ADDIS ABABA UNIVERSITY

College of natural and computational sciences

Department of chemistry

Determination of heavy metals in the soils of flower farms at Zeway, Sebeta and Holeta

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DECLARATION

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.

Dr. Negash Getachew ……………. ………………

Advisor **Signature** **Date**

As members of the Examining Board of the final MSc open Defence, we certify that we have read and evaluated the thesis prepared by Yenenesh Gemechu Jote entitled :$^{<<}$Determination of heavy metals in the soils of the flower farms at Zeway, Sebeta and Holeta, Ethiopia$^{>>}$, and Recommended that it can be accepted as fulfilling the thesis requirement for the degree of master of science in chemistry.

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Final approval and acceptance of the thesis is contingent upon the submission of the final copy of the thesis to the Council of Graduate Studies (CGS) through the Departmental Graduate Committee (DGC) of the candidate’s major department.

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Abstract

Soils polluted with heavy metals have become common across the globe due to increase in geologic and anthropogenic activities. Heavy metals in the soil refers to some significant heavy metals of biological toxicity, including mercury (Hg), cadmium (Cd), lead (Pb), chromium (Cr), nickel (Ni), arsenic (As), etc. With the development of the economy, more specific with the development of industry the presence of heavy metals in the soil caused by this activity have gradually increased in recent years. These in turn have resulted in serious environment deterioration. The aim of this research was to evaluate the real situation of the soil contamination with heavy metals within the Flower farm of Zeway, Sebeta and Holeta in Ethiopia, and particularly in Oromia region. The obtained values of reagents volume, temperature and time for optimal procedure were 6 mL of the mixture of HCl and HNO_3 with the ratio of 3:1, 210^{o}C and 3:00 hour to mineralize powdered samples during wet digestion. The concentration of some selected metals in the soil samples were determined by micro wave plasma atomic emission spectroscopy. The mean concentration of heavy metals in soil samples near the flower farm exhibited decreased trend in the order of Fe > Zn >Ni > Cu > Cr
.

Key words: soil, heavy metals, contamination flower farm and MP - AES

INTRODUCTION

1.1 Background of the study

Heavy metal contamination refers to the excessive deposition of toxic heavy metals in the soil caused by human activities. Heavy metals in the soil include some significant metals of biological toxicity, such as mercury (Hg), cadmium (Cd), lead (Pb), chromium (Cr), arsenic (As), etc. They also include other heavy metals of certain biological toxicity, such as zinc (Zn), copper (Cu), nickel (Ni), tin (Sn), vanadium (V), and so on. In recent years, with the development of the global economy, both type and content of heavy metals in the soil caused by human activities have gradually increased. Heavy metals are highly hazardous to the environment and organisms. It can be enriched through the food chain. Once the soil suffers from heavy metal contamination, it is difficult to be remediated. The term ‘heavy metal’ is often used to cover a diverse range of elements, which constitute an important class of pollutants. With the industrial development, the production and emission of heavy metals have increased. Some metals, e.g. Mn, Cu, Zn, Mo and Ni, are essential or beneficial micronutrients for microorganisms, plants, and animals, but at high concentrations all these metals have strong toxic effects and pose an environmental threat. Heavy metal pollution can be defined as an undesirable change in the physical, chemical or biological characteristics of land, water and air that may or will harmfully affect animals, plants and humans environmental protection worldwide. Trace metals have been referred to as common pollutants, which are widely distributed in the environments with sources mainly from anthropogenic activities and from the weathering of minerals and soils [1].

The presence of heavy metals in different foods constitutes serious health hazards, depending on their relative levels. For example, cadmium and mercury injure the kidney and cause symptoms of chronic toxicity, including impaired kidney function, poor reproductive capacity, hypertension, tumors and hepatic dysfunction. Lead causes renal failure and liver damage. Some other metals (*e.g.* chromium, zinc and copper) cause nephritis, anuria are extensive lesions in the kidney. Therefore, the problem of food contamination by toxic metals is receiving global attention.

Soil adjacent to the industrial area contains the highest concentration of heavy metals. In the past, soil contamination was not considered as important as air and water pollution, because soil contamination was often with wide range and was more difficult to be controlled and governed than air and water pollution. However, in recent years the soil contamination in developed countries becomes to be serious. It is thus paid more and more attention and became a hot topic of environmental protection worldwide. In Ethiopia, floriculture as an industry is only a decade old but has expanded from two in 2000 to 85 industries in 2011. This level of production has promoted Ethiopia as the second-largest producer of roses in Africa next to Kenya and sixth in the world after Holland, Colombia, Ecuador, Kenya and Israel. The industry is blamed for using too much chemicals which damage the environment through its discharge. The production uses more than 300 chemicals as pesticides and growth regulators, which kills useful organisms in the soil and disturbs the biodiversity. Intensive chemical fertilizers and pesticides that are frequently applied to produce a quality rose resulted in the negative impact on the environment. Although detailed research on floriculture effluent is scant, studies have shown the impact of industrial effluents and municipal wastes on soil quality [2].

Holeta, zeway and sebeta towns are the most industrial zones in Oromia region, Ethiopia, which have seen an upsurge in floriculture activities in recent years with extensive use of fertilizers and pesticides in the industry. The effluent from the flower industry is discharged into a channel that flows through agricultural farmland into the river and lakes.

The purpose of this study was to determine the levels of heavy metals (Cd, Zn, Co, Cu, Ni, Fe, Cr, and Hg) in the adjacent soil around the floriculture industry in Holeta, zeway and Sebeta towns in Ethiopia and assess their potentials as pollutants.

1.2 Objectives

General objectives

This study reports the input and distribution of heavy metals in the soil around Sebeta,Holeta and Zeway floriculture. Also, it aims at estimation of the impact of industrialization by comparing the pollution status of the soil with the standard.

Specific objectives

- To develop a procedure for digestion of soil samples.
- To determine trace metals (Cd, Pb, Zn, Cu, Ni, Fe, Cr, Hg and Co) contents of the collected soil samples.
- To evaluate the degree of pollution of soil sample collected and evaluate the distribution of those metals along the area.
- To compare the metal contents of soil sample collected from industrial area with soil sample with standard concentration of heavy metals.

1.3 Significance of the study

The major significance of this study is to provide information about the presence of heavy metals in soils around Zeway, Holeta and Sebeta flower farms in Ethiopia. Also the study gives some clues to further studies for toxicity and effect of heavy metals in soils around the area.

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 relatively high density (specific gravity greater than about 5) or of high relative atomic weight is defined as a heavy metal. The term "heavy metals" is used to describe more than a dozen elements that are metals or metalloids e.g. chromium, arsenic, cadmium, lead, mercury, manganese, etc. Heavy metals are natural constituents of the Earth's crust. Because they cannot be degraded or destroyed, heavy metals are persistent in all parts of the environment. In small amounts, they enter the human body via food, drinking water and air. Living organisms require varying amounts of "heavy metals". Iron, cobalt, copper, manganese, molybdenum, and zinc are required by humans.

Excessive levels can be damaging to the organisms. Therefore, heavy metals can be described as any metallic element that has a relatively high density and is toxic or poisonous at low concentrations [3].

Human activities affect the natural geological and biological distribution of heavy metals through pollution of air, water, and soil. Humans are also responsible for altering the chemical forms of heavy metals released to the environment. Such alterations often affect a heavy metal's toxicity by allowing it to bio-accumulate in plants and animals, bio-concentrate in the food chain, or attack specific organs of the body. Bioaccumulation refers to an increase in the concentration of a metal in a biological organism over time, compared to the normal concentration in the environment Many metals and other chemicals accumulate in living things any time they are taken up and stored faster than they are broken down' (metabolized) or excreted [4,10].

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.

Certain elements that are normally toxic are, for certain organisms or under certain conditions, may be beneficial. Examples include vanadium, tungsten, and even cadmium. Heavy metals are stable and persistent environmental contaminants since they cannot be degraded or destroyed. Therefore, they tend to accumulate in the soil, seawater, freshwater, and sediments [4].

In small quantities, certain heavy metals are nutritionally essential for a healthy life (e.g., iron, copper, manganese, and zinc). Some of these are referred to as the trace elements.

These elements, or some form of them, are commonly found naturally in foodstuffs, in fruits and vegetables, and in commercially available multivitamin products.

