. Five standard solutions were prepared by serial dilution of each stock solution.

Calibration curves were prepared to determine the concentration of the metals in the sample solution. The instrument was calibrated using five series of working standards. The working standard solutions of each metal was prepared from 100 mg/L intermediate standard solutions of their respective metals. Calibration curve for each metal ion to be analyzed was prepared by plotting the absorbance as a function of metal ion standard concentration.

Table 4. Standard solutions of the metals

Metal	**Salt of the metal used**	**Molecular weight (g/mol)**	**Amount needed for 1000 mg/L in 100 mL (g)**
Lead (Pb)	$Pb(NO_3)_2$	331.2	0.15092
Cadmium (Cd)	$Cd(NO_3)_2.4H_2O$	236.42	0.274
Zinc (Zn)	$ZnSO_4.7\ H_2O$	161.43	0.274
Copper (Cu)	$CuCl_2.2H_2O$	170.48	0.26850
Chromium (Cr)	$K_2Cr_2O_7$	294.185	0.2826

3.5. Sample Collection

3.5.1. Water Sample Collection

Water samples were collected in 250 mL capacity plastic bottles from MidegaWoreda from one ground water and threesurface water with 10-15 cm depth. Then the sample from the site were mixed well to represent the whole water in Midega Woreda. Before sampling, the bottles were washed with detergent followed by tap water and finally several times rinsed with distilled water. The samples were properly tagged and stored in a refrigerator till the complete analyses were carried out.

Table 5. Sample location

Sample	Kebelle	Name of water	Distance from the city (km)	Type of water	Duration	Purpose
1	Roba	Eskim water	2	Ground 300m depth	Through out the year	Washing, cooking Drinking for animal, delay time of food
2	Lencha	Hargaya Pond	4	Surface	5 - 6 month	For all purpose
3	Urju	Limayo Pond	3	Surface	4 - 5 month	For all purpose
4	Berzalla	-	1	Surface	3 - 4 month	For all purpose

3.5.2. Soil Sample Collection

Soil samples were taken from Midega Woreda in plastic bags near to each water sample area from 0-5 cm depth from the surface. Before sampling, the plastics were washed with detergent followed by tap water and finally several times rinsed with distilled water. Then the samples were kept properly until the complete analyses were carried out.

3.6. Sample Digestion

3.6.1. Water Sample Digestion

Wet digestion methods for elemental analysis involve the chemical degradation of sample matrices in solution, usually with a combination of acids to increase solubility. The various acid and flux treatments are carried out at high temperatures in specially designed vessels that help to minimize contamination of the sample with substances in the air, the local environment, and from the vessel walls. The use of closed systems, where the digestion reaction is completely isolated from the surroundings, may help to reduce both contamination and sample loss (Twyman, 2005). The metal percentage found in water were estimated by digestion of the water samples 50 mL with 3 mL concentrated HCl,1 mL concentrated HNO_3 and 2 drop of H_2O_2 at 90°C for one hour until a clear solution was observed.The clear solutions were diluted to 50 mL volumetric flask to make solution of known concentration and blank digestion was carried out in the same way.

3.6.2. Soil Sample Digestion

Sample of soil (5grams each) was weighed (samples that were taken for spiking and non-spiking) in to 250 mL conical flasks.Then, 1mL HNO_3, 3 mL HCl and two drops of H_2O_2 were added into each flask. The samples were dissolved in the acid mixture and digestedovera heating plate (at 100°C) for two hour. Finally, the mixture was filtered through Whatman filter paper and the filtrate was transferred into a 100 mL volumetric flask and diluted to the mark. Then the solution was kept inthe refrigerator until analysis.

3.7. Physico-Chemical Parameter Determinationfor Water and Soil Samples

The pH-meter were calibrated before the determination of pH of any sample by using appropriate buffer solution. Determination of pH of a soil is an important factor during analysis of the soil samples. In this experiment, five gram of soil sample was thoroughly mixed with 50 mL of deionised water and the pH value of the suspension was determined by using a pH-meter.

The conductivity meter was calibrated by using standard solution (0.01M KCl) till the reading becomes 1412 µs/cm, then the conductivity of water samples were determined.Water hardness is the traditional measure of the capacity of water to react with soap,hard water requiring considerably more soap to produce lather. Hard water often produces a noticeable deposit of precipitate (e.g. insoluble metals, soaps or salts) incontainers, including “bathtub ring”. It is not caused by a single substance but by avariety of dissolved polyvalent metallic ions, predominantly calcium and magnesium cations, although other cations (e.g. aluminium, barium, iron, manganese, strontium and zinc) also contribute.

Hardness is most commonly expressed as milligrams ofcalcium carbonate equivalent per litre. Water containing calcium carbonate atconcentrations below 60 mg/L is generally considered as soft; 60–120 mg/L,moderately hard; 120–180 mg/L, hard; and more than 180 mg/L, very hard (Gowan, 2000). Although hardness is caused by cations, it may also be discussed in terms of carbonate (temporary) and non-carbonate (permanent) hardness.

Hardness of the water samplewasdetermined by titration using appropriate titrant (EDTA) and indicator (Erichometric black T) then total hardness of the water sample as $CaCO_3$ was reported in ppm as follows.

$TH_{\text{due to CaCO3}} =$

Where,

TH = Total hardness

V_1 = Volume of titrant in mL

V_2 = Volume of sample in mL

Alkalinity of water sample was determined by titration through appropriate titrant (HCl) and indicator (phenophtaline) then alkalinity of the water sample in ppm was reported by the following formula.

Where,

TA = Total alkalinity

N = Normality of acid

B = Volume of HCl

V = Volume of sample in mL

3.8. Data Analysis

The data obtained from laboratory experiment were analyzed by using Microsoft Office Excel spreadsheet for the analysis of variance (ANOVA) to identify significant difference. The data was expressed in terms of descriptive statistics and the values are presented with mean ± standard deviation values.

4. RESULTS AND DISCUSSION

4.1. Calibration of the Instrument

Calibration of an instrument or a piece of equipment involves making a comparison of ameasured quantity against reference values. Instrumental calibration is particularly important and should be checked periodically during each measurement.

