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Analysis of Essential and Non-Essential Heavy Metals in Tomato and Soil in Ziway Urban Area, East Shoa Zone, Ethiopia

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Abstract

Heavy metals in agricultural soils posed significant dangers to human health and the ecosystem. In the current research, the concentration of Fe and Zn (needful metals) and Cd, Cr, and Pb (non-needful metals) were determined in tomato and tomato soil samples by flame atomic absorption spectrophotometry (FAAS). Samples were collected from three different agricultural land of Gerbi Gilgila irrigation land of east Shewa Zone, Ethiopia. A wet digestion method employing nitric acid (4 mL) and perchloric acid solution (1 mL) was used for the digestion of the samples. The findings showed the presence of various metals in tomato soil samples, measured in mg kg^{-1} on a dry weight basis, within the following ranges: Zn (3.454±0.069), Pb (0.814±0.016), Cr and Cd (0.001±0.002), and Fe (100.63±0.173). Overall, the metal levels in tomato soil from the Geribi Gilgila site decreased in this order: Fe was the biggest, followed by Zn, then Pb, while Cr and Cd were at the same level. Similarly, soil samples from non-tomato soil showed that Fe was greater than Zn, which was greater than Pb, while Cr and Cd were also equal. Interestingly, the tomato soil samples exhibited the exact same pattern, with Fe greater than Zn, which was greater than Pb, and Cr equal to Cd. The metal levels in the analyzed tomato samples were lower the WHO safe limit; indicating they are benign for human intake and can serve as a nice source of needful nutrients. The study results revealed that tomato grown in those areas is not contaminated so it is fit to use as food item.

Keywords: Needful metals, Atomic Absorption Spectrophotometry, Soil, Wet digestion

1. Introduction

The toxic trace element represents mainly transition elements, some metalloids, lanthanides, and actinides. Soil media is the primary source of toxic trace elements moved from the roots or foliage to plants. Some trace elements are well known to be plant nutrients, nevertheless plants cultivating in a contaminated environs can absorb trace elements and reach higher levels in their tissues, representing a crucial hazard to human health. Toxic trace elements have a highly detrimental impact; this toxicity is owing to their non-decomposable, extended biological lifetime in our body system, and propensity to accumulate in various body tissues. Normal cropping cannot eliminate them and pollution is not easily leached by rain [1-4]. The remainders of the trace elements are highly toxic because of their water solubility [5-6].

Trace elements in farmland and vegetation are a significant factor affecting human health. Numerous factors affect the extent of trace elements in vegetables and soil. These comprise irrigation practice, atmospheric deposition, the characteristics of the soil where the plants are cultivated, and the stage of plant maturation at the time of harvest [7]. A wastewater irrigation, solid waste disposal, and industrial activities are main contributors to soil pollution by toxic trace elements. As a result, food crops cultivated in such polluted soils often show higher levels of these elements being absorbed [8-9].

The absorption of elements using plants is determined by their soluble concentration in the soils. The type of plant species, application of fertilizers, soil composition, and soil pH, are all important factors [10-11]. The harmful effects and movement of trace elements in soil depend on both their overall concentration and the particular chemical forms they take. The interaction between element-binding properties and environmental conditions leads to increased levels of harmful trace elements, impacting food quality and posing risks to human health globally. The ingestion of dangerous trace elements from polluted food sources may contribute to the onset of numerous long-term health conditions [9, 12-14].

Vegetables are needed in human food intake, supplying necessary nutrients like proteins, vitamins, carbohydrates, minerals, and trace elements. However, both the edible and inedible portions of plants can also accumulate harmful substances. The concentration of trace elements in vegetables differ based on the kind of species, and the efficiency of a vegetable's capacity to absorb these elements is resolved on by factors such as vegetables intake or the soil to plant exchange ratio [15]. Numerous studies have confirmed that certain vegetables can accumulate significant amounts of elements from the soil [16-17]. This poses a notable exposure risk for individuals who consume crops cultivated in soil rich in trace elements.

Harmful trace elements are partially consumed through the edible portions of vegetable crops. Establishing baseline

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levels of elements for instance, zinc (Zn), cadmium (Cd), lead (Pb), chromium (Cr), iron (Fe), and others in these crops is essential to assess their potential health risks and define safety thresholds. In developing nations, urban farming is becoming increasingly common due to rapid urbanization, which brings challenges like heightened demand for food and job opportunities. Urban agriculture serves as a supplementary approach to alleviate food shortage, strengthen urban environmental management, and promote the efficient utilization of urban waste resources [18-19].

While urban agriculture offers numerous advantages, it is crucial to prioritize the safety of the produce. The rapid and often unplanned growth of urban areas, combined with industrial activities and insufficient waste management, leads to significant changes in the surroundings and a rise in urban leftover accumulation. An outstanding urgent challenge of urbanization in underdeveloped regions, particularly in Africa-including Ethiopia-is the management of different hazardous waste phases. These wastes can often be toxic or even radioactive in nature [20-21].

The objective of this research was to measure and analyze the extents of both indispensable and harmful metals, namely, Zn, Fe, Cd, Pb, and Cr, in urban soil samples, as well as selected vegetables from farms near urbanized areas. These farms are known to be contaminated because of the discharge of fertilizers, pesticides, and municipal waste. Tomatoes, a widely consumed vegetable, were chosen for analysis as they are often irrigated with river water or wastewater due to the scarcity of clean water. This research is critical because a large part of the population consumes vegetables grown in these areas. The absorption of trace elements by plants and vegetables differs and is dependent on point like soil acidity or basicity (pH) and organic matter content.

Vegetables and fruits are commonly regarded as "protective supplementary foods," providing an affordable and accessible source of essential minerals and nutrients for many people in developing nations [22-25]. Vegetables are abundant in vitamins, minerals, fiber, and antioxidants, which play a role in preventing chronic illnesses linked to aging. However, the increasing demand for vegetables has driven significant shifts in farming methods, such as mechanization, the application of agrochemicals, the use of selected seed types, irrigation, and post-harvest handling. Sadly, environmental pollution has become a significant issue, contaminating soil, water, and air, ultimately impacting crops and vegetables that are part of the human diet [26-27].

