

**DETERMINATION OF SELECTED HEAVY METALS IN SOIL, WATER  
AND TOMATO (*SOLANUM LYCOPERSICUM*) WITH THEIR HEALTH  
HAZARD INFLUENCE FROM ABUARIE IRRIGATION SITE, NORTH**



**By: Tilahun Tadesse (ID No GSE 13023)**

**MSc Thesis (Chem 6053) Submitted to the Department of Chemistry  
Faculty of Natural and Computational Science**

**Presented in Partial Fulfillment of the Requirement for the Degree of  
Master's in Analytical Chemistry**

**Office of Graduate Studies, Woldia University**

**May, 2023**

**Woldia, Ethiopia**

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Presented in Partial Fulfillment of the Requirement for the Degree of Master's in  
Chemistry (Analytical)

Office of Graduate Studies

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May, 2023, Woldia, Ethiopia

## DECLARATION

I hereby declare that this Master Thesis entitled “Determination of the Levels of Selected Heavy Metals and Health Risk Assessment in Soil, irrigation Water and Tomato (*Solanum Lycopersicum*) With their Health Hazard Influence from Abuarie Irrigation Site, North Wollo, Ethiopia” is my original work. That is, it has not been submitted for the award of any academic degree, diploma or certificate in any other university. All sources of materials that are used for this thesis have been duly acknowledged through citation.

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## RECOMMENDATION

I/we, the advisor(s) of this thesis, hereby certify that I/we have read the revised version of the thesis entitled “Determination of the Levels of Selected Heavy Metals and Health Risk Assessment Soil, irrigation Water and Tomato (*Solanum Lycopersicum*) With their Health Hazard Influence from Abuarie Irrigation Site’’ Prepared under my/our guidance by Tilahun Tadesse submitted in partial fulfillment of the requirements for the degree of Master’s of Science in chemistry (Analytical). Therefore, I/we recommend the submission of revised version of the thesis to the department following the applicable procedures.

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Major Advisor

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## Approval Sheet

I/we, the advisors of the thesis entitled “Determination of the Levels of Selected Heavy Metals and Health Risk Assessment in Soil, irrigation Water and Tomato (*Solanum Lycopersicum*) With their Health Hazard Influence from Abuare Irrigation Site” and developed by Tilahun Tadesse, hereby certify that the recommendation and suggestions made by the board of examiners are appropriately incorporated into the final version of the thesis.

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### III LIST OF ABBREVIATION

|                |                                                          |
|----------------|----------------------------------------------------------|
| ABS            | Skin Absorption Factor                                   |
| ADD            | Average Daily Dose                                       |
| AF             | Adhesive Factor                                          |
| ANOVA          | Analysis Of Variance                                     |
| AT             | Average Time                                             |
| ATSDR          | Agency for Toxic Substances and Disease Registry         |
| BDL            | Below the Detection Limit                                |
| BW             | Body Weight                                              |
| CF             | Conversion Factor                                        |
| CMH            | Chinese Ministry of Health                               |
| C <sub>T</sub> | Concentration of Tomato                                  |
| ED             | Exposure Duration                                        |
| EF             | Exposure Frequency                                       |
| EU             | European Union                                           |
| FAO            | Food and Agricultural Organization                       |
| ICP-OES        | Inductively Coupled Plasma-Optical Emission Spectrometry |
| IDL            | Instrumental Detection Limit                             |
| IngR           | Ingestion Rate                                           |
| InhR           | Ingestion Rate                                           |
| MDL            | Method Detection Limit                                   |
| PEF            | Particular Emission Factor                               |
| RMC            | Recommended Maximum Concentration                        |
| SD             | Standard Deviation                                       |
| SL             | Skin Adherence Factor                                    |
| SPSS           | Statistical Package for Social Science                   |
| TF             | Transfer Factor                                          |
| USEPA          | United States Environmental Protection Agency            |
| WHO            | World Health Organization                                |

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## V ABSTRACT

*Heavy metal (HMs) contaminants can be found on the surface and in the tissue of fresh tomatoes in different concentration ranges. Intake of these heavy metal-contaminated tomatoes may pose a risk to the human health. In this study the level and their health hazard influence of Chromium, Cadmium, Iron, Lead, Copper, Nickel, Zinc and Cobalt in soil, irrigation water and tomato samples collected from Abuarie Irrigation Site, North Wollo, Ethiopia were investigated using inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). Wet digestion method was used for the preparation of soil, tomato and irrigation water samples. The proposed method was validated by spiking the samples with a standard solution of each metal. The recoveries of the spiked, soil, tomato and water samples were in the range of 80–105%, 82–95% and 80–105%, respectively. The concentration of heavy metals in the soil, tomato and irrigation water sample found to be ranged from  $49,020 \pm 275$  (Fe) to  $10.06 \pm 0.44$  (Cd),  $170 \pm 1.98$  (Fe) to  $0.274 \pm 0.006$  (Cd)  $\text{mgkg}^{-1}$  and  $0.617 \pm 0.003$  (Fe) to  $0.002 \pm 0.001$   $\text{mgL}^{-1}$  (Co), respectively. The concentration of Fe, Pd, and Zn in soil sample, and Fe, Cr and Co in irrigation water sample were below the world health organization (WHO) value while the other HMs concentration in both irrigation water and soil were above WHO and USEPA. Similarly all the targeted heavy metals concentration in tomato sample were above the recommended limit of WHO/FAO and USEPA. The HI value for Cd, Pb, Zn, Ni, Co, Fe, Cr and Cu from this study were less than 1 ( $\text{HRI} < 1$ ) means that the exposed population is safe of metals health risk. The carcinogenic analysis of all Chromium, cadmium, nickel and lead is above  $1 \times 10^{-4}$  that revealed there is high probability to have cancer risk due to exposure to heavy metal. In this study the overall non-carcinogenic risks of irrigation water, tomato and soil for all targeted heavy metals has low effect on human health.*

**Keywords:** Heavy metal, Tomato, Soil, Irrigation water, Health risk





## 1. INTRODUCTION

Fruits and vegetables are rich sources of vitamins, minerals, and fibers, and also have beneficial for the human being and are great value and widely used for dietary purposes, importance in the diet because of the presence of vitamins and mineral salts [1]. They are very important protective food and useful for the maintenance of health and the prevention and treatment of various diseases. However, these plants contain both essential and toxic metals over a wide range of concentrations. For instance, elements such as cadmium, lead and mercury are major contaminants of food supply and may be imposed the most dangerous problem to our environment while others like iron, zinc and copper are essential for biochemical reactions in the body side [2]. Using vegetables and fruits grown on high heavy metals soil (near smelters, industrial factories, farm lands who use high amount of pesticides, herbicides and fertilizers) is also a cause of heavy metal in toxication. Generally, excess intakes of such elements have a negative health impact on humans [3].

The content of essential and non-essential elements in plants depends on the soil characteristics and the environment where the plant is grown and the ability of plants to selectively accumulate some metals [4]. Contamination of soil by HMs is often a direct or indirect consequence of anthropogenic activities. Sources of anthropogenic of metal contamination in soils include urban and industrial wastes mining, smelting of nonferrous metals and metallurgical industries, transportation facilities, fossil fuel burning for heating purposes. Moreover, pesticides, herbicides and both organic and inorganic fertilizer that are widely used in agriculture and increasing municipal effluent accompanying rapid urbanization are the root cause for heavy metals pollution for developing countries [5].

Various sources of environmental contamination have been implicated as route for heavy metals in food. Waste water irrigation, air deposition, spillage are major pathway to heavy metals bioaccumulation in tomato and a major part of Ethiopia diet and is very susceptible to environmental pollution due to the activities and processes going on or practiced in the area where it is cultivated or obtained from Thus, HMs are easily transferred into agricultural soil and water bodies, which resulting harm of humans through food chain through inhalation, ingestion and dermal contact to irrigation water and soil, as well as eating of contaminated food products grown in such area [6]. A number of studies have indicated that HMs could be stored in fatty tissues of human beings and consequently affect the functions of the vital organs and disturb the nervous system and endocrine system [9].

Tomato is one of the most widely grown vegetable crops in the world, second to potato. It use as a food originated in Mexico, and spread throughout the world following the Spanish colonization of the Americas [10]. In Ethiopia, there is no exact information as to when tomato was first introduced; however, the crop is cultivating in different major growing areas of the country. Reports in 2015 cropping calendar showed that tomato production in Ethiopia was about 22,788 tons from harvested area of 3,677 hectare. Moreover, Ethiopia tomato is one of the most important and widely grown vegetable crops, both during the rainy and dry seasons for its fruit by smallholder farmers, commercial state and private farms [11]. The total production of tomato in Ethiopia has shown a marked increase, indicating that it becomes the most profitable crop providing a higher income to smallholder farmers compared to other vegetable crops. However, average yield of tomato in Ethiopia is low, ranging from 6.5-24 Metric hectare as compared with average yields of 51, 41, 36 and 34 metric hectare in America, Europe, Asia and the entire world, respectively. The varieties that are adaptable to die rent agro-ecologies, poor quality seeds, disease and insect pests, high postharvest loss, lack of awareness of existing improved technology and poor marketing systems are some of the major constraints associated with tomato production in Ethiopia [12]. Amhara region has different agroecology and fertile soil that are suitable for producing various types of fruits and vegetables. The region has ideal opportunities for horticultural industry development including abundant surface and groundwater potentials, cheap labor force and increasing demand for horticultural produces both within the domestic and international market. In 2016/17 Autumn season, about 468, 689.1 hectares of land is under vegetable and root crops with a total production of 54.4 million kuntal in Ethiopia. The production of vegetables contributes 1.69% of the entire area under all crops at the national level and 2.17% of the production of the total crops. The country's onion Meher production were 3,274,752.45 kuntal and tomato accounting 283,648.27 kuntal during the year [3]. Habru district where this study conducted is one of naturally endowed areas for vegetable production due to its favorable agroecology and availability of irrigation water. It is mainly for commercial vegetable production in two rounds per year. In 2016/17 production year, about 7, 295 hectares cultivated for vegetables and 872,500 kuntal of vegetables produced in the district [12].

## 1.2 Statement of the problem

Vegetables and fruits are influenced by many factors, including: concentration of HMs in soil, composition and intensity of atmospheric deposition, including precipitations, phase of plant vegetation, agricultural technologies such as: irrigation with wastewater, the administration of organic and mineral fertilizers with the load of heavy metals, or application of pesticides which contain such chemical elements in their structure [7]. These toxic heavy metals are originated from different sources by different mechanisms of natural or anthropogenic process. The soil environmental, the irrigation water and the ground water problems directly affect the quality and the safety of the agricultural products including tomato. Thus, the fruit and vegetables growing in such area have ability to absorb and accumulate the heavy metals at different parts of the fruit and vegetables. For instance. The plants like tomato are highly contaminated HMs, if the community is utilized irrigation water that is coming from contaminated river or grown in a soil contaminated with HMs. Consequently, although many health benefits of fruit and vegetables, heavy metals that can be found on the surface and in the tissue of fruit and vegetables in different concentration range can pose a direct threat to human health [13].

Furthermore, the direct contact of contaminated irrigation water and soil with HMs also leads to many diseases including lung tissue damage, respiratory illness, liver and kidney failure and others. Chromium for instance is carcinogenic and can lead to nasal septum perforation, asthma and liver damage, whereas Ni, Cd and Cu has been reported to cause nasal and lung cancer [14]. North Wollo, particularly, Abuarie, is one of the potential farm lands used for the production of different types of vegetable and fruits by using both irrigation water. Moreover, farmers in the area have been used different types of fertilizers and pastes like herbicide and insecticide to increase the crop production and economic growth and in turn these dangerous chemicals accumulate in the soil and irrigation water. Hence, consumption of any agricultural products including tomato (largely produced in the area) produced in this area might be expected to have different health risks. Therefore, the present study was focused to determine the levels of selected heavy metals in soil, irrigation water and tomato along with estimating of health hazard influence by HMs at Abuarie irrigation farm land.

## **1.3 Objectives**

### **1.3.1 General Objective**

The general objective of the study was to quantify the levels of selected heavy metals in soil, irrigation water and tomato (*Solanum Lycopersicum*) with health hazard influence from Abuarie irrigation site, North Wollo Ethiopia.

### **1.3.2 Specific Objectives**

- To quantify the levels of Fe, Pb, Cu, Cr, Co, Zn, Ni and Cd in tomato, soil and irrigation water at the Abuarie irrigation site.
- To compare the concentration of HMs in soil, irrigation water and tomato with the standard value.
- To estimate carcinogenic and no-carcinogenic effect of the toxic heavy metals based on USEPA model.

## **1.4 Significance of the study**

The determination of toxic heavy metals in vegetables specially tomato, irrigation water and soil in the study area have been used as a baseline data sources for the inhabitants or the stake a holder which used to take remedial action or prevent further increment. Moreover, the out put of the study also used for the scholars who have an interest to do more in this area as a reference in the study area.

## 2. LITERATURE REVIEW

### 2.1 Vegetables

Vegetables are rich sources of vitamins, minerals, and fibers, and also have beneficial anti-oxidative effects. However, intake of heavy metal-contaminated vegetables may pose a risk to the human health. This is because, heavy metals have the ability to accumulate in living organisms and at elevated levels they can be toxic. It has been reported that prolonged consumption of unsafe concentrations of heavy metals through foodstuffs may lead to the chronic accumulation of the metals in the kidney and liver of humans causing disruption of numerous biochemical processes, leading to cardiovascular, nervous, and kidney and bone disease [15]. Eating vegetables in diet can have many health benefits by reducing many health related disease and used to convert the fats and carbohydrates into energy. Eating vegetable is one of the most important pathways for the human body to absorbed dietary mineral, necessary for its health development but unfortunately harmful element such as heavy metal [16].

*Solanum lycopersicum*, commonly known as tomato is an important fruit crop of Ethiopia in a warm season plant requiring an optimum temperature 20-24<sup>0</sup>C, grows on fertile moisture retentive soil. Mulching organic matter and nitrogen, phosphorus and potassium (NPK) favors the growth and to prevent weeds, reduces leaf diseases, helps in distribution of water and generally makes the tomato plant stronger. After flowering the fruits reach maturity in 50-60 days. Technically tomatoes are fruits rather than vegetables, and are consumed raw as well as cooked [17].

Tomatoes contribute to a healthy and well-balanced diet. They are rich in vitamins, minerals, proteins essential amino acids sugars and dietary fibers. They also contain vitamin C, vitamin E and low amounts of the water-soluble type B vitamins, thiamin, niacin and riboflavin. Tomatoes and tomato products are used as ingredients in many traditional dishes, because of their compatibility with other food ingredients and due to the concentration and availability of several nutrients in these products and to their wide spread consumption by humans all over the world However, heavy metals are one of a range of important types of contaminants that can be found on the surface and in the tissue of fresh tomatoes as well as processed tomato products. As a result, heavy metal accumulation in tomato and processed tomato products may pose a direct threat to human health [18].

### **2.1.1 Factors Affecting Heavy Metals Mobility and Bioavailability in Plants**

Plant uptake of trace elements is generally the first step of their entry into the agricultural food chain. Plant uptake is dependent on (i) movement of elements from the soil to the plant root, (ii) elements crossing the membrane of epidermal cells of the root, (iii) transport of elements from the epidermal cells to the xylem, in which a solution of elements is transported from roots to shoots, and possible mobilization, from leaves to storage tissues used as food (seeds, tubers, and fruit) in the phloem transport system [19].

Plant species, relative abundance and availability of necessary elements also control metal uptake rates. Abundant bio available amounts of essential nutrients can decrease plant uptake of non-essential but chemically similar elements. Bioavailability may also be related to the availability of other elements [20].

### **2.1.2 Heavy Metals in Vegetables**

Vegetables and fruits are very important part of the human diet as they contain proteins, carbohydrates, vitamins, minerals and trace elements. They contain both essential and toxic elements in various concentrations. Many researchers have shown that some common vegetables have ability of accumulating high level of metals from the soil. Distribution of heavy metals in plant body depends upon their concentration in soil and water as well as plant species and its population. Heavy metals play very important role in the metabolism and growth of plants and animals [21].

## **2.2 Waste water and Irrigation**

Wastewater may be defined as the combination of liquid wastes discharged from domestic households, farms, institutions, commercial and industrial establishments eventually mixed with groundwater, surface water, and storm water [22]. Wastewater has become an attractive option for conserving and expanding available water supplies. Wastewater can have many types of applications, including irrigation of agricultural land, aquaculture, landscape irrigation, urban and industrial uses, recreational and environmental uses, and artificial groundwater recharge. In principle, wastewater can be used for all purposes for which freshwater is used, given appropriate treatment [23].

The risks and benefits of wastewater use in agriculture is that Wastewater use in agriculture has substantial benefits for agriculture and water resources management, but can also pose

substantial risks to public health – especially when used untreated water for crop irrigation. There can also be chemical risks to plant health, and risks to the environment in the form of soil and groundwater pollution. Countries seeking to improve wastewater use in agriculture must reduce the risks, in particular those to public health, and maximize the benefits through properly planned, implemented and managed wastewater irrigation practices [24].