2.2 Occurrence of heavy metals in nature

Metals in the environment may be present in the solid, liquid or gaseous state. They may be present as individual elements, and as organic and inorganic compounds. The movement of metals between environmental reservoirs may or may not involve changes of state.

The geosphere is the original source of all metals (except those that enter the atmosphere from space in the form of meteorites and cosmic dust). Within the geosphere, metals may be present in minerals, glasses, and melts. In the hydrosphere, metals occur as dissolved ions and complexes, colloids, and suspended solids. In the atmosphere, metals may be present as gaseous elements and compounds and as particulates and aerosols. Gaseous and particulate metals may be inhaled and solid and liquid (aqueous-phase) metals may be ingested or absorbed, thereby entering the biosphere. In addition to being the original source of all terrestrial metals, the geosphere may represent a sink for metals. The atmosphere and hydrosphere also constitute sinks for metals; however, from a geological perspective, they are more likely to be considered as agents of transport [5, 6].

The movement of metals from one site to another depends on the linear and temporal scales of observation. For example, the oceans are a vast reservoir for a variety of chemical elements. They also serve as a conduit for elements derived from weathering of rocks to return to the geosphere through sedimentation. A reservoir may act as a catalyst for changes of state of metals and metal compounds, without actually having incorporated those metals, as in the case of some biologically mediated reactions.

2.3 Behavior of heavy metals in the Environment

The main source for metal input to plants and soils is atmospheric deposition. Volatile metalloids such as As, Hg, Se, and Sb can be transported over long distances in gaseous forms or enriched in particles, while trace metals such as Cu, Pb, and Zn are transported in particulate phases. In terrestrial ecosystems, soils are the major recipient of metal contaminants, while in aquatic systems sediments are the major sink for metals, Freshwater systems are contaminated due to runoff and drainage via sediments or disposal, while groundwater is impacted through leaching or transport via mobile colloids.

A number of biogeochemical processes take place at the heterogeneous interface between the rock, soil, water, air and living organisms. These processes or interactions in turn control the solubility, mobility, bioavailability and toxicity of metals. Metals are found in soil solution as free ions or complexed to inorganic or organic ligands. Both die free ions and the metal-ligand complexes can be (i) taken up by plants, (ii) retained on mineral surfaces, natural organic matter, and microbes, (iii) transported through the soil profile into groundwater via leaching or by colloid-facilitated transport, (iv) precipitated as solid phases, and (v) diffused in porous media such as soils [2,7].

Microorganisms can transform metals such as Hg, Se, Sn, As and Cr by means of oxidation-reduction and methylation (the process of replacing an atom, usually a H atom, with a methyl group) mechanisms and di-methylation reactions.

These processes affect transport or mobility and solubility or toxicity of metals. For example, methylated (organic) forms of Hg are more toxic than inorganic forms of the element and they bio-accumulate in organisms. Methylation is favored in environments characterized by low oxygen levels, low pH, and high soil organic matter (SOM) contents.

Heavy metal contamination of soil is a far more serious problem than air or water pollution because heavy metals are usually tightly bound by the organic components in the surface layers of the soil. Consequently, the soil is an important geochemical sink which accumulates heavy metals quickly and usually depletes them very slowly by leaching into groundwater aquifers or bio-accumulating into plants.

Heavy metals can also be very quickly trans-located through the environment by erosion of the soil particles to which they are adsorbed or bound and re-deposited elsewhere. The transport, cycling, fate, bioavailability and toxicity of heavy metals are markedly influenced by their physico-chemical forms in water, sediments and soil. Whenever a heavy metal or its compound is introduced into an aquatic environment, it is subjected to a wide variety of physical, chemical and biological processes. Often, heavy metals experience a change in the chemical form as a result of these processes and so their distribution, bioavailability and other interactions in the environment are also affected. They can leach into living systems from natural ore deposits and other sources such as waste disposal of heavy metal containing waste. In fact, waste disposal accounts for higher percentage of most heavy metals including manganese in the environment.

2.4 Uses of heavy metals

Heavy metals are important components of building materials, vehicles, appliances, tools and computers; and are essential in the infrastructure including highways, bridges, railroads, airports, electrical utilities and food production and distribution.

Civilization was founded upon the metals of antiquity, gold, copper, silver, lead, tin, iron and mercury. Natural and consumer products contain small concentrations of different heavy metals. For example, cadmium is mainly used in batteries, plastics and it is also found in cigarette smoke, in shellfish and vegetables [11, 12].

Mercury is found in batteries, dental amalgam, vacuum pumps and valves. Airborne mercury comes from the combustion of diesel, jet fuel and heating oil. Arsenic is high in seafood and may also be found as a contaminant in animal feeds. It is also present in wood preservatives, herbicides, corrosion inhibitors, in lead and copper alloys.

Cadmium is used industrially as an anti-friction agent, as a rust-proofer, in plastics manufacture, in alloys and in alkaline storage batteries. Chromium is found in fresh foods, copy machine toner and nickel in coins, kitchen utensils and milk. Copper is essential to all living organisms and has a wide range of effects depending on concentration and chemical formulation. It is used in the electrical industry in alloys such as brass, in chemical catalysts and in wood-preservatives. Lead has been used in batteries, electronic equipments, in petrol, toys, paint, etc. Lead has been used as fuel additive in many countries for several years, although this practice has since stopped in most of the countries of the world, because of the health implications of lead.

Manganese compounds are used in manufacturing of products such as batteries, steel and unleaded petrol. Manganese dioxide is commonly used in the production of dry-cell batteries, matches, fireworks, porcelain and glass-bonding materials. It is also used as the starting material for the production of other manganese compounds.

Manganese chloride is a precursor of other manganese compounds. It is used as a catalyst in the chlorination of organic compounds, in animal feed to supply essential trace minerals and in dry-cell batteries.

Manganese sulfate is used as a fertilizer, livestock nutritional supplement and in ceramics. As potassium permanganate, it is used as oxidizing agent and disinfectant in water purification and in waste treatment plants. It is used in metal cleaning, bleaching and as a preservative for fresh flowers and fruits.

2.5 The anthropogenic sources of heavy metals

Much research has been conducted on heavy metal contamination in soil from various anthropogenic sources such as industrial wastes, automobile emissions, mining activity and agricultural practices.

The anthropogenic heavy metals are believed to easily accumulate in the top soil, causing potential problems such as toxicity to plants and animals, accumulation in food chain, perturbation of the ecosystem and adverse health effects [7,11].

2.6 Human exposure and health hazards associated with heavy metals

Humans are always exposed to the natural levels of trace elements. Under normal circumstances; the body is able to control some of these amounts. However, continuous exposure to elevated levels of metals could cause serious illness or death. Increased exposure may occur through inhalation of airborne particles or through ingestion of contaminated soil by children or by absorption through the skin [16].

Metals and their compounds can accumulate in the body's tissues, such as bones or nerves. They can cross the placenta and harm an unborn child in pregnant women. Children are the most susceptible to health problems caused by heavy metals, because their bodies are smaller and still developing. The health hazards presented by heavy metals depend on the level and the length of exposure. In some cases, the health effects are immediately apparent; in others, the effects are delayed [16, 17].

High levels of toxic metals deposited in body tissues and subsequently in the brain, may cause significant developmental and neurological damage, including depression, increased irritability, anxiety, insomnia, hallucination, memory loss, aggression and many other disorders [18].

Cadmium

Cadmium is a toxic trace element which may accumulate in soils from various human activities. Natural source of cadmium is weathering of rocks while some cadmium enters air through forest fires and volcanoes. No cadmium ore is mined for the metal, because more than enough is produced as a byproduct of the smelting of zinc from its ore, sphalerite (ZnS), in which CdS is a significant impurity, making up as much as 3%. It is similar in many respects to zinc but it forms more complex compounds. About three-fourths of cadmium is used in Ni-Cd batteries, most of the remaining one-fourth is used mainly for pigments, coatings and plating, and as stabilizers for plastics. Cadmium has been used particularly to electroplate steel where a film of cadmium only 0.05 mm thick will provide complete protection against the sea. Cadmium has the ability to absorb neutrons, so it is used as a barrier to control nuclear fission. Metal plating and tire rubber are considered the likely sources of Cd in urban soil and street dust.

