JIMMA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

COLLEGE OF NATURAL SCIENCE

DEPARTMENT OF CHEMISTRY

Analysis of Trace Elements in Tomato Fruits from Ziway Lake Irrigated Farms

By: Zerihun Girma

Advisors: Fekadu Melak (PhD)

FeyisaWodajo (MSc)

June, 2019

Jimma, Ethiopia

Analysis of Trace Elements in Tomato Fruits from Ziway Lake Irrigated Farms

By: Zerihun Girma

Advisors:

Fekadu Melak (PhD)

Feyisa Wodajo(MSc)

A thesis Submitted to College of Natural Sciences, Department of Chemistry, Jimma University, in Partial Fulfillment of the Requirements for the Degree of Masters of Science in Chemistry (MSc.).

June, 2019

Jimma Ethiopia

Graduate Thesis Ownership Agreement

ACKNOWLEDGEMENTS

First and foremost, I would like to praise the Almighty God for bestowing up on me health, strength, patience and protection throughout my study period. I express my deepest and heartfelt gratitude to my advisors Dr. Fekadu and Mr. Feyisa Wodajo for their utmost cooperation, suggestions, valuable comments, supervision, appreciable and encouragement. I also like to appreciate their patience in following up this work from the very beginning to the end and for the provision of useful reference materials.

I would like to extend my gratitude to Chemistry Department of Jimma University for providing financial support to carry out this study. I would like to extend my gratitude to Chemistry Department of Arba Minch University for providing the necessary materials during my laboratory work and Mr. Ambaye Alemayehu for his technical assistance and valuable moral encouragement.

I am also indebted to all my family, especially to my aunt Aster Bezabih and Batu secondary school administrative staff and Chemistry Department teacher's for their unreserved encouragement, love, support and patience. Last but not least, my heartfelt gratitude goes to my friends and colleagues. They deserve special thanks for their valuable contributions and encouragements.

Table of Content

Contents **Page**

LIST OF TABLES

LISTS OF FIGURES

APPENDIX TABLE

APPENDIX FIGURE

ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
CRV	Central Rift Valley
DNA	Dioxribonucleic Acid
FAO	Food and Agricultural Organization
IDL	Instrumental Detection Limit
LOD	Limit of Detection
LOQ	Limit of Quantification
RNA	Ribonucleic Acid
WHO	World Health Organization

ABSTRUCT

Tomato is one of the most important edible and nutritional vegetable and can accumulate heavy metals when it is grown at polluted area. In this study, levels of selected heavy metals were determined in tomato, its farmland soil and water of Adami Tulu, Ethiopia. The samples were collected from four different localities of Adami Tulu. Tomato samples were collected from six sampling plots of each farm lands randomly. Composite soil samples were collected by digging up to the depth of 30 cm depth from where the tomato fruits collected. The irrigated water samples were collected in one liter polyethylene bottles after it has been diverted from Lake Ziway water in an open channel before entering into the farm plots of each four sampling site. The tomato, soil and water samples were digested following the protocol of microwave assisted digestion (wet digestion) method. The concentrations of the selected metals in tomato, soil and water samples were determined by flame atomic absorption spectroscopy. The results indicated that the concentration of metals in tomato samples were ranged from 5.56 to 10.37 mg/kg for Cu, 12.72 to 26.94 mg/kg for Zn, 3.16 to 8.64 mg/kg for Co, 0.13 to 0.27 mg/kg for Cd and 0.14 to 0.32 mg/kg for Pb. The concentrations of heavy metals in soil samples were ranged from 21.41 to 86.95 mg/kg for Cu, 52.76 to 66.21 mg/kg for Zn,11.52 to 13.91 mg/kg for Co, 0.38 to 0.67 mg/kg for Cd and 8.35 to10.34 mg/kg for Pb and in the water sample were ranged from 0.036 to 0.044 mg/L for Cu, 0.230 to 0.305 mg/L for Zn, 0.038 to 0.130 mg/L for Co, 0.011 to 0.021 mg/L for Cd and 0.019 mg/L to 0.041 mg/L for Pb. The content of Zn has the highest concentration in the tomato sample collected from all farm lands. The level of Cu, Co, Pb and Cd were higher in all sample sites and were below the permissible limit of WHO/FAO. The content of heavy metals such as Cd and Pb in tomato samples were slightly above the permissible value of WHO/FAO. Based on results obtained from this study we suggests concerned official body (ies) to take the necessary precaution measures for cleaning the source pollution.

Keywords: Tomato, Soil, Irrigated water, Heavy metals

CHAPTER ONE

1. Background of the study

The term heavy metals refer to any metallic element that has a relatively high density and is toxic or poisonous at low concentration [1]. These metals are released to the environment by natural and anthropogenic means, such as 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 [2].

Heavy metals have both positive and negative roles in human life [3]. Living organisms require trace amounts of some heavy metals, including copper (Cu), chromium (Cr), cobalt (Co), manganese (Mn) and zinc (Zn) but excessive levels can be detrimental to the organism [4]. Mercury (Hg), lead (Pb), cadmium (Cd), and arsenic (As) are recognized as health hazardous and all have caused major health problems because of environmental pollution [5]. These elements have no beneficial effects in humans, and there is no known homeostasis mechanism for them. They are generally considered as the most toxic substances to humans and animals [6]. Heavy metals are regarded as environmental pollutants due to their toxicity, persistency and bioaccumulation problem, and their effects on health [7]. Human exposures to heavy metals occur primarily through inhalation of air and ingestion of food and water [8].

Heavy metals are among the major contaminant of food supply and are considered as problem to the environment [9]. Many people could be at risk of adverse health effects from consuming vegetables cultivated in contaminated soil. Many researchers have shown that some vegetables are capable of accumulating high levels of metals from the soil. Studies have revealed that fruits and leafy vegetables are vulnerable to heavy metal contamination from soil, wastewater and air pollution [10].

Ethiopia has a variety of vegetables growing in different agro ecological zones produced through commercial as well as small farmers both as a source of income and food [11]. Tomato is a vegetable that is used worldwide in diets because of its excellent source of many nutrients and secondary metabolites that are important for human health [12]. In Ethiopia, tomato is produced in the state and private horticultural enterprises, commercial farms and small farmers scattered in different parts of Ethiopia [13]. It is produced mainly as a source of food and income both under rain-fed as well as irrigated conditions. Tomato is among the most important vegetable crops in Ethiopia [14]. The first record of commercial tomato cultivation was in 1980 with a production area of 80 ha in the upper Awash by Merti Agro-industry for both domestic and export markets [15].

Tomato production is a widely practiced activity in Batu (Ziway) and other surrounding woredas of East Shoa and West Arsi Zones of Oromia, lying in the belt of the Central Rift Valley (CRV) of Ethiopia. In this area tomato production is undertaken by smallholders and some large-scale commercial farming private investors [16]. It is consumed in every household in different modes [17].Tomatoes transport metal ions from the soil through their roots into the stem, leaf and fruits [18]. Trace amounts of heavy metals accumulate in tomato fruit, and they are known to transfer in trace quantities to consumers. Metals accumulation in vegetables may pose a direct threat to human health [19].

The concentration of heavy metals in the soil affects the amount of their accumulation in plant grown on it. The degree of accumulation of the metals from the soil depends on the type of soil, the pH value, the quality of water used for irrigation, the chemical composition of the metal, utilization of pesticides and fertilizers and the type of tomato species [20].

In general, most heavy metals are not biodegradable, have long biological half-lives and have the potential for accumulation in the different body organs leading to unwanted side effects [21]. Generally, different metals have different health effects. Heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, bone diseases and other vital organs. This fact necessitates for frequent determination of heavy metals in fruits, vegetables and soil to ensure that their levels meet the agreed international standards for the safety of consumers [15, 22].

Small holder farmers in the Batu (Ziway) and Adami Tulu area are highly engaged in vegetable production through the use of irrigation from Lake Denbel **(**Ziway). Especially onion and tomato is among widely grown vegetable types [14]. Lake Denbel (Ziway) is widely used for flower farm, vegetable irrigation, and other crops cultivation which vulnerable to agro-chemical pollution specially fertilizers and pesticides. Since the irrigation is practiced around the lake shore, it is susceptible to environmental pollution (soil, air, water, and food pollution) [23].

Previous study was done on the concentrations of heavy metals in different vegetables in this study area, however, there is no study conducted on the determination of heavy metals in tomato. Determination of levels heavy metals in edible vegetables are essential because their accumulation capacity of plants for heavy metals vary from plant to plant (some are hyper-accumulators and others not). Thus, in this study, the content of selective heavy metals such as Cu, Zn, Co, Cd and Pb in tomato fruit, its farmland soil and water were investigated using flame atomic absorption spectroscopy (FAAS). The correlation between the content of the target metals in tomato, its farmland soil and water were also studied using Pearson correlation.

1.1. Statement of the Problem

The Ethiopian Rift Valley is among the government's target areas for agricultural intensification where there are large, commercial agricultural investments in addition to smallholder farmers. Small holder farmers in the Batu (Ziway) and Adami Tulu are highly engaged in vegetable production using irrigation from Lake Denbel **(**Ziway). Especially onion and tomato are among widely grown vegetable types.

Several studies were reported on heavy metal concentrations in tomato samples in the different parts of the world using different techniques [24]. Some studies were carried out in Ethiopia on the levels of essential and non-essential metals [25]. However, to the best of our knowledge, there is no report in the literature on the levels of heavy metals in tomato fruit of Ziway Lake irrigated farms in Adami Tullu Woreda, Oromia Region, Ethiopia. Hence this study is intended to determine the levels of toxic heavy metals, Cd and Pb and other essential elements such as Zn, Co and Cu in tomato, its farmland soil and water of Adami Tulu Woreda, Oromia region, Ethiopia.

1.2. Objectives of the study

1.2.1. General objective

The main objective of this study was to investigate the contents of heavy metals in tomato fruit, its farmland soil and water of Adami Tulu Woreda, Oromia Regional state, Ethiopia.