The study centers on the issue of heavy metal pollution in Ethiopia, particularly in urban areas like Zeway. While tomatoes are a dietary staple, there is limited understanding of the heavy metals they contain and the health dangers related with elevated levels of iron and zinc. By comparing heavy metal concentrations in tomatoes and soil from two different locations, the research establishes a baseline for monitoring pollution. This highlights the urgent need for greater awareness and regulatory action to preserve public health and establish food security.

2. Materials and Methods

2.1. Explanation of the Study Area

Zeway is bordered by two administrative zones of the Oromia regional state. The western part is part of the East Shoa Zone, while the eastern part falls within the Arsi Zone (see Figure 1). The western shore of Lake Zeway is shared by the districts of Adamitullu Jiddo Kombolcha and Dugda. This lake is situated within the Great East African Rift Valley in Ethiopia, approximately 163 kilometers southeast of the capital city, Addis Ababa. The location is situated at an elevation of 1,650 meters beyond sea level, with coordinates ranging from 7° 98’ to 8° 05’ N latitude and 38° 72’ to 38° 92’ E longitude.

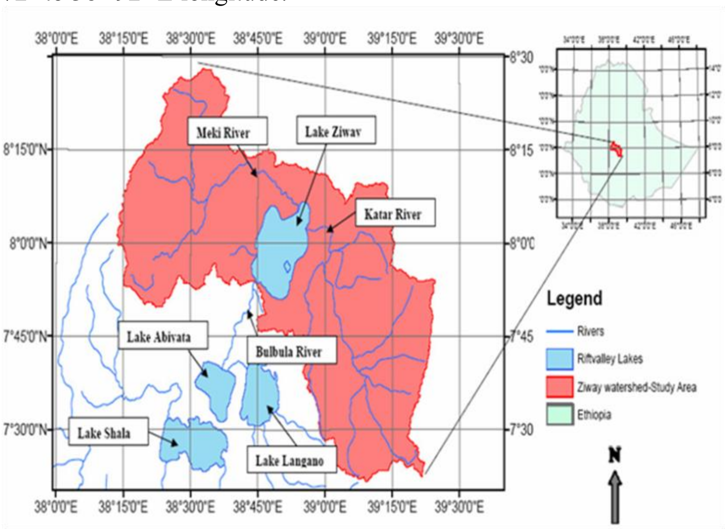


Figure 1. Absolute location of the study area.

2.2. Apparatus and Equipment

The extents of hazardous heavy metals in vegetable and soil samples were analyzed using Atomic Absorption Spectroscopy (FAAS, Agilent Technology, Model No. 210). A variety of laboratory instruments and materials were used in the study.

2.3. Chemicals and Reagents

All chemicals and reagents used in the research were of laboratory grade and high purity. Deionized water was utilized for the preparation and dilution practices during the research. The chemicals employed included nitric acid (HNO_3, 69%), hydrogen peroxide (H_2O_2, 30%), sulfuric acid (H_2SO_4, 98%), perchloric acid ($HClO_4$, 70-72%), and hydrochloric acid (HCl, 37%). A stock standard/reference solution with a concentration of 1000 mg L^{-1} was prepared for the targeted heavy metals, like iron (Fe), zinc (Zn), chromium (Cr), lead (Pb), and cadmium (Cd).

2.4. Collecting and Preparing Samples

2.4.1. Cleaning of Glassware and Sample Holders

All apparatus utilized for holding samples and adsorbing metal ions were carefully cleaned. They were rinsed first with tap water, then with deionized water, and finally dried in a clean area [28].

2.4.2. Preparation of Vegetable Sample

The vegetable sample was collected in August 2021, consisting of about 1.5 kg of the edible part of tomato (*Lycopersiconesulentum Miller*). For this purpose, three farmlands were selected, and sub-samples were reserved from the edible parts of tomato plants. Sampling was performed by hand. The collected samples were systematically mixed together to create a composite sample, representing a typical portion of the vegetables [29-30]. Any damaged or spoiled parts were discarded, and the unused samples were placed in polyethylene bags for transportation to the experimental center for digestion.

In the lab, the plant samples were first rinsed with distilled water to clean off any unwanted small particles. After being cut into smaller pieces with a knife (plastic), the samples were air dried for six to eight days and then dried in an oven at 90-100°C for two hours. Once dried, the materials were powdered into a fine powder, then sieved through a 2 mm mesh and kept in polyethylene bags within desiccators till the digestion process.

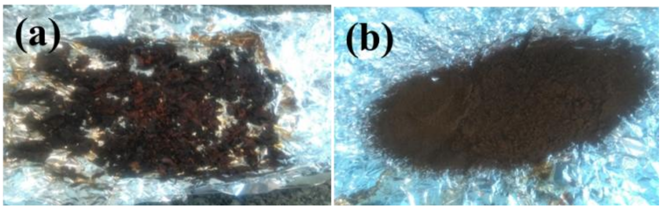


Figure 2. The dried (a) and pulverized into fine powder (b) vegetable sample.

2.4.3. Soil Sampling and Preparation

Soil sampling and preparation tactics were based on methods from prior studies [31-32]. A 1.0 g soil sample was took from a depth of 0-20 cm at the vegetable cultivation site using an auger, while a manage soil sample was collected 2 km distant from the study area. The samples were stored in polyethylene bags for pre-treatment also analysis. Initial preparation included the removal of larger particles and debris, followed by air dried at 25°C in a controlled able to a constant weight was reached, dust-free location for five days. The samples were subsequently ground and passed through a 2 mm mesh to ensure uniformity. The dried and homogenized soil samples were kept in polyethylene bags until the digestion process.