Cadmium (Cd) and its compounds are extremely toxic at all levels and tend to bio-accumulate in organisms and ecosystems. Cadmium derives its toxicological properties from its chemical similarity to zinc. Cadmium is bio-persistent and, once absorbed by an organism, remains resident for many years (over decades for humans) although it is eventually excreted. In humans, long-term exposure is associated with renal dysfunction. High exposure can lead to obstructive lung disease and has been linked to lung cancer, although data concerning the latter are difficult to interpret due to compounding factors. Cadmium may also produce bone defects in humans and animals.

Cadmium is strongly adsorbed to organic matter in soils. When cadmium is present in soils it can be extremely dangerous, as the uptake through food will increase. Soils that are acidified enhance the cadmium uptake by plants. Human uptake of cadmium takes place mainly through food. Foodstuffs that are rich in cadmium (liver, mushrooms, shellfish, mussels, cocoa powder and dried seaweed) can greatly increase the cadmium concentration in human body. Tobacco smoke transports cadmium into the lungs [9].

Blood will transport it to the rest of the body. Other high exposures can occur with people who live near hazardous waste sites or factories that release cadmium into the air and people that work in the metal refining industry. When people breathe in cadmium, it can severely damage the lungs. This may even cause death.

Cadmium transported to the liver binds with proteins to form complexes that are transported to the kidneys where it is likely to damage the filtering mechanism. This causes the excretion of essential proteins and sugars from the body damaging kidney further. The highest concentration of cadmium is found in liver and kidney with somewhat lower concentration in pancreas and spleen.

Ingestion of small amount of cadmium over a period of a few years may lead to the accumulation of chronically or even acutely toxic level of cadmium in body. It takes a very long time before cadmium that has accumulated in kidneys is excreted from a human body. Other health effects that can be caused by cadmium are: diarrhea, stomach pains and severe vomiting, bone fracture, reproductive failure and possibly even infertility, damage to the central nervous system, damage to the immune system, psychological disorders, and -possibly DNA damage or cancer development.

Cadmium poisoning causes softening of the bones and kidney failures and was responsible for the "itai-itai" disease (a name derived from the painful screams in Japanese language) due to the severe pain in the joints and the spine .The disease arose from increased uptake of cadmium in locally consumed rice grown in paddy fields irrigated with cadmium-contaminated river water.

Chromium

Chromium is used in metal alloys and pigments for paints, cement, paper, rubber, and other materials. Low-level exposure to Cr can irritate the skin and cause ulceration. Longterm exposure can cause kidney and liver damage, and also circulatory and nerve tissues. Chromium often accumulates in aquatic life, adding to the danger of eating fish that may have been exposed to high levels of chromium.

The level of chromium in air and water is generally low. In drinking water the level of chromium is usually low as well, but contaminated well water may contain the dangerous chromium (VI) or hexavalent chromium. For most people eating food that contains chromium

(III) is the main route of chromium uptake, as chromium (III) occurs naturally in many vegetables, fruits, meats, yeasts and grains. Various ways of food preparation and storage may alter the chromium contents of food. When food is stored in steel tanks or cans chromium concentrations may rise.

Chromium (III) is an essential nutrient for humans and shortages may cause heart conditions, disruptions of metabolisms and diabetes. But the uptake of too much chromium (III) can cause health effects as well, for instance skin rashes Chromium(VI)) is very toxic and is the real danger to human health, mainly for people who work in the steel and textile industry. People who smoke tobacco also have a higher chance of exposure to chromium.

Chromium (VI) in leather products can cause allergic reactions, such as skin rash. After breathing chromium (VI) in air, nose irritations and nose bleeds are quite common. Other health problems that are caused by chromium (VI) are: skin rashes, upset stomachs and ulcers, respiratory problems, weakened immune systems, kidney and liver damage, alteration of genetic material and lung cancer.

Cobalt

Cobalt is of relatively low abundance in the Earth's crust and in natural waters, from which it is precipitated as the highly insoluble cobalt sulfide, CoS. Cobalt is used in many alloys (super alloys for parts in gas turbine aircraft engines, corrosion resistant alloys, high speed steels, cemented carbides), in magnets and magnetic recording media, as catalysts for the petroleum and chemical industries, as drying agents for paints and inks.

Human exposure to Co takes place through air, drinking water and food. Cobalt is not freely available in the environment, but when cobalt particles are not bound to soil or sediment particles the uptake by plants and animals is higher andaccumulation in plants and animals may occur.

Cobalt is contained in vitamin B_{12}, essential for human health. Cobalt is used to treat effects from Co may also arise due to exposure to radiations from radioactive cobalt isotopes. This can cause sterility, hair loss, vomiting, bleeding, diarrhea, coma and even death. When this radiation is used in cancer-patients to destroy tumors, it stimulates the production of red blood cells. The total daily intake of cobalt may be as high as 1 mg, but almost all will pass through the body unabsorbed, except that in vitaminB_{12}.

Copper

Presence of Cu in water impacts taste and color. Cu content of soil ranges from 10-80mg/kg depending upon the nature of the parent material and the pedeologic processes. It exists in soils mostly as cupric (Cu^{2+}) and less frequently as cuprous (Cu^{+}) ions.

Cu is a component of many plant enzymes (oxidase for example) and is involved in many electron transfer processes. Plants absorb copper in the form of cupric ions. The most common soil mineral with copper is chalcopyrite ($CuFeS_2$) with Cu in the Cu^{+} form. Cu exists in both exchangeable and less exchangeable forms, and also in the form of soluble organic complexes or chelates.

Copper is strongly adsorbed to many solids (clays, alumina, iron hydrous oxides, and manganese oxides). Copper, generally forms stronger bonds with organic ligands than most other metal ions.

Copper is an essential element for human life, but excessive intake results in its accumulation in the liver and produces gastrointestinal problems, anemia, liver and kidney damage. Continued inhalation of copper-containing sprays is linked with an increase in lung cancer. People with Wilson's disease are at greater risk for health effects from overexposure to copper.

Copper can be released into the environment by both natural sources (e.g. wind-blown dust, decaying vegetation, forest fires and sea spray) and human activities (mining, metal production, wood production and phosphate fertilizer production). Because copper is released both naturally and through human activities, it is very widespread in the environment. Copper is often found near amines, industrial settings, landfills and waste disposals.

Long-term exposure to copper can cause irritation of the nose, mouth and eyes and headaches, stomachaches, dizziness, vomiting and diarrhea. Intentionally high uptakes of copper may cause liver and kidney damage and even death. Industrial exposure to copper fumes, dusts, or mists may result in metal fume fever with atrophic changes in nasal mucous membranes.

Iron

Most of the rocks contain iron as one of the common elements and it is also an important component of many soils especially clay soil where it is usually a major constituent. Iron occurs as particulate ferric hydroxide or in the form of organometallic compound in natural system. Fe(III) oxide and Fe(II) are ubiquitous in anoxic environments and they affect the distribution, transport, and biogeochemistry of chemical contaminants by adsorption onto Fe(III) oxides and by control of oxidation and reduction reactions.

Iron is regarded as one of the essential elements for humans. Approximately 3000 to 5000 mg of iron exists in the human body. Therefore, as long as the quantity of iron in the environment is not too large, it may not be harmful to the human body.

However, iron can cause undesirable problems in industrial processes or ecosystems if its concentration in water is not managed properly. For example, the precipitates of iron hydroxide may block pipes, create turbidity problems, and iron deposits may act as a source material for an unpleasant taste or odor in water. Thus, excessive iron in water limits the usage of water for drinking or industrial processes. WHO has recommended a value of 0.3 mg/L as permissible limit for drinking water. For fresh water aquatic life, the limit is 1 mg/L.

Iron constitutes about 4.7% of the earth's crust. It is the second most important metallic element in the terrestrial environment. Iron is extremely useful, but can also be highly toxic to cellular constituents when present in excess. Iron is an important part of the plant's oxidation-reduction reactions. As much as 75% of the cell iron is associated with chloroplast. The major problem with iron availability is how to keep iron sufficiently soluble for plants to absorb enough of it. In strongly acidic solutions ($pH < 5$), iron becomes increasingly soluble, and is rarely deficient.It is essential for the physiological processes of all living organisms[8].

Mercury

Mercury poisoning symptoms include blindness, deafness, brain damage, digestive problems, kidney damage, lack of coordination and mental retardation.