In this study, atomic absorption spectroscopic standard solutions containing 1000 mg/L were used for preparing intermediate standard solutions (100 mg/L) in 100 mL volumetric flasks. Appropriate working standards (2, 4, 6, 8 and 10 ppm) were prepared for each metal ion solution by serial dilution of the intermediate solutions using deionized water. Each set of standard calibration solution was then aspirated one after the other into the atomic absorption spectrometer and its absorbance was recorded. Calibration curves were plotted with five points for the selected heavy metals standards using absorbance against concentrations (mg/L) and the calibration curves obtained are shown in the appendix Figures 1 up to5 for the selected metal. Immediately after calibration using the standard solutions, the sample solutions were aspirated into the AAS instrument and direct readings of the metal concentrations were recorded. The absorbance of blank solutions was recorded in the same way before the sample solution.

Table 6. Equation and correlation coefficent of the culibration curve

Metal	**Equation**	**Coefficient of determination (R^2)**
Lead	$Y = 0.010x - 0.001$	0.998
Cadmium	$Y = 0.119x + 0.055$	0.997
Copper	$Y = 0.142x - 0.051$	0.995
Chromium	$Y = 0.003x + 0.007$	0.996
Zinc	$Y = 0.092x - 0.005$	0.995

4.2. Physico Chemical Parameter Determinations

4.2.1. pH Determination

The pH meter was calibrated by using standard buffer solutions at pH 4.002, 6.86 and 10.22. Then the sample pH was recorded in triplicate measurement and the data were reported a follow.

Table 7. pH of water samples

Sample	Trial 1	Trial 2	Trial 3	Mean ± Sd
W1	6.84	6.67	6.72	6.74 ± 0.071
W2	7.65	7.50	7.60	7.58 ± 0.076
W3	7.77	7.71	7.77	7.75 ± 0.035
W4	7.78	7.75	7.72	7.75 ± 0.023

W1 = ground water
W2 = water from Lenchakebelle
W3 = water from Urjukebelle
W4 = water from Berzalakebelle

The ground water is less acidic because the pH value is bellow seven. But all the surface water is less basic as shown in the above table. The accessibility of metals in soil is directly dependent up on the pH of the soil. In alkaline soils, solubility may increase by formation of soluble organic and hydroxide complexes. Most of the trace metals added to the soil may not beavailable for plant uptake. They are strongly bound in near neutral soils and become moresoluble in acidic soils. Heavy metals are the least mobile in alkaline soils (Murray and Bride, 1994).

Table 8. pH of soil samples

Sample	Trial 1	Trial 2	Trial 3	Mean ± Sd
S1	8.70	8.59	8.65	8.647 ± 0.055
S2	8.56	8.49	8.46	8.503 ± 0.051
S3	8.79	8.79	8.77	8.783 ± 0.012
S4	8.75	8.60	8.69	8.680± 0.075

S1 = soil near to ground water
S2 = soil from Lencha kebelle
S3 = soil from Urju kebelle
S4 = soil from Berzala kebelle

The pH value of all soil at Midega Woreda was found to be less basic because all reading is above seven.

4.2.2. Conductivity of Water Samples

Conductivity is a measure of the ability of water to pass an electrical current. Conductivity in water is affected by the presence of inorganic dissolved solids such as chloride, nitrate, sulfate, and phosphate anions (ions that carry a negative charge) or sodium, magnesium, calcium, iron, and aluminum cations (ions that carry a positive charge).

The conductivity meter was calibrated by 0.01 M KCl standard solution until the calibration standard (1412 µs/cm). 0.01 M KCl solution, was prepared from the salt. Based on the findings of the present study, the ground water was found to be more conductor than the surface water, thise indicate the preenceof many cations in the soil that could be responsible for theoberved conductivity. High conductivity of water sample implies that there are a number of cations and anions in the ground and surface water, and is an indication for the saltiness of the water. The conductivities of the water samples collected from all the sites considered in this study were determined and reported at room temperature.

The values for all four water samples are displayed on Table 9. The values were in range 174.67 to 364.3 µS cm^{-1} for surface water samples and 3273 µS cm^{-1} for ground water samples.

Table 9. Conductivity of water samples

Sample	Trial 1 µs/cm	Trial 2µs/cm	Trial 3µs/cm	Mean ± Sd
W1	3300	3250	3270	3273±25.17
W2	248	241	249	246± 4.36
W3	174.2	174.9	174.9	174.67±0.40
W4	360	376	357	364.3±10.21

W1 = ground water W2 = water from Lencha kebelle

W3 = water from Urju kebelle W4 = water from Berzala kebelle

4.2.3. Alkalinity

Alkalinity is an aggregate property of the water sample which measures the acid-neutralizing capacity of a water sample. It can be interpreted in terms specific substances only when a complete chemical composition of the sample is also performed.

The alkalinity of surface water is due to the carbonate, bicarbonate and hydroxide content and is often interpreted in terms of the concentrations of these constituents. Higher the alkalinity, greater is the capacity of water to neutralize acids. Conversely, the lower the alkalinity, the lesser will be the neutralizing capacity.

Alkalinity of sample can be estimated by titration with standard H_2SO_4 or HCI solution. The titration was done by using 0.01 M HCl as titrant and Phenolphthalein indicator until light red color is observed. 0.01 M HCl titrant solution was prepared from the stock solution (12 M) by dilution.

Table 10. Alkalinity titration data

Sample	Volume of sample(mL)	Initial reading	Final reading	Volume of HCl	Average volume of HCl	Total alkalinity
W1	10	0	4.5	4.5	4.33	216.5
	10	0	4.6	4.6		
	10	14.6	18.5	3.9		
W2	10	0	1.2	1.2	1.4	70
	10	3	4.3	1.2		
	10	4.3	6.1	1.8		
W3	10	6.2	7.4	1.2	0.85	43.5
	10	7.4	8.5	1.1		
	10	8.5	9.6	1.1		
W4	10	0	1.6	1.6	1.7	80
	10	1.6	3.5	1.9		
	10	3.5	5.1	1.6		

W1 = ground water W2 = water from Lencha kebelle

W3 = water from Urju kebelle W4 = water from Berzala kebelle

The ground water is more alkaline than the surface water, implies the concentration of metal ion in the ground water is more. Based on the findings of the present study, the ground water can neutralize more acid than the surface water because of the observed alkalinity. Relatively surface water sample 3 is less alkaline.