Heavy metals like, Pb and Cd have no beneficial effects in humans, and there was no known homeostasis mechanism for them. Rather they are generally considered the most toxic to humans and animals even at low concentrations. The metals considered in this study include micro-nutrient such as iron, zinc and copper and non-essential/toxic heavy metal which were toxic to plant when present in the soil at concentrations above tolerance levels for the non-essential metals, Cr, Pb and Cd are recognized as health hazardous and all have caused major health problems as a result of environmental pollution [65].

## **2.3 Soil**

Soils are complex mixtures of minerals, water, air, organic matter, and countless organisms that are the decaying remains of once-living things. It forms at the surface of land – it is the “skin of the earth.” Soil is capable of supporting plant life and is vital to life on earth. It has physical, chemical and biological properties that continually change [25].

Considering all these factors, soil is a naturally occurring mixture of mineral and organic matter with a definite form, structure, and composition. Soil is composed primarily of minerals that are produced from rock (the parent material) that is weathered - broken down into small pieces. The organic matter of the soil includes both living organisms and dead organisms. Soils have four major components: mineral matter, organic matter, air, and water[26]. Generally speaking, the average soil sample is 45% minerals, 25% water, 25% air, and 5% organic matter. The amount of air and water filling the pore space in the soil varies depending on the amount of precipitation, location, and water holding capability of the soil. The air and water content of the soil is essential for most living organisms [27].

### **2.3.1 Soil Pollution**

Soil pollution in agricultural areas surrounding big cities is a major environmental problem. Soil is often contaminated by human activities and this is reflected in the high horizontal and vertical variability brought about by the anthropogenic influence on soil formation and development [19]. Environmental pollution is posing significant public health risks worldwide, becoming a major concern in developing countries because of rapid economic

activities and poor waste management. It is challenging to establish an association between environmental pollution and health effects because of the nature of pathways to exposure, limited data availability and the absence of a monitoring system. Furthermore, associations between environmental pollution and health are difficult due to the occurrence of multiple exposures, and the latency period of effect estimated that about 25 – 30% of the total burden of disease in the world is related to environmental factors, including chemical toxicants. For example, reported that lead is believed to be responsible for 3% of cerebrovascular disease burden worldwide. It has been reported that the prevalence level of lead in the blood of children worldwide is estimated at 40%, where the risk is more concerning in developing countries [8].

### **2.3.2 Soil Pollution by Heavy Metals**

Pollution of the soil by heavy metals have become a serious issue due to a number of human activities, such as those related to the mining, mineral, smelting, and tannery industries. Environmental pollution by heavy metals, even if it is at low concentrations and the long-term cumulative health effects that go with it, is of major health concerns all over the world [28]. For instance bioaccumulation of lead (Pb) in the human body interferes with proper functioning of the mitochondria thereby impairing respiration as well as causing constipation, swelling of the brain, paralysis and could eventually lead to death [29].

## **2.4 Selected Toxic Heavy Metals under Study and Their source**

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. 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 [30].

### **2.4.1 Chromium**

Chromium is one of the metallic elements for which maximum concentrations in the environment are limited by the law due to its toxic properties. In nature it may exist in two oxidation states: (III) and (VI). Chromium is widely distributed in the earth's crust. It can exist in oxidation states of +2 to +6. Soils and rocks may contain small amounts of chromium, almost always in the trivalent state [31].

**Toxicity of Cr:** Medical warning was issued that inhalation of dust containing Cr in high oxidation states (IV) and (VI) was associated with malignant growth in the respiratory tract and painless perforation in nasal spectrum among trivalent and hexavalent states, being the most stable and common in terrestrial environments greatest threat because of its high solubility, its ability to penetrate cell membranes and its strong oxidizing ability [32].

#### 2.4.2 Cadmium

Cadmium (Cd) is a naturally occurring metal situated in the periodic table of the elements between zinc (Zn) and mercury (Hg), with chemical behavior similar to Zn. It generally exists as a divalent cation, complexes with other elements (e.g.  $\text{CdCl}_2$ ). Cd exists in the earth's crust at about 0.1 part per million, usually being found as an impurity in Zn or lead (Pb) deposits, and therefore being produced primarily as a byproduct of Zn or Pb smelting [33].

**Toxicity of Cd:** The Agency for Toxic Substances and Disease Registry reports that the average American ingests about 30  $\mu\text{g}$  Cd/day. However, only about one tenth of this amount is actually absorbed into the tissues. Intake of Cd can double if one smokes cigarettes because each cigarette contains about 2  $\mu\text{g}$  Cd. Acute doses (10-30 mg/kg-day) of cadmium can cause severe gastrointestinal irritation, vomiting, diarrhea, and excessive salivation, and doses of 25 mg  $\text{CdI}_2$ /kg body weight can cause death. Low-level chronic exposure to Cd can cause adverse health effects including gastrointestinal and hematological activities [34].

#### 2.4.3 Lead

Lead is an abundant heavy metal in the Earth, about 14 parts per million by weight or 1 part per million by moles. It rarely occurs in pure form in nature. Lead is usually found in ores, mostly with copper, zinc and silver. The most common lead mineral is galena, which is lead sulfide ( $\text{PbS}$ ). Other minerals include lead carbonate ( $\text{PbCO}_3$ ) and lead sulfate ( $\text{PbSO}_4$ ) [35].

**Toxicity of Pb:** Most of the accumulated lead is sequestered in the bones and teeth. This causes brittle bones and weakness in the wrists and fingers. Lead that is stored in bones can reenter the blood stream during periods of increased bone mineral recycling (i.e. pregnancy, lactation, menopause, advancing age, etc.). Mobilized lead can be re-deposited in the soft tissues of the body and can cause musculoskeletal, renal, ocular, immunological, neurological, reproductive, and developmental effects. Impaired kidney function and a weakened immune system can also result from over-exposure to lead [36].

#### **2.4.4 Copper**

Metallic copper is malleable, ductile and a good thermal and electrical conductor. It has many commercial uses because of its versatility. Copper is used to make electrical wiring, pipes, valves, fittings, coins, cooking utensils and building materials [37]. It is present in munitions, alloys (brass, bronze) and coatings. Copper compounds are used as or in fungicides, algicides, insecticides and wood preservatives and in electroplating, azo dye manufacture, engraving, lithography, petroleum refining and pyrotechnics [38].

#### **2.4.5 Iron**

Iron is the second most abundant metal on the earth's crust. Iron occupies the 26<sup>th</sup> elemental position in the periodic table. Iron is a most crucial element for growth and survival of almost all living organisms [39]

Iron (Fe) is a constant and necessary component of the animal and human. Used for the synthesis of hemoglobin and myoglobin muscle. The daily requirement of iron is covered in food. When the deficiency disorders are formed (anemia), which is treated with the administration of iron salts as a medicament. Iron is found in all organs and tissues, and the largest quantities are stored in the liver and spleen. Iron salts taken orally do not poison, but can produce side effects such as constipation and vomiting [40].

Iron deficiency is a highly prevalent form of under nutrition, affecting around one-fourth of the world's women and children, and is one of the most common causes of anaemia. We conducted comprehensive reviews of published literature linking iron deficiency to disability and death for four potential outcomes: child mortality, perinatal mortality, maternal mortality and mild mental retardation. For all of these outcomes, the best available data were prospective observational studies in which anaemia or haemoglobin concentration was the risk factor [41].

#### **2.4.6 Cobalt**

Cobalt released into the atmosphere is deposited on soil, and cobalt released to water may sorb to particles and settle into sediment or sorb directly to sediment. The distribution coefficient of cobalt (e.g. from water to sediment) varies due to pH, redox conditions, ionic strength, and dissolved organic matter concentrations [42]. Factors affecting the speciation and fate of cobalt in water, sediments, and soil include organic ligands such as humic acids, anions, pH, and redox potential. The soil mobility of cobalt is inversely related to the strength

of adsorption by soil constituents. Although plants may take up cobalt from the soil, the translocation of cobalt from the roots to other parts of the plant is not significant [43].

Measured atmospheric concentrations of cobalt are about  $1\text{ ng/m}^3$  or less in non-source areas and generally less than  $10\text{ ng/m}^3$  in source areas although higher concentrations in source areas have been reported. Surface water and groundwater concentrations of cobalt are low, below  $1\text{ }\mu\text{g/l}$  in pristine areas and  $1\text{--}10\text{ }\mu\text{g/l}$  in populated areas. Surface water and groundwater concentrations can be much higher in mining and agricultural areas as much as several hundred milligrams per liter. Mean cobalt concentrations in seawater have been reported to be less than  $1\text{ }\mu\text{g/l}$  [44].

## **2.5 Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES)**

ICP-OES is one of the most powerful and popular analytical tools for the determination of trace elements in a myriad of sample types. The technique is based upon the spontaneous emission of photons from atoms and ions that have been excited in a radio frequency discharge. Liquid and gas samples may be injected directly into the instrument, while solid samples require extraction or acid digestion so that the analyses were present in a solution [45]. The sample solution is converted to an aerosol and directed into the central channel of the plasma. At its core the inductively coupled plasma (ICP) sustains a temperature of approximately  $10000\text{ K}$ , so the aerosol is quickly vaporized [46].

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) is a multi-element method with very good detection power and offers the right conditions for reliable and rapid determination. By using ICP-OES, the sample organic matrix components do not contribute to interferences and have no effect on the final measurements, due to high plasma temperature [47].

In ICP-OES analysis the thermal excitation sources can populate a large number of different energy levels for several different elements at the same time. All of the excited atoms and ions can then emit their characteristic radiation at the same time. This results in the flexibility to choose from several different emissions and allows detection of multiple elements concurrently [48]. Simultaneous ICP instruments can screen for up to 60 elements in a single sample run of less than one minute, with no compromise of precision or detection limits. Simultaneous ICP instruments can screen for up to 60 elements in a single sample run of less than one minute, with no compromise of precision or detection limits. Sequential ICPs can provide analytical results for about five elements per minute [49].

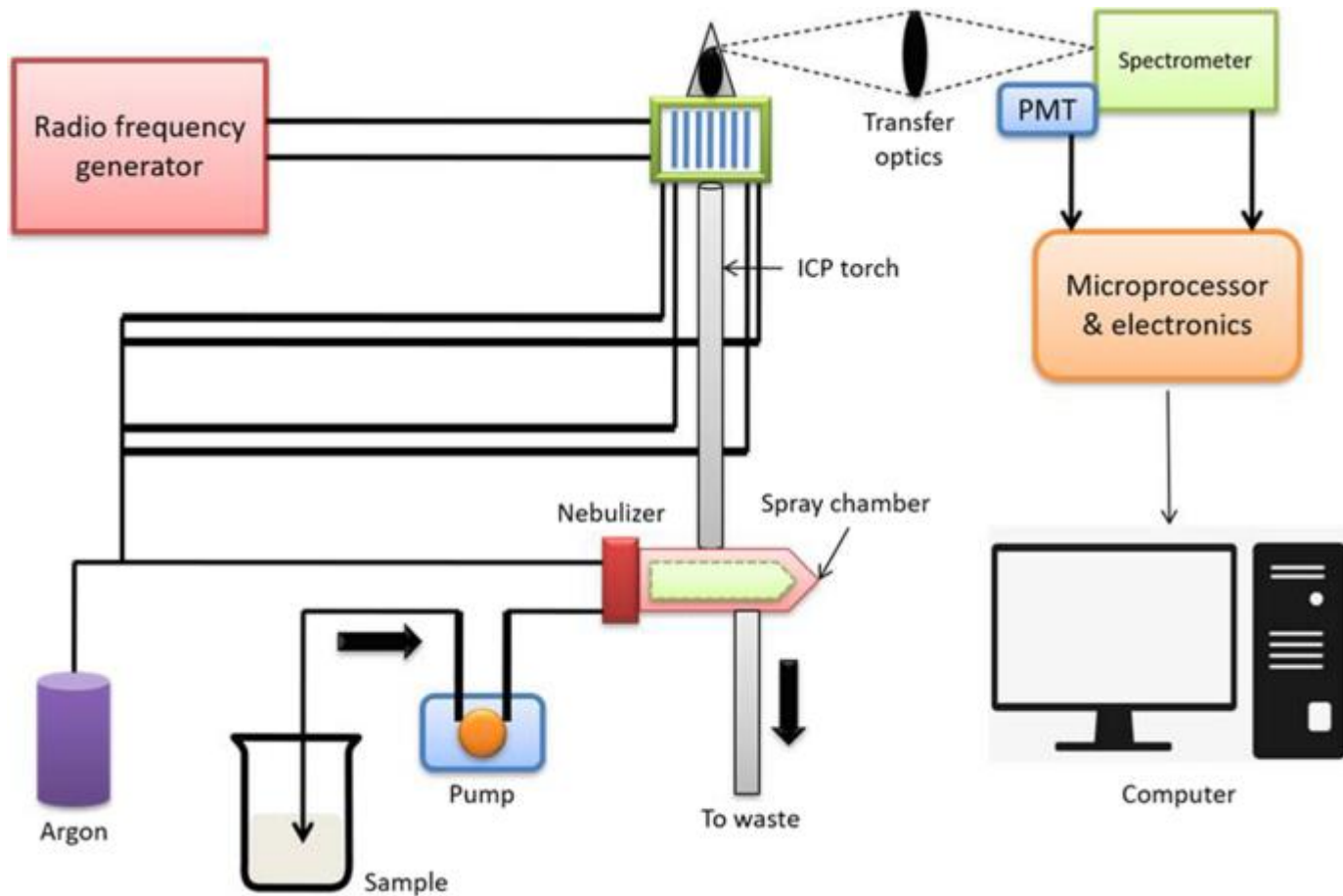
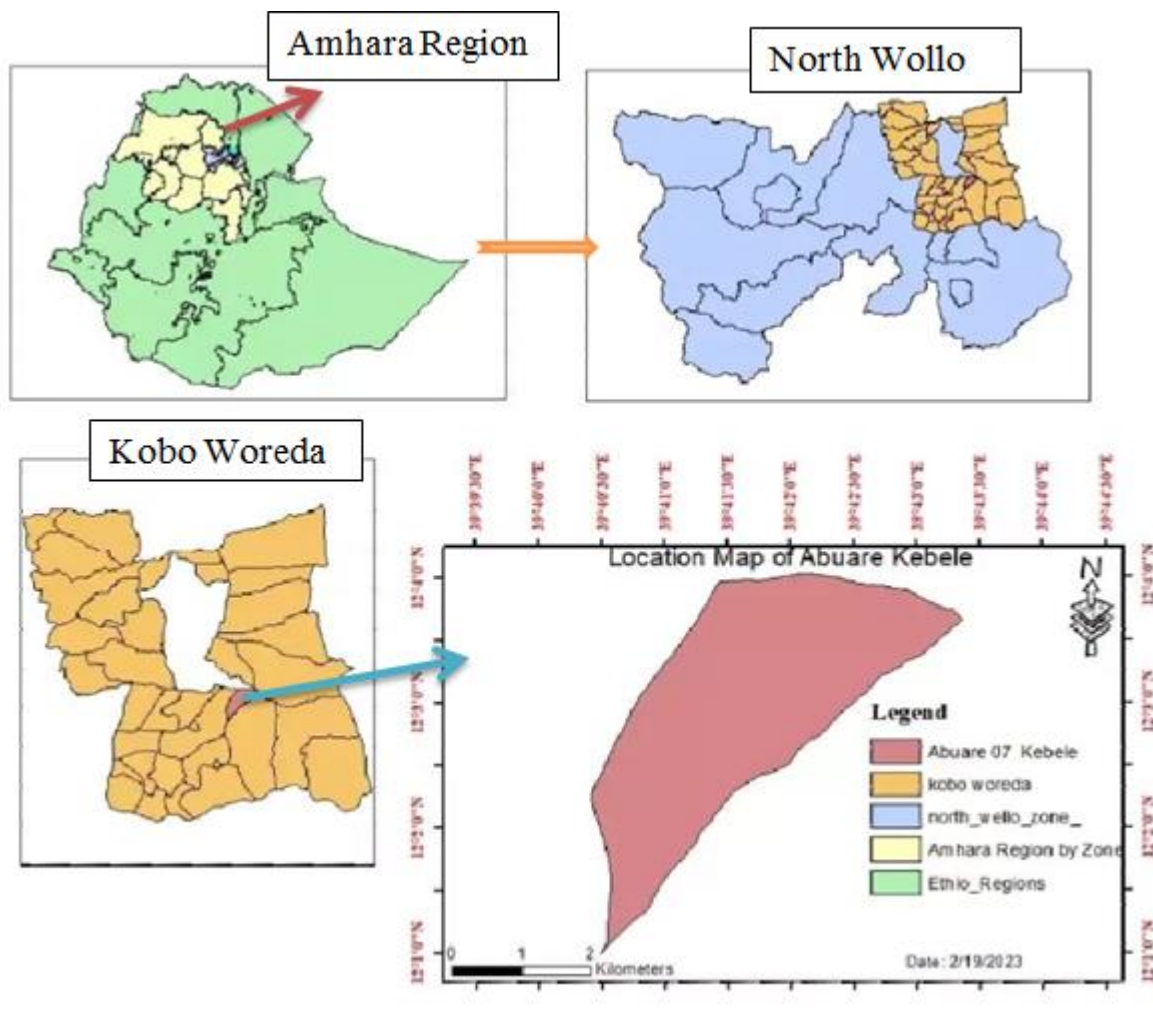


Figure 1: Schematic diagram of inductively coupled plasma-optical emission spectrometry (ICP-OES) [50].

