HAWASSA UNIVERSITY
COLLEGE OF NATURAL AND COMPUTATIONAL SCIENCE
DEPARTEMENT OF CHEMISTRY

DETERMINATION OF SELECTED HEAVY METALS (Cu, Cr, Pb. Ni, Mn AND Co) IN SOIL SAMPLES AROUND MIDROC GOLD MINING IN SHAKISO DISTRICT, GUJI ZONE, OROMIA REGION ETHIOPIA.

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JUNE 2025
HAWASSA, ETHIOPIA

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A MASTER THESIS SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES OF HAWASA UNIVERSITY, COLLEGE OF NATURAL AND COMPUTATIONAL SCIENCE DEPARTMENT OF CHEMISTRY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN CHEMISTRY.

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JUNE 2025
HAWASSA, ETHIOPIA

DECLARATION

I hereby declare that this MSc thesis is my original work and has not been presented for a degree in any other university, and all sources of material used for this thesis/dissertation have been duly acknowledged.

Name: ____________________________________

Signature: _________________________________

This MSc thesis has been submitted for examination with my approval as thesis advisor.

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This is to certify that the thesis entitled **“Determination of selected heavy metals (Pb ,Cu, Cr, Co, Mn and Ni) in soil samples around MIDROC Gold mining in Shakiso district, Guji Zone, Oromia Region Ethiopia”** is prepared by Dejene Genene Ashenafi (PGChemk/006/11) under my/our supervision has been submitted for examination with my/our approval as university advisor.

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We, the undersigned, members of the Board of Examiners of the final open defense by Dejene Genene Ashenafi have read and evaluated his/her thesis entitled **“Determination of selected heavy metals (Pb, Cu, Cr, Co, Mn and Ni) in soil samples around MIDROC Gold mining in Shakiso district, Guji Zone, Oromia Region Ethiopia’’** and examined the candidate. This is, therefore, to certify that the thesis has been accepted in partial fulfillment of the requirements for the degree of Master of Science in Chemistry.

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DEDICATION

This thesis is dedicated to my beloved mother and father

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List of Abbreviations

AAS	Atomic Absorption Spectroscopy
ANOVA	Analysis of Variance
CL	Confidence Level
ES EPA	Environmental services and Environmental Protection Agency
FAO	Food and Agriculture Organization
MCL	Maximum Contamination Level
QA	Quality Assurance
QC	Quality Control
%R	Percentage of Recovery
%RSD	Percentage Relative Standard Deviation
R	Correlation coefficient
RL	Recommended Limit
SD	Standard Deviation
WHO	World Health Organization

Abstract

Soil supports all terrestrial life, and it is a medium in which nearly all food-producing crops grow. However, soil pollution, mainly due to anthropogenic origin, is a significant problem worldwide, affecting soil fertility, plant growth, and human health. Heavy metal contamination of soils is mostly due to mining and smelting of metal ores. Therefore, in this study, soil samples were taken from three sampling sites, such as Dadola, Reji, and Legedembi, around the MIDROC gold mining company to assess the levels of heavy metal contamination of the sampling sites. The soils samples (0 to 15 cm deep) were collected from across 9 sites within three selected areas by using stainless steel applying a random sampling technique. After proper samples pre-treatment of dried, crushed and homogenized, known weight of Soils sample was wet digested using 3:2mL of HNO_3*, of* $HClO_4$ *for 2:00 hr at 250* ^oC *and Soil samples were prepared through an optimized wet digestion procedure is a material to ensure safety and accurany., and the concentrations of the selected heavy metals (Cu, Cr, Co, Pb, Mn, and Ni) were determined by using FAAS. All these heavy metals statically analyzed by using one way ANOVA are significantly difference* ($p<0.05$)*.*

The average concentrations of the heavy metals were found to be in the range of Cu (161.5–312) mg/kg, Cr (127–276.66) mg/kg, Mn (446.27–644.44) mg/kg, Pb (52–77) mg/kg, Ni (25.5–42.83) mg/kg, and Co (13.18–18) mg/kg. The levels of the heavy metals in the soil samples were found in the decreasing order Mn > Cu > Cr > Pb > Ni > Co, and the concentrations of Cu, Cr, Pb, and Mn were above the WHO-recommended limits. This result showed the sampling sites were polluted with heavy metals, and this could affect soil quality, the environment, and human health. Therefore, the concerned bodies should take necessary measures to reduce the effect of soil pollution from MIDROC gold mining companies in the host community.

Keywords*: Soil pollution, Heavy metal, Shakiso, Guji Zone, MIDROC gold mining*

1. Introduction

1.1. Background of the study

Soil is the thin, porous layer of material consisting of both organic and inorganic components that covers the rocky surface of the Earth [1]. The organic part, which comes from the decomposition of plant and animal remains, is concentrated in the dark topsoil. The inorganic part of rock fragments was created over millennia by the physical and chemical weathering of bedrock [2]. Soil is created on the earth's surface through the processes of mechanical, chemical, and biological weathering and contains mineral components such as sand, clay, and silt, as well as organic matter, microorganisms, gases, and water [3, 4]. These components play a crucial role in soil fertility and directly affect plant growth and the health of the surrounding ecosystem [5].

Soil supports all terrestrial life. It is involved in the regulation and provision of many key ecosystem services that are essential to the environment and to human health and well-being. Soil is the foundation of the agri-food system and the medium in which nearly all food-producing crops grow—about 95% of the food we eat comes from the soil [5]. Soil also provides building materials, fuel, and fiber. They are the basis for human infrastructure. Therefore, soil plays a crucial role in sustainable economic and social development, impacting both human health and the construction process. However, soil pollution, the contamination of soil by harmful substances, has emerged as a significant environmental threat that poses serious threats to human and ecosystem health [6]. Soils are crucial in providing numerous ecosystem services essential for sustaining life on Earth. However, the alarming reality is that we have been witnessing a rapid loss of the quality of soils and the invaluable benefits they offer.

The primary source of soil contaminants is of anthropogenic origin. Both organic and inorganic pollutants can enter the soil matrix through various pathways, including the application of fertilizers and pesticides, improper disposal of wastewater, pharmaceuticals, plastics, and the burning of fossil fuels, and industrial activities, particularly the mining and smelting of metal ores [6]. Furthermore, toxic substances such as heavy metals and metalloids are also the main threats to healthy soil. Common heavy metals associated with soil pollution include lead (Pb), cadmium (Cd), mercury (Hg), arsenic (As), chromium (Cr), nickel (Ni), antimony (Sb), zinc (Zn), selenium (Se), beryllium (Be), thallium (Tl), and copper (Cu). Some of these metals are essential micronutrients for microorganisms, plants, and animals in low concentrations, but at high concentrations, all these heavy metals have strong toxic effects and pose an environmental threat [7] and can accumulate in the soil, adversely affecting plant growth and causing harm to organisms in the soil and the food chain even at low concentrations.

Industrial activities have been major contributors to soil pollution over the past century [1]. Particularly, mining and manufacturing industries contribute significantly to soil contamination through the discharge of hazardous chemicals, heavy metals, and toxic substances [8]. This is because most industries depend on extracting minerals from the earth [1]. As a result, the mining and smelting of metal ores have significantly contributed to the surge in heavy metal contamination on the Earth's surface. This issue is recognized as a substantial global environmental problem [9]. Particularly, soils in the vicinity of mining sites are highly impacted, and this contamination often extends to other components of the environment, including surface and groundwater sources, the air, and agricultural crops [10].

Gold mining activity plays a great role in enhancing the livelihoods of the host communities in different parts of the world [11]. However, gold mining tends to have huge negative impacts on the environment because of the nature and quantities of chemicals used in processing gold that lead to a huge amount of toxic waste and pits and tailings. It also produces noise pollution, which is caused by blasting and the movement of large vehicles [12]. The environmental impacts of gold mining are particularly severe because of the chemical processes often used to extract gold. At the present time, the cyanide leaching technique is used in extracting gold. This process is particularly damaging to the environment, infringes the principle of sustainable development, consumes large quantities of water and energy, contributes to global warming, emits hydrogen cyanide, and creates a morass of hazardous waste [12].

Ethiopia is rich in gold deposits, which are found in the north, south, and west parts of the country. Ethiopia has been producing gold since the late 1930s as a state-owned gold mine and the MIDROC PLC gold company [11]. These mining corporations, as well as illegal miners, have been producing gold without regard to environmental sustainability. As a result, the Guji zone, particularly the Shakiso district, is facing several environmental challenges, such as soil erosion, land degradation, and contamination of water due to a lack of environmental policies and responsibility related to mining activity [11]. Therefore, the primary objective of the study is to determine the concentration of selected heavy metals (Cr, Pb, Mn, Ni, Cu, and Co) present in the soil across various MIDROC Gold mining sites in the Shakiso district, encompassing the Legedembi, Reji, and Dadola areas.