2.5. Sample Digestion

2.5.1. Digestion of vegetable samples

A 1.0 g fine powdered vegetable sample was added in a borosilicate digestion flask, and 10 mL of an acid mixture comprising nitric acid, perchloric acid, and hydrogen peroxide in a 5:1:1 (v/v/v) ratio was introduced. The mixture was heated at 270-300°C for 2 hours using a block digester [33]. Once digestion, the clear and colorless solution was purified into a 50 mL volumetric flask. The digestion tubes were washed with distilled water to combine any remaining left over, which was introduced to the flask. The solution was then diluted to the mark with distilled water. The diluted samples were stored in 50 mL high density polyethylene bottles till analysis. A blank solution was prepared by combining 5 mL nitric acid, 1 mL perchloric acid, and 1 mL hydrogen peroxide, following the same procedure as the sample [30, 33]. The heavy metal concentration was determined using FAAS at Addis Ababa University, Soil Chemistry Laboratory.

2.5.2. Wet digestion of soil sample

A 1.0 g of dried and homogenized soil sample was moved in a 100 mL digestion flask. To each flask, 5 mL of deionized water and 30 mL of a 5:1 volume ratio of HNO_3 plus $HClO_4$ were added. The soil sample was dissolved by the acid mixture and digested in a fume hood at a temperature range of 270-300°C for 2 hours, after which it was left to cool. Once cooled, 2 mL of H_2O_2 was introduced into the mixture, which was subsequently filtered using filter paper into a 100 mL volumetric flask. The purified solution was then diluted to the mark with distilled water [31, 34]. The filtrates obtained were analyzed by Flame Atomic Absorption Spectrometry (FAAS). A blank reagent was also prepared and subjected to the same digestion process for comparison.

2.6. Physicochemical Properties of Soil Samples

2.6.1. Soil sampling and treatment

Surface soil samples (0-20 cm depth) were taken from tomato-growing fields in January 2021 using a stainless steel auger [31]. At each sampling location within the district, individual soil samples were joined to generate a single merged sample. Three such composite samples were prepared, placed in labeled plastic bags, and transported to Debre Berhan University for laboratory analysis. The samples were air dried under shade for seven days, then ground and passed through a < 0.5 mm mesh. Soil properties, including pH and electrical conductivity, were analyzed as part of the study.

2. 6.2. Soil pH

A 10 g portion of air dried and finely ground soil, passed through a 2 mm stainless steel mesh, was weighed and moved into a 100 mL beaker. To create a 1:2.5 soil to water ratio (dry weight in grams to water in milliliters), 25 mL of deionized water was introduced to the beaker. The mixture was stirred for 30 minutes using stirrer. After stirring, the sample was left undisturbed for 5 minutes to allow the soil particles to settle down. The pH was then measured by placing the electrodes into the clear supernatant of the soil-water suspension [35].

2.6.3. Electrical conductivity

The conductivity level quantifies the ability of a solution to conduct electricity. To prepare the soil suspension, 10 g of air dried soil (passed to < 2 mm mesh) was weighed and transferred into a bottle. Next, 50 mL of deionized water was added to create a 1:5 soil to water ratio. The mixture was shaken mechanically at 15 rpm for 1 hour to ensure the dissolution of soluble salts. The electrical conductivity of a 0.01 M KCl solution was determined at the same temperature as the soil suspension. Prior to measurement, the conductivity cell was properly rinsed with the soil suspension and carefully fill up without troubling the settled soil particles [36]. The reading displayed on the conductivity meter was then record counts.

2.7. Heavy Metal Analysis

2.7.1. Atomic absorption spectroscopy

The technique employs absorption spectrometry to measure the concentration of target analyte in a sample. It operates by comparing the measured signal to a standard with a known analyte concentration, adhering to Beer-Lambert's law. The sample is first converted into atomic vapors through a process called atomization. The accuracy and precision of this method depend significantly on the atomization step, making the selection of an appropriate atomization method essential.

Atomizers are classified into two main types: continuous and discrete. Continuous atomizers introduce the sample at a steady rate, producing a consistent spectral signal over time. Examples include flame, inductively coupled argon plasma, and direct current argon plasma atomizers. Discrete atomizers, on the other hand, introduce a specific quantity of the sample as a liquid or solid plug, generating a spectral signal that rises to a peak before declining. Electrothermal atomizers are a common example of discrete atomizers. Once atomized, the atoms absorb radiation at specific wavelengths from an external source. This technique is widely applied for elemental analysis in various matrices, including soils, water, nuts, wine, and wine products [37].

Figure 3. Flame Atomic Absorption Spectroscopy (FAAS)

2.7.2. Instrument's operating conditions

The concentrations of Fe, Zn, Cr, Cd, and Pb in the extracted vegetable and soil samples were measured using Atomic Absorption Spectrometry (AAS). The instrument was calibrated using 1000 ppm standard solutions of each heavy metal, along with drift blanks. Calibration curves were established for each metal to make sure the accuracy of the instrument and to verify the reliability of the results. Standard stock solutions of 1000 ppm for all metals were prepared and diluted to the required concentrations for calibration. A multi-element solution having Fe, Zn, Cr, Cd, and Pb at 1000 ppm was used to create calibration standards, which were further diluted with 2% nitric acid to achieve the desired working concentrations.

Instrument parameters, including burner and lamp alignment, slit width, and wavelength, were optimized according to the manufacturer's instructions to achieve maximum signal intensity. Three replicate measurements were performed for each soil and vegetable sample. Hollow cathode lamps for each metal, operated at the manufacturer-recommended settings, were used at their own primary wavelengths. The acetylene and airflow rates were adjusted to maintain optimal flame conditions. All five metals (Fe, Zn, Cr, Cd, and Pb) were analyzed in absorption mode. Three readings were recorded for each digest under different FAAS conditions, as outlined in Table 1, to ensure the highest signal intensity.

Table 1. Instrumental operating condition for the analysis of metal in sample of vegetable and their respective soil vegetable growing.

