DETERMINATION OF SELECTED HEAVY METALS IN SUGARCANE (*SACCHARUM OFFICINARUM L.*)ALONG WITH IT'S SOIL OF PLANTATION AND ASSOCIATED HEALTH RISKS IN SANKA IRRIGATION FARMLAND, NORTH WOLLO ETHIOPIA

By Tigabu Awraris Dejen

A Thesis Submitted to the department of chemistry School of Natural and Computational Science.

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

Office of Graduate Studies

Woldia Science and Technology University

February.2023

Woldia, Ethiopia

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Declaration

I hereby declare that this Master Thesis entitled "**Determination of Selected Heavy Metals in Sugarcane** (*Saccharum Officinarum L.*)**Along with its Soil of Plantation and Associated Health Risks in Sanka Irrigation Farmland, North Wollo Ethiopia"** is my original work. That is, it has not been submitted for the award of any academic degree, diploma, or certificate in any other university .All sources of materials that are used for this thesis have been duly acknowledged through citation

_____	_____	_____
Name of the student	Signature	Date

Recommendation

I, the advisor of this thesis, here by certify that I have read the revised version of the thesis entitled "**Determination of Selected Heavy Metals in Sugarcane** (*Saccharum Officinarum L.*)**Along with its Soil of Plantation and Associated Health Risks in Sanka Irrigation Farmland, North Wollo Ethiopia"** prepared under my guidance by Tigabu Awraris submitted in partial fulfillment of the requirements for the degree of Mater's of Science in Analytical chemistry. Therefore, I recommend the submission of a revised version of the thesis to the department following the applicable procedures.

_____	_____	_____
Major Advisor	Signature	Date

Approval Page

I,the advisor of the thesis entitled"**Determination of Selected Heavy Metals in Sugarcane** (*Saccharum Officinarum L.*)**Along with its Soil of Plantation and Associated Health Risks in Sanka Irrigation Farmland, North Wollo Ethiopia"**and developed by Tigabu Awraris, here by certify that the recommendation and suggestions made by the board of examiners are appropriately incorporated in to the final version of the thesis.

MajorAdvisor	Signature	Date

We,the undersigned ,members of the Board of Examiners of the thesis by Tigabu Awraris have read and evaluated the thesis entitled"**Determination of Selected Heavy Metals in Sugarcane** (*SaccharumOfficinarum L.*)**Along With its Soil of Plantation and Associated Health Risks in Sanka Irrigation Farmland, North Wollo Ethiopia**" and examined the candidate during the open defense. This is, therefore, to certify that the thesis is accepted for partial fulfillment of the requirement of the degree ofMaster of Science in Analytical Chemistry.

Chairperson	Signature	Date
InternalExaminer	Signature	Date
ExternalExaminer	Signature	Date

Final approval and acceptance of the thesis is contingent up on submission of its final copy to the Office of Postgraduate Studies (OPGS) through the Department Graduate Council (DGC)andFacultyGraduate Committee(SGC).

Head, Department	Signature	Date
Faculty Dean	Signature	Date
Office of Postgraduate Studies,Dean	Signature	Date

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II. CONTENTS

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V. ACRONYMS AND ABBREVIATION

ADD	Average Daily Dose
ABS	Skin Absorption Factor
AF	Adhesive Factor
ANOVA	Analysis of Variance
AT	Average Time
BW	Body Weight
CF	Conversion Factor
CSA	Central Statistical Agency of Ethiopia
ED	Exposure Duration
EF	Exposure Frequency
FAO	Food & Agricultural Organization
GPS	Global Positioning Satellite
HI	Hazard Index
HM_S	Heavy Metals
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
IngR	Ingestion Rate
InhR	Inhalation Rate
MDL	Method Detection Limit
MQL	Method Quantization Limit
PEF	Particular Emission Factor
RSD	Relative Standard Deviation
SD	Standard Deviation
SPSS	Statistical Package for Social Science.
THQ	Target Hazard Quotient
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

VI. ABSTRACT

Heavy metals (HMs) pollution is among the leading health concerns all over the world. Because of their long-term cumulative effects; Consumption of food crops contaminated with heavy metals is a major food chain route for human exposure. In this study, the levels of heavy metals (Fe,Pb,Cr, Zn,Co, Ni, and Cd) in soil and commonly consumed sugarcane from Sanka farmland in northern Ethiopia have been determined by using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).The mean concentration of metals in soil samples(mgkg^{-1})were Fe(22975±5.520),Pb(101±3.820*),Cr(129±4.160),Zn(120± 3.940),Co(3.750 ± 0.086) Ni (7.067± 0.104), Cd (14.740± 0.089), while that of sugarcane (mgL^{-1})were Fe (0.557 ±0.008) Pb (0.033 ±0.001),Cr(0.127±0.002),Zn (0.020 ±0.001),Co(0.036 ±0.002) Ni (0.026 ±0.004), Cd (0.022 ± 0.004). The transfer factors of heavy metals from soil to sugarcane were: 0.000, 0.013, 0.039, 0.006, 0.384, 0.147,and 0.059 for Fe, Pd, Cr, Zn, Co, Ni,and Cd respectively).Health Risk assessments of soil HMs to individuals exposed through non-dietary routes and consuming locally grown sugarcane (juice) were conducted. Results indicated that the ranking for risks of HM exposure was juice drinking > non-dietary oral intake > dermal contact > inhalation. For non-carcinogenic risks, Cr and Cd in sugarcane juice posed the most significant risks, whereas As and Pb posed the highest risks through non-dietary exposure routes. The cancer risks of Pb in sugarcane juice posed the most significant risks, whereas Ni posed the lowest risks through non-dietary exposure routes. The Target hazard quotient(THQs) of heavy metals by Oral (Fe > Cr >Pb> Zn > Co >Ni > Cd),Inhalation (Fe > Cr >Pd> Zn > Co > Cd > Ni), Derma (Fe> Cr>Pb> Zn > C> Ni> Cd) and Juice (Fe > Cr >Pb> Co > Cd > Ni) are determined but all heavy metals in the three non-dietary exposure routes and Juice were below unity(<1) and from the consumption of sugarcane juice and non-dietary exposure routes, Hazard Index of target metals were order as Cr>Cd>Fe>Zn>Pd>Ni>Co. The HI (the sum of individual metals THQ for each exposure route was found alarmingly less than unity (<1). So in this case there is no apparent health impact due to the metals considered. The study concluded that sugarcane grown on this farm is almost safe for human consumption in terms of the studied metals but, it is recommended that the level of heavy metals in the soil should be monitored to avoid unnecessary accumulation beyond the WHO safe limit.*

Keywords: Heavy Metals, Sugarcane, Soil, Transfer Factors, Health Risk Assessments

1. INTRODUCTION

1.1. Background of the Study

The interaction of heavy metals with the environment is an important issue in science. These elements are a collection of metals or metalloids that have large specific densities and are usual constituents of the earth's crust [1]. Even though heavy metals are abundant in the earth's crust they are usually found in trace quantities in plants and the human body [2]. Some of these metals are important for metabolic processes and organisms may show nutrient deficiency when these elements are at relatively low availability. On the other hand, heavy metals can be toxic if they are in excess amounts in the body while some are poisonous even in trace amounts[3].

The source of heavy metals in the human body is primary food. Human beings are exposed to heavy metals by inhalation, ingestion, and dermal contact absorption [4]. However, it is the ingestion of food contaminated with heavy metals that contributes upto 90% of exposure to toxic elements [5]. This is because there is a constant need to consume food crops since they are the source of essential nutrients. Some of the plants can absorb and retain heavy metals using parts that are exposed to air in a polluted environment or from contaminated soils. Therefore, it has generated numerous studies on harmful food contaminants such as heavy metals [6].

Soil is considered to be an important resource that provides a habitable environment and plays a major role in food production and is hence important in sustaining essential human needs. Consequently, any heavy metal contamination of this resource will result in the possible contamination of food crops. Indeed, high amounts of heavy metals in soils are resulting in increased concentrations of these elements in food crops. Elevated concentrations of heavy metals in soil can be attributed to both natural and anthropogenic causes [7]. The heavy metal contamination of food is a vital environmental problem that is increasingly becoming severe all over the world and particularly, in developing nations [8]. Due to increased population and high levels of poverty, developing countries are under pressure to industrialize. This has led to rapid urbanization with increased growth in the number of industries. Consequently, industrial waste with elevated amounts of heavy metals is mounting. Most developing countries have poor methods of waste disposal and therefore industrial effluent rich in toxic metals is dumped into rivers and landfills. As a result, crops cultivated in urbanareas are often found to contain heavy metals levels that are beyond the permitted amounts[6, 9].

It is the properties of heavy metals in the environment and their interaction with plants that make these elements interesting. These metals are non-biodegradable and tend to persist in the environment, and form soluble compounds. In addition, plants are inclined to bioaccumulate heavy metals whereby plants absorb and retain these elements over time. The concentrations of elements tend to increase through the food chain in a process known as bio-magnification. Human beings are usually at the tail end of the food chain and therefore at great risk of having unhealthy concentrations of heavy metals [10].

Urban agriculture is one of the activities that contribute significantly to heavy metal bioaccumulation and consequent bio magnification. It is often done in waste dump sites as a result of their organic matter deposits and plant nutrients. However, waste dump sites are poorly managed and are used to discard sewage and industrial wastes which have heavy metals, dangerous organic chemicals, salt, and high pH. Plants cultivated under these environments could absorb and retain high amounts of these metals.When crops or plants are consumed over a period they pose a health risk to human beings. generally,in addition to urbanization, improper waste disposal, and industrialization; fertilizers, pesticides, and herbicides are the main sources in the studding area [6].

Sugarcane is associated with the *Graminae* family and its genus is *Saccharin*. It exists three species: *Saccharumofficinarum, Saccharumspontaneum, and SaccharumRobustum* [11].It originates from tropical South and Southeast Asia. In the 7thcentury, the knowledge of growing sugarcane was transferred to China. Around the 8th century, sugarcane was introduced by the Arabs to Mesopotamia, Egypt, North Africa, and Spain, from where it was introduced to Central and South America. Christopher Columbus brought sugarcane to the Caribbean islands, today's Haiti, and the Dominican Republic. Driven by the interests of major European colonial powers, sugarcane production had a great influence on many tropical islands and colonies in the Caribbean, South America, and the Pacific [12]. In Ethiopia, there are two types of sugarcane, namely 'Tafach shenkora' and 'key shenkora' in Amharic which belongs to *the Saccharum spontaneum* species. In the studying area, only key shenkora (*Saccharum spontaneum)* is cultivated in a large coverage, that the researcher select sugarcane rather than the other crops (source; Teshome Ashagrie (PhD), expert for fruits and vegetable in Sirinka agricultural research center) [13].

Generally, agricultural products including sugarcane is a vital plant to human beings and in fact, is the top-ranking crop worldwide with a production of more than 1.59 billion tons annually. However, the plant has been shown to accumulate heavy metals in concentrations that are beyond permitted levels by the World Health Organization. This implies that prolonged consumption of contaminated sugarcane could be detrimental to human health [14].Thus, monitoring these pollutants in food and agricultural products and actions to eliminate them in source emissions is a major concern for health policymakers. However, as far as my survey, there is no study conducted for the determination of heavy metals in sugarcane and its plantation soil in Ethiopia. Therefore, the present study was focused on the determination of Iron(Fe), Lead(Pb), Chromium(Cr), Zinc(Zn), Cobalt(Co),Nickel(Ni),and Cadmium(Cd)in sugarcane and its underlining soil samples with their associated health risk assessment taken from Sanka irrigation farmland, North Wollo, Ethiopia.

1.2. Statement of the Problem

There is a great concern arising from food contamination from heavy metals. This is because more than 90% of human exposure to harmful heavy metals is through the ingestion of contaminated food. Foods are primarily contaminated by the cultivation of plants in polluted soil. Rapid and unorganized industrialization, the use of a large number of pesticides, herbicides, and both organic and inorganic fertilizers, and poor management of waste have resulted in large amounts of heavy metals in environments of developing countries, particularly in soils [15]. Thus, plants grown in these environments could absorb and retain high amounts of heavy metals. Sugarcane is among the most important grown in the world and therefore a concern that very few studies have paid attention to the number of heavy metals in sugarcane. Furthermore, the consumption of sugarcane grown in potentially polluted soil could lead to adverse health effects on human beings [16].

Although, several studies have shown that sugarcane is capable of absorbing and retaining heavy metals in significant amounts, most studies have ignored HMs determination in sugarcane which is [1,13]. Ethiopia is one of the developing countries that accompanies rapid urbanization and the use of a large amounts of pesticides, herbicides, and both organic and inorganic fertilizers which rich in heavy metals. Hence, the use of these chemicals to cultivate crops and sugarcane in the studding area might cause mental contamination and different health problems.

Besides, there was no adequate information on the heavy metals levels in sugar cane and its growing soil along Sanka farmland, where a large amount of sugarcane have been produced as compared to other areas found in North Wollo districts. Therefore, there is a need to study the heavy metal content in sugarcane and its underlying soil in the Sanka farmland, and their health risk assessments

1.3. Objectives of the Study

1.3.1. General Objective

- To determine the level of selected heavy metals in sugarcane along with its soil of plantation and their associated health risk assessment at Sanka irrigation Farmland, NorthWollo.