1.2. Statement of the problem

Gold mining activities are associated with a potential risk of environmental pollution and human health. In Oromia Regional State, Ethiopia, the Shakiso district and its surrounding areas, including Dadola, Legedembi, and Reji, are major centers for gold mining due to abundant deposits existence of MIDROC Gold mining factory. In these areas, both legal and illegal gold mining activities have been ongoing for several years. These activities have the potential to release toxic heavy metals into the surrounding soil, leading to soil, water, and air contamination, which potentially affect the health of the local population. The lack of comprehensive data on the levels of heavy metals in soil surrounding gold mining operations hinders effective environmental management and and policy-making, Therefore, this study seeks to fill this gap by providing a detailed analysis of the concentration of Cu, Cr, Co, Pb, Mn, and Ni in soil samples collected from the Dadola, Reji, and Legedembi sites around the MIDROC gold mine in the Shakiso district, Guji zone, Oromia region, Ethiopia.

1.3. Objectives of the study

1.3.1. General objectives of the study

The main objective of this study was to determine the concentration of selected heavy metals (Cr, Pb, Mn, Ni, Cu, and Co) in soil samples taken from the Legedembi, Reji, and Dadola sites around the MIDROC Gold mining factory using flame atomic absorption spectroscopy (FAAS).

1.3.2. Specific objectives of the study

- To investigate the concentration of heavy metals (Cr, Pb, Mn, Ni, Cu and Co) in soil sample taken from Legedembi, Reji and Dadola sites.
- To compare the concentration of heavy metals among the three selected sites.
- To compare the concentration of heavy metals (Cr, Pb, Mn, Ni, Cu and Co) with the WHO and ESEPA permissible limits.

1.4. Significance of the study

The study was conducted to determine the levels of selected heavy metals assessed in three selected sites around MIDROC gold mining in the Shakiso district, Guji zone, Oromia region, Ethiopia. This study would provide background information regarding the levels of heavy metal contamination in the study sites, which in turn would provide information the concerned bodies to protect the environment and take necessary actions for the well-being of the host community.

1.5. Scope of the study

This study aims to determine the level of selected heavy metals (Cr, Pb, Mn, Ni, Cu, and Co) in soil around the MIDROC Gold mining area in the Shakiso district in the Guji Zone, Oromia Regional State, Ethiopia. The study focused on the determination of the selected heavy metals in soil samples taken from the three sites, Dadola, Reji, and Legedembi, around the MIDROC Gold mining area in the Shakiso district. These sites were selected due to their proximity to active gold mining operations that might contaminate the surrounding soil with toxic heavy metals. Furthermore, MIDROC Gold Mining Company is one of the biggest gold mining companies actively producing gold in the Shakiso district, Guji zone, Oromia Regional State, Ethiopia. As a result, the company covers a large area for gold extraction that could have a huge impact on the surrounding environment and human health.

2. Literature review

2.1. Heavy metals

Heavy metals, naturally occurring elements found in the Earth's crust, can be referred to as any metallic element that has a relatively high density and is toxic or poisonous even at low concentrations [13]. Therefore, heavy metals are chemical elements with a specific gravity that is at least five times the specific gravity of water. The specific gravity of water is 1 at 4°C. Heavy metals can also refer to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations [14]. The most commonly found heavy metals at contaminated sites are lead, chromium, arsenic, zinc, cadmium, copper, mercury, and nickel [15].

Heavy metals have become concerning due to heightened human activities such as industrial processes, mining, agriculture, and urbanization [16]. These activities contribute to heavy metal pollution through various pathways, including emissions, effluents, and improper waste disposal, with common heavy metals such as lead, mercury, cadmium, chromium, and arsenic being associated [17].

Soils may become contaminated by the accumulation of heavy metals and metalloids through emissions from the rapidly expanding industrial areas, mine tailings, disposal of high-metal wastes, leaded gasoline and paints, land application of fertilizers, animal manures, sewage sludge, pesticides, wastewater irrigation, coal combustion residues, spillage of petrochemicals, and atmospheric deposition [18]. Therefore, soils are the major sink for heavy metals released into the environment by aforementioned anthropogenic activities, and unlike organic contaminants, which are oxidized to carbon (IV) oxide by microbial action, most metals do not undergo microbial or chemical degradation [19], and their total concentration in soils persists for a long time after their introduction [20]. Changes in their chemical forms (speciation) and bioavailability are, however, possible. The presence of toxic metals in soil can severely inhibit the biodegradation of organic contaminants [21]. Heavy metal contamination of soil may pose risks and hazards to humans and the ecosystem through direct ingestion or contact with contaminated soil, the food chain (soil-plant-human or soil-plant-animal-human), drinking of contaminated groundwater, reduction in food quality (safety and marketability) via phytotoxicity, reduction in land usability for agricultural production causing food insecurity, and land tenure problems [22].

2.2. Sources of heavy metal contamination in soil

Heavy metals occur naturally in the soil environment from the pedogenetic processes of weathering of parent materials at levels that are regarded as trace (<1000 mg/kg) and rarely toxic [23, 24]. Due to the disturbance and acceleration of nature's slowly occurring geochemical cycle of metals by man, most soils of rural and urban environments may accumulate one or more of the heavy metals above defined background values high enough to cause risks to human health, plants, animals, ecosystems, or other media [25]. The heavy metals essentially become contaminants in the soil environments because (i) their rates of generation via manmade cycles are more rapid relative to natural ones, (ii) they become transferred from mines to random environmental locations where higher potentials of direct exposure occur, (iii) the concentrations of the metals in discarded products are relatively high compared to those in the receiving environment, and (iv) the chemical form (species) in which a metal is found in the receiving environmental system may render it more bioavailable [25]. Heavy metals in the soil from anthropogenic sources are often more mobile and bioavailable compared to pedogenic and lithogenic sources. Mobility refers to the ability of metals to move through the soil matrix, while bioavailability indicates the extent to which metals can be absorbed by living organisms [26]. Metal-bearing solids at contaminated sites can originate from a wide variety of anthropogenic sources in the form of metal mine tailings, disposal of high-metal wastes in improperly protected landfills, leaded gasoline and lead-based paints, land application of fertilizer, animal manures, biosolids (sewage sludge), compost, pesticides, coal combustion residues, petrochemicals, and atmospheric deposition [27, 28]. picture of the source of high toxicity heavy metals contamination are shown in below (see figure 1).

Figure 1. The source of heavy metals contamination.

2.2.1. Fertilizers

Fertilizers are substances that are applied to soils or plants to supply essential nutrients that promote growth and enhance agricultural productivity. The primary nutrients typically included in fertilizers are nitrogen (N), phosphorus (P), and potassium (K), often referred to as NPK. These macronutrients play critical roles in plant metabolism, influencing processes such as photosynthesis, energy transfer, and nutrient uptake [29]. In addition to macronutrients, fertilizers may also contain secondary nutrients, such as calcium, magnesium, and sulfur, as well as micronutrients like iron, manganese, and zinc, which are vital for various physiological functions in plants [30].

The classification of fertilizers can be broadly divided into two categories: organic and inorganic. Organic fertilizers are derived from natural sources, such as animal manure, compost, and plant residues, and they often improve soil structure and microbial activity [31]. In contrast, inorganic fertilizers are synthetically manufactured and typically provide nutrients in a readily available form for plant uptake. While inorganic fertilizers can lead to rapid improvements in crop yield, their excessive use has raised concerns regarding environmental sustainability, soil health, and water quality [32].

The application of fertilizers is guided by soil nutrient status, crop requirements, and environmental considerations. Soil testing is a critical step in determining the nutrient needs of crops and preventing over-fertilization, which can lead to nutrient runoff and subsequent eutrophication of water bodies [33]. Moreover, the timing and method of fertilizer application are essential factors that influence nutrient efficiency and minimize environmental impacts [29].The picture urine of fertilizer is shown below (see figure 2).

Figure 2.The urine of fertilizers.

2.2.2. Wastewater

Wastewater can be classified into several categories, including domestic, industrial, and agricultural wastewater. Domestic wastewater, often referred to as sewage, originates from households and includes water from toilets, sinks, and showers. Industrial wastewater is generated from manufacturing processes and may contain a variety of pollutants, including heavy metals, organic compounds, and chemicals [34]. Agricultural wastewater arises from agricultural activities, particularly from runoff containing fertilizers and pesticides [35]. The improper management of wastewater can lead to severe environmental and health consequences. Contaminated water bodies can result in the proliferation of waterborne diseases, loss of biodiversity, and degradation of aquatic habitats [36]. Furthermore, untreated wastewater can contribute to soil degradation and affect agricultural productivity. Farmers generally are not bothered about environmental benefits or hazards and are primarily interested in maximizing their yields and profits. Although the metal concentrations in wastewater effluents are usually relatively low, long-term irrigation of land with such can eventually result in heavy metal accumulation in the soil. The pictures of waste water area are shown below (see figure 3).

Figure 3.picture of waste water

2.2.3. Metal Mining and Milling Processes and Industrial Wastes

Metal mining and milling are critical components of the global economy, providing essential materials for various industries. However, these processes generate significant industrial waste, which poses environmental and health risks. Metal mining encompasses several stages, including exploration, extraction, and processing, each contributing to environmental degradation [37]. The milling process, which involves crushing and grinding ore to liberate valuable minerals, further exacerbates waste generation [38]. Industrial wastes from metal mining can be categorized into several types, including tailings, waste rock, and smelting by-products. Tailings, the residual materials left after the extraction of valuable minerals, are particularly concerning due to their potential to contaminate soil and water [39]. Waste rock, which consists of non-valuable material removed during mining, can also lead to landscape disruption and erosion [40].