4.2.4. Hardness

Water hardness is the traditional measure of the capacity of water to react with soap,hard water requiring considerably more soap to produce a lather. Hard water often produces a noticeable deposit of precipitate (e.g. insoluble metals, soaps or salts) incontainers, including “bathtub ring”. It is not caused by a single substance but by avariety of dissolved polyvalent metallic ions, predominantly calcium and magnesium cations, although other cations (e.g. aluminium, barium, iron, manganese, strontium and zinc) also contribute. Hardness is most commonly expressed as milligrams of calcium carbonate equivalent per litre (WHO,2009).

Table 11. Hardness titration data

Code	**Volume of sample (mL)**	**Initial reading**	**Final reading**	**Volume of EDTA**	**Average volume of EDTA**	**Total hardness as $CaCO_3$ (ppm)**
W1	10	0	19.1	19.1	18.43	18430
	10	19.2	37.5	18.3		
	10	0.2	18.1	17.9		
W2	10	18.1	19.4	1.3	1.23	1230
	10	19.4	20.6	1.2		
	10	20.7	21.9	1.2		
W3	10	9.3	10.4	1.1	1.2	1200
	10	10.4	11.5	1.1		
	10	11.5	12.9	1.4		
W4	10	12.9	14.2	1.3	1.567	1567
	10	14.2	15.9	1.7		
	10	18.1	19.8	1.7		

W1 = ground water W2 = water from Lencha kebelle

W3 = water from Urju kebelle W4 = water from Berzala kebelle

The titration was done by using EDTA as titrant and 2 mL ammonium buffer (prepared from 57 mL ammonium hydroxide and 7 gram ammonium chloride in 100 mL round bottom flask). The titrant EDTA, was standardized by 0.01 M $CaCO_3$ and the titration is carried out by using Phenolphthalein indicator that reveals the equivalence point of titration. EDTA draws the calcium and magnesium ions into a complex, so neither one has free ions in solution.

The principal natural sources of hardness in water are dissolved polyvalent metallicions. Total hardness is largely due to calcium and magnesium ions, a minor contribution to the total hardness of water is also made by other polyvalent ions, such as aluminium, barium, iron, manganese, strontium and zinc.

Total hardness is defined as the sum of calcium and magnesium hardness, in mg/L as $CaCO_3$. High levels of hard-water ions such as Ca^{2+} and Mg^{2+} can cause scaly deposits in plumbing, appliances and boilers. These two ions also combine chemically with soap molecules, resulting in decreased cleansing action. Both calcium and magnesium are essential minerals and beneficial to human health in several respects (WHO, 2009).

Generally the total hardness of ground water was found to be 18430 ppm as calcium carbonate, which is hard but the hardness value of the surface water is not that much. This means using the ground water for drinking purpose can cause different health problem, but the risk of using surface water for drinking purpose is not significant with repect to hardness.

4.3. Levels of Heavy Metals in Water and Soil Samples

Calibration curves for Pb, Cu, Cd, Cr and Zn were obtained by using suitable standard solutions prepared from stock solutions. Absorbance of appropriate Pb, Cu, Cd, Cr and Zn solutions were measured by AAS. The correlation coefficients of the elements were determined using prepared standards versus their corresponding absorbances. The absorbance of the standard solution for each metal is given in the appendix table 3 and their corresponding correlation coefficients of the calibration is given in table 6.

Table 12. Concentration of the investigated metal in water and soil samples

Metal	S1	S2	S3	S4	W1	W2	W3	W4
Lead	0.06 ± 0.001	0.12 ± 0.021	0.14 ± 0.010	0.28 ± 0.020	____	____	____	____
Cadmium	____	____	____	____	____	____	____	____
Zinc	0.597 ± 0.003	0.294 ± 0.001	1.032 ± 0.002	0.206 ± 0.002	2.816 ± 0.002	4.131 ± 0.004	2.108 ± 0.002	0.804 ± 0.003
Copper	0.487 ± 0.0015	0.641 ± 0.0031	0.557 ± 0.0015	0.711 ± 0.0015	0.424 ± 0.0010	0.507 ± 0.0020	0.459 ± 0.0015	0.415 ± 0.0021
Chromium	____	____	____	____	____	____	____	____

S1 = Soil near to ground water S2 = Soil from Lencha kebelle

S3 = Soil from Urju kebelle S4 = Soil from Berzala kebelle

W1 = Ground water W2 = Water from Lencha kebelle

W3 = Water from Urju kebelle W4 = Water from Berzala kebelle

____ = undetected i.e. the concentration of the corresponding metal is bellow the detection limit of the instrument.

4.3.1. Lead

Lead is regarded as highly hazardous for plants, animals and particularly for microorganisms. Long-term exposure to lead can result in a buildup of lead in the body and severe symptoms. These include anemia, pale skin, a decrease handgrip strength, abdominal pain, nausea, vomiting and paralysis of the wrist joint. Prolonged exposure may also result in kidney damage.

If the nervous system is affected, usually due to very high exposure, the resulting effects include severe headache, coma, delirium and death. Continued exposure can lead to decreased fertility and/or increased chance of miscarriage or birth defects (Dobrzanski *et al.,* 2005).

Lead is not detected in ground and surface water samples by the instrument. Even though lead is found in soil samples, its amount was found to be bellow the maximum permissible limit given by WHO. The relative amount of lead is maximum in sample 4 soil collected from Berzala kebelle and minimum in sample 1 soil taken near the ground water.

4.3.2. Zinc

Zinc is an essential element for human, animal, and certain types of plant. The cell of living organisms contains zinc as one of the main component of various enzymes, such as carbonate anhydrase, carboxy-peptidase, superoxide dismutase, lactase, dehydrogenase, phosphatase and glutamatede hydrogenase. It is also necessary for a healthy immune system, cell division and synthesis of protein and collagen which is great for wound healing and healthy skin. However, a higher amount of it can cause anemia, pancreas damage and lower levels of high density of lipoprotein cholesterol (Finkelman, 2005).