1.2.2. Specific objective

- To analyze the level of Zn, Cu, Co, Cd and Pb in tomato fruit.
- To determine level of Zn, Cu, Fe, Cd and Pb in the farmland soil.
- To analyze the level of Zn,Cu,Fe, Cd and Pb in the irrigated water.
- To compare the level of metals in tomato fruits cultivated at different irrigated farmlands.
- To investigate the relationship among the content of the target metals in the tomato fruits, its farmland soils and water.

1.3. Significance of the study

This study was investigating the concentration of selective heavy metals in tomato, its farmland soil and water of Adami Tulu Woreda. Thus the study will be important,

- Providing information about the concentration of the metals in tomato product of the Woreda.
- It can be used as valuable document for further research work.
- It could be important for designing appropriate preventive measures to ensure tomato quality.
- It will be used to create awareness to the people the health risk of toxic metals.

CHAPTER TWO

2. REVIEW LITERATURE

2.1. Tomato (Solanum lycopersicum Mill)

Tomato is one of the most important edible and nutritional vegetable crops in the world. It is the second most widely consumed vegetable after the potato [26]. According to FAO 126 Million tons of tomatoes were produced in the world. Tomatoes are important not only because of the large amount consumed, but also because of their healthy aspects and nutrition. It is an excellent source of many nutrients and secondary metabolites that are important for human health, including mineral matter, vitamins, lycopene, flavonoids, organic acids, phenolics and chlorophyll [11]. Additionally, tomato fruits contain several antioxidants, such as vitamin C, carotenoids, phenolic compounds, flavonoids and phenolic acids [27]. Most importantly, tomato consumption has been shown to reduce the risks of cardiovascular disease and certain types of cancer, such as prostate, lung, and stomach [28]. The first record of commercial tomato cultivation is from 1980 with a production area of 80 ha [13] in the upper Awash by Merti Agro industry for both domestic as well as export markets.

In 2015 cropping calendar, tomato production in Ethiopia was about 22,788 tons from harvested area of 3,677 ha [29]. It is used as canned vegetable. It is popularly used for both commercial and home use purposes. The fresh produce is sliced and used as salad [30]. It is mainly produced under irrigation during off season because under rainy condition, it is susceptible to a disease complex. Successful cultivation of tomato is based essentially upon the choice of suitable varieties for a particular location [31].

Vegetables have become an integral part of human's diet due to their nutritional values thus any form of contamination especially by heavy metals is of great concern [17].Tomato is an important source of heavy metals when it is grown on contaminated soil [32]. The presence of toxic elements in tomato samples depends on the growing conditions and the utilization of pesticides and fertilizers. In addition, the accumulation of metals varies greatly both between species and cultivars [21].

2.2. Heavy Metals

The term Heavy Metals refer to any metallic element that has a relatively high density and is toxic or poisonous at low concentration [1]. It mainly includes the transition metals, some metalloids, lanthanides, and actinides [33]. Heavy Metals are also defined as those elements with a specific density at least five times the specific gravity of water [34].

Heavy Metals include Cd, Cu, Pb, Zn, Hg, As, Ag, Cr, Fe, Co and Pt group elements [35]. Some heavy metals such as Fe, Cu, Zn and Co are essential for plant growth and to maintain normal human body functions at trace amounts. They play important role in biological systems (essential for the metabolic activities of living organisms) [36] but excessive levels can be detrimental to the organism [4]. Heavy metals Cd, Hg and Pb and As have no known essential role in living organisms exhibit extreme toxicity even at very low (trace) concentration and all have caused major health problems as a result of environmental pollution [5]. Heavy metals are present in all types of ecosystems. Their existence is mainly due to anthropogenic sources such as industrial and agricultural activities [37].

Plants are important components of ecosystems as they transfer elements from abiotic into biotic environments. The primary sources of elements from the environment to plants are: air, water and the soil [38]. Heavy metals are among the major contaminants of food supply and may be considered the most important problem of pollution [39].

Heavy metals may be present either as a deposit on the surface of fruits or may be taken up by the crop roots and incorporated into the edible part of plant tissues. Heavy metals deposited on the surface can often be eliminated simply by washing prior to consumption, where as bio accumulated metals are difficult to remove and are of major concern [40]. Irrigation by sewage water effluents is the main reason for the accumulation of heavy metals in vegetables [41]. Long term irrigation with sewage water can induce changes in the quality of soil and trace element inputs are sustained over long periods [42]. Tomato plant takes up metals by absorbing them from contaminated soils, as well as from deposits on different parts of the tomato plant that exposed to the air from polluted environments and can accumulate in its different parts of the body [10].

Heavy metals may enter the human body through inhalation of dust, consumption of contaminated drinking water, direct ingestion of soil, smoking tobacco and consumption of food plants grown in metal contaminated soil [43]. Heavy metals are not biodegradable, have long biological half-lives, toxic in nature and potential for accumulation in the different body organs leading to unwanted side effect. This situation cause varying degrees of illnesses based on acute and chronic exposures potentially toxic metals are also present in commercially produced food stuffs [44].

The excessive content of heavy metals in food was reported to be associated with etiology of a number of diseases, especially with cardiovascular, kidney, nervous, as well as bone diseases. The implication associated with heavy metal contamination is of great concern, particularly in agricultural production system.

2.2.1. Lead

Lead is a naturally occurring heavy metal**.** 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 [45]. Lead has many industrial and commercial uses. It is used in the production of ammunition, as solder, in ceramic glass, and the production of batteries. 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 [46].

Lead is regarded as highly hazardous for plants, animals and particularly for micro-organisms. The main sources of lead pollution in agriculture and plants are lead mines, fuel combustion, sewage sludge applications, industrial wastewater, pesticides and farm yard manure [47]. Lead has no essential function in man.

Lead circulates in the bloodstream and accumulates in tissues and bones, or is eliminated from the body, primarily in urine. The blood brain barrier of children and infants is relatively impermeable lead to lead but they are at high risk of accumulating in the brain and central nervous system which may cause neuron degeneration [37]. Therefore, lead poisoning is a greater concern in children.

It can damage the kidneys, liver, heart and the vascular, immune and neural systems, especially in young children, and causes a number of hemotological and neurological illness [48].

According to Heidary-Monfared (2011), Lead is absorbed by root hairs and stored mainly in cell walls with concentration differing among the different organs of a plant [49]. He reported that translocation of Pb from roots to tops is limited as only 3% of Pb absorbed via the root will accumulate in the shoot. Non-smoking adults are exposed to lead through food and water. High Pb content in vegetables grown in contaminated areas can potentially pose a health risk to consumers.

2.2.2. Cadmium

Cadmium is a non-essential to both plant and human. Although Cadmium is a naturally occurring element, it is rarely found as a pure metal in nature. It is generally associated with oxygen, chlorides, sulfates, and sulfides. Cadmium is naturally present in the environment: in air, soils, sediments and even in unpolluted seawater. Volcanism is the largest natural source of Cadmium [50]. 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. Cadmium is also present as a pollutant in phosphate fertilizers. Natural as well as anthropogenic sources of cadmium, including industrial emissions and the application of fertilizer and sewage sludge to farm land, may lead to contamination of soils, and increase cadmium uptake by crops and vegetables, grown for human consumption [51].

Food is the most important source of cadmium exposure in the general non-smoking population in most countries. Immobilization can increase the Cadmium concentration of the soil and ultimately lead to the increased toxicity of the contaminated soil. Higher soil Cadmium concentrations can result in higher levels of uptake by plants. Cadmium is a toxic and non-essential element that accumulates mainly in blood, the kidneys and liver tissues. International Agency for the Research on Cancer (IARC) has classified Cadmium and Cadmium salts as possible human carcinogens [52].

2.2.3. Zinc

Zinc is an essential element, necessary for the growth, development and the normal functioning of the body. Zinc is required to maintain the proper functions of the immune system, normal brain activity and it is also the key component of many enzymes and vital elements for humans, animals, plants and microorganisms. Zinc is also involved in Dioxribonuclic acid (DNA) and ribonucleic acid (RNA) synthesis. Nevertheless, increased concentrations of zinc in the body can have a detrimental effect on human health. Studies have shown that the increased intake of zinc into the body can lead to a deficiency of copper in the liver, the serum and the heart, and the decrease of the activity of copper metalloenzymes [44].

Zinc is a ubiquitous metal present in the environment, naturally most rocks and many minerals contain zinc which can be used for the zinc industry. Anthropogenic sources are mining, zinc production facilities, iron and steel production, corrosion of galvanized structures, coal and fuel combustion, waste disposal and the use of zinc-containing fertilizers and pesticides [53].

2.2.4. Copper

Copper occurs naturally in ores. It is mined as a primary ore product from copper sulfide and oxide ores. It is released into the environment through mining, agriculture and industrial activities. Copper is used extensively in the manufacture of textiles, antifouling paints, electrical conductors, plumbing fixtures, pipes, coins, cooking utensils, wood preservatives, pesticides and fungicides, and copper sulfate fertilizers [48].

The mobility of copper in soil depends on the soil pH and the content of organic compounds and other minerals with which copper might interact. In general, copper has low mobility in plants relative to other elements [54].

Sensitivity to the toxic effects of excess dietary copper is influenced by its chemical form, species, and interaction with other dietary minerals. High levels can cause symptoms of acute toxicity, including nausea, abdominal discomfort, diarrhoea, haemoglobinuria and/or haematuria, jaundice, oliguria/anuria, hypotension, coma and death. Histopathological effects have been observed in the gastrointestinal tract, liver and kidney. There is limited information on chronic toxicity of Copper. However, copper does not appear to be a cumulative toxic hazard for man, except for individuals suffer from Wilson's disease. Copper is not considered to be mutagenic, carcinogenic or affect reproduction [55].

2.2.5. Cobalt

Cobalt is an essential element, necessary to human because it is part of vitamin B12. It is a key constituent of cobalamin which is known as vitamin B_{12}, the primary biological reservoir of cobalt as an ultratrace element. Bacteria in the guts of ruminant animals convert cobalt salts into vitamin B_{12}, a compound which can only be produced by bacteria or arches. The minimum presence of cobalt in soils therefore markedly improves the health of grazing animals and an uptake of 0.20 mg/kg a day is recommended for them, as they can obtain vitamin B_{12} in no other way [48].

