ADDIS ABABA UNIVERSITY

COLLEGE OF NATURAL AND COMPUTATIONALSCIENCES

DEPARTMENT OF CHEMISTRY

GRADUATE THESIS (Chem.750)

Determination of metal contents in carrot and its corresponding soil of the plant Cultivated in Akaki Kality farms in Addis Ababa, Ethiopia by Flame Atomic Absorption Spectroscopy (FAAS)

By; Seare G/micheal

Id no; GSR/2525/14

Advisor: Dr. Negussie Negash

Addis Ababa, Ethiopia

ADDIS ABABA UNIVERSITY

COLLEGE OF NATURAL AND COMPUTATIONAL SCIENCES

Declaration

I the undersigned, hereby declare that this research study is my own original work and that all references have been correctly recorded and acknowledged, and that it has not previously been submitted in full or in part to any university for academic qualification. The thesis "Determination of metal contents in carrot and their corresponding soil of the plant Cultivated in Akaki kality farms in Addis Ababa, Ethiopia by Flame Atomic Absorption Spectroscopy (FAAS)" is conducted under the supervision of Doctor Negussie Negash, Department of Chemistry, and Addis Ababa University, Ethiopia.

Name: Seare G/micheal

Signature: ___________________

This thesis has been submitted for examination with my approval as university advisor. As thesis advisor, I hereby certify that I have read this thesis prepared under my guidance and recommended that it can be accepted as fulfilling the thesis requirement.

Advisor's Name: Doctor Negussie Negash

Signature: _____________________________

2023, Addis Ababa University

ADDIS ABABA UNIVERSITY

COLLEGE OF NATURAL AND COMPUTATIONAL SCIENCES

DEPARTMENT OF CHEMISTRY

Determination of metal contents in carrot and their corresponding soil of the plant Cultivated in Akaki Kality farms in Addis Ababa, Ethiopia by Flame Atomic Absorption Spectroscopy (FAAS)

Approved by the examining board

Name	Signature	Date
Dr. Negussie Negash	__________	___________
(Advisor)		
Prof. Negussie Megeresa	__________	__________
(Examiner)		
Dr. Weldegebriel Yohanness	__________	__________
(Examiner)		

Acknowledgements

I praise the almighty God who gave me this opportunity and helped me to accomplish my study. I also thank him for upholding me from the problem in my life at any moment.

I would like to express my deepest gratitude to my advisor Dr. Negussie Negash for his patience, friendly approach, sincere, and immense devotion to help me for the accomplishment of this work. I have a special respect and appreciation for his support whenever he is requested.

I would like to express my special gratitude and thanks to Dr. Weldegebriel for his unreserved cooperation during AAS analysis.

Finally, I would like to thank my beloved families who gave support during my study.

Table of contents

List of figures

List of tables

Abbreviations

AES	Atomic emission spectroscopy
ANOVA	Analysis of variation
ASV	Anodic stripping voltammetry
BDL	Below detection limit
DF	Degree of freedom
FAAS	Flame atomic absorption spectrometry
FAO	Food and agriculture organization
GFAAS	Graphite furnace atomic absorption spectrometry
HMs	Heavy metals
ICP-MS	Inductively coupled plasma mass spectrometry
LOD	Limit of detection
MDL	Method detection limit
ND	Not detected
NAA	Neutron activation analysis
NEMA	National environmental management authority
%RSD	Percentage relative standard deviation
%R	Percent recovery
R^2	Regression correlation coefficient
SD	Standard deviation
TCAS	Thermolysis-coupled atomic absorption spectroscopy
XRF	X-ray fluorescence
WHO	World health organization

Abstract

The aim of this study is to determine the metal concentration of carrot and the corresponding soil sample collected from akaki kality farms in Addis Ababa, Ethiopia. Levels of selected metals (Fe, Cu, Ni, Zn, Pb and Cd) were determined using flame atomic absorption spectroscopy. After proper samples pre-treatment of washing, dried, crushed and homogenized, known weight of carrot sample was wet digested using 3:1 mL of HNO_3, of HCl for 3:00 h at 300 ^{o}C and for soil sample 3:1 mL of HNO_3 and of HCl and 1 mL for 3:00 hr at 300^{o}C. Then using the optimized conditions sample preparation was made and levels of metals was determined by FAAS.

The mean concentration range (mg/kg) of each metal in carrot were Zn (52.30)> Cu (25.3)> Pb (25.18) >Fe (23.94) > Cd (2.43), Ni was below the detection limit and in soil samples Zn (134.46) > Cu (71.45) > Pb (22.18) >Cd (4.02), respectively. Ni and Fe were below the detection limit. The result indicates that concentration of Cd, Zn, Cu, Fe, and Pb metals in carrot sample and Cd, Zn, Cu, and Pb metals in its soil is higher than the WHO guidelines. ANOVA indicated that there is significant difference between the mean concentration of Cd Cu, and Zn and the mean concentration of the metal Pb does not significantly differ between the samples means among carrot and soil samples at 95% confidence level, respectively. The accuracy of the optimized procedure was evaluated by analysing the digestion of the spiked samples with standard solution and the percentage recoveries varied from 93.5 % to 101.6%.

Keywords: Carrot, Soil, heavy metals, minerals, Digestion, Optimization, flame atomic absorption spectrometry

1. Introduction

1.1 Background of the study

Natural contamination is an undesirable alteration within the climate, the hydrosphere, and the lithosphere. Progressed industrialization forms have given consolation to human creatures on the one hand, but it has moreover brought about an aimless discharge of gasses and fluids that contaminate the environment of the natural framework on the other hand. Quick industrialization and urbanization have contaminated the environment with overwhelming metals, and the rate of relocation and transport of these metals within the environment has expanded drastically since the 1940s [1]. Contamination due to overwhelming metals poses a natural risk and is right now a major concern [2]. Fast mechanical advancement has brought about a genuine concern for common assets such as soil and water in numerous nations [3]. Businesses are one of the anthropogenic exercises that have contributed to expanded concentrations of numerous overwhelming metals within the environment [4].

Heavy metals are among the foremost vital contaminants debilitating human well-being [5]. They are not biodegradable and stay within the environment. They sully the nourishment chain and cause different well-being issues in creatures and people due to their poisonous quality. Approximately one-fourth of human infections are due to the introduction of natural poisons [6]. Overwhelming metals such as cadmium (Cd), lead (Pb), arsenic (As), and mercury (Hg) constitute one of the most natural toxins that can cause a basic issue for all life forms, such as soil microbial populaces, plants as well as people and hurt human wellbeing [7]. For case, introduction to tall Pb concentrations brings well-being problems such as the skeletal, circulatory, anxious, enzymatic, endocrine, and resistant frameworks within the human body, and introduction to Cd can cause cancer [8].

Industrialization in numerous nations has driven genuine natural contamination. The quick development of businesses and expanded transfer of dangerous squander has disintegrated the quality of water assets [9]. Mechanical releases are one of the major sources of overwhelming metals dependable for biological contamination. Human exercises without a doubt make numerous natural issues, which significantly influence the encompassing soil and water assets [10]. Concurring to [11], utilizing treated and untreated wastewater for water systems may result in the amassing of heavy metals in soils and thus in plants and foodstuffs. Soil contamination happens due to different human exercises such as mechanical exercises and chemical applications [12]. Soil is for the most part respected as the extreme sink for overwhelming metals discharged into the environment [13]. Soil contamination by businesses is one of the most prominent natural issues and poses major issues to the environment, life forms, and people. Subsequently, human wellbeing dangers as a result of uncovering the soil to overwhelming metals ought to not be disregarded [4].

These days expansive sums of untreated sewage/industrial water are being released into surface bodies for transfer. In times of water deficiency, hence, agriculturists utilize this squandered water to flood their vegetable areas in city conurbations. Such water systems hones donate exceptionally great edit yields as they contain huge sums of natural fabric and inorganic components fundamental for plant development. But it too may contain non-essential overwhelming metals which, when displayed in a huge sum, may be exchanged to creatures and human creatures through the nourishment chain [14]. By and large, the ranchers are not mindful of such consequences of a tall build-up of overwhelming metals within the nourishment chain; subsequently, they proceed to develop vegetables on sewage and mechanical effluents.

In developing nations like Ethiopia, agrarian arrive is sullied with overwhelming metals, which may be a genuine natural issue due to their poisonous quality [15]. Water system water sullied by mechanical effluents has driven extremely overwhelming metal defilement in soil and plants. Due to the utilization of wastewater for soil irrigation, the concentration of heavy metals within the consumable parts of developing plants is expanding [16].

The major sources of heavy metal defilement within the environment are human exercises such as mechanical waste generation, inevitably coming about within the genuine defilement of the encompassing water assets on neighbourhood, territorial, and worldwide scales and causing critical well-being issues in people and creatures [17]. One of the most prominent water quality issues is overwhelming metal defilement. New water is beneath weight due to mechanical exercises. Hence, deciding the chemical substance of water assets sometime recently any human utilize is fundamental [18]. The gushing produced by businesses, as sketched out in quintessence, regularly comprises an over-awareness of overwhelming metals such as cadmium (Cd), arsenic (As), mercury (Hg), copper (Cu), and lead (Pb) which is natural issues [19].

The presence of heavy metals in completely different foods constitutes genuine well-being risks, depending on their relative levels. For illustration, cadmium and mercury harm the kidney and cause indications of inveterate poisonous quality, counting disabled kidney work, destitute regenerative capacity, hypertension, tumours, and hepatic brokenness. tall lead concentrations bring around well-being issues, causes such as the skeletal, circulatory, nervous, enzymatic, endocrine, and safe frameworks within the human body [4,12]. and renal disappointment and liver harm. A few other metals (e.g. chromium, zinc, and copper) cause nephritis, and anuria is a broad injury within the kidney. In this manner, the issue of nourishment defilement by harmful metals is accepting worldwide consideration.

The assurance of trace or ultra-trace sums of components has become increasingly critical in areas such as natural, natural, and fabric sciences [20]. In any case, it is exceptionally troublesome to decide to follow ultra-trace components straightforwardly indeed with the profoundly touchy rebellious presently accessible, since the discovery affectability is some of the time inadequate and the impact of frameworks in tests cannot be ignored. The improvement of the components to be analyzed in conjunction with the elimination of frameworks in test arrangements is imperative to realize the specified affectability with fewer types of impedance from networks in nuclear spectroscopic strategies, such as AAS, and ICP-AES [21].

The water and soil contamination of heavy metals has ended up an address of significant open and logical concern in light of proof of their extraordinary harmfulness to human wellbeing and natural frameworks. The central requirement for in situ perception of the heavy metal is due to the truth that the issues depend unequivocally on the particular nearby mechanical forms. For field perception, dregs have been broadly utilized as natural markers, and their capacity to follow defilement sources is broadly recognized [22]. The flame atomic absorption spectrometry strategy is utilized, which offers quick multi-elemental investigation, moo running costs, exceptionally great exactness, and tall affectability.

This study aimed to determine the concentrations of heavy metals on carrot and its soils around akaki river farms to evaluate their status and their impacts on carrots and its soil produced using untreated urban, agricultural, municipal and industrial wastewater effluents.

1.2 Statement of the problem

Water basins like rivers, ponds especially Akaki River are polluted with toxic heavy metals that come from untreated urban, agricultural and industrial effluents. This may result in bio-accumulation of heavy metals in humans using water directly and eating agricultural products. Since, Akaki River passes through populated residential areas, towns, industrial and agricultural sites. Heavy metal contamination has become a very serious issue to public health since they are non-biodegradable and highly toxic. Heavy metal accumulation gives rise to toxic concentrations in the body, while some elements (e.g., Arsenic, cadmium, chromium) act as carcinogens and others (e.g., mercury, copper and lead) are associated with developmental abnormalities in children [10]. The analysis of heavy metals that include zinc, copper, cadmium, lead, iron and nickel is therefore justified to provide precautionary use of water, as well as provide a basis to aware government authorities such as National Environmental Management Authority (NEMA) towards management of discharge pollutant wastes into the river.

1.3. Objectives of the study

1.3.1. General objective

- ✓ The overall objective of this research is to determine the concentration of toxic and trace heavy metals in the Carrot and its soil collected from the farm areas of Akaki kality river Addis Ababa, Ethiopia.

1.3.2. Specific objective

- ✓ To develop and validate sample preparation procedure (digestion procedure) for the extraction of selected trace metal concentration from carrot and soil samples for their subsequent determination by using flame atomic absorption spectrometry (FAAS).
- ✓ To compare the concentration of metals determined with the acceptable limits of by WHO/FAO
- ✓ To study the correlation of the analyzed metals in carrot and the corresponding soil.
- ✓ To compare the metal concentration of carrot and soil sample collected with others literatures reported value.

1.4. Significance of the study

The potential hazard from the accumulation of metals from plants grown on contaminated soil is becoming an increasing problem in many countries, as are food safety issues and potential health risks from the accumulation of heavy metals in soils, water and plants one of the biggest problems is serious environmental concerns from environmentalists and health practitioners.

The major significance of this study is to provide information about the presence of heavy metals in carrots and its soils around akaki kality river farms in Addis Ababa, Ethiopia. Also the study gives some hints to further studies for toxicity and effect of heavy metals in soils and carrot around the area and also to provide some helpful information as a stepping stone for other researchers.