Based on the findings of this study, the concentration of zinc was found to be maximum in water sample 2 (from Lencha kebelle) and minimum in water sample 4 collected from Berzala kebelle.

Relatively the concentration of zinc was maximum in watersamples, but the value is not beyond the maximum permissible limit given by WHO. Zinc is detected in both samples. The concentration of zinc is relatively maximum in water samples. Only water sample 4 has less concentration than soil sample 3. The concentration of zinc is maximum in water sample 2 and minimum in soil sample 4. In all case the concentration of the metal ion does not exceed the maximum permissible limit.

4.3.3. Copper

Copper is an essential trace element to plants, animals and even humans, and although the concentration of copper is usually low in nature, it happens in adequate quantities for growth in all aquatic environments. It is required for bone formation, maintenance of myelin within the nervous system, synthesis of hemoglobin, component of key metalloenzymes, plus it forms an important part of cytochrome oxidase and assorted other enzymes involved in the redox reactions in the cells of animals. It is also essential for cellular metabolism, where its concentration is well regulated, but becomes toxic at elevated levels (Pelgorm *et al.,* 1995). Although copper is important, it is toxic when concentrations exceed that of natural concentrations (< 0.05 µmol/L) (Stouthart *et al.,* 1996).

Copper was detected in both samples. Relatively maximum concentration of copper is found in soil sample 4 (0.711 ± 0.0015 mg/L) and the minimum concentration is seen in water sample 4 (0.415 ± 0.0021 mg/L). In all sample the concentration of copper is bellow the maximum limit.

4.4. Method Validation

4.4.1. Precision and Accuracy

Accuracy and precision are probably the most often quoted terms to express the extent of errors in a given analytical result. Analytical results must be evaluated to decide on the best values to report and to establish the probable limits of errors of these values (Kikuchi *et al*., 2002).The analyst will thus be concerned with the question of precision (repeatability of results), that is, the agreement between a set of results for the same quantity and also with accuracy, that is the difference between the measured value and the true value of the quantity (Dean, 1997).The precision of an analytical procedure is usually expressed as the variance, relative standard deviation and percentage relative standard deviation of a series of measurements (Matusiewicz and kopras, 1997). The precision of the results were evaluated by mean and standard deviation of the results of readings for each sample. In this study,the accuracy and validity of the measurements were determined by analyzing spiked samples.

4.4.2. Limit of Detection and Limit of Quantification

Limit of detection (LOD) and limit of quantitation (LOQ) are concepts and terms used to describe the lowest concentration of a measurand that can be reliably measured by a particular measurement procedure.

4.4.2.1.Limit of detection

Method detection limit is the smallest quantity of analyte that can be distinguished from statistical fluctuations in the blank, which usually corresponds to the standard deviation of the blank solution times a constant. The limit of detection is most commonly defined as the amount of analyte that gives a signal equal to three times the standard deviation of a blank (Butcher and Senddon, 1998).

In this study the MDL values for the analysis of the selected heavy metals in soil and water samples were determined by AAS using reagent blank, i.e. 1 mL of 69-72% HNO_3, 3 mL of 70% HCl and two drops of hydrogen peroxide were added into 50 mL of deionized water. Then the method detection limit of each element was determined as three times the standard deviation of the blank solution.

As it can be seen from Table 13, the method detection limit values of the investigated elements by AAS were found to be 0.023 and 0.006 ppm for copper and zinc in water, respectively. Similarly in soil samples, LOD for the detected metals namely lead, copper and zinc were determined to be 0.011, 0.025 and 0.006 ppm, respectively. These results indicate that the method can be used for the determination of metals at trace levels for both soil and water samples.

4.4.2.2. Limit of quantitation

The lowest concentration level at which a measurement is quantitavely meaningful with an acceptable level of repeatability, precision and trueness is called the limit of quantitation (LOQ).

Limit of quantitation of the studied elements were calculated by multiplying SD of the blank by ten (Mitra, 2003). In this study, LOQ was obtained from seven reagent blankreadings,which were digested in the same digestion procedure for soil,ground and surface water samples. The LOQ was calculated by multiplying standard deviation of the reagent blank by 10 and the value for the analysis was given in table 13.

As it can be seen from Table 13, the limit of quantification values of the investigated elements for water sample by AAS were found to be 0.078 and 0.019 ppm for copper and zinc respectively. Similarly LOD for the detected metals (i.e., lead, copper and zinc) were determined to be 0.035, 0.082 and 0.019 ppm, respectively.These results indicate that the method can be used for the determination of metals at trace levels for soil and water samples.

Table 13. Limit of detection and limit of quantification for water sample

Metal ion	IDL	LOD	LOQ
Cu in water	0.02	0.023	0.078
Zn in water	0.005	0.006	0.019
Pb in soil	0.01	0.011	0.035

Cu in soil	0.02	0.025	0.082
Zn in soil	0.005	0.006	0.019

IDL = Instrument detection limit LOD = Limit of detection LOD = Limit of quantification

4.4.3.Recovery

The digestion method and AAS analysis were validated by undertaking recovery experiments for Cu, Zn, Cd, Cr and Pb in the soil,ground and surface water samples. In this study, the recovery tests were done by spiking known concentrations of each metal in the sample. The amount of spiked metals recovered after the digestion of spiked samples was used to calculate percentage recovery using the recovery formula described by Burns *et al.* (2002).

$$\% \text{ Recovery} = \frac{\text{(Amount after spike – Amount before spike)}}{\text{Amount added}} \times 100$$

During the recovery test, from stock solution (1000 mg/L) intermediate standard solution (10 mg/L) was prepared and appropriate concentrations of the heavy metals were spiked in each sample. The results obtained for this recovery test was shown in table 14 and 15 for the water and soil sample, respectively.