1.3.2. Specific Objectives:

- To determine levels of Fe, Pb, Cr, Zn, Co, Ni, and Cd in Sugarcane and its Soil of plantation.
- To evaluate the transfer factor of selected heavy metals from soil to sugarcane plant.
- To estimate the health risk of inhabitants due to agricultural soil via ingestion, inhalation and dermal contact exposure pathways
- To estimate the health risk of inhabitants due to sugarcane juice by ingestion rout
- To compare the concentration of heavy metals determined with the acceptable limits proposed by WHO/FAO

1.4. Significance of the Study

The analytical results from this study used as baseline data on the levels of selected heavy metals in sugarcane and its soil of plantations around Sanka irrigation farmland in North Wollo Ethiopia besides being an important assessment of environmental pollution in rural areas where different farming is predominant. Moreover, the outcome of this research work ultimately helps:

- As a baseline data for the health policymakers in Ethiopia on the daily intake of heavy metals consummations.
- To provide accurate and reliable information on the accumulation of heavy metals in sugarcane and its soil of plantation in the studding area
- To initiate further studies on nutritional, medicinal, and toxicological effects that can be caused due to the use of sugarcane through diet.

2. LITERATURE REVIEW

2.1. Heavy Metals

A metal of relatively high density (specific gravity greater than about 5) or 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 into 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 [17]. 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 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 [18].

2.2. Sources of heavy metals

Heavy metals may come from natural and anthropogenic processes and end up in various environmental compartments (soil, water, air, and their interface).

2.2.1. Natural sources

Various natural sources of HMs have been recorded in several studies. Natural emissions of HMs occur under numerous and certain environmental conditions. Volcanic eruptions, sea-salt sprays, forest fires, rock weathering, biogenic sources, and particles of wind-borne soil are included in these pollutants. The release of metals from their endemic spheres to different environmental compartments will lead to natural weathering processes. In the form of hydroxides, oxides, sulfides, sulfates, phosphates, silicates, and organic compounds, heavy metals can be found. Lead (Pb), nickel (Ni), chromium (Cr), cadmium (Cd), arsenic (As), mercury (Hg), selenium (Se), zinc (Zn), and copper (Cu) are the most popular heavy metals. While the above-mentioned heavy metals can be present in traces, humans and other mammals still cause significant health problems [19].

2.2.2. Anthropogenic sources

Industries, irrigation, drainage, mining, and metallurgical processes, as well as runoff, also contribute to the release of pollutants into various compartments of the ecosystem. For certain metals, anthropogenic heavy metal processes have been noted to go beyond natural fluxes. In wind-blown dust, metals naturally released are mainly from industrial areas. Car exhaust releases lead; smelting that releases arsenic, copper, and zinc; insecticides that release arsenic and burning [20].

2.3. Occurrence of Heavy Metals in Nature

Metals in the environment may be present in a 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 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 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 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 inthe state of metals and metal compounds, without actually having incorporated those metals, as in the case of some biologically mediated reactions [6].

2.4. Accumulation of Heavy Metals in Soils

Heavy metals' origins in soil are both natural (geogenic or pathogenic) and anthropogenic. They are constituents of the earth’s crust and therefore it is expected that soil will have a substantial amount of these elements. However human activities have also resulted in additional amounts of the elements in the environment. The fact that the metals in the environments could be attributed to these two sources has been illustrated by the high levels of Zn and Fe in Lakes Nakuru and Bogoria sediment. They concluded that an elevated Fe level was because of the volcanic activities in the area. Fe is the most plentiful metal in the earth's crust and so that observation was expected [15,20].

Heavy metals from geogenic sources are usually present in forms that have low availability to plants. The processes of sorption and desorption determine the availability of specific chemical species and their content in the soil [23]. This is determined by the interaction between metals and soil’s solid phase, water content, and constituent air which is comprised of four physicochemical processes: cation exchange, co-precipitation, specific adsorption, and organic–ligand complexation [24]. These processes are dependent on covalent bonding with the matrix of the soil, metal-anion exchange at the surface of the soil, and the creation of water-insoluble precipitates. The metals availability plant uptake is highly influenced by the elements’ solubility and mobility. It has been found that heavy metals in soils resulting from natural sources have relatively low mobility and hence low phytoavailability. Several surveys indicated that despite

the high levels of heavy metals in soil from natural sources, the elements had low mobility and a photo-availability that was below the threshold [25].

Anthropogenic activities are the main cause of the increase in metal levels in soils and accumulation in plants [26]. The accumulation of heavy metals in the plant is influenced largely by the bioavailability of the elements in the soil. The dynamic process of heavy metal bioavailability in the soil is dependent on a combination of biological, chemical, and environmental parameters. Metals resulting from anthropogenic sources have speciation that influences positively their bioavailability in soil [24, 25].

Soils play an important role in our society as it is the basis on which food crops are grown. However, it is also the sink for most heavy metals. Heavy metals are not subject to chemical or biological degradation and therefore heavy metal pollution of soil poses a long-term environmental problem with serious health implications for human beings and animals. Moreover, contaminated soil is the primary route of heavy metal exposure to human beings. It has been suggested that soil ingestion is the main source of Pb in children's blood [26–29].

Although heavy metals do not degrade, the chemical conditions in the soil determine the fate and transport of the metals from the source [24]. The chemical form of a metal element in soil controls its availability, non-availability, and bioaccumulation in soils and plants. Several factors influence the chemical form of an element in soil: parent materials, soil organic matter, crop residues, soil pH, and solubility, presence of other metals, fertilizers, and the type and amount of clay. These factors create chemical characteristics of the soil that determines the solubility and mobility of the metals. For instance, the pH of the soil and organic constituent influences significantly mobility of metals in soils [30–32].

Activities such as industrialization, urbanization, agriculture, and mining are among the main causes of elevated amounts of heavy metals. Mining and application of wastewater or sludge have been singled out as the leading sources of heavy metal pollution of soil.It is projected that approximately 240, 0.5, 310, and 250 million tonnes of Pb, Cd, Cu, and Zn respectively, have ended up in the soil as a result of mining activities. The notably elevated values were attributed to the increasing anthropogenic activities [35].

2.5. Accumulation of Heavy Metals in Sugarcane

The importance of sugarcane (*Saccharum officinarum*) cannot be underestimated. It is the highest-ranking crop worldwide with a yearly production of over 1.59 billion tonnes. It is the main raw material for the production of sucrose, molasses, and bioethanol. Despite its obvious usefulness, it is therefore a concern that very few studies have concentrated on the number of heavy metals in sugarcane. The plant and its products are consumed by billions of people and hence the lack of enough information on the heavy metal accumulation by the plant could adversely affect human health [25].

Several studies have found that sugarcane can uptake and retain heavy metals in significant amounts. For instance, a study in Nigeria reported sugarcane could bioaccumulate heavy metals and therefore pose a health risk to humans by biomagnification of the elements through the food chain study found out that even though the concentrations of Pb and Cd were not detected (below the detection limit of AAS) in irrigation water, the elements were detected in sugarcane juice extracted from plants farmed in the same area (0.16 - 0.42 mg/l for Pb and 0.01 - 0.02 mg/l). These amounts were beyond the permitted levels of World Health Organization standards for drinking water (0.05 mg/l for Pb and 0.01 mg/l for Cd). They also found a significant correlation (95% confidence limit) between the two elements which suggested a common source of the pollutants.in Zimbabwe also reported that amounts of Zn and Cu in sugarcane stalks were beyond the permitted levels by European Union (50 mg/kg for Zn) and United Kingdom (20 mg/kg for Cu) guidelines [13,36].

It has been reported that amounts of heavy metals in soil influence the amounts of these elements in sugarcane. There was survey also reported that the concentration of Cu (29.45 ± 2.03 21mg/kg), Pb (12.09 ± 1.27 mg/kg), Cr (4.21 ± 1.20 mg/kg), and Ni (6.19 ± 1.42 mg/kg) in sugarcane stems were above the permitted limits by Food and Agriculture Organisation/World Health Organisation. They singled out Cu contamination and attributed it to the large amounts of Cu in the soils (219 ± 25.34 mg/kg) from copper mines. Aresearcher found out that sugarcane cultivated in a reclaimed Mn mine had Pb (1.3 mg/kg) and Cd (0.19 mg/kg) levels in their edible parts that were beyond the safety limits and thus not safe for human consumption. This was attributed to large amounts of the two elements in the soil. A report in Nigeria showed an increase in the concentrations of Cu ($p<0.05$), Ni ($p<0.05$), and Zn ($p<0.01$) in soil with the amount in the sugarcane juice[1]. They, however, could not find correlations for Se and Cr which

was an indication that heavy metal amounts in the soil were not the only factor determining levels in the plant. The other factors include the type of soil, plant species, and other elements in the soil. There was a strong correlation between the metal levels in irrigation water and the concentrations of heavy metals in two varieties of sugarcane juice (r = 0.9848 and 0.7570). There was also a strong association between the metal concentrations in juice with those in topsoil (r = 0.5677). The study concluded that indiscriminate farming of sugarcane along riverbeds, on which untreated industrial effluents and heavy domestic waste were dumped, was a serious health risk [9].

Some sugarcane varieties have been observed to have relatively lower abilities to uptake and retain heavy metal in their biomass. Finding work on a selection of cane varieties reported that a sugarcane variety had comparatively lower heavy metal accumulation in contrast to six other varieties in the study. They also found that there was no significant correlation between the concentration of heavy metal in sugar cane juice and soil's heavy metal concentration. They suggested that the level of heavy metals in the cane's juice is influenced by the relative ability of the cane to enrich the metals. This finding was similar to another finding who reported that there was a correlation between total heavy metal concentration in soil and subsequent heavy metal levels in juice. The highest correlation coefficient (r2) observed was for Cu (0.19) [17,37].On the other hand, sugarcane has been thought of as an alternative plant for phytoremediation, a plant-based method to remove heavy metals from polluted soils. A suitable plant species suited for phytoremediation should be an efficient accumulator of the metal, produce high biomass, and is tolerant to heavy metal concentration in soil. Sugarcane is an outstanding biomass producer and is known to be tolerant to heavy metals. In an investigation by one survey soil was induced with Cu (60–125 mg/kg), Zn (150–300 mg/kg), and Pb (500–1000 mg/kg). Despite very high extractable metal concentrations and heavy metal contents greater than the concentration threshold, sugarcane root biomass increased ($p < 0.01$).). Another report also showed that sugarcane is an outstanding Cd accumulator and also tolerant to high amounts of Cd. They demonstrated that the sugarcane could tolerate 500 μM Cd whereas most convection plants are affected by amounts below 20 μM.The plant also showed Cd accumulation in its shoot tissues to 451 mg/kg. They also reported that sugarcane could accumulate a significant amount of Cu (45 mg/kg) even though it is not highly tolerant to the metal. Some studies have shown uneven distributions of various metal elements between the various parts of the sugarcane[14,18]. Zhang

found out that the distribution of heavy metal in the sugarcane stem was irregular. The top part of the cane had a higher Zn concentration ($p < 0.001$) in the juice while higher amounts of Pb, Sn, and Cu were found to be in the juice from the bottom parts. The retention of most metals in the lower parts is due to the because of heavy metal bindings to negatively charged walls and extracellular precipitation. Furthermore, transfer factors show most heavy metals were retained mainly in the roots. The soils to root transfer factors for Cu, Mn, Pb, and Zn were 0.25, 1.28, 0.93, and 0.67 respectively as compared to the soil-to-stem transfer factors which were 0.23, 1.03, 0.79, and 0.64 respectively. They further noted that amounts of these elements in comestible parts of sugar cane were about 80% to 90% of the amounts detected in the root [17].

2.6. Behavior of Heavy Metals in the Environment

Atmospheric deposition is the primary source of metal input to plants and soils. Trace metals like Cu, Pb, and Zn are carried in particulate phases, but volatile metalloids like As, Hg, Se, and Sb can be transported over long distances in gaseous forms or enriched in particles. Freshwater systems are contaminated by runoff and drainage via sediments or disposal, while groundwater is impacted by leaching or transport via mobile colloids. Soils are the primary recipient of metal contaminants in terrestrial ecosystems, while sediments are the primary sink for metals in aquatic systems. Many biogeochemical processes take place in the heterogeneous interface of rock, soil, water, air, and living beings. Via these interactions or processes, the toxicity, bioavailability, solubility, and mobility are in turn controlled.[38]

In the heterogeneous interface of rock, soil, water, air, and living things, several biogeochemical activities take occur. The solubility, mobility, bioavailability, and toxicity of metals are in turn governed by these processes or interactions. In soil solutions, metals can be found as free ions or complexed with inorganic or organic ligands. Both the metal-ligand complexes and the die-free ions can be I absorbed 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 like soils. Metals like Hg, Se, Sn, as, and Cr can be changed by microorganisms through oxidation-reduction, methylation (the process of replacing an atom, typically a H atom, with a methyl group), and di-methylation processes. These procedures have an impact on the solubility, mobility, and transport of metals. For instance, methylated (organic) forms of mercury

are more poisonous than the element's inorganic forms, and they bio-accumulate in living things. Environments with low oxygen content, a low pH, and high soil organic matter (SOM) contents support methylation. Metals like Hg, Se, Sn, As, and Cr can be changed by microorganisms through oxidation-reduction, methylation (the process of replacing an atom, typically a H atom, with a methyl group), and di-methylation processes. These procedures have an impact on the solubility, mobility, and transport of metals. For instance, methylated (organic) forms of mercury are more poisonous than the element's inorganic forms, and they bio-accumulate in living things. Environments with low oxygen content, a low pH, and high soil organic matter (SOM) contents support methylation [39].