### **3. MATERIALS AND METHODS**

#### **3.1 Description of the Study Area**

This study was conducted around Ray Kobo in the North Wollo, Amhara Region, Ethiopia. It is 60 km far from Woldia, which is administrative zone of Kobo or Raya Kobo [51]. The sampling place is located in the northeast corner of the North Wollo Zone, and bordered on the south by the Logiya River, on the west by Gidan, on the north by Tigray Region, and on the east by the Afar Region [52]. The landscape of this district is characterized by a broad fertile plain that is separated from the lowlands of the Afar Region by the Zobil Mountains, which are over 2000 meters high with mean annual rainfall of 670 mm that ranges from 500 mm to 850 mm and the temperature varies from a minimum of 19 °C to a maximum of 33 °C annually [53]. In general, the altitude of Kobo ranges from 1100 meters on the plains to slightly more than 3000 meters above sea level along the border with Gidan. Kobo, as well as the other seven rural districts of this Zone, has been grouped amongst the 48 districts identified as the most drought prone and food insecure in the Amhara Region at position 12°04'29.75"N with 39°40'05.40"E [54]. To combat increasing droughts and improve crop yields, two irrigation projects have been undertaken in this district by the Commission for Sustainable Agriculture and Environmental Rehabilitation in the Amhara Region and the affecting 302 hectares and benefiting 1,017 households [55]. The sampling site and geographical location of the sampling points was presented in Figure 2 and Table 1 respectively.



**Figure 2:** Geographical location of Kobo Woreda and the study area Abuarie

**Table 1:** Geographical location of sampling points and the sample type in the studding area

| Sample type      | Sampling Location | Latitude                    | Longitude                   | Altitude(m) |
|------------------|-------------------|-----------------------------|-----------------------------|-------------|
| *Soil and Tomato | 1                 | 12 <sup>0</sup> 04'31.54''N | 39 <sup>0</sup> 40'05.91''E | 1387        |
|                  | 2                 | 12 <sup>0</sup> 04'31.65''N | 39 <sup>0</sup> 40'05.89''E | 1376        |
|                  | 3                 | 12 <sup>0</sup> 04'30.24''N | 39 <sup>0</sup> 40'04.24''E | 1381        |
| Water            | 1                 | 12 <sup>0</sup> 04'31.97''N | 39 <sup>0</sup> 39'46.14''E | 1392        |
|                  | 2                 | 12 <sup>0</sup> 04'33.38''N | 39 <sup>0</sup> 39'51.00''E | 1492        |
|                  | 3                 | 12 <sup>0</sup> 04'33.11''N | 39 <sup>0</sup> 40'05.27''E | 1476        |

**Note:** \*soil and tomato collected in the same location

### 3.2 Apparatus and Equipment

ICP-OES Spectro-Arcos (Model: ARCOS FHS12, USA) was used for the determination of target heavy metals in irrigation water, tomato and soil samples, different size beakers,

Erlenmeyer flasks, funnels, filter paper (Whatman No.42), volumetric flasks, block digester, fume hood, Analytical balance (Model E11140, Switzerland), centrifuge, droppers, glass pipettes, spatula, measuring cylinders, plastic knife, Auger mining, vinyl gloves, steel less steel auger, conical flasks stirrer, polyethylene bags, GPS (global positioning satellite), drying Oven (Model: DHG-9123A) micropipette (Merck KGaA, Darmstadt, Germany) were used in this study.

### **3.3 Chemicals, Reagents and Standard Solutions**

All of the chemical used in this study were analytical grade reagent. Deionized water were used for all preparation and dilution purposes throughout the study. Nitric acid,  $\text{HNO}_3$  (70%), hydrogen peroxide,  $\text{H}_2\text{O}_2$  (30%) and hydrochloric acid,  $\text{HCl}$  (35%) (Research-Lab Fine Chem Industries Mumbai, India) were used for the digestion of samples. 1000 ppm stock standard solutions of the HMs (Cu, Pd, Cr, Zn, Co, Ni, Cd and Fe) were used to prepare calibration standard and spiking standard solutions.

### **3.4 Cleaning of Apparatus and Sample Containers**

All the apparatus using in study such as sample containers, mortar and pestles, crucible, glassware and plastics were washed using detergent and tap water, then rinsed with deionized water and soaked in 2 molar (M) nitric acid for 3 days to leach out adsorbed metal ion. Then, the apparatus were dried in Electric thermostatic heated dry box oven (202AB) at 105 °C for 5 hours [89].

### **3.5 Sample Collections and preparation**

#### **3.5.1 Collection and Preparation of Soil, Tomato and Irrigation Water Samples**

The top 0-30 cm depth of soil layer was considered as most of the soil's chemical interactions with the atmosphere are expected to take place [57]. Thus, the soil sample was collected from each three sub sampling points (from 0-30 cm depth) using soil steeliness steel auger and then the collected samples were mixed together to form 3 kg of composite a bulk sample. From a bulk sample, about 1 kg soil sample was taken, and then labeled, packed, and transported to laboratory then dried at room temperature for 3 days. The samples were then ground with a mortar and pestle to pass through a 1 mm sieve and homogenized. The dried, sieved, and homogenized soil samples were finally stored in polyethylene bags and kept in desiccators until digestion. On the other hand, the tomato sample was collected in similar manner of soil sample. Hence, 1 kg of tomato samples were taken from the composite 3 kg tomato samples, which made from three sampling point where the soil sample was taken.

Then, the tomato sample was tap water followed by repeated washing with de-ionized water to remove dirt, then the samples were air-dried for six days and further dried in an oven at 55 °C for 24 hours to remove moisture and maintain constant mass [93]. The dried representative sample of tomato was cut into small pieces using a steeliness steel knife and ground into fine powder using acid washed commercial mortar and pestle and then sieved to 1 mm mesh size. Finally, the dried samples were kept in a desiccator until the time of digestion.

Furthermore, 500 ml water samples from Golina river being used for irrigation purpose were collected from three different sites and form 1500 ml composite sample, then 250 ml water samples were taken by cleaned and dry polyethylene bottles. Finally, the sample was brought to the laboratory and it was kept in the refrigerator until needed for digestion.

### **3.6 Digestion of soil, tomato and irrigation water samples**

A 0.25 g of dried and powdered soil was digested with 20 ml aqua regia ( $\text{HCl}/\text{HNO}_3$  3:1) in a beaker (open-beaker digestion) on a thermostatically controlled hot plate. The digested were heated to near dryness and cooled to ambient temperature [61]. Then 5.0 ml of hydrogen peroxide was added in parts to complete the digested and the resulting mixture heated again to near dryness in a fume cupboard. The beaker walls were washed with 10 ml of deionized water and 5 ml HCl were added, mixed and heated again. The resulting digest was allowed to cool and put into 50 ml volumetric flask and fill it up to the mark with de-ionized water [62]. Finally, the solution was ready for Fe, Pb, Cd, Cu, Co, Cr, Ni and Zn analysis by ICP-OES.

A 0.5 g of homogenized tomato powdered sample was introduced from the desiccator into borosilicate digested flask. Then, 10 ml of acid mixture solution containing ( $\text{HNO}_3$ -  $\text{HCl}$ -  $\text{H}_2\text{O}_2$ ) with the ratio (8:1:1, v/v/v) was added into it, and then, the mixture was heated at 120 °C over 3 h on block digester. Next, the digested solution was filtered out into 100 ml volumetric flak [60]. Finally, the cooled solution was filled up to the mark with distilled water. All the solutions which used to determine the concentration of the target analyte of the sample were stored in refrigerator until the analysis was done.

First, the-sample bottles were shaken thoroughly by use of hand, and then a100 ml of the sample and 5 ml of concentrated nitric acid were mixed put in a conical flask. Secondly, the mixture was heated slowly at a temperature below 180 °C for two hour on a hot plate and evaporated to about 20 ml ensuring that the water did not boil, and then heating was continued after addition of 5 ml of fresh concentrated nitric acid by covering the beaker with a watch glass. Thirdly, 2 ml of concentrated hydrochloric acid was added and heated slightly

to dissolve any remaining residue. Fourthly, a few drops of hydrogen peroxide were then added to ensure complete digestion had taken place. Finally, the solution was filtered using the watts man filter paper and the filtrate was transferred to a 100 ml volumetric flask to cool and filled with deionized water until the mark of the flask [63].

### **3.7 Preparation of Standards and Analysis of Samples using ICP-OES**

A series of standard solution for each metal was prepared by dilution with 0.5% nitric acid from the standard stock solutions which is 1000 ppm in 3% nitric acid. Thus, all standard solutions were prepared in 50 ml volumetric flasks. Calibration curves were done for each element.

### **3.8 Method Validation and Recovery Test**

#### **3.8.1 Method Detection Limit (MDL) and Limit of Quantification (LOQ).**

The method detection limit (MDL) is defined as the lowest concentration of analyte that can be determined by the analytical method with a specific confidence limit [3]. Three replicate blank samples were digested using the same processes as the soil, tomato, and irrigation water samples for estimation of MDL. Thus, the standard deviation (SD) of the three replicate blanks was determined to obtain the Method Detection Limit (MDL), which is three times the standard deviation of the blank and ten times the standard deviation of the blank and equals the Limit of Quantification (LOQ) using standard formula 1 and 2, respectively.

$$\text{MDL} = 3 \times \text{SD} \quad \text{Equ 1}$$

$$\text{LOQ} = 10 \times \text{SD} \quad \text{Equ 2}$$

Where SD= Standard deviation of the blank

#### **3.8.2 Recovery test**

Method validation is the process of confirming that a certain analytical technique is appropriate for the intended use. A small and known amount of heavy metals from the stock solution were added or spiked into the soil, tomato, and irrigation water samples to be digested, and the concentrations of both spiked and non-spiked samples were read to test the effectiveness of the analytical process. The outcome was determined through calculation [85]. The relevant samples were digested using the same procedure, and the spiked and unspiked tomato, soil, and water samples were assessed under comparable circumstances. The percentage recoveries of the analytes were then determined using equation 3's formula. The percentage recoveries of the analytes were then calculated using equation 3's formula.

$$\% \text{Recovery} = \left( \frac{C_{\text{Minthespiksample}} - C_{\text{Minthenon spikesample}}}{\text{Amount added}} \right) \times 100 \quad \text{Equ}$$

3

Where, CM = concentration of metal of interest

### 3.9 Transfer Factor (TF)

The transfer factor (TF), which is frequently used in the scientific literature as a metric for the bio-transfer of heavy metals, was the ratio of the concentration of a heavy metal in a plant to the concentration of a heavy metal in soil. The heavy metal content of the soil that reached the tomato plants is indicated by the letter TF. To determine the degree of risk and related hazard due to ingestion as a result of heavy metal buildup in the edible portion of tomato vegetables, a transfer factor (TF) was determined.

$$TF = \frac{C_{\text{tomato}}}{C_{\text{soil}}} \quad \text{Equ 4}$$

Where: TF – transfer factor,  $C_{\text{tomato}}$  – metal content in tomato ( $\text{mg kg}^{-1}$ ),  $C_{\text{soil}}$  – metal content in soil ( $\text{mg kg}^{-1}$ )

### 3.10 Data Analysis

SPSS software version 26 was used to do statistical analysis, Pearson Correlation, and ANOVA (analysis of variance). The amounts of HMs were expressed as mean SD (standard deviation) in the soil, tomato, and water samples. The mean value of HMs in water, tomato, and soil are assessed, and their significance is assessed using ANOVA analysis. The HMs levels in each sample were also connected using Pearson correlation. A 95% confidence level was chosen in the study for all significant tests.

### 3.11 Health Risk Assessment

The most common sources of heavy metal in plants and vegetables are sewage sludge application, deposition from fossil fuel combustion, rock weathering and phosphate fertilizers. Heavy metal accumulates especially in the kidneys leading to dysfunction of the kidney with increased secretion of proteins in urine (proteinuria) and other effects [98]. Moreover, waste water irrigation and air deposition are also major pathway to heavy metals bioaccumulation in plants including tomato. Many studies in developing countries including a major part of Ethiopia are very susceptible to environmental pollution due to the activities and use of huge amount of fertilizers and HMs rich pesticides [99].

The potential health risks of HMs through consumption of tomato, contact of irrigation water and agricultural soil were assessed based on the Average daily dose (ADD), health risk index (HI) and the hazard quotient (HQ). Agricultural workers' exposure through ingestion and dermal contact of soil and irrigation water were also evaluated in a health risk assessment [64].

### 3.11.1 Average daily doses (ADD)

Residents may be exposed to HMs from the soil through a variety of routes, including cutaneous contact, inhalation, and oral absorption of soil particles. Additionally, HMs can also enter the body by the consumption of tomato and water. Using 5, 6, and 7 equations correspondingly, the estimated HMs intake from soil were expressed as the average daily dose, of inhalation, cutaneous exposure, and ingestion. While Equations 8 and 9 were used to evaluate the ADD of HMs by tomato consumption and irrigation water, respectively [95].

$$ADD_{oral} = \frac{Cs \times IngR \times CF \times EF \times ED}{BW \times AT} \times 10^{-6} \quad \text{Equ 5}$$

$$ADD_{inh} = \frac{Cs \times InhR \times EF \times ED}{BW \times AT \times PEF} \quad \text{Equ 6}$$

$$ADD_{derm} = \frac{Cs \times SL \times SA \times AF \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6} \quad \text{Equ 7}$$

$$ADD_{tomato} = \frac{Ct \times IngR \times EF \times ED}{BW \times AT} \times 10^{-6} \quad \text{Equ 8}$$

$$ADD_{water} = \frac{Cw \times IngR \times EF \times ED}{BW \times AT} \quad \text{Equ 8}$$

Where C metal is the heavy metal conc ( $\text{mg kg}^{-1}$ ), CF is the conversion factor. The conversion factor of 0.085 is to convert fresh vegetable weight to dry weight [95].  $ADD_{oral}$ ,  $ADD_{inh}$ ,  $ADD_{water}$  and  $ADD_{derm}$  are average daily doses taken by oral intake (exposure by non-dietary mouth intake of HM, e.g. dust or air-borne particles), inhalation, and dermal contact of soil dust (in  $\text{mg kg}^{-1} \text{ day}^{-1}$ ),  $ADD_{water}$   $ADD_{tomato}$  estimated average daily dose intake

through irrigation water ( $\text{mg L}^{-1} \text{ day}^{-1}$ ) and tomato ( $\text{mg kg}^{-1} \text{ day}^{-1}$ );  $C_s$  and  $C_t$  are HMs concentrations in soil and Tomato ( $\text{mg kg}^{-1}$ );  $C_w$  HMs concentrations irrigation water ( $\text{mg L}^{-1}$ ).  $\text{IngR}$  is the ingestion rate of soil dust and tomato;  $\text{InhR}$  is the air inhalation rate;  $\text{SL}$  is the skin adherence factor;  $\text{EF}$  is the exposure frequency;  $\text{ED}$  is the exposure duration;  $\text{AT}$  is the average time in days;  $\text{BW}$  is body weight;  $\text{PEF}$  is the particular emission factor  $\text{SA}$  is the skin area;  $\text{AF}$  is the adhesive factor, and  $\text{ABS}$  is the skin absorption factor.

The values of  $\text{IngR}$ ,  $\text{InhR}$ ,  $\text{SL}$ ,  $\text{EF}$ ,  $\text{ED}$ ,  $\text{AT}$ ,  $\text{BW}$ ,  $\text{PEF}$ ,  $\text{SA}$ ,  $\text{AF}$ , and  $\text{ABS}$  are described in Table 2 where  $\text{EF}$  is the exposure frequency ( $350 \text{ days year}^{-1}$ );  $\text{ED}$  is the exposure duration (54 years, we have used  $\text{FIR}$  is the food ingestion rate (metal in human consumption values for adult Ethiopian is  $65 \text{ g person}^{-1} \text{ day}^{-1}$ ) [102].  $\text{RfD}$  is the reference dose,  $\text{BW}$  is the average body weight (65 kg for adults vegetable consumer in Ethiopian); and  $\text{AT}$  is the average exposure time for non-carcinogens ( $\text{ED} \times 365 \text{ days/year}$ ) [103].