Table 14. Recovery of zinc and copper metal in water samples

	Metal	**Before spiking**	**Amount added (ppm)**	**Amount obtained**	**Recovery % Mean ± SD**
W1		2.815		6.743	98.20 ± 2.02
W2		4.130		8.094	99.10 ± 1.05
W3	Zinc	2.109	4	5.955	96.17 ± 0.06

W4		0.804		4.362	88.94 ± 2.04
W1	Copper	0.423	6	6.027	93.40 ± 1.06
W2		0.507		6.533	100.43 ± 2.05
W3		0.458		5.806	89.13 ± 2.03
W4		0.415		5.596	86.35 ± 1.04

W1 = ground water W2 = water from Lencha kebelle
W3 = water from Urju kebelle W4 = water from Berzala kebelle

The recovery percentages of the spiked soil and water samples were obtained as shown in table 14 and 15. The recovery results for the metals under investigation (Cu, Cr, Zn, Pb and Cd) varied in the range 86.35 - 100.59%. The obtained results are in acceptable range which is no less than 70% and no greater than125% (Duan *et al.,*2002) and which revealed that the digestion method and the AAS analysis utilized in the present study were reliable.

Table 15. Recovery of lead, zinc and copper metal in soil samples

Sample of soil	Metal	Before spiking	Amount added (ppm)	Amount obtained	Recovery % Mean ± Sd
S1	Lead	0.060	2	1.970	95.50 ± 2.01
S2		0.120		2.070	97.50 ± 1.04
S3		0.140 0.280		2.045	95.25 ± 2.01

S4				2.088	90.38 ± 1.11
S1	Zinc	0.598	4	4.490	97.30 ± 0.13
S2		0.281		4.217	98.10 ± 1.04
S3		1.033		4.669	90.90 ± 3.03
S4		0.207		4.083	96.90 ± 0.06
S1	Copper	0.486	6	6.522	100.59 ± 1.04
S2		0.641		6.492	97.51 ± 0.03
S3		0.556		6.211	94.24 ± 2.04
S4		0.711		6.421	95.16 ± 1.03

S1 = soil near to ground water

S2 = soil from Lencha kebelle

S3 = soil from Urju kebelle

S4 = soil from Berzala kebelle

5. SUMMARY, CONCLUSION AND RECOMMENDATION

5.1. Summary

In this study the levels of selected heavy metals (Pb, Cr,Zn, Cu and Cd) in samples of soil, ground and surface water in Eastern Hararghe at Midega Woreda were determined by flame atomic absorption spectroscopy.The samples were digested by using HNO_3, HCl and H_2O_2. Some phsico-chemical parameters like pH, conductivity, hardness and alkalinity of the samples were also determined by appropriate instruments. The result obtained from the analysis shows that the concentration of the selected heavy metals found in the tested samples was found to be below the critical levels of each heavy metal which were given by WEPA (World Environmental Protection Agency) and WHO. The concentrations of the detected heavy metalsin soil samples were found to be in the range of 0.06 – 0.28, 0.206 – 1.032 and 0.487 – 0.711 ppm for lead, zinc and copper, respectively. Similarly the concentrations of zinc and copper in water samples were found to be in the range of 0.804 – 4.131 and 0.415 – 0.507 ppm, respectively.

5.2. Conclusion

Only two metals (i.e., Cadmium and Chromium) were bellow the detection limits of the atomic absorption spectroscopy. The concentrations of the other metals (lead, zinc and copper) were not above the maximum permissible value. The results showed that the amount of zincfound insoil, ground and surface water samples was quiet higher than that of lead and copper. Yet all these values are much lower than the tolerance level set by WHO. The selected acid digestion procedure for the sample was found efficient for all of the metals. It was evaluated through the recovery experiment. And good percentage recoveries were obtained for all of the metals investigated.

The result obtained from pH determination showed that the soil sample was found to be more basic than the samples of both ground and surface water. Both total alkalinity and hardness confirmed the ground water to be hard (i.e., not recommended for drinking).

But the surface water can be used for drinking just with respect to hardness by humans. The hardness of surface water found in Midega Woreda is not a serious case but the ground water is so hard.

5.3. Recommendation

In light of the findings and the conclusion drawn above, the following recommendations are forwarded. In future research undertakings:

- Check the presence of the rest heavy metals that cause health problem in humans and investigate seasonal variation.
- Educate the people to have better water treatment technique and water storage practices.
- Conduct further study on other parameters that have significant health concern.

6. REFERENCES

Abollino A. M., Sarzani C, Mentasti E. 2000. The retention of metal species by different solid sorbents: Mechanisms for heavy metal speciation by sequential three column uptake. *Analytica Chimica Acta*, 411: 223-225.

Akcay H, Oguz A, KarapireC. 2003. Study of heavy metal pollution and speciation in Buyak Menderes and Gediz river sediments. *Water Research,* 37:813-822.

APHA. 2005. Standard methods for examination of water and waste water. American Public Health Association 21st edition. Washington DC, USA.

Appel, C. 2002. Concentration, pH, Surface Charge effects on Cadmium and Lead Sorption in Three Tropical soils. *Journal of Environmental Qual*itiy, 31: 581-589.

Atalay, A., Pao, S. James, M. Whitehead, B and Allen, A. 2008. Drinking water assessment at underserved farms in Virginia's coastal plain. *Journal of Environmental Monitoring and Assessment*, 4: 53-64.

ATSDR (Agency for Toxic Substance and Disease Registry). 2004. Toxicological Profile for Copper. U.S. Department of Health and Humans Services, Public Health Service, Centers for Diseases Control, Atlanta.

ATSDR. 2000. Case Studies in environmental medicine Lead Toxicity.U.S. Department of Health and Human Services, Atlanta, GA, Page 31-33.

ATSDR. 2007. Toxicological Profile for Lead U.S. Department of Health and Humans Services, Public Health Humans Services, Centers for Diseases Control, Atlanta.

ATSDR. 2008. Draft Toxicological Profile for Cadmium U.S. Department of Health and Humans Services, Public Health Humans Services, Centers for Diseases Control. Atlanta.

Baez A., R. Belmont, R.M. Garcia, H. Padilla, M.C. Torres. 2007. Chemical composition of rainwater collected at a southwest site of Mexico City, Mexico. *Review Atmospheric Research,* 86: 61-75.

Berman, E. 1980. *Toxic metal and their analysis*. New York: Hayden and Sons Ltd.

Bishnoi, M. and Arora, S. 2007. Potable ground water quality in some villages of Haryana, India: focus on fluoride. *Journal of Environmental Biology*, 28(2): 291-294.