By eroding the soil particles to which they are attached or adsorbed and re-depositing them elsewhere, heavy metals can also be translocated across the ecosystem very quickly. The physicochemical forms that heavy metals take in water, sediments, and soil have a significant impact on their transit, cycle, fate, bioavailability, and toxicity. A heavy metal or its compound is subjected to a range of physical, chemical, and biological processes whenever it is introduced into an aquatic environment. As a result of these activities, heavy metals frequently alter chemically, which has an impact on their distribution, bioavailability, and other interactions in the environment. Natural ore deposits and other sources, such as the disposal of garbage containing heavy metals, can cause them to seep into biological systems [40].

2.7. Heavy Metals and Their Harmful Nature to Human Health

Heavy metals have developed an interest in the scientific community as a result of their toxic effects on human beings. Heavy metals are those elements whose interactions with biological systems are determined by their Lewis acid and ionic indices properties. This narrows down to most of the transitional elements, rare earth elements, and some p-group elements that are either metals or metalloids [1]. Plants constantly uptake heavy metals and concentrations within the organisms could buildup to levels larger than those in the environment [1,38]. Since the toxicity of any material to a living system is dependent on the amount of that substance in the cells of the organism, these metals are not always considered toxic [10]. Some heavy metals, at trace levels, are essential. However, the metals are non-biodegradable and tend to have an extended biological half-life hence prolonged consumption of food crops with risky levels of heavy metals can result in a chronic accumulation of these elements in the kidney and liver of

human beings, thereby triggering disruptions of many biochemical processes. Therefore numerous studies have been done on heavy metals and their accumulation in food crops. [6, 38]Some heavy metal species have been singled out because of their toxicity even in trace amounts. Among the most common heavy metals are Pb, Cr, Ni, and Cd. Pb and Cd can accumulate in crucial organs of humans and their half-life could reach 30 years. Excessive exposure to Pb is associated with damage to the skeletal, enzymatic, circulatory, endocrine, nervous, and immune systems. Cd has been linked with lung cancer, hypertension, kidney dysfunction, and bone fractures among other complications. Pb and Cd are also known to cause teratogenesis and mutagenesis. Furthermore, hexavalent chromium is regarded to be carcinogenic to human beings by the International Agency for Research on Cancer and the United States Environment Protection Agency while Ni is associated with emphysema, asthma, chronic bronchitis, and cancer of the lungs [2,38].

Even though some metal elements are considered essential, they are harmful to human health when present in elevated amounts. Zn and Cu are needed for biochemical and physiological functions to maintain health. Their deficiencies lead to immunological defects and various abnormalities. Cu is a constituent of several enzymes and hence contributes to collagen synthesis and is also important to the formation of nerves, connective tissues, and the immune system. Zn plays a vital role in the well-functioning of biological systems such as the transport of proteins, enzyme structure and functions, hormonal activities, and specific receptor locations. However, the excessive concentration of Cu and Zn in food and feedstuff is known to have toxic effects on human beings and animals. Cu is known to irritate the mouth, nose, and eyes and also dizziness, headaches, stomach aches, and severe gastrointestinal problems. It is also associated with liver damage when in excess, while high amounts of Zn can lead to a reduction of immune faction and levels of high-density lipoproteins. Other essential elements, Iron and Manganese, have been associated with Parkinson’s disease, malfunction of the immune system, and infertility in mammals [29, 37–39].

Iron Iron is the fourth most abundant element in earth's crust (after oxygen, silicon, and aluminum). The mean iron content of soil, sediment, and rocks is about 5%. Most of the iron in soils is present as iron oxides; the typical soil colors (brown, red, yellow) are partly due to various iron oxides differing in their physical/chemical properties and their color. Iron,

aluminum, and manganese oxide soil minerals are important sinks for heavy metals in soil and residual-amended soils [43]. Iron can occur in either the divalent (Fe^{+2}) or trivalent (Fe^{+3}) states. Iron occurs predominantly as Fe^{+3} oxides in soils. The divalent state (or ferrous state) can be oxidized to the trivalent state (or ferric state), where it may form oxide or hydroxide precipitates, and become unavailable to plants as a micronutrient. Roots of some plants can reduce iron from the ferric to the ferrous state, and allow iron uptake into the plant [44]. Iron has many important functions in plant growth and development, such as involvement in the biosynthesis of chlorophyll, respiration, and chloroplast development, and improves the performance of photo systems. It is an essential part of many enzymes. Iron also participates in the oxidation process that releases energy from sugars and starches and in response to that converts nitrate to ammonium in the plant. It plays an essential role in nucleic acid metabolism.

The availability of Fe in soils is affected by soil properties such as soil pH, calcium carbonate content, and organic matter, accumulation of phosphorus, ion imbalance, soil texture, soil temperature, poor soil aeration, high humidity, and soil compaction. The availability of iron and most micronutrient is largely pH– dependent, availability decreases as pH increases. Iron in drinking water is present as Fe^{2+} or Fe^{3+} in suspended form. It causes staining in clothes and imparts a bitter taste. It comes into the water from natural geological sources, industrial wastes, domestic discharge, and also from by-products. Excess amount of iron (more than 10 mg/kg) causes a rapid increase in pulse rate and coagulation of blood in blood vessels, hypertension, and drowsiness. Although most mineral soils are rich in iron, the expression of iron toxicity symptoms in leaf tissues occurs only under flooded conditions, which involves the microbial reduction of insoluble Fe^{+3} insoluble Fe^{+2}. Iron toxicity in tobacco, canola, soybean, and Hydrillaverticillata is accompanied by a reduction of plant photosynthesis and yield and an increase in oxidative stress.

The appearance of iron toxicity in plants is related to high Fe^{+2} uptakes by roots and its transportation to leaves and via the transpiration stream. The Fe^{+2} excess cause free radical production that impairs cellular structure irreversibly and damages membranes, DNA, and proteins. Iron toxicity is not common, but some plants do secrete acids from the roots, which lowers soil pH. These plants can take up too much iron, leading to toxicity.

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 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 $pb^{2+}$to 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 women and can also damage the organs responsible for sperm production in the 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 children exposed to higher lead levels have been well documented. Lead acetate and lead phosphate are potential carcinogens based on studies in animals. However, there is inadequate evidence to determine lead carcinogenicity in humans. Lead poisoning damages the nervous system, kidneys, and liver and causes sterility, growth inhibition, and developmental retardation. Lead is toxic at all levels, hence lead based petrol, toys, and paints have been banned [8].

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. Long-term exposure can cause kidney and liver damage, as 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.

Naturally, Cr is found in all sorts of environmental components including air, water, and soil but in trace amounts. 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 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.In soils, its innate concentration varies within 10–50 mg kg-, depending on the mineralogy of the parent bedrock material. 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 a 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 the air, nose irritations and nose bleeds are quite common. Other health problems that are caused by chromium (VI) are skin rashes, upset stomachs, ulcers, respiratory problems, weakened immune systems, kidney and liver damage, alteration of genetic material, and lung cancer.

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 adults 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 the body, and chromosomal abnormalities. A zinc deficiency after birth may result in dwarfism, poor appetite, mental lethargy, etc. Excess amounts 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 rock, the 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 concentrations in soils (50 mg/kg on 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 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.

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. Cobalt is abundantly present in sedimentary vis-à-vis igneous rocks. Co is characterized bychalcophile, hydrophilic, and lithophilic in nature.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 and accumulation in plants and animals may occur [47,48].

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}.

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 a borderline element between hard and soft acid acceptors in chemical interactions with donor atoms. This is reflected in its abundance in the earth‟s crust as oxides, carbonates, silicates with iron, and magnesium, and as sulfides, arsenides, and tellurides. Nickel salts are soluble and can occur as leachate from nickel-bearing rocks. The effects of nickel exposure vary from skin irritation to damage to the lungs, the nervous system, and mucous membranes. It is also a known carcinogen.

Cadmium; Cadmium is a toxic trace element that may accumulate in soils from various human activities. A natural source of cadmium is weathering of rocks while some cadmium enters the 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, and 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 can 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.Besides, Zn, Pb, and Cu mining; ferrous and non-ferrous metal production; and cement production also contribute to the concentration of Cd in the environment [42].

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 the organic matter in soils.Which occurs at concentrations of 0.01 to 1 mg/kg. Weathering can Pbto Cd concentrations up to 5 μg/L [47]. 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 the 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 the liver and kidney with a somewhat lower concentration in the pancreas. Ingestion of a small amount of cadmium over a few years may lead to the accumulation of chronically or even acutely toxic levels of cadmium in the body. It takes a very long time before cadmium that has accumulated in kidneys is excreted from the 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 (Cd) is one of the most phytotoxic heavy metals, which is easily absorbed by vegetables due to its lipid solubility. Therefore, closely monitoring the Cd concentrations in the soil is crucial. [48].

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 the 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.

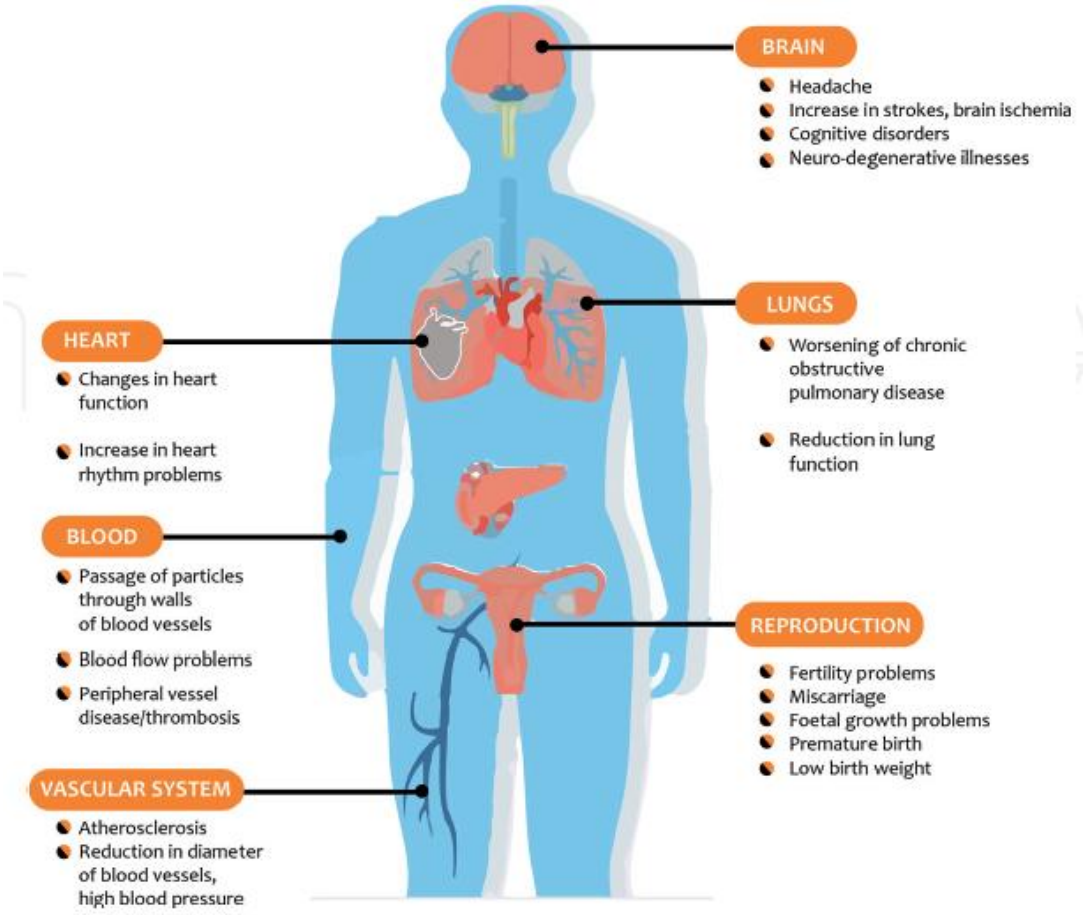


FIGURE 1. EFFECTS OF HEAVY METALS IN ORGANS OF HUMAN HEALTH [19]

2.8. 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, shellfish, and vegetables[49]

Cadmium is used industrially as an anti-friction agent, as a rust-proofer, in plastics manufacture, in alloys, and alkaline storage batteries. Chromium is found in fresh foods, copy machine toner, 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, chemical catalysts, and wood preservatives. Lead has been used in batteries, electronic equipment, petrol, toys, paint, etc. Lead has been used as a fuel additive in many countries for several years, although this practice has since stopped in most countries of the world, because of the health implications of lead. Manganese compounds are used in the 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 [50].

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 waste treatment plants. It is used in metal cleaning, bleaching, and as a preservative for fresh flowers and fruits [51].