**Table 2:** The values of the parameters for the estimation of human exposure [75]

|             | Parameters                 | Unit                               | Value                                                                |
|-------------|----------------------------|------------------------------------|----------------------------------------------------------------------|
| <b>IngR</b> | ingestion rate             | $\text{mgday}^{-1}$                | 30                                                                   |
| <b>InhR</b> | inhalation rate            | $\text{m}^3 \text{day}^{-1}$       | 7.6                                                                  |
| <b>ABS</b>  | skin absorption factor     | -                                  | 0.001                                                                |
| <b>AF</b>   | adhesive factor            | -                                  | 0.07                                                                 |
| <b>BW</b>   | body weight                | Kg                                 | 65                                                                   |
| <b>SL</b>   | skin adherence factor      | $\text{mgcm}^{-2} \text{day}^{-1}$ | 0.07                                                                 |
| <b>ED</b>   | exposure duration          | Year                               | 40                                                                   |
| <b>EF</b>   | exposure frequency         | $\text{dayyear}^{-1}$              | 300                                                                  |
| <b>PEF</b>  | Particular emission factor | $\text{m}^3 \text{kg}^{-1}$        | $1.36 \times 10^9$                                                   |
| <b>SA</b>   | skin area                  | $\text{cm}^2$                      | 5700                                                                 |
| <b>CF</b>   | conversion factor          | -                                  | 0.085                                                                |
| <b>AT</b>   | Average time               | -                                  | For cancer, $70 \times 365$<br>For non-cancer $\text{ED} \times 365$ |

### 3.11.2 Hazard Quotient and Health Risk Index

The ratio of the toxic element's average daily exposure dose to its specific reference dose is known as the "hazard quotient," or "HQ." A severe health risk to humans exists when the hazard quotient (HQ) is greater than one, whereas there are no serious adverse effects on human health when HQ is less than one [96]. Equation 10 was used to determine the reference dose, which is particular to the trace element being assessed.

$$HQ = \frac{ADD}{RfD} \quad \text{Equ 9}$$

Where ADD is the average daily doses of the population in  $\text{mg day}^{-1} \text{ kg}^{-1}$  body weight and RfD is the reference dose ( $\text{mg kg}^{-1} \text{ day}^{-1}$ ) values for each metals

The general risk assessment is called the health risk index (HI). Any index or indicator may be used to calculate the risk index. Equation 11 was used to calculate the likelihood and impact index composite [102]:

$$HI = \sum_{k=1}^n HQ \quad \text{Equ 10}$$

Where HQ is hazard quotient in all three exposure per three sample

**Table 3:** RfD and CSF value of heavy metals at different sample type and exposure routes

| HMs       | RfD in soil        |                    |                    | RfD in tomato      |                    | CF for soil and water |                    |
|-----------|--------------------|--------------------|--------------------|--------------------|--------------------|-----------------------|--------------------|
|           | RfD <sub>Inh</sub> | RfD <sub>Der</sub> | RfD <sub>Ing</sub> | RfD <sub>Inh</sub> | CSF <sub>Der</sub> | CSF <sub>Inh</sub>    | CSF <sub>Ing</sub> |
| <b>Fe</b> | 0.00022            | 0.07               | 0.84               | 0.7                |                    |                       |                    |
| <b>Zn</b> | 0.3                | 0.06               | 0.3                | 0.3                |                    |                       |                    |
| <b>Cu</b> | 0.04               | 0.012              | 0.04               | 0.04               |                    |                       |                    |
| <b>Pb</b> | 0.00352            | 0.000525           | 0.0035             | 0.0035             | 0.0085             | 0.00008               | 0.085              |
| <b>Cr</b> |                    | 0.00005            | 0.003              | 0.003              | 0.0065             | 0.012                 | 42                 |
| <b>Cd</b> | 0.001              | 0.00001            | 0.001              | 0.001              | 6.3                | 0.0018                | 6.3                |
| <b>Ni</b> | 0.0206             | 0.0054             | 0.02               | 0.02               | 0.84               | 0.00024               | 0.84               |
| <b>Co</b> |                    | 0.016              | 0.02               | 0.0003             |                    |                       | 9.8                |

*Note the RfD for water sample is 0.06 mg.*

### **3.12 Carcinogenic risk assessment**

The carcinogenic analysis is realized by the evaluation of the probable cancer risks due to exposure to heavy metal by calculation of the CR through Equation 12. In fact, the CR is the incremental probability of a person to develop any type of cancer over a lifetime as a result of 24 h per day exposure to a given daily amount of a carcinogenic element for 70 years. The permissible limits of CR for one or more heavy metals are  $10^{-6} < CR < 10^{-4}$ . If the values of CR are greater than  $10^{-4}$ , it indicates the cancer risk effects human health; if CR is lower than  $10^{-6}$ , it did not considered harm health [105].

$$CR = ADD \times CSF \quad \text{Equ 12}$$

Where: CR= Cancer risk over a lifetime by individual heavy metal ingestion, CSF = cancer slope factor in ( $\text{mg kg}^{-1}\text{day}^{-1}$ ) in three exposure and ADD = Average daily dose ( $\text{mg kg}^{-1}$ )

## 4. RESULTS AND DISCUSSION

### 4.1 Calibration of the Instrument

Iron, Lead, Chromium, Zinc, Cobalt, Nickel and Cadmium in the digest of tomato, irrigation water and soil samples were determined by (ICP-OES). The calibration curve demonstrated strong linearity, with  $R^2$  values varied between 0.9957 and 0.9999, which were greater than the permitted level for linearity (0.995) [70]. The concentration of the working standards, correlation coefficient and calibration equation of the calibration curve for each metal [87] are shown in Table 4.

**Table 4:** Working standard concentration, correlation coefficient and calibration equation of each metals.

| HMs | Concentration of standards ( $\text{mgkg}^{-1}$ ) | Correlation coefficient | Calibration equation   |
|-----|---------------------------------------------------|-------------------------|------------------------|
| Pb  | 0.2,0.4,0.6,0.8,1.0,1.2,1.4,1.6                   | 0.9968                  | $Y = 901.52x - 3.3379$ |
| Cr  | 0.5,1.0,1.5,2.0,2.5,3.0,3.5,4.0                   | 0.9976                  | $Y = 6488.8x - 81.911$ |
| Zn  | 0.2,0.4,0.6,0.8,1.0,1.2,1.4,1.6                   | 0.9999                  | $Y = 33137x + 78.394$  |
| Co  | 0.5,1.0,1.5,2.0,2.5,3.0,3.5,4.0                   | 0.9957                  | $Y = 9354.2x - 192.78$ |
| Ni  | 0.5,1.0,1.5,2.0,2.5,3.0,3.5,4.0                   | 0.9967                  | $Y = 5234.6x - 65.04$  |
| Cd  | 0.2,0.4,0.6,0.8,1.0,1.2,1.4,1.6                   | 0.9973                  | $Y = 16752x + 189$     |
| Fe  | 1,2,3,4,5,6,7,8                                   | 0.9967                  | $Y = 10400x + 780.2$   |
| Cu  | 0.2,0.4,0.6,0.8,1.0,1.2,1.4,1.6                   | 0.9996                  | $Y = 39443x - 133.6$   |

### 4.2 Method Detection Limit and Limit of Quantification

As shown in the table 5 almost all the value of MDL and LOQ of the experimental result in each sample were greater than the detection limit of the ICP-OES instrument. This indicates that the instrument used was good sensitivity for the analysis of the concentration of the selected heavy metals (Fe, Cd, Cu, Cr, Pb, Zn, Ni and Co) in the sample.

**Table 5:** Instrument, Method Detection and limit of quantification of selected heavy metals.

| HMs | IDL<br>( $\text{mgkg}^{-1}$ ) | Soil sample            |                        | Tomato sample          |                        | Water sample          |                       |
|-----|-------------------------------|------------------------|------------------------|------------------------|------------------------|-----------------------|-----------------------|
|     |                               | MDL                    | LOQ                    | MDL                    | LOQ                    | MDL                   | LOQ                   |
|     |                               | ( $\text{mgkg}^{-1}$ ) | ( $\text{mgkg}^{-1}$ ) | ( $\text{mgkg}^{-1}$ ) | ( $\text{mgkg}^{-1}$ ) | ( $\text{mgL}^{-1}$ ) | ( $\text{mgL}^{-1}$ ) |

|    |       |      |      |       |      |       |      |
|----|-------|------|------|-------|------|-------|------|
| Fe | 0.002 | 0.10 | 0.35 | 0.006 | 0.02 | 0.021 | 0.07 |
| Cu | 0.001 | 0.06 | 0.21 | 0.003 | 0.01 | 0.003 | 0.01 |
| Ni | 0.007 | 0.10 | 1.00 | 0.009 | 0.03 | 0.009 | 0.03 |
| Zn | 0.002 | 0.03 | 0.10 | 0.006 | 0.02 | 0.003 | 0.01 |
| Co | 0.005 | 0.21 | 0.72 | 0.006 | 0.02 | 0.006 | 0.01 |
| Cr | 0.004 | 0.13 | 0.44 | 0.006 | 0.02 | 0.009 | 0.03 |
| Cd | 0.002 | 0.20 | 0.69 | 0.003 | 0.01 | 0.003 | 0.01 |
| Pb | 0.001 | 0.13 | 0.40 | 0.006 | 0.02 | 0.006 | 0.02 |

### 4.3 Recovery Test

The percentage recovery for the soil and irrigation water and tomato samples lie in the range of 80.2% – 105%, 79.8% – 105% and 81.7% – 94.7% respectively. The obtained results were in acceptable range which was not less than 70% and no greater than 125%. Thus, the method utilized in the present study were good reliable [86]. The details of the result is presented in table 6.

**Table 6:** Values of the percent recovery analysis for soil, tomato and irrigation water samples.

| HMs           | Concentration before spiking<br>metal (mg kg <sup>-1</sup> ) | Concentration after<br>spiking (mg kg <sup>-1</sup> ) | Amount<br>Added (mg kg <sup>-1</sup> ) | %Recovery |
|---------------|--------------------------------------------------------------|-------------------------------------------------------|----------------------------------------|-----------|
| Soil sample   |                                                              |                                                       |                                        |           |
| Fe            | 49020 ±275                                                   | 50,070.00 ±6.10                                       | 1000                                   | 105       |
| Ni            | 211.42 ±1.02                                                 | 306.75 ±0.231                                         | 100                                    | 95.3      |
| Co            | 300.00 ±35.5                                                 | 396.95 ±0.0229                                        | 100                                    | 100       |
| Cu            | 116.08 ± 0.49                                                | 149.63 ±4.534                                         | 40                                     | 83.8      |
| Zn            | 120.76 ±0.14                                                 | 160.87 ±0.763                                         | 50                                     | 80.2      |
| Cd            | 11.84 ±0.44                                                  | 15.97 ±0.135                                          | 5                                      | 82.7      |
| Pb            | 58.14 ± 0.7                                                  | 78.12 ±1.409                                          | 20                                     | 100       |
| Cr            | 168.69 ±0.68                                                 | 242.27 ±0.368                                         | 80                                     | 92        |
| Tomato sample |                                                              |                                                       |                                        |           |
| Fe            | 170.17 ± 1.98                                                | 186.50 ± 0.668                                        | 20                                     | 81.7      |
| Co            | 1.553 ±0.015                                                 | 3.394 ±0.038                                          | 2                                      | 92.1      |
| Cu            | 3.203 ±0.021                                                 | 6.628 ±0.044                                          | 4                                      | 85.6      |
| Cd            | 0.297 ±0.006                                                 | 2.115 ±0.021                                          | 2                                      | 90.9      |
| Pb            | 1.417 ±0.068                                                 | 3.224 ±0.021                                          | 2                                      | 90.3      |
| Cr            | 1.653 ±0.015                                                 | 3.033 ±0.02                                           | 1.5                                    | 92        |

|    |              |              |   |      |
|----|--------------|--------------|---|------|
| Ni | 2.257 ±0.074 | 4.151 ±0.022 | 2 | 94.7 |
| Zn | 4.980 ±0.085 | 8.382 ±0.047 | 4 | 85   |

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| Irrigation water sample |              |              |   |      |
|-------------------------|--------------|--------------|---|------|
| Fe                      | 0.240 ±0.003 | 7.952±0.076  | 8 | 96.4 |
| Co                      | 0.030 ±0.001 | 1.019 ±0.011 | 1 | 98.9 |
| Cu                      | 0.069 ±0.001 | 3.699 ±0.019 | 4 | 90.7 |
| Cd                      | 0.034 ±0.001 | 1.030 ±0.006 | 1 | 99.6 |
| Pb                      | 0.097 ±0.002 | 0.980 ±0.191 | 1 | 88.3 |
| Cr                      | 0.066 ±0.003 | 0.864 ±0.008 | 1 | 79.8 |
| Ni                      | 0.025 ±0.005 | 1.078 ±0.017 | 1 | 105  |
| Zn                      | 0.098 ±0.018 | 7.542 ±0.047 | 8 | 93   |

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### 4.3.1 Precision and Accuracy of Results

The analyst concerned with the question of precision (repeatability of results) that is the agreement between the set of result. In this study precision of the results were evaluated by relative standard deviation of the results of triplicate samples with triplicate measurements of each sample ( $n = 3$ ) were used for the analysis of metals in the given all samples. It also determined by standard deviation, variance and range of series of measurements of triplicate measurements ( $n = 3$ ) were used for the analysis of determination of heavy metals in the soil, water and tomato sample was done using ICP-OES. The precision of the method was expressed in the three replicate readings.

As shown in Table 6 the percentage recovery for the soil, water and tomato samples lies in the range 80.2 - 105%, 79.8 - 105.3% and 81.6% - 94.7% respectively, which are within the acceptable range for all metals in all samples. The obtained results were in acceptable range which was not less than 80% and no greater than 120% [58]. Thus, the results revealed that the digestion method analysis utilized in the present study has showed a good reliability.

### 4.4 Levels of Heavy Metals in Soil, Tomato and Irrigation Water Samples

The determination of toxic heavy metals in vegetables, especially tomatoes, irrigation water, and soil in the study area has been used as a baseline data source for the inhabitants or stakeholder groups to take remedial action or prevent further increment. Moreover, the output of the study is also used as a reference for scholars who have an interest in doing more in this area [88]. Loading and accumulation of heavy metals in the soil depend on different factors

such as the chemical form of elements, pH, organic matter content, texture and cation exchange capacity (CEC) of the soil. With increasing pH, organic matter content, CEC and clay, the percentage and availability of the metals are reduced. In addition, the existence of carbonate, sulphate, phosphate and sulphide in the soil creates an increase in the metal precipitation and consequently decrease their availability to the plants [89].

#### 4.4.1 Level of heavy metals in soil sample

As shown in Table 7 and Figure 3, the concentrations of heavy metals in soil samples were found to range from 170 to 0.29 mg kg<sup>-1</sup>, with the decreasing order being Fe > Zn > Cu > Ni > Cr > Co > Pb > Cd. The present investigation's analysis of the heavy metals revealed that Fe had the highest concentration, with values in Abuarie irrigation land of 49020 mg kg<sup>-1</sup>. My investigation's findings made it abundantly evident that the irrigation land's soil was slightly below the permittivity limit for iron, which is 50,000 mg kg<sup>-1</sup>. The amount of heavy metals in the soil in the Koka Ejersa area was reported to be lower than previous reported levels (52,760 mg kg<sup>-1</sup>) [12], while higher than 46426.67, 41410, 38430 mg kg<sup>-1</sup> in Mojo area under tomato and cabbage cultivation and Koka Negewe area respectively [77,12]. The high level of Fe might be due to its fourth most abundant element in the earth's crust next to oxygen, silicon and Aluminum.

Lead concentration of soil in this study was higher than (37.93 and 35.8) mg kg<sup>-1</sup> in under tomato and under cabbage cultivation respectively in Mojo [77], (43.6 and 37.3) mg kg<sup>-1</sup> in Koka Ejersa area and Koka Negewe area in Koka [12] While, lower than (0.55-80.86 and 0 - 61.56) mg kg<sup>-1</sup> winter and summer ranges respectively in Philippi hortico in South Africa [18]. Zn concentration were found in Abuarie irrigation was lower than 300 mg kg<sup>-1</sup> WHO/FAO safe limit. However the current study of Zn were higher than the other studies in Mojo, 98.86 mg kg<sup>-1</sup> Koka Ejersa 108.26 mg kg<sup>-1</sup> and Koka Negewe 97.76 mg kg<sup>-1</sup> [77,12]. Likewise, concentration levels of Cr in this study was higher than the other studies in Ziway near flower garden and Ginch town on which onion was grown (4.06, 71.85 mg kg<sup>-1</sup>) respectively. As well as, the mean concentration of Ni levels was also compared to other study conducted in other countries and Ethiopia. The level of Ni were higher than 35.58, 30.50, 35 and 40.33 mg kg<sup>-1</sup> in Mojo area and Koka Negewe and Ejersa in Ethiopia And also the reported value range both summer and winter season 0-9.91 and 0.8.5 mg kg<sup>-1</sup> in Phillipi in South Africa [77, 12]. The levels of Cd obtained in soil samples of current study were found to be 11.85 mg kg<sup>-1</sup> which was higher than the reference value of 3 mg kg<sup>-1</sup> and the

reported value of 5.3, 4.76, 6.03 and 4.36 under tomato cultivation in mojo, under cabbage cultivation, Koka Ejersa and Negewe area respectively [77,12] in the country. Also the mean concentration of Cd in my study were higher than in Phillipi South Africa reported value ranges in summer season 0.009-1.77 and in winter season 0.004 - 4.72 mg kg<sup>-1</sup>.