2. Literature review

Over the past two decades, the term "heavy metals" have been used increasingly in various publications and legislation related to chemical hazards and the safe use of chemicals.

2.1 Heavy metals

A metal of moderately high density (particular gravity more prominent than around 5 g/cm^3) or of high relative nuclear weight is characterized as a heavy metal. The term "overwhelming metals" is utilized to depict more than a dozen components that are metals or metalloids e.g. chromium, arsenic, cadmium, lead, mercury, manganese, etc. Overwhelming metals are characteristic constituents of the Earth's outside. Since they cannot be corrupted or crushed and are diligent in all parts of the environment. In little sums, they enter the human body through nourishment, drinking water, and discussion. Living beings require shifting sums of "heavy metals". Iron, cobalt, copper, manganese, molybdenum, and zinc are required by people.

Human exercises influence the normal topographical and organic dispersion of overwhelming metals through contamination of air, water, and soil. People are moreover capable of modifying the chemical shapes of heavy metals discharged into the environment. Such modifications regularly influence a heavy metal's harmfulness by permitting it to bio-accumulate in plants and creatures, bio-concentrate within the nourishment chain, or assault particular organs of the body. Bioaccumulation refers to an increment within the concentration of a metal in a organic organism over time, compared to the ordinary concentration within the environment Numerous metals and other chemicals amass in living things any time they are taken up and put away speedier than they are broken down (metabolized) or excreted [25,26].

Some heavy metals such as mercury and lead are toxic metals that have no known vital or beneficial effect on organisms, and their accumulation over time in the bodies of animals can cause serious illness.

In small amounts, certain heavy metals are nutritiously fundamental for a solid life (e.g., press, copper, manganese, and zinc). A few of these are alluded to as the following components. These components, or a few shapes of them, are commonly found in foodstuffs, in natural products and vegetables, and in commercially accessible multivitamin items. There are reports of shifted concentrations of overwhelming metals building up in plants. Its over-the-top utilization has the potential to result in the admissions of noxious overwhelming metals, which might cause lethal complications such as aggregate harming, anxious disarranges, and cancer. When cadmium, copper, lead, nickel, mercury, and arsenic collect in plants at levels over the by and large allowed limits, it contaminates the environment and postures a genuine well-being hazard. For the reason of guaranteeing the security and quality of nourishment, it is essential to test plant extricates for the nearness of exceptionally noxious overwhelming metals such as arsenic, mercury, lead, and cadmium [27].

2.2. Accumulation of heavy metal on soil & plant

Since the lack or overabundance of these metals constitutes a well-being hazard to individuals and other animals when gathered inside the natural framework, the collection of these metals within the soil-plant framework has ended up a worldwide issue. When devoured over time, consumable trim plants developed on metal-enriched soils may gather these metals in sums that are destructive to human wellbeing [28].

The larger part of plants for the most part created by taking supplements from the soil. The sort of soil affects their capacity to realize this. A blend of sand, sediment, clay, and natural matter can be found in soil. The area influences this combo. The sum of supplements that are accessible to plants depends on the surface and pH of the soil. The way that metal takes to the plant is: soil > roots > stems > clears out [29].

2.3. Sources of heavy metals

One of the biggest sources of heavy metals is the earths outside. Heavy metal sources were part into two fundamental categories by researchers: anthropogenic and natural sources. In differentiate to anthropogenic sources, which incorporate industry, farming, mining, and residential effluents, natural sources incorporate sedimentary rocks, volcanic emissions, soil arrangement, and shake weathering [30].

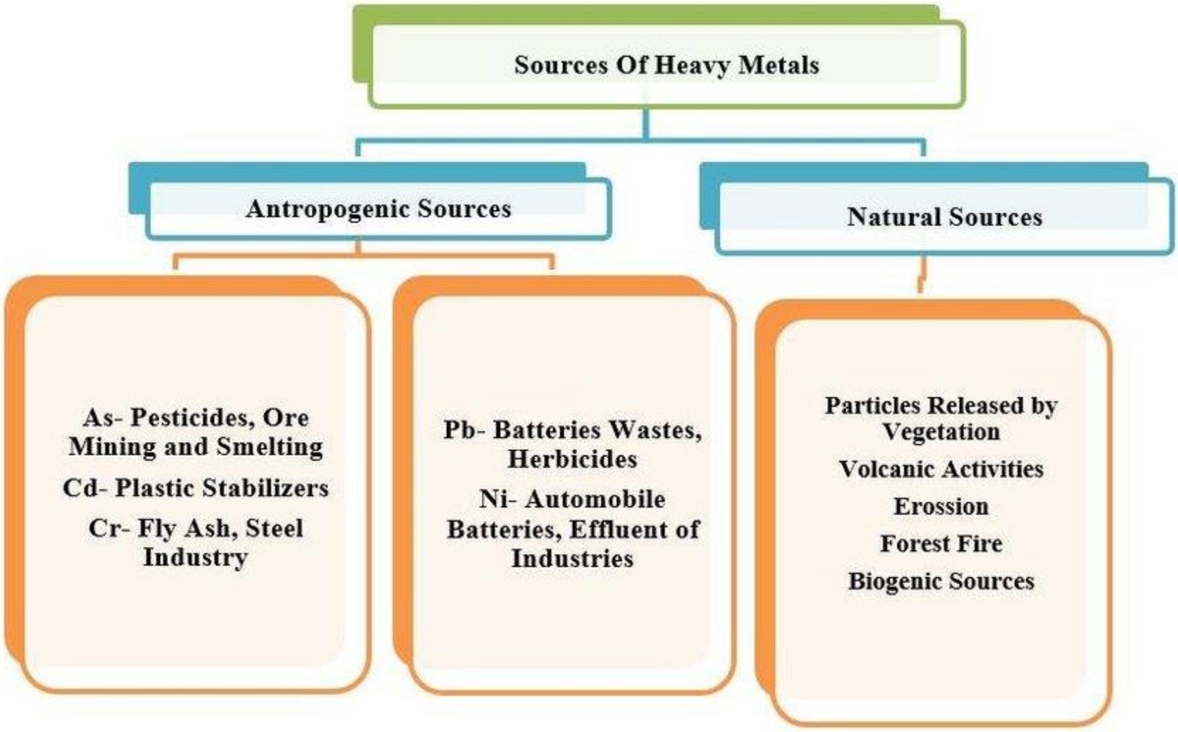

Figure 1: source of heavy metal

2.3.1. Natural sources of heavy metals

In terms of heavy metals' characteristic sources, molten and sedimentary rocks are thought to be the foremost predominant. It has been found that the extents of diverse components inside one shake sort, as well as between particular shake sorts, shift. The sort of rocks and the state of the nearby environment can be utilized to decide the concentration of heavy metals [30]. Alongside stream silt, soil arrangement is another vital figure in the build-up of heavy metals.

2.3.2. Anthropogenic sources of heavy metals.

Heavy metals are thought to come from anthropogenic sources such as businesses, farming, mining, domestic, and wastewater. These components altogether contribute to the increment within the concentration of heavy metals and contamination within the environment, such as the discharge of Cu, Zn, and As from refining; As from bug sprays; Hg from burning fossil fills, and Pb from car debilitate. Moreover, scheduled human exercises like cultivating, fabricating, and mechanical forms hurt the biospheres adjust [30].

2.4. Effect of heavy metals toxicity on plants

Naturally, the plant needs certain components to grow. Heavy metal exposure can seriously harm plants, despite the fact that these trace elements are necessary. The rhizosphere is where heavy metals first affect plants. The mineral oxidation and dissolution in the rhizospheres is indicated by the carbonate deposits transpiring on plant roots. It has been discovered that these mechanisms raise the metal ion concentrations in rhizosphere fluid. Plants that are exposed to cadmium become mineral deficient. The oxidative stress caused by the heavy metals' production of free radicals produces an increase in the quantities of reactive oxygen species (ROS) inside of cells, which in turn damages biological molecules such as proteins, nucleic acids, lipids, and enzymes. Numerous physiological issues, including DNA damage, cell death, and the suppression of enzyme activity, are brought on by the malfunction in all these biological molecules, which may finally cause the death of the entire plant [36].

2.5. Roles of some essential (trace) and non-essential metals

In understanding their relative concentrations within the body, minerals are ordinarily partitioned into two major classes. One of the bunches is composed of large-scale components or large-scale minerals, such as calcium, magnesium, potassium, and sodium, which are found in moderately high amounts and are required in amounts each day. Microelements, moreover known as the following components, are minerals that are shown in diminutive sums and are required in doses of a couple of milligrams or less per day. These minerals incorporate zinc, copper, nickel, and chromium. Other components, including aluminium, lead, cadmium, mercury, and arsenic, have been recognized as possibly unsafe. Really, in the event that devoured in fitting amounts and for long sufficient periods of time, all basic components may also be perilous to both people and creatures [29]. Underneath may be a brief portrayal of the physiological capacities of Cu, Zn, Cr, Ni, Cd, Pb, and Fe.

Cadmium

Cadmium could be a poisonous component that will be collected in soils from different human exercises. A natural source of cadmium is the weathering of rocks whereas a few cadmium enters the air through woodland fires and volcanoes. No cadmium mineral is mined for the metal, since more than sufficient is delivered as a by-product of the smelting of zinc from its mineral, sphalerite (ZnS), in which CdS may be a noteworthy debasement, and making up as much as 3%. It is comparable in numerous regards to zinc but it shapes more complex compounds. Around three-fourths of cadmium is utilized in Ni-Cd batteries, and most of the remaining one-fourth is utilized primarily for shades, coatings, and plating, and as stabilizers for plastics. Cadmium has been utilized especially to electroplate steel where a film of cadmium as it were 0.05 mm thick will give total assurance against the ocean. Cadmium has the capacity to retain neutrons, so it is utilized as a obstruction to control atomic parting. Metal plating and tire elastic are considered the likely sources of Cd in urban soil and road tidy [28].

Cadmium (Cd) and its compounds are amazingly poisonous at all levels and tend to bio accumulate in living beings and biological systems. Cadmium determines its toxicological properties from its chemical similitude to zinc. Cadmium is bio-persistent and, once retained by a life form, remains inhabitant for a long time (over decades for people) in spite of the fact that it is in the long run excreted. In people, long-term presentation is related to renal brokenness. The tall presentation can lead to obstructive lung illness and has been connected to lung cancer, although data concerning the last mentioned are troublesome to decipher due to compounding components [1].

Due to its event within the environment from a number of anthropogenic causes and the dangers it poses to the whole biological system, cadmium is respected as an unsafe and non-essential overwhelming metal. The lion's shares of Cd ions are taken up by plant roots because of their versatility, bioavailability, and concentration; the leftover portion can be taken up straight from the air. Furthermore, Cd builds up within the roots, shoots, and eatable segments of plants after entering plant cells by means of other transporters such as Calcium (Ca) channels. Plants uncovered to tall levels of Cd experience an assortment of physiological and biochemical changes. Also, the build-up of Cd in plants has destructive impacts, such as the concealment of a few exercises (mineral transport, photosynthetic device, and supplement admissions). Moreover, it may avoid the passage of Fe into plant shoots [28].

Zinc

Zinc is a fundamental trace component for people. Its insufficiency as well as overabundance is destructive. Later it appeared that zinc is greatly critical, particularly in fatal improvement and the nourishment of new-born children. The grown-up human body contains around 2.3 g of zinc which happens generally in over 100 proteins. The typical everyday prerequisite for zinc is 15 mg for grown-ups and 5 mg for children. Zinc plays a part in carbohydrate, lipid, and protein digestion systems and within the union and breakdown of DNA. Because of these functions, zinc insufficiency within the embryo will result in impeded development mutation of the body and chromosomal anomalies. A zinc insufficiency after birth may result in dwarfism, destitute cravings, mental laziness, etc. [28].

An abundance sum of zinc on the other hand can cause a sweet taste, dry throat, hack, throbbing shortcoming, fever, stomach issues, sickness, heaving, and central anxious framework clutter. [1].

Lead

Metallic lead does not break up in water and is not behind, be that as it may, lead can combine with other chemicals to make lead compounds or lead salts. A few lead salts break up in water way better than others. In spite of the fact that lead itself cannot be broken down, lead compounds in water may combine with diverse chemicals depending on the sharpness and temperature of the water.

Lead features a thickness of 11.3 g/cm3 nuclear number 82 and is derived from its sulfide mineral galena, carbonate cerus location, and sulfate anglesite. The minerals are habitually found in combination with other recoverable metals such as Cu, Zn, and Cd. Lead exists in different oxidation states (0, I, II, and IV), which are of natural significance with oxidation +2. Lead was put at position 2 on the Office for Poisonous Substances and Infection Registry’s (ATSDR) beat 20 lists of most perilous overwhelming metals and it accounts for most of the cases of pediatric heavy metal harming. Lead has been utilized in pipe making, channels, and patching materials as well as battery making, plumbing, ammo, fuel-added substances, paint shades, and pesticides. A few impacts of Pb harming incorporate lack in cognitive work due to the devastation of the central anxious framework, stomach torment and inconvenience, arrangement of frail bones as Pb replaces calcium, and frailty due to a decrease of proteins concerned with the amalgamation of ruddy blood cells. Lead too leads to diminished ripeness, causes cancer, and other minor impacts like spewing, queasiness, and cerebral pain. Introduction to tall Pb levels can seriously harm the brain and kidneys, cause unsuccessful labor in pregnant ladies, harm the organs capable of sperm generation in men, and may eventually cause passing [25, 31].