One of the most famous cases of mercury poisoning resulting from chronic exposure was the disaster that occurred in Minamata, Japan, where methyl mercury was discharged from a plastics manufacturing plant into the waters of Minamata Bay in the 50s and 60s. Fish in the harbor were contaminated and those who ate the contaminated fish were gradually poisoned.

Nickel

Nickel is one of the ubiquitous elements and ranks 23 in order of abundance. Its average concentration in the earth's crust is 75 mg/kg. Nickel is relatively toxic and widespread in the environment .Nickel enters the environment through two main pathways: natural-such as weathering of minerals and rocks, and geochemical emission, and anthropogenic such as industrial and vehicular emissions. The total world emission of nickel to the atmosphere has been estimated at 30,000 tones/annum with the natural and anthropogenic sources contributing about 15000 and 18000 tons per year, respectively.

Nickel particles in the air settle to the ground or are taken out of the air in rain. Much of the nickel in the environment is found in soil and sediments because nickel attaches to particles that contain iron or manganese, which are often present in soil and sediments. It is considered as a borderline element between hard and soft acid acceptors in chemical interactions towards donor atoms. This is reflected in its abundance in the earth's crust as oxides, carbonates, silicates with iron, magnesium and as sulfides, arsenides and telurides. Nickel salts are soluble and can occur as a lechate from nickel bearing rocks.

The affects of nickel exposure vary from skin irritation to damage to lungs, the nervous system, and mucous membranes. It is also a known carcinogen [13, 14].

Lead

Metallic lead does not dissolve in water and does not bum, however, lead can combine with other chemicals to form lead compounds or lead salts. Some lead salts dissolve in water better than others. Although lead itself cannot be broken down, lead compounds in water may combine with different chemicals depending on the acidity and temperature of the water.

Most of the lead used by industry comes from mined ores (primary) or from recycled scrap metal or batteries (secondary). The main sources of lead pollution are lead smelters, battery manufacturers, paper and pulp industries, boat and ship fuels and ammunition industries.

In addition, the production of television picture tubes, pigments, petroleum fuels, printing, glass industries, photographic materials, etc., also adds pb^{2+} the environment. People living near hazardous waste sites may be exposed to lead by breathing air, drinking water, eating foods or swallowing or touching dust or dirt that contains lead. For others (people who do not live near hazardous waste sites), exposure to lead may occur by eating foods or drinking water that contain lead, by spending time in areas where leaded paints have been used, by working in jobs where lead is used, by having hobbies in which lead may be used such as sculpturing (lead solder) and staining glass.

Cigarette smoke also contains small amounts of lead. Lead may enter foods if they are put into improperly glazed pottery or ceramic dishes and from leaded-crystal glassware.

The effects of lead exposure are the same whether it is breathed or swallowed. Low levels of lead have been identified with anemia as it causes injury to the blood forming systems while high levels cause severe dysfunction of the kidneys, liver, the central and peripheral nervous system and high blood pressure [24].

Hypertension has also been associated with lead exposure in the general population. At the typical levels to which individuals are exposed, lead can cross the placenta and damage developing fatal nervous systems. High level exposure to lead may cause miscarriage in pregnant woman and can also damage the organs responsible for sperm production in male.

The most severe neurological effect of lead in adults is lead encephalopathy, which is a general term to describe various diseases that affect brain function. Lead exposure may cause weakness in fingers, wrists, or ankles.

Children are more sensitive to the effects of lead than adults. A child who swallows large amounts of lead may develop blood anemia, kidney damage, severe stomachache, muscle weakness, and brain damage. The lower IQ levels and other neuropsychological deficiencies among the children exposed to higher lead levels have been well documented [24, 19,4].

Lead acetate and lead phosphate have been shown to be potential carcinogens based on studies in animals. However, there is inadequate evidence to clearly determine lead's carcinogenicity in humans.

Lead poisoning damages the nervous system, kidneys, liver and cause sterility, growth inhibition, developmental retardation. Lead is toxic at all levels, hence lead based petrol, toys and paints have been banned [8].

Zinc

Zinc is an essential trace element for humans. Its deficiency as well as excess is harmful. Recent research has shown that zinc is extremely important especially in fetal development and the nutrition of infants. The adult human body contains about 2.3 g of zinc which occurs mostly in over 100 enzymes. The normal daily requirement for zinc is 15 mg for adult and 5 mg for children. Zinc plays a role in carbohydrate, lipid and protein metabolism and in the synthesis and breakdown of DNA. Because of these functions, zinc deficiency in the fetus will result in retarded growth malformation of body, and chromosomal abnormalities. A zinc deficiency after birth may result in dwarfism, poor appetite, mental lethargy, etc.

Excess amount of zinc on the other hand can cause stomach cramps, nausea, vomiting and central nervous system disorder. Most of the rocks in the earth’s crust contain zinc in varying concentrations.

Depending on the type of the rock, highest concentration is found in basic eruptive rocks (e.g. basalt, 70-130 mg/kg). An average concentration of 50-60 mg/kg is generally found in acid eruptive rocks. Zinc is found in relatively high concentration in soils (50 mg/kg on an average). Zn content in soil is much higher in the vicinity of ore deposits and smelters. Atmospheric deposition increases Zn concentration in surface soil in Zn^{2+} form and in complexes. The concentration is low in the surface soil, but increases in greater depth. Zn is an essential growth element for plants and animals, but at elevated levels, it is toxic to some aquatic species. Excessive Zn in soil may cause damage to plants and at lower pH, the yield is reduced.

2.7 Heavy Metals pollution

Heavy metal is metallic elements with high atomic weight and density. These include the transition metals, some metalloids, lanthanides and actinides. Amounting to more than 20 metals generally exist in a positively charged form and can bind on to negatively-charged organic molecules [11, 12].

Being metals ions, heavy metal cannot be degraded or destroyed, therefore their stability make them as the persistent toxic substances in environment. Heavy metal as the environmental contaminants can be found in the air, soil and water, which pose health hazard to the general public. Presence of heavy metal in water as the contaminants is an indication of global problem [37].

2.8 Bioavailability of heavy Metals and chemical speciation

Bioavailability is defined as the fraction of the element from an ingested matrix such as soil, water or food that can be absorbed by an organism. The bioavailability and environmental mobility of the metals are dependent upon the form in which the metal is associated with the soil. However determining the total metal contents of soil provides little insight into their bio -availability. To determine bio -availability and the actual dangers posed by the heavy metals in soil, one approach is based on sequential extraction of the metals into different phases so that the labile fractions could be estimated in atmospheric particulate matter, sediment and soils. Bioavailability of metals from contaminated sites is a very important aspect of health risk assessment programs [35].

The distribution of trace elements in the environment, their accumulation by organisms, their bioavailability and their toxicity to organisms (including humans) can be understood only in terms of trace element species. Therefore, it is very important to identify elemental species so that environmental processes can be fully understood [5].

Soils consist of heterogeneous mixtures of organic and inorganic solid components as well as a variety of soluble substances. Therefore, metal distribution among specific forms varies widely based on the metal’s chemical properties and soil characteristics. Thus, it is important to evaluate the availability and mobility of heavy metals to establish environmental guidelines for potential toxic hazards and to understand the chemical behavior and fate of heavy metal contaminants in soils.

2.9. Analysis of heavy Metals in soil sample

Metals contained in samples are determined by a wide variety of analytical methods, with the choice often depending on the precision and sensitivity required. The selected heavy metals can be determined by various spectroscopic or chromatographic methods, such as atomic absorbance spectrometry using flame (FAAS) or graphite furnace (GFAAS) atomization, atomic emission spectrometry (AES), inductively coupled plasma atomic-emission spectrometry (ICP-AES), inductively coupled plasma-mass spectrometry (ICP-MS), X-ray fluorescence (XRF), and ion chromatography (IC) [35, 21].

The methods such as polarography and voltammetry can also be used to determine the metal levels in various samples.

All these methods require pre treatment of samples to be analyzed. One of these samples pre-treatment involve sample matrix break down or sample decomposition. In this project, MP-AES was employed for determination of metal levels in soil samples.

2. 10. Sample Decomposition

A common result of the sample preparation is the dissolution of the entire sample, producing a clear solution. The digestion method must be selected to suit the type of sample, the metals being determined, the analytical method and factors such as the matrix composition, the element contents, the possible interferences, the risk of loses and contaminations, the practicality and possible safety hazards in the laboratory [34, 21, 22].