2.3. Pathway of heavy metal contamination in gold mining company

Gold mining is a lucrative industry that has been a significant contributor to the global economy for centuries [41]. Mining, mineral processing, and metallurgical extraction are the three principal activities of gold mining industries that produce wastes. Mineral processing, also known as beneficiation, aims to physically separate and concentrate the ore mineral(s) using physical, chemical, and sometimes microbiological techniques. Metallurgical extraction breaks the crystallographic bonds in the ore mineral in order to recover the desired element or compound [42]. Large quantities of waste are produced during this activity. Particularly in gold mines, which release over 99% of extracted ore as waste to the environment [44].

One of the primary pathways of heavy metal contamination in a gold mining company is through the discharge of mine tailings. Mine tailings are the waste materials left over after the extraction of gold from the ore, and they often contain high concentrations of heavy metals [44]. These tailings are typically stored in tailing dams or ponds, where they can leach heavy metals into the surrounding soil and water [45]. Therefore, tailings are the major wastes produced from gold extraction, and they contain high amounts of heavy metals. These metals leach out in an uncontrolled manner into surrounding environments on exposure to water or through dispersal by wind. The presence of elevated concentrations of heavy metals in the environment is a serious health issue worldwide due to their non-degradative nature, which makes them persistent and thereby exerts long-term effects on the ecosystem [46]. Another pathway of heavy metal contamination in a gold mining company is the use of chemicals used to dissolve gold from the ore. Cyanide is commonly used to dissolve gold from the ore, but it can also mobilize other heavy metals present in the ore, leading to their release into the environment [47, 48]. Furthermore, the transportation and storage of chemicals used in the gold mining process can also contribute to heavy metal contamination. Spills or leaks of these chemicals can result in the release of heavy metals into the environment, contaminating soil, water, and air [49, 50]. It was found that improper handling and storage of chemicals at gold mining sites led to the contamination of nearby water sources with cadmium and lead, posing a risk to aquatic life and human health [49]. The picture of mining area are shown below (see figure 4).

Figure 4.picture of mining area

2.4. Human Health risk of heavy metals exposure

Heavy metal contamination poses a global concern with significant implications for both the environment and public health [51]. Metals such as lead, cadmium, mercury, arsenic, and chromium, although naturally occurring, enter ecosystems through industrial activities, mining operations, and agricultural practices [52, 53]. Released metals accumulate in soil, water, and food chains, posing serious health risks such as neurological disorders, organ damage, and cancer, underscoring the need for global intervention [54].Gold mining activities can introduce a range of environmental health hazards and risks to nearby communities [41]. Exposure to heavy metals like lead, mercury, cadmium, and arsenic is linked to neurological disorders, respiratory problems, cardiovascular diseases, and cancers and poses risks to ecosystems and biodiversity [55, 56]. These metals pose health risks through water contamination, with industrial activities and mining in Ethiopia notably contributing to pollution near mining sites. Furthermore, heavy metals can infiltrate soil and crops, contaminating food sources, especially in agricultural regions using contaminated water for irrigation [57]. Chronic heavy metal exposure is linked to neurological disorders, kidney damage, respiratory and cardiovascular issues, developmental delays, and cancers, especially for those near industrial or mining areas [56]. Children are particularly vulnerable due to their developing physiology and behaviors such as hand-to-mouth contact, potentially leading to developmental delays and cognitive impairments [58]. Heavy metal pollution also adversely affects ecosystems and wildlife, disrupting aquatic life and biodiversity [59]. These health impacts impose significant economic burdens on affected communities and healthcare systems, especially in low-resource settings.

2.5. Some selected heavy metals

2.5.1. Chromium

Chromium is the seventh most abundant element on earth [60]. It occurs in several oxidation states in the environment, ranging from Cr+2 to Cr+6. In the soil, the most commonly occurring forms of Cr are trivalent Cr + 3 and hexavalent Cr + 6, and both states are toxic to animals, humans, and plants [61]. Hexavalent chromium is thought to have 100-fold extra toxicity than trivalent chromium for each acute and persistent exposure, due to its excessive water solubility and mobility and easy reduction. The respiratory tract is the important target organ for hexavalent chromium after inhalation exposure in humans. It occurs naturally by the burning of oil and coal, petroleum from ferrochromate refractory material, pigment oxidants, catalysts, chromium steel, fertilizers, oil well drilling, and metal plating tanneries [14].

Exposure to chromium can lead to human health problems, cancer of the respiratory system, and skin irritation. Then also damage to the mucous membrane and liver and kidney damage [62]. Chronic human exposure to high concentrations of hexavalent chromium through inhalation or oral exposure may produce effects on the liver, kidney, gastrointestinal, and immune systems, and possibly the blood.

2.5.2. Lead

Naturally, lead is not found in its elemental form but is primarily extracted from ores. The most significant lead-bearing mineral is galena (PbS), which constitutes the primary source of lead in mining operations [63]. Other minerals containing lead include anglesite ($PbSO_4$) and cerussite ($PbCO_3$), which are secondary minerals formed through the weathering of [64]. Typical mean Pb concentration for surface soils worldwide averages 32 mg/kg and ranges from 10 to 67 mg/kg [65], but concentrations ranging between 80 mg/kg [66] and 510 mg/kg [67] have been reported in gold mine tailings. It occurs in the form of galena (PbS) in gold ore, and this form is found when the sulfide concentration of the ore is high [68].

Lead ranks fifth behind Fe, Cu, Al, and Zn in industrial production of metals. The most significant use of lead is in lead-acid batteries, which are widely employed in automotive and renewable energy applications. Other uses include solders, bearings, cable covers, ammunition, plumbing, pigments, and caulking [69]. Ionic lead, Pb (II), lead oxides and hydroxides, and lead metal oxyanion complexes are the general forms of Pb that are released into the soil, groundwater, and surface waters. Exposure to lead can result in a wide range of biological effects depending on the level and duration of exposure. However, the most serious source of exposure to soil lead is through direct ingestion (eating) of contaminated soil or dust [55].

Inhalation and ingestion are the two routes of exposure, and the effects from both are the same [55]. Pb accumulates in the body organs (i.e., brain), which may lead to poisoning (plumbism) or even death [55]. The gastrointestinal tract, kidneys, and central nervous system are also affected by the presence of lead. Children exposed to lead are at risk for impaired development, lower IQ, shortened attention span, hyperactivity, and mental deterioration, with children under the age of six being at a more substantial risk. Adults usually experience decreased reaction time, loss of memory, nausea, insomnia, anorexia, and weakness of the joints when exposed to lead [55].

In general, plants do not absorb or accumulate lead. However, in soils testing high in lead, it is possible for some lead to be taken up. Studies have shown that lead does not readily accumulate in the fruiting parts of vegetable and fruit crops (e.g., corn, beans, squash, tomatoes, strawberries, and apples). Higher concentrations are more likely to be found in leafy vegetables (e.g., lettuce) and on the surface of root crops (e.g., carrots). Since plants do not take up large quantities of soil lead, the lead levels in soil considered safe for plants will be much higher than soil lead levels where eating of soil is a concern (pica). Generally, it has been considered safe to use garden produce grown in soils with total lead levels less than 300 ppm. The risk of lead poisoning through the food chain increases as the soil lead level rises above this concentration. Even at soil levels above 300 ppm, most of the risk is from lead-contaminated soil or dust deposits on the plants rather than from uptake of lead by the plant [70].

2.5.3. Copper

Copper is an essential micronutrient required in the growth of both plants and animals. In humans, it helps in the production of blood hemoglobin. In plants, Cu is especially important in seed production, disease resistance, and regulation of water [62]. Copper is indeed essential, but acute exposure can lead to gastrointestinal distress, including nausea, vomiting, and abdominal pain. [69]

Copper is widely distributed in sulfides, arsenites, chlorides, and carbonates in gold ores. The mean concentration of 5 to 70 mg/kg exists in unpolluted soil, while higher concentrations are found in contaminated environments like mining sites [44]. Found a concentration of 92.17 mg/kg in gold mine tailings in Ghana [70]. Gold mining has greatly increased Cu concentration in the environment, which upon release binds to particles of organic matter, clay minerals, and sesquioxides, leading to great accumulation in the soil [71]. Copper exists in two states: oxidized state Cu (II) and reduced state Cu (I). The ability to exist in these two states makes this metal potentially toxic because the conversion between Cu (II) and Cu (I) could lead to a generation of superoxide and hydroxyl radicals [72]. Excessive Cu concentration has deleterious effects on soil microbes [73].

2.5.4. Nickel

Nickel is an element that occurs in the environment only at very low levels and is essential in small doses, but it can be dangerous when the maximum tolerable amounts are exceeded. This can cause various kinds of cancer on different sites within the bodies of animals, mainly those that live near refineries. The most common application of Ni is as an ingredient of steel and other metal products. The major sources of nickel contamination in the soil are metal plating industries, combustion of fossil fuels, and nickel mining and electroplating [74]. It is released into the air by power plants and trash incinerators and settles to the ground after undergoing precipitation reactions.

