



**HAWASSA UNIVERSITY**  
**COLLEGE OF NATURAL AND COMPUTATIONAL SCIENCES**  
**DEPARTEMENT OF CHEMISTRY**

**THE EFFECT OF IRRIGATION AROUND ZIWAY ON HEAVY METAL  
CONTENT OF MAIZE GRAIN AND SOIL**

**MSc THESIS**

**By**

**SILESHI TEFERRA**

**ADVISOR: Dr BEKELE LEMMA**

November, 2024

HAWASSA ETHIOPIA

**A MASTER THESIS SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES OF  
HAWASSA UNIVERSITY, COLLEGE OF NATURAL AND COMPUTATIONAL  
SCIENCES, DEPARTMENT OF CHEMISTRY IN PARTIAL FULFILLMENT OF THE  
REQUIREMENTS FOR THE DEGREE OF MASTERS IN CHEMISTRY**

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## **DECLARATION**

This Thesis entitled “Determination of the level of selected heavy metals in irrigated versus rain fall harvesting maize grain production around Ziway is my original work has not been presented for a degree in any other university and that all sources or materials used for the thesis have been accordingly acknowledged.

Name: Sileshi Teferra

Signature: \_\_\_\_\_

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

Advisor Name: Dr. Bekele Lemma

Signature: \_\_\_\_\_

# SCHOOL OF GRADUATE STUDIES

## HAWASSA UNIVERSITY

### APPROVAL SHEET-1

This is to certify that the thesis entitled “Determination of the level of selected heavy metals in irrigated versus rain fall harvesting maize grain production around Ziway” is submitted in partial fulfillment of the requirements for the degree of Master in of science Chemistry of the graduate program of the Department of Chemistry, Hawassa University, and is a record of original research carried out by Sileshi Teferra ( PG ChemK/013/11 ), under my supervision, and no part of the thesis has been submitted for any other degree or diploma. The assistance and help received during the course of this investigation have been accordingly acknowledged. Therefore, I recommend that it is accepted as fulfilling the thesis requirements.

Dr. Bekele Lemma

\_\_\_\_\_

\_\_\_\_\_

Name of advisor

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**APPROVAL SHEET-2**

We, the undersigned, members of the board of Examiners of the final defense by Sileshi Teferra have read and evaluated this thesis entitled “Determination of the level of selected heavy metals in irrigated versus rain fall harvesting maize grain production around Ziway” examined the candidate. This is therefore to certify that, the thesis has been accepted partial fulfillment of the requirements for the degree of Master of Science in Chemistry.

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SGS	Signature	Date

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## **Abstract**

*The aim of the current study was to determine the metallic concentration of maize of irrigated versus rain fed and soil of irrigated versus rain fed and the water used for irrigation. This is to investigate the influence of irrigation on the concentration of heavy metals in the maize grains and soil. This was done by comparing with rain fed farms. The concentrations of copper (Cu), zinc (Zn), chromium (Cr), nickel (Ni), and lead (Pb) in acid digested sample were determined using flame atomic absorption spectrometry. A composite purposive sampling method was used to collect samples from sample site of zaway city, Ethiopia. Microsoft Excel was used for Descriptive statistical analysis of the results and one way ANOVA was employed to compare the mean difference of heavy metals concentration between irrigated and rain fed. In maize samples (rain fed and irrigated maize) the mean concentrations of Pb, Cr, Ni, Cu and Zn were (0.42 – 1.25) for rain fed and irrigate maize, (not detected (nd) – 0.42) for rain fed and irrigated maize, (0.62 – 0.93) for rain fed and irrigated maize, (10.8 – 12.3) for rain fed and irrigated maize and (20.23 – 24.3) for rain fed and irrigated maize. In soil samples mean concentration of Pb, Cr, Ni, Cu and Zn were in the range of (9.46 – 12.36) for rain fed and irrigated, (4.4 – 5.36) for rain fed and irrigated, (4.3 – 6.4) for rain fed and irrigated, (56.4 – 66.3) for rain fed and irrigated and (74.26 – 86. 35) for rain fed and irrigated. The mean concentrations of metals in water used for irrigation were (mg/L) of Pb (0.24), Cr (0.065), Ni (0.051), Cu (1.23) and Zn (0.92) in the irrigated water samples were above the limit set by US EPA (2004). The study show that irrigated (maize and soil) contained higher concentration of heavy metals and were above the limit set by US EPA which show that it was contaminated and would be unsave for human consumption.*

**Keywords:** Atomic absorption, Heavy metal, Irrigation, Safe limits, Soil, Maize,

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## **Abbreviations**

FAAS	Flame Atomic Absorption Spectroscopic
CRV	Central Rift Valley
FAO	Food and Agricultural Organization
LDT	Limit of Detection
WHO	World Health Organization
EMEP	European Monitoring and Evaluation Program
CNC	Central Nervous System
SD	Standard Deviation

# 1. INTRODUCTION

## 1.1 Background of the study

Cereals are the important crops that serve as staple food for most people in Ethiopia and the main source of food in many countries. Generally speaking, cereals are necessary for a healthy diet and nowadays a daily consumption between 4 and 6 portions of cereals derived products is recommended due to their content in fiber, trace minerals and vitamins, which are supposed to prevent various diseases[1]. Maize among one of the most commonly cereals in Ethiopia .Since all items made from maize and cereals in general are high in carbohydrates, they form the foundation of a diet that is both well-balanced and healthful which explains why this particular food group is so important to us[2].

Maize is extensively grown as a cereal grain that was domesticated in Central America[3]. It is one of the most versatile emerging crops having wider adaptability. Globally, maize is known as queen of cereals because of its highest genetic yield potential [4]. Maize is the only food cereal crop that can be grown in diverse seasons, ecologies and uses [5]. Beside this maize have many types like normal yellow/white grain, sweet corn, baby corn, popcorn, waxy corn, high amylase corn, high oil corn, quality protein maize, *etc.* Apart from this, maize is an important industrial raw material and provides large opportunity for value addition [4].

Maize is one of Ethiopia's most significant cereal crops and about 9 million farmer produce maize and maize production was about 6 million tons annually [6]. Maize is the cheapest source of calorie, providing 16.7 % of per capita calorie intake nationally and thus maize is crucial crop for global food security [6].Maize Cereal is needed for balanced healthy diet. It is an essential energy sources because, it is rich in carbohydrates and protein nutritional compositions. In the last time it was mainly cultivated to use as food for human being and animals. In addition, maize is very well known as a model crop for plant breeding methodology. When present in small amounts, heavy metals are metallic elements with a relatively high density that are hazardous or dangerous [7].Heavy metals are naturally occurring elements, and are present in varying concentrations in all ecosystems. There are a huge number of heavy metals. They are found in elemental form and in a variety of other chemical compounds [7]. Those that are volatile and those that become attached to fine particles can be widely transported on very large

scales. Each form or compound has different properties which also affect what happens to it in food web, and how toxic it is. Human activities have drastically changed the biochemical cycles and balance of some heavy metals [8].

The combustion of fossil fuels and gasoline, waste incinerators, mining, and smelters are the primary human sources of heavy metals [9]. There are several ways in which heavy metals can enter into food chain. They can be absorbed from soils by plant roots or deposited on plant leaf surfaces by airborne particles or aerosols [10]. Furthermore, heavy metals have accumulated in the soil can spread to the different crops when grown as a result of long term - irrigated with waste water resulting in higher levels of contamination with concentration higher than maximum allowable limit [10].

The major heavy metals of concern to mercury ( Hg), cadmium (Cd )and lead (Pb), because they are the most toxic and have known serious effects [9]. High levels of heavy metal exposure in the environment have been connected to kidney damage and several malignancies. For example, some like Cd, Pb and Hg are major contaminants of food supply and may be considered the most important problem to our environment while others like iron (Fe), zinc (Zn) and copper (Cu) are essential for biochemical reactions in the body. The uptake and effects of pollutants in plants, animals, and humans are closely related to their micronutrient intake. The properties of the soil and the capacity of plants to accumulate specific metals selectively have an impact on the content of vital elements in plants [8].

## **1.2 Research gap**

The Ethiopian Rift Valley is among the government's target areas for agricultural intensification where there are large, commercial agricultural investments such as tomatoes, potato, cabbage, maize etc in addition to smallholder farmers. Among other things, small-holder farmers in Batu (Ziway) use irrigation to grow maize. Many flower farms, vegetable irrigation systems, and other agricultural practices that are susceptible to agrochemical pollution, particularly due to the intensive use of pesticides and fertilizers [11]. The irrigated activity rely on lake Denbel and the irrigation is practiced around the lake shore. The lake is susceptible to environmental pollution (soil, air, water, and food pollution), due to the closeness of the irrigation activities of commercial farmers intensive use of fertilizers, herbicides, and insecticides. Several studies have reported on heavy metal concentrations in tomato samples in the different parts of the world

using different techniques. Some studies were also carried out in Ethiopia on the levels of essential and non-essential metals. However, there are limited reports in the literature on the influence of Lake Ziway irrigation on heavy metals in maize grain of farms in Adami Tullu Woreda, Oromo Region, Ethiopia. Hence this study is intended to determine the levels of toxic heavy metals, Ni, Pb, and Cr and other essential elements such as Zn, and Cu in were investigated in maize grain and soil from irrigated farm in vicinity of Lake Ziway.

### **1.3. Objectives of the study**

#### **1.3.1 General objective**

The main objective of this study is to determine the concentration of heavy metals (Pb, Cr, Ni, Cu, and Zn) in maize grown by irrigation using Lake Ziway.

#### **1.3.2 Specific objective**

To investigate the influence of Lake Ziway irrigation on the concentration of heavy metals (Pb, Ni, Cr, Cu, & Zn) in maize grain and comparing it with that of maize grown in rain fed farms

To investigate the influence of Lake Ziway irrigation on the concentration of heavy metals (Pb, Ni, Cr, Cu, & Zn) in soil by comparing with rain fed farms.

To determine the level of heavy metals Pb, Ni, Cr, Cu and Zn in water used for irrigation.

### **1.4. Scope and Limitation of the Study**

The main aim of this study was to determine the levels of some selected heavy metals (Pb, Cr, Ni, Cu and Zn) in Maize, Soil and water around Adami Tulu or Batu district. The level of heavy metals in Maize, Soil and water sample were collected from East Shewa zone Oromia region around Adami Tulu district were analyzed by using Flame Atomic Absorption spectroscopic. The study focused on maize grains sample, water sample and Soil sample. Due to time and financial problems, this study was conducted with lower number of sample than required that consider different type of soil in selected locality

### **1.5. Significance of the study:**

Maize crops are good source of nutritive values (protein, carbohydrate, crude fiber, crude oil, ash content and moisture content) minerals and vitamins for human beings and animals. This study would provide some information on the concentration of selected heavy metals of maize sample, soil sample as well as and water sample. Consuming the cereals contaminated with heavy metals

has different effects on human health; therefore, monitoring contamination of heavy metals would provide the timely information to avoid unnecessary risk. So, the generated analytical data and information on the maize grain and soil samples cultivated around Adami Tulu district could be used as baseline information for future research in related various field in Ethiopia [12].