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 [32]. The digestion methods could be classified in to wet digestion, acid digestion, dry ashing, and microwave digestion.

2.10. 1. Wet digestion

Samples to be analyzed for elemental metal content are usually prepared by digesting the matrix in a strong acid. In the case of organic matrices, an oxidizing mixture is used to destroy the entire organic matrix and solubilize the sample. This yields a clear solution containing the metals for analysis by such techniques as AA, ICP, or ICP-MS. Nitric acid is commonly used, because there is no chance of forming insoluble salts as might happen with HCl or H_2SO_4. Hydrogen peroxide may be added to increase the oxidizing power of the digestion solution [21, 22 32]. The procedure could take place either in open system or closed system.

2.10.2. Dry ashing

For samples that contain much organic matter, which are being analyzed for non volatile metals, dry ashing is a relatively simple method of removing the organic matter that can be used for relatively large samples and requires little of the analysts time. In the open vessel method, the sample is placed in a suitable crucible and is ignited in a muffle furnace.

Crucibles used for ashing are usually made of silica, porcelain, platinum, or Pyrex. After decomposition the residue is dissolved in acid and transferred to a volumetric flask prior to analysis. Typical ashing temperatures are 450 to 550 °C. Magnesium nitrate is commonly used as an ashing aid. The major drawbacks of the method are the possible loss of some elements by volatilization, contamination of the sample by airborne dust, as it must be left open to the atmosphere and irreversible sorption of analyte into the walls of the vessel [32].

2. 10 .3. Microwave digestion

A microwave sample digestion system consists of a microwave oven, a rotating carousel holding several sample digestion bombs, and a system for venting these in a controlled fashion. It may also provide monitoring and recording of both temperature and pressure in the containers.

Digesting a sample in a closed container in a microwave oven has several advantages over open container dissolution methods.

The containers are fabricated of high-temperature polymers, which are less likely to contain metal contaminants than are glass or ceramic beakers or crucibles. The sealed container eliminates the chance of airborne dust contamination. The sealed, pressurized containers reduce evaporation, so that less acid digestion solution is required, reducing blanks. The sealed container also eliminates losses of more volatile metal species, which can be a problem in open container sample decomposition, especially in dry ashing [21].

2.10.4. Fusion

Fusion is a powerful technique especially both for organic matrices and those with a high silica and alumina content. Since solid and aggressive fusion reagents are difficult to purify. Fusion cannot be recommended as ultra trace analysis. A second disadvantage is that the method is carried out in contact with ambient air. Risks of volatilizations are large [9].

3. EXPERIMENTAL

3.1.1 Equipment, reagents or chemicals

3.1.1.1 Equipments

Mortar and pestle was used to grind soil sample. Analytical balance (Larko, LA114, 110 g/0.1 g) with precision of ± 0.0001 g was used to weigh the soil samples. 100 mL round bottomed flasks fitted with reflux condensers were used in Kjeldahl apparatus hot plate to digest the dried and powdered soil samples. Borosilicate volumetric flasks (25, 50 and 100 mL) were used during dilution of sample and preparation of metal standard solutions.

Measuring cylinders, pipettes, micropipettes, were used during measuring different quantities of volumes of sample solution, acid reagents and metal standard solutions. Micro wave plasma atomic emission spectroscopy was used for the analysis of the analyte metals (Cu, Zn, Hg, Ni, Fe, Co, Cr, Pb and Cd in the soil sample.

3.1.1.2. Reagents and chemicals

Reagents that were used in the analysis were all analytical grade. HNO_3 (69-72%) and HCl(37%). Aqua-regia prepared from 3:1 ratio of 37% HCl and (69-72%) HNO_3 and extra pure hydrogen peroxide 30% were used for digestion of soil sample.

De-ionized water was used for dilution of sample and intermediate metal standard solutions prior to analysis rinsing glassware and sample bottles.

3.2 Procedure

3.2.1. Cleaning apparatus

Apparatus such as volumetric flasks, measuring cylinder and digestion flasks were washed with detergents and tap water, rinsed with de ionized water. Dried in oven and kept in dust free place until analysis begins. Prior to each use the apparatus were soaked and rinsed in de-ionized water**.**

3.2.2. Description of sampling areas

Samples were collected from three major flower production area in Ethiopia namely Sebeta,Holeta and Zeway, in Oromia region around Addis Ababa.

Figure1.Sebetalapheto rose flower farm

Figure 2. Zeway lake around share Ethiopia flower farm

3.2.3 Sample collection and preparation

The soil samples used for the study were collected from different geographical coordinates on the site with plastic ladles. Each soil sample was collected at the depth of about 30cm from the surface of the soil to obtain through layer of the soil. Samples were labeled and stored in polythene bags prior to analysis[33].

The soil samples were first air-dried at room temperature ground in a ceramic mortar and sieved at 500 microns. About 0.5 g of the pulverized sample was digested with HNO_3, and HCl [34].

3.2.4 Determination of moisture content of the sample

To determine the moisture content of soil sample, first it was carefully exposed to air to vaporize water on the surface of it. Then it was weighed with electronic balance to record the initial weight with its moisture content. After oven drying at 80^0c for two days it was re-weighed and re-dried until it gave constant mass. As can be seen from Table 1, the moisture content of three samples was between 25-40%.

Table 1.Moisture content of sample

Sampling area	The mass before drying(g)	The mass after drying(g)	Moisture content (%)
Zeway	500	380	24
Sebeta	500	320	36
Holeta	500	325	35

3.2.5. Digestion procedure and sample digestion

Digestion of soil with acids in an electrical heating block has been well established and widely used for the determination of nutrient concentrations in soil samples. Adding the strong mineral acids or their combinations (commonly nitric or/and hydrochloric acid as they are strong oxidizing agent and forms soluble salts with metals) to the soil in appropriate vessel (test tube, beaker, digestion flask, etc) and heating with a Bunsen burner, hot plate, or aluminum block with programmed temperature is the most common procedure employed.

aluminum block with programmed temperature is the most common procedure employed

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Figure 3. Digesting of soil samples

3.2.5.1 Optimization of digestion procedure of soil samples

The basic requirements for sample preparation for analysis are to get an optimum condition for digestion. The optimum condition is the one which required minimum reagent volume consumption, minimum reflux time, clarity of digests, and ease of simplicity. In this study, to prepare a clear colorless sample solution that is suitable for the analysis using MP- AES, digestion procedures were optimized using the HNO_3 and HCl acid mixtures by varying parameters such as volume of the acid mixture, digestion time and digestion temperature (Table 2). From the optimization procedures, 6 ml of the acid mixture of HNO_3 (69-70%) and HCl (70%) with the ratio of 3:1, digestion time of 3 hours and digestion temperature of 210^0C were the optimal condition for 0.5 g soil sample.

These optimum conditions were selected based on clarity of digests, minimum reagent volume consumption, minimum digestion time, simplicity and minimum temperature applied for complete digestion of sample.

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

Trial no	Reagent(s) used	Reagent(s)volume(mL)	Temp. (^{o}C)	Digestion time(h)	Observation

I. Optimization for reagent volume

1	Aqua-regia	3mL	300	3:00	
2	Aqua-regia	4 mL	300	3:00	
3	Aqua- regia	5 mL	300	3:00	
4	**Aqua-regia**	**6 mL***	**300**	**3:00**	**Clear and colorless**
5	Aqua- regia	7mL	300	3:00	
6	Aqua-regia	8mL	300	3:00	

II. Optimization for Temperature

1	Aqua- regia	6mL	150	3:00	
2	A qua-regia	6 mL	180	3:00	
3	**Aqua-regia**	**6 mL**	**210***	**3:00**	**Clear and colorless**
4	Aqua- regia	6 mL	240	3:00	
5	Aqua-regia	6 mL	270	3:00	
6	Aqua-regia	6 mL	300	3:00	

II. Optimization for time

1	Aqua-regia	6 mL	210	1:45	
2	Aqua-regia	6 mL	210	2:00	
3	Aqua-regia	6 mL	210	2:15	
4	Aqua-regia	6 mL	210	2:30	
5	Aqua-regia	6 mL	210	2:45	
6	**Aqua-regia**	**6 mL**	**210**	**3:00***	**Clear and colorless**

* Indicate the optimal condition for the given parameter.