Nickel levels in soils greatly depend on the concentration of the parent rocks, and this concentration has been estimated to range from 3 to 100 mg/kg for world soils [75]. In gold mine tailings, a higher concentration of 583 mg/kg was found by Matshusa et al. [76] in South Africa. Bitala et al. [77] also reported concentrations as high as 11,200 mg/kg in Tanzania. Nickel exists in gold-bearing ore as pyrrhotite (Fe(1 - x)S), which can contain up to 5% Ni, and pentlandite (FeNi)S8. Other mineral sources are chalcopyrite ($CuFeS_2$) and gersdorffite (NiAsS). It exists in the 0 and +2 oxidation states and less often in the 1, +1, +3, and +4 oxidation states. Among its species, the +4 oxidation state is known to be more toxic and carcinogenic compared to +2 [78]. Nickel toxicity arises due to its tendency to substitute other metal ions in proteins or enzymes or attach to cellular compounds [79]. It also intermingles with no less than 13 essential elements in living organisms.

2.5.5. Manganese

Manganese in soils comes from natural sources such as weathering of manganese-containing minerals, volcanic eruption, atmospheric deposition, plant leaching, and anthropogenic sources like wastewater discharges from industrial activity and fossil fuel combustion [80]. Manganese is an essential micronutrient in most organisms that is required for the activity of a diverse set of enzymatic proteins (e.g., arginase and glutamine synthase) [81, 82]. It contributes to the structure of photosynthetic proteins and enzymes in plants. Thus, manganese plays two roles in plant metabolism: as an important micronutrient and, when present in excess, as a harmful element [83]. Manganese is essential for human health, supporting the brain and immune systems, enzyme cofactors, and regulating blood sugar levels [84].

2.5.6. Cobalt

Cobalt is a naturally occurring element that is primarily obtained from the mining of cobaltite, a cobalt-bearing mineral, and is often a byproduct of nickel and copper extraction [85]. Small amounts of cobalt are naturally found in most rocks, soil, water, plants, and animals, typically in small amounts. It is widely distributed naturally in rocks, soils, water, and vegetation (Nilsson et al. 1985), and always occurs in nature in association with nickel and usually with arsenic [86]. The most important cobalt minerals are smaltite ($CoAs_2$) and cobaltite (CoAsS); however, the chief technical sources of cobalt are residues called "speisses," which are obtained in the smelting of arsenical ores of nickel, copper, and lead [86].

Cobalt may enter the environment from both natural sources and human activities. Cobalt occurs naturally in small amounts in soil, rock, air, water, plants, and animals. The most frequent form of cobalt presence in the soil is Co^{2+} (ionic form), Co^{3+} (coordination compounds), as well as $CoOH^{+}$ and $Co(OH)_3^{-}$. Furthermore, the contamination of soil with cobalt has an effect on other trace elements in soil; e.g., it may increase the content of lead, chromium, nickel, and zinc in soil [86].

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, and as drying specialists for paints and inks [85]. Cobalt is an essential element, required for good health in animals and humans, and therefore, it is important that foodstuffs contain adequate quantities of cobalt. Cobalt is part of vitamin B12, which is essential to keep the body’s nervous system and red blood cells healthy [85].

The main causes of increasing the soil cobalt content include improper fertilizer management, the use of some pesticides, and inappropriately used sludge from municipal sewage treatment plants. The emission of cobalt compounds, mainly during the combustion of hard coal and petroleum, transferred to the soil environment during intensive precipitation. Furthermore, the extraction of different kinds of raw materials, particularly metallic, also leads to soil pollution with cobalt [87].

2.6. Quantitative Analysis of heavy Metals in Soil Sample

2.6.1. Atomic absorption spectrometry

Flame atomic absorption spectroscopy is very useful for the determination of a large number of elements, especially at trace levels. It is a widely used technique for the analysis of a wide variety of sample matrices, including biota, soils, and water.

Flame atomic absorption spectroscopy is a very reputable technique that is inexpensive and delivers accurate results even though this method determines a single element per analysis [88]. In FAAS, samples are vaporized at very high temperatures, and the concentrations of selected atoms are determined by measuring absorption at their characteristic wavelengths. This is typically accomplished by converting the sample into an atomic vapor by spraying a solution into a flame [88]. The amount of analyze present in the study sample is determined based on how much light is absorbed after passing through the flame [89]. Typical AAS spectrometer used in this study is shown in Figure.1

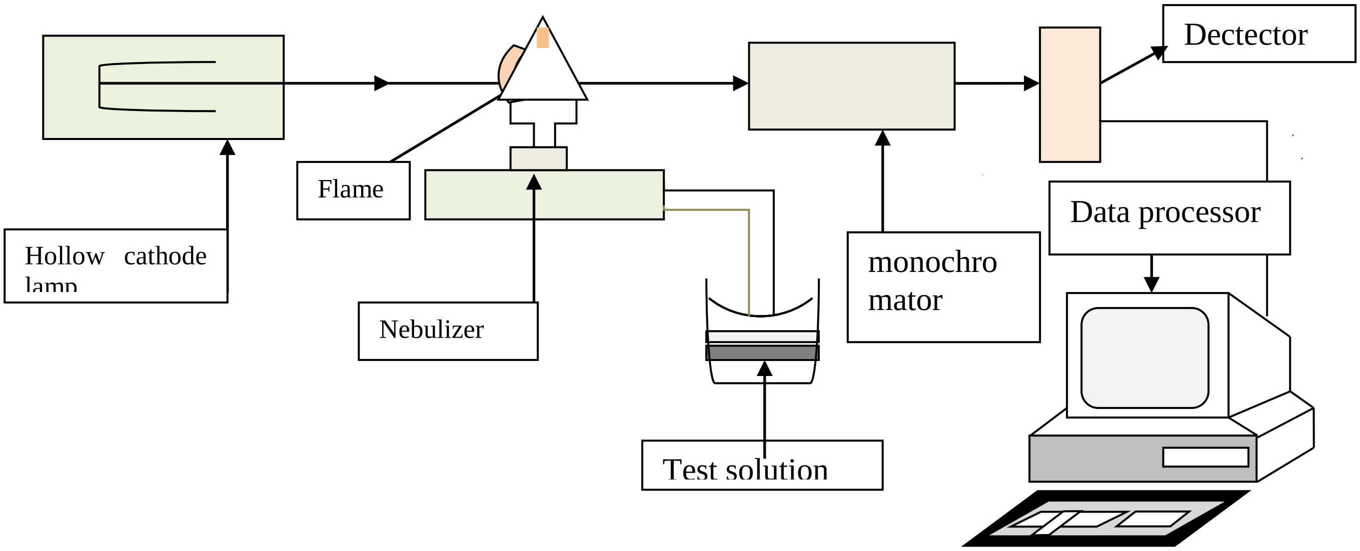

Figure 5.Schematic diagram of Atomic Absorption spectroscopy (AAS)

Solid samples have to be brought into solution before elemental analysis is performed using atomic spectroscopy techniques. This is because of the instrumentation requirements dedicated to the analysis of liquid samples [90]. Therefore, solid samples are converted into solution, and therefore dissolution of sample matrices prior to determination is a vital stage of analysis aimed at releasing analyses into simple chemical form [90]. The composition of solid sample matrices varies from purely inorganic (e.g., ash, rocks, metallurgical samples) and purely organic (e.g., fats) to mixed matrices (e.g., soils, sediments, plant and animal tissues). Dissolution of inorganic matrices leads to clear solutions, where analyses are in their ionic forms. Both purely organic and mixed matrices are more troublesome, and dissolution does not guarantee complete matrix decomposition. A method for total decomposition of organic samples includes dry ashing, wet digestion, and microwave digestion. In this way, the wet digestion method was used [91].

2.6.2. Wet Digestion

Wet acid digestion is one of the methods that are usually used to oxidize the organic part of samples or to extract elements from inorganic matrices. Compared to dry ashing, wet digestion presents a wide range of varieties concerning the choice of reagents as well as devices used. However, the sample's nature and its composition, as well as the composition and concentration of the reactive mixture, should be considered before analysis. It includes the strength of the acid, its oxidizing power and boiling point, the solubility of resulting salts, and the safety and purity of the reagent. In general, HNO_3, HCl, H_2SO_4, H_3PO_4, $HClO_4$, HF, and H_2O_2 are used for organic samples, alloys, minerals, soils, rocks, and silicates [90]. In this study wet digestion method using a mixture of HNO_4 and $HClO_4$ was used after the optimization experiment. The optimization of the digestion procedure was determined based on the usage of a smaller reagent volume, a shorter digestion time, and a reasonably mild temperature for obtaining clear and colorless solutions of the resulting digests [91, 92].

2.6.3. Optimization of digestion procedure soil samples

For each of the soil samples, 2.0 g of powder and homogenized sample was weighed and transferred to 250 mL of a round-bottom flask. Then different volumes of HNO_3 and $HClO_4$ at quantified proportions (v/v) were added and digested at different temperatures for different periods of time. The optimized procedure was determined based on the formation of a clear, colorless solution. The digested solution was allowed to cool, and 5 mL of distilled water was added to dissolve residue formed on cooling and gradually swirled and filtered into a 100 mL volumetric flask through Whatman No. 42 filter paper. Then the clear solution was diluted up to 100 mL in a volumetric flask with 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 heavy metal contents was made as shown in Appendix A.