## 2. REVIEW OF LITERATURES

### 2.1 Maize Production in Ethiopia

Maize (*Zea mays* spp.) is one of the most important cereal crops worldwide, cultivated under several conditions and for numerous purposes, including food, feed, and bio fuels [13]. Maize is the second most widely cultivated crop in Ethiopia and is grown under diverse agro-ecologies and socioeconomic conditions. It is mostly grown during the meher growing season, which depends on rainfall from May to September [14]. Maize has expanded rapidly (in terms of both area and production) and yield has also shown an increasing trend. About 70% of maize production concentrates in Oromia and Amhara regions [14]. With increased productivity, maize has already spread to new regions (such as west and east Gojam) where it was previously not widely recognized. Since the introduction of suitable highland varieties like BH660 (bako hibride), Jibat, and Wonchi, maize has also expanded into previously unexplored agro ecological areas, including the highlands of Ethiopia. Corn had a beneficial effect on the decrease of poverty in many regions of the nation after a notable improvement in productivity due to the wise investment in improved seeds and chemical fertilizers to boost maize production and productivity [15].

Ethiopia comes in fifth place when it comes to the area used for maize cultivation, but it comes in second place, right after South Africa, when it comes to prospective output [16]. Among the most significant crops grown domestically, maize accounts for 30% of total production and 18.5% of the total land used for grain crops. Comparatively, teff occupies 24.3% of the land but produces only 17.2% of the grain. In comparison to 2005, the number of producers, the area allotted, the production and productivity were 44.1% ,55.2%, 184.5% and 82.5%, respectively. The agro commercial clusters (ACC) program has resulted in a 12.8% increase in average country-level maize production [17].

Although there have been a few better varieties of maize published, Ethiopian farmers grew mostly native, low-yielding, tall-growing types prior to 1992, which is why the country's maize productivity was poor in the early 1990s [14]. Adoption of improved maize varieties was noticed from 1993 onwards following the release of improved maize hybrids (BH140 in 1988

and BH660 in 1993). Maize agronomic research was also initiated shortly after the release of the new maize varieties. Several maize agronomic recommendations were developed for different locations. The recommendations include optimum plant density and optimum fertilizer rates, which are key determinants of maize productivity. However, the extent to which farmers are using these agronomic recommendations is not well known, since the maize yield gap is still high in Ethiopia [17].

For example, there is not enough information on the actual amount of fertilizer rate that farmers currently apply to maize, despite the fact that there are various recommendations at different times regarding fertilizer, such as blanket and regional recommendations from the past two decades or more and Ethio SIS(soil international system) map/soil based-test recommendations as of late. Numerous studies have shown that farmers develop superior varieties of maize, but it's unclear which kinds—hybrids or) OPV (open pollinated variety) are being widely grown from the released types currently in use [14].

After rice and wheat, maize is the third-most important food crop in the world in terms of output value and calorie intake [18]. Maize has a diverse form of utilization for human food and feed and as a raw material for industrial processing. In Africa, a greater proportion of maize grains produced are used for human food whereas industrial processing of the bulk of maize grains are carried out in developed countries. With the lowest calorie content of all the major cereals, it is the most affordable food grain that offers high-quality protein and energy. It is also a crucial crop for Ethiopia's food security [19]. Food security is the major development agenda in Ethiopia and maize is one of the major food sources for most of the Ethiopian population. It is also one of the strategic crops considered in the national agricultural sector development plan of the country. The role of maize in meeting the food security requirements of the population and in promoting emerging agro industries will therefore continue to be important in the country. Understanding the status and future outlook of maize is crucial [17].

## **2.2. Heavy Metals**

Heavy metals are stable substances that the body is unable to digest. Their density is at least five times greater than that of water. Additionally, they are not biodegradable and may accumulate in various human organs, potentially causing unfavorable side effects [12]. These days, heavy metals are a major environmental concern. These metals are hazardous to

both people and animals due to their tendency to bio accumulate in the food chain. When a chemical's concentration in a biological organism rises over time relative to its concentration in the environment, this is referred to as bioaccumulation. Heavy metals' long-term environmental persistence exacerbates the damage they represent to human and animal health [20]. Heavy metals Cd, Hg, 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. Heavy metals are present in all types of ecosystems. Their existence is mainly due to anthropogenic sources such as industrial and agricultural activities [21].

Heavy metals can either be deposited on the crop's surface or they can be absorbed by the roots and integrated into the plant tissues' edible portions. If heavy metals are deposited on the surface, they may usually be removed by washing before eating, although bio-metal accumulation is a serious hazard and is challenging to eliminate. The main cause of the buildup of heavy metals in crops is irrigation with sewage water effluent. Extended use of sewage water for irrigation can lead to alterations in soil quality and prolonged sustenance of trace element inputs. Metals are absorbed by maize plants through deposits on various sections of the plant and from polluted soil s [22].

### **2.2.1 Chromium**

Chromium (Cr) is the 21<sup>st</sup> most abundant element, by weight, in the Earth's crust. Any element in groups 3–12 of the periodic table that is in the d-block is referred to as a transition element or transition metal [23]. It is the first element in group 6. It is a steely-grey, lustrous, hard, and brittle transition metal. Cr metal is valued for its high corrosion resistance and hardness. A major development in steel production was the discovery that steel could be made highly resistant to corrosion and discoloration by adding metallic chromium to form stainless steel. Stainless steel and chrome plating (electroplating with chromium) together comprise 85% of the commercial use. Health concerns with chromium are primarily related to hexavalent compounds owing to their toxic effects on humans, animals, and microorganism [24]. Medical warning was issued that inhalation of dust containing Cr in high oxidation states (IV) and (VI) was associated with malignant growth in there aspiratory tract and painless perforation in nasal spectrum among trivalent and hexavalent states, being the most stable and common in terrestrial environments.

Hexavalent Cr is the form considered to be the greatest threat because of its high solubility, its ability to penetrate cell membranes and its strong oxidizing ability. Hence, Cr (VI) is more toxic than Cr (III) because of its high rate of absorption on living surface. Because of its poisonous qualities, it is one of the metallic elements whose maximum concentrations in the environment are regulated by law. Numerous industries, including metal plating, leather tanning, and other metallurgical processes, require chromium compounds [9].

The inadequate disposal of their wastes may give rise to concentrations above the natural values. Food contains Cr at concentrations ranging from 10 to 1300  $\mu\text{g}/\text{kg}$ . Highest concentrations have been found in meat, fish, fruit, and vegetables. Cr levels in soil vary according to area and the degree of contamination from anthropogenic Cr sources [25].

### **2.2.2 Lead**

Lead (Pb) is a heavy metal that is denser than most common materials. It is soft and malleable, and has a relatively low melting point. When freshly cut, Pb is silvery with a hint of blue; it tarnishes to a dull gray color when exposed to air. Pb is the element with the greatest atomic number among all stable elements, and it ends three major chains of heavier element decay [26]. According to the covalent index, Pb belongs to a small class of elements that can only be described as poisonous. This class includes some metals and metalloids. Widespread use has caused extensive environmental contamination and health problems in many parts of the world. Pb is a cumulative toxicant that affects many bodily systems. It is a byproduct of human activity and is present in the earth's crust at low levels. And they have no known level beneficial effect in body. Pb can get into our body when we breathe Pb contaminated air [7]. Pb is one of the most toxic heavy metals found in the environment and has become the most widely distributed toxic heavy metal in the urban environment as a result of its extensive use as antiknock additive in gasoline in the past [27]. Consideration of Pb intake by man must take into account other routes in addition to ingestion in food. Pb concentrations in the air change according to the level of industrial pollution and urbanization. As a result, when breathing in Pb, some of it is subsequently absorbed by the body. Similar to this, Pb amounts in drinking water might vary depending on where you live. Hence, the amount of Pb ingested from food, water, and the air varies, and their relative contribution to the total amount of Pb absorbed in the body relies on the percentage of lead the body retains from each source. People are exposed to a variety of pathways. These exposures could be brought on by breathing in ambient Pb in the air [2].

### 2.2.3 Nickel

Nickel (Ni) is one of the essential elements found in abundance in the earth's crust occurring at an average concentration of about 75µg/g. It is a metallic element in the periodic table's group VIII B [27]. It is a nutritionally essential trace metal for at least several animal species, microorganisms and plants [28]. Ni is an essential trace element in animals, although the functional importance of Ni has not been clearly demonstrated. It is considered essential based on reports of Ni deficiency in several animal species. In humans, essential component of the haemopoietic process, and play important role in physiological processes as a co-factor in the absorption of iron from the intestine. Additionally, Ni has been linked to decreased body weights, noticeably faster heartbeats, and decreased liver weights. Moreover, Ni compounds are carcinogenic when inhaled, primarily from occupational exposures [7]. Accumulation of Ni and Ni compounds in the body through chronic exposure may be responsible for a variety of adverse effects on the health of human beings, such as lung fibrosis, kidney and cardiovascular diseases and cancer of the respiratory tract [29]. The effects of nickel exposure vary from skin irritation to damage to lungs, the nervous system, and mucous membranes. It is also a known carcinogen. Ni deficiency is manifested primarily in the liver; effects include abnormal cellular morphology, oxidative metabolism, and increases and decreases in lipid levels. Decreases in growth and hemoglobin concentration and impaired glucose metabolism have also been observed. The essentiality of Ni in humans has not been established. Ni compounds are known carcinogens in both human and animal models. There are two primary ways that Ni enters the environment: natural processes like the weathering of rocks, minerals and geochemical emissions, and man-made processes like industrial and vehicle emissions. An estimated 330,000 tons of Ni are released into the atmosphere annually worldwide, with roughly 150000 and 180000 tons coming from anthropogenic and natural sources, respectively [7]. Ni particles in the air settle to the ground or are taken out of the air in rain. Much of the Ni in the environment is found in soil and sediments because Ni attaches to particles that contain iron or manganese, which are often present in soil and sediments. This is reflected in its abundance in the earth's crust as oxides, carbonates, silicates with iron, magnesium and as sulphides and arsenides. Ni salts are soluble and can occur as a leachate from Ni bearing rocks [30].

#### **2.2.4. Copper**

Copper (Cu) occurs naturally in ores. It is found mostly as sulphides in igneous rocks. Samples from the Kearsage flows, Greenstone, and Michigan show that it is mostly present as sulphides rather than mixed with silicates.