Element	Wavelength (nm)	Slit Width Limit (nm)	Lamp Current (mA)	Instrumental Detection mg L^{-1}
Fe	248.3	0.2	4.00	0.006
Zn	213.5	0.5	2.00	0.001
Cr	357.9	0.2	4.00	0.001
Cd	228.8	1.2	2.00	0.002
Pb	383.3	1.2	2.00	0.006

2.8. Instrumental Calibration

Calibration curves for Fe, Zn, Cd, and Pb were created using standard solutions prepared from stock solutions. The precision of heavy metal analysis using FAAS relies heavily on accurate calibration and proper preparation of standard solutions. Calibration standards were considered for each element, allowing for their optimum working ranges. A correlation coefficient (R^2) value approaching 1 signifies a strong linear relationship between variables, while values closer to 0 indicate a lack of linear correlation [38]. As indicated in Tables 2 and 3, the correlation coefficients for the metals ranged between 0.993 and 0.999, reflecting a robust linear relationship. These coefficients were calculated by associating the absorbance values of the prepared standards with their corresponding concentrations. Tables 1 and 2 present the standard concentrations and their respective correlation coefficients for the calibration curves of each metal in soil and vegetable samples. Furthermore, calibration graphs for each metal in both samples are included.

Table 2. Concentrations of the prepared working standard solutions and the corresponding correlation coefficients (R^2) of the calibration curves for heavy metal analysis in soil samples.

Element	Concentration (mgkg^{-1})	Coefficients of determination (R^2)	Equation
Fe	1.00, 2.00, 3.00, 4.00	0.9994	Y=0.0095x-0.0002
Zn	0.25, 0.50, 0.75, 1.00	0.9998	Y=0.0878x-0.0030
Cr	0.50, 1.00, 1.50, 2.00	0.9815	Y=0.0093x+0.0008
Cd	0.25, 0.50, 0.75, 1.00	0.9724	Y=0.0274x+0.0069
Pb	0.40, 0.80, 1.20, 1.60	0.9993	Y=0.0059x+0.0025

2.9. Digestion and Optimization of Metals

Several digestion techniques for vegetable samples were evaluated and optimized via a combination of nitric acid and perchloric acid. Key parameters, such as the volume of the acid mixture, digestion duration, and temperature, were varied to identify the most efficient method. The best digestion process was selected based on achieving a clear solution, minimizing reagent usage, reducing digestion time, and ensuring complete digestion of the vegetable samples without any remaining undigested material.

2.9.1. Method detection limit

The Method Detection Limit (MDL) refers to the smallest amount of the analytes that can be reliably identified and quantified. It indicates the minimal concentration at which the analyte can be differentiated from background variations in blank samples [38]. To determine the MDL, five blank samples were prepared and subjected to the same digestion process as the soil and vegetable samples. These blanks were analyzed for their metal content (Fe, Zn, Cd, Cr, and Pb) using FAAS. The standard deviation (SD) of the five replicate blank measurements was estimated, and the MDL was derived using the appropriate formula [39].

MDL=3x SD of Blank Where: SD = Standard deviation

2.9.2. Statistical data analysis and data processing

All the statistical analyses were conducted on Lenovo pc computer via the Microsoft EXCEL (version 2010). All experimental measurements were performed in triplicate; the results of the three replicates were reported as the mean value along with the standard deviation.

2.9.3. Method validation

In this study, since qualified reference materials for soil, vegetable, and effluents were unavailable in the laboratory, the reliability of the digestion method, as well as the precision and accuracy of FAAS were verified using spiked and non-spiked samples. Both spiked and non-spiked vegetable, soil and effluent samples were processed using the same digestion procedure applied to the original samples and analyzed under identical conditions. The percentage recoveries of the analytes were then determined using the formula provided [29,30].

$$\text{Recovery} = \frac{\text{amount after spiked} - \text{amount before spiked}}{\text{amount added}} x100$$

3. Results and Discussion

3.1. Physicochemical Properties of the Soil Samples

3.1.1. Soil pH

The pH of a soil sample has a significant impact on metal dynamics for the reason that it controls precipitation and adsorption, which is the foremost mechanism of metal retention in soils. Soil pH levels and various soil traits play a critical role in influencing the processes that determine the mobility and solubility of heavy metals within the soil. As soil pH drops, the solubility of cationic metal forms increases, making them more accessible to plants. The typical pH range for normal soil is between 5.5 and 7.5. [40]. In this study, soil samples from tomato growing regions had a pH value of 7.45, while soil samples from non-tomato-growing areas had a pH value of 8.01 as introduced in Table 3. The pH of soil samples collected from tomato growing areas of the soil sample is in the range normal soil and pH of soil samples gained from non-tomato growing areas of the soil sample have a basic pH [30, 41].

According to Kidanemariam [42] decreasing of the soil pH (increasing acidity) was as a result of demanding rainfalls that can leaches soluble nutrients like magnesium and calcium, with consequent replacement by Al^{3+} and H^{+} ions [43]. The pH value below 5.50 is regarded as a problematic for most microbial activity, and this directly impacts availability of nutrients to plant [44]. Since the pH of soil sample that collected from Gerbi Giligila was between normal and basic, so the chance of accumulating metal in to the soil and the transfer of metal to the tomato were lower.

3.1.2. Soil electrical conductivity

Electrical conductivity (EC) reflects the concentration of water-soluble salts in the soil. It is influenced by the level of dissolved minerals and measures the capacity of a substance to transmit an electric current at a standardized temperature of 25°C. The soil EC classifications are: non saline less than 2, moderately saline 2-8, very saline 8-16, and extremely saline greater than 16 $mScm^{-1}$ [36]. According to this grouping, the EC findings from this study suggest that the soil is moderately saline, as it contains relatively low levels of ions.

The conductivities in the tomato-growing soil samples were determined to be 3.1 and 3.7 $mScm^{-1}$ at the Gerbi Giligila tomato irrigation site and non-tomato irrigation site, respectively. This demonstrated that pesticides, fertilizers, and irrigation can produce hazardous amounts of metal from a tiny amount of soil in soils with low 45, 46].

Table 3. Average values of soil pH and EC for selected fields of each unit farm.