Copper (Cu) and cobalt (Co) were also found in higher concentration collected from sampling locations with concentration range of 116 mg kg<sup>-1</sup> for Cu and 300 mg kg<sup>-1</sup> for Co. The levels of Cu obtained in this study were found to be much higher than the WHO limit values of 100 mg kg<sup>-1</sup> and the reported value range of 2.58–72.95 mg kg<sup>-1</sup> in summer and 2.68-53.96 mg kg<sup>-1</sup> in winter season in Philippi south Africa [18], 35 mg kg<sup>-1</sup> in Koka Ejersa and 40.33 mg kg<sup>-1</sup> in Negewe [12]. Likewise, the level of Co obtained in this study were also found to be higher than soil reference value (50 mg kg<sup>-1</sup>) reported and other reported values in Mojo 15.13 mg kg<sup>-1</sup> and Koka Ejersa area 13.53 mg kg<sup>-1</sup> [77, 12]. Distribution of heavy metals in soil was continuously altered that might be due to various soil processes and different usage of agro-chemical application and other human activities at each sampling site under the influence of environmental factors [29].

In the other hand the results from this study showed that concentration value of Ni, Cu, Co, Cd and Cr in the samples were generally higher than the WHO/FAO maximum permissible limits. The remaining elements Fe, Zn and Pb were below the recommended value. The levels of these low concentration of heavy metals are indicative of low levels of contamination of farmlands were cultivated by these heavy metals in spite of increasing use of fertilizers and pesticides in modern agriculture, as well as emissions from other anthropogenic sources. Even though these heavy metal concentrations fell below the critical permissible concentration level in most heavy metals, it seems that their persistence in the soils of the study site may lead to increased uptake of these heavy metals by plants.

**Table 7:** Concentration of selected heavy metals in soil, tomato and irrigation water samples with the recommended value.

| HMs       | Soil sample in mg kg <sup>-1</sup> |             |               | Tomato sample in mg kg <sup>-1</sup> |      |               | Water sample in mg L <sup>-1</sup> |             |               |
|-----------|------------------------------------|-------------|---------------|--------------------------------------|------|---------------|------------------------------------|-------------|---------------|
|           | Mean                               | WHO/<br>FAO | USEPA<br>2002 | Mean                                 | WHO  | USEPA<br>2012 | Mean                               | WHO/<br>FAO | USEPA<br>2012 |
| <b>Fe</b> | 49,020±275                         | 50,000      | -             | 170±1.98                             | 150  | -             | 0.24±0.003                         | 0.3         | 5             |
| <b>Ni</b> | 211±1.02                           | 50          | -             | 2.25±0.074                           | 0.02 | -             | 0.025±0.005                        | 0.02        | 0.2           |
| <b>Cu</b> | 116±0.49                           | 100         | 160           | 3.20±0.021                           | 2    | 1.3           | 0.069±0.001                        | 0.01        | 1             |

|           |            |     |     |            |      |       |             |       |       |
|-----------|------------|-----|-----|------------|------|-------|-------------|-------|-------|
| <b>Co</b> | 300±35.5   | -   | -   | 1.55±0.015 | 0.17 | -     | 0.03±0.001  | -     | 0.05  |
| <b>Zn</b> | 121±0.14   | 300 | 300 | 4.98±0.085 | 1.5  | -     | 0.098±0.018 | -     | -     |
| <b>Cd</b> | 11.85±0.44 | 3   | 3   | 0.29±0.006 | 0.2  | 0.005 | 0.034±0.001 | 0.003 | 0.005 |
| <b>Pb</b> | 58.14±0.7  | 100 | -   | 1.41±0.068 | 0.5  | 0.005 | 0.097±0.002 | 0.05  | 0.015 |
| <b>Cr</b> | 169±0.68   | 100 | 150 | 1.65±0.015 | 1.2  | 0.5-1 | 0.066±0.003 | 0.1   | 0.1   |

#### 4.4.2 Level of Heavy Metals in Tomato Sample:

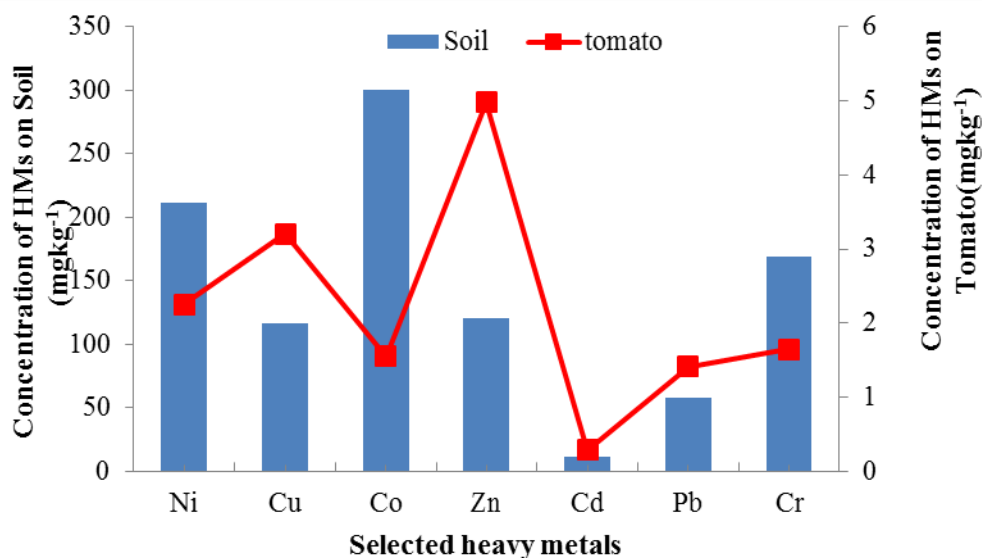
All the concentrations of heavy metals in tomato (*Solanum lycopersicum*) samples around Kobo area irrigation lands have been investigated and the result were found above the permissible limits given by WHO and USEPA. The levels of heavy metals in tomato samples were found to be in the range of 170 to 0.29 mg kg<sup>-1</sup> with the decreasing order of Fe > Zn > Cu > Ni > Cr > Co > Pb > Cd presented in Table 7. The results of the investigation have shown that the mean levels of iron were 170 mg kg<sup>-1</sup> (dry weight) in tomato sample analyzed which is higher than the recommended value of 150 mg kg<sup>-1</sup>. The level of heavy metals in tomato vegetable varies by the ability of its accumulation of some of these elements selectively. Bioavailability of the elements depends on the nature of their association with the constituents of a soil, pH, conductivity, salinity of irrigation water and soil. Additional sources of these elements for plants are rainfall, atmospheric dusts, plant protection agents and fertilizers that can be absorbed through the leaf blades and transfer to the fruit [71]. In this study, high concentration of these elements present in the parts of the plant may be due to the type of soil and the absorption ability of the plants to get the trace heavy metals from the polluted soils and their ability to accumulate heavy metals in their tissues as well as cultivation of different tomato species and application of displease do not repeat different methods of farming.

All the concentration of these selected heavy metals in tomato sample were above the maximum permissible limit set for tomato sample by FAO/WHO. This may be due to different usage of agro-chemical application and other human activities at each sampling site. The general trend for heavy metals content in soil samples was decline in the following order: Fe > Zn > Cu > Ni > Cr > Co > Pb > Cd. The high concentration of Fe and the other trace heavy metals present in the parts of the plants may be due to the absorption ability of the plants to get the trace heavy metals from the polluted soils. Iron as an essential element for all plants has many important biological roles in the processes as diverse as photosynthesis, chloroplast development and chlorophyll biosynthesis that is why it has highest value compared from other metals [73].

The levels Pb, Cu, Cd and Cr metals in tomato sample were found to be 1.4, 3.2, 0.29 and 1.65 mg kg<sup>-1</sup>, respectively, which is higher than the other studies conducted in Ziway (Near flower garden) 0.48, 0.39, 0.025 and 0.32 and far flower garden of 0.399, 0.16, 0.013 and 0.11 respectively [31], while lower than the values in Mojo area under tomato cultivation 3.63, 16.27, 0.56 and 1.69 mg kg<sup>-1</sup> and under cabbage cultivation 7.56, 9.42, 1.56 and 4.63 mg kg<sup>-1</sup> respectively [77].

For lead in vegetables, the safe limit is 0.2 mg kg<sup>-1</sup>, and for zinc, it is 20 mg kg<sup>-1</sup>, according to the Chinese Department of Protective Medicines [90]. According to the food being evaluated, the nation or organization occasionally, and various heavy metals, there are different recommended limits for each. In certain nations, the health sectors have documented safe levels of heavy metals, while in others, there is no such document to direct the consumption of heavy metals by its population [91]. According to the guidelines set forth by the WHO and FAO, the amount of heavy metals in the average person's daily consumption is below the level considered safe and has no impact on those who work with tomato plants at the sample location.

From the reported literature concentration value of selected heavy metals in tomato sample in Koka Ejersa area found to be 56.06, 0.90 and 0.33 mg kg<sup>-1</sup> and in Koka Negewe area 70.66, 1.33 and 0.46 were much lower concentration than the data we have obtained Fe, Ni and Co which is 170, 2.25 and 1.55 mg kg<sup>-1</sup> respectively, but the concentration of Zn in koka Ejersa area, 17.86 mg kg<sup>-1</sup> and Koka Negewe area, 18.16 mg kg<sup>-1</sup> [12], were higher than 4.98 mg kg<sup>-1</sup> of my study value at Abuarie irrigation site as shown in the table 7 and figure 3.



**Figure 3: Concentration of heavy metals on soil and tomato sample**

#### 4.4.3 Level of Heavy Metals in irrigation water Sample

As shown in Table 7, the result obtained revealed that the concentration of the heavy metals in irrigation water were found to be in the order of  $\text{Fe} > \text{Zn} > \text{Pb} > \text{Cu} > \text{Cr} > \text{Cd} > \text{Co} > \text{Ni}$  with the value ranged from 0.24 to 0.025 mg L<sup>-1</sup>. Almost all these concentration data ( Ni, Cu, Cd, Pb and Cr) were found in line with heavy metal concentration of irrigation water collected in winter (0-0.06, 0-0.09, 0-0.06, 0-0.12 and 0-0.16) and summer (0-0.05, 0-0.07, 0-0.05, 0-0.14 and 0-0.23) mg L<sup>-1</sup> cropping seasons from the Philippi horticultural area south Africa [96].

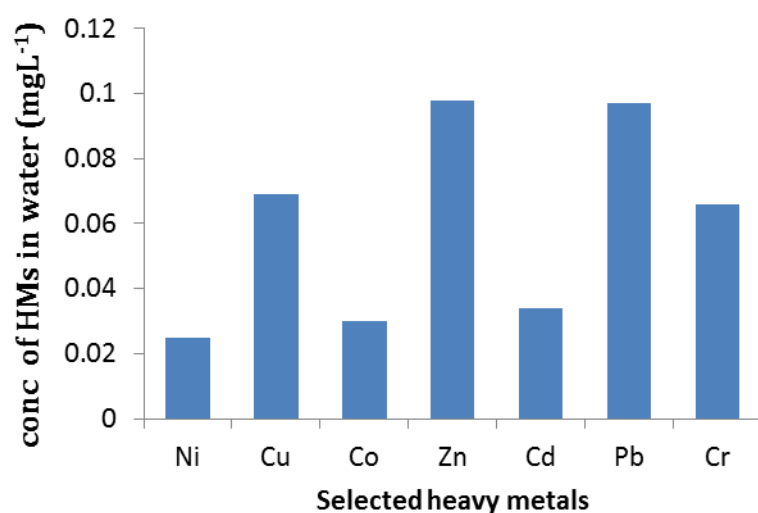
Even though the concentration of iron was recorded the highest one but iron, chromium and cobalt concentrations in Abuarie irrigation water sample were below the recommended maximum concentration (RMC) value of WHO, and USEPA on the Table 7. On the other side the concentration of nickel, copper, cadmium and lead on this study found to be above the WHO primitive value. So this high concentration of trace heavy metals (Cd, Pb, Ni and Cu) containing Irrigation water may be cause to be increase soil acidity and diminish essential phosphorous and molybdenum in soil [78].

Lead was one of the metals that have the most damaging effects on human health. A concentration of lead in the irrigation water samples was 0.097 mg L<sup>-1</sup>. The lead value was higher than recommended limit in irrigation water set by WHO and USEPA. This makes the water unsuitable for human consumption as Pb was known to be toxic even at low levels with

resultant ill-health effects as chronic exposure has been linked to growth retardation in children.

The mean concentration of heavy metals in water ranges from 0.025 mg L<sup>-1</sup> (Ni) to 0.24 mg L<sup>-1</sup> (Fe). Almost all the concentration of Ni, Cd, Pb and Cu were above while Fe, Cr and Co were below maximum permissible limit set for water sample by FAO/WHO. The general trend for heavy metals content in water samples was decline in the following order: Fe > Zn > Pb > Cu > Cr > Cd > Co > Ni. As shown in Table 7 and figure 4, the recorded results of accumulated iron, zinc, copper and lead in irrigated water sample showed relatively higher values for lands irrigated from Golina river around the Abuarie irrigation site. This indicates that they were used chemicals for the difference purpose like pesticide and herbicide might contain more sources of these metals from the agricultural waste such as chemicals.

In general the concentration of heavy metal in the irrigation water sample were lower when compeer to the heavy metal concentration of the soil sample and the tomato sample which means the source of heavy metals in the tomato sample come from the soil. Because the concentration of heavy metal in the soil sample was gravy grate than the water.



**Figure 4:** Concentration of selected heavy metals in water Samples

#### 4.5 Comparison of HMs Concentration in Soil, Tomato and Irrigation Water

Up on comparing the levels of heavy metals in tomato and the growth media soil and irrigation water, all the concentration of essential and nonessential heavy metals in soil were the highest than tomato and water sample. This indicates that only a small portion of soil

metals was transferred to the tomato and the root acts as a barrier to the translocation of heavy metals within tomato [72]. This may reveal that the main source of metal contents of tomato was from their soil content which might be affected by chemical use for farm, the environmental interferences like pesticides, fertilizers and other additives that farmers used. In addition, the variations in transfer factor among metals in the tomato may be attribute to differences in the concentration of metals in the soil and differences in element uptake by tomato.

Furthermore, the level of heavy metals concentration of the current study in soil sample and tomato samples from farm irrigated with the water in the Abuarie irrigation site were compared reported literature values and the details are given in table 8.