It is most prevalent in minerals containing ferrous iron. From Cu sulfide and oxide ores, copper is extracted as a principal ore product [31]. Cu is released into the environment through mining, agriculture and industrial activities. A wide range of products, including fabrics, coatings that prevent fouling, electrical conductors, plumbing fittings, pipelines, coins, cooking utensils, wood preservatives, fungicides and insecticides, and Cu sulfate fertilizers, are made with copper [11]. Cu and Cu alloys have been widely used in light industry, machinery manufacturing, building industry, defense industry and other fields in recent years, especially in the electronic industry, because of its popular price, good electrical and thermal conductivity. Actually, with the development of electronic information industry, more and more requirements are put forward for Cu and Cu alloy materials, in especially, high strength and high conductivity. High strength and high conductivity of Cu alloys are contradictory [32]. Sensitivity to the toxic effects of excess dietary Cu is influenced by its chemical form, species, and interaction with other dietary minerals. Many 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. Information regarding Cu chronic toxicity is scarce. However, aside from those who have Wilson's disease, Cu does not seem to pose a cumulative hazardous risk to humans. It is not believed that Cu is carcinogenic, mutagenic, or affects reproduction [33].

#### **2.2.5 Zinc**

Zinc(Zn) is a naturally occurring element found in the earth surface rocks. Because of its reactivity, metal is not found as the free element in nature. There are approximately 55 mineralized forms of Zn. The most important Zn minerals in the world are sphalerite (ZnS), smithsonite (ZnCO<sub>3</sub>), and hemimorphite Zn<sub>4</sub>(Si<sub>2</sub>O<sub>7</sub>)(OH).H<sub>2</sub>O. The periodic table features two common oxidation states for Zn: Zn(0) and Zn (+2). Zn is found in Group IIB. Zn can be found in many various forms, including zinc oxide, zinc sulfate, and Zn chloride. Small quantities of Zn can be found in practically all igneous rocks. The main ores of Zn are sulfides, like wurtzite

and sphalerite. An estimated 1–300 mg/kg of Zn is naturally present in soils [34]. Zn is an essential element for people, animals, plants, and microorganisms. It is also necessary for the immune system to operate properly and for appropriate brain activity. Nevertheless, increased concentrations of Zn in the body can have a detrimental effect on human health. Study has indicated that an elevated consumption of Zn within the body may result in a deficit of Cu in the liver, serum, and heart, as well as a reduction in Cu metallo enzyme activity. Zn is ubiquitous metal present in the environment, naturally most rocks and many minerals contain Zn which can be used for the zinc industry. Anthropogenic sources are mining, Zn production facilities, Fe and steel production, corrosion of galvanized structures, coal and fuel combustion, waste disposal and the use of Zn containing fertilizers and pesticides [35]

## **2.3 Source of Heavy metals**

### **2.3.1. Fertilizers**

Historically, the first significant human impact on the land was from agriculture. Plants require both micronutrients (Co, Cu, Fe, Mn, Mo, Ni and Zn) and macronutrients (N, P, K, S, Ca, and Mg) to grow and complete their life cycle. Certain soils lack these micronutrients that are necessary plant growth; they can be added to the soil or sprayed on crops [2]. Large quantities of fertilizers are regularly added to soils in intensive farming systems to provide adequate N, P, and K for crop growth. The compounds (DAP, Urea, UAN and ammonia) used to supply these elements contain trace amounts of heavy metals (e.g., Cd and Pb) as impurities, which, after continued fertilizer, application may significantly increase their content in the soil. Metals, such as Cd and Pb, have no known physiological activity. Application of certain phosphatic fertilizers inadvertently adds Cd and other potentially toxic elements to the soil, including F, Hg, and Pb [36].

### **2.2.2 Horticulture Industry**

Horticulture industry is major potential source of pollutions. Industries in the area, depending on their process, might release metal containing waste water or air emissions. Factories processing using-containing chemicals are specially suspected. Intensive horticultural practices over the twentieth century, coupled with growing greenhouse production, have dramatically increase pollution on the horticultural landscape. Land and soil degradation caused by erosion (wind and water), organic matter decline, compaction, salinization, reduced fertility and pollution all have

the potential of environmental mismanagement within horticulture. This in turn leads to degradation and as a result impede on the biosecurity of future production [37].

### **2.3.3 Pesticides**

Humans use pesticides to kill or discourage species (pests) that pose a threat to our health and well-being, the health and well-being of our pets and animals, or that harm crops [38]. Several common pesticides used fairly extensively in agriculture and horticulture in the past contained substantial concentrations of metals. Some pesticides which contain heavy metals are Methamidophos and Imidacloprid. For instance in the recent past, about 10% of the chemicals have approved for use as insecticides and fungicides in UK were based on compounds which contain Cu, Hg, Mn, Pb, or Zn. Examples of such pesticides are copper-containing fungicidal sprays such as Bordeaux mixture (copper sulphate) and copper oxychloride [2]. Lead arsenate was used in fruit orchards for many years to control some parasitic insects. Arsenic-containing compounds were also used extensively to control cattle ticks and to control pests in banana in New Zealand and Australia, timbers have been preserved with formulations of Cu, Cr and Mn. There are now many derelict sites where soil concentrations of these elements greatly exceed background concentration [39].

### **2.3.4. Polluted water**

Polluted Water is one of the major today's environmental problems. Among the natural resource water is the most vulnerable in terms of pollution. Water can be polluted by following factor: industrialization (Horticulture industry), pesticides and fertilizers, sewage and others. Polluted water and water sources have intolerable smell and contains less flora and fauna [2]. Large quantity of domestic sewage is drained in to lake and most of the sewage is untreated. Domestic sewage contains solid waste, toxicants, bacterial contaminants and these toxic materials causes pollution. Different industrial waste that is drained in to lake without treatment is also one of the main causes of pollution. Water pollution is one of major significant for the health of all living organisms; especially mankind. When water is polluted, it becomes unsafe for human consumption because the water contains dangerous or toxic substances and disease-causing bacteria and organisms [36].

*Table 1 Maximum permissible in mg/L of toxic and /or disease-cause in drinking water*

Substance	WHO	Health Canada	EU Standard
copper	2	1	2
Zinc	3	5	--
Nickel	0.07	----	0.02
Chromium	0.05	0.05	0.05
Lead	0.01	0.005	0.01

#### **2.4 Heavy metal pollution in Ethiopia**

Heavy metal pollution has grown to be a serious worldwide issue, particularly for African nations like Ethiopia where disposing of waste is a big issue. Even while heavy metals are naturally present in soil, human activities like mining, urbanization, industrialization, and agriculture (which uses pesticides and fertilizers) greatly increase the amounts of heavy metals in the environment [2,36]. The use of agrochemicals, untreated or partially treated industrial effluent disposal, urban waste, and fast industrialization and urbanization have all contributed to Ethiopia's alarmingly high pollution levels, which are causing rising metal levels and declining agricultural soil quality [40]. At present, agricultural soils in Ethiopia are becoming increasingly polluted with heavy metals, especially, in urban centers. The dominant heavy metal pollutant sources in Ethiopian agricultural soils are irrigation with rivers/streams laden with industrial effluents and application of fertilizer and pesticides [40]. In addition, the environment has been negatively impacted by the alarming rise in heavy metal population, agricultural transformation, rapid urbanization, mechanization, and sewage pollution. Currently, migration from rural to large cities causing rapid expansion of urban towns, informal settlements, and imbalance of infrastructure cause contamination of surroundings and key health problems in Ethiopia. Accordingly, unplanned urbanization and industrialization in Ethiopia have had a negative impact on diversity of and wildlife [41].

#### **2.5 Effect of irrigation with polluted water on crop and soil**

The probability of occurrence and magnitude of the negative effects of wastewater pollutants on soil and crops vary depending on the concentration, solubility and toxicity of pollutants, climatic conditions, rate and frequency of application of wastewater as irrigation water, type of crop and expected productivity, initial soil properties, level technological and socio-economic status of farmers. The various techniques available for the application of irrigation water help to reduce or minimize some of these negative effects [42].

The results of this study has shown the effects of irrigation with wastewater on growth and yield of maize crop, on soil properties and the effect on enrichment and bio accumulation of nutrients and metals in soil and maize crop[43] . Growth and yield characters of maize crop were not improved as a result of irrigation with wastewater; the high concentration of trace metals in wastewater affected ultimately by lowering the growth and yield when irrigated by wastewater and as compared to rain fed farm crop. The effects could be attributed to higher accumulation of micronutrients and macronutrients in soil and plant, when the mean values were not highly significant as indicated by the present study as compared to rain fed maize grain. Bio-accumulation factor values were high with wastewater grown crop, whereas lowest Bio-accumulation factor values were found for rain fed site [42,43 ].

### 3. MATERIALS AND METHODS

#### 3.1. Experimental site

The study was conducted on farmland of Tulu kebele in the vicinity of Lake Ziway. Lake Ziway basin is about 150 km south of the capital city, Addis Ababa. The town of Ziway (recently named Batu) is situated on the lake's western shore. The altitude of Lake Ziway is approximately 1636 m above sea level (masl), with a maximum water depth of 4 m, a total basin area of about 7300 km<sup>2</sup> (Figure 1) and a lake volume of 1.5 million cubic meters. Most of the basin is characterized by low to moderately undulating topography but bounded by a steep slope and abrupt faults in the eastern and southeastern escarpments, ranging from 4200 to 1600 masl (Figure 1). Lake Ziway Basin experiences the monsoon agro-climate zone characteristics. The mean annual rainfall of the basin spatially varies from 500 to 1150 mm, with a noticeable temporal variation at a monthly time scale. The mean annual temperature ranges from approximately 15°C for the highlands to 25°C close to the lake [44].