3. Materials and method

3.1. Description of the study

The Shakiso district in the Guji Zone, Oromia Region State (Figure 2), is located at a latitude and longitude of 5°45′N, 38°55′E, respectively, and an elevation of 1758 meters above sea level [11]. MIDROC Lega Dambi Gold Mine plc, is located in the Oromia regional state, Guji Zone, Odo Shakiso district, about 470 km away from Addis Ababa, the capital city of Ethiopia, in the south direction. Based on the Central Statistical Agency (CSA, 2017), Shakiso has an estimated total population of 259,641; specifically, 134,523 are males and 125,118 are females. The climate of the district was characterized by an equatorial type with two rainfall characteristics: February to July is a rainy month, while September to December is a dry month [11]. The temperature of the district is high, with records showing significant seasonal and daily variations in all respects. The annual temperature ranges between 26 and 29 °C, and the rainfall ranges from 500 mm to 1250 mm [93]. Major socio-economic activities in the study area include mixed farming and large-scale and small-scale gold mining. Most of the population (90%) is engaged in farming activity, which provides their main source of livelihood. Crops grown in the districts are mostly cash crops and subsistence crops. Subsistence farming, such as vegetable and cash crop cultivation, is practiced in Shakiso Districts. Cash crop production mainly involved cultivation of the palm crop, coffee, and khat [11].

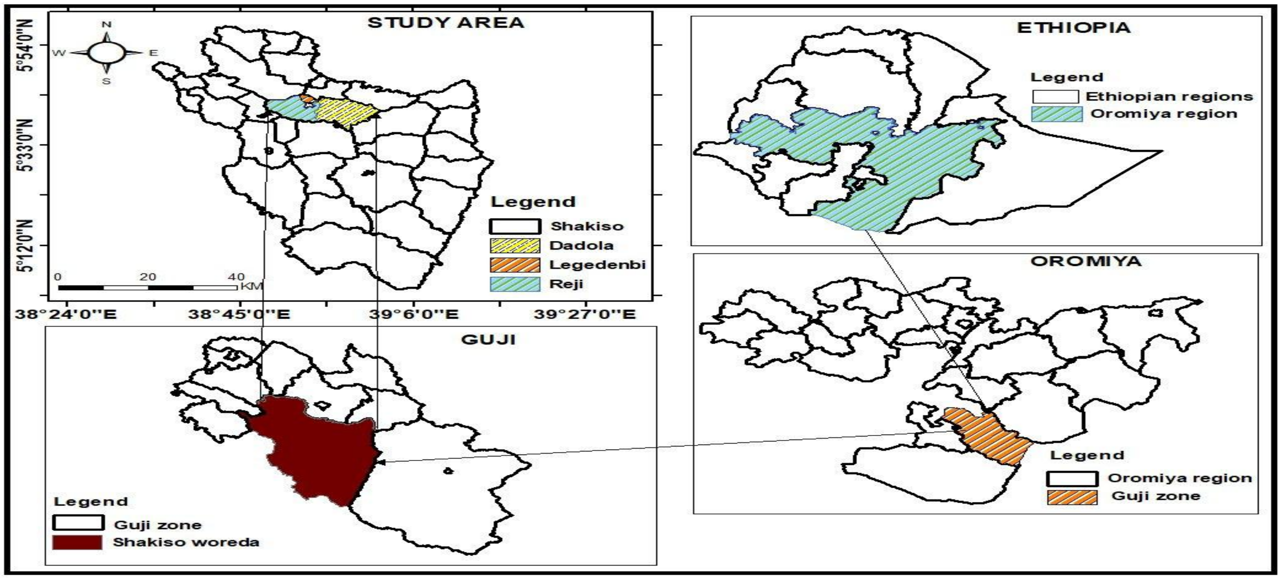

Figure 6. Location Map of the study area (source, finance and economic development office of guji zone)

3.2. Sample collection method and preparation

3.2.1. Sample collection method

In this study, soil samples were collected in the month of July 2024 E.C. from three sites, such as Legedembi, Dadola, and Reji. These sites were selected based on their proximity to the gold mining company. Three soil samples were collected from the topsoil at a depth of 0-15 cm at each sampling site using clean stainless steel by applying a random sampling technique. Then, after the three soil samples of each of the sites were mixed, homogenized, placed into clean polyethylene bags in triplicate, labeled (site 1, site 2, and site 3), and transported to Hawassa University, Department of Chemistry Laboratory, for sample preparation.

3.2.2. Sample preparation

In the laboratory, the samples were taken in clean plastic and then first dried in air in the direction of sunlight for one week to evaporate the moisture. Then, the soil samples were ground with a mortar and pestle and sieved through a 2 mm sieve to obtain the fine soil powder. A 2.0 g sieved soil sample was taken and digested, and finally the selected heavy metals were analyzed by Flame Atomic Absorption Spectrophotometer (FAAS).

3.3. Chemicals and apparatus

3.3.1. Chemicals

Nitric acid (68%) (Spectrosol®, BDH, England) and perchloric acid (38%) (Aldrich, A.C.S. Reagent, Germany) were used for soil sample digestion. Stock standard solution containing 1000 mg/L of metals. Mn, Ni, Cu, Cr, Pb, and Co were used to prepare 10 mg/L intermediate standard solutions, which were used for the preparation of calibration standard solutions for each metal.

3.3.2. Equipment and apparatus

In this study, a digital balance (ADAM, England) for weighing soil samples was used; a round-bottom flask fitted with a reflux condenser was used for digesting samples; measuring cylinders, pipettes, and micropipettes (Pyrex, USA) were used for measuring different volumes of sample solution, acid reagents, and metal standard solutions; and a flame atomic absorption spectrophotometer (FAAS) (Buck Scientific, model 210 VGP AAS, USA) equipped with a hollow cathode lamp background corrector and an air-acetylene flame atomizer was used for determination of the selected metals in the soil sample.

3.4. Digestion of Soil Sample

Using the optimized conditions (Appendix A), 2.0 g soil powder samples were weighed and transferred to 250 mL round-bottom flasks, and 10 mL of 3:2 ratios of HNO_3 and $HClO_4$ were added. Then the solution was digested on a reflux setup/closed digestion/apparatus at 250 °C for 2:00 hours of digestion time, and the digested solution was kept to cool at room temperature for about 25 min without disassembling the condenser. Digested solutions were allowed to cool, and 20 mL of distilled water was added to dissolve the residue formed on cooling and vigorously swirled and then filtered into a 100 mL volumetric flask through Whatman No. 42 filter paper. Finally, the clear solution was diluted by distilled water. This procedure was done three times for each soil sample. The digestion of the blank reagent was done simultaneously without the samples. All the solutions were stored in the refrigerator until the analysis was done. The solutions were used to determine the concentration of the selected heavy metals in the sample. Figure 3 shows the digestion of soil samples using the reflux condenser/closed setup apparatus.

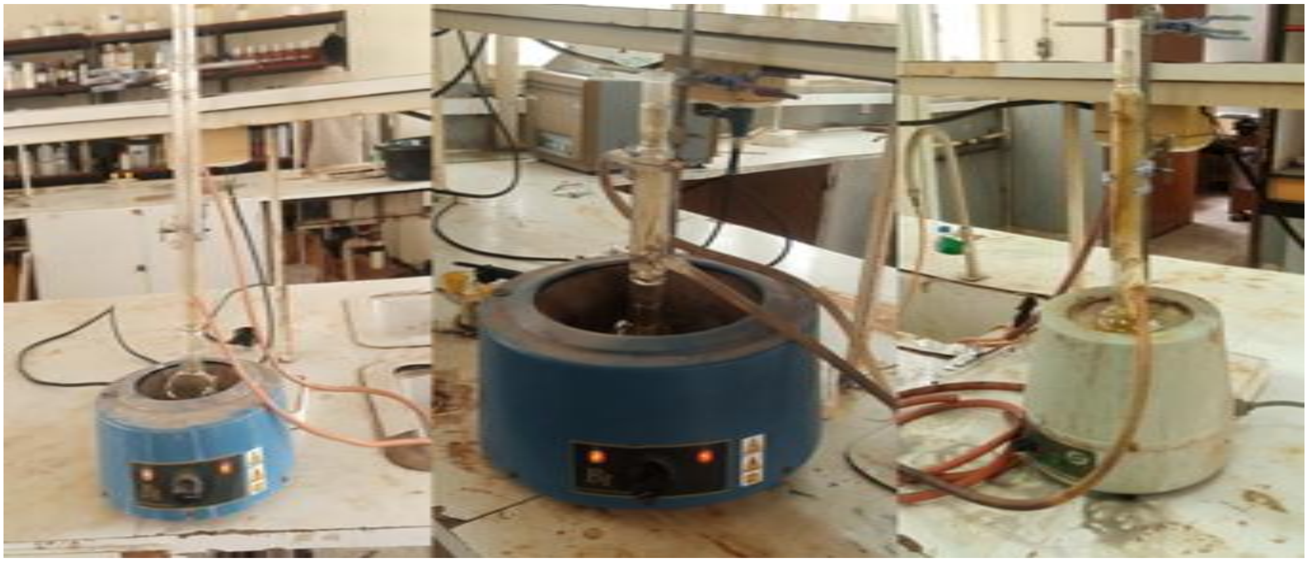

Figure 7.Schematic diagram of Atomic Absorption spectroscopy (AAS)

3.5. Instrumental operating conditions and calibration

3.5.1. Instrumental operating conditions

The analyses of heavy metals in soil samples were carried out by flame atomic absorption spectrometry after parameters such as lamp alignment, slit width, and wavelength adjustment were optimized for maximum signal intensity for each metal. The operating conditions for Cr, Cu, Pb, Ni, Mn, and Co analysis by FAAS were indicated in Table 3.1.