Sample Site	pH	EC ($mScm^{-1}$)
Non tomato soil	8.01	3.10
Tomato soil	7.45	3.70

EC= Electrical Conductivity

3.2. Stages of Heavy Metals in Soil Samples

The levels of Cr, Cd, Zn, Pb, and Fe in the digested soil samples were measured using Flame Atomic Absorption Spectrometry (FAAS). The results for these metals are displayed in Table 4 and Figure 4. Iron was found to be significantly more abundant than the other metals across all soil samples. As indicated in Table 4, the concentrations of zinc, iron, and lead were notably higher in soils irrigated with water from the Eastern Industry Zone compared to other heavy metals, suggesting that the water may contain elevated sources of these elements.

In general, heavy metals such as lead (Pb) and cadmium (Cd) have no known beneficial effects on humans, and there are no natural mechanisms in the body to regulate them [47]. These metals are highly hazard to both humans and animals, with even low levels of exposure linked to various adverse health effects, plus neurotoxicity and carcinogenicity [48]. The metals examined in this study include essential micronutrients like iron and zinc, as well as non-essential or toxic heavy metals that can harm plants when present in soil above certain thresholds. Chromium (Cr), lead (Pb), and cadmium (Cd) are particularly hazardous to health and have been associated with significant health issues due to environmental contamination [47].

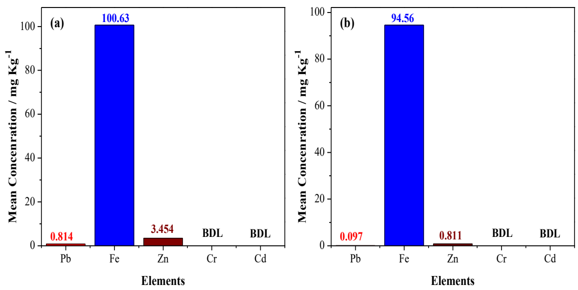
Table 4. Average concentrations of Cr, Cd, Zn, Fe, and Pb in soil samples analyzed using the wet digestion method (n = 3, $mgkg^{-1}$).

Sample Site	Pb	Fe	Zn	Cr	Cd
Tomato Soil	0.814±0.016	100.63±0.173	3.454±0.069	BDL	BDL
Non-Tomato Soil	0.0397±0.007	94.56±0.092	0.811±0.017	BDL	BDL

Figure 4. The concentration of Cr, Cd, Zn, Fe, and Pb of (a) Tomato and (b) Non-tomato soil samples.

3.2.1. Chromium in soil samples

Chromium is essential for the metabolism of cholesterol, fats, and glucose. A deficiency in chromium can



lead to hyperglycemia, increased body fat, and reduced sperm count, while excessive levels can be toxic and carcinogenic [49]. As shown in Table 4, the chromium content in the soil samples ranged below detectable levels (BDL), specifically less than 0.001±0.002 mgkg^{-1}. Both tomato-growing and non-growing soils (non-irrigated) exhibited the lowest chromium concentrations. The permissible limit for chromium in soil is 50 mgkg^{-1}[50]. Therefore, the chromium levels detected in soil samples from areas irrigated with water near the Eastern Ziway zone are unlikely to endanger to human health. Primary sources of chromium pollutants typically include emissions from electroplating activities and the disposal of chromium-containing waste [51]. However, this study suggests that no significant electroplating processes or wastewater use for irrigation are present at the site. A comparison of chromium levels in tomato-irrigated soils with non-irrigated soils indicates that wastewater discharge from the industrial zone and town into the river is unlikely to have an impact. Similar studies have reported chromium concentrations in soil ranging from 20.83 to 104.83 mgkg^{-1}[39] and 20.71-41.45 mgkg^{-1} [51].

3.2.2. Cadmium in soil samples

Cadmium (Cd) is an inessential heavy metal that is highly hazard even at low concentrations. It has been linked to learning disabilities and hyperactivity in early-child age [52]. As indicated in Table 4, the experimental outcomes revealed that Cd concentrations in both tomato-growing and non-tomato soil samples were below detectable levels (BDL). As a non-essential metal, cadmium is considered highly toxic. In similar studies, Amde et al.,[39] reported Cd concentrations in soil ranging from 2.82 to 4.77 mgkg^{-1}, while Singh et al., [51] found levels between 0.79 and 412.16 mgkg^{-1}. The permissible limit for Cd in soil is 3 mgkg^{-1} [50]. Therefore, the BDL (0.001±0.002 mgkg^{-1}) Cd concentrations detected in vegetable-growing and non-tomato soil samples from areas irrigated around the Eastern Ziway and Gerbi Giligila irrigation sites are unlikely to pose a risk to human health. The Cd levels in these soil samples with non-tomato soils suggests that the low concentrations may be due to the absence of wastewater discharge from industrial zones into the river and the minimal impact of chemicals used in pesticides and fertilizers.

3.2.3. Zinc in soil samples

Zinc is a fundamental component of numerous enzymes and serves as in various roles in biological processes. It is essential for DNA synthesis, normal growth, brain development, bone formation, and wound healing. But, at elevated levels, zinc can act as a neurotoxin [30, 53]. As presented in Table 4, the zinc amount in the soil in this research fell within natural ranges, varying from 0.811±0.017 to 3.454±0.069 mgkg^{-1}. Similarly, earlier studies reported zinc concentrations in soil ranging from 60.09 to 414.12 mgkg^{-1}, with uncontaminated soils typically containing around 200 mgkg^{-1} [54] and 133 mgkg^{-1}, respectively. Awokunmi et al., [55] found upper zinc levels in soil samples, ranging between 350 and 3052 mgkg^{-1}, compared to this study. In the Gerbi Giligila irrigation site, tomato-growing soil had the highest zinc content (3.454±0.069 mgkg^{-1}), while non-tomato soil had the lowest (0.811±0.017 mgkg^{-1}) (Figure 5). The WHO/FAO tolerated limit for zinc in soil is 300 mgkg^{-1}. Since the zinc concentrations in this study were well below this limit, all soil samples contained zinc levels within the acceptable range.

A lack of zinc in humans can result in stunted growth, reduced energy levels, and insufficient protein absorption. Conversely, excessive zinc intake from plants may cause symptoms such as vomiting, dehydration, electrolyte imbalances, abdominal pain, and a loss of muscle coordination.