3. MATERIALS AND METHODOLOGY

3.1. Apparatuses and Instruments

Auger mining, properly cleaned and sterilized polyethylene bags, and stainless steel knife has been employed for soil and sugarcane samples collection:1.0 mm sieve was used for sieving mechanically dried and crushed soil. A Milestone Microwave (Model:STRAT D 134348, EVISA),Drying Oven (Model: DHG-9123A) and Analytical balance (Model E11140, Switzerland) were used for the digestion of sugarcane and soil samples, dry the soil samples and weigh the processed samples, respectively. Measuring cylinders, pipette, and micropipette (Merck KGaA, Darmstadt, Germany) were used to measure different volumes of sample, acid reagents, and metal standard solutions. The digested samples were filtered with Whatman No. 42 filter paper:GPS (global positioning satellite) was used to take the sampling point locations within sampling site. The inductively coupled plasma optical emission spectroscopy ICP-OES Spectro-Arcos (Model: ARCOS FHS12, USA) was used for the determination of target heavy metals in study the samples

3.2. Chemicals and Reagents

All reagents and chemicals used in this study were analytical grades unless otherwise stated. distilled water was used for all preparation and dilution purposes of solutions through out the experimental procedures. Chemicals such as HNO_3 (69%),H_2O_2 (30%), and HCl (37%) (All from Sigma Aldrich, USA) were used during sample digestion procedures. 1000 ppm stock standard solutions of the heavy metals (Fe, Pd, Cr, Zn, Co, Ni, Cd, and Cu), were used to prepare calibration standard and spiking standard solutions.

3.3. Description of Study Area

The study was conducted in the Amhara region North Wollo Zone, Gubalafto Woreda Sanka irrigation farmland. Sanka is a small city located at a distance of 23 km from Woldia,(which is the capital city of North Wollo Zone) in the western direction in Amhara Region at an altitude of 2077,position $11^0$53’40.325”N with $39^0$27’24.852”E and the average annual minimum and maximum temperatures are 7^oC and 27^oC, respectively; while the average annual minimum and maximum rainfall are 1.2 mm and 414.8 mm and the relative humidity ranged from 40 to 74% [52].

According to the Central Statistical Agency of Ethiopia (CSA) (2007) survey,Sanka has a total population of 15,536 which shows an increase of 0.48%. Of these, 50.6% are men, and 49.4% are women. The average number of persons in a household was 4.15. The majority of the population (86.6%) was followers of Ethiopian Orthodox Christianity, while 13.32% of the population reported as Muslim. Almost all of the population was from Amhara ethnic groups and spoke Amharic as their first language [52].

Table 1. The geographical location of sampling pointsin the studying area

No	Location	Sampling site	Latitude	Longitude	Altitude(m)	Accuracy
1	Anoba	1	$11^0$53’33.408’’N	$39^0$27’13.212”E	2103	±4
		2	$11^0$53’37.530”N	$39^0$27’07.044”E	2125	±5
2	Woyniye	1	$11^0$53’38.327”N	$39^0$27’14.916”E	2102	±4
		2	$11^0$53’40.325”N	$39^0$27’24.852”E	2077	±4
3	Geshober	1	$11^0$53’43.649”N	$39^0$28’13.001”E	2023	±3
		2	$11^0$53’46.290”N	$39^0$28’05.783”E	2030	±4

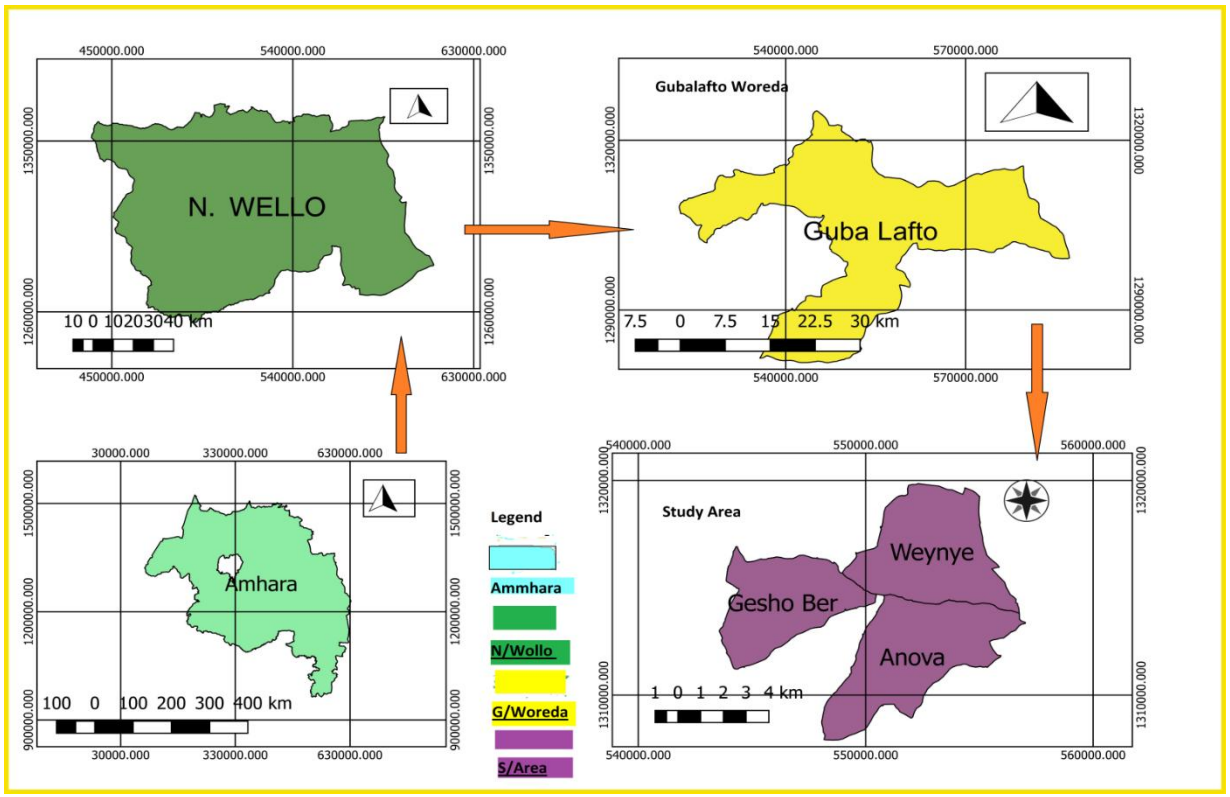


FIGURE 2. THE GEOGRAPHICAL LOCATION OF THE STUDDING AREA

3.4. Working Procedure

Cleaning apparatus all glass wares and other apparatus such as volumetric flask, round bottom flask, beaker, measuring cylinder, pipette, mortar, and pestle were washed with detergents and tap water and then soaked with dilute nitric acid for three days and then rinsed in distilled water. The glass wares and other apparatus were dried in a hot air oven and kept in a clean place till analysis begins.

3.4.1. Sampling Procedures

The first reconnaissance survey was conducted to identify sugarcane farms in the studying area. Sugarcane stems and soil samples were collected at every sampling point concurrently. The coordinates of the sampling location within the sampling site were obtained with the aid of GPS (global positioning satellite) that were only sampled when the instrument indicated that the point could be mapped with an accuracy of 3-5meter (m). The soil sample was collected at the place where the sugarcane was sampled. The samples were put in plastic bags, labeled, sealed, and taken to the laboratory for digestion followed by analysis.

3.4.2. Sugarcane sample collection and preparation

Six sampling points were established from three sampling sites namely Geshober, Anoba, and Woynye, and then six sugarcane plants 0.5 kg weight each were collected from where the soil sample was collected by using a stainless steel knife. The shoots were removed and the stems were cut into smaller sizes and tied by robe properly then taken to the laboratory. Then sugarcane was rinsed with de-ionized water to remove dirt. The sugarcane juice was squeezed out into a 50 mL flask with the aid of a pre-cleaned extractor and kept refrigerated until further analysis.

FIGURE 3. SUGARCANE PLANT, SAMPLE AND WELL-PREPARED JUICE

3.4.3. Soil sample collection and preparation

3 kg composite Soil sample was collected into clean polyethylene bags from the same sites where the sugarcane samples were collected with the consent of the farmers at 0–20 cm depth usinga steel auger and pooled together to form a composite sample. The collected carefully packed and labeled soil samples were then transported to the Laboratory for analysis.

In the laboratory, the soil samples were air dried in a dry and dust-free place at room temperature (25˚C) for one week , followed by an oven dry until constant weights were attained. The samples were then grind with a mortar and pestle to pass through a 2 mm sieve and homogenized. The dried, sieved, and homogenized soil samples were finally stored in polyethylene bags and kept in desiccators until digestion and analysis.

FIGURE4. A PLACE WHERE SOIL SAMPLESARE TAKEN AND SOIL SAMPLE

3.5. Digestion of Sugarcane juice Sample

20mL of the sugarcane juice sample was transferred to a 250 mL round bottom flask and 6mL of Aqua-regia(3:1 ratio of HNO_3 and HCl) was added. Then the solution was digested on microwave digestion for 3:00 h at the temperature of 210^{o}C. After 3:00 h of the digestion time the digested solution was permitted to cool to room temperature for about 30 min without disassembling the condenser. Then at the time of disassembling the setup, 10 mL of distilled water was added to the solution. This was done by rinsing the neck of the round bottom flask and the tip of the condenser that was in contact to dissolve the residue formed to cooling and minimizing dilution of filter paper by digesting residue while filtering with Whatman 110 mm filter paper into 50 mL volumetric flask [15].

Finally, the cooled solution was filled up to the mark with distilled water. This procedure was done three times for the sugarcane juice sample. The digestion of the blank reagent was done by following similar procedures simultaneously with the sample. All the solutions were stored in the refrigerator until the analysis was done. The solutions were used to determine the concentration of the target analyte of the sample.

3.6. Digestion of soil samples

The soil sample was dried in the open air for one week of crushing and sieved mechanically by using a 1.0 mm sieve.

After which, 1.25 g of composite sample was digested with 20mL Aqua-regia (3:1 ratio of HNO_3 and HCl) in abeaker (open beaker digestion) on a thermostatically controlled hot plate. The digest was heated to near dryness and cooled to ambient temperature. Then 5mL of H_2O_2 was added in parts to complete the digestion and the resulting mixture was heated again to near dryness in a fume cupboard. The beaker walls were washed with 10mL of deionized water and 5mL HCl was added, mixed, and heated again. The resulting digest was allowed to cool and transferred into 50mL of the standard flask through Whatman 110 mm filter paper and make up to mark with deionized water [53].Fe, Pb, Cr, Zn, Co, Ni, and Cd heavy metal elements were then analyzed by direct aspiration of the sample solution into inductively coupled plasma optical emission spectroscopy (ICP-OES) at Horticoop Ethiopia (Horticulture) PLC, heavy metal analysis laboratory. Debire Zeit, Ethiopia

3.7. Analysis of Sugarcane Juice and Soil Samples

For the analysis of sugarcane and soil samples, calibration of the instrument with the known concentration of standard solutions was done for each target analyte. Calibration metal standard solutions were prepared for each of the heavy metals from an intermediate standard solution containing 10 mg/L which was prepared from the Inductively Coupled Plasma–Optical Emission Spectrometry (ICP-OES) standard stock solutions that contained 1000 mg/L. These standards were diluted with distilled water to obtain eight working standards for each metal of interest.

Three replicate determinations were carried out for each sample. All the metals which were determined by absorption and concentration mode and instrument read out were recorded for each sample of sugarcane juice and soil with the blank solution.

3.8. Method Performance and Validation

The validation parameters included in this study were linearity, accuracy, precision, and detection limit (DL). The validation method followed the protocol guidelines for the validation of analytical methods.

Linearity; Linearity is the ability of a method to elicit test results that are directly proportional to analyte concentration within a given range. The equation of the calibration curve that relates the dependent (y) and independent (x) variables is $y = ax+b$. The mathematical method known as linear regression was used to estimate the coefficients of the calibration curve, from one set of experimental measurements. The value of 0.99 was used for the coefficient of correlation (R^2) as the limit for setting the coefficients of the curve [54].

