The contents of essential and toxic metals in coffee bean and soil in Dale Woreda, Sidama Regional State, Southern Ethiopia

Yohannes Seifu Berego Corresp., 1 , **Solomon Sorsa Sota** 1 , **Mihret Ulsido** 2 , **Embialle Mengistie Beyene** 3

1 Biology, Hawassa University, Hawassa, Sidama Region, Ethiopia

2 Departement of Water Supply and Environmental Engineering, Institute of Technology, Faculty of Biosystems and Water Resources Engineering, Hawassa University, Hawassa, Sidama Region, Ethiopia, Hawassa University, Hawassa, Sidama Region, Ethiopia

3 Environmental Health, Hawassa University, Hawassa, Sidama Region, Ethiopia

Corresponding Author: Yohannes Seifu Berego
Email address: yohannesseifu@hu.edu.et

Background: For developing countries like Ethiopia, coffee is a commodity of great economic, social, and environmental importance. There are no detailed investigations performed on the contents of essential and toxic metals in coffee bean and soil in this study area. **Methods:**The levels of essential metals (Na, K, Ca, Zn, Mn, Cu, Co, Cr, Ni), and toxic elements (Pb and Cd) were investigated in coffee beans (coffee growing farmland and coffee washing plants) and soil samples (from farmland) using Flame Atomic Absorption Spectrometer (FAAS) and flame emission atomic spectroscopy. We selected 6 (20%) of administrative units (Kebele) with purposive sampling technique based on their coffee production capacity in Dale Woreda for the soil testing. After coffee sample preparation in Microwave system with $HNO_3$and H_2O_2reagents, the accuracy of the optimized procedure was evaluated by analyzing the digest of the spiked samples. Soil samples were abridged accompanying slight revision of EPA 3050B acid digesting method. ANOVA was used to determine the significant differences in the mean concentration of metal within coffee bean from farmland at the various sampled sites at $p< 0.05$ significant level. To correlate the effect of one metal concentration on other metal in the coffee beans samples, the Pearson correlation matrices were used. **Results:**Calcium had the highest concentration (1355±18.02mg kg^{-1}) of macro elements in soil samples, followed by K (681.43±1.52mg kg^{-1}).Similarly, Na (111.63±0.35 mg kg^{-1}), Cu (49.96±0.99mg kg^{-1}), Co (5.43±0.31 mg kg^{-1}), Mn (0.62±0.238mg kg^{-1}), Ni (0.194±0.01mg kg^{-1}), and Zn (0.163±0.007mg kg^{-1}) were detected among the microelements in soil samples. Pb, and Cr were not detected in all soil sample. Potassium (K) was found to have the highest concentration (99.93±0.037mg kg^{-1}) followed by Ca (17.23± 0.36 mg kg^{-1}) among the macro elements in coffee beans from farmers' farms. Like coffee beans from farmland, samples from washing plants also contained highest K (77.93±0.115mg kg^{-1}), followed by Ca (4.33±0.035 mg kg^{-1}). Metal levels in coffee bean samples from farmland are in the following order: K>Na>Ca >Mn>Cu> Ni>Zn. Metal levels were found to be K>Na>Ca >Mn>Cu> Zn>Ni in coffee beans from the washing plants. Co, Cr, Pb and Cd were not detection in all coffee bean samples. Except for calcium, potassium and manganese, the levels of metals in coffee beans from farmland and washing plants were not significantly different at 95% confidence level within a kebele. **Conclusions:**We observed permitted levels of macro and trace elements in coffee beans from farmlands and washing plants. Only in the soil samples, cadmium concentrations are higher than those permitted for agricultural soil recommended by WHO and FAO. Overall, there is no health danger linked with the use of coffee beans due to detrimental and trace heavy metals.

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Yohannes Seifu Berego[1], Solomon Sorsa Sota[2], Mihret Dananto Ulsido[3, 5], Embialle Mengistie Beyene [4]

[1] Biology, Hawassa University, Hawassa, Ethiopia
[2] Biology, Hawassa University, Hawassa, Ethiopia
[3] Departement of Water Supply and Environmental Engineering, Institute of Technology, Faculty of Biosystems and Water Resources Engineering, Hawassa University, Hawassa, Ethiopia
[4] Departments of Environmental Health, Hawassa University, Hawassa, Ethiopia
[5]Center for Ethiopian Rift Valley Studies (CERVaS)

Corresponding Author:
Yohannes Seifu Berego[1]
Atote, Hawassa, Sidama Region, 05, EthiopiaEmail address: yohannesseifu@hu.edu.et.