Children are more sensitive to the impacts of lead than grown-ups. A child who swallows expansive sums of lead may create blood frailty, kidney harm, extreme stomach-ache, muscle shortcoming, and brain harm. The lower IQ levels and other neuropsychological lacks among children uncovered to higher lead levels have been well recorded [25].

Nickel

Nickel (Ni) is required by both plants and creatures for the work of particular proteins and possibly for the press digestion system. When eating a shifted count calories, individuals have never illustrated a nickel insufficiency. Grown-ups are thought to require between 100 and 300 g of nickel day by day [32].

Various items, including stainless steel and other amalgams, castings, catalysts, batteries, gadgets, ceramics, shades, and indeed coinage, require nickel metal and its subsidiaries. Ni poses a hazard to human wellbeing indeed in spite of the fact that it isn't a substance that's habitually discharged into the environment. Ni is generally unsafe to people due to its capacity to trigger touchy reactions in expansion to its carcinogenicity. The foremost negative well-being result within the common populace is unfavourably susceptible contact dermatitis, which is brought on by delayed skin contact with Ni for those who are as of now touchy to it. It has been proposed that Ni2+ is the atomic cause of the harmful Ni species that are capable of genuine well-being impacts, such as unfavourably susceptible contact dermatitis and respiratory tract cancer. The taking-after organ frameworks are affected by cardiovascular (heart and blood vessels), respiratory (from the nose to the lungs), dermal (skin), and immunological [33].

Mercury

Mercury (Hg), a worldwide toxin created by anthropogenic and characteristic implies acts as a bio accumulative poison that seriously influences our environment and human lives. Mercury exists actually and is a man-made contaminant. The normal wealth of Hg within the earth’s outside is 0.09 ppm; in soils 30 to 160 ppb; in streams 0.07 µg/L, and in-ground waters 0.5 to 1 µg/L. Mercury happens free in nature, but the chief source is cinnabar (HgS). The discharge of prepared mercury can lead to a dynamic increment within the sum of climatic mercury, which enters the atmospheric-soil-water dissemination cycles where it can stay in circulation for a long time. Due to the capacity to travel over long separations within the air as vaporous essential species, distant from the point outflow source, mercury is respected as a `global pollutant'. The most common pathway of defilement of people with mercury is the nourishment chain, where the foremost poisonous species, methyl mercury, bio accumulates. Amid combustion mercury in coal is nearly completely transmitted to the atmosphere. With a gigantic sum of coal expended, coal combustion is one of the most anthropogenic sources of this component within the environment. The Hg substance in coals changes totally different coal bowls, geographical ages, and coal positions [34]. Mercury is utilized in amalgams, reflect coatings, vapour lights, paints, measuring gadgets (thermometers, indicators, and manometers), pharmaceuticals, pesticides, and fungicides.

Mercury may be an omnipresent natural poison that causes a wide run of unfavourable well-being impacts in people. Three shapes of mercury (elemental, inorganic, and natural) exist, and each has its claim profile of toxicity. Introduction to mercury ordinarily happens by inward breath or ingestion. Promptly ingested after its inward breath, mercury can be an indoor poison, for illustration, after spills of natural mercury within the domestic; in any case, industry outflows with coming about surrounding discuss contamination stay the foremost critical source of breathed-in mercury. The creating hatchling and youthful children are thought to be excessively influenced by mercury presentation, since numerous perspectives of improvement, especially brain development, can be irritated by the nearness of mercury. Minimizing mercury presentation is, subsequently, fundamental to ideal child well-being.

Chromium

A few people's chromium deficiency may be connected to diabetes. The support of glucose retention in cells is the property of chromium that has gotten the foremost inquiries about. Chromium enters the cell and likely boosts the development of glucose over the cell layer or increments the number of affront receptors. A chromium deficiency is characterized by diminished glucose resilience, expanded serum cholesterol, and triglycerides in both people and creatures. Chromium's ESADDI, or evaluated secure and satisfactory everyday dietary admissions, ranges from 50 to 200 g per day. The elderly may have a better chance of getting diabetes because of their negligible to destitute chromium admissions. An impressive division of the populace with as it were gently expanded blood glucose may have chromium utilization of less than 20 g/day. Tall chromium is impalpable and has been connected to lung cancer, liver harm and circulatory and nerve tissues [34].

Copper

Cu may be a component of numerous plant proteins (oxidase for case) and is included in many-electron exchange forms. Plants retain copper in the shape of cupric particles. The foremost common soil mineral with copper is chalcopyrite (CuFeS2) with Cu within the Cu+ frame. Cu exists in both interchangeable and less replaceable shapes, additionally within the frame of solvent natural complexes or chelates [1].

Copper is unequivocally adsorbed to numerous solids (clays, alumina, press hydrous oxides, and manganese oxides). Copper by and large shapes more grounded bonds with natural ligands than most other metal particles.

Copper is a basic component for plant and mammalian life and is crucial for the digestion system of carbohydrates and lipids. Being both a fundamental and destructive component, it has various organic impacts. Intemperate admissions come about in its aggregation within the liver and produce gastrointestinal issues, frailty, and liver and kidney harm. Proceeded inward breath of copper-containing showers is connected with an increment in lung cancer. Individuals with Wilson's illness have a more noteworthy chance for well-being impacts from overexposure to copper [25].

Copper can be discharged into the environment by both common sources (e.g. wind-blown tidy, rotting vegetation, timberland fires, and ocean showers) and human exercises (mining, metal generation, wood generation, and phosphate fertilizer generation). Since copper is discharged both normally and through human exercises, it is exceptionally far-reaching within the environment. Copper is frequently found close to amines, mechanical settings, landfills, and squander transfers.

Long-term presentation to copper can cause aggravation of the nose, mouth, and eyes and cerebral pains, stomach-aches, tipsiness, spewing, and loose bowels. Intentioned tall uptakes of copper may cause liver and kidney harm and indeed pass. Mechanical presentation to copper exhaust, clean, or fogs may result in metal smolder fever with atrophic changes in nasal mucous films. Of hereditary fabric and lung cancer [33].

Cobalt

Cobalt is of moderately low wealth within the Earth's outside and in common waters, from which it is accelerated as the profoundly insoluble cobalt sulfide, CoS. Cobalt is utilized in numerous amalgams (super amalgams for parts in gas turbine airplane motors, erosion-safe combinations, high-speed steels, cemented carbides), in magnets and attractive recording media, as catalysts for the petroleum and chemical businesses, as drying specialists for paints and inks.

Human presentation to Co takes put through air, drinking water, and food. Cobalt isn't unreservedly accessible within the environment, but when cobalt particles are not bound to soil or dregs particles the take-up by plants and creatures is higher and aggregation in plants and creatures may happen.

Cobalt is contained in vitamin B12, basic for human well-being. Cobalt is utilized to treat impacts from Co may also arise due to presentation to radiations from radioactive cobalt isotopes. This may cause sterility, hair misfortune, heaving, dying, runs, coma, and indeed passing. When this radiation is utilized in cancer patients to devastate tumors, it fortifies the generation of ruddy blood cells. The overall everyday admissions of cobalt may be as tall as 1 mg, but nearly all will pass through the body unabsorbed, but that in vitamin B12.

Iron

Most of the rocks contain iron as one of the common components and it is additionally a vital component of numerous soils particularly clay soil where it is more often than not a major constituent. Iron happens as particulate ferric hydroxide or within the shape of an organometallic compound in a normal framework. Fe (III) oxide and Fe (II) are omnipresent in anoxic situations and they influence the dispersion, transport, and biogeochemistry of chemical contaminants by adsorption onto Fe (III) oxides and by control of oxidation and decrease responses.

Iron is respected as one of the basic components for people. Approximately 3000 to 5000 mg of iron exists within the human body. Therefore, as long as the amount of iron within the environment isn't as expansive, it may not be hurtful to the human body.

2.6. Detection method of the heavy metals

There are a few strategies like atomic emission spectroscopy (AES), X-ray fluorescence (XRF), neutron activation investigation (NAA), anodic stripping voltammetry (ASV), thermolysis-coupled nuclear absorption spectroscopy (TCAS), nuclear absorption spectrometry (AAS), and graphite furnace nuclear absorption spectrometry (GFAAS) which are utilized for the evaluation of the HMs in plant tests [35].

Atomic Absorption Spectroscopy (AAS) is the favoured explanatory method for the following reasons: AAS is the foremost broadly utilized method that employments basic, effortlessly accessible, reasonably instrumented, and is quick. AAS can be utilized to analyse the concentration of over 67 diverse metals in an arrangement. AAS is exceptionally touchy and can degree down to parts per million of a gram (mg/L) in a test. AAS can moreover be utilized for the investigation of metals like arsenic, antimony, tin, selenium, bismuth, and mercury [36].

2.7. Determination of metals utilizing flame atomic absorption spectroscopy

Atomic absorption spectrometry (AAS) may be a broadly utilized strategy for deciding follow and ultra-trace components in all sorts of tests. With AAS, a light beam passes the test. Depending on the concentration of the component, a certain extent of the light is absorbed. By comparing the escalation of the first pillar and the beam after passing the test, the concentration of the component can be calculated. Since each component absorbs light of a characterized wavelength, the AAS instruments have personal light sources for each component. Ordinarily, AAS could be a strategy for deciding as it were a single component per investigation.

The advantage is that this expository strategy empowers the assurance of components in exceptionally low mass concentrations (g L^{-1} range). Depending on the anticipated mass concentration run and the sum of tests accessible, the examination can be performed with either fire AAS (FAAS) or graphite tube AAS (GF-AAS). For the previous, a test volume of a number of mL is required, for the last mentioned, as it were little sums of tests are required. In this manner, GF-AAS permits much lower discovery limits than FAAS. GF-AAS can also be utilized to enhance the analyte over and over pipetting the test into the graphite tube.

By changing the pipetting speed of the auto sampler, the impacts of physical unsettling influences due to the higher thickness of arrangements such as spit or sweat arrangements can be minimized. Chemical modifiers can be utilized to maintain a strategic distance from chemical induction. AAS could be a single-element strategy that works in a successive mode. It is reasonable to check considers of particular components such as Cd, Cr, Ni, and Pb, which indeed in exceptionally moo mass concentrations have negative impacts on human wellbeing. The drawback of GF-AAS is the long investigation time per test and much care is required, on a much more constrained scale, ordinarily for moo follow components. An imperative application of this strategy is the observation of wastewater [42]. The piece graph of FAAS and GF-AAS appears in Figure 2. In common, empty cathode lights are utilized as a source, fire or graphite heater as an atomizer grinding as wavelength selector, and photomultiplier as a finder.

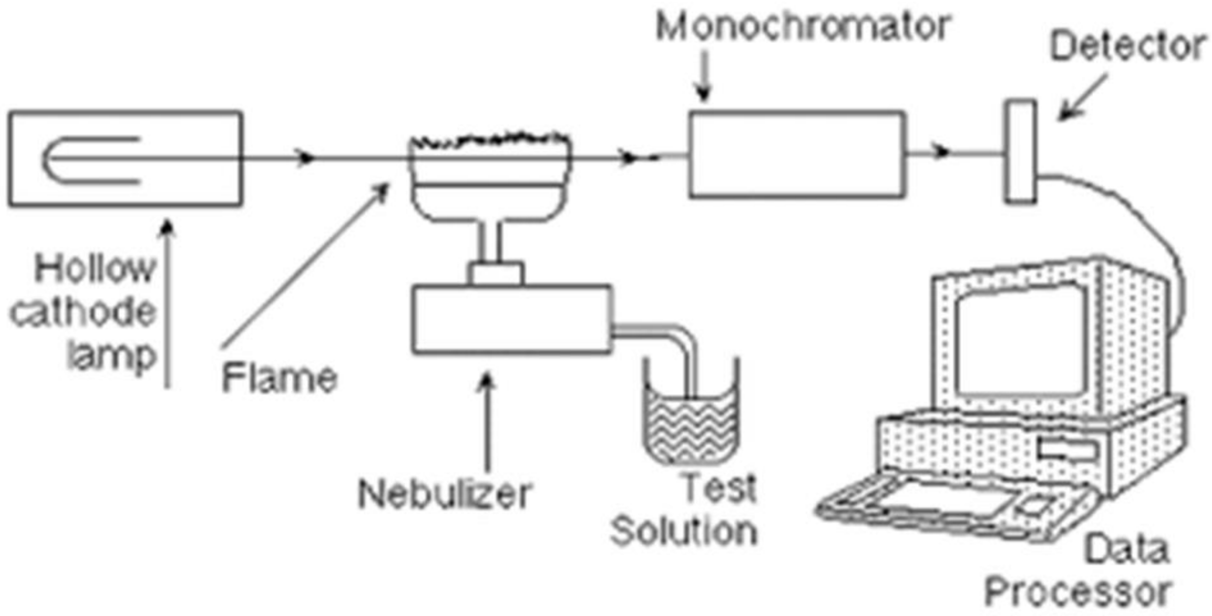

Figure 2. Schematic diagram of FAAS experimental setup.