Precision; Precision is an analytical parameter called variability. It expresses the variations within the same laboratory, when the same sample is analyzed by the same procedure, by instrument, and/or by different analysts in different time intervals. The variation or error in analytical results must be evaluated by applying different statistical methods. Most of the common statistical methods applied in analytical chemistry are the standard deviation, variance, coefficient of variance, relative standard deviation, and range of series of measurements. In this particular study, the results of the measurements are expressed as the mean of the measurements together with the standard deviation of the triplicate samples with triplicate measurements of each sample [70]. The mean, standard deviation, and relative standard deviation were calculated mathematically as follows (equations 1, 2, and 3).

$$\text{mean} = \frac{\sum_{i=1}^{n} xi}{n} \quad \ldots\ldots 1$$

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (xi - mean)}{n-1}} \quad \ldots\ldots 2$$

$$\%RSD = \frac{SD}{mean} \quad \ldots\ldots 3$$

Accuracy; Accuracy of an analytical method, also called recovery, is defined as the closeness between the true value of the analysis in the sample and the value obtained by the analytical procedure.Which is expressed as percentage recovery (%R). It is a parameter that

ensures that no loss or contamination occurred during the test procedure, contributing to quantifying the sample [55].The experiment was done on the validity of the analytical procedure for each sugarcane and soil sample that was collected from the sample sites. The spiked and none spiked samples were digested and analyzed in the same way using the analytical procedure of sample analysis. The percentage of the analytes was calculated by using the formula:

$$\%\text{Recovery test} = \frac{\text{Amount after spike} - \text{Amount before spike}}{\text{Amount added}} \times 100 \quad \ldots\ldots 4$$

Method Detection Limit (MDL) and Method of Quantification Limit (MQL),the method detection limit is the minimum concentration that can be detected by the analytical method with a given certainty. It is also the smallest concentration or amount of analyte that can be reliably shown to be present and measured under a specific confidence level. The limit of detection can be calculated by multiplying the standard deviation of the blank (SD_b) three times (LOD = $3SD_b$).The detection limit (with all steps of the analysis included) is called the MDL. The practical method for determining the MDL is to analyze samples of concentration near the expected limit of detection [55].

$$LOD = 3SD \quad \ldots\ldots 6$$

The limit of quantification (LOQ) is the minimum concentration that can be quantified and it is 10 times the standard deviation.

$$LOQ = 10\ SD \quad \ldots\ldots 7$$

In this case, the value of the method detection limit of each element is should be more or less higher than that of the instrumental detection and lower than limit of quantification. This confirms that the method was good and acceptable.

3.9. Determination of heavy metals

The digested samples were determined for the concentrations of heavy metals Fe, Pb, Cr, Zn, Co, Ni, and Cd by using The ICP-OES Spectro-Arcos (Model: ARCOS FHS12, USA) Final concentrations of the metals in the soil samples were calculated using the following formula [54].

$$\text{Concentration } (mgkg^{-1}) = \frac{\text{Concentration } (mgL^{-1}) \times V}{W} \quad \ldots\ldots 5$$

Where

V = Final volume (50 mL^{-1}) of the solution, and

W = Initial weight (1.25 g) of the sample measured

3.10. Transfer factor of heavy metals from soil to sugarcane

Transmission of heavy metals from soil to sugarcane is studied using an index which is called transfer factor (TF). It is calculated as a ratio of the concentration of a specific heavy metal in the sugarcane to the concentration of the same heavy metal in soil both represented in the same units. If TF is greater or equal to one the absorption of heavy metal from the soil by the sugarcane is higher. On the other hand, a lower value TF indicates the poor response of the sugarcane plant towards heavy metal absorption and the sugarcane plant can be used for human consumption. TF is calculated by the formula [56]:

$TF = C_{plant} / C_{soil}$……...…….. 8

Where,

$\mathbf{C}_{plant}$ and $\mathbf{C}_{soil}$ are the concentration of metals in the plant and the concentration of metals in the soil respectively.

3.11. Data Analysis

All data in this study were subjected to statistical analysis of Pearson Correlation and Paired -Samples T-test analysis by using SPSS software version 26 and Stata IC/13. The means for the levels of HMs in sugarcane and soil samples were reported as mean ± SD. Paired -Samples T-test analysis is used to compare the mean value of HMs in the soil and sugarcane juice and as well as used to test whether they are significantly different or not. Pearson correlation was also used to relate the levels of heavy metals in sugarcane and soil. The study used a 95% confidence level for all significant tests [57].

3.12. Health Risk Assessments

Average daily doses (ADD), HM from the soil could be taken up by residents following different absorption routes, including oral ingestion (non-dietary or dietary), dermal contact, and inhalation. The estimated HM from soil (expressed as the average daily dose, ADD) was assessed using the following formulas by the Eqs. (9)–(12):[65– 67].

$$ADD_{oral} = \frac{Cs\ xIngR\ x\ CF\ x\ EF\ xED}{BW\ xAT}\ x10^{-6} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 9$$

$$ADD_{inh} = \frac{Cs\ xInhR\ xEF\ xED}{BW\ xAT\ xPEF} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 10$$

$$ADD_{derm} = \frac{Cs\ xSL\ xSA\ xAF\ xABS\ xEF\ xED}{BW\ xAT}\ x\ 10^{-6} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 11$$

$$ADD_{juice} = \frac{Cj\ x\ \mathrm{IngR}\ x\mathrm{EF}\ x\ \mathrm{ED}}{\mathrm{BW}\ x\mathrm{AT}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 12$$

Where

ADD_{oral}, ADD_{inh}, and ADD_{derm} are average daily doses taken by oral intake (defined as the un intentional exposure by non-dietary mouth intake of HM, e.g., dust or air-borne particles) ,inhalation, and dermal contact of soil dust (with the value of mg kg^{-1} day^{-1}) respectively; ADD_{juice} is estimated average daily dose intake through sugarcane juice (mg kg^{-1} day^{-1});*C*s and *C*j are HM concentrations respectively in soil and in squeezed sugarcane juice (mg kg^{-1}); IngR is the ingestion rate of soil dust and juice; InhR is the air inhalation rate; SL is the skin adherence factor; EF is the exposure frequency;ED is the exposure duration; AT is the average time in days; BW is body weight; PEF is the particular emission factor; SA is the skin area;; AF is the adhesive factor, and ABS is the skin absorption factor. Values and units of IngR, InhR,SL, EF, ED, AT, BW, PEF, SA, AF, and ABS are described in Table 3.

Target hazard quotient (THQ); To assess non-carcinogenic human health risks from three non-dietary pathways for each HMs, the target hazard quotient (THQ)values were estimated. The THQ values of the local population due to the three non-dietary pathways were calculated using Eq (13) [61].

THQ = ADD/RfD……..……..13

Where

ADD is the average daily dose of the population in mg/day/kg body weight and RfD is the oral reference dose (mgL^{-1} day^{-1}) values for each metal of interest and as listed in table 2. If the value of THQ is <1, it is generally presumed to be safe for the risk of noncarcinogenic effects and if it is >1, it is supposed that there is a chance of noncarcinogenic effects with an increasing probability as the value upsurges [61].

The target cancer risk (TCR; the cancer risk (CR) posed to human health due to the ingestion of individual possibly carcinogenic metals was estimated using Eq (14). Then, the target cancer risk (TCR) resulting from heavy metals Pb, Cr, Cd, and Ni ingestion, which may promote carcinogenic effects depending on the exposure dose, was calculated using Eq (15) [43,64].

CR = ADD × SF……14

$TCR = \sum_{(n=1)}^{i} \mathrm{CR}, \mathrm{i} = 1,2,3 \ldots . \mathrm{n}$……...…….……15

Where

CR= cancer risk, TCR= target cancer risk; SF = slope factor for carcinogenicity; ADD = average daily dose of heavy metal in mg kg^{-1} day^{-1}; the human health risks posed by seven HMs (Fe, Zn, Pb, Cd, Co, Cr and Ni) were assessed. Four HMs (Pb,Cd, Cr, and Ni) classified as carcinogens were assessed for their carcinogenic risks [58]. The RfDs values of the evaluated HMs and SFs values of the evaluated HM could be found in Tables 2 [67–69].

Table 2. RfD and SF value of target heavy metals

Heavy metals	RfD value in mg kg^{-1} day^{-1}	SF value in mg kg^{-1} day^{-1}
Fe	$1x10^{-3}$	-
Pb	$3.6x10^{-3}$	0.042
Cr	$3\ x10^{-3}$	0.5
Zn	$2\ x10^{-2}$	-
Co	$2\ x10^{-2}$	-
Ni	$3\ x10^{-1}$	0.91
Cd	$5\ x10^{-1}$	15

Hazard Index (HI);To further investigate the health risks induced through non-dietary exposures of HM, the hazard index (HI) of three non-dietary pathways for each HM was calculated usingEq. (15) [58].

$$HI = HQ_{oral} + HQ_{inh} + HQ_{der} \quad \text{.....15}$$

Where

HI is the sum of various metals hazards. If the HI value became <1.0, there is no apparent health impact due to the metals considered. However, an HI value of >1.0 indicates potential health impact implications. A serious chronic health impact has been suggested for HI >10.0 [61].

Table 3. Values of the parameters for the estimation of human exposure [66, 70]

No	Parameters	Unit	Value
1	IngR (ingestion rate)	mg day^{-1}	30
2	InhR (inhalation rate)	m^3day^{-1}	7.6
3	ABS (skin absorption factor)	Unitless	0.001
4	AF (adhesive factor)	Unitless	0.07
5	AT(average time)	Unitless	for non-cancer ED×365 for cancer, 70 × 365
6	BW (body weight)	Kg	60
7	SL (skin adherence factor)	$mg/cm^2\,day^{-1}$	0.07
8	ED(exposure duration)	Year	40
9	EF (exposure frequency)	Day $year^{-1}$	300
10	PE (particular emission factor)	$m^3\,kg^{-1}$	1.36×10^9
11	SA (skin area)	cm^2	5700
12	CF (the conversion factor)	Unitless	0.085

4. RESULTS AND DISCUSSION

4.1. Calibration of the Instrument in the Determination of Selected Metals

The heavy metals Fe, Pb, Cr, Zn, Co, Ni, and Cd in the digest of sugarcane juice and soil samples from one composite sample of six different areas were determined three times by (ICP-OES).The calibration curve exhibited good linearity with R^2 values ranging between 0.9957 and 0.9999, which were greater than the acceptable limit (0.995) for the linearity. Based on the information from the correlation coefficients and their corresponding calibration curves of each metal, it is possible to say the two variables (concentration and absorbance) have a good positive correlation and linearity. The concentration of the working standards, correlation coefficient and calibration equation of the calibration curve for each metal are shown in Table S1 of Supplementary Material and figure 5-8 [54].

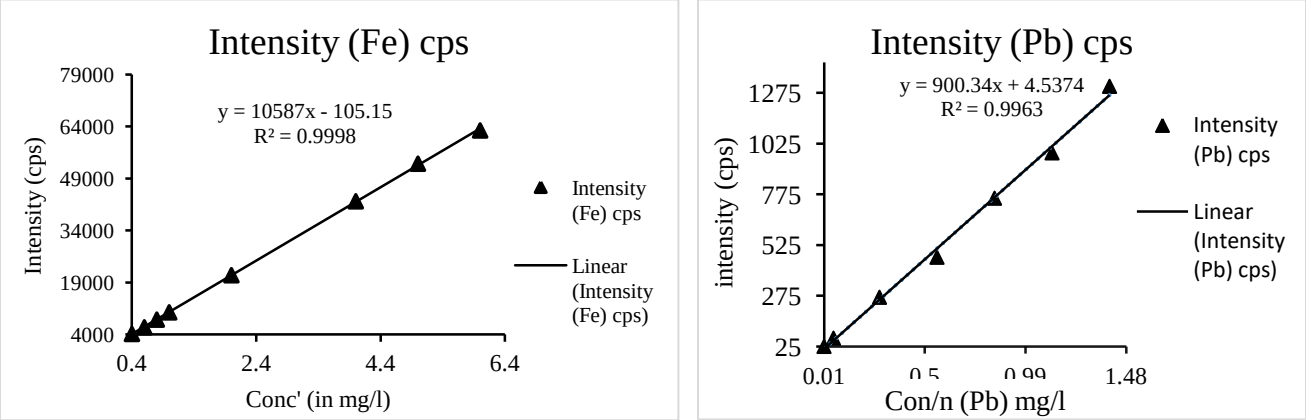
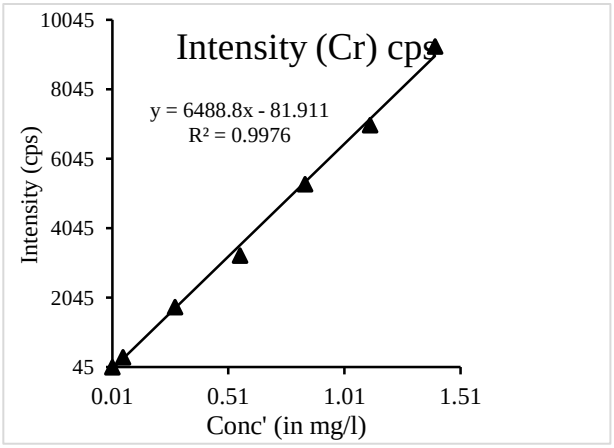