Table 3.1. FAAS Instrumental operating conditions

Elements	Wave length λ in (nm)	Slit width in (nm)	Current in (mA)	Flame, oxidant and fuel type
Cr	357.9	0.7	2.0	Air-acetylene
Cu	324.7	0.7	1.5	Air-acetylene
Pb	283.3	1.2	2.0	Air-acetylene
Ni	341.5	0.2	3.0	Air-acetylene
Mn	279.5	0.7	3.0	Air-acetylene
Co	240.7	0.7	4.5	Air-acetylene

3.5.2. Instrumental calibration

Calibration of the instrument for each metal analyzed was carried out with four standard solutions. The concentrations of the standard solutions used for each metal are shown in Table 3.2. Then, the absorbance of the standard solutions was measured, and the calibration curves for each of the analyzed metals were constructed, and the calibration graph for each metal was shown in Appendix B.

Table 3.2: Concentrations of working standards for each metal analysed using FAAS

Elements	Concentration (ppm)	Elements	Concentration (ppm)
Cr	2, 1, 0.5, 0.05	Mn	1, 0.5, 0.1, 0.05
Cu	2, 1.5, 0.5, 0.08	Co	2, 1, 0.5, 0.06
Pb	1, 0.5, 0.25, 0.09	Ni	1, 0.5, 0.1, 0.06

3.6. Heavy metal analysis

After calibration, the samples were aspirated into the FAAS instrument, and the metal concentrations were read off directly. Then, the final concentrations of the metals in the soil samples were calculated using the following formula.

$$\text{Concentration (mg/kg)} = \frac{\text{Concentration of AAS reading (mg/L)} \times \text{V (L)}}{\text{Weight of sample (kg)}}$$

Where, V = Final volume (100 mL) of solution & W= Initial weight (2.0 g) of soil sample measured.

3.7. Method detection limit (MDL)

The method detection limits for each metal were estimated using blank digests for selected soil samples. Each blank solution was run with FAAS for the level of the metal in a similar manner as the samples, and triplicate readings were recorded. Then, the standard deviations of the blank concentrations were calculated and used to calculate the method detection limit as follows [94].

MDL=3×Standard deviation of the blank

3.8. Recovery test

The digestion method and AAS analysis were validated by measuring the recovery of Cr, Cu, Pb, Ni, Mn, and Co spiked into soil samples. The known volume and concentration of standard solutions were employed on the samples in order to determine recovery. 0.05 mg/L of Cr, Mn, Pb, Cu, Co, and Ni were spiked at once to 2.0 g of powdered soil sample. The spiked samples were then digested in the same way as the soil samples. The final volume of the digestion was diluted to 100 mL and run on AAS, and metal contents were determined from the calibration curve. The amount of spiked metals recovered after the digestion of spiked samples was used to calculate percentage recovery using the formula [95].

$$\%\ \text{Recovery} = \frac{\text{CM (in the spiked sample)} - \text{CM (in the non−spiked sample)}\ \text{x}100\ \%}{\text{CM added for spiking}}$$

Where: C_M is concentration of heavy metals.

3.9. Statically analysis

Statistical analysis of data was carried out using the SPSS 16.0 statistical package program. One-way ANOVA (analysis of variance) was performed for statistically significant differences in the mean value of heavy metal concentrations between the three sampling sites. Differences in mean values were accepted as being statistically significant if $P < 0.05$.

4. Result and discussion

4.1. Regression equation

Calibration curves were constructed by first preparing a set of standard solutions with known concentrations of the selected heavy metals. The instrument response is measured for each and plotted vs. the concentration of the standard solution. The correlation coefficients (R²) for the calibration curves for all the selected metals analyzed were greater than or equal to 0.999, which assured the linearity of instrumental response for individual metals, or these correlation coefficients showed that there was a very good correlation (linear relationship) between concentration and absorbance. The equation of the graph and its R² value for each metal are shown in Table 4.1. The calibration graphs for the selected metal analyzed are shown in Appendix B.

Table 4.1: Calibration graph equation and R² value

Metal	Calibration Equation	R^2 Value
Cr	$y = 0.0075x + 0.0003$	0.9998
Cu	$y = 0.0305x + 0.0028$	0.9999
Pb	$y = 0.0277x - 0.0003$	0.9997
Ni	$y = 0.0285x + 0.0012$	0.9998
Mn	$y = 0.1127x - 0.0008$	0.9997
Co	$y = 0.0691x + 0.0035$	0.9998

4.2. Method of validation

The method detection limit values for each element analyzed in soil samples are shown in Table 3. These values were above the detection limit of the instrument.

Table 3: Method detection limit for the elements determined in soil samples

Element	Cr	Cu	Pb	Ni	Mn	Co
IDL mg/L	0.04	0.005	0.08	0.05	0.03	0.05
MDL mg/L	0.05	0.008	0.09	0.07	0.05	0.06

The method detection limits estimated indicated that if the concentration of the respective element is at least equal to the detection limit, it can be detected but not quantified.

4.3. Results of the Recovery Experiment

The recovery experiment was carried out using a selected soil sample (Legedembi). The results of the % recovery experiment for the elements found in the soil sample were shown in Table 4.3.

Table 4.3: Recovery test results (mean ± SD, n=3, mg/kg) for the analysed elements in soil sample collected from Legedembi site

Metal	Conc. of unspiked sample (mg/kg)	Amount added (mg/kg)	Conc. Spiked sample (mg/kg)	Recovery (%)
Cu	314.65 ± 3.5	0.5	315.17 ±2.3	104
Cr	280.7 ± 2.21	0.5	281.21 ±6.2	102
Co	14.4 ± 0.1	0.5	14.9 ±0.4	100
Mn	450.85 ± 3.4	0.5	451.39 ±3.5	108
Pb	82.5 ± 0.7	0.5	82.99 ±0.3	98
Ni	33.55 ± 1.1	0.5	34.1 ± 1.0	110

The % recovery values for all the analyzed elements lie within the range of 98% to 110.0%, which is in the acceptable range (80–120%) [96], which suggests that the experimental procedures and the method of analysis were accurate and valid.

4.4. Concentration of metals in Soil samples

The concentration of six heavy metals—Cu, Cr, Co, Mn, Pb, and Ni—was analyzed in the digested soil samples by using flame atomic absorption spectroscopy. The concentrations of the heavy metals are shown in Table 4.4

Table 4.4. Average concentration (mean ± SD, n=9, mg/kg) and relative standard deviation (%RSD) of heavy metals in each soil sample

Metals	Dadola (mg/kg)	%RSD	Reji conc. (mg/kg)	%RSD	Legedembi (mg/kg)	%RSD	FAO /WHO/ (2019) [97]	ES EPA (2020) [98]
Cu	207.6±2.9	3.895	161.5±3.4	2.1	314.65 ± 3.5	1.19	100	1000
Cr	174.17±1.18	6.79	127±6.71	5.29	280.7 ± 2.21	2.01	150	100
Co	18±1.04	5.78	17±0.89	5.26	14.4 ± 0.1	0.98	25	50
Mn	644.4±2.04	3.16	592.72±2.14	3.61	450.85 ± 3.4	7.57	500	500
Pb	60.33±3.28	5.43	52±0.833	1.60	82.5 ± 0.7	0.857	50	400
Ni	25.5±1.54	6.07	42.83±2.22	5.181	33.55 ± 1.1	3.16	50	100

The result shown in Table 4.4 indicates that the mean concentration of Cu, Cr, and Pb was determined in soil samples collected from Legedembi to be greater than both the Dadola and Reji gold mining sites, while the mean concentration of Mn and Co analyzed from samples collected from the Dadola site is higher than both the the Legedembi and Reji sites. And the mean concentration of Ni in soil samples collected from Reji is greater than both Legedembi and Dadola sites. Comparing the selected metals' concentration in general, the highest content in the soil is manganese, and the lowest one of the metals' concentration is cobalt. The mean concentration of heavy metals in soils collected from all sampling sites decreased in the order of Mn > Cu > Cr > Ni > Pb > Co (Figure 4).