Comparing FAAS and GFAAS The flame atomic absorption spectrometry method, which offers quick multi-elemental investigation, low running costs, and exceptionally great accuracy, endures from destitute affectability within the assurance of overwhelming metals in natural tests such as characteristic water and other genuine tests is utilized for all levels of screening and is utilized for employments a constrained run of common components [41].

The explanatory method which was utilized in this investigation for the assurance of levels of chosen overwhelming metals in carrots and their comparing soil test was flame atomic absorption spectrometry (FAAS) (ZEEnit 700, Germany) prepared with deuterium ark foundation corrector, nebulizer, monochromator, locator, fire, information processor and empty cathode lights comparing to metals of intrigued after devastation of natural matric.

3. Experimental

3.1. Equipment and apparatus

Ceramic pestle and mortar were used for grinding and homogenizing the dried carrot and its soil, digital analytical balance (OPTECH, A205EC, Italy) with ±0.0001 g precision used to measure mass of the sample and polyethylene plastic bags were used for collecting the samples. Quick-fit 24/29 and 29/32 round bottom flasks (250 mL) fitted with reflux condenser were used in kjeldahl apparatus hot plate to digest the samples. A micropipette (Dragon med, 1-100 µL, 100-1000 µL) were used for measuring different amounts of acids and standard solutions and for spiking of known concentration for recovery test. 50 mL and 100 mL volumetric flasks were used to dilute sample solutions and prepare standard solutions. ZEEnit 700 scientific model Analytikjena (Germany) Flame Atomic Absorption Spectrometer equipped with deuterium arc background corrector using air-acetylene flame was used for analysis of the metals (Cu, Zn, Ni, Cd, Fe and Pb).

3.2. Chemicals and reagents

69.5% HNO3 (Scharlau AC 1600, Spain) and 37% HCl (Riedel-de Haan, Germany) were employed to break down carrot and its soils. To create calibration curves for the detection of metals in samples, 1,000 mg/L stock standard solutions of the metals Cu, Zn, Ni, Cd, Pb, and Fe were used. For the preparation of standard solutions, dilution, and cleaning (rinsing) purposes, distilled-de-ionized water was employed. All of the reagents utilized in the analysis were of the analytical variety.

3.3. Procedures

3.3.1. Description of sampling areas

The samples for this study were collected from the area in Ethiopia, namely Akaki kality in the city of Addis Ababa which is located 8.8972889 N latitude and 38.77157 E longitude and its elevation 2161 m, The selection of these sampling points was based on the consideration of the relative amount of wastewater that discharges pollutants into the surrounding area and the accessibility of the investigation points.

3.3.2. Sample collection and preparation

Representative amount of carrot and soil samples were collected from Akaki kality in the city of Addis Ababa, Ethiopia as mentioned above. Samples were used to store and transport the samples in laboratory. After being delivered to the lab, samples were immediately rinsed with de-ionized water after being repeatedly cleaned with tap water to get rid of any possible. After cutting the carrot into small pieces with a stainless steel knife and allowing it to dry with its soil for seven days at room temperature and two days in an oven at 700C for complete dried of samples, using a mortar and pestle it is crushed and ground to powder. The samples were then pulverized, screened using the specified sieve size 0.5 mm, and kept in a dry, clean sample bottle. Finally, a solution for the final metal determination was created after 0.5 g of powder samples from each sample were obtained for digestion and run individually.

Figure 3. Picture of plant of carrot and it's homogenized of carrot and soil sample

3.3.3. Apparatus cleaning

The necessity of cleaning any equipment that will be utilized cannot be overstated because the major goal of this study was to identify trace metals at the trace level. In order to prevent contamination, all analytical glassware, including micropipette vials, volumetric flasks, filter funnels, and digestion flasks, should be washed with detergents and tap water, soaked in dilute nitric acid (10% HNO3) for a hours, rinsed with de-ionized water, dried at room temperature, and kept in a dust-free place until needed for use. When handling the carrot and its soil sample, sterile disposable powder-free plastic gloves were worn. Until analysis, the digested solutions were also stored in the refrigerator.

3.4. Sample decomposition

The purpose of sample decomposition is for converting all the species in which a given element is present in such a way that it becomes present in one defined form, eliminating interfering substances from the matrix, and obtaining the element in a homogeneous and easily accessible matrix. The digestion methods could be classified in to wet (acid) digestion, dry ashing, and microwave digestion. In this study wet digestion method was used.

3.5. Optimization of digestion procedure

Optimization of digestion procedure is important to create optimum working conditions before starting analysis of real samples. Which means before preparing for analysis the volume of reagents, digestion time and temperature should be optimized. Wet acid digestion is one the method which is usually used for samples of organic matrix is based on varying different digestion parameters like volume ratio of reagents, digestion time and temperature. Kjeldhal apparatus is one of Wet acid digestion apparatus in which organic components are assumed to be decomposed in the form of different gaseous forms and other metallic elements are left in the solutions. The Optimization of digestion procedure was determined based on the usage of smaller reagent volume, shorter digestion time and reasonable mild temperature for obtaining clear and colourless solutions of the resulting digests.

3.5.1. Optimization of digestion procedure soil samples

For each of the soil samples, 0.5 g of powder and homogenized was balanced and transferred to 250 mL of a round bottom flask. Then different volumes of HNO3 and HCl at quantified proportions (v/v) was added and digested at different temperatures (150, 180, 210, 240, 270 and 300 oC) for different period of time (105, 120, 135, 165 and 180 min). The optimized procedure was determined based on the formation of a clear colourless solution. The digested solution were allowed to cool and 5 mL of distilled water was added to dissolve residue formed on cooling and gradually swirled and filtered into 50 mL volumetric flask through What man 93 filter paper. Then the clear solution was diluted up to 50 mL volumetric flask distilled water. Finally, it was stored for analysis using flame atomic absorption spectrometry (FAAS). Hence the optimization procedure for the sample preparation for the determination of toxic and trace metal contents were made as shown in Table 1

Figure 4. Digestion of carrot and soil samples in Kjeldahl apparatus hot plate.

Table 1. Different conditions tested for optimization of digestion procedure for 0.5 g Soil samples.

Optimization for reagent volume	Trial no	Weight of sample	Reagents	Reagent volume (mL)	Temp. (^0C)	Digestion time (hr.)	Observation
	1	0.5g	HNO_3:HCl	3:3	300	3	Deep yellow
	2	0.5g	HNO_3:HCl	3:2	300	3	Deep yellow
	3	0.5g	HNO_3:HCl	**3:1***	300	3	**Clear and colorless**
	4	0.5g	HNO_3:HCl	2:3	300	3	Deep yellow
	5	0.5g	HNO_3:HCl	5:1	300	3	Light yellow
	6	0.5g	HNO_3:HCl	4:2	300	3	Deep yellow

Optimization for time	Trial no	Weight of sample	Reagents	Reagent volume (mL)	Temp. (^0C)	Digestion time (hr.)	Observation
	1	0.5g	HNO_3:HCl	3:1	300	**3:00***	**Clear and colorless**
	2	0.5g	HNO_3:HCl	3:1	300	2:45	Clear and light yellow
	3	0.5g	HNO_3:HCl	3:1	300	2:30	Clear and light yellow
	4	0.5g	HNO_3:HCl	3:1	300	2:15	Deep yellow
	5	0.5g	HNO_3:HCl	3:1	300	2:00	Deep yellow
	6	0.5g	HNO_3:HCl	3:1	300	1:45	Deep yellow

Optimization for Temperature	Trial no	Weight of sample	Reagents	Reagent volume (mL)	Temp. (^0C)	Digestion time (hr.)	Observation
	1	0.5g	HNO_3:HCl	3:1	**300***	3	**Clear and colorless**
	2	0.5g	HNO_3:HCl	3:1	270	3	Clear and light yellow
	3	0.5g	HNO_3:HCl	3:1	240	3	Clear and light yellow
	4	0.5g	HNO_3:HCl	3:1	210	3	Deep yellow
	5	0.5g	HNO_3:HCl	3:1	180	3	Deep yellow
	6	0.5g	HNO_3:HCl	3:1	150	3	Deep yellow

Note. * Indicate the shows the optimized volume ratio, time and temperature

3.5.2. Optimization of digestion procedure for carrots samples

For each of the carrot samples, 0.5 g of powder and homogenized was balanced and transferred to 250 ml of a round bottom flask. Then different volumes of HNO3 and HCl4 at quantified proportions (v/v) was added and digested at different temperatures (150, 180, 210, 240, 270 and 300 oC) for different period of time (105, 120, 135, 165 and 180 min). The optimized procedure was determined based on the formation of a clear colorless solution. The digested solution were allowed to cool and 5 mL of distilled water was added to dissolve residue formed on cooling and gradually swirled and filtered into 50 mL volumetric flask through Whatman 93 filter paper. Then the clear solution was diluted up to 50 mL volumetric flask distilled water. Finally, it was stored for analysis using Flame atomic absorption spectrometry.

Table 2. Different conditions tested for optimization of digestion procedure for 0.5 g carrot samples.

	Trial no	Weight of sample	Reagents	Reagent volume (mL)	Temp. (^{0}C)	Digestion time (hr.)	Observation
Optimization for reagent	**1**	0.5g	HNO$_3$:HCl	**3:1***	300^0	3:00	Clear and colorless
	2	0.5g	HNO$_3$:HCl	3:2	300^0	3:00	Clear and light yellow
	3	0.5g	HNO$_3$:HCl	3:3	300^0	3:00	Clear and light yellow
	4	0.5g	HNO$_3$:HCl	4:1	300^0	3:00	Clear and yellow
	5	0.5g	HNO$_3$:HCl	4:1	300^0	3:00	Clear and yellow
	6	0.5g	HNO$_3$:HCl	5:1	300^0	3:00	Clear and yellow

	Trial no	Weight of sample	Reagents	Reagent volume (mL)	Temp (^{0}C)	Digestion time (hr.)	Observation
Optimization for Temperature	1	0.5g	HNO$_3$:HCl	3:1	**300^{0*}**	3:00	Clear and colorless
	2	0.5g	HNO$_3$:HCl	3:1	270^0	3:00	Clear and light yellow
	3	0.5g	HNO$_3$:HCl	3:1	240^0	3:00	Clear and light yellow
	4	0.5g	HNO$_3$:HCl	3:1	210^0	3:00	Clear and light yellow
	5	0.5g	HNO$_3$:HCl	3:1	180^0	3:00	Clear and yellow
	6	0.5g	HNO$_3$:HCl	3:1	150^0	3:00	Clear and yellow

	Trial no	Weight of sample	Reagents	Reagent volume (mL)	Temp. (^{0}C)	Digestion time (hr.)	Observation
Optimization for time	1	0.5g	HNO_3:HCl	3:1	300^0	**3:00***	Clear and colorless
	2	0.5g	HNO_3:HCl	3:1	300^0	2:45	Clear and color
	3	0.5g	HNO_3:HCl	3:1	300^0	2:30	Clear and light yellow
	4	0.5g	HNO_3:HCl	3:1	300^0	2:15	Clear and light yellow
	5	0.5g	HNO_3:HCl	3:1	300^0	2:00	Clear and light yellow
	6	0.5g	HNO_3:HCl	3:1	300^0	1:45	Clear and yellow

Note. * Indicate the shows the optimized volume ratio, time and temperature.

3.6. Digestion of soil samples

Using the optimized conditions (Table 3), 0.5 g soil powder samples were weighed and transferred to 250 mL round bottom flask and 4 mL of 3:1 ratio of HNO3 and HCl were added. Then the solution was digested on a Kjeldhal digestion for the optimized time 3:00 hr. at the optimized temperature 300 oC. After 3:00 h of the digestion time the digested solution was permitted to cool to room temperature for about 30 min without disassembling the condenser. Digested solutions were allowed to cool and 20 mL distilled water was added to dissolve the residue formed on cooling and vigorously swirled and then filtered into 50 mL volumetric flask through What man 93 mm filter paper. Finally the clear solution was diluted by distilled water. This procedure was done three times for each soil samples.

The digestion of the blank reagent was done simultaneously without the samples. All the solutions were stored in refrigerator until the analysis was done. The solutions were used to determine the concentration of the target analyte of the sample.

3.7. Digestion of Carrot samples

Using the optimized conditions (Table 3 and 4), 0.5 g carrot powder sample was transferred to 250 mL round bottom flask and 4 mL of 3:1 of 69.5% HNO3 and 70% HCl was added. Then the solution was digested on a Kjeldhal digestion for the optimized time 3:00 h at the optimized temperature 300 oC. After 3:00 hr of the digestion time the digested solution was permitted to cool to room temperature for about 30 min without disassembling the condenser.

Then at the time of disassembling the setup, 10 mL of distilled water was added to the solution. This was done by rinsing the neck of the round bottom flask and tip of condenser that was in contact to dissolve the residue formed to cooling and minimizing dilution of filter paper by digest residue while filtering with what man 93 mm filter paper into 50 mL volumetric flask. Finally, the cooled solution was filled up to the mark with distilled water. This procedure was done three times for each carrot samples.