**Table 8:** Comparison of HMs concentration with reported result for tomato, Irrigation water and soil samples

| Heavy metals in mg kg <sup>-1</sup> |        |        |        |      |        |        |        |        |           |
|-------------------------------------|--------|--------|--------|------|--------|--------|--------|--------|-----------|
| Sample                              | Fe     | Ni     | Cu     | Co   | Zn     | Cd     | Pb     | Cr     | Reference |
| Soil                                | 49,020 | 211.42 | 116.08 | 300  | 120.76 | 11.85  | 58.14  | 168.69 | CS        |
|                                     | 11.25  | 0.208  | 0.25   | 0.31 | 8.03   | BDL    | BDL    | 23     | [77, 78]  |
|                                     | 15.25  | 0.132  | 0.65   | 0.37 | 8.79   | 0.0115 | 0.155  | 6.6    | [79, 80]  |
| Tomato                              | 170    | 2.25   | 3.20   | 1.55 | 4.98   | 0.29   | 1.41   | 1.65   | RT        |
|                                     | 3.2    | 5.70   | 0.045  | 1.2  | 3.8    | 0.2    | 5.5    | 4.94   | [81, 82]  |
|                                     | 12     | BDL    | 0.900  | 0.8  | 3.28   | BDL    | 0.004  | 0.070  | [83, 84]  |
| irrigation<br>water                 | 0.24   | 0.025  | 0.069  | 0.03 | 0.098  | 0.034  | 0.097  | 0.066  | Cw        |
|                                     | -      | 0-0.05 | 0-0.09 | -    | 0-0.07 | 0-0.05 | 0-0.12 | 0-0.16 | [18]      |
|                                     | -      | -      | 1.8    | -    | 12.8   | 0.012  | 2.04   | 1.1    | [80]      |

*Note: CS current study on soil, CT current study on tomato, sample, CW current study on water,*

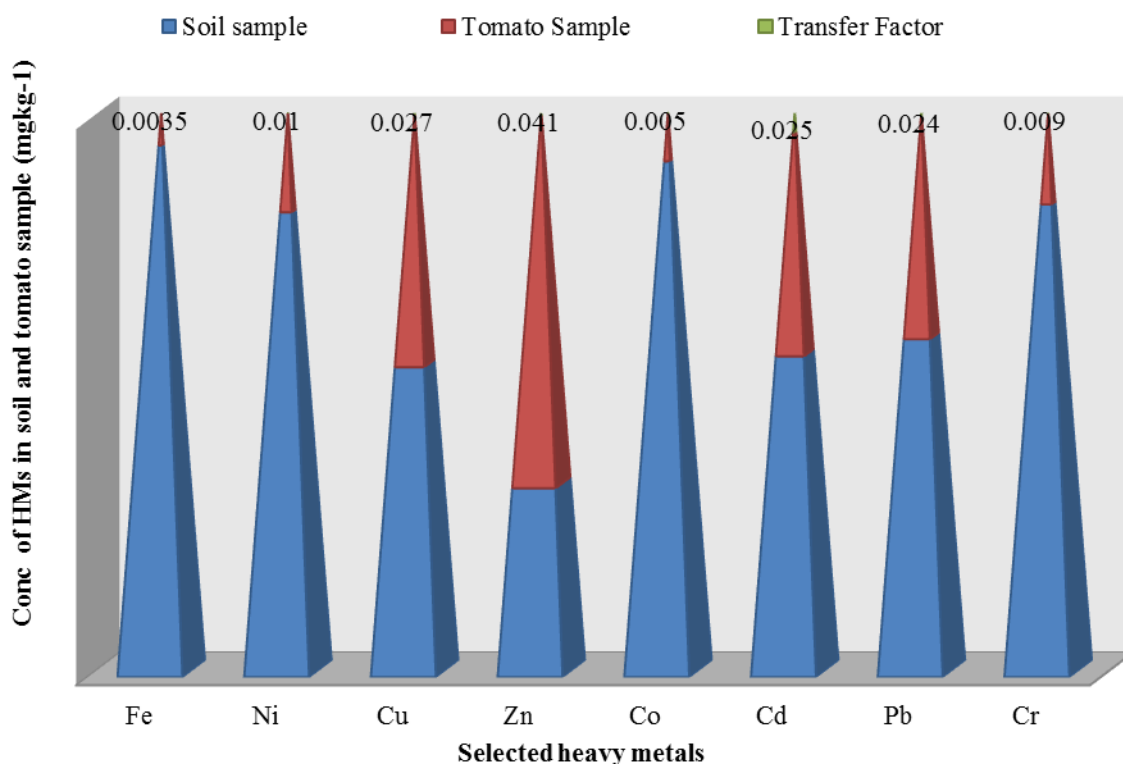
As it was seen in Table 8 the concentration of all selected heavy metals in this study except Ni, Pb and Cr in tomato were greater than the reported results but the concentrations of irrigation water in the current study were lower than the review results of irrigation water sample at the study area of Banglabazar at the country Bangiladish. In the same way all the concentration of the heavy metals in the soil sample were greatly higher than the concentration on the review sample. These might be due to the used different chemicals like fertilizers and pesticides was the best sources for heavy metals in these irrigation area and so the environment was highly affect by contaminated heavy metal from the farm chemicals.

#### 4.7 Heavy Metal Transfer Factor (TF) from Soil to tomato

**Table 9:** Transfer factors (TF) for heavy metals from soil to tomato plants

|               | Heavy metals in mg kg <sup>-1</sup> |       |       |       |       |       |       |       |
|---------------|-------------------------------------|-------|-------|-------|-------|-------|-------|-------|
|               | Fe                                  | Ni    | Cu    | Zn    | Co    | Cd    | Pb    | Cr    |
| <b>Soil</b>   | 49,020                              | 211   | 116   | 120   | 300   | 11.85 | 58.14 | 168   |
| <b>Tomato</b> | 170                                 | 2.25  | 3.20  | 4.98  | 1.55  | 0.29  | 1.41  | 1.65  |
| <b>TF</b>     | 0.0035                              | 0.010 | 0.027 | 0.041 | 0.005 | 0.025 | 0.024 | 0.009 |

In the present study, the TF of different heavy metal from soil to tomato vegetable are presented in Table 9. Thus, the TF value were ranges from 0.0035 (Fe) – 0.041 (Zn) as listed the trend of TF for heavy metal in tomato samples investigated were in order; Zn > Cu > Cd > Pb > Ni > Cr > Co > Fe. Higher transfer factors reflect relatively poor retention in soils or greater efficiency of tomato vegetables to absorbs metals while low transfer factor reflects the strong sorption of metals to the soil colloids [76]. Relative to the other heavy metals, the highest TF values were found to be 0.041 and 0.027 for Zn and Cu respectively. However the transferability of all the selected heavy metal elements (Fe, Pb, Co, Cr, Cu, Zn, Ni and Cd) were less than 1 which is metal bioavailability or mobility of these heavy metals with a natural occurrence in the soil might be very low and there was little the transfer factor transfer ratios. Therefore the transfer factors of all elements are within normal range in plant [98].



**Figure 5:** The level of HMs in soil and tomato along with the transfer of HMs from soil totomato (note that the data labeled value indicates the TF of each elements)

## 4.8 Correlation Analysis of Heavy Metals

### 4.8.1 Pearson Correlation

The Pearson correlation coefficient ( $r$ ) indicates that how far away all these data points are the best fit through the data of variables and the measure of the strength of linear association between variables. High correlation coefficient (near +1 or -1) means a good relation between two variables. If the correlation coefficient( $r$ ) is +1, there is a strong positive correlation relationship between the two variables which have directly related. Whereas if the correlation coefficient ( $r$ ) is -1, there is a strong negative correlation between the two variables which have inversely proportional relation. The range of the correlation values  $r < 0.2$  (no correlation), when  $r$  is between (0.20-0.39) low correlation, (0.50 – 0.69) moderate correlation, and if  $r$  is greater than 0.70 have highly correlated [99].

Generally from Table 10 the results of the Pearson correlation coefficients between heavy metals concentration in soil, tomato and irrigation water samples are summarized as follow.

**Table 10:** Pearson correlation coefficients between heavy metals concentration.

| In soil sample   |          |        |          |         |        |         |        |    |
|------------------|----------|--------|----------|---------|--------|---------|--------|----|
| HMS              | Cd       | Co     | Cr       | Cu      | Fe     | Ni      | Pb     | Zn |
| <b>Cd</b>        | 1        |        |          |         |        |         |        |    |
| <b>Co</b>        | -0.461   | 1      |          |         |        |         |        |    |
| <b>Cr</b>        | -0.952   | 0.711  | 1        |         |        |         |        |    |
| <b>Cu</b>        | 0.161    | -0.950 | -0.456   | 1       |        |         |        |    |
| <b>Fe</b>        | -0.701   | -0.310 | 0.449    | 0.591   | 1      |         |        |    |
| <b>Ni</b>        | -0.212   | 0.965  | 0.501    | -0.999* | -0.549 | 1       |        |    |
| <b>Pb</b>        | 0.914    | -0.781 | -0.994   | 0.548   | -0.351 | -0.591  | 1      |    |
| <b>Zn</b>        | -0.229   | -0.759 | -0.081   | 0.924   | 0.855  | -0.903  | 0.186  | 1  |
| In tomato sample |          |        |          |         |        |         |        |    |
| <b>Cd</b>        | 1        |        |          |         |        |         |        |    |
| <b>Co</b>        | 0.189    | 1      |          |         |        |         |        |    |
| <b>Cr</b>        | -0.945   | 0.143  | 1        |         |        |         |        |    |
| <b>Cu</b>        | -0.277   | 0.891  | 0.577    | 1       |        |         |        |    |
| <b>Fe</b>        | 0.945    | -0.143 | -1.000** | -0.577  | 1      |         |        |    |
| <b>Ni</b>        | 0.313    | 0.992  | 0.015    | 0.826   | -0.015 | 1       |        |    |
| <b>Pb</b>        | -0.297   | -0.994 | -0.032   | -0.835  | 0.032  | -1.000* | 1      |    |
| <b>Zn</b>        | 0.912    | 0.575  | -0.728   | 0.141   | 0.728  | 0.675   | -0.662 | 1  |
| In tomato sample |          |        |          |         |        |         |        |    |
| <b>Cd</b>        | 1        |        |          |         |        |         |        |    |
| <b>Co</b>        | -1.000** | 1      |          |         |        |         |        |    |
| <b>Cr</b>        | -0.500   | 0.500  | 1        |         |        |         |        |    |
| <b>Cu</b>        | -0.500   | 0.500  | -0.500   | 1       |        |         |        |    |
| <b>Fe</b>        | 0.982    | -0.982 | -0.655   | -0.327  | 1      |         |        |    |
| <b>Ni</b>        | 0.503    | -0.503 | 1.000**  | 0.497   | 0.657  | 1       |        |    |
| <b>Pb</b>        | 0.500    | -0.500 | 1.000**  | 0.500   | 0.655  | 1.000** | 1      |    |
| <b>Zn</b>        | 0.277    | -0.277 | 0.693    | -0.971  | 0.091  | -0.691  | -0.693 | 1  |

\*\**. Correlation is significant at the 0.01 level (2-tailed).* \**. Correlation is significant at the 0.05 level (2-tailed).*

The results from the Table 10 indicated that most metal pairs have strong and positive correlations on **soil** sample. Based on these there were strong positive correlation between Co with Cr and Ni, Pb with Cd ( $r = 0.914$ ), Zn with Cu and Fe. This correlation shows that the elements are closely associated. There were also moderate positive correlations between Fe with Cu ( $r = 0.591$ ) and Ni with Cr ( $r = 0.501$ ). Some metal pairs have Strong negative

correlations were found between Cd with Cr and Fe, Cu with Co and Ni with Cu, Pb with Co and Cr, Zn with Co and Ni. There are moderate negative correlations were found between Ni with Fe and Pb.

However some coordination of selected heavy metals like Cu with Cd, Fe with Co, Ni with Cd, Zn with Cd, Zn with Cr and Zn with Pd have the value close to zero in both direction shows that they have almost no correlation between them.

In **tomato** sample the elements between Cu with Co ( $r = 0.891$ ), Fe with Cd ( $r = 0.945$ ), Ni with Co and Cu, Zn with Cd and Fe ( $r = 0.728$ ) has strong and positive correlation. This correlation shows that the elements are closely associated. There were also moderate positive correlations between Cu with Cr, Zn with Co and Ni.

Most of metal pairs have strong negative correlations between Cr with Cd ( $r = -0.945$ ), Fe with Cr ( $r = -1.000^{**}$ ), Pb with Co, Cu and Ni, and Zn with Cr. Moderate negative correlations were found between Fe with Cu and Zn with Pb. Some pair of heavy metals between of Co with Cd, Cr with Co, Cu with Cd, Fe with Co, Ni with Cr and Fe, Pb with Cr and Fe and Zn with Cu have the value close to zero in both direction shows that they have almost no correlation between them.

The results of correlation coefficients between each elements from **irrigation water** samples were strong positive correlation between Fe with Cd and Pb with Ni. This correlation shows that the elements are closely associated. There were also moderate positive correlations between Cr with Co ( $r = 0.500$ ), Cu with Co ( $r = 0.500$ ), Ni with Cd and Fe, Pb with Cd, Cu and Fe and Zn with Cr. Strong negative correlations of selected heavy metals in irrigation water were found between Co with Cd ( $r = -1.000$ ), Fe with Co ( $r = -0.982$ ), Ni with Cr ( $r = -1.000$ ), Pb with Cr ( $r = -1.000$ ) and Zn with Cu ( $r = -0.971$ ). There are moderate negative correlations between Cr with Cd, Cu with Cd and Cr, Fe with Cr ( $r = -0.655$ ), Ni with Co ( $r = -0.503$ ), Pb with Co ( $r = -0.500$ ), Zn with Ni and Pb. Similarly some pair of elements like Zn with Cd and Co have the value shows that they have almost no correlation.

#### **4.8.2 Analysis of Variance (ANOVA)**

Student F-test was calculated to identify whether the means of the concentration of selected heavy metals (Fe, Pb, Ni, Zn, Co, Cu, Cd and Cr) between tomato, water and soil samples vary significantly and the detailed result was summarized in Appendix 1

As can be observed the bolded numerical values from the appendix part Table 14, the ANOVA analysis on the multiple comparison of heavy metals concentration between soil, tomato and water indicates that, almost all of the heavy metal concentration in each soil, tomato and water sample has a significant at 95% probability levels that have less than 0.05 ( $P < 0.05$ ) which means significantly related while Pb of tomato with Pb of water and the vice versa has the value of 0.083, Fe of tomato with Fe of water and the vice versa has the value of 0.440 and Co of tomato with Co of water and the vice versa has the value of 0.995 which are far from 0.05. These indicate that they do not have a relation one to another and for detail information see appendix part.

#### 4.9 Health Risk Assessment

The evaluation of the health risk of heavy metals has been realized by the risk level estimation and by the classification as carcinogenic or non-carcinogenic health hazards. So, the hazard quotients (HQ), the hazard index (HI), and the cancer risk (CR) were used to estimate the carcinogenic and non-cancer health risk of heavy metals in hydro-alcoholic gels of Abidjan caused via dermal absorption [92].

Metal concentrations from irrigation water, soil, and tomatoes were utilized to determine the adverse effect on human exposure by ingestion, inhalation, and skin contact pathways. On the other hand, the estimation of ADD, HQ, and HI was set up using the CR determination.

**Table 11:** Average daily dose (ADD) of eight heavy metals in soil, tomato and irrigation sample

| Sample        | Exposure   | Fe                    | Pb                    | Cr                     | Zn                    | Co                    | Ni                    | Cd                    | Cu                    |
|---------------|------------|-----------------------|-----------------------|------------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| <b>Soil</b>   | Oral       | $0.43 \times 10^{-3}$ | $0.49 \times 10^{-6}$ | $0.15 \times 10^{-5}$  | $0.67 \times 10^{-6}$ | $0.20 \times 10^{-5}$ | $0.18 \times 10^{-5}$ | $0.88 \times 10^{-7}$ | $0.76 \times 10^{-5}$ |
|               | Inhalation | $0.37 \times 10^{-2}$ | $0.42 \times 10^{-3}$ | $1.3 \times 10^{-2}$   | $0.58 \times 10^{-3}$ | $0.22 \times 10^{-2}$ | $0.16 \times 10^{-2}$ | $0.77 \times 10^{-4}$ | $0.19 \times 10^{-3}$ |
|               | Dermal     | $0.18 \times 10^{-4}$ | $0.21 \times 10^{-7}$ | $0.633 \times 10^{-7}$ | $0.29 \times 10^{-7}$ | $0.11 \times 10^{-6}$ | $0.79 \times 10^{-7}$ | $0.38 \times 10^{-8}$ | $0.23 \times 10^{-7}$ |
| <b>Water</b>  | Ingestion  | $0.61 \times 10^{-2}$ | $0.25 \times 10^{-2}$ | $0.17 \times 10^{-1}$  | $0.25 \times 10^{-2}$ | $0.8 \times 10^{-3}$  | $0.6 \times 10^{-3}$  | $0.9 \times 10^{-3}$  | $0.17 \times 10^{-2}$ |
| <b>Tomato</b> | Tomato     | $6.45 \times 10^{-5}$ | $5.37 \times 10^{-7}$ | $6.27 \times 10^{-7}$  | $1.98 \times 10^{-6}$ | $5.87 \times 10^{-7}$ | $8.56 \times 10^{-7}$ | $1.13 \times 10^{-7}$ | $1.21 \times 10^{-6}$ |

In Table 11 the sequence value of the average daily dose for Adult people in each of the three exposures to the soil, tomato, and irrigation water sample were presented:  $Fe > Co > Ni > Cr > Zn > Cu > Pb > Cd$  for dermal contact,  $Cr > Fe > Pb = Zn > Cu > Cd > Co > Ni$  for ingestion of irrigation water, and its ranges from  $0.17 \times 10^{-1}$  to  $0.6 \times 10^{-3}$  for Cr and Ni, respectively. Similarly order of ingestion of tomato was  $Fe > Zn > Cu > Ni > Cr > Co > Pb > Cd$  and the ranges from  $6.45 \times 10^{-5}$  to  $1.13 \times 10^{-7}$  for Fe and Cd respectively. Cd was the least ADD value while Fe was the highest value in all

exposure. This could be the result of its abundance because iron is the fourth most abundant element in the earth's crust.

#### 4.9.2 Non-carcinogenic Health Risk

Table 12 displays the various exposure routes, such as skin contact, ingestion, and inhalation, that were used to evaluate the health consequences of HMs. For adult communities, the non-carcinogenic risk was calculated by HQ and HI using various significant routes. The overall mean value of HI intake ranged from 0.7956 (Cr) to 0.00115 (Cd) for all three samples (soil, irrigation water, and tomato), maintaining the following ordering:  $Cr > Fe > Co > Zn > Ni > Cu > Pb > Cd$ . The value of HQ ingestion in irrigation water and tomato were  $Cr > Fe > Co > Ni > Pb > Zn > Cu > Cd$ , and  $Fe > Zn > Ni > Cr > Co > Pb > Cu > Cd$  respectively. The ranges between 0.75 to 0.0013 for irrigation water and  $6.44 \times 10^{-6}$  to  $1.12 \times 10^{-8}$ . Highest HQ (dermal) was recorded for Fe that rendered the value of  $1.8 \times 10^{-2}$ . This might be the occurrence (percentage abundant of) iron in the earth's crust.