Boukhalfa, C. 2007. Heavy metals in the water and sediments of OuedEs-Souk, Algeria, a river receiving acid effluents from an abandoned mine. *African Journal of Aquatic Science*, 32 (3): 245-249.

Bunzl, K.,Trautmannsheimer, M., Schramel, P., Reifenhauser, W. 2001. Availability of arsenic, copper, lead, thallium, and zinc to various vegetables grown in slag-contaminatedsoils. *Journal of Environmental Quality,* 30: 934-939.

Butcher, D. J. and J. Senddon. 1998. A Practical Guide to Graphite Furnace Atomic Absorption Spectrometry, John Wiley and Sons, New York, Page 34-149.

Castro Gonzalez, M. I. and Mendez Armenta, M. 2008. Heavy metals: Implications associated to fish consumption. *Environmental Toxicology and Pharmacology*, 26: 263-271.

Cezary, K. and Singh, B. R. 2001. Fractionation and mobility of copper, lead, and zinc in soil profiles in the vicinity of a copper smelter. *Journal of Environmental Qual*ity, 30: 485-492.

Chalermsupanimit, S. 2006. Accumulation of heavy metals in water, sediment and aquatic plants in Snakes kin Gourami Fish raising pond at Amphawa Distric. Samut Songkhram Provisio n.MSc. Thesis.Faculty of Graduate Studies, Mahido University.

Chapman, G.H. 1978. Effects of continuous zinc exposure on Sockere Salmon during adult tosmolt Freshwater Residency. *Fish Science*, 107(6): 828-836.

Clemente, R., Dickinson, N. M. and Lepp, N. W. 2008. Mobility of metals and metalloids in a multi element contaminated soil 20 years after cessation of the pollution source activity*E nvironmental Pollut*ion (in press).

Couture, P. and Rajotte, J.W. 2003. Morphometric and metabolic indicators of metal stress in wild yellow perch (Percaflaveseens) from Sudbury, Ontario. *Journal of Environmental Monit*oring, 5: 216–221.

Dallas, H.F. and Day, J. A. 1993. The effect of water quality variables on river ecosystem. A review: Water Research commission Report No. 351: 240.

D'Amore, J., Abedb, S. R., Scheckelb, K. G. and Ryanb, J. A. 2005. Methods for Speciation of Metals in Soils. *Journal of Environmental Qual*ity, 34: 1707-1745.

David, W.O., B. H. Colin and F.O. Thomas. 2008. Heavy metals adsorbents prepared from the modification of cellulose. *Journal of Biosource Technology*, 99: 6709-6724.

De Vries, W., Romkens, P. F. and Schutze, G. 2007. Critical soil concentrations of cadmium, lead, and mercury in view of health effects on humans and animals. *Review on Environmental Contamination Toxicology,* 191: 91-130.

Dean, J. R. 1997. Atomic Absorption and Plasma Spectroscopy. John Wiley and Sons: Chichester, page 84.

Dobrzanski, Z., R. Kalaeu, H. Gorecka, K. Cholnaka, and Barkowalk. 2005. The content of micro elements and Trace Elements in Raw Milk from cows in Silesian Region. *Polish Journal of Environmental Studies*, 14 (5): 685-689.

Duan, T., Kang, J., Chen, H. and Zeng, X. 2002. Determination of ultra trace concentration ofelements in high purity tellurium by inductively coupled plasma spectrometry afteriron(III) hydroxide co precipitation. *Journal of Spectrochemicalacta part B,* 58: 1679-1685.

El-Ghawi, U.M., Al-Fakhri, S.M., Al-Sadeq, A. A., Bejey, M.M. and Doubali, K. K. 2007.The level of selenium and some other trace elements in different Libyan arable soils using instrumental neutron activation analysis. *Biological Trace Element Research*, 119 (1): 89-96.

Ene, A., I.V. Popescu, C. Stihi. 2009. Applications of proton induced Xray emission technique in materials and environmental science. *Journal of Analytical Chem*istry, 20(1): 35 - 37.

Farrukh, A., Iqbal A, Zafar M. 2006. Antioxidant and free radical scavenging properties of twelve traditionally used Indian medicinal plants. *Journal of Biology*, 30: 177-183.

Figueroa, E. 2008. Are more restrictive food cadmium standards justifiable health safety measures or opportunistic barriers to trade? An answer from economics and public health. *Science of the Total Environment*, 389: 1-9.

Filep, G.1998. Behaviour and fate of pollutants in soil.FilepGy. (ed), Soil Pollution. Agricultural University of Debrecens, Page 21-49.

Finkelman, R. B. 2005. Source and health effects of metals and trace elements in our environment : an over view about metal contaminants in New Zealand Resolution press, Christ church. New Zealand, Page 25-46.

Garcia R., Belmont, H. Padilla, M.C. Torres and A. Baez. 2009. Trace metals and inorganic ions measurements in rain from Mexico City and a nearby rural area. *Review Chemistry and Ecology*, 25(2): 71-86.

Ghaedi, M., Fathi, M. R., Marahel, F. and Ahmadi F. 2005. Simultaneous preconcentration and determination of copper, nickel, cobalt and lead ions content by fame atomic absorption spectrometry. *Bulletin of Environmental Contamination and Toxicology*, 14:1158-1165.

Gowan W. 2000. *Water processing: residential, commercial, light-industrial*, 3rd ed. Lisle, IL, Water Quality Association.

Goyer, R. A. and T. M. Clarkson. 2001.Toxic effects of metals. Chapter 23. In: Klaassen, C. D.,C asarett and Doulls toxicology. New York: McGraw-Hill, Page 811-868.

Han, F. X., Kingery, W. L., Selim, H. M. and Derard, P. D. 2000. Accumulation of heavy metals in a long-term poultry waste-amended soil.*Soil Sci*ence, 165: 260-268.

Johnson, D. B., and K. B. Hallberg. 2005. Acid mine drainage remediation options. A review: *Science Total Environment*, 338: 3-14.

Karczewska, A., Szerszen, L. and Kabala, C. 1998. Forms of selected heavy metals and their transformation in soils polluted by the emissions from copper smelters. *Advanced Geo-Ecology,* 31:705-712.