The digestion of the blank reagent was done in simultaneously without the samples. All the solutions were stored in refrigerator until the analysis was done. The solutions were used to determine the concentration of the target analyte of the sample.

3.8. Determination of the metals by FAAS

After the instrument working settings were optimized for the instrument's maximum signal intensity, the amounts of each metal in the two samples were assessed using FAAS. Each of the rue samples was determined in triplicate. At the corresponding primary source line, a hollow cathode lamp for each metal (Cu, Zn, Cd, Ni, Fe and Pb) was utilized. The lamp was run under the manufacturer's specified settings. In order to achieve proper flame conditions, the air and acetylene flow rates were controlled. The components in the digested blank solutions were identified using the same analytical method.

3.9. Method performance and validation

Based on the information from the correlation coefficients and their corresponding calibration curves of each metal the two variable concentration and intensity have a good positive correlation and linearity.

3.9.1. Method detection limits (MDL)

The smallest concentration that an analytical method can reliably detect is known as the method detection limit (MDL). The limit of detection is the lowest concentration level that can be determined statistically distinct from a blank (with a 95% confidence interval). It is also the smallest concentration or amount of an analyte that can reliably be proved to be present or measured under certain conditions. Although it is not often specified as a precise figure, the MDL/LOD is typically found to be in the region where the signal to noise ratio is larger than 3. You can figure it out by increasing the reagent blank's standard deviation by three (MDL = 3* Sample blank).

3.9.2. Limit of quantification (LOQ)

Limit of quantification (or limit of determination) is the lowest concentration of the analyte that can be measured in the sample matrix at an acceptable level of precision and accuracy. An acceptable level of precision is typically 10 to 20 % of relative standard deviation depending upon the concentration level measured. However, in the absence of specified precision, the limit of quantification is the same as the concentration that gives a signal 10 times the standard deviation of the blank(LOQ=10*Sample blank)[14] .

3.9.3 Precision and accuracy

Accuracy and precision are used most frequently to indicate errors in analytical results. The accuracy of an analytical procedure expresses the closeness of measurements to the true value, whereas the precision of an analytical procedure expresses the closeness of agreement (degree of scatter) between a series of measurements obtained from multiple sampling of the same homogeneous sample under the prescribed conditions [38]. In most cases, the variance, standard deviation, or coefficient of variation of a set of measurements is used to indicate the precision of an analytical technique.

In the present study, the precision of the results were evaluated by relative standard deviation of the results of two samples (n = 2) with a triplicate measurement of each sample. These parameters are useful in estimating and reporting the probable size of random error. The results of the present analysis are reported with corresponding pooled standard deviation of 9-measurements for a bulk sample of triplicate reading per sample and relative standard deviation.

3.10. Validation of the optimized procedure

Spiking tests were run to confirm the effectiveness of the improved process. For this aim, standard solutions containing 1,000 mg/L of each metal were utilized, and from these solutions, intermediate standards containing 10 mg/L of each metal (Pb, Cd, and Cu,) were prepared. The sample of carrot was chosen for the recovery measurement, and the spiking was carried out in three groups in triplicate. In the first group, 515 µL of Fe was spiked and introduced to a 250 ml round-bottomed flask that already contained 0.5 g of sample and 4 mL of an acid mixture (comprising 3 mL of HNO3 and 1 mL of HCl), in the second group, 420 µL of Cd was spiked and added in 250 mL round bottomed flasks containing the same volume of sample and acid. And in the third group, 430 µL of Cu was spiked and added. Then, using the same optimal digestion process employed in sample analysis, the round-bottomed flasks containing the mixes were equipped with the condenser and digested concurrently with the blank sample on a hot plate Kjeldahl device. Then, using this equation, the percentage recoveries of the analyte were determined.

$$\text{Percent Recovery}=\frac{(C_M\ in\ the\ spiked\ sample)-(C_M\ in\ the\ non-spiked\ sample)}{C_M\ added\ for\ spiking}\text{X } 100$$

Where, CM = Concentration of metal of interest

Table 6 concludes with a list of the recovery analysis findings, with the percentage recoveries falling between 93.5-a101.6 percent. As a result, for the selected metals, the % recoveries for the carrot sample are within the permissible range

N.B.: The amount of element still present in the original sample or recovered after digestion is the percentage of recovery, which is connected to accuracy.

Table 3: Recovery test using optimized procedure of metals in carrot sample.

Metals	Concentration of metal in un-spiked sample carrot (mg/kg)	% spiked	Amount spiked (mg/kg)	Concentration of metal in spiked sample (mg/kg)	% Recovery
Pb	25.18	20%	5.036	29.88	93.5
Cd	2.43	20%	0.486	3.37	94
Cu	25.3	20%	5.06	30.44	101.6

4. Results and Discussion

The concentration of metals in both Carrot and their corresponding soils samples were determined by using flame atomic absorption spectrometry and the precision of the result was evaluated as mean and standard deviation. Triplicate analyses were done to determine the mean values of each sample and triplicate samples were used for all sample sites.

4.1. Calibration of the instrument and determination of the metals by AAS

4.1.1. Calibration of the instrument

10 mg/L intermediate standard solutions of metals of interest were prepared from the atomic absorption spectrometer standard stock solutions that contained 1000 mg/L. The standards were diluted with deionized water to obtain working standards of each metal, i.e. Cu, Zn, Fe,

Cd, Ni and Pb. The absorbance of the working standard solutions were measured and the calibration curves for each of the analyte metals (Cu, Zn, Cd, Ni, Fe and Pb) were constructed. The operating conditions and working standard solution for FAAS employed for each analyte were given in Table 4.

Table 4, Wavelength (nm), Working standard concentrations Limit of detection (mg/L), Limit of quantification, correlation coefficient and equation of the calibration curves for determination of metals using FAAS

No	Metal	Wavelength (nm)	Working standard concentrations (mg/L)	(LOD) (mg/L)	(LOQ) (mg/L)	Equation of the calibration curves	Correlation coefficient (R2)
1	Pb	283	0.25,0.5,0.75,1	0.0389	0.3	Y= 0.254x-0.0018	0.9972
2	Fe	248	0.25,0.5,1,2	0.0581	1.927	Y= 0.0642x+0.0031	0.9991
3	cu	324	0.25,0.5,0.75,1	0.0830	0.876	Y= 0.1031x+0.0014	0.9975
4	Zn	213	0.25,0.5,0.75,1	0.0119	0.799	Y= 0.5003x+0.024	0.9967
5	Ni	232	0.25,0.5,0.75,1	0.0185	0.616	Y= 0.0539x+0.0005	0.9971
6	Cd	228	0.25,0.5,0.75,1	0.0141	0.347	Y= 0.1926x+0.0184	0.9911