The  $HQ_{\text{tomato}}$ ,  $HQ_{\text{water}}$ ,  $HQ_{\text{ing}}$ ,  $HQ_{\text{inh}}$ , and  $HQ_{\text{derm}}$ , values were found to be in the order of  $Fe > Zn > Ni > Cr > Co > Pb > Cu > Cd$ ,  $Cr > Fe > Co > Ni > Pb > Zn > Cu > Cd$ ,  $Fe > Cr > Pb > Co > Ni > Zn > Cu > Cd$ ,  $Cr > Zn > Cu > Co > Ni > Fe > Cd > Pb$  and  $Fe > Cr > Cu > Pb > Co > Zn > Cd > Ni$  respectively. Whereas, HI value of HMs in all exposure in soil found to be in the decreasing order of  $Cr > Zn > Fe > Cu > Co > Ni > Cd > Pb$ .

Moreover, the overall HI value with in all exposure with all samples decline in order of  $Cr > Fe > Co > Zn > Ni > Cu > Pb > Cd$ . The highest score was observed 0.7956 (Cr) while the lowest value was found 0.00115 (Cd). The non-carcinogenic risks of HMs by three non-dietary exposure routes were dermal contact > inhalation > oral. Fe had the highest non-carcinogenic risk for all three non-dietary routes. The value of HI in each element with each exposure from this study were less than 1 ( $HI < 1$ ) [104] means that the exposed population is safe of metals health risk. However the sum of overall HI value of each elements in each exposure is greater than the recommended limit, then the population is therefore at greater risk.

The non-carcinogenic human health risk from the consumption of tomato contaminated by heavy metals was estimated through the calculation of hazard quotient. In these work no one the HQ value on the site is greater than one. It is evident from the data in Table 14 that the HQs of all heavy metals in all sample analyzed with HQ values of less than one.

**Table 12:** General health risk assessment of each and all selected HM elements and exposure in soil, tomato and irrigation water quantitatively.

| HM                      | Soil                          |                               |                             |                              | Water             | Tomato                       |                              | HI <sub>Ing in</sub> | HI <sub>in</sub> |
|-------------------------|-------------------------------|-------------------------------|-----------------------------|------------------------------|-------------------|------------------------------|------------------------------|----------------------|------------------|
|                         | HQ <sub>oral</sub>            | HQ <sub>inhal</sub>           | HQ <sub>derml</sub>         | HI                           | HQ <sub>ing</sub> | HQ <sub>Tomat</sub>          | HI <sub>W+T</sub>            | SWT                  | STW/elmnt        |
| <b>Fe</b>               | 0.34 x 10 <sup>-2</sup>       | 0.37 x 10 <sup>-2</sup>       | 0.18 x 10 <sup>-1</sup>     | 2.51 x 10 <sup>-2</sup>      | 0.07              | 6.44 x 10 <sup>-6</sup>      | 7 x 10 <sup>-2</sup>         | <b>0.0734</b>        | <b>0.0951</b>    |
| <b>Pb</b>               | 0.13 x 10 <sup>-3</sup>       | 0.12 x 10 <sup>-3</sup>       | 0.58 x 10 <sup>-5</sup>     | 2.56 x 10 <sup>-4</sup>      | 0.016             | 5.37 x 10 <sup>-8</sup>      | 1.6 x 10 <sup>-2</sup>       | <b>0.0161</b>        | <b>0.01626</b>   |
| <b>Cr</b>               | 0.5 x 10 <sup>-3</sup>        | 0.43 x 10 <sup>-1</sup>       | 0.21 x 10 <sup>-2</sup>     | 4.56 x 10 <sup>-2</sup>      | 0.75              | 6.27 x 10 <sup>-8</sup>      | 7.5 x 10 <sup>-1</sup>       | <b>0.7505</b>        | <b>0.7956</b>    |
| <b>Zn</b>               | 0.33 x 10 <sup>-4</sup>       | 0.29 x 10 <sup>-1</sup>       | 0.14 x 10 <sup>-5</sup>     | 2.9 x 10 <sup>-2</sup>       | 0.015             | 1.89 x 10 <sup>-7</sup>      | 1.5 x 10 <sup>-2</sup>       | <b>0.01503</b>       | <b>0.044</b>     |
| <b>Co</b>               | 0.10 x 10 <sup>-3</sup>       | 0.11 x 10 <sup>-1</sup>       | 0.55 x 10 <sup>-5</sup>     | 1.1 x 10 <sup>-2</sup>       | 0.04              | 5.89 x 10 <sup>-8</sup>      | 4 x 10 <sup>-2</sup>         | <b>0.0401</b>        | <b>0.0511</b>    |
| <b>Ni</b>               | 0.60 x 10 <sup>-4</sup>       | 0.53 x 10 <sup>-2</sup>       | 0.26 x 10 <sup>-6</sup>     | 5.36 x 10 <sup>-3</sup>      | 0.033             | 8.56 x 10 <sup>-8</sup>      | 3.3 x 10 <sup>-2</sup>       | <b>0.03306</b>       | <b>0.03836</b>   |
| <b>Cd</b>               | 0.17 x 10 <sup>-6</sup>       | 0.15 x 10 <sup>-3</sup>       | 0.76 x 10 <sup>-6</sup>     | 1.5 x 10 <sup>-4</sup>       | 0.0013            | 1.12 x 10 <sup>-8</sup>      | 1.3 x 10 <sup>-2</sup>       | <b>0.013</b>         | <b>0.00115</b>   |
| <b>Cu</b>               | 0.53 x 10 <sup>-6</sup>       | 0.24 x 10 <sup>-1</sup>       | 0.87 x 10 <sup>-5</sup>     | 2.4 x 10 <sup>-2</sup>       | 0.012             | 1.2 x 10 <sup>-8</sup>       | 1.2 x 10 <sup>-2</sup>       | <b>0.012</b>         | <b>0.036</b>     |
| <b>HI<sub>Tot</sub></b> | <b>0.43 x 10<sup>-2</sup></b> | <b>0.12 x 10<sup>-1</sup></b> | <b>0.2x 10<sup>-1</sup></b> | <b>1.4 x 10<sup>-1</sup></b> | <b>0.9373</b>     | <b>3.6 x 10<sup>-7</sup></b> | <b>9.3 x 10<sup>-1</sup></b> | 0.9343               | <b>1.0776</b>    |

Note: HI<sub>Total</sub> = total health index, HQ = hazard quotient wst = irrigated water, soil and tomato

In addition, four different expression were used to determine the HM intake amount for each exposure: (1) Each metal intake by each exposure route, (2) each metal intake by all three exposure routes, (3) all metal intake by each exposure route, and (4) all metal intake by any of the three exposure routes. Due to these the sum of HQ value of each element in each exposure, Oral ( $0.43 \times 10^{-2}$ ), inhalation ( $0.116 \times 10^{-1}$ ) and dermal ( $0.201 \times 10^{-1}$ ) in soil per each exposure were less than One as can be seen from the table 14. Also the HI value of all and each elements in the soil less than one. Therefore each and all the value of HQ and HI in soil indicates that their effect on health impact were very low.

The total HI value of HMs in tomato were than the value at water and soil sample.  $HQ_{\text{irrig water}} > HI_{\text{soil}} > HI_{\text{tomato}}$  ( $0.9373 > 0.14 > 3.6 \times 10^{-7}$ ). It might be due to absorption ability of tomato, favorability of topography, plant species and biological availability of the plant. All the concentration of HMs in tomato were higher than the permissible WHO/FAO value, However all the HI value of HMs in tomato were less than one. This shows that the estimated amount of fertilizers and pesticides used as well as the pollution coming from the cities in the form of dust might not be the cause for increased the amount of heavy metals in the area. In my study, the overall health risk assessment (HI) order of each elements in all exposure in all soil, tomato and irrigation water sample were in order of  $Cr > Fe > Co > Zn > Ni > Cu > Pb > Cd$  with the range between 0.7956 to 0.00115 for chromium and cadmium respectively. Although the value of HQ and HI is less than one, heavy metals could cause various type of diseases by entering in large quantities and accumulating for along time.

In general the banding of all elements through all exposure pathway of HI in all three samples (soil, tomato and irrigation water) were found to be less than 10 (1.0776) which shows that it might not be causes a serious chronic health risk. But I suggest that in order to take the aware that using them as in a vegetables form by cooking with food instead of eating tomato as a fruit.

#### 4.9.1 Carcinogenic Analysis

The Adults' ADD values obtained by ingestion, inhalation, and dermal techniques were arranged in the order of Cr > Cd > Ni > Pb, Cr > Ni > Cd > Pb, and Ni > Cd > Cr > Pb, respectively. The results show that Cr was the most consumed and absorbed metal, with an average intake of  $3.9 \times 10^{-2} \text{ mg kg}^{-1}\text{day}^{-1}$  from ingestion, compared to Pb consumption of  $1.1 \times 10^{-4} \text{ mg kg}^{-1}\text{day}^{-1}$  through dermal absorption present in Table 11.

The CR index was only estimated for Pb, Cr, Cd, and Ni because the elements' carcinogenic slope factors (CRF) were available. For all of the targeted adult participants in this investigation, a higher level of CR value of 0.039 was discovered. The range of CR was  $3.9 \times 10^{-2}$  for Cr to  $1.2 \times 10^{-4}$  for Pb for the three routes (ingestion, inhalation, and dermal contact). The CR across all three samples' absorption ranged from  $1.6 \times 10^{-5}$  for tomato sample to  $3.9 \times 10^{-2}$  for irrigation water in ingestion. The cumulative CR value also performed above the  $10^{-6}$  to  $10^{-4}$  range. According to this study, the majority of the mean CR values for each individual in each exposure are lower than the allowable value, which has no effect on human health. However, when the CR value of the targeted heavy metals is exceeded in their combined form, the risk level poses a major hazard to the local population's health. As a result, the investigated ideals ought to pose a danger to the local community.

Table 13: Carcinogenic risk of targeted heavy metals in soil, tomato and irrigation water

| HM                  |            | Cancer risk                 |                             |                             | CRin soil                  | Through Ingestion          |                            | CR <sub>Ingestion</sub> WT |
|---------------------|------------|-----------------------------|-----------------------------|-----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|
|                     |            | Ingestion                   | Inhalation                  | Dermal contact              |                            | Water ingestion            | Tomato ingestion           |                            |
| <b>Pb</b>           | <b>ADD</b> | 8.5x10 <sup>-7</sup>        | 7.4x10 <sup>-4</sup>        | 0.37x10 <sup>-7</sup>       |                            | 1.4x10 <sup>-3</sup>       | 3.1x 10 <sup>-7</sup>      | 1.2x10 <sup>-4</sup>       |
|                     | CSF        | 0.085                       | 0.00008                     | 0.0085                      |                            | 0.085                      | 0.085                      |                            |
|                     | CR         | <b>7.2x10<sup>-8</sup></b>  | <b>5.9x10<sup>-8</sup></b>  | <b>3.1x10<sup>-10</sup></b> | 1.3x10 <sup>-7</sup>       | <b>1.2x10<sup>-4</sup></b> | <b>2.6x10<sup>-8</sup></b> |                            |
| <b>Cr</b>           | <b>ADD</b> | 2.6x10 <sup>-6</sup>        | 2.3x10 <sup>-3</sup>        | 0.11x10 <sup>-6</sup>       |                            | 9.5x10 <sup>-4</sup>       | 3.6x 10 <sup>-7</sup>      | 3.9x10 <sup>-2</sup>       |
|                     | CSF        | 42                          | 0.012                       | 0.0065                      |                            | 42                         | 42                         |                            |
|                     | CR         | <b>1.09x10<sup>-4</sup></b> | <b>2.76x10<sup>-5</sup></b> | <b>7.2x10<sup>-10</sup></b> | 1.3x10 <sup>-4</sup>       | <b>3.9x10<sup>-2</sup></b> | <b>1.5x10<sup>-5</sup></b> |                            |
| <b>Cd</b>           | <b>ADD</b> | 0.15x10 <sup>-6</sup>       | 1.3x10 <sup>-4</sup>        | 0.66x10 <sup>-8</sup>       |                            | 4.9x10 <sup>-4</sup>       | 6.3 x 10 <sup>-8</sup>     | 3.1x10 <sup>-4</sup>       |
|                     | CSF        | 6.3                         | 0.0018                      | 6.3                         |                            | 6.3                        | 6.3                        |                            |
|                     | CR         | <b>9.5x10<sup>-7</sup></b>  | <b>2.3x10<sup>-7</sup></b>  | <b>4.2x10<sup>-8</sup></b>  | 1.2x10 <sup>-6</sup>       | <b>3.1x10<sup>-4</sup></b> | <b>3.9x10<sup>-7</sup></b> |                            |
| <b>Ni</b>           | <b>ADD</b> | 0.32x10 <sup>-5</sup>       | 2.8x10 <sup>-3</sup>        | 0.14x10 <sup>-6</sup>       |                            | 3.6x10 <sup>-4</sup>       | 4.9x 10 <sup>-7</sup>      | 3x10 <sup>-4</sup>         |
|                     | CSF        | 0.84                        | 0.00024                     | 0.84                        |                            | 0.84                       | 0.84                       |                            |
|                     | CR         | <b>2.68x10<sup>-6</sup></b> | <b>6.7x10<sup>-7</sup></b>  | <b>1.2x10<sup>-7</sup></b>  | 3.5x10 <sup>-6</sup>       | <b>3x10<sup>-4</sup></b>   | <b>4.1x10<sup>-7</sup></b> |                            |
| CR <sub>Total</sub> |            | <b>1.13x10<sup>-4</sup></b> | <b>2.85x10<sup>-5</sup></b> | <b>1.63x10<sup>-7</sup></b> | <b>1.4x10<sup>-4</sup></b> | <b>3.9x10<sup>-2</sup></b> | <b>1.6x10<sup>-5</sup></b> | <b>4x10<sup>-2</sup></b>   |

Note: CR<sub>total</sub> = total cancer risk, wt = water and tomato, wst = water, soil and tomato

## 5. CONCLUSION AND RECOMMENDATION

### 5.1 Conclusion

In this study tomato, irrigation water and the soil where the tomato was grown were analyzed for their concentrations of Cr, Cd, Zn, Pb, Fe, Cu, Co and Ni using wet-digestion method and inductively coupled plasma optical emission spectrometer instrument and their health risk assessment in each exposure from Abuarie irrigation land, North Wollo, Ethiopia.

The concentrations of Cr, Ni, Zn, Cd, Cu, Co, Fe and Pb for soil, tomato and water samples were found to be ranged from 49,020 ( Fe ) to 11 ( Cd), 170 (Fe) to 0.29 ( Cd) and 0.24 ( Fe) to 0.025 (Ni)  $\text{mg kg}^{-1}$  respectively. The concentrations of Ni, Cr, Co, Cu and Cd in the soil sample were higher than the WHO/FAO maximum permissive limits while the remaining Fe, Pb and Zn were lower than the maximum permissive limits. On the other hand, in tomato, all the concentrations these elements were higher than the guide line of WHO which were found to be ranged from 170 (Fe) to 0.274 (Cd)  $\text{mg kg}^{-1}$ . Therefore mean concentration and health index indicate tomato containing heavy metals beyond the limit were dangerous. My study leads that the used amount of fertilizers and pesticides in the land might be causes for high amount of heavy metals present in tomato and not good for health if we consume them directly as a fruit rather than vegetable.

The general trend of TF for heavy metal in tomato sample were in order;  $\text{Zn} > \text{Cu} > \text{Cd} > \text{Pb} > \text{Ni} > \text{Cr} > \text{Co} > \text{Fe}$  and ranges between Fe (0.0035) – Zn (0.064). Variations in transfer factor among metals in the tomato may be attributed to differences in the concentration of metals in the soil and characteristics or nature of element. In addition, the metal contents of tomato might be affected by the environmental interferences like pesticides, fertilizers and other additives that farmers use.

Almost all the HQ and HI value of HMs in tomato, soil and irrigation water were less than one. The banding of all elements through all exposure pathway of HI in all three samples (soil, tomato and water) were found to be less than 10 which has no chronic health risk.

The CR across all three samples' absorption ranged from  $1.6 \times 10^{-5}$  for tomato sample to  $3.9 \times 10^{-2}$  for irrigation water in ingestion. The cumulative CR value also performed above the  $10^{-6}$  to  $10^{-4}$  range. According to this study, the majority of the mean CR values for each individual in each exposure are lower than the allowable value, which has no effect on human health.