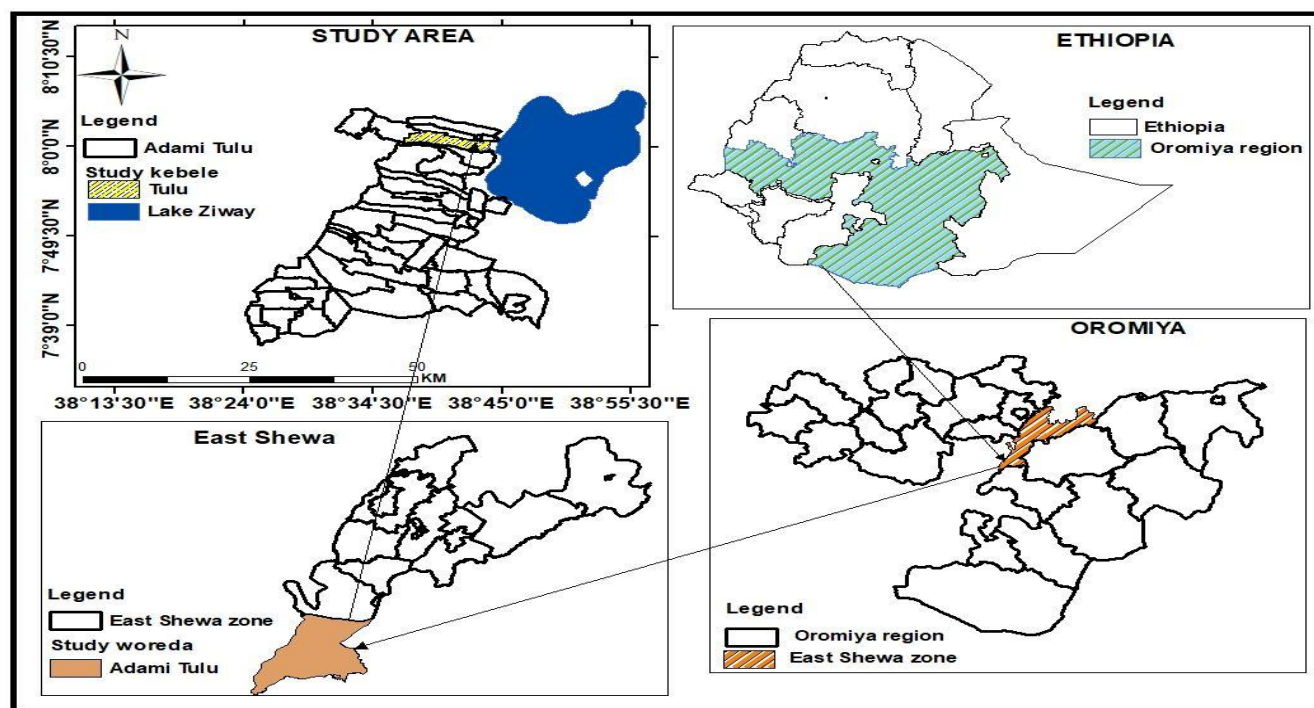


Figure : 1 The Map of the study area

#### 3.2. Sample of Collection

Samples of maize (irrigated and rain fed) 1kg of each were collected from Tulu kebele, around Batu (Adami Tulu). Sampling of maize was done randomly from two farmland site (irrigated site

and rain fed site) each farm land site has three sample size within these local areas. All the samples were collected and stored in polyethene bags according to their type and was brought to Hawassa University Research Laboratory for preparation and pretreatment.

Samples of soil (irrigated and rain fed) 1kg of each were collected from 0.30cm depth from the same site where the maize were collected at Tulu kebele, around Batu (Adami Tulu). The soil sample was done randomly from two farmer site (rain fed farm and irrigated farm) each have three samples with total of six samples within these local areas. All the samples were collected and stored in polyethene bags and were brought to Hawassa University Research Laboratory for preparation and treatment [11].

Samples of water (irrigated) 1 L of each were collected from three place at lake Ziway. All the samples were collected and stored in polyethene plastic bottle and were brought to Hawassa University Research Laboratory for preparation and treatment.

### **3.3 Reagents and Materials**

The Reagent used in the analyses were  $\text{HNO}_3$  (69%),  $\text{HCl}$  (37%),  $\text{HF}$ ,  $\text{HClO}_4$ , dionized water and  $\text{H}_2\text{O}_2$  (30%) were used for the digestion of maize samples, soil and water samples. Stock standard solutions containing 1000 mg/L of the metals Cr, Ni, Cu, Zn, and Pb from which 10 mg/L of intermediate standard obtained were used for preparation of calibration standards of each metal. Double distilled water was used for dilution, cleaning and for preparation of all solution throughout the laboratory work.

The apparatus and instruments were used in this study include: polyethylene bag, glass bottles, plastics, funnel, beakers { different size}, electronic balance, flasks of different size, measuring cylinder, round bottom flask, Whatman filter paper, equipped with deuterium background corrector and air-acetylene flame atomizer was used for analysis of the selected metals (Cr, Ni, Cu, Zn and Pb. All glassware, which was used for laboratory work were washed, with liquid soap, rinsed with water, soaked in 10 % nitric acid for 24 hrs, cleaned thoroughly with distilled water and dried in such a manner to ensure that any contamination do not occur.

### **3.4 sample pre-treatment**

The collected maize samples was first washed with tap water to remove dust and any items adhering to the surfaces. The washed samples were dried in open air on paper for about 2 hrs to

eliminate excess moisture. The sample was weighed, dried in an oven at 105 °C for several hours and reweighed until constant weight will be obtained. The dried samples were then ground in a mortar and pestle and sieved with 1.5 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.

### 3.5 Sample Digestion

5g of grounded samples was weighed and transferred to a clean crucible, which was labeled according to the sample number and dry ashing process was carried out in a muffle furnace by step wise increase of the temperature from 450<sup>0</sup>C up to 500<sup>0</sup>C and then left to ash at this temperature for 5 hrs . After the ash was wetted with distilled water and treated with 2 mL of concentrated HNO<sub>3</sub>. Then the crucible was covered with watch glass and placed on hot plate. The digestion was performed at a temperature 90<sup>0</sup>C for 1 h. The ash was dissolved in 5 mL of 9% HCl and digested again on hot plate until the white fumes ceased to exist and sample reached to 2 mL. After cooling, 20 mL of distilled water was added and filtered using what man filter paper. The filtered samples were diluted up to the mark of 50 mL standard volumetric flask. All samples were prepared identically in triplicates [2].

Soil sample were mixed thoroughly to achieve homogeneity and sieved 0.5g of dried and homogenized soil sample was were weighed by using electrical balance and placed into 50ml refluxing flask. After that, 6ml of 68% HNO<sub>3</sub> and 3ml 37% HClO<sub>4</sub> of freshly (3:1 v/v ratio) were added. The mixture was digested on reflux set up/ closed digestion apparatus at 200<sup>0</sup>C for 2hr and kept to cool at room temperature. After cooling the digested sample were filtered through what man No.42 filter paper. The filtered solution was transfer into 50ml volumetric flask by adding 50ml of distilled water, and kept for metal analysis [11].

The water sample bottles were shaken thoroughly in their plastic containers by use of hand. A Volume of 100 ml of the sample was measured using a 100 ml volumetric flask and put in a Conical flask and 5 ml of concentrated nitric acid was then added. The mixture was heated slowly on a hot plate and evaporated to about 20 ml ensuring that the water did not boil. A further 5 ml of concentrated nitric acid was added and the beaker was covered with a watch glass while heating continued. Nitric acid continued to be added until the solution appeared light

colored and clear. Lastly, 2 ml of concentrated hydrochloric acid was added and heated slightly to dissolve any remaining residue. Few drops of hydrogen peroxide were then added to ensure complete digestion had taken place. The solution was filtered and the filtrate was transferred to a 100 ml volumetric flask to cool and the filtrate was made up to the mark with distilled [45].

### 3.6 Operating Conditions of FAAS for Analysis of Metals

In this study a total of five metals for each maize, soil and water sample were analyzed using Flame Atomic Absorption Spectroscopic (FAAS) with external calibration curve after the parameters such as burner and lamp alignment, slit width and wavelength adjustment were optimized for maximum signal intensity of the instrument. Five elements (Pb, Cr, Ni, Cu and Zn) were analyzed by absorption mode of the instrument. The operating conditions of the instrument employed for each analyte are shown in table 2.

*Table 2: Instrumental Operating Conditions for Determination of Selected Metals in Maize Sample Using FAAS*

Metals	Wave length (nm)	Slit width (nm)	Lamp current (mA)	Energy (eV)	Instrumental detection limit (mg/L)
Cr	357.9	0.7	2.0	2.712	0.040
Ni	341.5	0.2	7.0	2.624	0.020
Cu	324.7	0.7	1.5	3.938	0.005
Zn	213.9	0.7	2.0	3.237	0.005
Pb	283.2	0.7	2.0	2.874	0.040

### 3.7 Instrument Calibration and Measurement of Selected Metals Concentration

Determination of trace metals concentration was done using FAAS. Intermediate standard solutions (10 mg/L) of metals of interest were prepared from the 1000 mg/L standard stock solutions. These solutions were diluted to the desired concentrations to calibrate the instrument (A 10 ppm multi-element solution containing Cr, Zn, Ni, Pb, and Cu was utilized to prepare elemental calibration solutions). These intermediate standards were diluted with deionized water to obtain four working standards of each metal. The same analytical procedure was engaged for the determination of elements in digestion blank solutions.

*Table 3: Concentrations of the Standard Solutions Used to Begin Calibration Graphs for the Determination of Metals in maize soil and water Samples*

Analyte (metal)	Intermediate Standard concentration in mg/L	Standard concentration in mg/L	Correlation coefficient of calibration curve in %
Cr	10	0.05, 0.5, 1, 2	0.998
Cu	10	0.01, 0.05, 0.5, 1	0.999
Ni	10	0.05, 0.1, 0.5, 1	0.999
Zn	10	0.1, 0.5, 1, 2	0.995
Pb	10	0.05, 0.1, 0.5, 1	0.998

### 3.8. Data Analysis.

The significance of variation between samples of maize and soil were analyzed using one-way ANOVA. From ANOVA Table the mean concentrations of all metals (Ni, Cu, Zn, Cr and Pb) were analysis to assess significant difference ( $P < 0.05$  at 95% confidence interval) between maize of irrigated and that of rain fed and also soil of irrigated and rain fed.

### 3.9 Method validation

As it can be seen from Tables 4, 5, and 6 the mean percent recoveries for the studied metals in the Spike sample ranged between 90 to 116 %. All the recovery values were within the acceptable range of 80–120% for metal analysis [46]. The RSD values obtained for water, maize and soil spike samples ranged from 0.99 to 11.28 % (Table 4 and 6), which was under the required control limits  $\leq 15\%$  [47]. These results indicate that the proposed method was precise and accurate.