Kikuchi, Y. T. Nomiyama, N. Kumagai, T. Uemura, K. 2002. Cadmium concentration in current Japanese food and beverages.*Journal of Occupational Health*, 44: 240-247.

Kumar, Y.,P.P. King and V.S.R.K. Prasad. 2006. Removal of copper from aqueous solution: A marine green algae. *Journal of Hazardous Materials*, 137: 367-368.

Lee G.J., Kim C, K., Lee M, K., Rhee C. K. 2010. Simultaneous voltammetric determination of Zn , Cd and Pb at bismuth nano powder electrodes with various particle size distributions. Electroanalysis, 22: 530-535.

Lewis, S.D. and Lewis W. M. 1971. The effect of zinc and copper on the osmolality blood serumof the channel catfish (Ictalarius punctatus) Rafinesque, and golden shiner (NotemigonusCrysoleucas) Mitchell. *Transactions of the American Fisheries Society*, 100: 639-643.

Luoma, N.S. and Rainbow, S.P. 2008. Metals Contamination in Aquatic Environments: Science and Lateral Management. Cambridge University Press,UK.

Matusiewicz, H. and M. Kopras. 1997. Methods for improving the sensitivity in Atom Trapping FAAS. *Journal of Analytical Atomic spectrometry*,12: 1287-1291.

McLean, J. E., Bledsoe, B. E. 1992. Behaviour of metals is soils: USEPA Ground Water Issue. Environmental Protection Agency, Washington D.C.

Ming-Ho,Y. 2005. Environmental Toxicology: Biological and Health Effects of Pollutants, Chapter 12, CRC Press LLC, ISBN 1-56670-670-2, 2nd Edition, Boca Raton, USA.

Mitra, S. 2003. Sample preparation Techniques in Analytical Chemistry, John Wiley and Sons, Inc. Hoboken, 227-244.

Moore, P. A., Daniel, T. C., Gilmour, J.T., Shreve B. R., Edwards, D. R. and Wood, B. H. 1998. Decreasing metal runoff from poultry litter with aluminum sulfate. *Journal of Environmental Qual*ity, 27: 92-99.

Murray B. and M. Bride, 1994. Environmental chemistry of soils, 1st edition, Oxford University Press, *Network*, 7:69-80.

Murray, K. S., Cauvet, D., Lybeer, M. and Thomas, J. C. 1999. Particle size and chemical control of heavy metals in bed sediment from the Rouge River, southeast Michigan. *Environmental Science Technology,* 33: 987-992.

Murray, K.S., Rogersb, D.T. and Kaufman, M.M.2004.Heavy metals in an urban watershed in southeastern Michigan. *Journal* o*f Environmental Qual*ity, 33: 163-172..

Novotry, K.,Turzikova A, Komarek J. 2000. Speciation of copper, lead and cadmium in aquatic systems by circulating dialysis combined with flame atomic absorption spectroscopy. *Fresenius Journal of Analytical Chem*istry, 366: 209-212.

Nriagu, J. O. and Pacyna, J. M. 1988. Quantitative assessment of worldwide contamination of air,water and soils by trace metals. *Nature publishing group, 333*: 101-192.

Nussey, G. 1998. Metal ecotoxicology of the upper Oliphant River at selected localities and the effect of copper and zinc on fish blood physiology. Ph.D-thesis. Rand Afrikaans University, SA

Ogoyi O., C. J. M. wita, E. K. Nguu and P. M. Shiundu. 2011. Determination of Heavy Metal Content in Water, Sediment and Microalgae from Lake Victoria, East Africa. *Open Environmental Engineering Journal*, 4:1-3.

Opydo and Jadwiga. 1989. The determination of Zn, Cd, Pb and Cu in soil extracts by anodic stripping Voltammeter. *Water, Air and Soil pollution,* 45:43-48.

Pandey, J. and Pandey,U. 2008. Accumulation of heavy metals in dietary vegetables and cultivated soil horizon in organic farming system in relation to atmospheric deposition in a seasonally dry tropical region of India. *Environmental Monitoring Assessment,* 1: 1-14.

Patil.P. N, Sawant. D.V, Deshmukh. R. N. 2012. Physico-chemical parameters for testing of water. A review:*International Journal of Environmental Sciences*, 3: 3-4.

Poggio. L., B. R. S. Erwin.H. and Ajmone F. 2009. Metals pollution and human bio accessibilityo f topsoil's in Grugliasco. Italy. *Environmental Pollution*, 157: 680- 689.

Rajendran, P., J. Muthukrishnan and P. Gunasekaran. 2003. Microbes in heavy metal remediation. *Indian Journal of Experimental Biol*ogy, 41(9):935-944.

Richard, S. R. 1993. Review: Alzheimer's disease and environmental aluminum. *Age and Ageing*, 22:138-153.

Rodriguez, D., Fernandez, P., Perez Conde, C., Gutierrez, A., Camara, C. 1994. Determination of lead in natural waters using flow injection with on line preconcentration and flame atomic absorption spectroscopy detection. *Fresenius Journal of Analytical Chemistry*, 349: 442–446.

Sammut, M. L., Noack, Y., Rose, J., Hazemann, J. L., Proux, O., Depoux, M. 2010. Speciation of Cd and Pb in dust emitted from sinter plant. *Chemosphere*, 78: 445.

Sanayei, Y., Ismail, N and Talebi, S. M. 2009. Determination of heavy metals in Zayandeh rood, Isfahan-Iran.*World Applied Sciences Journal*, 6(9):1209-1214.

Sharma, D. C. and C. F. Foster. 1995. Column studies in to the adsorption of chromium (VI) using sphagnum moss peat. *Bioresource Technology*, 52: 261.

Singh, S and Mosley, L. M. 2003. Trace metal levels in drinking water on Viti Levu, Fiji Islands. *Journal of Natural Science*, 21:31- 34.

Soriano Disla, J. M., Gomez, I., Guerrero, C., Navarro Pedreno, J., Mataix Beneyto, J., Jordan and M. M. 2008. Edaphic factors related to heavy metals and nutrients behavior following a single sewage sludge application. *Geophysical Research Abs*tract, 10:00769.

Sosmasundaram.B.,King,P.E. and Shackely, S. 1984. The effects of Zinc on postfertilization development in eggs of *Clupeaharengus L. Aquatic Toxicology*, 5: 167-178.