FIGURE 5. INTENSITY VERSUS CONCENTRATION CURVE FOR Fe AND Pb



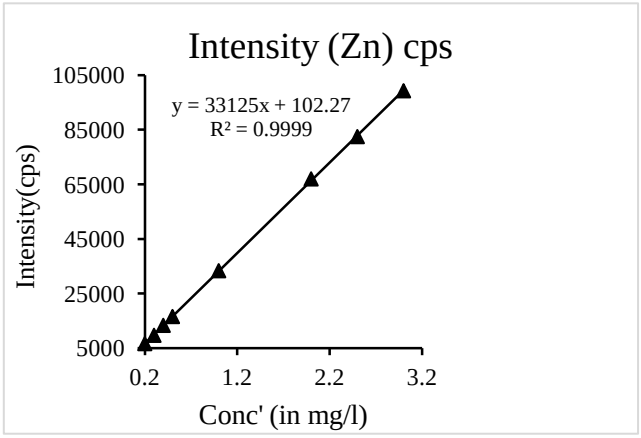
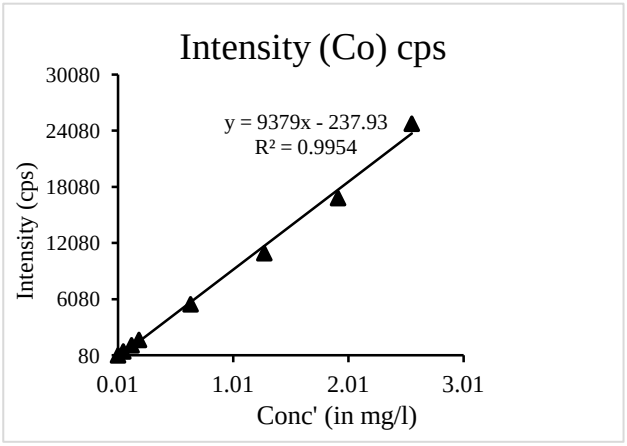


FIGURE 6. INTENSITY VERSUS CONCENTRATION CURVE FOR Cr AND Zn



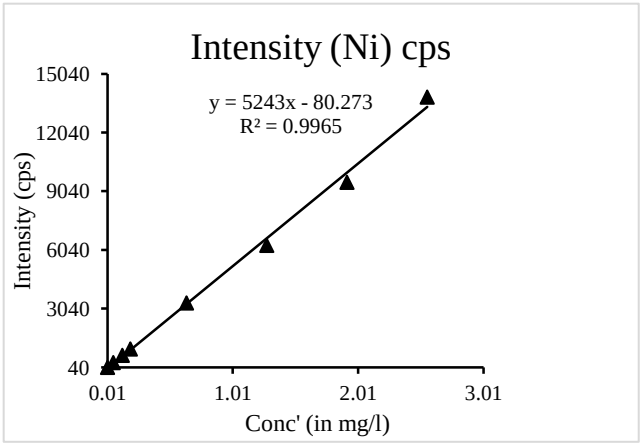


FIGURE 7. INTENSITY VERSUS CONCENTRATION CURVE FOR Co AND Ni

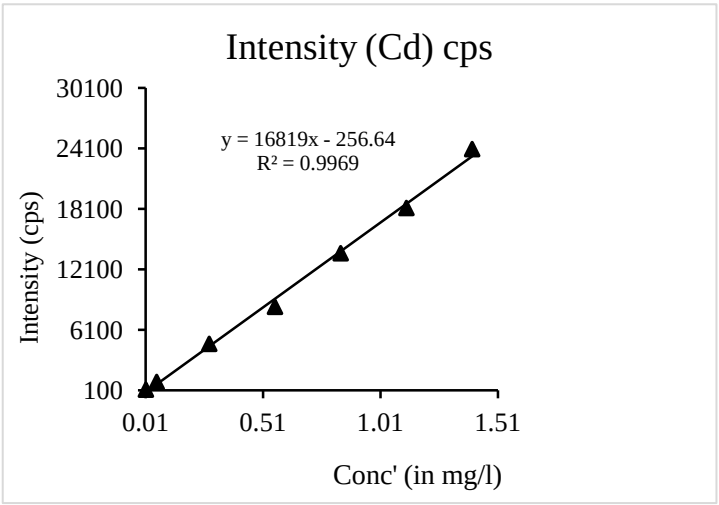


FIGURE 8. INTENSITY VERSUS CONCENTRATION CURVE FOR Cd

4.2. Method Detection Limits (MDL) and Limit of Quantification (LOQ).

The Limit of Quantification (LOQ) and Method Detection Limits (MDL) for all the metals considered in this study have been calculated from the response of seven replicates of the calibration reagent blank using a standard formula LOQ = 3 × SD and MDL = 10×SD and the data are presented in table 4.The instrumental detection limits (IDL) as obtained from the instrument's operation manual ranged from 0.001 to 0.009 mg/kg which were below the Method Detection Limits (MDL),that laid for sugarcane juice simple; in the range of 0.003–0.252 mgL^{-1}, for soil sample; in the range of 0.009-0.015 $mgkg^{-1}$. The Method Quantification Limit (MQL) value lay for the sugarcane juice sample in between 0.01 and 0.84 mgL^{-1}, for the soil sample in between 0.09-21 $mgkg^{-1}$ The result shows both the MDL and MQL values were greater than that of the IDL; hence, the results of the analysis could be reliable.

Table 4. The instrumental detection limit, method detection limit and method of quantification

Target	IDL	Sugarcane juice sample		Soil sample	
Metals	($mgkg^{-1}$)	MDL(mgL^{-1})	MQL (mgL^{-1})	MDL ($mgkg^{-1}$)	MQL ($mgkg^{-1}$)
Fe	0.002	0.018	0.06	0.021	0.21
Pb	0.001	0.003	0.01	0.012	0.21
Cr	0.006	0.008	0.02	0.009	0.09
Zn	0.002	0.003	0.01	0.009	0.09
Co	0.007	0.009	0.02	0.012	0.21
Ni	0.009	0.015	0.05	0.015	0.15
Cd	0.002	0.252	0.84	0.006	0.06

4.3 Accuracy and Precision

As can be seen from Table 5 and 6, the mean percent recoveries for the studied metals in the soil spiked samples ranged between 81.98 and 105% and in the sugarcane juice spike sample ranged between 89.4 and 105.2% and. All the recovery values were within the acceptable range of 80–120% for metal analysis. The precision of the method was expressed as the RSD of the three replicate readings. The RSD values obtained for sugarcane juice spike samples ranged from 0.02-5.00 % (Table 6) and for soil spike samples ranged from 0.60-3.78 %.which was under the

required control limits of ≤15% [54].So these results indicate that the proposed method was precise and accurate.

Table 5. Recovery test results for soil samples

	Heavy metals in the soi sample						
	Fe	Pd	Cr	Zn	Co	Ni	Cd
Un spiked Sample (mg/kg)	22975.32	100.880	129.320	120.398	3.750	7.067	14.740
Added amount ($mgkg^{-1}$)	1000.00	100.00	800.000	800.00	100.00	100.00	800.00
Spiked sample ($mgkg^{-1}$)	127975	10098.88	73713.32	65711.61	9699.75	9540.08	66190.74
%Recovery	105	99.98	91.98	81.98	96.96	95.33	82.72
% RSD	0.96	3.78	3.22	0.68	2.32	1.47	0.60

Table 6. Recovery test results for sugarcane juice samples

	Heavy metals in sugarcane juice sample						
	Fe	Pd	Cr	Zn	Co	Ni	Cd
Un spiked sample (mgL^{-1})	0.557	0.033	0.127	0.020	0.036	0.026	0.022
The amount added (mgL^{-1})	8.000	2.000	1.500	4.000	2.000	2.000	2.000
Spiked sample (mgL^{-1})	8.277	2.062	1.651	3.595	2.053	2.130	1.962
% Recovery	96.50	101.5	101.6	89.4	100.9	105.2	97.00
% RSD	1.43	3.03	0.02	5.00	0.55	3.84	4.54

4.4. Concentration of heavy metals in a soil sample

The mean concentrations of heavy metals in the soil samples are shown in Table 7.The data revealed that all the analyzed metals accumulated in the soil at different concentrations. Results are expressed as the mean and standard deviation of three replicate analyses.

Iron (Fe); In a composite soil sample, iron (Fe) was found to have the highest concentration of all the heavy metals examined from the sample sites, with a level of 22875-23075 $mgkg^{-1}$. This outcome was found to be below the FAO/WHO guideline from 2001. (50,000 $mgkg^{-1}$). but greater than the 4642 $mgkg^{-1}$ in Dukem, Ethiopia and the 24352 $mgkg^{-1}$ in Nigeria reported in the earlier research [40,41]. The availability of iron in nature and the amount of fertilizer, pesticides, and herbicides that farmers employ could be the cause of the high level of iron.

Lead (Pb); the average lead (Pb) value in the examined soil samples was 101$mgkg^{-1}$. The mean Pb concentration in this study was different from the mean Pb concentrations reported in farmland in China and Shanghi agricultural soil, respectively, which were 51.87 $mgkg^{-1}$and 25.57 $mgkg^{-1}$ [66, 67] The use of various farming techniques, as well as the geographic and climatic diversity of the nations, may be the cause of this. The Pb levels in this study 101 $mgkg^{-1}$ were greater than the Pb values in soil of Southern Ethiopia that was reported in soil samples at 46.47 mg/kg^{-1} [71, 65]. The cultivation of various soil types in the two regions and the use of various farming techniques may be the cause of this. The level of Pb in the current study was approximately similar to that of the permissible limits, (100 $mgkg^{-1}$) for agricultural land (FAO/WHO, 2001).So this indicated that the soil is suitable for the cultivation of different plants.

Chromium(Cr); The results of the chromium (Cr) concentration ranged from 127.2 to 131.20 $mgkg^{-1}$ and were much greater than those discovered in soil samples from East Gojam, Ethiopia and Pakistan, which ranged from 1.50 to 2.86 $mgkg^{-1}$ and 1.222 to 1.310 $mgkg^{-1}$ respectively [20-67]. This is a result of different agricultural strategies used by farmers in each nation as well as variations in the Cr levels in soil parent material. The allowable limits for agricultural land (100$mgkg^{-1}$) were exceeded in the current study's Cr levels. (FAO/WHO, 2001) This demonstrates that the soil in the study region has been contaminated with chromium as a result of a contaminated landfill and the presence of topsoil and pebbles.

Zinc (Zn); Zinc concentrations ranged from 120.858 to 121.018 $mgkg^{-1}$. The average Zn concentration in this study is significantly lower than the average Zn concentrations reported for Nigerian farmland, Chinese farmland, and Indian farmland, respectively, which were 0.432-0.8079 $mgkg^{-1}$, 4.55-48.9 $mgkg^{-1}$, and 49.10-57.09 $mgkg^{-1}$ [65-67]. The excessive use of several kinds of pesticides, fertilizers, and herbicides may be the cause of the highest amount of Zn in this agricultural site. According to FAO/WHO (2001), the allowed limits for Zn on agricultural land are 300 $mgkg^{-1}$. The level of Zn in the current study was lower than that. As a result, the soil in the tillage regions is appropriate for planting a variety of plants.

Cobalt (Co); as the experimental analyses show in Table 7, the concentrations of cobalt ranged from 3.650-3.800 $mgkg^{-1}$. This level of Co in this study was lower than 22.20 $mgkg^{-1}$ reported in soil samples in Iraq and 140.7 $mgkg^{-1}$ in soils used for cultivation of plants in East Gojjam Zone, Ethiopia respectivly [52, 63]. The difference in Co levels in the countries could be attributed to the difference in Co levels in parent rocks as well as agricultural practices employed by farmers in each country. The levels of Co obtained in this study were lower than the 2001 WHO recommended limit, which is 50 $mgkg^{-1}$. In this case, the widespread use of various pesticides and fertilizers may not have contributed to the increased availability of Co in the soil.

Nickel (Ni); Nickel is present in soil grown at an average value of 7.067 $mgkg^{-1}$. This study's Ni concentration was lower than the levels of 20 to 30 $mgkg^{-1}$ reported for soil samples taken in Brazil [68] and 87.5 to 123.5 $mgkg^{-1}$ in East Gojjam Zone, Ethiopia [54]. The cause of this may be anthropogenic activities like mining, smelting, and the application of some organic amendments, such as compost made from sewage sludge or sewage sludge, which are less prevalent in this area than in other regions. Ni levels were lower than the allowed limits (50 $mgkg^{-1}$) for agricultural land in the current investigation (FAO/WHO, 2001). Due to this, when compared to other cancer-causing heavy metals, Ni presents a lower risk of cancer in the soil of the research area.

Cadmium (Cd) The soil at the test location had a cadmium concentration of 14.740 $mgkg^{-1}$. It's possible that the use of phosphate fertilizers that include cadmium is to blame for the high amount of cadmium. Herbicides, pesticides, insecticides, and exposure from dust contaminated with cadmium. also, it was shown from this study that local agricultural practices did not result in an increase in the amount of Cd in the soils..

The Cd concentrations in this investigation were lower than the levels of 27.93–45.33 $mgkg^{-1}$ that were found in soil samples taken in Dukem, Ethiopia [74]. Pesticides, fertilizer, and municipal and industrial sewage effluents are known to be released into nearby irrigation farms, which may be the cause of the increased levels. The amounts of Cd found in this study were higher than the levels of Cadmium found in soil samples from east Gojam, ethiopia (2.5 mg kg^{-1}) [54].The fact that the Cd concentrations in this investigation were found to be significantly greater than the recommended limits (3 $mgkg^{-1}$) established by WHO/FAO suggests that the soil was contaminated with Cd. The usage of phosphate fertilizers and manure may have led to the increased availability of Cd in the environment.

Generally, as stated in the above all discussion of heavy metals: fertilizers, pesticides, herbicides insecticides, and anthropogenic activities might be affected the distribution of heavy metals in the soil.