*Table 4: Recovery Values of Metals for the Analyzed water Samples*

Metals	Conc. in	Amoun	Concentration in	% Recovery	RSD
--------	----------	-------	------------------	------------	-----

	sample (mg/L)	t added (mg/L)	spiked sample (mg/L)		
Pb	0.24 ± 0.01	0.1	0.34 ± 0.01	110 ± 10	9.09
Cr	0.065 ± 0.02	0.1	0.15 ± 0.01	90 ± 10	11.11
Ni	0.051 ± 0.01	0.1	0.14 ± 0.005	102.3 ± 11.54	11.28
Cu	1.23 ± 0.02	0.1	1.33 ± 0.02	108.33 ± 7.63	7.05
Zn	0.92 ± 0.02	0.1	1.03 ± 0.05	116 .66 ± 5.77	4.94

*Table 5: Recovery Values of Metals for the Analyzed maize Samples*

Metals	Conc. in sample (mg/L)	Amount added (mg/L)	Concentration in spiked sample (mg/L)	% Recovery	RSD
Pb	0.123 ± 0.002	0.1	0.223 ± 0.002	100.33±2.08	2.07
Cr	0.085 ± 0.002	0.1	0.185 ± 0.001	106.33±11.8 4	11.14
Ni	0.093 ± 0.0015	0.1	0.194 ± 0.001	101.66 ± 1.52	1.50
Cu	1.21 ± 0.01	0.1	1.35 ± 0.001	102.3 ± 1.57	1.49
Zn	2.43 ± 0.01	0.1	2.52 ± 0.01	110 ± 10	9.09

*Table 6: Recovery Values of Metals for Analyzed soil Samples*

Metal	Conc. in	Amount	Concentration in	%	RSD
-------	----------	--------	------------------	---	-----

s	sample (mg/L)	added (mg/L)	spiked sample (mg/L)	Recov ery	
Pb	0.12 ± 0.001	0.1	0.22 ± 0.001	101.6 ±1.52	1.51
Cr	0.050 ± 0.001	0.1	0.151 ± 0.002	99.2 ± 2.01	2.02
Ni	0.063 ± 0.002	0.1	0.163 ± 0.001	99.3 ± 1.52	1.53
Cu	0.663 ± 0.001	0.1	0.764 ± 0.001	101.1 ± 1.1	0.99
Zn	0.863 ± 0.0015	0.1	0.964 ± 0.001	100.66 ± 1.15	1.14

## 4. RESULTS AND DISCUSSION

### 4.1 Physicochemical Characteristics of soil and sample water used for irrigation

Physico-Chemical Analysis of water and soil sample is essential to have full information about any kind of water and soil system. Selection of parameters for testing of water and soil is solely depends upon for what purpose we going to used that water and soil and what extent we need its quality and purity. Assessment and control of irrigation water quality depend upon physico-chemical properties like pH and electrical conductivity (EC). These are used to know the status of water whether it is fit or unfit for different purposes.

*Table:7 Physical characteristics of water used for irrigation and soil were presented*

Sample type	Ph	Conductivity (Ns/ cm)
Irrigation water	$8.02 \pm 0.015$	$0.921 \pm 0.002$
Irrigation soil	$5.2 \pm 0.1$	$102.2 \pm 0.208$

The pH of irrigated (soil and water) has a major effect on metal dynamics because it controls adsorption and precipitation, which is the main mechanism of metal retention in soils as well as water. As pH decreases, the solubility of cationic forms of metal in the soil and water increases and therefore become more readily available to plants. The pH value for normal soil is 5.5–7.5, but the pH value of these soil samples was found to be without this range (5.2). And Ph of irrigated water recorded higher (8.02) than Ph of irrigated soil [48].

Electrical Conductivity of irrigated (soil and water); these values indicate the relative water-soluble salt content of the soil. Electrical conductivity depends on the amount of dissolved minerals and gives the ability of a substance to conduct an electric current at a specific temperature (25 0C). The electrical conductivity of irrigated water was recorder 0.92Ns/cm while the conductivity of irrigated soil was recorded 102.2Ns/cm [49]

### 4.2 Concentration of metals in maize of irrigated and rain fed farming

Maize plant can absorb heavy metals from soil and water and accumulate in the maize grain. In this study as shown in table 8 and figure 2 the higher content of Cu was obtained from irrigated maize (12.3 mg/kg) and the lower concentration of Cu was found in sample of rain fed (10.8 mg/kg). The concentrations of Cu in rain fed maize (10.8 mg/kg) and in irrigated (12.3mg/kg) were without significant differences (appendix 1). The content of Cu was with the standard permissible set by WHO/FAO [50].

The higher content of Zn was obtained irrigated maize (24.3 mg/kg) and the lower concentration of Zn was found in sample of rain fed (20.23mg/kg). The concentrations of Zn in rain fed (20.23 mg/kg) and in irrigated (24.3mg/kg) were without significant difference (appendix 1). The concentration of Zn was with standard permissible limit of WHO/FAO recommended value for daily and provisional tolerable weakly intake of 5 mg/L and 25 mg/L respectively [50].

The concentration of Pb was higher with the range (0.42 – 1.25 mg/kg). The higher value of Pb was (1.25 mg/kg) obtained from irrigated maize sample and the lower content of Pb is found in rain fed maize site (0.42 mg/kg). The concentrations of Pb in rain fed and in irrigated were without significant difference (appendix 1). The concentration of Pb in both irrigated and rain fed maize samples were slightly above from the permissible limit set by WHO/FAO [50]. The higher level of Pb in irrigated maize grain species is an indication of food toxicity to consumers.

The concentration of Cr in irrigated maize sample was  $0.85 \pm 0.02$  mg/kg while the concentration of Cr in rain fed maize sample was not detected. The content of Cr was with the standard permissible set by WHO/FAO [50].

The mean concentration of Ni contents in maize samples range from (0.62 mg/kg) to (0.93 mg/kg). The higher value of Ni was ( $0.93 \pm 0.01$  5 mg/kg) obtained from irrigated site and the lower content of Ni is found in rain farm site ( $0.62 \pm 0.01$  5mg/kg). The concentrations of Ni in rain fed and in irrigated were without significant difference (appendix 1). The concentration of Ni was slightly above from the permissible limit set by WHO/FAO [50].

In general, the concentration order of metals in irrigated maize grain sample was found in order of  $Zn > Cu > Pb > Ni > Cr$  and the concentration patter of metals in rain fed maize grain sample was found in order of  $Zn > Cu > Ni > Pb$ . The mean concentrations of Pb and Ni detected in maize were slightly higher than the limit set by the WHO/FAO [50], while the levels of Cu, Zn, and Cr concentrations were within the standard [51].

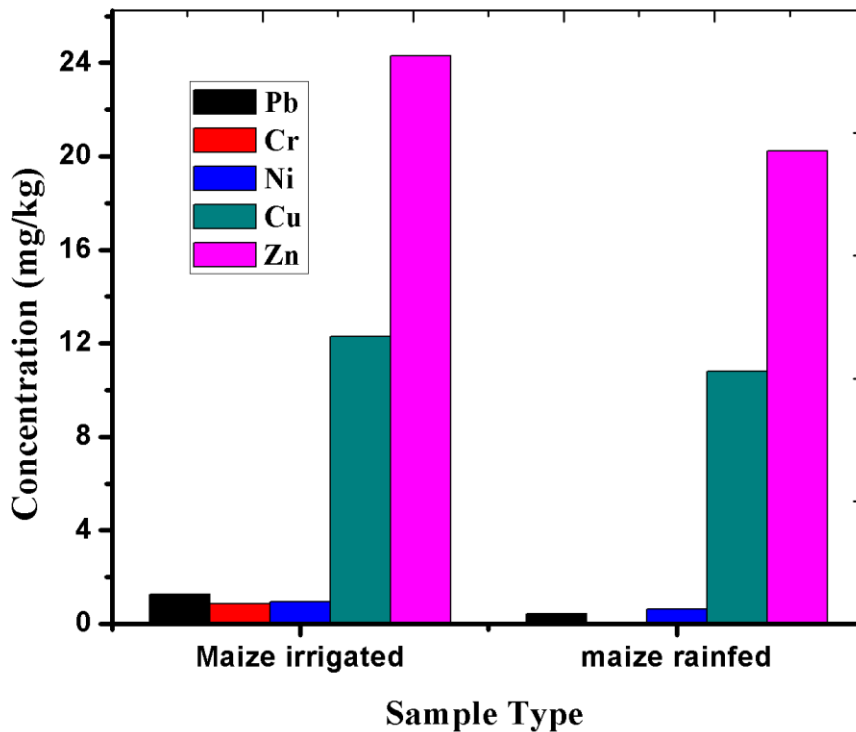
In Table 8 and figure 2 the concentration of metals in irrigated maize is higher than that of maize of rain fed this might be the accumulation of metals from irrigated soil to maize. The soil used for irrigation might be polluted by different anthropological source and the discharge of waste from different industries into water used for irrigation.

*Table 8 Mean concentrations of metals (mean  $\pm$  SD, n = 3, mg/kg dry weight) in maize of irrigated and rain fed*

Sample	Pb	Cr	Ni	Cu	Zn
Maize (irrigated)	1.25 $\pm$ 0.01 <sup>b</sup>	0.85 $\pm$ 0.02	0.93 $\pm$ 0.15 <sup>b</sup>	12.3 $\pm$ 0.2 <sup>b</sup>	24.3 $\pm$ 0.2 <sup>b</sup>
Maize (rainfed)	0.42 $\pm$ 0.01 <sup>b</sup>	ND	0.62 $\pm$ 0.01 <sup>b</sup>	10.8 $\pm$ 0.1 <sup>b</sup>	20.23 $\pm$ 0.15 <sup>b</sup>
WHO/FAO permissible limit (Aderinola et al at 2012)	0.3	2.3	0.1	73	99

ND= Not detected

Mean values with same letter are not statically difference



*Figure 2: Level of heavy metals in maize of irrigated and rain fed*

#### 4.3 Concentration of metals in soil of irrigated and rain fed farms

Copper (Cu) is an essential micronutrient which functions as a biocatalyst, required for body pigmentation in addition to iron, maintain a healthy central nervous system, prevents anemia and interrelated with the function of Zn and Fe in the body. Most plants contain the amount of copper which is inadequate for normal growth and is usually ensured through chemical or organic fertilizers [52]. The mean concentration of Cu contents in soil samples range from (56.4 mg/kg) to (66.3 mg/kg). The higher value of Cu was (66.3mg/kg) obtained from irrigated sample site and the lower content of Cu is found in rain farm site (56.4 mg/kg). There was no significant difference on the values among of Cu concentration in two soil sample (appendix 2). Recent study by Girma (2019) reported that the mean concentration of Cu in soils of Ziway area was 23.25 mg/kg, which have lower concentration value from this study.

Zinc (Zn) is an essential element for plants and animals similar to Cu, but only a small increase in its level may cause interference with physiological processes. The presence of Zn seems to be essential to neutralize the toxic effects of Cd [53]. The mean concentration of Zn in the digested

soil sample ranges from (74.26 mg/kg to 86.35 mg/kg). The sample from irrigated soil was resulted higher concentration (86.35 mg/kg) while the sample from rain fed soil had lower concentration (74.26mg/kg). There was no significant difference on the values among Zn concentration in irrigated and rain fed soil sample (appendix 2). The study conducted by Girma (2019) the mean concentration of Zn in this area was 52.76 mg/kg, which lower than the present study result.