3.2.5.2 Digestion of soil samples

Applying the optimized condition (Table 2), 0.5 g of dried and homogenized soil samples were transferred into a 100 mL round bottomed flask. To this 6 ml of aqua-regia (3:1 ratio of 37% HCl to (69-72%) HNO_3, respectively) were added and the mixture was digested on a Kjeldahl digestion apparatus fitting the flask to a reflux condenser by setting the temperature first to dial at 6 (150^0C) for the first 30 min and then raised to dial 8 (180 ^{0}C) for the next 30 min and finally raised to dial 9 (210^0C) for the remaining 2 hours.

Figure 4. Optimized soil samples

3.3 Soil heavy metal analysis

Heavy metals (Fe, Zn, Cu, Pb, Cr, Hg, Ni, Co and Cd) in soil samples were analyzed using aqua- regia digestion method and determined by micro wave plasma atomic emission spectrscopy.

Table 3.Instrumental operating conditions for the determination of metals using MP –AES.

metal	Wave length(nm)	Blank correction	Replicate	Pump speed	Blank subtraction	Stablization time	Sample uptake	Sample uptake fast	Rinse time	Nebulizer flow
Fe	371.993	Auto	3	15	on	16	30	On	10	0.65
Cu	327.395	Auto	3	15	On	18	30	On	12	0.7
Zn	213.857	Auto	3	15	On	21	28	On	10	0.45
Pb	283.305	Auto	3	15	On	21	28	On	10	.75
Cd	226.502	Auto	3	15	On	18	30	On	12	.5
Ni	305.081	Auto	3	15	On	18	30	On	12	0.7
Co	340.512	Auto	3	15	On	14	25	On	10	0.75
Hg	253.652	Auto	3	15	On	10	18	On	12	0.75
Cr	427.480	Auto	3	15	on	21	28	on	10	0.9

3.4 Data analysis

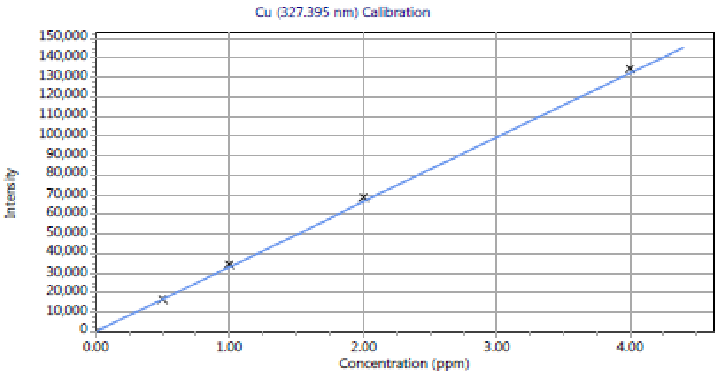
All the data were acquired and entered in to computer and using Microsoft excels statistically using SPSS 16.0. Variation of each parameter between sites was analyzed using one way ANOVA at 95% confidence level were calculated and the results were presented as mean and standard deviation (Mean ± SD).

3.5 Instrument calibration

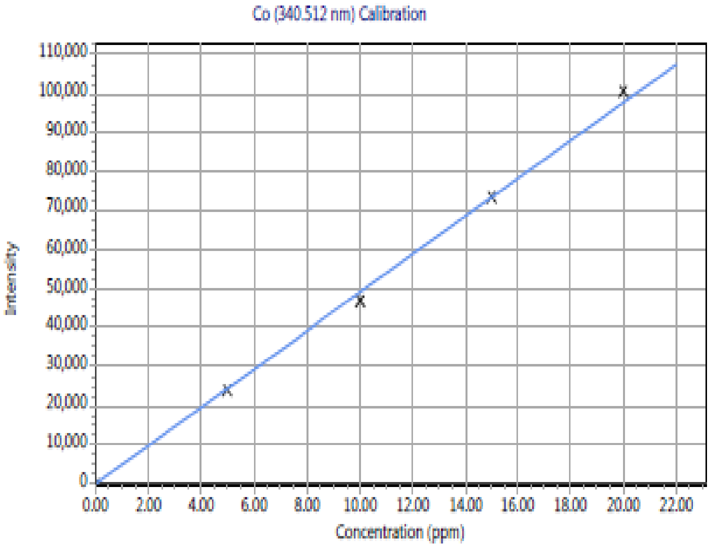
From the corresponding calibration curves in figure 5for each metal it is possible to conclude that the change in intensity with concentration is in good positive correlation and give a linear graph.

Cd,Cu--Yenenesh.mpws

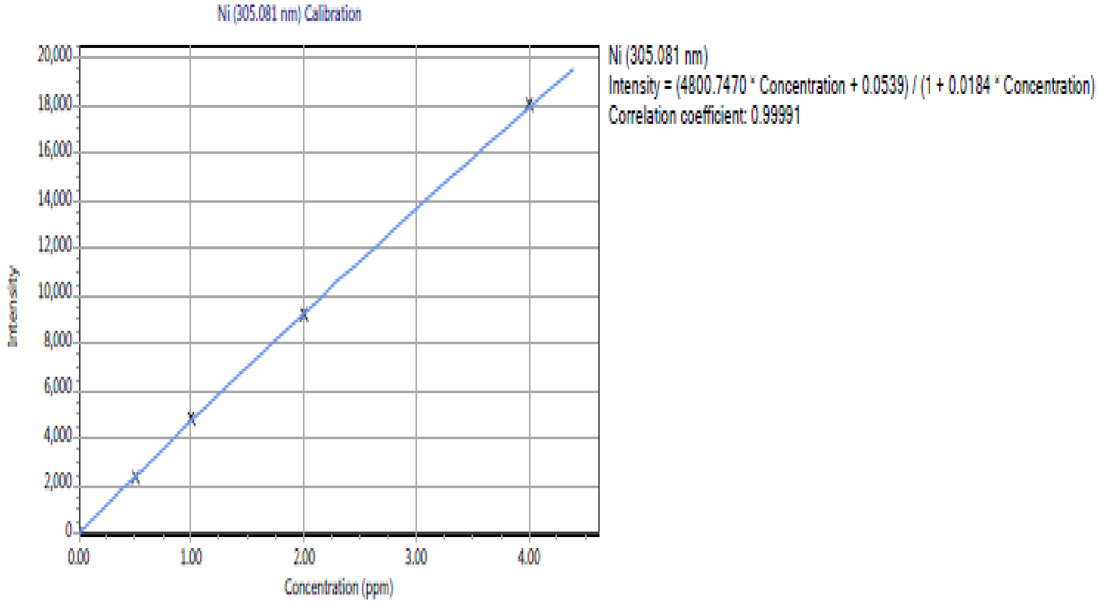
Instrument used: MY15110003



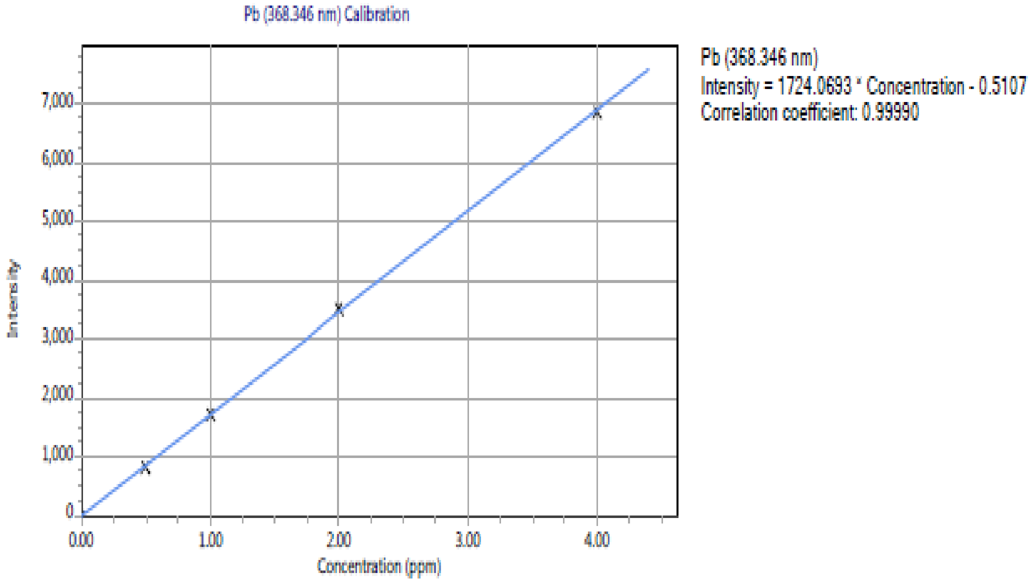
Cu (327.395 nm)
Intensity = 33057.4631 * Concentration - 45.1071
Correlation coefficient: 0.99990