Cobalt released into the atmosphere is deposited on soil, and cobalt released to water may sorbs to particles and settle into sediment or sorbs directly to sediment. Cobalt has been found in a variety of media, including air, surface water, leachate from hazardous waste sites, groundwater, soil, and sediment [48]. Sources of exposure to cobalt and inorganic cobalt compounds are both natural and anthropogenic. Natural sources include wind-blown dust, seawater spray, volcanoes, forest fires, and continental and marine biogenic emissions. Anthropogenic sources include the burning of fossil fuels, sewage sludge, phosphate fertilizers, mining and smelting of cobalt ores, processing of cobalt alloys, and industries that use or process cobalt compounds. Exposure to high levels of cobalt results in lung and heart diseases and dermatitis. Cobalt has been found to have reproductive and developmental effects in animals [56].

2.3. Soil

Soil is an environmental and biochemical reaction system comprising of three important phases: solid (i.e. mineral particles, organic debris, plant roots), solution (i.e. groundwater, rain water, biological excreta, products of biochemical reactions), and gas (i.e. atmospheric, product of biochemical reactions) which move towards equilibrium with one another. Agricultural soil is the most important sink for heavy metals due to soils' high metal retention capacities [35]. Heavy metals soil contamination may occur due to irrigation with contaminated water, the addition of fertilizers, metal-based pesticides, and industrial emissions [57]. These toxic heavy metals transferred and concentrated into plant tissues from the soil due to absorption that commonly occurs in the root system, where it is in direct contact with pollutants. Heavy metals in soluble form have high relation to their uptake by plants. The vegetable from the contaminated soil can accumulate some high concentration of heavy metal and cause some serious risk to human health [58].

2.4. Waste Water

Water contamination by heavy metals in some areas is practically inevitable due to natural process (weathering of rocks) and anthropogenic activities (industrial, agricultural and domestic effluents).The use of waste water can increase the crop productivity, but also increases the contamination of heavy metals in the plants [21].Waste water from the industries of mining, electroplating, paint or chemical laboratories often contains high concentrations of heavy metals, including Cd, Cu and Pb. Heavy metal contamination of agricultural soils from wastewater irrigation is of serious concern since it has implications on human health [40].

CHAPTER THREE

3. MATERIALS AND METHODS

3.1. Description of Study Area and study period

The study was conducted on four irrigation farms (ElkaChalamo, Tulu, Kontola, and Bochessa) that are adjacent to Lake Ziway (Lake Dambal) around Batu (Ziway), Oromia Region, Ethiopia, which is located 160 km from Addis Ababa, the capital city of Ethiopia. The study was conducted from September 2018 to March 2019.

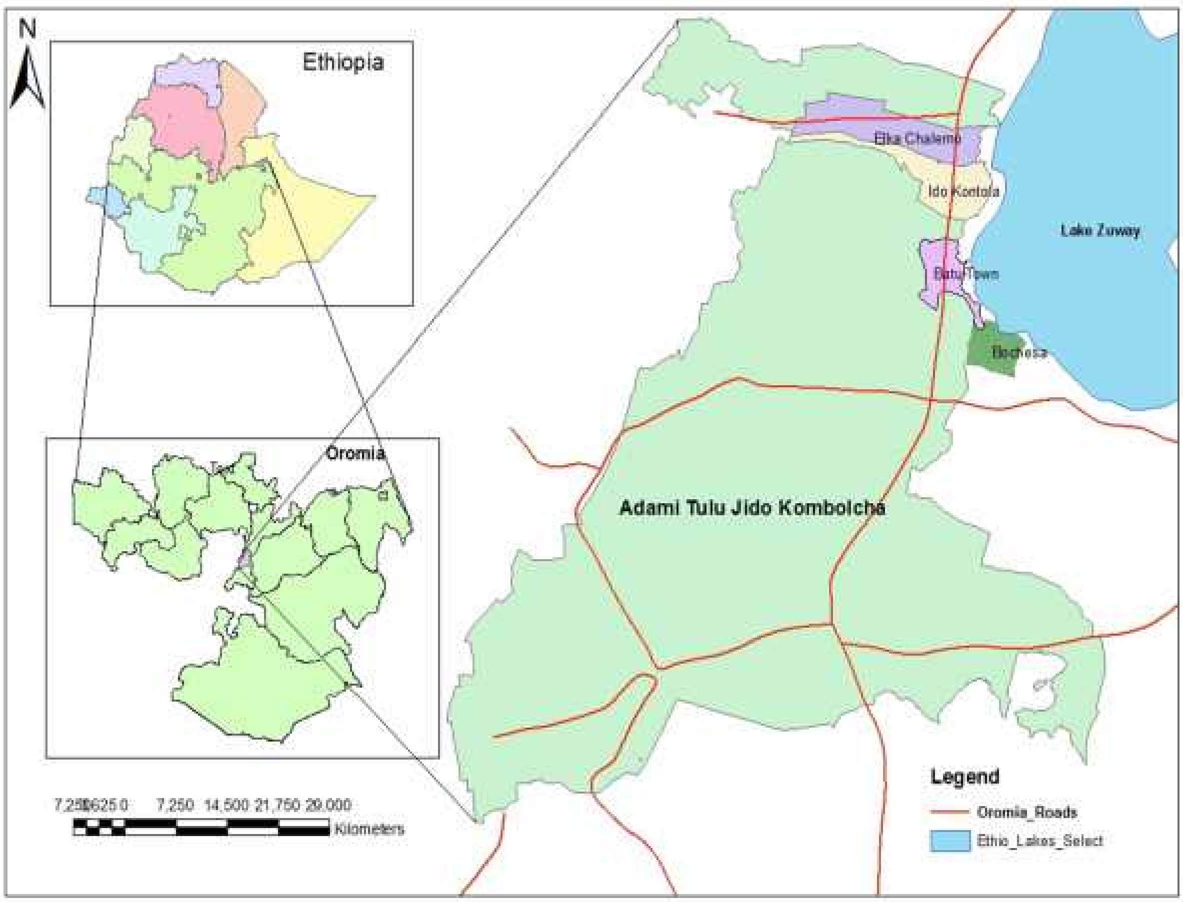

Figure1. Map showing Study Areas

3.2. Reagents

Reagent that were used in this analysis are analytical grade, such as HNO_3 (69%) , HCl (37%) and HF(40%) all from Loba *Chemie* Pvt. Ltd (Mumbai, Maharashtra, India) and H_2O_2 (30%) from RdH Labor chemikalien GmbH & CO.KG (Seelze, Germany), were used for the digestion of tomato, soil and water samples. From stock standards solutions containing (1000 mg/L) of Cu, Zn, Co, Cd and Pb from Blulux Laboratories Pvt Ltd (Faridabod, Haryana, India) for spiking recovery test and calibration curve preparation for each metal. Double distilled water was used for dilution, cleaning and for preparation of all solution throughout the laboratory work.

3.3. Instruments and apparatus

Microwave digester was used for the digestion of tomato, soil and water samples. Flam atomic absorption spectrometry (FAAS), ZEE nit 700p, from Analytik Jena (Germany) with deuterium lamps as background corrector and hollow cathode lamps with air-acetylene flam was used for determination of heavy metals.

3.4. Study Design

Experimental design was employed in the study.

3.5. Sample collection

At each four tomato farmlands fresh tomatoes of uniform size and level of maturity were collected randomly from six sampling points to represent the farm land tomato. The tomato samples were sub-sampled and thoroughly mixed to form a composite sample. Then all samples were packed, labeled and transported to laboratory for analysis.

The soil samples were collected from a depth of 0-30 cm where the tomato fruits collected at six positions of each farmland and the collected sample were combined to get a uniform homogenized sample. The samples were sealed in a clean separate polythene bags and were labeled according to their farmland.

The irrigated water samples were collected in one liter polyethylene bottles (pre-cleaned with 10% nitric acid followed by repeated rinsing with bi-distilled water) diverted from Lake Ziway water in an open channel before entering into the farm plot from each sampling site. Sampling was done for three consecutive days. The samples were preserved in a cool place (about 4˚C). Finally, the samples were taken to Arba Minch University laboratory for preparation and analysis.

3.6. Experimental

3.6.1. Sample pre-treatment

The collected tomato samples were first washed with tap water and were rinsed three times with distilled water to remove surface pollutants and any items adhering to the surfaces. The washed samples were sliced into small pieces and were dried in open air on paper for about 2 hours to eliminate excess moisture. The sample was weighed, dried in an oven at 105 °C for several hours and reweighed until constant weight was obtained. The dried sample was then ground in a mortar and pestle and sieved with 2 mm sieve. The powdered sample was then placed in pre-cleaned screw capped polyethylene container and stored in desiccators containing calcium chloride to keep to constant dry weight till digestion [59].

The soil samples were dried in an open air, mechanically grounded, sieved with a 2 mm sieve and stored properly for preparation.

The water samples were preserved with 5 ml 70% conc. HNO_3 and stored for preparation [61].

3.6.2. Digestion of Tomato, Soil and Water

3.6.2.1. Digestion of Tomato Samples

0.5 g of powdered tomato samples were taken and added in to microwave-closed vessel and a mixture of 6 mL of HNO_3 and 2 mL of H_2O_2 (3:1) were added. The mixtures were then inserted into a microwave digester. The heating program was performed in four successive steps. Digestion conditions for the microwave system were applied as 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W, 8 min for 550 W. The system was stopped heating the sample whenever T reached 180 ^{0}C.

After the digestion procedure and subsequent cooling, the digested samples were diluted to a final volume of 25 mL with deionized water. After that, filtration and analysis of metal concentration was took place [24].

3.6.2.2. Digestion of Soil Samples

0.5 g of powdered soil samples were weight and added into microwave digestion tube. Mixture of 9 mL of HNO3, 3 mL of HF and 2 mL of HCl (3:2:0.7) with addition a 1 mL of H_2O_2 was added in to each digestion teflon tube and then, inserted in to microwave digester.Then the following heating program: In a first step the power of the microwave was increased to 250 W in 2 min and kept constant at that power for 6 min. Then, the power was increased from 250 W to 400 W in 1 min, and held at that value for 4 min. In a third step, the power was increased to 600 W in 1 min and held constant for 4 min. The system was stopped heating the sample whenever T reached 200 ^{0}C or 40 bars inside the extraction vessel. Finally, the suspension was allowed to cool down in a last step of 15 min. After cooling, the solution was diluted to 25 mL with deionized water. Then it was filtered and stored at 4 ^{0}C until analysis [60].