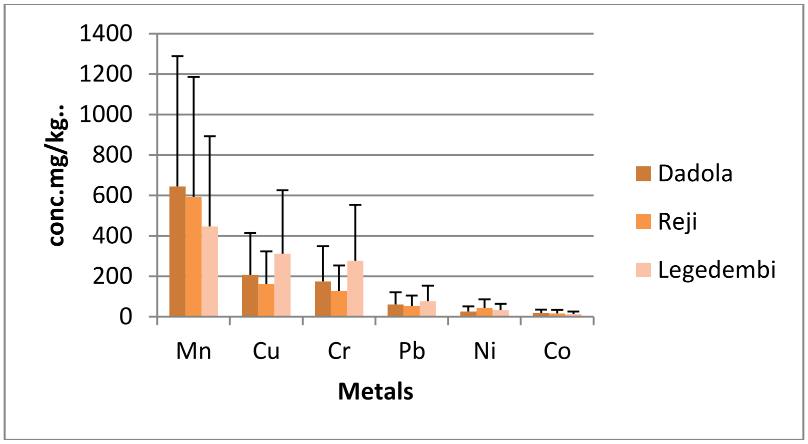

Figure 8.Comparison of the mean concentrations of heavy from the three soil sampling sites.

4.5. Statically Analysis of heavy metals (Cr Cu, Co, Mn, Pb, and Ni)

ANOVA analysis (Table 4.5) showed that the mean concentration of all the heavy metals analyzed was significantly different among the selected soil sampling sites at a 95% ($p < 0.05$) confidence level.

Table 4.5. Results of ANOVA analysis among the three soil sampling sites

Metals compared at 95% confidence level and their p-values Cr Cu, Co, Mn, Pb, and Ni						
soil sample R/D/L	Cr	Cu	Co	Mn	Pb	Ni
p-values	1×10^{-4}	1×10^{-4}	6×10^{-4}	1×10^{-4}	1×10^{-4}	1×10^{-4}
Result	significant difference	significant difference	significant difference	significant difference	significant difference	significant difference

The results of the heavy metals analyzed in the study areas showed that their concentration levels of chromium and manganese are above the standard guidelines for the maximum permissible limit of the ES EPA, and the concentrations of Mn, Pb, Ni, and Co are below the maximum permissible limit of the ES EPA. While the concentration levels of Ni and Co are below permitted limit values of the FAO/WHO, the concentration levels of Cu, Cr, Pb, and Mn are above permitted limit values of the FAO/WHO (Table 4.4), which could lead to negative effects on human health and the environment. The high concentrations of Cu, Cr, Pb, and Mn in soil from MIDROC gold mining sites are likely due to the use of cyanide acid and the leaching of these metals from the ore during the mining process. These metals can accumulate in the soil over time, leading to increased levels that exceed permissible limits. The presence of these metals in soil can have detrimental effects on plant growth, soil fertility, and groundwater quality. Through the consumption of contaminated food or water can lead to serious health issues, including neurological disorders, respiratory problems, and cancer.

5. Conclusion and Recommendation

5.1. Conclusion

Except for Ni and Co, high amounts of heavy metals such as Cu, Cr, Pb, and Mn were found in soil samples from all three sites, and the levels decrease in the order of Mn > Cu > Cr > Pb. The concentrations of these heavy metals were above the maximum recommended limits of the FAO/WHO. Gold mining factories are one of the main sources of toxic heavy metal contamination of soil. This result indicated that the selected soil sampling sites were contaminated with these heavy metals, and it poses a potential risk to the environment and causes adverse effects on plants, animals, and humans.

5.2. Recommendation

The investigation revealed the areas around the MIDROC Gold mining factory, particularly Legedembi, Reji, and Dadola, were highly contaminated with toxic heavy metals. Therefore, comprehensive corrective action should be taken to curb the existing soil pollution. Furthermore, host communities should be given awareness training regarding soil pollution to reduce the risk of exposure to heavy metal contamination and its associated environmental and health impacts.

The future researcher should be investigating further study of the remains metals that did not investigated in present study.

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Appendixes

Appendix A: Different trials tested during the optimization of digestion method for soil sample

Optimization for reagent volume						
Trial1	Weight of sample	Reagent	Reagent volume	Temp (°C)	Digestion Time (hr)	Observation
1	2g	HNO_3:$HCLO_4$	3:3	250	2:00	Color less and yellow precipitate
2	2g	HNO_3:$HCLO_4$	**3:2***	250	2:00	Color less and white precipitate
3	2g	HNO_3:$HCLO_4$	3:1	250	2:00	Color less and white precipitate
4	2g	HNO_3:$HCLO_4$	2:3	250	2:00	Color less and white precipitate
5	2g	HNO_3:$HCLO_4$	4:2	250	2:00	Color less and white precipitate

Optimization for time						
Trial1	Weight of sample	Reagent	Reagent volume	Temp (°C)	Digestion Time (hr)	Observation
1	2g	HNO_3:$HCLO_4$	3:2	250	**2:00***	yellowish 2
2	2g	HNO_3:$HCLO_4$	3:2	250	1:30	Color less and white precipitate
3	2g	HNO_3:$HCLO_4$	3:2	250	1:45	Color less and white precipitate
4	2g	HNO_3:$HCLO_4$	3:2	250	1:35	Color less and white precipitate
5	2g	HNO_3:$HCLO_4$	3:2	250	1:50	Color less and white precipitate

Optimization for temperature						
Trial1	Weight of sample	Reagent	Reagent volume	Temp (°C)	Digestion Time (hr)	Observation
1	2g	HNO_3:$HCLO_4$	3:2	240	2:00	yellowish 2

2	2g	HNO_3:$HCLO_4$	3:2	**250***	2:00	Light yellow
3	2g	HNO_3:$HCLO_4$	3:2	180	2:00	Color less and white precipitate
4	2g	HNO_3:$HCLO_4$	3:2	230	2:00	Color less and white precipitate
5	2g	HNO_3:$HCLO_4$	3:2	220	2:00	Color less and white precipitate

Appendix B: Figure of Callibration curve for metals of Cr, Cu, Co, Pb, Mn and Ni (absorbance versus concentration)