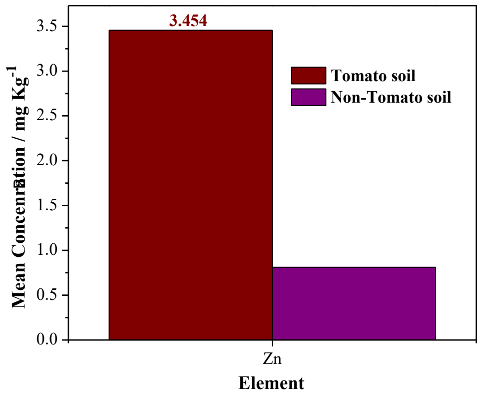


Figure 5. The concentration of Zn in Tomato and Non-Tomato soil sample**.**

3.2.4. Iron in soil samples

Iron is a vital and abundant element essential for both plants and animals. However, excessive iron levels can lead to tissue damage and various diseases in humans, including anemia and neurodegenerative conditions [56]. As shown in Table 4, the iron concentrations in the soil samples ranged from 94.56±0.092 to 100.63±0.173 mgkg^{-1} (Figure 6). These results are below the iron content described by McGrath et al., [54], which was 80,000 mgkg^{-1} in certain contaminated soils. However, other studies have reported lower iron levels compared to this study. For instance, Akubugwo et al., [57] recorded iron concentrations in soils ranging from 73.62 to 226.39 mgkg^{-1}, while Tsafe et al., [58] reported a value of 195.25 mgkg^{-1}. In this study, tomato-growing soil had the highest iron content (100.63±0.173 mgkg^{-1}), while non-tomato soil contained the lowest (94.56±0.092 mgkg^{-1}). The WHO/FAO [59] tolerated limit for Fe in soil is 5,000 mgkg^{-1}. Therefore, the iron content found in soil samples from areas irrigated with river water around the Eastern Ziway Zone and Gerbi Giligila irrigation site are unlikely to endanger to human health. However, the relatively low iron levels in these soils may contribute to iron deficiency in humans if the crops grown in these soils are a primary dietary source. A relationship of iron levels in the soil samples with the permissible limit suggests that the iron content is within safe ranges but may not be sufficient to address potential iron deficiency.

Sample	Pb	Fe	Zn	Cr	Cd
Tomato Sample	0.5445±0.011	7.672±0.153	2.556±0.051	BDL	BDL

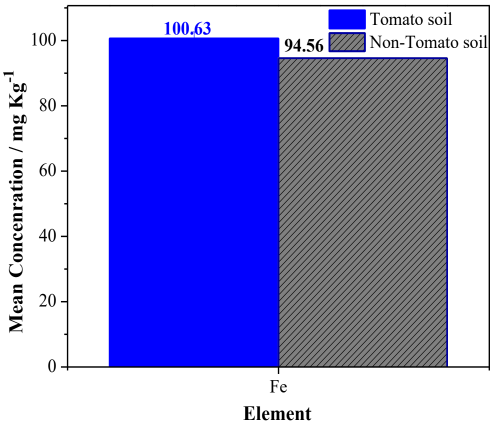


Figure 6. The concentration of Fe in Tomato and Non-Tomato soil sample.

3.2.5. Lead in soil samples

Lead (Pb) is a persistent metal, remaining in soil for 150 to 5,000 years [60]. It causes oxidative stress and disrupts antioxidant balance, leading to poisoning. High levels can result in anemia, brain damage, and nervous system disorders [61]. In this study, soil lead levels ranged from 0.0397±0.007 to 0.814±0.016 mgkg^{-1} (Figure 7), well below the WHO/FAO [59] limit of 100 mgkg^{-1}. Even low lead exposure above 0.01 mgkg^{-1}can harm fetuses and children [62]. Thus, lead levels in soils irrigated near Eastern Ziway Zone and Gerbi Giligila are unlikely to pose significant health risks.

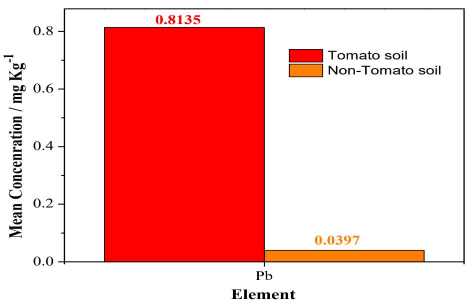


Figure 7. The concentration of Pb in Tomato and Non-Tomato soil samples.

3.3. Heavy Metal Concentration in Vegetable Samples

Vegetables such as tomatoes (*Lycopersicon esculentum Miller*) were analysed for their total metal content, with extents of heavy metals varying based on the plant's ability to accumulate specific elements and their interaction with soil components. Further sources of these elements consist of atmospheric dust, rainfall, plant protection agents, and fertilizers, which can be absorbed through leaves [38, 63-64]. The concentrations of Cr, Zn, Pb, Cd, and Fe in tomato samples grown with river water from the Gerbi Gilgila irrigation farmland are presented in Table 5, revealing that most metals were accumulated to varying degrees compared to WHO standards. These vegetables, consumed by urban populations in Zeway and nearby cities like Addis Ababa and Debre Zeit, show no significant health risks, as the plants appear healthy and grow even with accumulating heavy metals within safe limits for human consumption. The mean concentrations of Cr, Cd, Zn, Fe, and Pb in vegetable samples, analyzed using the wet digestion method (mean ± SD mgkg^{-1}, n=3), are displayed in Table 5.

Table 5. Concentration in dry weight of heavy metals in tomato samples (mgkg^{-1}).

Sample	Pb	Fe	Zn	Cr	Cd
Tomato Sample	0.5445±0.011	7.672±0.153	2.556±0.051	BDL	BDL

The concentration of metal in the tomato Cr, Cd, and Pb, sample that were collected from Gerbi Gilgila around irrigation farm land cultivated area were found to be ranged from BDL to 0.5445±0.011. In this study, lead (Pb) was identified as the metal with the highest concentration, reaching 0.5445±0.011 mgkg^{-1} in tomatoes grown using water from the Gerbi Gilgila irrigation farmland. But the concentration of all elements that were analyzed in this experiment was lower than permissible limit.