3.6.2.3. Digestion of Water Samples

100 mL filtered water of each sample were taken in a microwave vessel. Then the mixture 4 mL concentrated HNO_3 and 2 mL H_2O_2 was added in to each vessel. After that the samples were inserted in to microwave digester. The samples were digested for 5 min at 650 W. After digestion the samples were allowed to cool and filtered into a 100 ml volumetric flask using Whatman No. 42 filter paper and were made up to the mark with distilled water. The metals will be then analyzed [61].

Triplicate was carried out for each sample. The blank solutions were prepared by digesting the mixture of reagents following the same digestion procedure and diluted to 25 mL with de ionized water.

3.4.3. Procedure of Spiking

To confirm the efficiency of the utilized procedures recovery study was conducted, by spiking experiments in which known volume and concentration of standard solutions, were employed. A mixture of (1 mg/L) of Cu, Co and Zn (0.5 mg/L) of Cd and (2 mg/L) Pb in 10 mL volumetric flask was prepared from the stock solution containing (1000 mg/L) and were added in to in to 0.5 g of powdered tomato and soil samples and water samples in each vessels for spiking.

3.4.4. Method of Data Analysis

Statistical data analysis of the sample were analyzed by one way ANOVA analysis at confidence level of 95% was employed to assess the presence or absence of significant difference among tomato, soil and water samples collected from different farmlands of the study area and the statistic result was reported using(Mean ±SD). Data were analyzed using SPSS statistical software (version 25) and MS Excel.

3.4.5. Precision and Accuracy

In this study, the precision of the results were evaluated by the standard deviation of the results of triplicate samples (n = 3), analyzed under the same condition. Alternatively, the accuracy of the result was evaluated by recovery studies.

To perform a recovery study, known concentration of target metals were added into tomato, soil and water samples. From known (1000 mg/L) stock standard solutions of 10 mg/L (Pb, Cd, Co, Zn and Cu) of intermediate solutions were prepared. From the intermediate solutions based upon the amount that make the concentration of the final solution of 1 mg/L of (Cu, Zn and Co) and 0.5 mg/L of (Cd) and 2 mg/L of (Pb) were added to 0.5 g of tomato, soil and water samples. Then they were digested in microwave digester with the same digestion method and condition for tomato, soil and water samples. After digestion the spiked tomato, soil and water samples were diluted to the required volume with double -distilled water, and analyzed with the same method used for the analysis of the tomato, soil and water samples. Triplicate samples were prepared and triplicate analyses were carried out.

$$(\%R) = \frac{Csp - Cusp}{Cad} \times 100 \qquad \textbf{(1)}$$

Where, Csp, Cusp and Cad are concentrations of the analyte in spiked, unspiked and added respectively

The quantitative determination of the metals using FAAS, calibration curves were construct by using five working standard solution. Intermediate standard solutions of each metal containing 10 mg/L were prepared in 100 mL volumetric flask from the standard stock solutions that contained 1000 mg/L. The intermediate standards were diluted with double-distilled water to obtain five working standards solution of each metal interest for calibration purpose. The instrument was calibrated using five series of working standards.

Concentrations of working standards and value of correlation coefficient (Table 1 of the appendix) obtained from intensity verses concentration calibration curve for each metal and all selected metals have good linearity with a coefficients of (R^2 = 0.994 to 0.999).

3.4.6. Method Detection Limit (LOD)

Method detection limit is the smallest concentration of analyte that can be distinguished from jstatistical fluctuations in the blank, which usually corresponds to the standard deviation of the blank solution times a constant. In this study, the digested blank solutions containing HNO_3 and H_2O_2 and HNO_3, HF, HCl and H_2O_2 then analyzed by FAAS triplicate readings were taken for each blank and the standard deviation of the blank solution was calculated. The method of detection limit of each element was obtained by multiplying the standard deviation of the reagent blank by three and the mean concentration of the blank was added [62].

$$\mathbf{LOD = 3s_b + mean_b} \qquad \mathbf{(2)}$$

Where: $\mathbf{s_b}$ and $mean_\mathbf{b}$ are standard deviation and mean of blank reagent readings

3. 4. 7. Limit of Quantification (LOQ)

The lowest concentration at which a measurement is quantitatively meaningful .The LOQ is most often defined as 10 times the signal/noise ratio plus the mean concentration of blank if the noise is approximated as the standard deviation of the blank. In this study, LOQ was obtained from triplicate analysis of five reagent blanks which were digested in the same digestion procedure for tomato , soil and water samples .The LOQ was calculated by multiplying mean of standard deviation of the reagent blank and the values for the elements [63] was listed in table 1.

$$LOQ = \mathbf{10s_b + mean_b} \qquad (3)$$

CHAPTER FOUR

4. RESULTS AND DISCUSSION

4.1. Validation of the Procedure

The procedure was validated by determining metal concentration of a sample spiked with a known amount of each metal. Accordingly, known amounts and concentration from stock solution of each metal element were spiked on 0.5 g samples. The spiked and non-spiked samples were digested in parallel using the wet digestion method and concentration of each metal was determined in triplicate samples by taking three reading for each. The obtained recoveries were in the range of 84.3 – 104%, 85 – 104% and 84.7 – 105% for tomato, soil and water samples, respectively. The results are given in Table 3. These values are within the accepted range. But recoveries of same metals in sample were higher in all tomato, soil and water samples, but the precision is good. In general, the proposed method demonstrated its good accuracy and precision [64].

Table 3: Recovery (%R) tests) for the Tomato, Soil and Water Samples (n = 3)

	Recovery (%R)														
Metals	**Cu**			**Zn**			**Co**			**Cd**			**Pb**		
Sample Site	**T**	**S**	**W**	**T**	**S**	**W**	**T**	**S**	**W**	**T**	**S**	**W**	**T**	**S**	**W**
Tulu	94.5	87.9	84.7	95.6	102.8	94	93	98.6	94.8	93.5	87.3	90	92	104	99.1
Kontola	89.6	100	95.3	88.5	92.5	89.5	95	86.1	100	98.4	92.4	103	84.3	93.7	85.5
Elkachalmo	91.0	90.7	90.7	87.4	88	92	87	102	85.3	91	89.2	105	93.4	86.6	97.3
Bochesa	93.3	87.4	101	104	85	99	96	96.5	87.5	93.3	97.9	89	101	95	89.5

T= Tomato *S= Soil* *W= Water*

4.2. Concentration of Metals in Tomato Samples

The Table 4 shows the mean concentration metals in tomato samples.

Table 4: Average concentration (mean mg/kg ± SD, n = 3) of metals in tomato samples from the four sites (mg/kg)

Sample site	Cu	Zn	Co	Cd	Pb
Tulu	9.91 ± 0.22	12.75 ± 0.26	5.75 ± 0.002	0.18 ± 0.02	0.25 ± 0.02
Kontola	5.56 ± 0.04	15.92 ± 0.37	4.65 ± 0.001	0.15 ± 0.01	0.18 ± 0.01
Elkachalamo	7.34 ± 0.10	26.94 ± 1.01	8.64 ± 0.13	0.13 ± 0.01	0.14 ± 0.01
Bochesa	10.37±0.14	22.44 ± 0.67	3.16 ± 0.07	0.27 ± 0.02	0.32 ± 0.02

Tomato plant can absorb heavy metals from soil and water and accumulate in the fruit. In this study as shown in Table 4 the highest content of Cu was obtained in tomato from Bochesa (10.37 mg/kg) and the lowest concentration of Cu was found in sample Kontola (5.56 mg/kg) of Adami Tulu Woreda. The concentrations of Cu in Tulu (9.91 mg/kg) and in Bochesa (10.37 mg/kg) were without significant differences. The content of Cu was below the permissible set by WHO/FAO.

The mean of the Zn contents in tomato samples range from (12.75mg/kg) to (26.94 mg/kg) with the maximum value of (26.94 mg/kg) from the sample location Elkachalamo and the minimum value was (12.75mg/kg) from Tulu (Table 4). The concentration of Zn was below permissible limit of WHO/FAO recommended value for daily and provisional tolerable weakly intake of 5 mg/L and 25 mg/L respectively.

The mean concentration of the Co contents in tomato samples range from (3.16 – 8.64 mg/kg).The maximum value of Co was (8.64 mg/kg) obtained from sample site Elkachalamo and the minimum content of Co is found in Bochesa site (3.15 mg/kg) as shown in Table 4. The mean concentration of the Cd contents in tomato samples is very small and range from (0.13-0.27 mg/kg). The maximum value of Cd was (mg/L) obtained from sample site Bochesa and the minimum content of Cd is found in Elkachelemo site (0.13 mg/kg) as shown in Table 4 .The concentration of Cd was slightly above from the permissible limit set by WHO/FAO. The concentration of Pb was high with the range (0.14 - 0.32 mg/kg). The maximum value of Pb was (0.32 mg/kg) obtained from sample site Bochesa and the minimum content of Pb is found in Elkachalamo site (0.14 mg/kg). The concentration of Pb was slightly above from the permissible limit set by WHO/FAO.

In almost all tomato samples, Zn was found in higher concentration than Cu, Zn, Co, Cd and Pb while the lowest concentration of Cd was observed. As shown in Table 4.

In general the concentration of metals in all tomato samples was:

Zn > Cu > Co > Pb> Cd in sample area Elkachalamo and Bochesa but in sample area Bochesa Zn > Cu >Pb > Co > Cd. Result in this study indicates that the tomato vegetables grown near the floriculture industrial area contain the higher level of heavy metals than that of far from it. The statistical analysis (ANOVA) performed on the results obtained showed that metal concentrations in tomato were significantly different at 95% ($P < 0.05$) from each other.

4.3. Concentration of Heavy Metals in Soil Sample

The Table 5 shows that the concentration metals obtained from the soil

Table 5: Average concentration (mean mg/kg ± SD, n = 3) of metals in soil samples from the four sites (mg/kg).