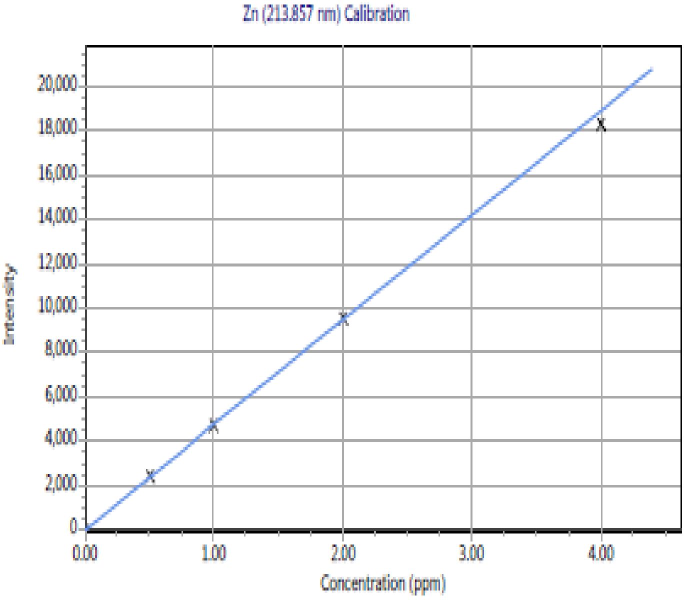
Co (340.512 nm)
Intensity = 4887.5685 * Concentration - 0.0027
Correlation coefficient: 0.99940



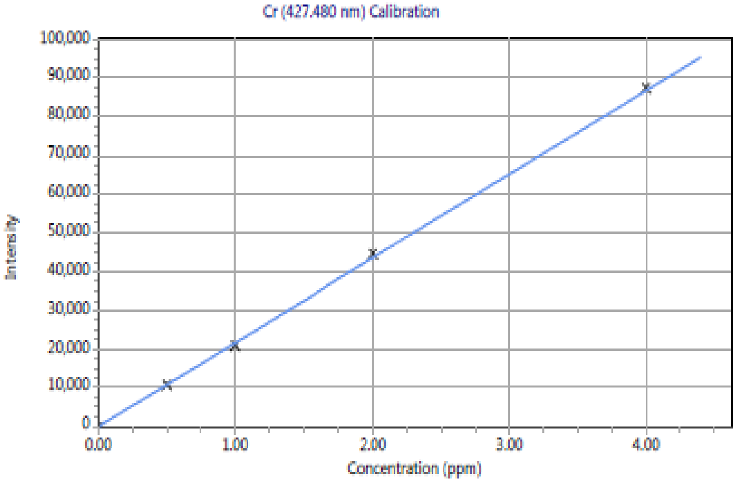
Ni (305.081 nm)
Intensity = (4800.7470 * Concentration + 0.0539) / (1 + 0.0184 * Concentration)
Correlation coefficient: 0.99991



Pb (368.346 nm)
Intensity = 1724.0693 * Concentration - 0.5107
Correlation coefficient: 0.99990



Zn (213.857 nm)
Intensity = 4732.9653 * Concentration + 24.0989
Correlation coefficient: 0.99969



Cr (427.480 nm)
Intensity = 21715.1442 * Concentration - 1.0411
Correlation coefficient: 0.99987

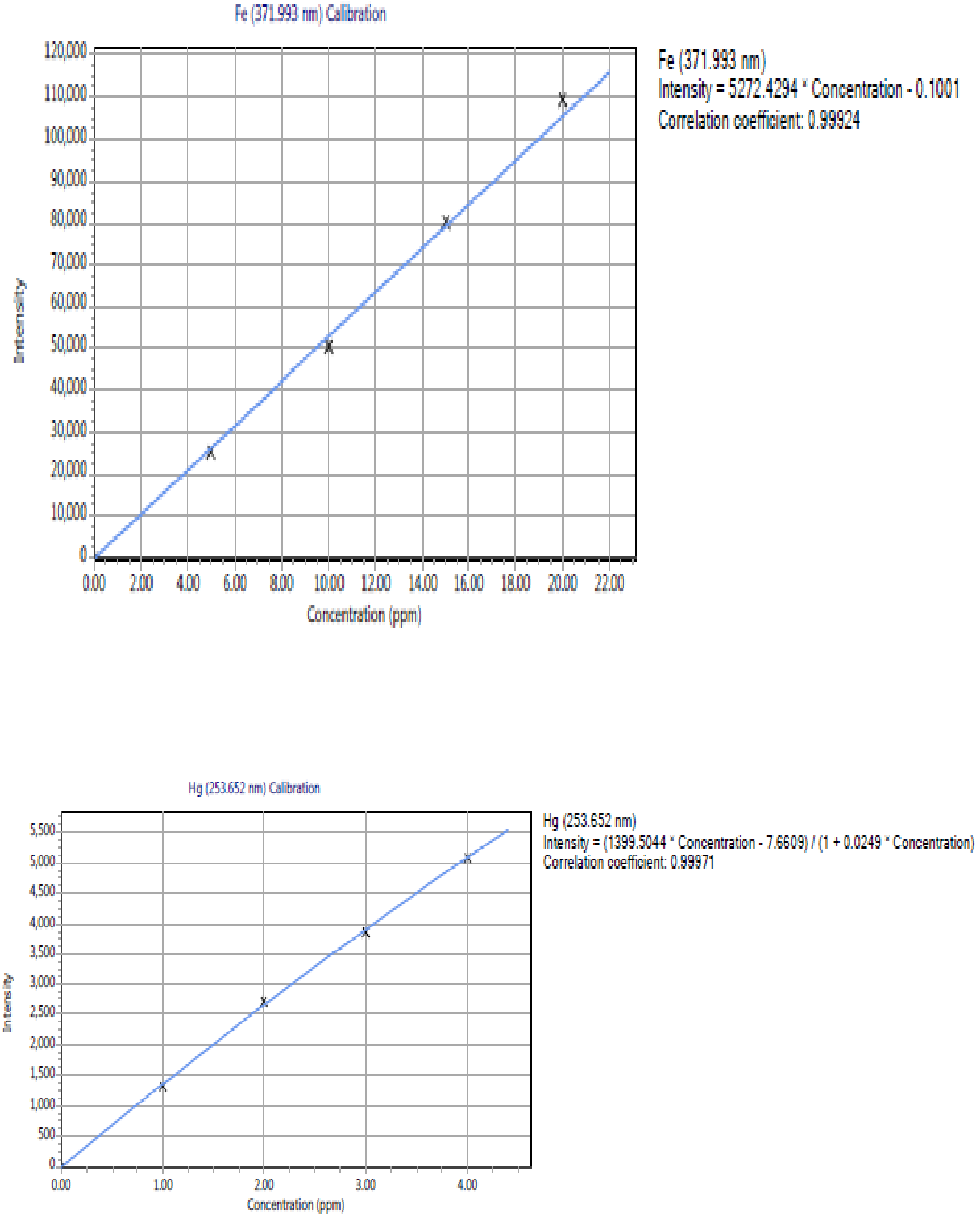


Figure 5. Calibration results of metals

3.5. Method performance and method validation

The criteria used for evaluating analytical methods are called figures of merit. Based on these characteristics, one can predict whether a method meets the needs of intended purpose. These figures of merit are accuracy, precision, sensitivity, detection limits, and the quantitation limits [32].

3.5.1. Precision and accuracy

The precision of an analytical procedure expresses the closeness or agreement between a replicate measurements obtained from multiple sampling of the same homogeneous sample under the prescribed conditions (repeatability or reproducibility). The common term used to measure variability is the coefficient of variation (CV) or relative standard deviation (RSD), which may also be expressed as a percentage and it is the parameter of choice for expressing precision in analytical sciences [32].

In this study, the precision of the results were evaluated by the pooled standard deviation, and relative standard deviation of the results of nine measurements for a given bulk sample.