Table 7. Concentration of heavy metals in soil and sugarcane juice sample

Metals	The concentration of heavy metals in soil sample ($mgkg^{-1}$)				The concentration of heavy metals in sugarcane juice sample (mgL^{-1})			
	Mean ± SD	Min	Max	WHO/ FAO	Mean ± SD	Min	Max	WHO/ FAO
Fe	22975±220	22740	23178	50,000	0.557 ±0.008	0.549	0.564	0.01
Pb	101±3.820	100.400	101.20	100	0.033 ±0.001	0.176	0.204	0.01
Cr	129±4.160	127.200	131.20	100	0.127±0.002	0.124	0.130	0.10
Zn	121±3.940	120.858	121.018	300	0.020 ±0.001	0.010	0.030	5.00
Co	3.750±0.087	3.650	3.800	50.0	0.036 ±0.002	0.034	0.038	0.001
Ni	7.067±0.104	6.950	7.150	50.0	0.026 ±0.004	0.023	0.031	0.002
Cd	14.740±0.089	6.950	7.150	3.00	0.022 ± 0.004	0.020	0.020	0.10

4.5. Heavy Metals Concentration in Sugar Cane Juice

The sugarcane juice was extracted from collected sugarcane stalks and analyzed for heavy metal contents. All the determined heavy metals in this study were found in the sugar cane juice. in this study the mean concentration of some target heavy metals Cadmium and zinc were below the acceptable permissible limits. Whereas Chromium, Iron, Cobalt, Nickel, and Lead were above the acceptable permissible limits set for food as stipulated by FAO/WHO regulatory bodies.

Iron (Fe);The results in Table 7 reveal that the average concentration of iron was highest among the heavy metals analyzed from the composite sample and the level obtained was found to be 0.557 mgL^{-1} in the composite sugarcane sample. which was higher than the WHO recommended limits of 0.01 mgL^{-1} and lower than the previous studies found to be in a range of 1.6- 12.5 mgL^{-1},0.17 - 0.61 mgL^{-1}, and 0.76-3.61 mgL^{-1} in Nigeria and 4.63- 49.07 mgL^{-1} in Kenya [14,42].The level of iron in the current study was between WHO recommended value and the previous studies. In this case, it was possible to say that the amount of iron was an optimum concentration in the current study.

Lead (Pb); in the studied sugarcane juice sample, the average result of lead (Pb) concentration was 0.033± 0.001 mgL^{-1}. Which was above the WHO recommended limit of 0.01 mgL^{-1}. and also the current study level of lead was higher than that of the previous studies that recorded 0.01-1.11mgL^{-1} lead levels in sugarcane juice from India [73], 0.16-0.42mgL^{-1}in Nigeria [14]**,**.The reason for this is due to the application of different methods of farming, geographical and climatic variation between countries and which was almost similar to that of 0.029 mgL^{-1}studied in China [76]. The reason for this might be the application of the same methods of farming, geographical and mineral content similarities of the two countries

Chromium (Cr);The result of Chromium(Cr) concentration was in the range of 0.124-0.130 mgL^{-1} slightly higher than the WHO-recommended levels of 0.1 mgL^{-1} of chromium in drinking juices. Previously recorded levels of chromium in sugarcane juice were in the range of 10.54-60.22 mgL^{-1} in India [73]. In the current study, recorded value was lower than the level in this Indian study. This might be because Chromium contaminations mostly emanate from fertilizers

and organic manure as well as, anthropogenic activities, sewage sludge, and industrial sludge, could have less contribution in the current studying area.

Zinc (Zn); in the current study the mean concentration of zinc (Zn) was 0.020 mgL^{-1}. which is lower than that of WHO limits in juices were 5 mgL^{-1}.The levels in the present study were also lower compared to levels in another study in China and Kenya which reported levels of 10.64 mgL^{-1},1.80-2.50 mgL^{-1}, and 0.37-12.32 mgL^{-1} in sugarcane juice respectively [71,72].Zinc is dispensed by fertilizers, pesticides, and industrial waste and also naturally occurs in soil. This might be due to low concentrations the target metal in soil of the tillage regions.

Nickel (Ni); The safe limit as WHO/FAO for Ni was 0.001 mgL^{-1} but in the current study, the average Ni concentration in sugarcane was 0.026 mgL^{-1}, which was higher than The safe limit as WHO/FAO and lower than when compared with another study that recorded 1.87 mgL^{-1} in India [76]. The variation might be in heavy metal uptake depends upon soil physicochemical properties and plant biological features.

Cadmium (Cd); the cadmium content of sugarcane juice in the sampling site was 0.022 mgL^{-1}, which is lower than that of the permissible WHO limits for cadmium in juice (0.1 mgL^{-1}). It has also showed the value of Cd in this study is lower than the previous studies in different regions in the world recorded that would be 0.1 mgL^{-1} in India, 0.18 mgL^{-1} and 0.152 mgL^{-1} in China [73-75].The reason might be the amount of Soil, pH, type and distribution of organic matter, plant age, availability of micro and macronutrients, and plant genotypes differ from country to country [78]**.** Due to this reason, the juice had less cancer risk through Cd when we compare the other cancer-risk heavy metals.

4.6. Correlation Analysis

The Pearson correlation coefficient (r) is used to measure the strength of linear association between two variables and attempts to draw a line of best fit through the data of two variables. The Pearson correlation coefficient (r) indicates how far away all these data points are from the line best fit. A correlation coefficient of +1 indicates that there is a strong (perfect positive) correlation relationship between the two variables this means the one variable increases the other variables also increase and vise verse whereas A correlation coefficient of -1 indicates that there is a weak (negative) correlation relationship between the two variables this means the one variable increases the other variables decrease and Vis verse [54]. The correlation values are categorized as no correlation (r = 0.00-0.19), low correlation (r = 0.20-0.39), medium correlation (r = 0.40-0.59), higher correlation (r = 0.60-0.79) and highest correlation (r = 0.8-1.00) [82]. Linear regression correlations test were performed to investigate the correlation between heavy metal concentration in the sugarcane samples are summarized in Tables 8.as can be seen from Table 8, the correlation coefficients between heavy metals in sugarcane juice shows highest correlation between Cr/Fe, Ni/Pb, and Cd/Fe. Medium positive correlation between Cr/Pb, Co/Zn, and Ni/Cr. Pb/Fe, Ni/Fe, and Cd/Zn has no correlation. All the correlation between Zn/Pb, Zn/Cr, , Co/Fe, Co/Fe, Co/Cr, Ni/Zn, Ni/Co, Cd/Pb, Cd/Co, and Cd/Ni, show negative correlation.

Table 8. Person correlation coefficients between metals concentration in sugarcane juice Sample

	Fe	Pd	Cr	Zn	Co	Ni	Cd
Fe	1.000						
Pb	0.135	1.000					
Cr	0.917	0.519	1.000				
Zn	0.030	-0.986	-0.371	1.000			
Co	-0.798	-0.705	-0.972	0.579	1.000		
Ni	0.137	1.000	0.520	-0.986	-0.706	1.000	
Cd	0.990	-0.009	0.850	0.173	-0.703	-0.007	1.000

According to Table 8 the correlation between Co with Pb, Fe, and Cr have negative correlation, this indicates that when the concentration of Co increase in sugarcane juice. the concentration of Pb, Fe, and Cr decreases and vice versa. Fe has highest correlation with the Cr

and Cd as well as it has medium correlation with the Ni and Pb. This shows the when the concentration of Fe and Ni increases/ decreases the concentration of Cr, Cd increases/ decreases strongly and it also increases/decreases moderately as Ni and Pb increases/decreases. Ni has strong (perfect positive) correlation with Zn, its value is 1.00. This indicates that Ni/Zn has a good linearity in the sugarcane juice sample.

Table 9. Person correlation coefficients between heavy metals concentration in soil Sample

	Fe	Pd	Cr	Zn	Co	Ni	Cd
Fe	1.000						
Pb	0.3791	1.00					
Cr	0.3718	-0.2579	1.00				
Zn	-0.0348	0.4217	0.4433	1.00			
Co	-0.5553	0.6410	0.8359	0.8544	1.00		
Ni	0.5236	0.5642	-0.2782	0.1836	0.4519	1.00	
Cd	-0.7237	0.6161	0.9270	0.9019	0.6670	0.8071	1.00

According to Table 9, the correlation coefficients between metals in soil shows highest correlation between Co/Cr, Co/Zn, Cd/Cr, Cd/Zn, and Cd/Ni. Higher positive correlation between Co/Pb, Cd/Pd and Cd/Co. Medium positive correlation between Zn/Pb, Zn/Cr, Ni/Co, Ni/Fe, and Ni/Pb. The correlation coefficients between metals Pb/Fe and Cr/Fe in the soil sample have low positive correlation. The correlation coefficients between metal Zn/Fe and Pb/Cu in the soil have no correlation coefficient between them. All the correlation between Cr/Pd, Zn/Fe, Co/Fe, Ni/Cr and Cd/Fe has negative correlation.

Table 10.Paired -Samples T-test for soil and sugarcane juice

Heavy metals	Type of sample	Mean± SD	T-value	Significant
Fe	Soil	22975 ± 220	180	0.000
	Sugarcane juice	0.557 ± 0.008		
Pd	Soil	101 ± 3.82	45	0.000
	Sugarcane juice	0.033 ± 0.001		
Cr	Soil	129 ± 4.16	53	0.000
	Sugarcane juice	0.127± 0.002		
Zn	Soil	121 ± 3.94	214	0.000
	Sugarcane juice	0.020± 0.001		
Co	Soil	3.750 ± 0.087	71	0.000
	Sugarcane juice	0.026± 0.004		
Ni	Soil	7.0675 ± 0.104	293	0.000
	Sugarcane juice	0.026 ± 0.004		
Cd	Soil	14.740 ± 0.089	112	0.000
	Sugarcane juice	0.022 ± 0.004		

Paired -Samples T-test was made at 95% confidence level. The results showed that there were significant differences ($p < 0.05$) in the concentrations of all heavy metals (Fe, Pb, Cr Zn, Ni, Co and Cd) in soil and sugarcane juice samples.

4.7. Transfer Factor of Heavy Metals from Soil to Sugarcane

From Table 11 the distribution of heavy metals in sugarcane juice was Co> Ni> Cd> Cr> Pb> Zn> Fe. The TF value of all target heavy metals was less than one in all sample sites, which indicates that the poor response of the sugarcane plant towards heavy metal absorption and the sugarcane plant can be used for human consumption [12].

Table 11. Transfer factors from soil to sugarcane

Heavy Metals	Fe	Pb	Cr	Zn	Co	Ni	Cd
Transfer factor	0.000	0.013	0.039	0.006	0.384	0.147	0.059

4.8. Health Risk Assessments

4.8.1. Exposure Doses

The *ADD*s of HMs by different routes of exposure were derived using Eq. 9-12. The estimated daily carcinogenic and non-carcinogenic doses are presented in Tables 12 and 13, respectively. For all three non-dietary routes of exposure, the major exposure route was oral, followed by dermal, and then inhalation.

4.8.2. Characterization of Human Cancer Risks

The calculated ADDs for carcinogenic effects and cancer risks of different exposure routes are listed in Table 12. For non-dietary exposure, the ranking of total cancer risks of four HM was Pb> Cr> Cd> Ni. The most significant exposure route was oral, followed by dermal contact, and then inhalation. For drinking sugarcane juice, Cd and Cr posed the highest risks, which were much higher than the risk induced by oral intake of corresponding HMs and over the upper limit of the threshold of cancer risk $1.0x10^{-4}$ recommended by EPA (USEPA 2001), whereas the values for Pb and Cd were lower than the corresponding oral intake and dermal contact values. The low-risk values for Pb and Cd through juice consumption were attributed to their very low bioavailability in sugarcane juice. Overall, the total cancer risks induced by four different exposure pathways were juice drinking > oral intake > dermal contact> inhalation (Table 12).

4.8.3. Characterization of Non-carcinogenic Health Risks

The toxicological (non-carcinogenic) risks of HMs by three non-dietary exposure routes were identified as oral intake > dermal contact > inhalation. Iron (Fe) had the highest non-carcinogenic risk for all three non-dietary routes. For other HMs, the order of non-carcinogenic risks (high to low) for oral intake was Pb> Cr >Fe> Cd >Zn > Ni>Co. For dermal contact, it was Pb> Cr >Fe>Cd >Co Ni > Zn, for inhalation, it was Fe >Cr>Zn>Pb> Cd > Ni > Co, and for juice Pb>Cr> Fe>Ni >Co>Zn>Cd(Table 13). All the heavy metals are below the acceptance limit (1.0) (MEPC 2014). The sum of risks induced by three non-dietary exposures (HI) for each HM was calculated by Eq. (15) (Table 13) and compared with the non-carcinogenic risks of drinking sugarcane juice. Drinking sugarcane juice may lead to have higher overall non-carcinogenic risks. Moreover, the data also showed that the risk levels of juice drinking for all target heavy metals are almost similar to that of their corresponding non-dietary risks.