Nickel is an essential trace element in animals, although the functional importance of nickel has not been clearly demonstrated. It is considered essential based on reports of nickel deficiency in several animal species. In humans, essential component of the haemopoietic process, and play important role in physiological processes as a co-factor in the absorption of iron from the intestine [54]. The Ni content of soil were range from (4.36 mg/kg to 6.46 mg/kg). Higher concentration of Ni were obtained in irrigated soil sample area (6.46 mg/kg) while, lower concentration of Ni was found in rain fed soil sample (4.36 mg/kg). The result showed that there was no significant difference on the values of the concentration of Ni among the sites (appendix 2).The study conducted by Lelisa (2018) the mean concentration of Ni in this area was 8.2mg/kg, which higher than the present study result.

Chromium (Cr) is a toxic naturally occurring element that may be released into the environment through sewage and fertilizers [55]. The mean concentration of Cr contents in soil samples range from (4.4 mg/kg) to (5.36mg/kg). Higher value of Cr was (5.36 mg/kg) obtained from irrigated sample site and lower content of Cr is found in rain fed soil (4.4 mg/kg). The result showed that there was no significant difference on the values of the concentration of Cr among the sites (appendix 2). Mean Cr concentration (8.44 mg/kg) was reported by Hailu (2007) in this area which is higher than the present study(5.36mg/kg). Lead (Pb) is a highly toxic heavy metal whose widespread use has caused extensive environmental contamination and health problems in many parts of the world [56]. The Pb content of soil was range from (9.46mg/kg to 12.36 mg/kg). Higher concentration of Pb were obtained in irrigated sample area (12.36 mg/kg) while, lower concentration of Pb was found in rain fed soil sample (9.46 mg/kg). The result showed that there was no significant difference one the values of the concentration of Pb among the sites (appendix 2). The study conducted by Girma (2019) reported that the mean concentration of Pb in soils around this area was 9.86 mg/kg, which have lower concentration value from this study. In general, the concentration patter of metals in irrigated soil sample was found in order of Zn > Cu > Pb > Ni >Cr *and* concentration patter of metals in rain fed soil sample was found in order of Zn > Cu > Pb> Cr >Ni. The physiology of the various plants may determine the level of accumulation of heavy metals

starting from up taking in soil to a preferential storage in the plant parts such as roots and leaves [57]. PH level of soil can determine the mobility and uptake of heavy metals by plants. The reported slightly high level of heavy metals in soils indicated that the irrigation water has been possibly contaminated by anthropogenic sources. High level of heavy metals is due to rapid development Horticulture industry and excessive use of pesticides and fertilizer. The bio-accumulative nature of these heavy metals in the human body could bring a long-term health impact [20]. The current results showed that soils in which maize were grown are contaminated by metals. Therefore, the exceeded value found in the maize parts is likely the result of the contaminated soil.

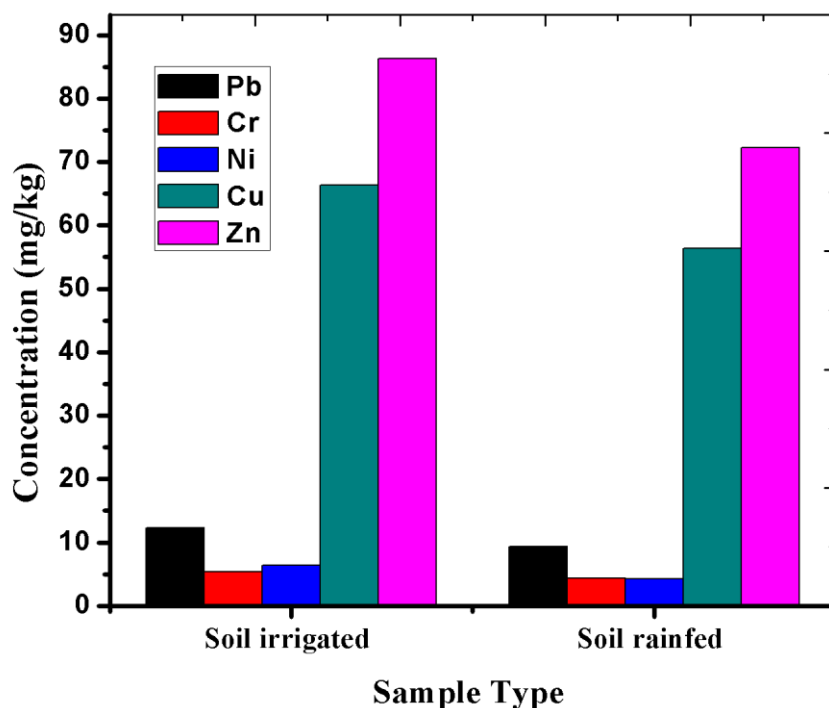
#### 4.4 Comparison of Heavy Metals in the maize and Soil Sample

Up on comparing the levels of metals in the maize and the growth media soil, Pb, Ni, Zn, Cr and Cu were higher in the soil and maize grain. Therefore, these metals were taken up by the plants significantly from the irrigation water applied. Mostly, the concentrations of essential and nonessential metals were higher in soils than maize grain. This indicates that only a small portion of soil metals was transferred to the maize and the root acts as a barrier to the translocation of heavy metals within maize. The concentrations of all essential and non-essential heavy metals were found to be higher in the soil sample than in the maize. This may reveal that the main source of metal contents of maize was from their soil content which might be affected by irrigation waste effluent, the environmental interferences like pesticides, fertilizers and other additives that farmers used. Variations in transfer factor among the maize may be attributed to differences in the concentration of metals in the soil and differences in element uptake by maize.

*Table 9 Metals Mean Concentration in Soil (mg/kg) of irrigated and rain fed*

Sample	Pb	Cr	Ni	Cu	Zn
Soil (irrigated )	12.36± 0.25 <sup>a</sup>	5.36 ± 0.15 <sup>a</sup>	6.46 ± 0.20 <sup>a</sup>	66.3 ± 0.1 <sup>a</sup>	86.35 ± 0.15 <sup>a</sup>
soil (rain fed)	9.46 ± 0.15 <sup>a</sup>	4.4 ± 0.2 <sup>a</sup>	4.36 ± 0.25 <sup>a</sup>	56.4 ± 0.1 <sup>a</sup>	74.26 ± 0.20 <sup>a</sup>

Mean values with same letter are not statically difference



*Figure 3: Level of heavy metals in soil of irrigated and rain fed*

#### 4.5 Concentration metals in Irrigated Water

Concentrations of metals in the irrigation water samples collected from Lake Ziway are given in Table 10 and Figure 4. The concentrations of all metals for the irrigated water obtained from Ziway lake sources are detected. A relatively high concentration of Cu and Zn obtained from the irrigated water which is used to irrigate the maize farms. Cu, Ni and Zn have mean concentration lower than the recommended maximum level for irrigation WHO [58]. While the mean concentration of Pb and Cr exceeds the maximum permissible limit set by EU Standard [59]. Elevated concentrations of heavy metals, especially Cr and Pb, will result in cancer risk when the daily intake exceeds the recommended value [60]. In general, the mean concentration of metal in irrigation water follows the order of Cu > Zn > Pb > Cr > Ni. T

#### 4.6 Comparison the concentration of heavy metal in irrigation water with soil and maize

The concentrations of all essential and non-essential heavy metals were found to be higher in the soil sample, maize and water sample. The maximum value (0.24mg/L) of Pb was obtained from

irrigated water sample site and the minimum content (0.12mg/L) of Pb is found in soil sample site. The study conducted by Girma (2019) reported that the mean concentration of Pb in irrigated water around this area was 0.032 mg/L, which have lower concentration value from this study. The concentration of Pb was slightly above from the permissible limit set by WHO [60].

The highest value (1.23mg/L) of Cu concentration was found from irrigated water sample and the lowest concentration (0.66mg/L) of Cu was found soil sample. Recent study by Girma (2019) reported that the mean concentration of Cu in in irrigated water of Ziway area was 0.036 mg/L, which have lower concentration value from this study. The content of Cu was with the standard permissible set by Healthy Canada [61].

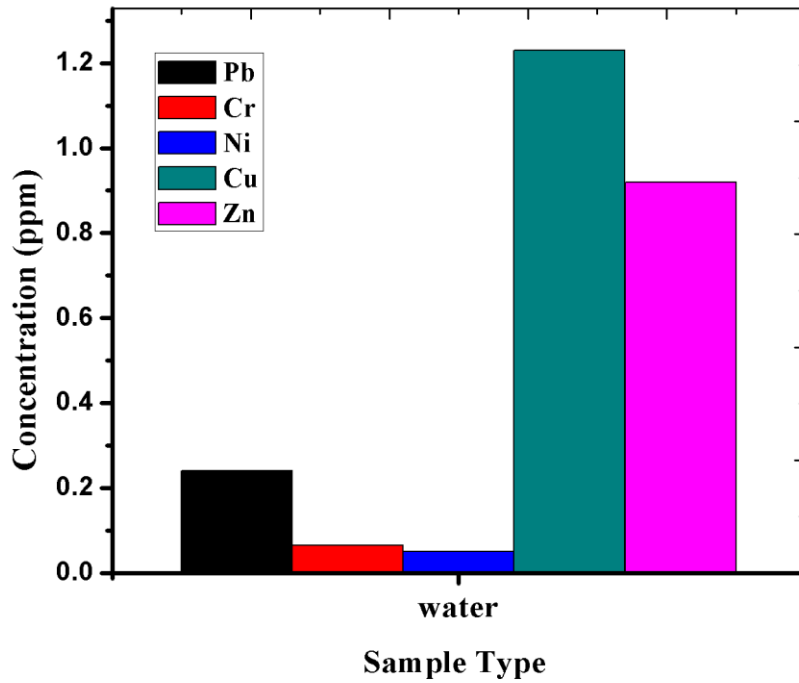
The highest value (2.43mg/L) of Zn concentration was found from irrigated maize sample and the lowest concentration (0.863mg/L) of Zn was found in soil sample. The study conducted by Girma (2019) the mean concentration of Zn in in irrigated water was 0.23 mg/L, which lower than the present study result. The concentration of Zn was with standard permissible set by WHO recommended [58].

The highest value (0.093mg/L) of Ni concentration was found from irrigated maize sample and the lowest concentration (0.051mg/L) of Ni was found in irrigated water sample. Mean Ni concentration (0.01 mg/L) reported by Solomon (2019) was lower than the present study (0.051 mg/L). The content of Ni was with the standard permissible set by EU Standard [59].

The highest value (0.085mg/L) of Cr concentration was found from irrigated maize sample and the lowest concentration of (0.05mg/L) Cr was found in irrigated soil sample. Mean Cr concentration was reported by Hailu (2007) was not detected while the present study was higher (0.065mg/L). The concentration of Cr was slightly above from the permissible limit set by WHO [58].