(i.e. three samples (n = 3) and triplicate readings for each sample).

3.5.2. Method detection limit

According to IUPAC, the limit of detection (LOD) is defined as the smallest concentration or amount of an analyte that can be reliably shown to be present or measured under defined condition, and the limit of detection is the lowest concentration level that can be determined to be statistically different from a blank (99% confidence). The LOD is typically determined to be in the region where the signal-to-noise ratio is greater than 3 but not necessarily quantitated as an exact value.

In the present study, method detection limit for each metal was estimated by digesting three analytical blanks with the optimized procedure for soil samples. Triplicate analyses of three blank samples for all elements were performed and the pooled standard deviation of the three blank reagents was calculated. The detection limits were obtained by multiplying the pooled standard deviation of the reagent blank by three. The method detection limit of each element is above the instrument detection limit.

3.5.3. Method limit of Quantitation (LOQ)

The lowest concentration level at which a measurement is quantitatively meaningful is called the limit of quantitation (LOQ). The LOQ is most often defined as 10 times the signal/noise ratio. If the noise is approximated as the standard deviation of the blank the LOQ is 10 x standard deviation of the blank. [32].

In this study, LOQ was obtained from triplicate analysis of three reagents blanks which were digested in the same digestion procedure as soil samples. The LOQ was calculated by multiplying pooled standard deviation of the reagent blank by ten.

Table 4.The values of LOD, IDL and LOQ with their r^2 and equation

metals	LOD(mg/g)	LOQ(mg/g)	IDL(mg/g)	Coefficient of deter.r^2	Linear regression equation
Fe	0.40	1.33	0.002	0.9995	Y=5024.3x+203.51
Zn	0.22	.73	0.002	0.9995	Y=4541.8x+301.91
Ni	0.27	0.90	0.002	0.9997	Y=4453.4x+207.29
Cu	0.40	1.33	0.002	0.9997	Y=33562x+525.38
Cr	0.34	1.13	0.002	0.9946	Y=327.3x+50.34

3.6. Validation of optimized procedure

The accuracy of the optimized procedure is checked by various methods. These are certified standard reference material analyzing and spiking sample with known concentration of the analyte. In this work, the method validation was established by spiking experiments. The spiked samples were prepared by adding a small known quantity of metal standard solutions.

The spiked and non-spiked samples were digested and analysed in similar condition. Then the percentage recovery of the analyte was calculated by:

$$\%R = \frac{c_m \text{ in the spiked sample} - c_m \text{ in the non} - \text{spiked sample}}{c_m \text{ added for spiking}} x100\%$$

Where, C_m = concentration of metal of interest.

As shown in Table 5 the results of percentage recoveries for the studied metal in soil samples were within the acceptable range (93-110%).

Therefore, this verifies that the optimized digestion procedure was valid for soil sample analysis.

Metal	Concentration of metal in un - spiked sample(mg/kg)	%spiked	Concentration of metal in spiked sample(mg/kg)	Amount added(mg/kg)	Amount recovered(mg/kg)	(%R)
Fe	273	20	868.1	5.41	7.7	110
Zn	120	30	405.6	2.72	6.6	105
Cu	21	60	35.o1	0.15	3	93.4
Ni	23	50	91.37	0.71	5.75	96.3
Cr	12	40	52.53	0.428	5	94.7

Table 5. Recovery test for the optimized procedure of soil sample

4. RESULTS AND DISCUSSION

4.1 Determination of metals in soil samples

The concentration of eight elements (Fe, Zn, Cu, Co, Cr, Ni, Cd, and Pb) in the digested samples of soil were analysed by MP- AES. Among the analysed metals Pb, Hg, Co and Cd were below the method detection limit and the level of the detected is metals shown with their respective %RSD in Table 6. The most abundant metal among the macro-elements in the soil samples is Fe, followed by Zn, Ni, Cu and Cr.

Table 6. Average concentration (mean, n = 3, mg/kg dry weight basis) and relative standard deviation (% RSD) of some selected heavy metals in soil samples from Zeway, Sebeta and Holeta.

metal	Zeway conc. Mean(mg/kg)	%RSD	Sebeta conc. Mean(mg/kg)	% RSD	Holeta conc. Mean(mg/kg)	%RSD
Fe	273	0.45	383	0.89	476	0.87
Zn	120	0.98	158	1.3	170	0.81
Cu	21	0.80	52	0.92	38	1.1
Ni	23	1.54	56	1.1	50	1.0
Cr	12	1.09	19	1.1	28	0.67
Cd	BDL	BDL	BDL	BDL	BDL	BDL
Pb						
Hg						
Co						

ND: BDL Concentration of the tested heavy metal below the method detection limit (< 0.002 mg/g).

4.2.2. Distribution pattern of metals in soil sample

The soil sample collected from three sampling areas were found to contain detectable metal content of Fe, Zn, Cu, Cr Hg, Pb, Cd and Ni in all the three soil samples and their values are given in Table 6. Among the analysed metals, pb, Cd, Co and Hg were found to be below the detection limit of the method used in this study.

There is significant difference in concentration of different metals within soil sample and appreciable difference in the same metals of different sample.

The determined concentration range of metals from three soil sampling area are given in Table 6.

In general, the concentration pattern of metals in soil was decreased as Fe >Zn > Ni > Cu >Cr.

4.5. Comparison of metal level in soil with literature values

The natural content of metals in the soil is directly related to the mineralogic and granulometric composition and the origin of the matrix soil and its range is very wide. [35]. The concentrations of Fe (273-467 mg/kg), Zn (120-170 mg/kg), Cu (21-52mg/kg) and Cr (12-28 mg/kg) and Ni (23-56 mg/kg) in the soil in this study were comparable with the value of Fe (200-480 mg/kg), Zn (100-240 mg/kg), Cr (7-150 mg/kg) and Cu (1-100 mg/kg) and Ni (20-80mg/kg)reported Soils of the farmland with clay texture and dark reddish brown color, is an indicative of the presence of excess amount of hematite, Fe_2O_3. Thus, Fe is the predominant metal within the concentration range of 200-480 mg/kg in these soils. Also when we compare the concentration of iron in the three samples, the sample collected from Zeway contains small amount of iron than samples collected from Sebeta and Holeta.

The level of pb, Cd, Co and Hg are the other tested toxic metal in the studied soils. However, in all samples they were found to be below the method detection limit and which was in agreement with the reported value [35].

4.6. Statistical analysis

4.6.1 Analysis of variance

T-tests and analysis of variance (ANOVA) are widely used statistical methods to compare group means. While the independent sample t-test is limited to comparing the means of two groups, while the one-way ANOVA can compare the mean of more than two groups of sample. ANOVA use the F statistic to compare whether the difference between samples means are significant or not [36].

If the calculated value of F (the ratio of SD between samples to SD within samples) is greater than the value obtained from the table at specified confidence level and degree of freedom, the differences in sample means are significant. In this study, soil samples were collected from three different areas and the metal level of each sample was analyzed by MP-AES. During the processes of sample preparation and analysis a number of random errors may be introduced in each aliquot and in each replicate measurement. The variation in sample mean of the analyte was tested by using ANOVA, whether the source for variation was from experimental procedure or heterogeneity among the samples.

Table 7. Analysis of variance (ANOVA) between soil samples at 95%confidence level.

metal	F_{cal}	F_{cri}	Remark
Fe	5.09	4.07	Significant difference between sample mean
Zn	5.89	4.07	Significant difference between sample mean
cu	8.32	4.07	Significant difference between sample mean
Cr	4.93	4.07	Significant difference between sample mean
Ni	3.14	4.07	Almost no significant difference between sample mean

5. CONCLUSION AND RECOMMENDATIONS

The present study revealed that open beaker digestion was a reliable method for quantitative determination of heavy metals in the soil samples. The metals such as Cd, Cr, Hg Co, Fe, Zn, Cu and Ni were analyzed by using MP- AES in the soil samples around the flower garden in Zeway, Sebeta and Menagesha in Ethiopia. To gain a better understanding of how soils might be used and yet protected in waste management efforts, soil scientists must devote a fair share of their research effort to environmental quality problems. Also the concentration of the metals in the areas were almost comparable with the literature value indicates the factories gave much attention for the disposal of their wastes and the soils around the factories not much polluted with heavy metals.

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