However, the mean value of the CR value of the targeted heavy metals (Cr, Cd, Ni and Pb) is exceeded in their all exposure (above  $1 \times 10^{-4}$ ) combined form, and the risk level poses a major hazard to the local population's health. As a result, the investigated ideals ought to pose a danger to the local community.

Tomato for the evaluation of potential non-carcinogenic and cancer-causing health concerns to Abuarie's population and surrounding areas. Because only a portion of the population in the study area was considered in the study's findings, there is a chance that the health hazards associated with heavy metal exposure from consuming tomatoes may have been overestimated.

## 5.2 Recommendation

Based on this study, the following points are recommended.

- Further investigation could be conducted to look at the effects of water and soil on local fruits and vegetables near the Abuarie irrigation location.
- The concerned Administrative bodies, district and regional level agricultural offices and of course, farmers in the area should be aware of the problem associated with environmental interferences like pesticides, fertilizers and other additives that farmers use.
- In the tomato and the soil sample they had a high level of toxic heavy metals coupled with the fact that the residents had low knowledge on the health risks posed by the problem associated with environmental interferences like pesticides, fertilizers and other additives that farmers use so the health minister must be teach about the heavy metal risk.
- Further research similar to this one was carried out in the area with the different vegetables and fruit.

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## APPENDIX

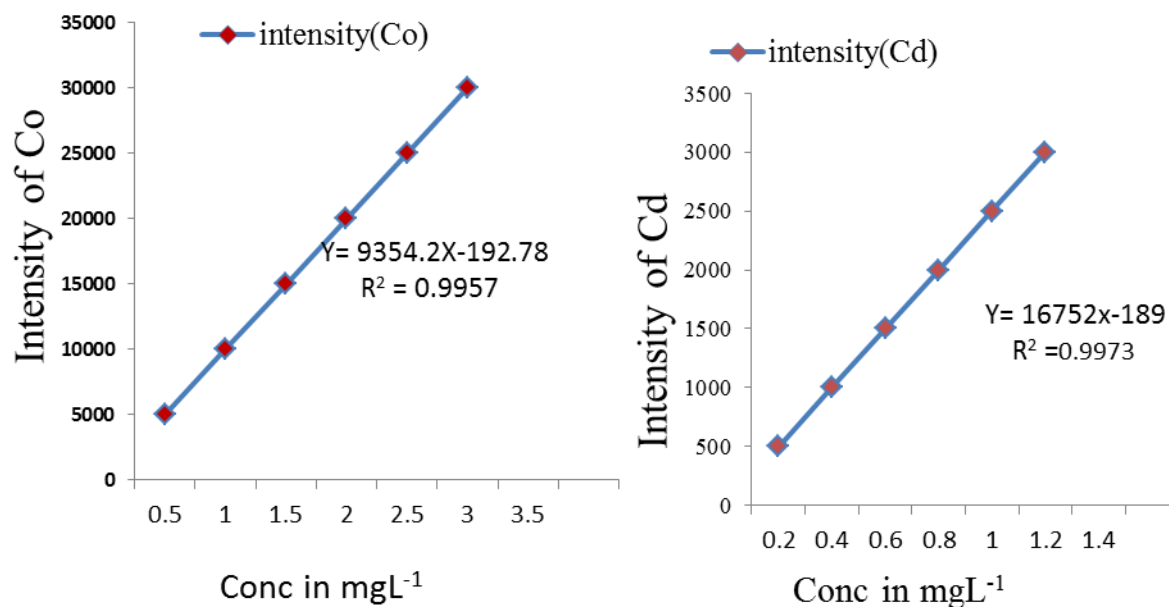


Figure 6: Intensity versus concentration curve for Co and Cd

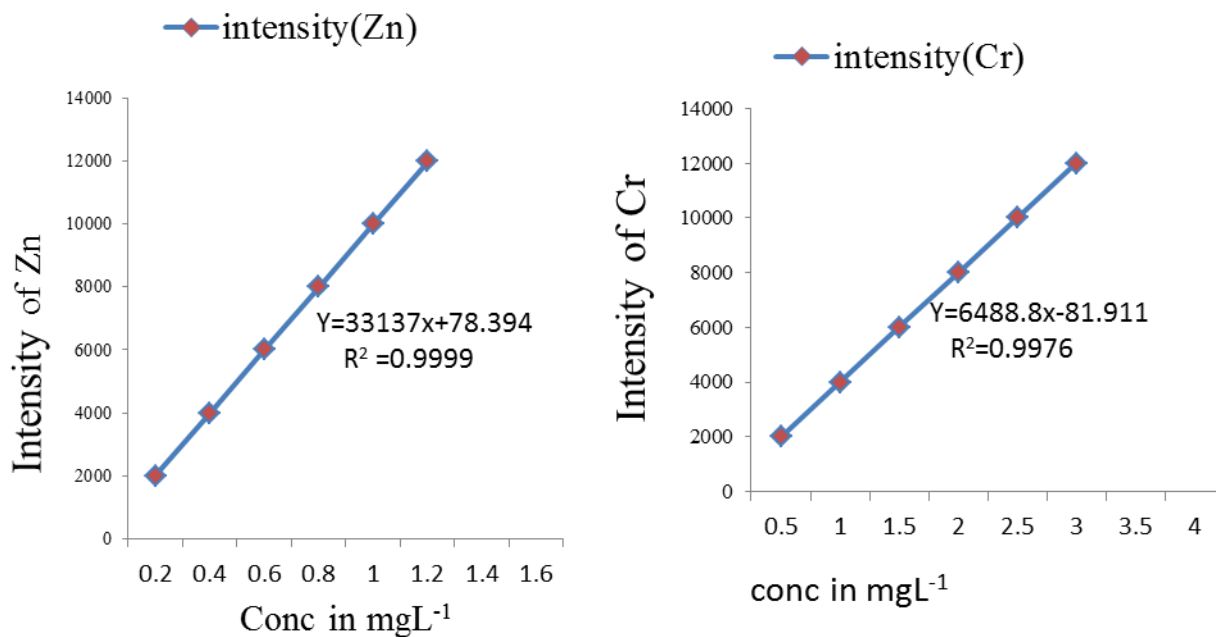
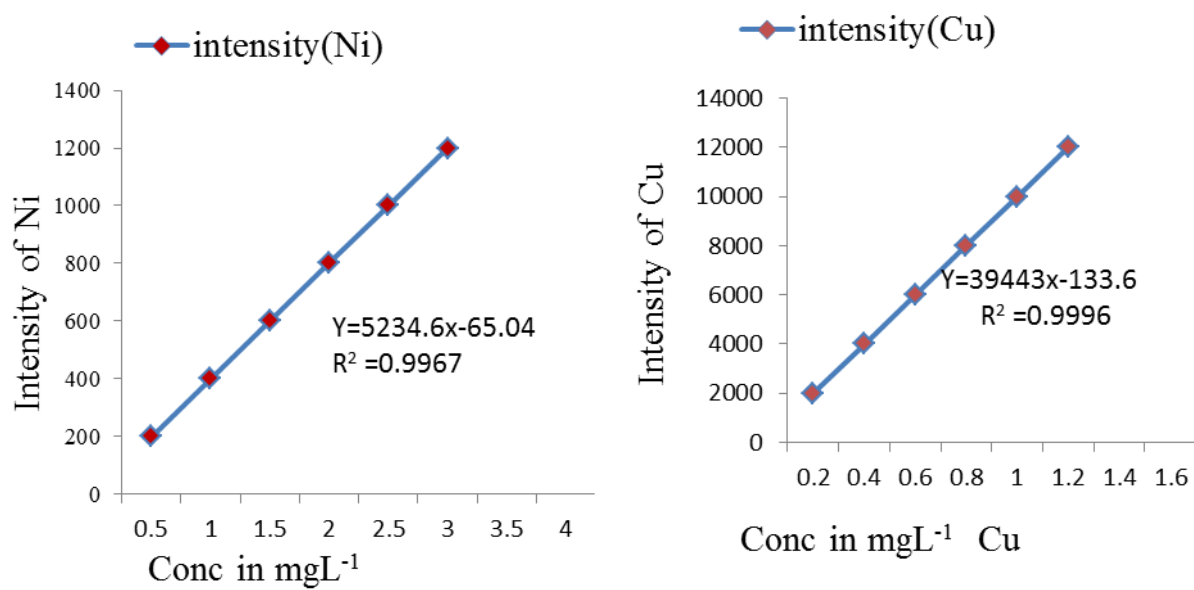
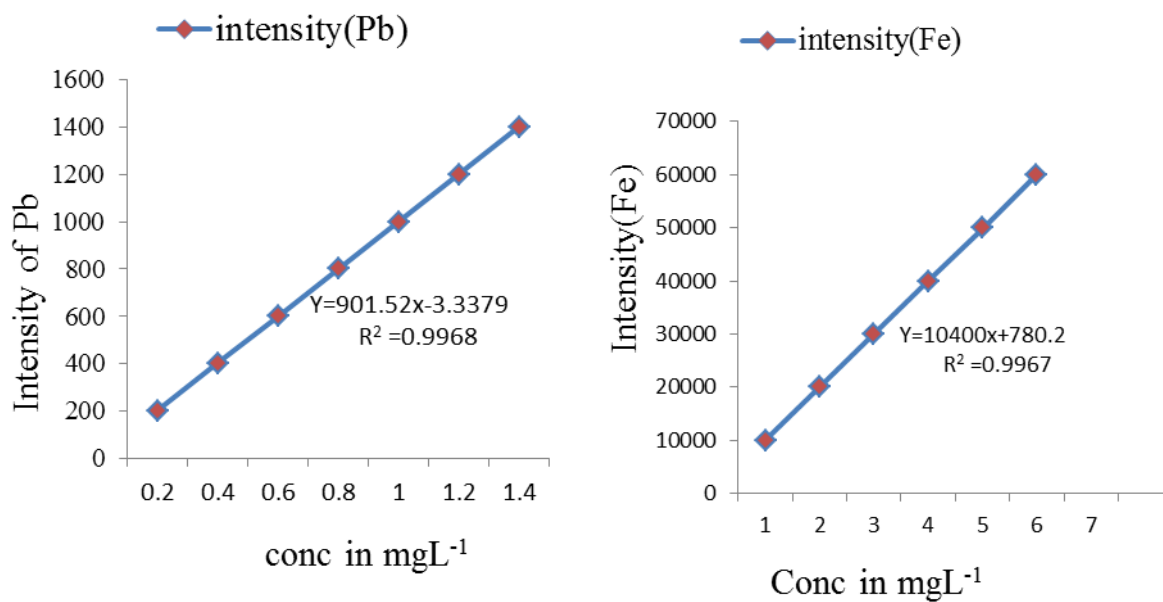


Figure 7: Intensity versus concentration curve for Zn and Cr



**Figure 8: Intensity versus concentration curve for Ni and Cu**



**Figure 9: Intensity versus concentration curve for Pd and Fe**

Table 14: Multiple Comparisons of heavy metals concentration in each sample using ANOVA Analysis

| Dependent Variable |        |        | Mean Difference           | Sig.         | 95% Confidence Interval |             |
|--------------------|--------|--------|---------------------------|--------------|-------------------------|-------------|
|                    |        |        |                           |              | Lower Bound             | Upper Bound |
| Cd                 | Soil   | tomato | 11.55000 <sup>*</sup>     | 0.000        | 11.3503                 | 11.7497     |
|                    |        | Water  | 11.81233 <sup>*</sup>     | 0.000        | 11.6126                 | 12.0121     |
|                    | tomato | Soil   | -11.55000 <sup>*</sup>    | 0.000        | -11.7497                | -11.3503    |
|                    |        | Water  | .26233 <sup>*</sup>       | 0.016        | 0.0626                  | 0.4621      |
|                    | Water  | Soil   | -11.81233 <sup>*</sup>    | 0.000        | -12.0121                | -11.6126    |
|                    |        | tomato | -.26233 <sup>*</sup>      | 0.016        | -0.4621                 | -0.0626     |
| Co                 | Soil   | tomato | 298.44667 <sup>*</sup>    | 0.000        | 247.0232                | 349.8702    |
|                    |        | Water  | 299.99000 <sup>*</sup>    | 0.000        | 248.5665                | 351.4135    |
|                    | tomato | Soil   | -298.44667 <sup>*</sup>   | 0.000        | -349.8702               | -247.0232   |
|                    |        | Water  | 1.54333                   | <b>0.995</b> | -49.8802                | 52.9668     |
|                    | Water  | Soil   | -299.99000 <sup>*</sup>   | 0.000        | -351.4135               | -248.5665   |
|                    |        | tomato | -1.54333                  | <b>0.995</b> | -52.9668                | 49.8802     |
| Cr                 | Soil   | tomato | 167.04000 <sup>*</sup>    | 0.000        | 166.0630                | 168.0170    |
|                    |        | Water  | 168.62667 <sup>*</sup>    | 0.000        | 167.6496                | 169.6037    |
|                    | tomato | Soil   | -167.04000 <sup>*</sup>   | 0.000        | -168.0170               | -166.0630   |
|                    |        | Water  | 1.58667 <sup>*</sup>      | 0.006        | 0.6096                  | 2.5637      |
|                    | Water  | Soil   | -168.62667 <sup>*</sup>   | 0.000        | -169.6037               | -167.6496   |
|                    |        | tomato | -1.58667 <sup>*</sup>     | 0.006        | -2.5637                 | -0.6096     |
| Cu                 | Soil   | tomato | 69.14667 <sup>*</sup>     | 0.000        | 68.4368                 | 69.8565     |
|                    |        | Water  | 72.28333 <sup>*</sup>     | 0.000        | 71.5735                 | 72.9932     |
|                    | tomato | Soil   | -69.14667 <sup>*</sup>    | 0.000        | -69.8565                | -68.4368    |
|                    |        | Water  | 3.13667 <sup>*</sup>      | 0.000        | 2.4268                  | 3.8465      |
|                    | Water  | Soil   | -72.28333 <sup>*</sup>    | 0.000        | -72.9932                | -71.5735    |
|                    |        | tomato | -3.13667 <sup>*</sup>     | 0.000        | -3.8465                 | -2.4268     |
| Fe                 | Soil   | tomato | 48849.83333 <sup>*</sup>  | 0.000        | 46849.8036              | 49849.7653  |
|                    |        | Water  | 49019.18000 <sup>*</sup>  | 0.000        | 47019.1803              | 50219.1832  |
|                    | tomato | Soil   | -48849.83333 <sup>*</sup> | 0.000        | -50219.1832             | -47065.1324 |
|                    |        | Water  | 169.34667                 | <b>0.442</b> | -228.5258               | 567.2192    |
|                    | Water  | Soil   | -49019.18000 <sup>*</sup> | 0.000        | -51042.3342             | -48324.3214 |
|                    |        | tomato | -169.34667 <sup>*</sup>   | <b>0.442</b> | -567.2192               | 228.5258    |
| Ni                 | Soil   | tomato | 209.16667 <sup>*</sup>    | 0.000        | 207.6743                | 210.6591    |
|                    |        | Water  | 211.28633 <sup>*</sup>    | 0.000        | 209.7939                | 212.7787    |
|                    | tomato | Soil   | -209.16667 <sup>*</sup>   | 0.000        | -210.6591               | -207.6743   |
|                    |        | Water  | 2.11967 <sup>*</sup>      | 0.011        | 0.6273                  | 3.6121      |
|                    | Water  | Soil   | -211.28633 <sup>*</sup>   | 0.000        | -212.7787               | -209.7939   |

|    |        |        |                        |              |          |          |
|----|--------|--------|------------------------|--------------|----------|----------|
|    |        | tomato | -2.11967 <sup>*</sup>  | 0.011        | -3.6121  | -0.6273  |
| Pb | Soil   | tomato | 56.72667 <sup>*</sup>  | 0.000        | 55.2003  | 58.2531  |
|    |        | Water  | 58.05067 <sup>*</sup>  | 0.000        | 56.5243  | 59.5771  |
|    | tomato | Soil   | -56.72667 <sup>*</sup> | 0.000        | -58.2531 | -55.2003 |
|    |        | Water  | 1.32400                | <b>0.083</b> | -0.2024  | 2.8504   |
|    | Water  | Soil   | -58.05067 <sup>*</sup> | 0.000        | -59.5771 | -56.5243 |
|    |        | tomato | -1.32400               | <b>0.083</b> | -2.8504  | 0.2024   |
| Zn | Soil   | tomato | 74.36667 <sup>*</sup>  | 0.000        | 73.7733  | 74.9600  |
|    |        | Water  | 79.25000 <sup>*</sup>  | 0.000        | 78.6567  | 79.8433  |
|    | tomato | Soil   | -74.36667 <sup>*</sup> | 0.000        | -74.9600 | -73.7733 |
|    |        | Water  | 4.88333 <sup>*</sup>   | 0.000        | 4.2900   | 5.4767   |
|    | Water  | Soil   | -79.25000 <sup>*</sup> | 0.000        | -79.8433 | -78.6567 |
|    |        | tomato | -4.88333 <sup>*</sup>  | 0.000        | -5.4767  | -4.2900  |

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