Figure.1.Calibration curve of Pb standard solution

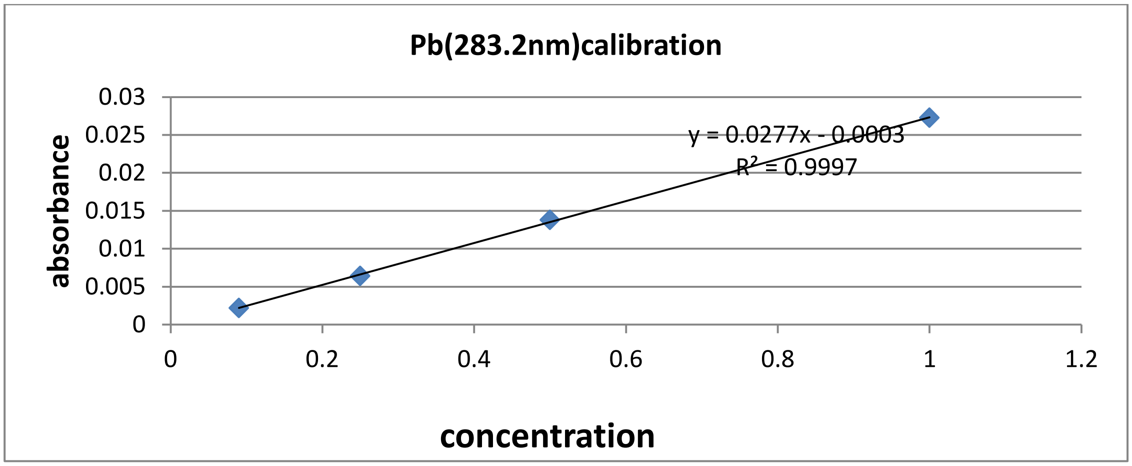

Figure.2.Calibration curve of Cr standard solution

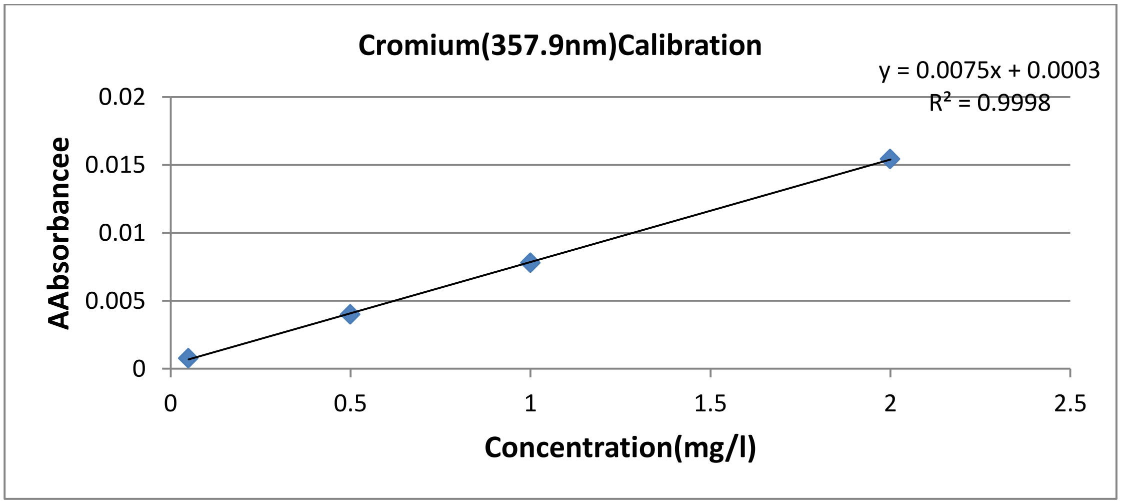

Figure.3.Calibration curve of Cu standard solution

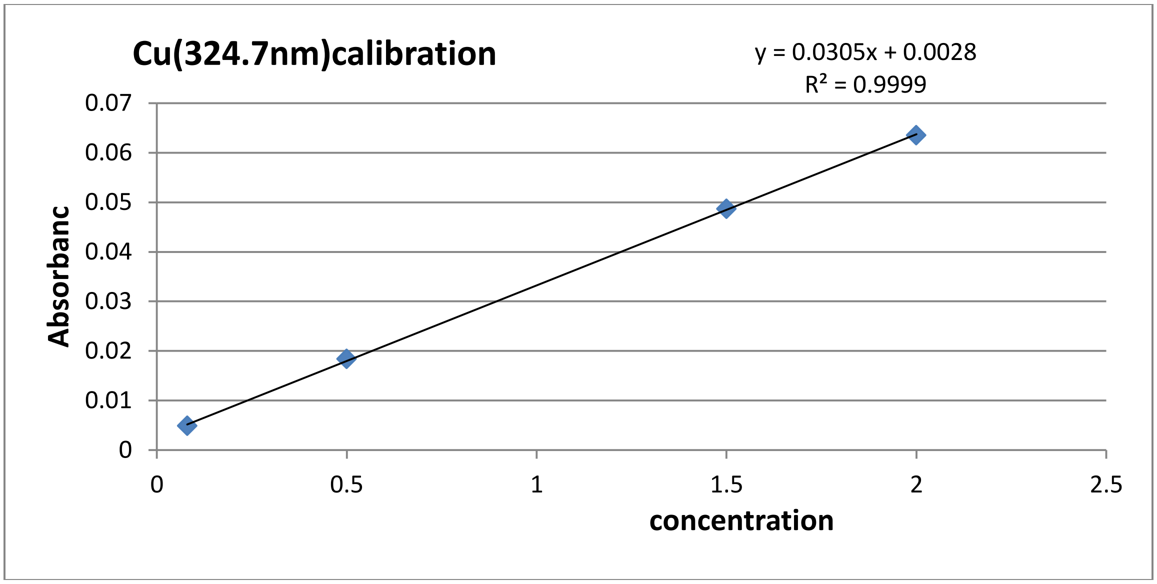

Figure.4.Calibration curve of Ni standard solution

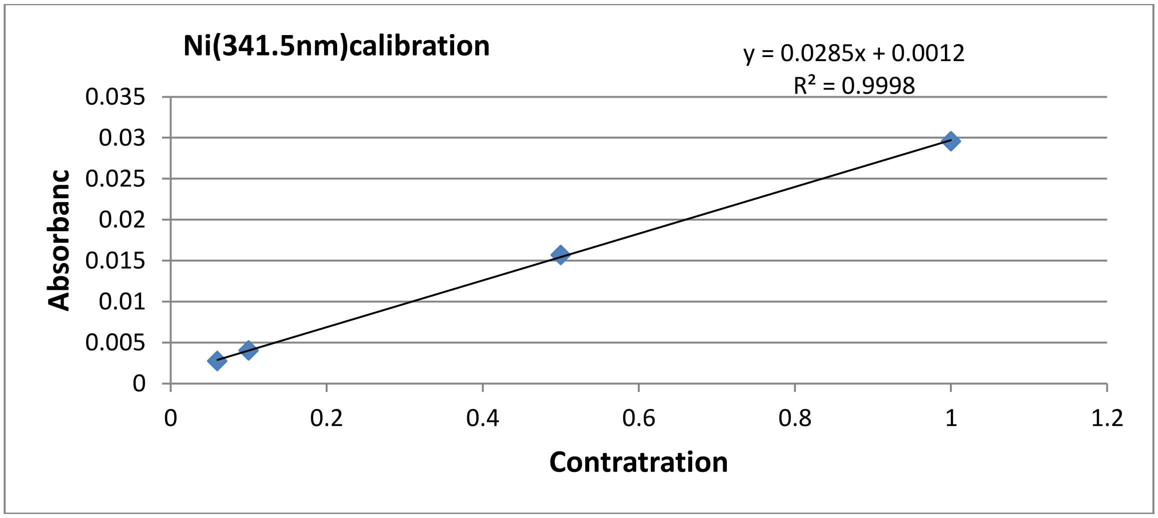

Figure.5.Calibration curve of Co standard solution

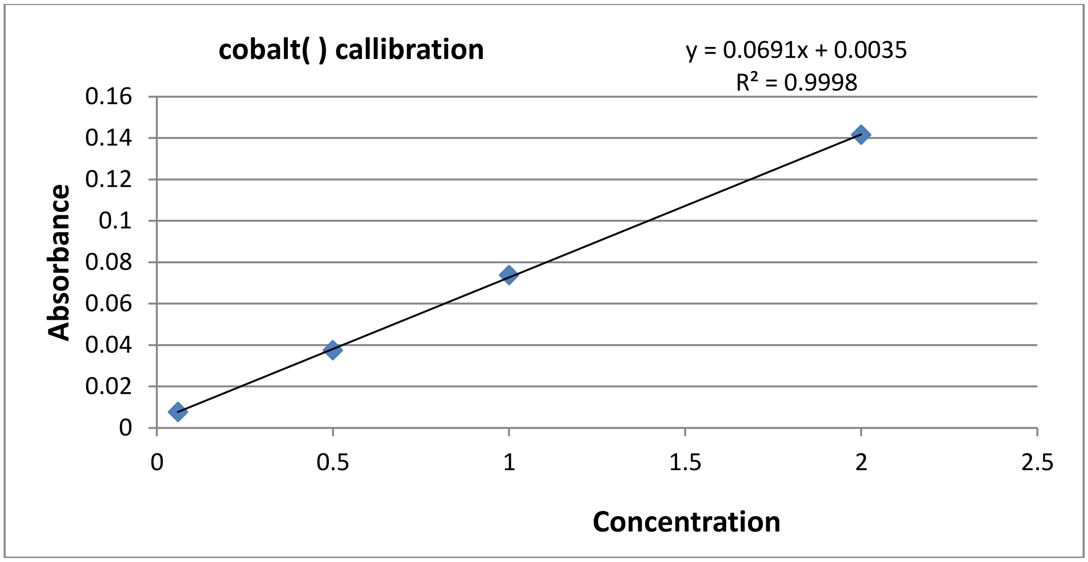

Figure.1.6.Callibration curve of Mn standard solution

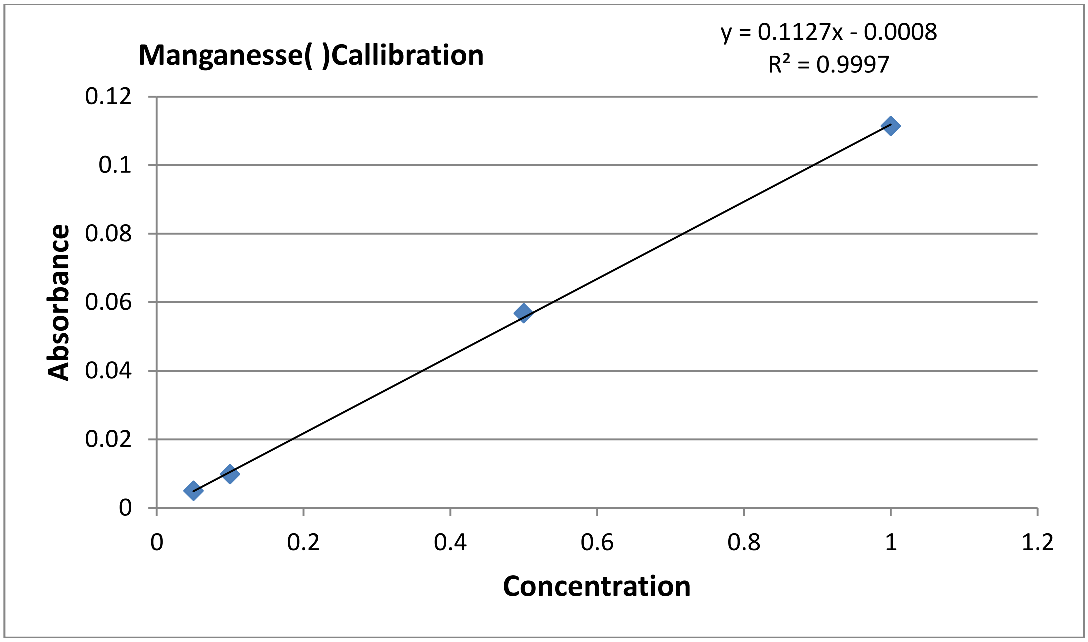

Figure.1.7.Callibration curve of Mn standard solution