*Table 10: Metals Mean Concentration in irrigation water (mg/L)*

Sample	Pb	Cr	Ni	Cu	Zn
Water used for irrigation	0.24 ± 0.01	0.065 ± 0.02	0.051 ± 0.01	1.23 ± 0.02	0.92 ± 0.02



*Figure 4 : Level of heavy metals in water used for irrigation*

#### **4.7 Data Analysis**

The significance of variation between samples of maize of irrigated and maize of rain fed and also soil of irrigated and rains fed were analyzed using one-way ANOVA. From ANOVA Table the mean concentrations of all metals (Ni, Cu, Zn, Cr and Pb) were not showed significant difference ( $P < 0.05$  at 95% confidence interval) between maize of irrigated and that of rain fed and also soil of irrigated and rain fed.

## 5. CONCLUSION AND RECOMMENDATIONS

### 5.1 Conclusion

The mean concentrations of Pb and Ni detected in maize at irrigated sites were slightly higher than the limit set by the WHO/FAO, while the levels of Cu, Zn, and Cr concentrations were within the standard. The mean concentrations of Pb, Cr, Ni, Cu and Zn in maize grain samples were higher at irrigated sites than rain fed farms. The mean concentration of Pb, Cr, Ni, Cu and Zn in the soils was also higher at irrigated sites than at rain fed sites. This may indicate the influence of irrigation water, which might be affected from the surrounding herbicide and fertilizer intensive agricultural activity. Similarly, the mean concentration of the studied metals in maize was in the order metals  $Zn > Cu > Pb > Ni > Cr$  while in the irrigated soil samples of  $Zn > Cu > Pb > Ni > Cr$ , and in the irrigation water  $Cu > Zn > Pb > Cr > Ni$ . The study indicates that the water used for irrigation slightly serve as the potential source of the heavy metals in the environment and the concentration of the heavy metals: Zn and Cu, are all far below the maximum tolerable levels set by WHO but the values of Pb, Ni and Cr were slightly higher than maximum tolerable levels set by WHO.

### 5.2 Recommendation

Based on the result obtained the following recommendation were forwarded.

- ✓ Monitoring of the levels of heavy metals in maize 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 maize harvested from this area.
- ✓ Government and Non-Governmental Organizations should provide storage facility at different locations to guard against spoilage..
- ✓ The ministries of Public Health and Sanitation and that of Agriculture should come up with health education programmes for the general population on the dangers of consumption of crops grown in and around polluted Lake and waste disposal sites.
- ✓ The farmers growing edible crops around the site and other concerning bodies should be advised to stop use of polluted water.

## Reference

1. Wodaje Addis Tegegn 2015. Assesment of some heavy metals concentration in selected cereals collected from local markets Ambo city Ethiopia
2. Woyyessa, Alemayew . 2017. “Levels of Selected Heavy Metals in Cereals Produced Around Chiro Town, Western Hararghe A,” no. May.
3. Kumar, Bhupender. 2012. “No TitleMaize Biology an Introduction.”
4. Nleya, Thandiwe, and Jonathan Kleinjan. 2019. “Corn Growth and Development,” no. March.
5. Brown, Jack. 2008. *An Introduction to Plant Breeding*.
6. Alemu, Dawit. n.d. *Situation and Outlook of Maize in Ethiopia of Maize in Ethiopia*.
7. LLISA, BLISTI. 2018. “assessment of heavy metal status in fresh and canned fruits, vegetable collected from supermarket and irrigation farms of akaki, awash, arba minch areas, ethiopia.
8. Duruibe, M. Ogwuegbu, and J. Egwurugwu, "Heavy metal pollution and human biotoxic effects," International Journal of physical sciences, vol. 2, pp. 112-118, 2007.”
9. Getu solomon. 2019. “determination of heavy metals in soil, water and tomato and analysis of physico-chemical parameters of soil and water.
10. Zegde, Melaku. 2009. “Determination of the Level of Selected Essential and Toxic Metals in Canned Tomatoes Paste,” no. July.
- 11 . Girma, : Zerihun. 2019. “Analysis of Trace Elements in Tomato Fruits from Ziway Lake Irrigated Farm.”
12. Habtamu. 2021. “determination of the concentration of some selected heavy metals and nutritional composition in barley (*hordeum vulgare*) around chacha district,” no. February.
13. Giovanna, Andrea, and Niño Savala. 2022. “Heavy Metals from Phosphate Fertilizers in Maize-Based Food-Feed Energy Systems Submitted By.”
- 14 . Balemi, Tesfaye, Mesfin Kebede, Tolera Abera, Gebresilasie Hailu, and Gebreyes Gurmu. 2019. “Some Maize Agronomic Practices in Ethiopia : A Review of Research Experiences and Lessons from Agronomic Panel Survey in Oromia and Amhara Regions” 14 (33): 1749–63. <https://doi.org/10.5897/AJAR2019.14338>.
15. Gudeta N, Twumasi-Afriyie S, Demisew AK, Bayisa A, Demoz N, Kassa Y, Habtamu Z, Leta T, Habte J, Wondimu F, Solomon A, Abiy A, Jemal A, Abrha K, Hintsu G, Habtamu T (2011). Development of improved maize germplasm for highland agro-ecologies of Ethiopia. In: Mosisa W, Twumasi-Afriyie S, Legesse W, Berhanu T, Girma D, Gezahegn B, Dagne W, Prasanna, BM, editors. Proceedings of the Third National Maize Workshop of Ethiopia. 18-20, April, Addis Ababa. pp. 43-46
16. Deribe, Yared, Adam Bekele, Ali Mohammed Oumer, and Tamrat Fikadu. 2022. Technical Efficiency of Maize Production in the Central Rift Valley of Ethiopia: Panel Data

Stochastic Frontier Model.

17. Louhichi K, Temursho U, Colen L, and Gomez Y, and Paloma S. 2019. Upscaling the productivity performance of the Agricultural Commercialization Cluster Initiative in Ethiopia. Publications Office of the European Union, Luxembourg. doi:10.2760/57450, JRC117562
18. Ransom, K. 19932 “FIRST NATIONAL MAIZE FIRST NATIONAL MAIZE.”
19. Yetneberk, Senayit, Mulugeta Teamir, and Adefris Teklewold. 2000. “Maize Based Food Products in Ethiopia: A Review of Traditional Practices and Research Outputs,” 1–16.
20. Hailu, Amare. 2007. “metal concentration in vegetables grown in northern addis ababa and part of rift valley ( zaway ), ethiopia a thesis submitted to the school of graduate studies,” no. August.
21. Yebrzaf, Y. Review on heavy metal concentration in vegetables grown in Ethiopia and its economic welfare implication. Journal of Biology, Agriculture and Healthcare, 2017, 7, 2224-3208
22. 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.
23. Lunk, Hans-joachim. 2015. “Discovery , Properties and Applications of Chromium and Its Compounds,” no. September. <https://doi.org/10.1007/s40828-015-0007-z>.
24. Iskra, Fedorus 2022. 2022. “Chromium , Its Properties , Transformation , and Impact on Humans,” no. Iii: 89–97.
25. G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, et al., "A chromium terephthalate-based solid with unusually large pore volumes and surface area," Science, vol. 309, pp. 2040-2042, 2005.
26. Boldyrev, Mikhail. 2018. “Lead : Properties , History , and Applications” 1 (2): 1–23. <https://doi.org/10.15347/wjs/2018.007>.
27. Wainwright H et al. Environmental Impact of Production Horticulture 2014.
28. Cempel, M, and G Nickel. 2006. “Nickel : A Review of Its Sources and Environmental Toxicology” 15 (3): 375–82.
29. Genchi, Giuseppe, Alessia Carocci, Graziantonio Lauria, Maria Stefania Sinicropi, and Alessia Catalano. 2020. “Nickel : Human Health and Environmental Toxicology.” <https://doi.org/10.3390/ijerph17030679>.
30. Ferder, J.; A. Gnirke and W. Thomas.; A novel MHC class I-like gene is mutated in patients with hereditary hemochromatosis. Nat Genet, (1996) 13(1), 399-408.
31. Granie, Precambrian. 1937. “A STUDY OF THE DISTRIBUTION OF TRACES OF COPPER , LEAD , AND ZINC IN THE MINERALS.

32. Zhong, Mingjun 2019. n.d. "Effects of Trace Elements on the Properties of Copper from First-Principles Calculations Effects of Trace Elements on the Properties of Copper from First-Principles Calculations," no. I. <https://doi.org/10.1088/1755-1315/300/2/022010>.
33. Järup, L. Hazards of Heavy Metal Contamination. *British Medical Bulletin*. 2003, 68,167-179
34. C.-D. Dong, C.-F. Chen, and C.-W. Chen, "Contamination of zinc in sediments at river mouths and channel in northern Kaohsiung Harbor, Taiwan," *International Journal of Environmental Science and Development*, vol. 3, p. 517, 2012
35. Heidary-Monfared, S. Community Garden Heavy Metal Study. 2011, 8-18.
36. Kamble, SM. (2014). Water pollution and public health issues in Kolhapur city in Maharashtra. *International Journal of Scientific and Research Publications*, 4, 1-6.
37. Goodwin, Frank E. 2017. "Zinc Compounds," no. June. <https://doi.org/10.1002/0471238961.2609140307151504.a02.pub3>
38. Giliomee, Jan H. 2014. "https://Www.Researchgate.Net/Puplication/269398458," no. January 2009.
39. Lukaski, 1999. Can we detrmine the biological availability of sedment-bounded trace element? *Hydro Biological*, 176(4): 376-379
40. Beksam10@gmail.c;m. 2020. "Heavy Metals Contamination of Soil in the Vicinity of Hawassa Industrial Zone , Ethiopia."
41. Gelaye, Yohannes, and Sintayehu Musie. 2023. "Impacts of Heavy Metal Pollution on Ethiopian Agriculture: A Review on the Safety and Quality of Vegetable Crops." *Article* 2023.
42. Ungureanu, Nicoleta, Technology Politehnica Bucharest, Valentin Vladut, and Sorin-stefan Biris. 2021. "The Effects of Wastewater Irrigation on Agricultural Soils the effects of wastewater irrigation on agricultural soils," no. november. <https://doi.org/10.52846/aamc.2021.02.66>.
43. Alghobar, Mohammed Abdullah, and Sidduraiah Suresha. 2016. "Effect of Wastewater Irrigation on Growth and Yield of Rice Crop and Uptake and Accumulation of Nutrient and Heavy Metals in Soil" 4 (3): 53–60. <https://doi.org/10.12691/aees-4-3-1>.
44. Hordofa, Aster Tesfaye, Olkeba T Leta, Tena Alamirew, and Nafyad Kawo. 2021. "Performance Evaluation and Comparison of Satellite-Derived Rainfall Datasets over the Ziway Lake
45. B. Zarcinas, B. Cartwright, and L. Spouncer, "Nitric acid digestion and multi-element analysis of plant material by inductively coupled plasma spectrometry," *Communications in Soil Science and Plant Analysis*, vol. 18, pp. 131-146, 1987.
46. Harvey, David. 2000. "C h e m i s t r Y."