Sample site	Cu	Zn	Co	Cd	Pb
Tulu	23.25 ± 0.311	52.76 ± 0.16	11.52 ± 0.21	0.53 ± 0.02	9.86 ± 0.41
Kontola	21.41 ± 0.52	66.21 ± 0.11	13.91 ± 0.32	0.38 ± 0.01	8.35 ± 0.30
Elkachalamo	70.69 ± 1.45	61.35 ± 1.43	12.95 ± 0.35	0.43 ± 0.01	8.76 ± 0.33
Bochesa	86.95 ± 1.59	59.35 ± 1.07	13.41 ± 0.24	0.67 ± 0.02	10.34 ± 0.11

The mean concentration of Cu contents in soil samples range from (21.41 mg/kg) to (86.95 mg/kg). The maximum value of Cu was (86.95 mg/kg) obtained from sample site Bochesa and the minimum content of Cu is found in Kontola site (21.41 mg/kg). There was much difference on the values among of Cu concentration in each sample site as shown in (Table 5). Recent study by Tamiru *et al*. (2010) reported that the mean concentration of Cu in soils of Ziway area was 56.72 mg/kg, which have lower concentration value from this study.

The mean concentration of Zn in the digested soil sample range from (52.76 mg/kg to 66.21 mg/kg).The sample from Kontola was resulted the highest concentration (66.21 mg/kg) while the sample from Tulu was found to be the least (52.76 mg/kg) among the soil samples (see Table 5). There was no much difference on the values among of Zn concentration in each sample site is close to each other as noted in (Table 5). The study conducted by Amare Hailu (2007) the mean concentration of Zn in this area was 49.9 mg/kg, which lower than the present study result. The Co content of soil were range from (11.52 mg/kg to 13.91 mg/kg).The highest concentration of Co were obtained in Kontola sample area (13.91 mg/kg) while, the lowest concentration of Co was found in Tulu soil sample (11.52 mg/kg) (Table 5). The result showed that there was no much difference one the values of the concentration of Co among the sites.

The mean concentration of Cd contents in soil samples range from (0.38 mg/kg) to (0.67 mg/kg). The maximum value of Cd was (0.67 mg/kg) obtained from sample site Bochesa and the minimum content of Cd is found in Kontola site (0.38 mg/kg). The result showed that the concentration of Cd in soil sample collected from Bochesa site was highly differing from the other sites (Table 5). Mean Cd concentration (0.22 mg/kg) was reported by Tamiru Alemayehu (2006) in this area which is lower than the present study (0.67 mg/kg).

The Pb content of soil were range from (8.35 mg/kg to 10.34 mg/kg).The highest concentration of Pb were obtained in Bochsa sample area (10.34 mg/kg) while, the lowest concentration of Pb was found in Kontola soil sample (8.35 mg/L) (Table 5). The study conducted by Tamiru Alemayehu (2006) reported that the mean concentration of Pb in soils around this area was 5.79 mg/kg, which have lower concentration value from this study.

In soil sample the concentration of metals was: Cu > Zn > Pb > Co > Cd in sample area Bochesa (Cu,Cd and Pb), and Kontola (Zn and Co) and but in sample area Bochesa Cu > Zn > Pb > Co>Cd were the highest concentrations metals. The result showed that mean concentration of metals in soil were significantly different from each other at 5% confidence interval.

4.3. Concentration of Heavy Metals in the Water Sample

The Table 6 shows that the concentration metals obtained from the water samples

Table 6: Average concentration (mean mg/L ± SD, n = 3) of metals in water samples from the four sites (mg/L)

Sample site	Cu	Zn	Co	Cd	Pb
Tulu	0.036 ± 0.001	0.230 ± 0.001	0.055 ± 0.001	0.014 ± 0.001	0.032 ± 0.007
Kontola	0.044 ± 0.001	0.305 ± 0.004	0.044 ± 0.001	0.01 ± 0.00	0.025 ± 0.004
Elkachalamo	0.041 ± 0.000	0.241 ± 0.024	0.038 ± 0.000	0.011 ± 00	0.019 ± 0.002
Bochesa	0.036 ± 0.001	0.266 ± 0.010	0.130 ± 0.000	0.021 ± 001	0.041 ± 0.001

The mean concentration of Cu contents in water samples range from (0.036 mg/L) to (0.044 mg/L). The maximum value of Cu was (0.044 mg/L) obtained from sample site Kontola and the minimum content of Cu is found in Tulu and Bochesa site in similar amount (0.036 mg/L). There was no much difference on the values among of Cu concentration in each water sample site as shown in (Table 6). In similar study, Reta et al. (2012) reported that Cu concentration in water of Ziway Lake 0.014 mg/L. Also, Berhan *et al*. (2018) reported 0.01 mg/L. These results were similar and less than the present study.

The result showed that Zn content in water samples were range from (0.230 mg/L to 0.305 mg/L). The highest concentration of Zn was obtained in Kontola sample area (0.305 mg/L) while, the lowest concentration of Zn was found in Elkachalamo water sample (0.230 mg/L) (Table 6). The mean concentration of Zn in water sample sites Tulu, Elkachalamo and Bochesa was almost similar (Table 6). Reta *et al*. (2012) reported Zn levels (0.084mg/L) in water of Ziway Lake smaller than those obtained in this study ranging between (0.230-0.305) mg/L.

The mean concentration of Co determined in water samples was range from (0.038 mg/L to 0.130 mg/L). The highest concentration of Co was recorded in Tulu sample area (0.130 mg/L) while the lowest concentration of Co was found in Tulu water sample (0.038 mg/L) (Table 6). The study conducted by Reta et al. (2012) had different Co concentration of 0.055 mg/L in water of Lake Ziway.

The Cd content of water was range from (0.010 mg/L to 0.021 mg/L).The maximum concentration of Cd was obtained in Bochesa sample area (0.021 mg/L) while, the minimum concentration of Cd was found in Kontola water sample (0.010 mg/L) (Table 6). There was no much difference on the values among of Cd concentration in Tulu, Kontola and Elkachalamo sample sites or close to each other as noted in (Table 6). Recent study by Kiflom *et al*. (2015) reported that the mean concentration of Cd in water of Lake Ziway was 0.06 mg/L, which have higher concentration value from this study. Also, Reta *et al*. (2012) reported 0.0062 mg/L, which is lower than the present study.

The mean concentration of Pb in the digested water sample range from (0.041 mg/L to 0.032 mg/L).The sample from Bochesa was resulted the highest concentration (0.041 mg/L) while the sample from Elkachelemo was found to be the least (0.019 mg/L) among the water samples (see Table6).The value of the concentrations of Pb in sample site Kontola and Elkachalamo was close to each other. As well as the value of the content of Pb in water obtained Tulu and Bochesa was close to each other. Mean Cd concentration (0.28 mg/L) was reported by Kiflom *et al.* (2015) in water of Lake Ziway which is higher than the present study (0.041 mg/L).

The result showed that the concentration of metals in water samples in decreasing order: Zn> Co > Cu > Pb > Cd in sample site Kontola (Zn and Cu) and Bochesa (Co, Pb and Cd). But in the sample area of Bochesa was Zn > Co > Pb > Cu > Cd. Result in this study indicated that the metal contents of water slightly varied. The results obtained showed that metal concentrations in water were significantly different at 95% ($P < 0.05$) from each other.

4.4. Analysis of Variance (ANOVA)

Analysis of variance (ANOVA) is the widely used statistical method to compare group mean. The one- way ANOVA can compare the mean of more than two groups of sample. ANOVA uses F-statistical test to compare whether the difference between samples means are significant or not [65]. During the process of sample preparation and analysis of tomato, soil and water sample, random error may be introduced in each sample solution and in each replicate measurement. The variation in sample mean of the analyte was tasted using ANOVA. The Analysis one-way ANOVA (Table 3, 4 and 5 of the appendix) showed that there was the statistical significant difference at 95% ($P < 0.05$) confidence level in mean concentration of all metals of tomato, soil and water sample.

4.5. Pearson Correlation of Metals in Tomato and Soil Sample and Tomato and Water sample

To compare the effect of metal concentration on tomato with the concentration of metal in the soil and water sample, Pearson correlation matrices was used to correlate for the sample.

The Tables 13 and 14 below show that the correlation between metals in soil and tomato sample and water and tomato sample.

Table 10: The Pearson correlation coefficient metal in tomato and soil sample

Metals	Cu in soil	Zn in soil	Co in soil	Cd in soil	Pb in soil
Cu in tomato	0.382	0.433	-0.278	0.908**	0.337
Zn in tomato	-0.781**	0.336	-0.022	-0.059	0.030
Co in tomato	-0.620*	0.306	-0.193	0.158	.207
Cd in tomato	0.606*	-0.028	-0.683*	0.980**	0.727**
Pb in tomato	0.842**	-0.057	-0.508	0.901**	0.550

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

The content of Cu in the soil has weak positive correlation with Cu in tomato this verifies that the dependence of Cu concentration in the tomato on the amount of metals under supporting soil of the plant was low. Zn in soil with Zn in tomato also has weak positive correlation. Co in soil with Co in tomato has negligible relationship. The concentration of Cd in tomato has strong positive correlation with Cd this showed that dependence of Cu concentration in the tomato on the amount of metals under supporting soil of the plant was high. Pb in soil with Pb in tomato has moderately positive relation. This shows that the concentration of Pb in tomato is dependent on concentration of Pb metals in the soil (Table 10).

Table 11: The Pearson correlation coefficient metal in tomato and water sample

Metals	Cu in water	Zn in water	Co in water	Cd in water	Pb in water
Cu tomato	-0.943**	0.233	0.330	-0.589*	-0.346
Zn tomato	-0.674*	0.002	-0.067	-0.280	0.045
Co tomato	0.091	-0.595*	0.169	-0.708**	-0.227
Cd tomato	0.615*	-0.0	-0.686*	0.977**	0.729**
Pb tomato	0.979**	-0.535	-0.635*	0.628*	0.646*

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

The concentration of Cu in water has a strong negative correlation with Cu in tomato this shows that there is no relationship between Cu in tomato and Cu in the supporting water. Zn in water with Zn in tomato have negligible relationship, Co in the soil has weak positive correlation with Cu in tomato this verifies that the dependence of Co concentration in the tomato on the amount of metals under supporting soil of the plant was low. The content of Cd in the water has strong positive correlation with Cd in tomato this verifies that the dependence of Cd concentration in the tomato on the amount of metals under supporting soil of the plant was high. The concentration of Pb in the water has strong positive correlation with Pb in tomato this verifies there was a high relationship between Pb in water and the plant (Table 11).