Stobrawa, K. and Lorenc-Plucińska, G. 2008. Thresholds of heavy-metal toxicity in cuttings of European black poplar (Populusnigra L.) determined according to antioxidant status of fine roots and morphometrical disorders. *Science Total Environment,* 390 (1): 86-96.

Stouthart, X. J. H., Haans, J. L. M, Lock, A. C. and Wendelaarbonga, S. E. 1996. Effect of water pH on copper toxicity to early life stages of the common Carb (*CyprinusCarpio).Aquatic Toxicology and Chemistry*, 15(3): 376- 383.

Tahir, N.M., Chee, P.S. and Maisarah, J. 2007. Determination of heavy metals content in soils and indoor dusts from nurseries in dungun, terengganu. *The MalaysianJournal of Analytical Sciences,* 11(1): 280-286.

Tsoumbaris, P. and H. Tsoukali Papadopoulou. 1994. Heavy metals in common foodstuff: quantit ative analysis. *Bulletin of Environmental Contamination and Toxicology,* 53: 267-269.

Tunali,S., A.Cabuk, A., Akar. 2006. Removal of lead and copper ions from aqueous solutions by bacterial strain isolated from soil. *Chemical Engineering Journal*, 115: 203-211.

TWAS. 2002. Safe drinking water-the need, the problem, solutions and an action plan, Third world academy of sciences, Trieste, Italy.

Twyman, R. M. 2005. Sample dissolution for elemental analysis: wet digestion, University of York, UK.

USEPA. 1995. Method 1638: Determination of trace metals in ambient waters by Inductively Coupled Plasma-Mass Spectrometry. EPA, 821-R-95–031. Washington, DC.

Voegelin, A., Barmettler, K. and Kretzschmar, R. 2003. Heavy metal release from contaminated soils: comparision of column leaching and batch extraction results. *Journal of Environmental Quality,* 32(3): 865-875.

Weiner, R. 2008. Application of environmental aquatic chemistry, Taylor and Francis, LLC.
USA.

Welz, B., Sperling, M. 1999. Atomic Absorption Spectrometry, 3rd Ed. Wiley VCH:Weinhem, New York.

WHO. 1996. Trace elements in human nutrition and health, (A Report of a re-evaluation of the role of trace elements in human health and nutrition), Geneva.

WHO. 1984. Guideline for drinking water quality. *Health Criteria and Supporting Information,* 2 : 63-315.

WHO. 2004a. Guidelines for drinking-water quality.Sixty-first meeting, Rome, 10-19 June 2003.

WHO. 2004b. Evaluation of certain food additives contaminants. Sixty-first report of the joint FAO/WHO Expert Committee on Food Additives.WHO Technical Report Series, No. 922.

WHO. 2006. Evaluation of certain food contaminants; Sixty-fourth report of the Joint FAO/WHO Expert Committee on Food Additives. WHO Technical Report Series, No. 930.

WHO. 2009. Calcium and magnesium in drinking-water: public health significance. Geneva, World Health Organization.

Yilmaz S., Yagmur S., Saglikoglu G., and Sadikoglu M. 2009. Direct determination of Zn Heavy Metal in Tap Water of Cana kale by anodic striping voltametry.*International Journal of Electrochemistry*, 4: 288-294.

Zhang, M., He, Z., Calvert, D. V., Stoffella, P. J. and Yang, X. 2003. Surface Runoff Losses of Copper and Zinc in Sandy Soils. *Journal of Environmental Quality* 1, 32(3): 909-915.

7. APPENDIX

7.1. Atomic Absorption Spectroscopy Readings

Table 1. Blank Solution Reading for water sample

Element	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Mean ± SD
Cu	0.005	0.02	0.004	0.001	0.007	0.005	0.02	0.009 ± 0.008
Zn	0.003	0.007	0.004	0.001	0.004	0.003	0.002	0.003 ± 0.002

Table 2. Blank Solution Reading for soil sample

Element	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Mean ± SD
Pb	0.001	0.001	0.008	0.004	0.003	0.01	0.002	0.004± 0.004
Cu	0.002	0.007	0.004	0.001	0.02	0.004	0.02	0.008± 0.008
Zn	0.002	0.004	0.002	0.006	0.001	0.005	0.002	0.003± 0.002

Table 3. Standard Solution Reading for each metal

Element	2 ppm	4 ppm	6 ppm	8 ppm	10 ppm
Pb	0.008	0.021	0.031	0.042	0.052
Cd	0.162	0.308	0.412	0.536	0.643
Cr	0.0116	0.0148	0.0176	0.0216	0.0253
Zn	0.087	0.168	0.282	0.372	0.446
Cu	0.108	0.221	0.37	0.506	0.68

Figure 1. Calibration curve for lead

Figure 2. Calibration curve for cadmium

Figure 3. Calibration curve for zinc

Figure 4. Calibration curve for copper

Figure 5. Calibration curve for chromium

Table 4. Instrumental operating conditions for determination of metals

Element	**Wavelength (nm)**	**Detection limit (mg/L)**	**Slit width (nm)**	**Lamp current (mA)**
Cd	228.8	0.005	0.7	2
Cu	324.7	0.02	0.7	1.5
Zn	213.9	0.005	0.7	2
Pb	217	0.016	1.0	5
Cr	357.9	0.051	0.7	2

Table 5. Acceptable values of metal content in water

Element	Maximum permissible limit in ppm	Source of reference
Cadmium	0.003	WHO
Lead	0.01	WHO
Chromium	0.05	WHO
Zinc	3	WHO
Copper	1	WHO

(Adapted from Engineering Services Division, Ministry of Health Malaysia, 2000)

Table 6. The world average concentration of metals in soil (mg/kg) by Ure and Berrow (1982)

Element	Maximum permissible limit in ppm	Source of reference
Cadmium	0.62	WHO
Lead	29.2	WHO
Chromium	32.4	WHO
Zinc	59.8	WHO
Copper	25.8	WHO

Figure 6. Concentration of lead in soil samples

Figure 7. Concentration of zinc in water and soil samples

Figure 8. Concentration of copper in water and soil samples