47. Ararso, Abebeye. 2013. "Call for Access and Benefit Sharing of *Rhamnus Prinoidea* ( Gesho ) Taya Birhanu Belay Genetic Resource Access and Benefit Sharing Directorate Ethiopian Biodiversity Institute.
48. J. Gichuki and J. Gichumbi, "Physico-chemical analysis of ground water from Kihara Division, Kiambu County, Kenya," *Journal of Chemical, Biological and Physical Sciences (JCBPS)*, vol. 2, p. 2193, 2012.
49. E. C. Brevik, T. E. Fenton, and A. Lazari, "Soil electrical conductivity as a function of soil water content and implications for soil mapping," *Precision Agriculture*, vol. 7, pp. 393-404, 2006.
50. WHO/FAO permissible limit (Aderinola et al 2012)
51. Codex Alimentarius Commission. 2001. "alinorm 01/38 joint fao/who food standards programme Codex Alimentarius Commission Twenty-Fourth Session," no. July: 2–7.
52. Tanna F. (2002) Metals in leafy vegetables grown in Addis Ababa and toxicology implications. *Eth. J. Health Dev't.*, Vol. 16(1), 295-302.
53. Cherif, J.; Mediouni, C.; Ammar, W. B.; Jemal, F. (2011) Interactions of zinc and cadmium toxicity in their effects on growth and in anti-oxidative systems in tomato plants (*Solanum lycopersicum*). *J. Env'tl Sci.*, 23(5), 837–844
54. Klasing, K.; Mineral tolerance of animals. *Mineral Tolerance of Animals*, (2005). 64. Ferder, J.; A. Gnirke and W. Thomas.; A novel MHC class I-like gene is mutated in,
55. Ghani A. (2011) Effect of chromium toxicity on growth, chlorophyll and some mineral nutrients of *Brassica juncea* L. *Egyptian Acad. J. Biol. Sci.*, Vol. 2(1), 9–15.
56. Sharma P. and Dubey R. S. (2005) Lead toxicity in plants. *Braz. J. Plant Physiol.*, Vol. 17(1), 35–52
57. Misganaw, Ermias. 2017. "Heavy Metal Concentration in Soil and Swiss Chard Grown in the Vicinity of Addis Ababa , Ethiopia" 17 (1): 58–62. [https://doi.org/10.5829/idosi.ajeaes.2017.58.62. .](https://doi.org/10.5829/idosi.ajeaes.2017.58.62.)
58. WHO Guideline For drinking-Water Quality, Geneva, second addendum WHO;2008, Vol 1 Recommendations 3<sup>rd</sup> Ed.
59. EU standard. Council Directive 98/83 EC on the quality of water intended for human consumption. Adopted by the council, on 3 November 1998.
60. Singh, S, M Zacharias, S Kalpana, and S Mishra. 2014. "Heavy Metals Accumulation and Distribution Pattern in Different Vegetable Crops," no. October. <https://doi.org/10.5897/JECE11.076>.
61. Healthy Canada. Guideline for Canadian Drinking Water Quality-Summary Table Water and Air Quality Bureau, Healthy Environment and Consumer Safety Branch Health Canada, Ottawa, Ontario, 2019.

## Appendix 1 result for ANOVAs single factor

Table 11 analysis of anova for maize of irrigated and rain fed

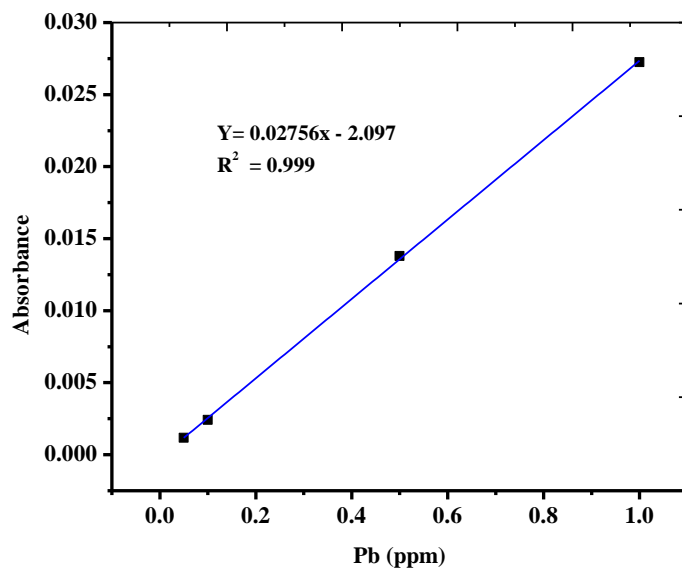
	Factor	Sum of square	Df	Mean square	F calculated	P value	F critical
Pb	Between Groups	0.0003	2	0.00015	0.00045	0.99	9.55
	Within Groups	0.9925	3	0.3308			
	Total		5				
Ni	Between Groups	0.0004	2	0.0002	0.000412	0.99	9.55
	Within Groups	0.14415	3	0.04805			
	Total	0.14415	5				
Cu	Between Groups	0.0133	2	0.006667	0.00043	0.99	9.52
	Within Groups	4.56	3	1.52			
	Total	4.57	5				
Zn	Between Groups	0.00823	2	0.000411	0.0005	0.99	9.52
	Within Groups	24.69	3	8.232			

*Table 12 analysis of anova for soil of irrigated and rain fed*

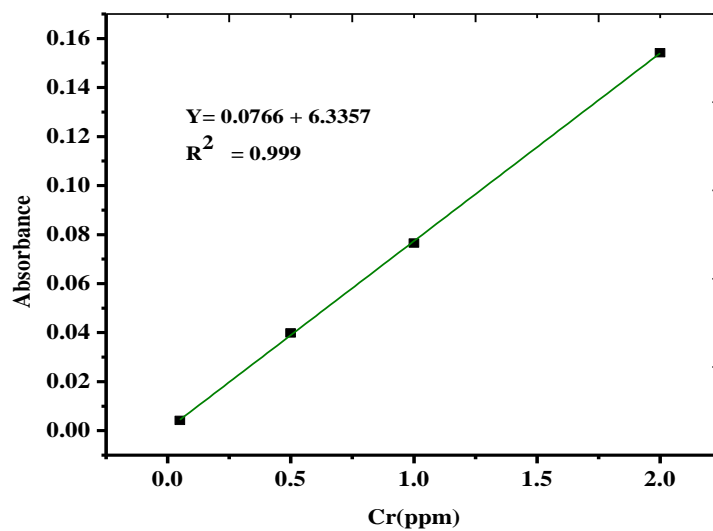
	Factor	Sum of square	Df	Mean square	F calculated	P value	F critical
Pb	Between Groups	0.0025	2	0.01267	0.0003	0.99	9.55
	Within Groups	12.67	3	4.22			
	Tota		5				
Cr	Between Groups	0.005733	2	0.002867	0.006044	0.99	9.55
	Within Groups	1.42	3	0.4742			
	Total		5				
Ni	Between Groups	0.000233	2	0.000117	0.00526	0.99	9.52
	Within Groups	6.657	3	2.219			
	Total		5				
Cu	Between Groups	0.0133	2	0.00666	0.000134	0.99	9.52
	Within Groups	149.015	3	49.67			
	Total		5				
Zn	Between Groups	0.001033	2	0.000517	0.0000007	0.99	9.55

## Appendix 3 Calibration graph

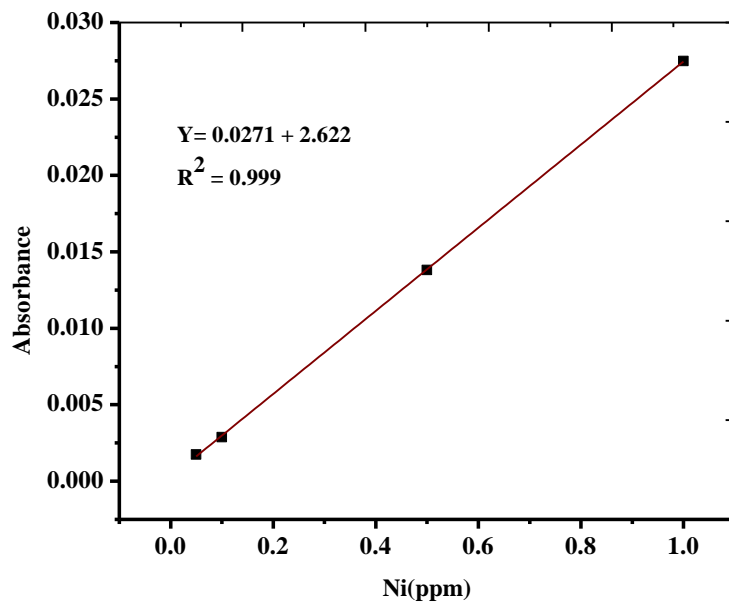
### 2.1 Calibration graph of lead



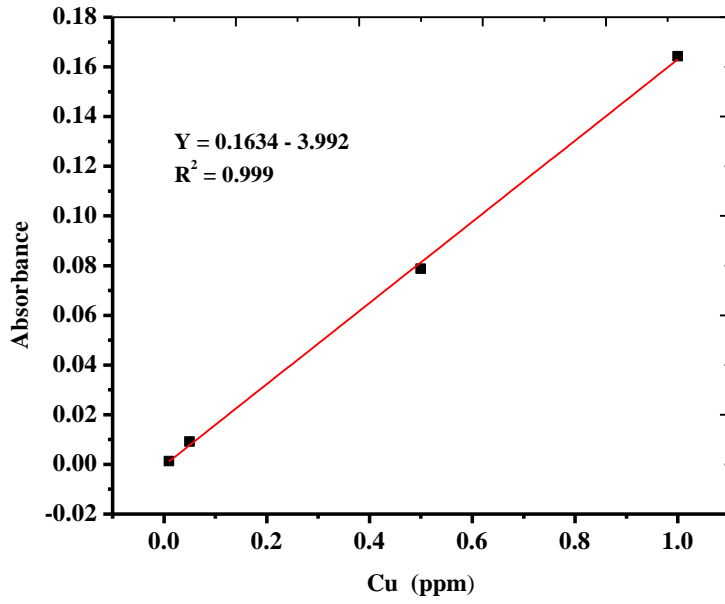
### 2.2 Calibration graph of chromium



### 2.3 Calibration graph of nickel



### 2.4 Calibration graph of copper



### 2.5 Calibration graph of zinc