4.1.2. Calibration curves of working standard concentrations of metals versus absorbance

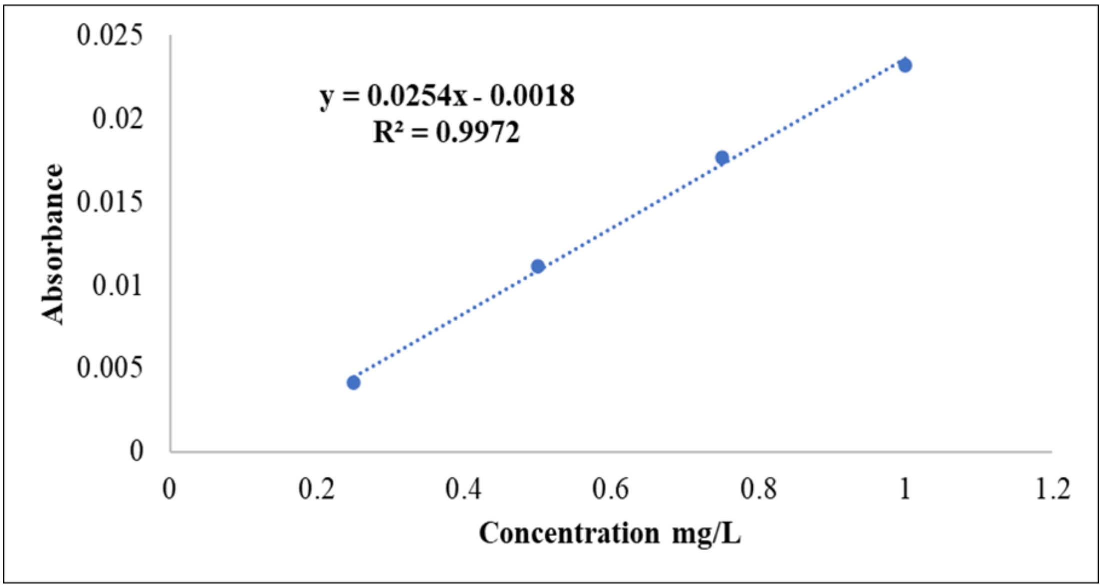

Figure 5. Calibration curve of lead standard solution

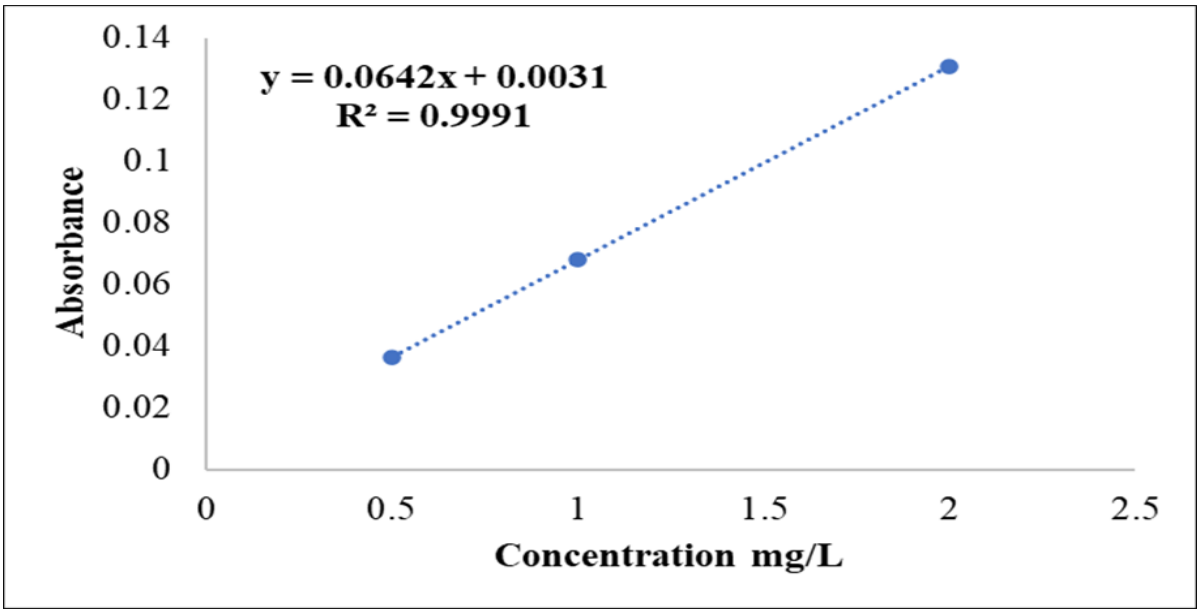

Figure 6. Calibration curve of iron standard solution

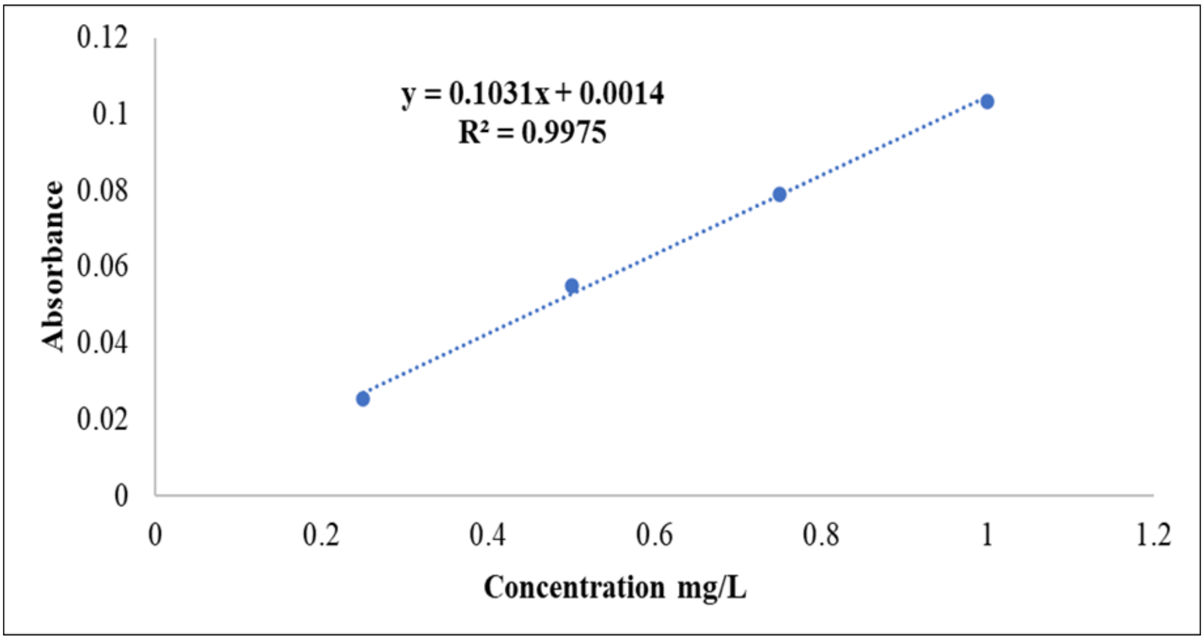

Figure 7. Calibration curve of copper standard solution

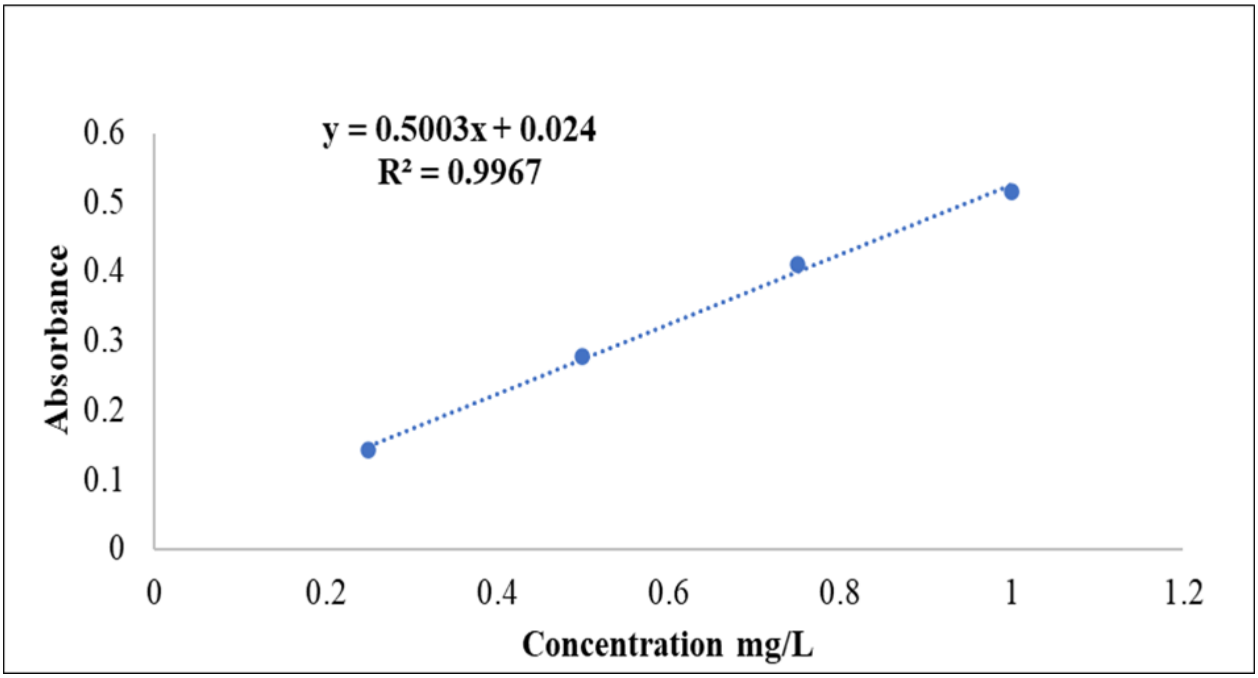

Figure 8. Calibration curve of zinc standard solution

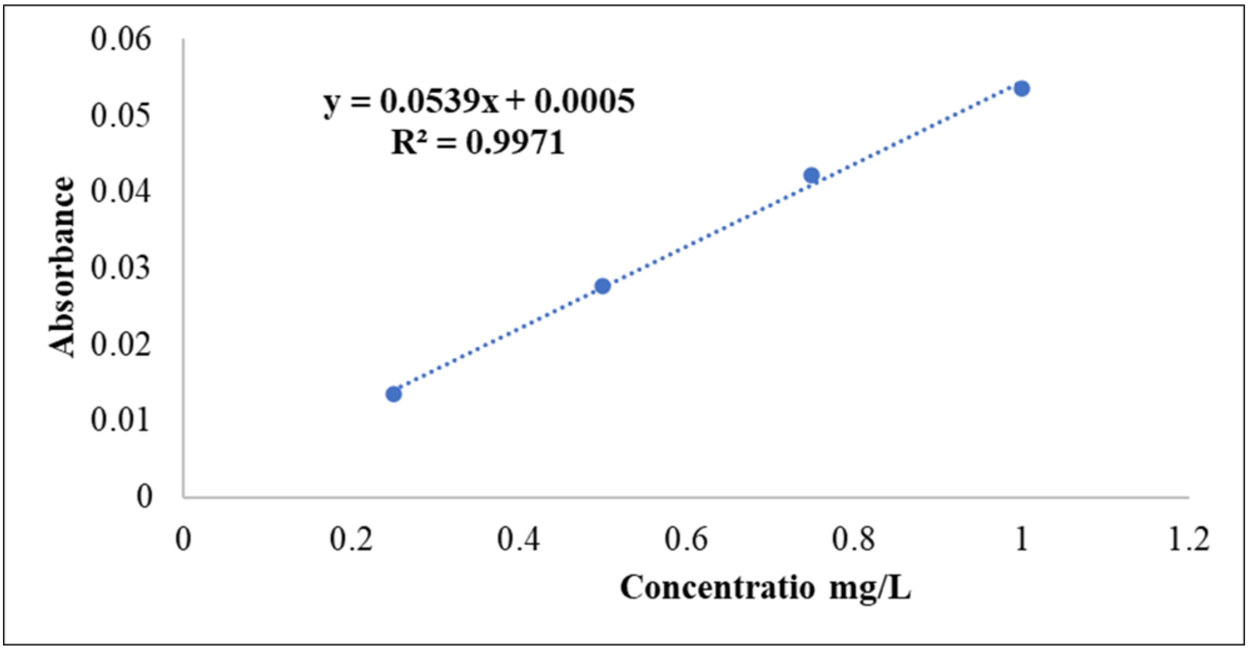

Figure 9. Calibration curve of nickel standard solution

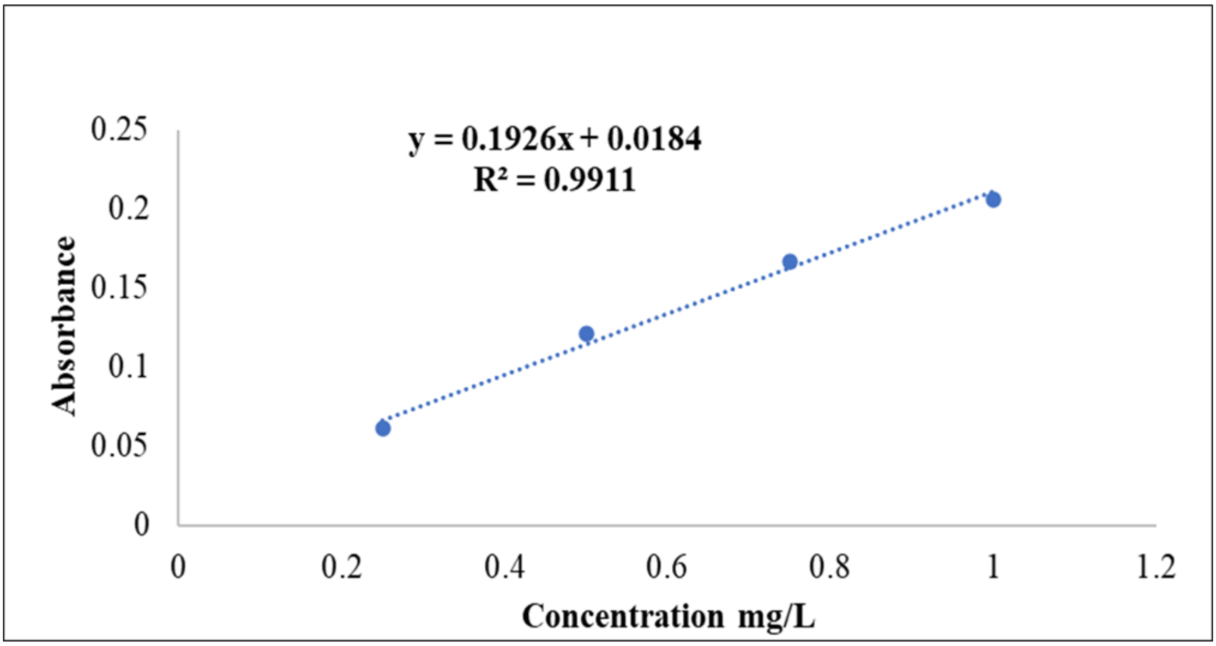

Figure 10. Calibration curve of cadmium standard solution

4.2. Levels of metals in the carrot and its soil samples

Plants gather metals from many sources in a variety of bodily sections, including the roots, stems, leaves, seeds, and other components. The amount of metals that collect in the body parts of plants varies, with certain concentrations being higher in the roots, some in the seeds, and others in the stems and other plant parts [30].The developed FAAS method was applied for the determination of the levels of six metals (Cu, Zn, Cd, Ni, Fe and Pb) in carrot and its soil samples collected from Akaki kality selected farm areas in Addis Ababa. The mean values were determined from triplicate analysis of each sample and the accuracy and precision of the results were checked by the aid of different statistical methods after the determination of the levels of metals in the carrot and its soil samples. Results obtained for each sample in terms of mg/kg dry weight basis together with values for standard deviation are shown in Table 5.

Table 5; Mean concentration (mean) ± SD, mg/kg) and % RSD of determined metals in carrot and its soil sample analyzed by FAAS.

		Sample sites, concentration of metals in (mg/kg)and %RSD			
NO	Metal	Carrot (mean)±SD, mg/kg)	%RSD	Soil (mean) ± SD, mg/kg)	%RSD
1	Pb	25.18±2.1903	8.69846686	22.18±1.9547	8.812949752
2	Fe	23.94±2.359	9.848979745	ND	ND
3	Cu	25.3±2.388	9.438864281	71.45±5.9596	8.3409222
4	Zn	52.30±4.029	7.703756988	134.46±9.039	6.722104328
5	Ni	ND	ND	ND	ND
6	Cd	2.43±0.1155	4.758381339	4.02±0.3101	7.719180717

where ND=Not detected

4.2.1. Concentration of metals in the carrot

Zn is present in the highest amount, as indicated in Table 5 and Figure 11, with a concentration of 52.30 mg/kg, followed by Cu 25.3mg/kg, Pb 25.18 mg/kg, Fe 23.94 and Cd 2.43 mg/kg. Metals Ni are not present because they are below the detection limit. These findings demonstrated that non-essential trace metals were either absent or detected at far lower concentrations than the essential trace metals. From the perspective of health, this is advantageous. Metal levels in carrots obtained are typically arranged in the following order: Zn> Cu>Pb> Fe > Cd, when compared within other literature Pb (0.026), Cd (0.004), Zn (7.54), Cu (9.2) Ni (0.248) and Fe (0.445) [48]. all the result obtained in this study is highest result than the literature because of used untreated industrials and municipal wastes.

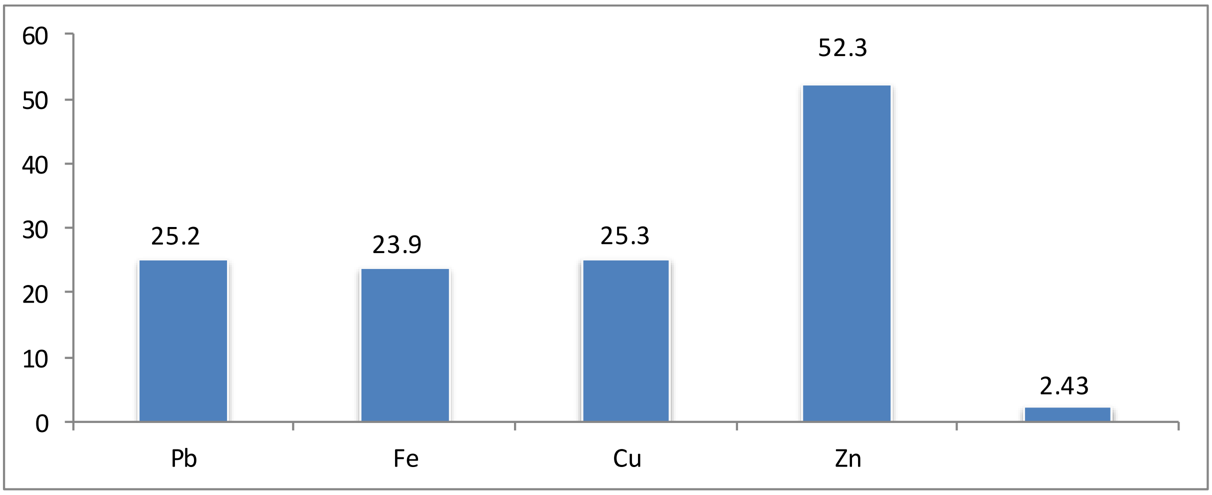

Figure 11: concentration (mg/kg) in carrot sample

4.2.2. Concentration of metals in soil

Zn is also found in the highest quantity in the soil samples, with a concentration of 134.46 mg/kg, followed by Cu 71.45 mg/kg, Pb 22.18 mg/kg Cd 4.02 mg/kg and the other two metals, Fe, and Ni, were observed below the instrument's detection limit. The order of the metal levels was discovered to be Zn >Cu>Pb > Cd. The results are shown in Table 5 & Figure 12. When compared with other literature result Zn 44 mg/kg, Cu 148 mg/kg, Cd 2.7 mg/kg & Pb 74 mg/kg [47]. Zn is highest result because of used untreated industrials and municipal wastes. & other is below the literature result.