The concentration of essential metal in the tomato Fe and Zn, as sample that were collected from Gerbi Gilgila around irrigation farm land cultivated area were found to be ranged from 2.556±0.051-7.672±0.153 mgkg^{-1}. Among this study, Fe was found in highest concentration metals analyzed with concentration of 7.672±0.153 mgkg^{-1} in tomato cultivated Gerbi Gilgila around irrigation farm land and the lowest concentration obtained from this study was Zn. The experimental results show that the trace metals under analysis were observed the concentration of heavy metal in the tomato that were analyzed cultivated at Gerbi Gilgila around irrigation farm land that is: Pb, Cr, Zn, Cd and Fe were lower than the detection limit [65].

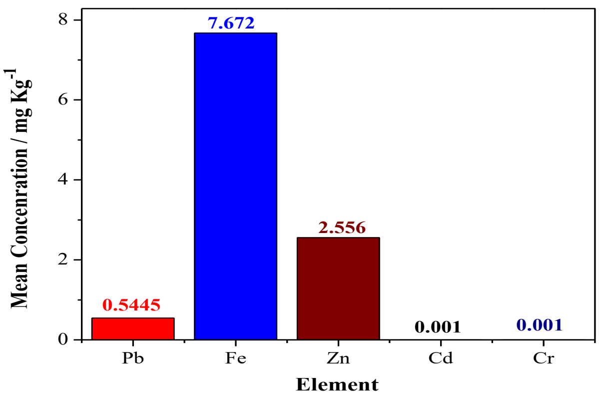


Figure 8. The concentration of metal in tomato sample.

Table 5 reveal that the concentration Fe was highest among the trace metals and the levels obtained was found to be 7.672±0.153 mgkg^{-1} in water Gerbi Gilgila around irrigation farm site. The findings indicated levels below the WHO's maximum allowable limit of 425 mgkg^{-1} for vegetables. The levels of Fe gained in this work were smaller than 545 mgkg^{-1} described by Skinner et al., [66] the concentration of tomato cultivated at water Gerbi Gilgila around irrigation farm less than with the value 138.2 mgkg^{-1} and 148.5-184.3 mgkg^{-1} reported elsewhere [67]. Iron plays a critical role in supporting plant development and ensuring nutritional quality.

Zinc is a key nutrient necessary for healthy growth and development in humans. Deficiency may arise from inadequate diet, poor absorption, excessive loss, or genetic issues related to zinc processing. In this experiment zinc level was in the value of 2.556±0.051 mgkg^{-1} as displayed in Table 5. The WHO suggested limit of zinc in vegetable is 100 mgkg^{-1} [68-69]. However, in this study, the zinc levels detected in tomatoes collected from the irrigation farms in Gerbi Gilgila were below the WHO-recommended threshold. The concentration of Zn in this finding was lower than values of 120 mgkg^{-1} reported elsewhere [70]. Zinc is essential for protein kinases involved in signal transduction and acts as an activator of transcription factors that regulate gene expression. A lack of zinc can disrupt its balance in the human body, leading to symptoms such as stunted growth, neuropsychiatric issues, skin conditions like dermatitis, hair loss (alopecia), digestive problems such as diarrhea, weakened immunity, and reduced appetite [71].

Mining, smelting operations, and household waste items (such as galvanized steel, skincare cosmetics, and pigments) are primary sources contributing to zinc contamination in local soil and groundwater. Zinc tends to be most accessible in acidic soil conditions [72]. The concentration of Zn at this sampling site was lower than the standard so it may be by the cause of soil basicity. In the considered tomato samples, the results of Pb amounts were 0.5445±0.011 mgkg^{-1}. The suggested maximum limit of lead for vegetable is 0.3 mgkg^{-1} [68]. In this work, the metal concentrations of Pb in tomato at Gerbi Gilgila sampling site found lower than the permitted level and the concentrations of lead were minor than 97.7 mgkg^{-1} and 4.88–94.63 mgkg^{-1} [73].

This may clarify why the tomatoes contained lead (Pb) levels below the acceptable limit. Lead accumulation in various vegetables can often exceed permissible thresholds for human consumption by several hundred times. The elevated Pb levels could be ascribed to the frequent usage of organophosphorus fertilizers, such as single superphosphate and triple superphosphate, by farmers. These fertilizers often contain significant amounts of cadmium (Cd) and lead (Pb). However, the bioavailability of Pb is reduced through the formation of complexes with anions like hydroxide, carbonate, sulfate, sulfide, and particularly phosphates. At this specific sampling site, the lower Pb levels might be due to reduced use of certain pesticides, for instance lead arsenates, during cultivation, the absence of wastewater for irrigation, and the presence of anions like hydroxide, carbonate, sulfate, sulfide, and phosphates in the soil [69]. Additionally, the regular consumption of tomatoes from these areas is considered safe.

Pb has no known biological purpose and tends to accumulate inside the body. Exposure to lead can cause serious health issues, particularly in children and pregnant women, as it is a neurotoxin that permanently disrupts brain development. It also builds up in bones, and its release during pregnancy and breastfeeding can lead to additional exposure [74]. As shown in Table 5, the cadmium (Cd) levels in tomatoes from the sampling sites were very low, measuring 0.001±0.002 mgkg^{-1}. These levels were significantly below the maximum limit of 0.3 mgkg^{-1} recommended by the Organization, [68] for vegetables. The highest Cd content in this study was much lower than the 2.5 mgkg^{-1} reported by Lokhande et al., [70] and 151.8 mgkg^{-1} reported by Ata et al., [73]. Cadmium was the least detected trace metal in this study. The low cadmium levels may be as a result of the absence of Cd-holding phosphate fertilizers, the use of river water for irrigation, and the potential use of natural fertilizers by farmers.