4.6. Comparison of Concentration of Metals of Adami Tullu Woreda Tomato with Literature Value

The table below shows that comparison of metals concentration in Adami Tullu tomato with other Ethiopia tomato sample**.**

Table 12: Comparison of metal concentration (Mean ± SD) In Adami Tullu tomato with other Ethiopian sample location (mg/kg)

Metal	Adami Tullu	Dukem	Bahir Dar	Adet
Cu	10.37±0.14	10.2±0.235	3.430±0.013	0.962±0.038
Zn	26.94±1.01	45.63±1.5	4.136±0.055	3.902±0.012
Cd	0.27±0.02	2.2±0.011	0.536±0.010	0.115±0.028
Pb	0.32± 0.02	4.6±0.021	0.98±0.017	0.244±0.010

The mean concentrations of Cu and Zn in tomato of this study area were higher than those of result from Bahir Dar and Adet [22]. The levels of Cd and Pb in tomato of present study were lower than obtained from Dukem and Bahir Dar [19, 22]. The concentration Zn obtained from Adami Tullu Woreda was lower than the result from Dukem [19]. Generally the highest content of metal concentrations was indicated at Dukem tomato farmlands.

4.7. Comparison of heavy metals concentration in Ethiopia tomato with literature values

Many researchers have reported the concentration of metals in tomato. The report indicated that Cd contents of tomato as Turkey (5.12 ± 0.28), Iran (0.28 ± 0.36) and from Libya (0.250±0.025) mg/kg or ppm [66]. There are also other literatures which reported the contents of some metals such as Cu (7.67 – 14.27), Zn (1.36–3.07), Pb (4.31–5.51) and Cd (0.17- 0.40) µg/g dw in Turkey [67]. The other literature reported the concentrations of metal Cu (0.41-1.44), Zn (2.98-3.75), Co (0.01), Cd (0.01) and Pb (2.96-3.92) mg/kg in Nigeria [68]. The report indicated that toxic heavy metals Pb and Cd contents of tomato as Kuwait (23.3-32.1 and 13.8-31.1), Pakistan (1560 and 330), Brazil (0.02 and 2.50), Egyptian (0.26 and 0.01), Greece (90.0-119 and 1.00-8.00), Bangladesh (14150 and 2390) and Spain (30.3-67.7 14.2-19.9) µg/kg respectively [69]. The comparison of the obtained heavy metal contents with results published in existing literature varies widely among different countries. Levels of heavy metals found in this study were lower than those obtained in several countries with exception of Brazil and Egypt. Bangladesh presents the highest lead (14,150 µg/kg) and cadmium (2,395µg/kg) concentrations in tomatoes, perhaps due to low standards of environmental protection and contaminated soils and water [70].

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

In this study the concentration of toxic metals Cd and Pb and essential metals Cu, Co, and Zn were determined in fruit of tomato its farmland soil and water of four kebeles of Adami Tulu Woreda, Oromia state, Ethiopia. The metal contents of the soil, tomato and water sample of each element are significantly different, indicating the concentrations of heavy metals were varied sample to sample and from site to site. The content of Zn has the highest concentration in the tomato sample collected from all farm lands. The level of Cu, Co, Pb and Cd were higher in all sample sites and were below the permissible limit of WHO/FAO. Although, the concentrations of Cd and Pb in tomato collected from Bochesa and Tulu were high and slightly above the permissible limit set by WHO/FAO.

5.2. Recommendation

Based the findings and the conclusion drawn above, the following recommendations are forwarded.

- ✓ Where the tomato and other vegetable grown must be far from floricultures industry.
- ✓ Monitoring of the levels of heavy metals in tomato should be encouraged.
- ✓ Use of good agricultural practices under supervision for proper fertilizer, herbicides and pesticides application.
- ✓ Health science researchers are advised to launch additional assessment and supplementary information on consumers who obtain or buy tomatoes harvested from this area.
- ✓ Concerned official body (ies) to take the necessary precaution measures for cleaning the source pollution.

6. REFERENCES

1. Duffus, J. “Heavy Metals”A meaningless term? (IUPAC Technical Report) Edinburgh, Scotland, United Kingdom. **2002,** 74(5), 793-807.
2. Ming-Ho, Y. *Environ Toxico: Biological* and Health Effects of Pollutants, Chap 12, CRC Press LLC, 2nd Edition, Boca Raton, USA. **2005**, 7, 112-125.
3. Colak, H.;Soylak, M.; Turkoglu, O. Determination of trace metal content of various herbal and fruit teas produced and marketed from Turkey. Trace Element Electrolytes, **2005**, 22, 192-195.
4. Manohara, B.; Belagali, S.L. Characterization of essential nutrients and heavy metals during municipal solid state composting. *International Journal of Innovative Research in Science*, *Engineering and Technology*, **2014**, *3*(2), 9664-9672.
5. Yebrzaf, Y. Review on heavy metal concentration in vegetables grown in Ethiopia and its economic welfre implication. *Journal of Biology*, *Agriculture and Healthcare*, **2017**, 7, 2224- 3208.
6. Draghici, C.; Coman, G.; Jelescu, C.; Dima, C.;Chirila, E. Heavy metals Determination in environmental and biological samples, In: *Environ* Heavy Metal Pollution and Effects on Child Mental Development- Risk Assessment and Prevention Strategies, NATO Advanced Research Workshop, Sofia, Bulgaria, **2010**, 19, 151- 158.
7. Oti, W.J.O.;Nwabue, F. I. Heavy Metals Effect due to contamination of vegetables from Enyigba Lead Mine in Ebonyi State, Nigeria. Environment and Pollution. **2013**, *2*(1), 19-26
8. Khan, K.; Cao, Q.; Zheng, M.; Huang, Y.; Zhu, Y. Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. Environ Pollution, **2008**, *152*(3), 686-92.
9. Jomova, K.; Valko, M. Advances in metal-induced oxidative stress and Human disease. *Toxicology*, **2010**, *283*, 65–87
10. Zaidi, M. I.; Asrar, A.; Mansoor, A.; Farooqu,M. A. The heavy metal concentration along roadside trees of Quetta and its effects on public health. *Journal of Applied Science*, **2005**, *4*, 708-711.
11. Dawit, A.; Abera, D.; Lemma, D.; Chemdo A. Domestic vegetable seed production and marketing. Research Report EARO, Ethiopia, **2004,** 5, 17.

12. Giovanelli, G.; Paradiso A. Stability of dried and intermediate moisture tomato pulp during storage. *Journal of Agriculture and Food Chemistry*, **2002**, 50, 7277-7281.
13. Ethiopia Agricultural Research Organization (EARO). Directory of released crop varieties and their recommended cultural practices. Ethiopian Agricultural Research Organization, Addis Ababa, Ethiopia, **2004.**
14. Jiregna, T.; Derbew, B.; Kassahin, B. Genetic association analysis among some traits of tomato (*Lycopersiconesculentum Mill*.) Genotypes. *International Journal of Plant Breeding and Genetics*, **2012**, *6*(3), 129-139.
15. Lemma, D. Tomatoes research experiences and production prospects. Research Report N EARO, Ethiopia, **2002**, 5.
16. Feyera, S. Graduation of households from social protection programmes in Ethiopia: Implications of market conditions and value chains on graduation. www.future- agricultures organization, **2013**.
17. Cobb, G.P.; Sands, K.; Waters M.; WixsonB.G.; Dorward-King, E. Accumulation of Heavy Metals by Vegetables Grown in Mine Wastes. Environmental Toxicology and Chemistry, **2000**, *19*(3), 600-607.
18. Feudo, G. L.;Naccarato, A.;Sindona, G.;Tagarelli, A. Investigation the origin of tomatoes and triple concentrated tomato paste through multielement determination by inductively coupled plasma mass spectrometry and statistical analysis. *Journal of Agriculture and Food Chemistry*, **2010,** *58*, 3801-3807.
19. Dagne, B. B.; Endale, T.; Tesfahun, K.; Negash D. Levels of some toxic heavy metals (Cr, Cd and Pb) in selected vegetables and soil around eastern industry zone, central Ethiopia. *African Journal of Agricultural Research*, **2019**, 14(2), 92-101.
20. Memon, A.R.; Aktoprakligul, D.; Demur, A.;Vertii, A.; Butak, T.A. Heavy metal accumulation and detoxification mechanism in plants. *Turkey Journal of Botany*, **2001**, *25*, 111-121.
21. Deribachew, B.; Made, M.; Nigussie, D.; Tadesse, A. M. Selected heavy metals in some vegetables produced through wastewater irrigation and their toxicological implications in eastern Ethiopia. *African Journal of Food Agriculture Nutrition and Development*, **2015**, 15(3), 98-112.