Table 12. Average daily doses (ADDs) and cancer risks of four heavy metals

Target metals	Average daily doses (mg/ kg/day)				Cancer risk			
	Oral	Inhalation	Dermal	Juice	Oral	Inhalation	Dermal	Juice
Pb	$0.30x10^{-5}$	$0.76x10^{-8}$	$0.50x10^{-6}$	$0.40x10^{-4}$	$0.12x10^{-4}$	$0.34x10^{-9}$	$0.25x10^{-7}$	$0.23x10^{-5}$
Cr	$0.36x10^{-5}$	$0.98x10^{-8}$	$0.64x10^{-6}$	$0.51x10^{-4}$	$0.20x10^{-5}$	$0.41x10^{-8}$	$0.36x10^{-6}$	$0.22x10^{-4}$
Cd	$0.40x10^{-6}$	$0.11x10^{-8}$	$0.70x10^{-7}$	$0.60x10^{-5}$	$0.61x10^{-5}$	$0.23x10^{-7}$	$0.13x10^{-5}$	$0.21x10^{-4}$
Ni	$0.20x10^{-6}$	$0.53x10^{-9}$	$0.30x10^{-7}$	$0.30x10^{-5}$	$0.18x10^{-6}$	$0.48x10^{-9}$	$0.27x10^{-5}$	$0.27x10^{-5}$

Table 13. Hazard quotients (HQ) of seven heavy metals

HMs	Oral	Inhalation	Dermal	Juice	HQ_{oral}	HQ_{inh}	HQ_{der}	HQ_{juice}
Fe	$0.65x10^{-3}$	$0.17x10^{-5}$	$0.11x10^{-3}$	$0.92x10^{-2}$	$0.13x10^{-2}$	$0.34x10^{-5}$	$0.22x10^{-3}$	$0.18x10^{-1}$
Pb	$0.30x10^{-5}$	$0.76x10^{-8}$	$0.50x10^{-6}$	$0.40x10^{-4}$	$0.10x10^{-1}$	$0.21x10^{-5}$	$0.13x10^{-3}$	$0.11x10^{-1}$
Cr	$0.36x10^{-5}$	$0.98x10^{-8}$	$0.64x10^{-6}$	$0.51x10^{-4}$	$0.12x10^{-2}$	$0.32x10^{-5}$	$0.21x10^{-3}$	$0.17x10^{-1}$
Zn	$0.39x10^{-5}$	$0.91x10^{-8}$	$0.60x10^{-6}$	$0.50x10^{-4}$	$0.13x10^{-4}$	$0.30x10^{-5}$	$0.20x10^{-5}$	$0.16x10^{-2}$
Co	$0.10x10^{-6}$	$0.28x10^{-9}$	$0.20x10^{-7}$	$0.20x10^{-3}$	$0.05x10^{-4}$	$0.14x10^{-7}$	$0.10x10^{-5}$	$0.10x10^{-2}$
Ni	$0.20x10^{-6}$	$0.53x10^{-9}$	$0.30x10^{-7}$	$0.30x10^{-5}$	$0.10x10^{-4}$	$0.26x10^{-7}$	$0.15x10^{-5}$	$0.05x10^{-2}$
Cd	$0.40x10^{-6}$	$0.11x10^{-8}$	$0.70x10^{-7}$	$0.60x10^{-5}$	$0.40x10^{-3}$	$0.11x10^{-5}$	$0.70x10^{-4}$	$0.60x10^{-2}$

It is evident from the data in Table 13, The ADD value of heavy metals as cancer by Oral (Pb> Cr > Ni > Cd), Inhalation (Cd >Pb >Cr > Ni), Derma (Pb> Cr > Ni> Cd) and Juice (Pb> Cr > Ni> Cd) whereas The ADD value of heavy metals as HQ in Table 13; Oral (Fe> Pb> Cr >Zn > Co >Ni> Cd), Inhalation (Fe> Cd> Co> Pb> Zn> Cr > Ni), Dermal (Fe> Pb> Zn> Cr > Co> Ni> Cd) and Juice (Fe> Co> Pb> Zn > Cr > Ni> Cd)

Target Hazard Quotient (THQ). The non-carcinogenic human health risk from the consumption of sugarcane juice contaminated by heavy metals and taken by three non-dietary exposure routes was estimated through the calculation of the target hazard quotient (THQ) as expressed under the methods section using Eq (13) and the data obtained are presented in Table 14. It is evident from the data in Table 14,The THQs of heavy metals by Oral (Fe> Cr> Pb> Zn> Co> Ni> Cd), Inhalation (Fe> Cr> Pd>Zn> Co> Cd>Ni), Derma (Fe> Cr> Pb> Zn> Co> Ni>Cd) and Juice(Fe> Cr> Pb> Co> Cd>Ni) are determined but all heavy metals in the three non-dietary exposure routes and Juice were below unity(<1). This indicated the potential non-carcinogenic human health risk due to the consumption of sugarcane juice and exposure routes generally presumed to be safe for the risk of non-carcinogenic effects.

Hazard Index (HI*)*. The hazard index, which considers the cumulative effect of the consumption of various potentially hazardous metals (elements) from the consumption of sugarcane juice and non-dietary exposure routes, has also been computed and the data is indicated in Table 12. Based on the data, Cr> Cd> Fe> Zn> Pd> Ni> Co. The HI (the sum of individual metals THQ for each exposure route) was found alarmingly less than unity (<1).So in this case there is no apparent health impact due to the metals considere

Table 14. the value of THQ and HI for target heavy metals

HMs	**THQ value**				**HI value**
	Oral	Inhalation	Dermal	Juice	
Fe	0.65	$0.17x10^{-2}$	0.11	0.92	$0.87x10^{-16}$
Pb	$0.08x10^{-2}$	$0.21x10^{-5}$	$0.13x10^{-3}$	$0.11x10^{-1}$	$0.55x10^{-16}$
Cr	$0.12x10^{-2}$	$0.32x10^{-5}$	$0.21x10^{-3}$	$0.17x10^{-1}$	$0.82x10^{-11}$
Zn	$0.20x10^{-3}$	$0.50x10^{-6}$	$0.30x10^{-4}$	$0.25x10^{-2}$	$0.79x10^{-16}$
Co	$0.05x10^{-4}$	$0.14x10^{-7}$	$0.10x10^{-5}$	$0.10x10^{-1}$	$0.39x10^{-21}$
Ni	$0.06x10^{-5}$	$0.18x10^{-8}$	$0.18x10^{-6}$	$0.10x10^{-4}$	$0.56x10^{-18}$
Cd	$0.08x10^{-5}$	$0.02x10^{-7}$	$0.14x10^{-6}$	$0.12x10^{-4}$	$0.18x10^{-15}$

Results of both cancer and non-carcinogenic health risk assessments show that drinking HM-contaminated sugarcane juice posed higher risks than the overall non-dietary exposures for the investigated HM and highlights the bio accumulative effects of HM in the soil environments of this region (Table 12 and 13). When considering non-dietary risks, the dominant factors are the environmental concentrations and toxicity of HM. For example, Pd and Cr possess high non-dietary risks because of their relatively high concentrations, whereas Fe had the highest concentration in our study, but possessed a low non-dietary risks due to low toxicity. The relationship between soil HM and the non-carcinogenic risks to humans through non-dietary exposure routes was examined to evaluate how factors such as HM in the environment (soil) can affect human health in the studied area through non-dietary pathways.

For dietary exposure (in this case, drinking sugarcane juice), the bioavailability of HM should be considered. For example, Cd had the lowest soil level but induced the highest cancer risk and the lowest non-carcinogenic risk in sugarcane juice. The high risk of Cd in the juice was likely attributed to its high bioavailability. The bioavailability of Cr was also high and posed a very high health risk following the consumption of contaminated sugarcane juice (the second highest for no carcinogenic risk) in the present study. In contrast, exposure to the other three

HMs with low toxicity (Fe, Zn, and Co) will likely pose a low risk following sugarcane juice drinking (table 13). The current study result shows that the bioavailability (from dietary exposure) and the toxicities of HMs depending on their soil concentrations can pose health risks to the human beings through different exposure pathways.So in this study as the data indicated that Cd has the highest toxic effect whereas Ni has the lowest toxic effect from the target metals.

5. CONCULUSION AND RECCOMENDATION

5.1. Conclusion

The concentrations of heavy metals in soil samples used for the cultivation of sugarcane in North Wollo Zone Sanka Irrigation farmland of the Amhara Regional State Ethiopia have been analyzed by inductively coupled plasma optical emission spectrometer (ICP-OES).The sequence of concentration of those analyzed heavy metals in soil was Fe> Cr>Zn> Pb> Cd>Ni> Co where as in sugarcane, Fe> Pd> Cr> Co>Ni> Cd>Zn.The level of heavy metals (Pb, Cr, and Cd) in soil and (Fe, Pb, Cr, Ni, and Co) in sugarcane juice were above the maximum tolerable levels set by FAO/WHO. Whereas, the level of heavy metals (Fe, Co, Ni, and Zn) in soil and (Zn and Cd) in sugarcane juice were below the maximum tolerable levels set by FAO/WHO.

The percentage of recovery lay between 89.4 to 105.2 % and 81.98 to 105% for sugarcane and soil samples respectively, which were with in the acceptable range for all heavy metals. The linearity of the calibration curves in each standard was acceptable since the correlation factors (R^2) are greater than 0.99 whereas the value of the method detection limit of each element is more or less higher than that of the instrumental detection and lower than the method of quantification. This confirms that the method was good and acceptable.

The correlation between Co with Pb, Fe, and Cr has a negative correlation, this indicates that when the concentration of Co increase in both sugarcane juice and soil the concentration of Pb, Fe, and Cr decreases and vice versa. Fe has the highest correlation with the Cr and Cd as well as a medium correlation with the Ni and Pb. This shows that when the concentration of Fe and Ni increases/ decreases the concentration of Cr, and Cd increases/ decreases strongly and it also increases/decreases moderately as Ni and Pb increase/decrease. Ni has a strong (perfect positive) correlation with Zn, its value is 1.00. This indicates that Ni/Zn has good linearity in the sugarcane and soil sample.

Health Risk assessments of soil HMs to individuals exposed through non-dietary routes and consuming locally grown sugarcane (juice) were conducted. Results indicated that the ranking for risks of HM exposure was juice drinking > non-dietary oral intake > dermal contact > inhalation. For non-carcinogenic risks, Cr and Cd in sugarcane juice posed the most significant risks, whereas As and Pb posed the highest risks through non-dietary exposure routes. For cancer risks, Pb in sugarcane juice posed the most significant risks, whereas Ni posed the lowest risks

through non-dietary exposure routes. The THQs of heavy metals by Oral (Fe > Cr >Pb> Zn > Co >Ni > Cd), Inhalation (Fe > Cr >Pd> Zn > Co > Cd > Ni), Derma (Fe> Cr>Pb> Zn > C> Ni> Cd) and Juice (Fe > Cr >Pb> Co > Cd > Ni) are determined but all heavy metals in the three non-dietary exposure routes and Juice were below unity(<1) and from the consumption of sugarcane juice and non-dietary exposure routes, Hazard Index of target metals Cr>Cd>Fe>Zn>Pd>Ni>Co. The HI (the sum of individual metals THQ for each exposure route was) found alarmingly less than unity (<1). So in this case there is no apparent health impact due to the metals considered. The study concluded that sugarcane grown on this farm is almost safe for human consumption in terms of the studied metals but, it is recommended that the level of heavy metals in the soil should be monitored to avoid unnecessary accumulation beyond the WHO safe limit.

5.2. Recommendation

Further study of the relationship between the heavy metal levels of the sugarcane plant and soil samples is recommended by taking a large number of sites and different methods to come up with a comprehensive conclusion. Additional investigation on soil pH, salinity, alkalinity, electrical conductivity and the nature of agricultural inputs like fertilizers, pesticides, and herbicides are also recommended. Generally, the following recommendations were made:

1) Since some heavy metals in sugarcane juice sample from the studding area were found to have high levels when which compared with WHO/FAO recommended, Farmers should be use fertilizers, pesticides and herbicides properly to monitored and avoid unnecessary accumulation beyond the WHO/FAO safe limit.
2) In addition, more studies should be done on the heavy metal concentration of sugarcane Bagasse and compared with the concentration in juice.
3) The current study indicated the transfer of heavy metals from soil to sugarcane plant only but not from water to sugarcane. So more studies should be done on the transfer of heavy metals from water to sugarcane.
4) It also recommended that to conduct a research for other types of agricultural products that are commonly produced in the studying area

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Appendix

Table S1 Working standard concentration, correlation coefficientand calibration equation of each metals.

Metals	Concentration of standards(mg/kg)	Correlation coefficient	Calibration equation
Pb	0.01,0.06,0.28,0.56,0.84,1.12,1.4	0.9968	*Y* = 901.52x-81.911
Cr	0.01,0.056,0.28,0.56,0.84,1.12,1.4	0.9976	*Y* = 6488.8x-81.911
Zn	0.2,0.3,0.4,0.5,1,2,2.5,	0.9999	*Y* = 33137x78.394
Co	0.01,0.06,0.13,0.19,0.64,1.28,1.92,	0.9957	*Y* = 9354.2x-192.78
Ni	0.01,0.06,0.13,0.19,0.64,1.28,1.92,	0.9967	*Y* = 5234 .6x-65.04
Cd	0.01,0.06,0.28,0.56,0.84,1.12,1.4	0.9973	*Y* = 16752x-18.9