Cd concentration in all vegetable are generally low (Table 5). Apart from the low level in soil, the weak to slightly alkaline soil pH. Soil pH is an extremely important influence in monitoring metal uptake in crops, conclude that the total soil Cd content and soil pH are the most important soil factor that affect the concentration of Cd in food crops. The levels of the metals in the tomato are given in Table 5. The result demonstrate that out of the five examined metals the chromium metals was with lower amount compared to all heavy metals. The concentration of Cr in the tomato samples was less than 0.001±0.002 mgkg^{-1} at sampling site. The chromium (Cr) levels measured in this study were below the maximum tolerable limit of 2.3 mgkg^{-1} set for vegetables [73].

Soil and groundwater contamination by Cr(VI) primarily results from the leaching of waste generated by industries like tanning, pigment production, and steel manufacturing. Trivalent chromium, Cr(III), is a necessary trace element for humans, with a safe daily intake of 50-200 µg, and it becomes toxic only at high concentrations. On the other hand, Cr(VI) is highly toxic, and long-term exposure can cause kidney and liver damage, as well as increase the risk of cancer. Although Cr(VI) is more harmful to plants, they tend to absorb it in greater quantities. Cr(VI) is more soluble in soil moisture and water, while Cr(III) mostly exists in soil as insoluble ions or hydroxides. This is due to Cr(III) undergoing hydrolysis at neutral pH, making it highly insoluble [75]. So if Cr (VI) is largely present in soil the vegetable may be absorb the ions from the soil. So in this experiment the concentration of Cr in tomato was very low it may be due to the soil basicity and the farm land may not be contaminated by the source of chromium ions.

3.4. Heavy Metal Transfer Factor (TF) from Soil to Vegetables

The transfer coefficient measures the relative bioavailability of metals to plants and depends on both soil and plant characteristics. It is determined by dividing the metal concentration in a vegetable crop by the total metal concentration in the soil [76]. A higher transfer coefficient indicates weaker retention of metals in the soil or better efficiency of plants in absorbing metals, but a lower coefficient advises strong binding of metals to soil particles. Plant uptake from soil is a critical factor in human experience to metals through the food chain. The Transfer Factor (TF) or Plant Concentration Factor (PCF) is a criterion used to quantify the movement of trace elements from soil to plants, and it is also affect the properties of soil and vegetables.

$$TF = \frac{CMV}{CMS} \quad (2)$$

Where, CMV = Concentration of metal in edible part of vegetable and CMS = Concentration of metal in soil [76].

In this study, the Transfer Factors (TF) of many heavy metals from soil to vegetables are detailed in Table 6. Higher TF values indicate weaker retention of metals in the soil or more efficiency of vegetables in absorbing metals, while lower TF values suggest strong binding of metals to soil particles [77]. The TF or Plant Concentration Factor (PCF) ranges were as follows: Zn (0.74–3.149), Fe (0.076–0.0811), and Pb (0.668–13.115). The trend of TF for heavy metals in the vegetable samples followed the order: Pb > Zn > Fe = Cr = Cd. The movement of metals from soil to plants depends on the physicochemical properties of the soil and the specific vegetable species, and is influenced by numerous environmental and human factors [78]. The big TF values were observed for Pb (13.115) and Zn (3.149), likely due to the higher mobility of these naturally occurring heavy metals in the soil and their lower retention compared to other toxic cations [30, 78].

Table 6. The transfer factors (TF) measure the movement of heavy metals from soil into vegetables.

TF	Pb	Fe	Zn	Cr	Cd
TF of Tomato Soil	0.668	0.076	0.74	-	-
TF of Non-Tomato Soil	13.12	0.081	3.149	-	-

3.5. Method Validation

The methods used in this study were validated using the spiking technique, and the recovery values are presented in Table 7 for tomato samples cultivated in Gerbi Giligila. To assess the efficiency of the analytical procedure, the percentage recovery was calculated by adding a known quantity of heavy metals from a stock solution to the tomato samples, which were then digested. The concentrations of both spiked and non-spiked samples were measured, and results were derived through calculations. Method validation ensures that the analytical method is suitable for its intended purpose. As shown in Table 7, the percentage recovery for the tomato samples from Gerbi Giligila ranged between 78.7% and 117%, falling within the acceptable range of 70% to 125%. This confirms the reliability of the digestion and analysis methods used in this study [79].

Table 7. Values of the recovery analysis of tomato sample.

Heavy metal	Concentration before spiking	Concentration after spiking	Amount added	% Recovery
Pd	0.97	2.93	2.00	98.20
Zn	1.67	3.61	2.00	97.12
Cd	1.15	2.86	1.60	107.00
Fe	1.65	3.37	2.00	86.00
Cr	1.50	3.03	1.60	95.50

4. Conclusion

The most important aim of this work was to evaluate the concentrations of certain toxic heavy metals, essential metals, and physicochemical variables such as conductivity and pH from collected samples (the Gerbi Gilgila irrigation site). Samples were analyzed for physical and chemical properties and heavy metals (Fe, Cr, Pb, Cd, and Zn). The levels of these heavy metals in tomato samples from Ziway, Ethiopia, were determined using Flame Atomic Absorption Spectrometry (FAAS) following wet digestion. The optimized method proved to be effective, defined, and accurate for the metals analyzed, as confirmed by recovery experiments, which yielded satisfactory recovery percentages for the selected heavy metals. The results aligned with the FAO/WHO guidelines for permissible elemental concentrations in human nutrition, showing that the tomato samples are safe for consumption. These findings offer baseline data for heavy metal analysis in tomatoes from the study area. Regular monitoring of metal levels in vegetables is crucial to prevent their entry into the food chain, and further research should focus on soil samples where tomatoes are cultivated. The pH of the soil samples was within the normal to slightly basic range, and the electrical conductivity (EC) was below the WHO permissible limits. Additionally, a assessment of heavy metal concentrations in this study with literature reviews revealed lower levels, suggesting that wastewater discharge into the river from the town, factories, and farm chemicals has not significantly impacted heavy metal contamination.

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