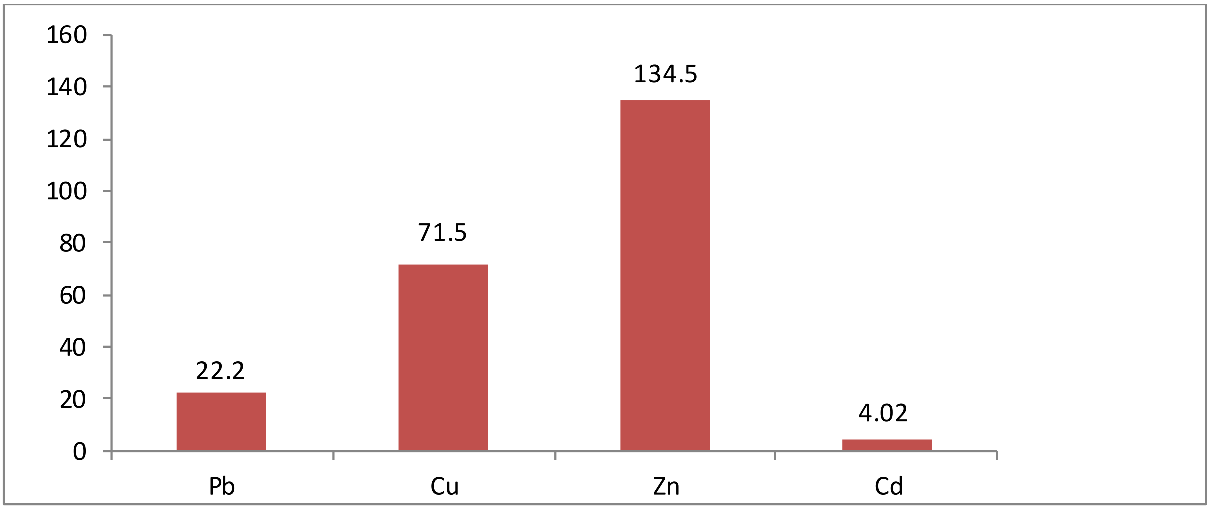

Figure 12: concentration (mg/kg) in soil sample

4.2.3. Comparison of the concentration of metals in carrot and its soil samples

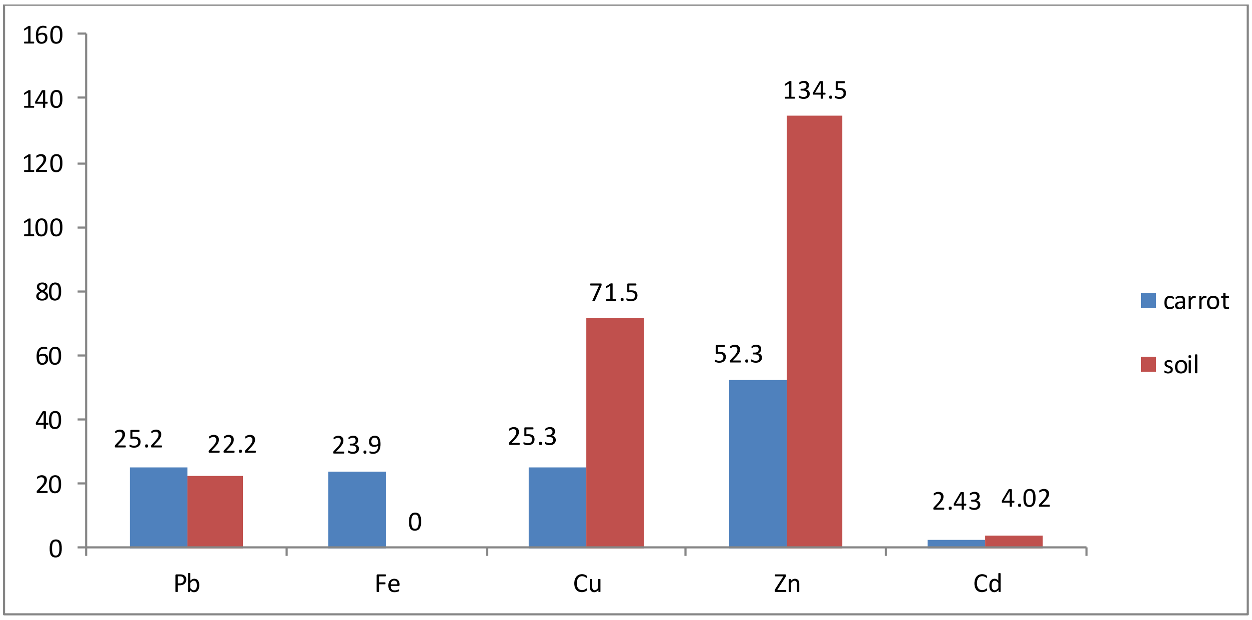

Figure 13: comparison of concentration (mg/kg) in carrot and soil samples

4.3. Comparison of concentrations (mg/kg) of selected metal levels in carrot and its soil obtained in the present study with permissible values from FAO/WHO.

The findings of the current study can be compared to the accepted references provided by the WHO. Table 6: Comparison of concentrations (mg/kg) of selected metal levels in carrot & soil obtained in the present study with permissible values from FAO/WHO.

No	Metal	Conc of carrot sample (mg/kg)	WHO recommended limit of metal in carrot (mg/kg)	Conc of soil sample (mg/kg)	WHO recommended limit of metal in soil (mg/kg)
1	Zn	52.30	50	134.46	50
2	Pb	25.18	0.3	22.18	10
3	Fe	23.94	20	ND	500
4	Cu	25.3	20	71.45	36
5	Cd	2.43	0.2	4.02	0.8
6	Ni	ND	1.5	ND	35
	reference	This study	[23,25]	This study	[45,46,47]

Table 7. Comparison of heavy metal concentration in soil samples with other reported Values (mg/kg)

Country	Methods	Cu	Zn	Ni	Pb	Cd	reference
Ethiopia	ICP- MS	201	749	318	81	1.0	[45]
India	AAS	ND	ND	1.57	1.10	1.52	[44]
China	ICP- MS	7.9	28	9.5-	22	0.07	[46]
Nigeria	AAS	20.5	8.70	2.60	9.6	ND	[43]
Ethiopia	FAAS	71.45	134.46	ND	22.18	4.02	This study

Table 8. Comparison of heavy metal concentration in carrot samples with other reported Values (mg/kg)

Country	Methods	Fe	Cu	Zn	Ni	Pb	Cd	reference
Bangladesh	AAS	7.2	3.68	11.18	0.38	0.75	0.30	[49]
Poland	AAS	4.32	3.41	3.62	0.700	0.040	0.060	[32]
china	AAS	12.2	0.227	1.591	ND	0.233	0.023	[41]
Libya	AAS	9.2	3.36	8.15	0.0231	24.8	13.3	[24]
Ethiopia	AAS	23.94	25.3	52.30	ND	25.18	2.43	This study

4.4. Analysis of variance (ANOVA)

One-Way ANOVA is a statistical technique used to compare sample mean values to determine if there is a statistically significant difference between them [35]. The technique only employs one independent variable. The variation in samples can be attributed to a variety of factors, including experimental design or sample heterogeneity (i.e., variations in the mineral content of the soil, the pH of the soil, the water, and the atmosphere; variations in how agrochemicals such as fertilizers, pesticides, and herbicides are applied; and other variations in cultivation practices) [54].

Microsoft Excel's ANOVA for a single factor was used in this investigation to determine whether or not the variance in sample means of the analyte had a significant difference (Table 9).

Table 9. shows that the mean concentration of the metal Pb does not significantly differ between the samples means at a 95% confidence level when F-calculated (at $p \geq 0.05$) is less than the critical value and F-**C**alculated larger than F-critical and $p < 0.05$, there is significant difference between the sample, so based on this idea results of variance analysis showed that there were significant differences in the mean values of Cu, Cd and Zn between carrot and soil sample. The variation in the mineral contents of the soil or the pH of the soil, which mostly results from soil contamination and predicts the degree of mineral absorption by carrot plant, may be the cause of this considerable discrepancy between sample averages.

Table 9: Analysis of variance (ANOVA) between carrot and its soil samples at 95% confidence level.

Metal	Source of Variation	Df	F-cal	F-cri	p-value	Remark
Pb	Between samples	1	3.132904783	7.708647422	0.151439352	There is no significant difference among the sample means
	Within samples	4				
	Total	5				
Cd	Between samples	1	69.28410475	7.708647422	0.001138176	There is significant difference among the sample means
	Within samples	4				
	Total	5				
Cu	Between samples	1	155.0111719	7.708647422	0.000239317	There is significant difference among the sample means
	Within samples	4				
	Total	5				
Zn	Between samples	1	206.7867579	7.708647422	0.000135904	There is significant difference among the sample means
	Within samples	4				
	Total	5				

4.5. Pearson correlation coefficients between metals concentrations of Carrot and soil samples.

The values of the product moment-correlation coefficient (r) fall between -1 and +1. Additionally, a perfect negative correlation has r value of -1, meaning that all experimental data points lie on a straight line with a negative slope. Similar to this, r value of +1 denotes a perfect positive correlation, with each point precisely falling along a line with a positive slope. However, a zero r value just indicates that the two components (in the formula, y and x) are not linearly connected and does not imply that they are completely unrelated

Table 10: Pearson correlation matrices for metals in Carrot sample.

Correlation matrix	Pb	Fe	Cu	Zn	Cd
Pb	1				
Fe	0.950546	1			
Cu	0.204389846	-0.109744349	1		
Zn	-0.978718233	-0.994051313	0.000836611	1	
Cd	-0.858009164	-0.65605138	-0.678159696	0.734346958	1

5. Conclusion

This work focused on the determination of (Zn, Cu, Pb, Cd, Co, and Fe) concentrations in Akaki kality farm of carrots its corresponding soil of the plant. The concentrations of (Zn, Cu, Pb, Cd, Co, and Fe) were determined by using FAAS technique. The mean concentration range (mg/kg) of each metal in carrot were Zn (52.30)> Cu (25.3)> Pb (25.18) >Fe (23.94) >Cd (2.43), Ni was below the detection limit and in soil samples Zn (134.46) > Cu (71.45) > Pb (22.18), >Cd (4.02) respectively, Ni and Fe were below the detection limit. The result indicates that concentration of Cd, Zn, Cu, Fe, and Pb metals in carrot sample and Cd, Zn, Cu, and Pb metals in its soil is higher than the WHO guidelines.

The level of lead, cadmium, zinc, iron and copper obtained in this study were higher than all the guidelines or standards reported in the literature. This may expose to health risk for people living around the area of the river because the river is used intensively for irrigation even for drinking and other purposes. When the recovery test was used to evaluate the improved wet acid digestion method for the examination of carrot, it was discovered to be effective for the selected metals. A satisfactory percentage recovery ranges from 93.5 % to 101.6% was obtained for the identified metals.

6. Recommendations

Akaki River is found within the transfer region of distinctive businesses, family and rural, restorative wastes, etc. On the other hand, waterway water is utilized for an assortment of purposes such as water systems, cattle drinking, and residential purposes without earlier treatment.

Subsequently, it is suggested that the utilization of vegetables developed in the mechanically sullied rural arrive around the zone be a tall chance to human health and creatures unless remedial activity is taken in existing contamination laws to avoid both developing vegetables and to raise community mindfulness of the dangers related with mechanically sullied farmland.

For feasible administration of this water asset all concerned bodies such as the Natural Assurance Office, the Wellbeing Division, the Office of Horticulture, the Addis Ababa Water and Wastewater Division, colleges and inquiries about organizations, etc......are working together to form a common stage to decrease the dangers related with mechanically sullied wastewater and center on a fitting methodology for mechanical squander administration and coordinates into mechanical improvement and Requirement of law and engendering natural instruction to the community with a special target to those donors of the show degradation might be one arrangement.