22. Gebregziabher, B.; Tesfaye, S.2, Assessment of levels of Lead, Cadmium, Copper and Zinc contamination in selected edible vegetables. International Journal of Innovation and Applied Studies, **2014**, 7 (1) 78-86.
23. Sobukola, O. P.; Adeniran, O. M.; Odedairo, A. A.; Kajihausa, O. E. Heavy metal levels of some fruits and leafy vegetables from selected markets in Lagos, Nigeria. *African Journal of Food Science*, **2010**, *4*(2), 82-88.
24. Fernanda, C. B.; Geysa B. B.; Isa, S. B.; Leonardo, S.G.T.; Maria, G.A.K. Determination of trace element concentrations in tomato samples at different stages of maturation by ICP OES and ICP-MS following microwave-assisted digestion. *Microchemical Journal*, **2013**, 109, 145-149.
25. Kelly, D. S.; Bateman, A. S. Comparison of mineral concentrations in commercially grown organic and conventional crops — tomatoes (*Lycopersicon esculentum*) and lettuces (*Lactuca sativa*). *Journal of Experimental Food Chemistry*, **2010**, 119, 738-745.
26. Miteva E.; Maneva S.; Hristova,D.; Bojinova, P. Heavy metal accumulation in virus- infected tomatoes. *Journal of Psychopathology*, **2001**, *149*, 179-184.
27. Gebregziabher, B.; Shiferaw, T. Assessment of levels of lead, cadmium, copper and zinc contamination in selected edible vegetables. *International Journal of Innovation and Applied Studies*. **2014**, *7*, 78-86.
28. Flora, S. J. S.; Mittal, M.; Mehta, A. Heavy metal induced oxidative stress and its reversal by chelation therapy. *Indian Journal of Medical Research*, **2008**, 128, 501–523.
29. Jan, A.T.; Ali, A.; Haq, Q. M. R. Glutathione as an antioxidant in inorganic mercury induced nephrotoxicity. *Journal of Postgraduate Med*ical, **2011**, 57, 72–77.
30. Teklu, M. B.; Adriaanse, P.; Assefa, G.; Wolde, A. A. Inventory of agro environmental characteristics and existing environmental standards in Ethiopia, Pesticide Risk Reduction Program-Ethiopia, Accessed from: **2012**, 5, 56-62.
31. Zoran, S. I.; NikolaosKapoulas, L. S.; Dragoljub, B.; Natasa, M.Heavy Metals and Nitrate Content in Tomato Fruit Grown in Organic and Conventional Production Systems. *Poland Journal of Environmental Studies*, **2014**, *23*(6), 2027-2032.

32. Basu, A.; Imrhan, V. Tomatoes versus Lycopene in oxidative stress and carcinogenesis: conclusion from clinical trials. *European Journal of Clinical Nutrition*, **2007,** *61*(3), 295-303.
33. Canene-Adams, k.; Campbell, J. K.; Zaripheh, S.; Jeffery, E. H.; Erdman, J, W. The tomato as a functional food. *Journal of Nutrition.* **2005**, *135*(5), 1226.
34. FAO. FAOSTAT, Available at http://faostat.fao.org, accessed on 20, **2015**.
35. CSA (Central Statistical Agency). Crop Production Forecast Sample Survey, 2013/14.Report on Area and Production for Major Crops (for Private Peasant Holdings 'Meher' season) Addis Ababa, Ethiopia, **2015**.
36. Chaerani, R. Early blight resistance in tomato: Screening and genetic study. PhD Thesis, Wageningen University, Wageningen, Netherlands, **2006,** 188.
37. John, H. D. Heavy metals: a meaningless term (IUPAC Technical Report)" Pure and Applied Chemistry, **2002,** *74*, 793-807.
38. Fiona, M.; Ravi, A.; Rana, P.B. Executive summary of technical report. Heavy metal contamination of vegetables in Delhi. **2003,** 248-256.
39. Harvey, D. Modern Analytical Chemistry, McGraw –Hill Companies, Inc. **2000**, 418.
40. Reta, B. K and Bhagwan, S. C. Concentration levels of major and trace metals in onion (*Allium Cepa L.*) and irrigation water around Meki town and Lake Ziway, Ethiopia. *Bulletin of the Chemical Society of Ethiopia*, **2012**, *26*(1), 27-42.
41. Lokhande R. S.; Singare P. U.; Pimple, D. S. Toxicity study of heavy metals pollutants in waste water effluent samples collected from Taloja industrial estate of Mumbai, India. *Resource of Environment*, **2011**, *1*(1), 13-19.
42. Hamilton, E. I. State of the art of trace element determinations in plant matrices: determination of the chemical elements in plant matrices, an overview. *Science of Total Environment,* **1995,** *176*, 3 – 14.
43. Al Jassir, M. S.; Shaker, A.; Khaliq, M. A. Deposition of heavy metals on green leafy vegetables sold on road sides of Riyadh City, Saudi Arabia. *Bulletin of Environmental Contamination and Toxicology*, **2005**, *75*(5), 1020–1027.
44. Amin, N.; Hussain, A.; Alamzeb, S.; Begum, S. Accumulation of heavy metals in edible parts of vegetables irrigated with waste water and their daily intake to adults and children. *District Mardan, Pakistan. Food Chem*istry, **2013,** 136, 1515–1523.

45. Gupta, N.; Khan, D.K.; Santra, S.C. An assessment of heavy metal contamination in vegetables grown in waste water-irrigated areas of Titagarh, West Bengal, India. Bull Environ. *Contamination and Toxicolology,* **2008**, *80*, 115–118.
46. Etem, O.; Ibrahim I.O.; Zeliha, L.; Goksel, D.;Memduh, S. Determination of heavy metals concentrations in Tomato (*Lycopersiconesculentum miller*) grown in different station types. *Romanian Biotechnological letters*. **2012**, *17*, 6962-6974.
47. Jarup, L. Hazard of heavy metal contamination. *British Journal of Medical Science*, **2003**, *68*, 167-182.
48. Gebregziabher, B.;Shiferaw T. Assessment of levels of lead, cadmium, copper and zinc contamination in selected edible vegetables. *International Journal of Innovation and Applied Studies,* **2014,** *7*, 78-86.
49. Oehlenschlager, J. Identifying heavy metals in fish In: Safety and Quality issues in fish processing, Bremner, H.A(Ed). *Wood head Publishing Limited*. **2002,** 95-113, 978-1- 84569-019-9, Cambridge.
50. Harrison, N. Inorganic contaminants in food, In: Food Chemical Safety Contaminants, Watson, D.H. (Ed.), pp. 148-168, Ltd, first Edition, Woodhead Publishing, 1-85573-462- 1, Cambridge.
51. Dobrzanski, Z.; Kalaeu, R.;Gorecka, H.; Cholnaka, K.; Barkowalk. The content of micro elements and Trace Elements in Raw Milk from cows in Silesian Region. *Polish Journal of Environmental Studies*, **2005**, *14* (5), 685-689.
52. Baysal, A.;Ozcan, M.;Akman S. A rapid method for the determination of Pb, Cu and Sn in dried tomato sauces with solid sampling electrothermal atomic absorption spectrometry. *Food Chemistry Toxicology*, **2013**, *49*, 1399-1403.
53. Heidary-Monfared**,** S. Community Garden Heavy Metal Study. **2011**, 8-18.
54. Queirolo, F.; Stegen, S.; Restovic, M.; Paz, M.;Ostapczuk, P.;Schwuger, M. J.; Munoz, L. Total arsenic, lead, and cadmium levels in vegetables cultivated at the Andean villages of northern Chile. *Science of Total Environment*, **2000**, *255,* 75 – 84.
55. Järup**,** L. Hazards of Heavy Metal Contamination. British Medical Bulletin. **2003**, *68*,167-179.

56. CodexAlimentarius Commission. Joint FAO/WHO Food Standards Programme Codex Committee on Contaminants in Foods Fifth Session: Working Document for Information and Use in Discussions related to Contaminants and Toxins in the GSCTFF The Hague, The Netherlands. **2011**, 11-88.
57. Sobukola, O. P.; Adeniran, O. M.;Odedairo, A. A.; Kajihausa, O. E. Heavy metal levels of some fruits and leafy vegetables from selected markets in Lagos, Nigeria. *African Journal of Food Sci*ence, **2010**, *4*, 389-393.
58. Nida, M.S.; Luma, S. A.; Akl, M. A. Toxic heavy metals accumulation in tomato plant (Solanum lycopersicum). *Journal of Agricultural and Biological Science*, **2016**, 11(10), 399-402.
59. Radwan, M.A.; Salama, A.K. Market basket Surrey for some heavy metals in Egyptian fruits and vegetables. *Food Chemistry and Toxicology*, **2006**, 44, 1273-78.
60. Gabriel, N.; Anislt, M.; Chukumah, C. O.; Mens M.; Obarakpor, K. I.; Edafe, E. A.; Morka, W. E. Determination of heavy metals in tomato (Solanum Lycopersicum) leaves, fruits and soil samples collected from Asaba Metropolis Southern Nigeria. *Canadian Journal of pure and Applied Sciences,* **2014**, 8(1), 2715-2720.
61. Josu, T.; Maite, M.; Hector, M.; Ziortza, G.; Alberto, D.; Juan, M. M. Uptake of metals by tomato plants (Solanum lycopersicum) and distribution inside the plant, *Journal of Food composition and Analysis,* **2017**, 59, 161-169.
62. Luis, G.; Hernandez, C.; Rubio, C.; González-Weller, D.; Gutiérrez, A.; Revert, C.; Hardisson, A. Trace elements and toxic metals in intensively produced tomatoes (lycopersicom esculentum). *Nutration of Hospital*. **2012**, 27(5), 1605-1609.
63. Gebre, A; Singh, B. C. Level of essential and nonessential metals in gesho (Rhamnus Prinoides) cultivated in ethiopia. *Bulletin of Chemical Society of Ethiopia*, **2011**, 26 329-342.
64. Menegesha, T.; Maheswara, V. F. Gezahegn. Determination of essential and non-essential metals concentration in papaya (carica papaya) seeds, leaves and supporting soil of odo-shakiso district in south east Oromia region, Ethiopia. *Science Journal of Analytical Chemistry*. **2014,** *4, 1*, 202-216.
65. ICH. Harmonised Tripratite Guideline "Text on validation of analytical procedures,**1994,** Htt //www.ich.org
66. Gure, A.; Chandravanshi, B. S. T. W. Godeto, Metal in green Coffee beans from major coffee growing region of Ethiopia. *Chemistry International*. **2017,** *3*,359-369.

67. Lugwisha, E. H.; Othman, C.O. Heavy Metal Levels in Soil, Tomatoes and Selected Vegetables from Morogoro Region, Tanzania. *International Journal of Environmental Monitoring and Analysis*, **2016**, 4(3), 82-88.

68. Soad, S.; Abdel G. Concentrations of heavy metals in water, sediment and mollusk gastropod,Lanistes carinatusfrom Lake Manzala, Egypt. *Egyptian Aquatic Journal Research, **2018**, 44, 77-82.*

69. Josu, T.; Maite, M.; Hector, M.; Ziortza, G.; Alberto, D.; Juan, M. M. Uptake of metals by tomato plants (Solanum lycopersicum) and distribution inside the plant, *Journal of Food composition and Analysis*, **2017**, 59, 161-169.