7. References

[1]. Khan, F.U., Rahman, A.U., Jan, A., Riaz, M. (2004). Toxic and trace metals (Pb, Cd, Zn,Cu, Mn, Ni, Co and Cr) in dust, dustfall/ Soil. *Journal- Chemical Society of Pakistan 4 (26), 453–456.*

[2]. Ali, H., Khan, E., Sajad, M.A. (2013). Phytoremediation of heavy metals-Concepts and applications. *Chemosphere 91 (7), 869–881.*

[3]. Abbasnia, A., Radfard, M., Mahvi, A.H., Nabizadeh, R., Yousefi, M., Soleimani, H.,Alimohammadi, M. (2018). Groundwater quality assessment for irrigation purposes based on irrigation water quality index and it's zoning with GIS in the villages of Chabahar, Sistan and Baluchistan, *Iran. Data Brief 19, 623–631.*

[4]. Mohammadi, A.A., Zarei, A., Esmaeilzadeh, M., Taghvi, M., Yousefi, M., Yousefi, Z., Sedighi, F., Javan, S. (2019). Assessment of Heavy Metal Pollution and Human Health Risks Assessment in Soils around an Industrial Zone in Neyshabur, Iran. *Biological Trace Element Research. 195(1), 343-352*

[5]. Dehghani, M., Heibati, B., Asadi, A., Tyagi, I., Agarwal, S., Gupta, V. (2016). Reduction of noxious Cr (VI) ion to Cr (III) ion in aqueous solutions using H_2O_2 and UV/H_2O_2 systems. *Journal of Industrial and Engineering Chemistry, 33, 197–200.*

[6]. Basma, G., Alhogbi, A.F.A. (2017). Soil pollution: a case study on the determination of toxic elements in soil in Jeddah City. *International Journal of Chemistry, 9 (2), 37–44.*

[7]. Lenart, A., Wolny-Koładka, K. (2013). The effect of heavy metal concentration and soil Ph on the abundance of selected microbial groups within Arcel or Mittal Poland steelworks in Cracow. *Bulletin of Environmental Contamination and Toxicology, 90 (1), 85–90.*

[8]. Zhou, H., Guo, X. (2015). Soil heavy metal pollution evaluation around mine area with traditional and ecological assessment methods. *Journal of Geoscience and Environment Protection, 3 (10), 28–33.*

[9]. Shams, M., Nezhad, N.T., Dehghan, A., Alidadi, H., Paydar, M., Mohammadi, A.A., Zarei, A. (2020). Heavy metals exposure, carcinogenic and noncarcinogenic human health risks assessment of groundwater around mines in Joghatai, Iran. *International Journal of Environmental Analytical Chemistry. 102(8, 1–17.*

[10]. Miri, M., Akbari, E., Amrane, A., Jafari, S.J., Eslami, H., Hoseinzadeh, E., Zarrabi, M., Salimi, J., Sayyad-Arbabi, M., Taghavi, M. (2017). Health risk assessment of heavy metal intake due to fish consumption in the Sistan region, Iran. *Environmental Monitoring and Assessment. 189 (11), 583.*

[11]. Karimi, A., Naghizadeh, A., Biglari, H., Peirovi, R., Ghasemi, A., Zarei, A. (2020). Assessment of human health risks and pollution index for heavy metals in farmlands irrigated by effluents of stabilization ponds. *Environmental Science and Pollution Research, 27, 10317–10327.*

[12]. Esmaeilzadeh, M., Jaafari, J., Mohammadi, A.A., Panahandeh, M., Javid, A., Javan, S. (2019). Investigation of the extent of contamination of heavy metals in agricultural soil F. Lemessa et al. Heliyon 8 (2022) e12429 using statistical analyses and contamination indices. *Human and Ecological Risk Assessment 25(5),1-12.*

[13]. Qingjie, G., Jun, D., Yunchuan, X., Qingfei, W., Liqiang, Y. (2008). Calculating pollution indices by heavy metals in ecological geochemistry assessment and a case study in parks of Beijing. *Journal of China University of Geosciences 19(3), 230-241.*

[14]. Saleemi, M. A. (1993). Environmental assessment and management of irrigation and drainage scheme for sustainable agriculture growth. *International journal of agricultural and biology.* 05(4), 533–535.

[15]. Agca, N., Ozdel, E. (2014). Assessment of spatial distribution and possible sources of heavy metals in the soils of Sariseki-Dortyol District in Hatay Province (Turkey). *Environmental Earth Sciences 71(3), 1033–1047.*

[16]. Arora, M., Kiran, B., Rani, S., Rani, A., Kaur, B., Mittal, N. (2008). Heavy metal accumulation in vegetables irrigated with water from different sources. *Journal of Agricultural Science and Technology 20(2), 811–815.*

[17]. Radfard, M., Yunesian, M., Nabizadeh, R., Biglari, H., Nazmara, S., Hadi, M., Yousefi, N., Yousefi, M., Abbasnia, A., Mahvi, A.H. (2019). Drinking water quality and arsenic health risk assessment in Sistan and Baluchestan, Southeastern Province, Iran. *Human and Ecological Risk Assessment 25(4), 1-17.*

[18]. Almasi, A.D.A., Amrane, A., Fazlzadeh, M., Mahmoudi, M., Hashemian, A. (2014). Effect of the retention time and the phenol concentration on the stabilization pond efficiency

in the treatment of oil refinery wastewater. *Fresenius Environmental Bulletin 23(10), 2541–2548.*

[19]. Bigdeli, M., Seilsepour, M. (2008). Investigation of metals accumulation in some vegetables irrigated with waste water in Shahre Rey-Iran and toxicological implications. *Journal of agricultural and environment science. 4(1) 86–92.*

[20]. Oliver, K., Joachim D., & Dietrich, A. V. (1999). Automated matrix separation and preconcentration for trace level determination of metal impurities in ultrapure inorganic salts by High-Resolution ICP-MS. *Fresenius Journal of Analytical Chemistry. 364, 694-699.*

[21]. K. H. Lee, Y. Muraoka, M. Oshima and S. Motomizu. (2004). Determination of heavy metals and rare earth elements in environmental samples by ICPMS after solid phase preconcentration with chelating resin fibers and anion exchanger filters. *Analytical Sciences, 20,183-187*

[22]. Soares, R. A., Boaventura, R., Machado, A., and Esteves, S. (1999). Sediments as monitors of heavy metal contamination in the Ave River Basin (Portugal): Multivariate analysis of data. *Environmental Pollution, 105,311-323*

[23]. Katsuro, A,. Yasuhiko, K,. Yoshinori, S,. Takashi T, & Hayao S. (2004). Heavy metal distribution in river and sediment around a "Firefly Village", Shikoku, Japan: Application of multivariate analysis. *Analytical Sciences, 20, 79-84*

[24]. Ademoroti, C.M.A. (1996). Environmental Chemistry and Toxicology, Foludex Press Ltd, Ibadan, Nigeria, *Environmental Pollution*, 162-203.

[25]. Agbo, S. (1997) Effects of Lead Poisoning In Children, In Proceedings at a Workshop on Vehicular Emission and Lead Poisoning in Nigeria, Edited By A.A. Falomo and C.C Chikwedu, Organized By Friends Of The Environment (Fote), Lagos. *Analytical Sciences, 20-28.*

[26]. Bieby.T, Siti, R.,Sheikh, A. (2011) "A Review on Heavy Metals (As, Pb, and Hg) Uptake by Plants through Phytoremediation", *International Journal of Chemical Engineering, Article ID 939161, 31.*

[27]. S. Gaudino, C. Galas, M. Belli, S. Barbizzi, P.Zorzi, R. Jacimovic, Z. Jeran, A. Pati and U. Sansone (2007). The role of different soil sample digestion methods on trace elements

analysis: a comparison of ICP-MS and INAA measurement results, *Journal for Quality, Comparability and Reliability in Chemical Measurement, 12, , 84- 93.*

[28]. Sutkowska K, Teper L, Czech T, Hulok T, Olszak M, Zogal J (2020). Quality of Peri-Urban Soil Developed from Ore-Bearing Carbonates, Heavy Metal Levels and Source Apportionment Assessed Using Pollution Indices. *Minerals. 10, 1140.*

[29]. Gemechu T. (2014). Quantitative Determinaton of the Accumulation level of selected essential and toxic heavy metals in korarima (Aframomum corrorima), Ginger (Zingibr officinale), Tumeric(Curcuma longa) and Black pepper (piper nigrum) Spice plants and their Corresponding Soils Cultivated in Jimma Zone , West Ethiopia *http://etd.aau.edu.et/handle/123456789/18.*

[30]. Alengebawy A, Abdelkhalek S T, Qureshi S R and Wang M (2021). Heavy Metals and Pesticides Toxicity in Agricultural Soil and Plants, Ecological Risks and Human Health Implications, *Toxics, 9: 42-85.*

[31]. Han FX, Banin A. (2002). Industrial age anthropogenic inputs of heavy metals into the pedosphere *.Naturwissenschaften, 89, 497-504.*

[32]. Zerihun, A. (2014). level of selected metals in leaves of Cannabis Sativa. L Cultivated in Ethiopia. *http://etd.aau.edu.et/handle/123456789/24591*

[33]. Mersha, S, A. (2018). Determination of levels of selected metals in the leaves ‘Tena Adam’ (Ruta chalepensis L.) collected from four selected areas around Addis Ababa, *http://etd.aau.edu.et/handle/123456789/18/discover.*

[34]. Hagos, M. (2011). Determination of Some Essential and Non-Essential Metals in Fenugreek Seed Cultivated in Different Parts of Ethiopia. *http://etd.aau.edu.et/handle/123456789/18/discover.*

[35]. Vinogradova N, Glukhov A, Chaplygin V, Kumar P, Mandzhieva S, Minkina T, Rajput V D. (2023). The content of Heavy metal in medicinal plant in various environmentally condition: *A Review, Journal of Horticulture, 9,239.*

[36]. Sahan S, Sahin U. (2010). Determination of Copper (II) Using Atomic Absorption Spectrometry and Erio-chrome Blue Black R Loaded Amberlite XAD-1180 Resin. *CLEAN - Soil Air Water 38(5-6), 485 - 491*

[37]. Ozyigit, I, I., Karahan, F., Yalcin, I E., Ozyigit, A H., and Ilcim, A. (2022). Heavy metals and trace elements detected in the leaves of medicinal plants collected in the southeast part of Turkey, *Arabian Journal of Geosciences, 15(1) 27-28.*

[38]. Hlihor R M, Ros M , Zaleschi L H, Simion I M, Mihait G, and Stoleru V. (2022). A review, Medicinal Plant Growth in Heavy Metals Contaminated Soils, Responses to Metal Stress and Induced Risks to Human Health. *Journal of Toxics, 10, 499-512.*

[39]. Gemechu (2014). Quantitative Determinaton of the Accumulation level of selected essential and toxic heavy metals in korarima (Aframomum corrorima), Ginger (Zingibr officinale), Tumeric(Curcuma longa) and Black pepper (piper nigrum) Spice plants and their Corresponding Soils Cultivated in Jimma Zone , West Ethiopia. *http://etd.aau.edu.et/handle/123456789/18.*

[40]. Yishak E and Dadebo T. (2022). Determination of the levels of some selected metals in ocimu lamiifolium in Wolaita Zone, Southern Ethiopia, *East African Journal of Biophysical and Computational Sciences, 3(2), 48-60.*

[41]. Annan K, Kojo A I, Cindy A , Samuel A N, Tunkumgnen B M. (2010). Profile of heavy metals in some medicinal plants from Ghana commonly used as components of herbal formulations. *Journal of Pharmacognosy Research, 2 2(1), 41-4.*

[42]. Baye, H., and Hymete, A. (*2013).* Level of heavy metal in common medicinal plants collected from environmentally different site. *Middle-East Journal of Scientific Research, 13(7), 938-943.*

[43].Olatunde,K.A.,Sosanya, P.A., Bada, B.S., Ojekunle ,Z.O., Abdussalaam, S.A. (2020). Distribution and ecological risk assessment of heavy metals in soils around a major cement factory, Ibese, Nigeria. *Scientific Africa*

[44]. Vinod, K., Anket, S., Parminder, K., Gagan, P., Aditi S. B., Renu B., Ashwani, K. (2019). Pollution assessment of heavy metals in soils of India and ecological risk assessment: A state-of-the-art. *Chemosphere, 216, 449-462*

[45]. Fentahun, A., Melaku, M., & Banchalem, K. Determination of heavy metals in soil used for potato cultivation by atomic absorption spectroscopy in awi Zone, Amhara Region, Ethiopia. Ecology & Environmental Science

[46]. Chuanghong, S., Jing, M., Yunqiao, Z., Ran, B.(2022) Heavy Metals in Soils From Intense Industrial Areas in South China: Spatial Distribution, Source Apportionment, and Risk Assessment. *Toxicology, Pollution and the Environment*

[47]. Milena, R., Željko Ć., Danijela, M., Tamara, B., Jelena, L., Slavka S., and Antonije, O. (2020). Ecological Risk Assessment of Heavy Metals in the Soil at a Former Painting Industry Facility. *Toxicology, Pollution and the Environment, 8, 43-89*

[48[. Somtobechukwu, S., Sab-Udeh, I. (2017). Determination of Heavy Metal Levels of some Cereals and Vegetables sold in Eke-Awka Market Awka, Anambra State, Nigeria. *Journal of Natural Sciences Research, 2, 42-98*

[49]. Romana, S., Rahamat, U., Kazi, A., Afrose, S., & Nadiruzzaman, M.(2022). Heavy Metals in Commonly Consumed Root and Leafy Vegetables in Dhaka City, Bangladesh, and Assessment of Associated Public Health Risks. *Environmental Systems Research*, 15, 148-160.