70. Manan, A.; Ying Hui, C.; Xinxin, G.; Xing-Min Z. Microwave assisted digestion followed by ICP-MS for determination of trace metals in atmospheric and lake ecosystem. *Journal of Environmental Sciences*, **2017**, 55, 1-10.

7. APPENDICES

Table 1: Concentrations of working standards solution and correlation coefficients

Metal	Working Standard Solutions (mg/L)	Correlation coefficient(r)
Cu	0.02, 0.05, 0.5, 1, 3	0.999
Zn	0.02, 0.05, 0.5, 1, 3	0.999
Co	0.02, 0.05, 0.5, 1, 3	0.996
Cd	0.02, 0.05, 0.5, 1, 3	0.997
Pb	0.5, 1, 1.5, 2,3	0.994

Table 2: IDL, LOD and LOQ for determination of metals in tomato, soil and water samples (mg/L)

Metals	**Cu**	**Zn**	**Co**	**Cd**	**Pb**
IDL	0.004	0.0059	0.0001	0.0027	0.007
LOD	0.005	0.010	0.0013	0.005	0.009
LOQ	0.015	0.017	0.012	0.008	0.01

Table 3: ANOVA between and within tomato sample at 95% confidence level

Metals	Source of variation	DF	F calculated	P-Value	F-critical
Cu	Between sample	3			
	Within sample	8	214.158	0.000	4.07
	Total	11			
Zn	Between sample	3			
	Within sample	8	1353.742	0.000	4.07
	Total	11			
Co	Between sample	3			
	Within sample	8	3430.242	0.000	4.07
	Total	11			
Cd	Between sample	3			
	Within sample	8	79.803	0.000	4.07
	Total	11			
Pb	Between sample	3			
	Within sample	8	1191.610	0.000	4.07
	Total	11			

Table 4: ANOVA between and within soil sample at 95% confidence level

Metals	Source of variation	DF	F calculated	P-Value	F-critical
Cu	Between sample	3			
	Within sample	8	35450.679	0.000	4.07
	Total	11			
Zn	Between sample	3			
	Within sample	8	347.631	0.000	4.07
	Total	11			
Co	Between sample	3			
	Within sample	8	54.887	0.000	4.07
	Total	11			
Cd	Between sample	3			
	Within sample	8	95368.001	0.000	4.07
	Total	11			
Pb	Between sample	3			
	Within sample	8	83798.047	0.000	4.07
	Total	11			

Table 5: ANOVA between and within water sample at 95% confidence level

Metals	Source of variation	DF	F calculated	P-Value	F-critical
Cu	Between sample	3			
	Within sample	8	55.259	0.000	4.07
	Total	11			
Zn	Between sample	3			
	Within sample	8	6.673	0.01	4.07
	Total	11			
Co	Between sample	3			
	Within sample	8	254.175	0.000	4.07
	Total	11			
Cd	Between sample	3			
	Within sample	8	26440.825	0.000	4.07
	Total	11			
Pb	Between sample	3			
	Within sample	8	1101.319	0.000	4.07
	Total	11			

Calibration curve of the five metals

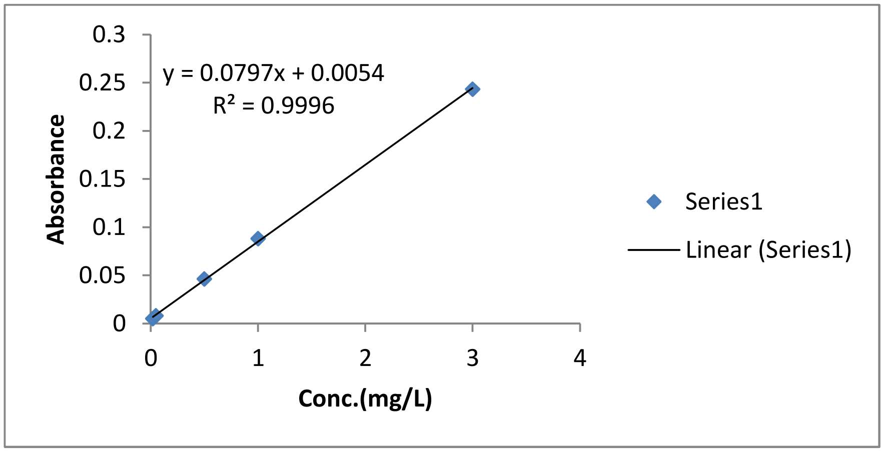

Figure 2: Calibration curve of Cu

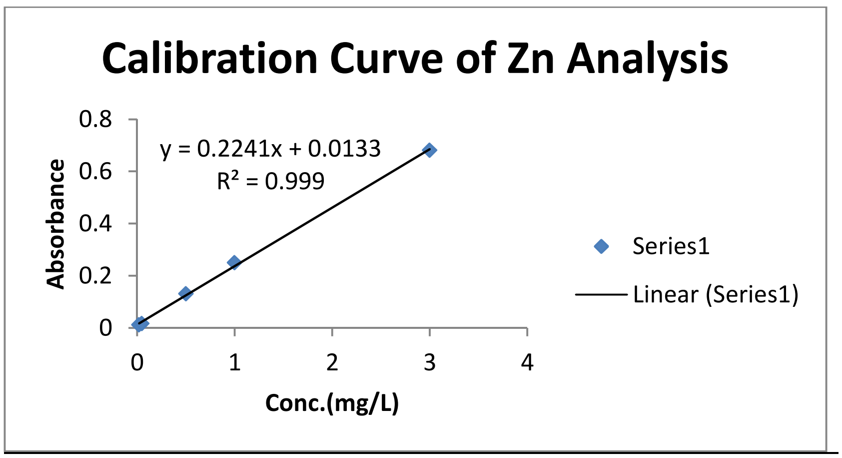

Figure 3: Calibration curve of Zn

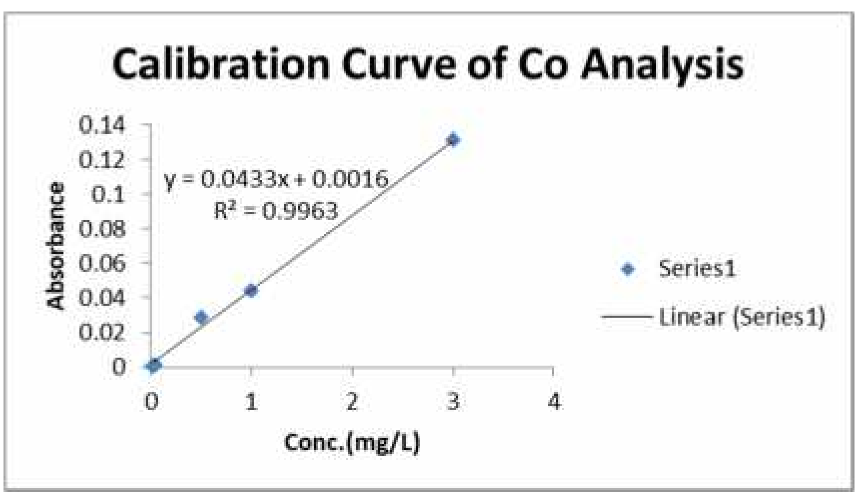

Figure 4: Calibration curve of Co

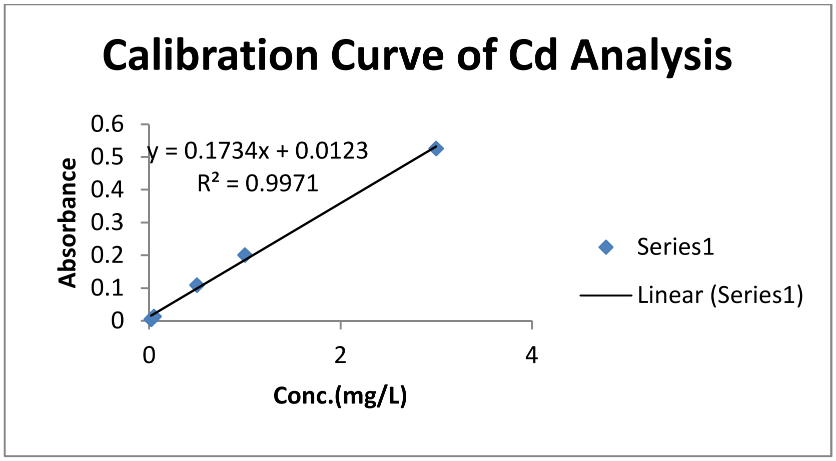

Figure 5: Calibration curve of Cd

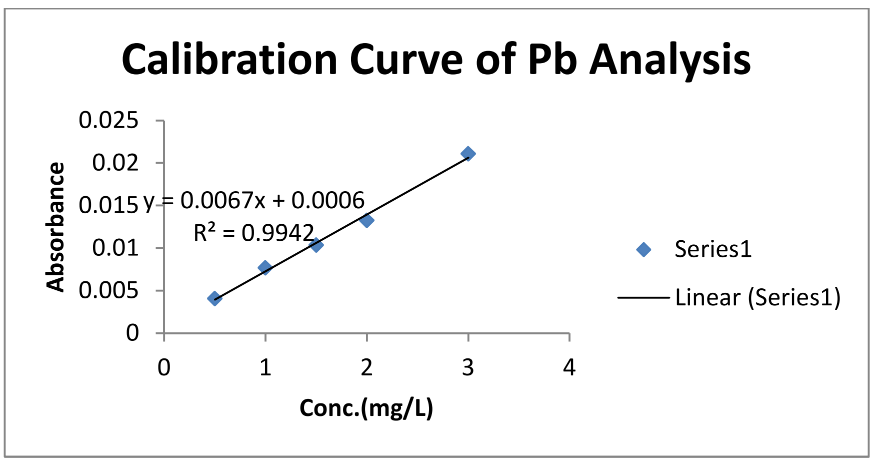

Figure 6: Calibration curve of Pb