Abstract

Background: For developing countries like Ethiopia, coffee is a commodity of great economic, social, and environmental importance. There are no detailed investigations performed on the contents of essential and toxic metals in coffee bean and soil in this study area.

Methods: The levels of essential metals (Na, K, Ca, Zn, Mn, Cu, Co, Cr, Ni), and toxic elements (Pb and Cd) were investigated in coffee beans (coffee growing farmland and coffee washing plants) and soil samples (from farmland) using Flame Atomic Absorption Spectrometer (FAAS) and flame emission atomic spectroscopy. We selected 6 (20%) of administrative units (Kebele) with purposive sampling technique based on their coffee production capacity in Dale Woreda for the soil testing. After coffee sample preparation in Microwave system with HNO_3 and H_2O_2 reagents, the accuracy of the optimized procedure was evaluated by analyzing the digest of the spiked samples. Soil samples were abridged accompanying slight revision of EPA 3050B acid digesting method. ANOVA was used to determine the significant differences in the mean concentration of metal within coffee bean from farmland at the various sampled sites at $p< 0.05$

significant level. To correlate the effect of one metal concentration on other metal in the coffee beans samples, the Pearson correlation matrices were used.

Results: Calcium had the highest concentration (1355±18.02mg kg^{-1}) of macro elements in soil samples, followed by K (681.43±1.52mg kg^{-1}).Similarly, Na (111.63±0.35 mg kg^{-1}), Cu (49.96±0.99mg kg^{-1}), Co (5.43±0.31 mg kg^{-1}), Mn (0.62±0.238mg kg^{-1}), Ni (0.194±0.01mg kg^{-1}), and Zn (0.163±0.007mg kg^{-1}) were detected among the microelements in soil samples. Pb, and Cr were not detected in all soil sample. Potassium (K) was found to have the highest concentration (99.93±0.037mg kg^{-1}) followed by Ca (17.23± 0.36 mg kg^{-1}) among the macro elements in coffee beans from farmers' farms. Like coffee beans from farmland, samples from washing plants also contained highest K (77.93±0.115mg kg^{-1}), followed by Ca (4.33±0.035 mg kg^{-1}). Metal levels in coffee bean samples from farmland are in the following order: K>Na>Ca >Mn>Cu> Ni>Zn. Metal levels were found to be K>Na>Ca >Mn>Cu> Zn>Ni in coffee beans from the washing plants. Co, Cr, Pb and Cd were not detection in all coffee bean samples. Except for calcium, potassium and manganese, the levels of metals in coffee beans from farmland and washing plants were not significantly different at 95% confidence level within a kebele.

Conclusions: We observed permitted levels of macro and trace elements in coffee beans from farmlands and washing plants. Only in the soil samples, cadmium concentrations are higher than those permitted for agricultural soil recommended by WHO and FAO. Overall, there is no health danger linked with the use of coffee beans due to detrimental and trace heavy metals.

Introduction

According to International Coffee Organization (ICO) (2021), coffee is the third most consumed beverage in the world after water and tea, and it is the world's second most traded commodity after oil. Various literature reports have taken note of the importance of moderate consumption of coffee on human health through the regulation of the level of sugar in the blood, as well as prevention of diseases of the circulatory system and digestive system, cancers, and Parkinson's and Alzheimer's diseases (Tan et at., 2007, Kotyczka et al., 2011).

Coffee is a commodity of great economic, social and environmental importance in Ethiopia (Gure et al., 2017) According to data from Ethiopian Tea and Coffee Authority(2022), Ethiopia exported 300,000 metric tons of coffee in 2021, bringing in $1.4 billion and accounting for almost 30% of all export revenue and supporting the livelihoods of over 25% of its population (Tefera and Tefera, 2014). According to ICO (2021), Ethiopia ranks fifth in the world as a coffee producer and exporter after Brazil, Vietnam, Colombia and Indonesia and is the third largest consumer, after Brazil and Indonesia (ICO, 2021). The Ethiopian output in 2020 reached 7.375 million bags (of 60 kg each) of processed coffee, nearly 4.3% of the global production (ICO, 2021).

Heavy metals by definition are metallic elements which have a high atomic weight and have much high density at least 5 times that of water. They are stable elements i.e. they cannot be metabolized by the body and bio-accumulative i.e. passed up the food chain to humans. Even at very low concentrations, they are highly toxic and can cause damaging effects (Mohiuddin et al., 2011). However, essential elements are those which even in small amount play important roles as far as healthy animals or plant life is concerned. Essential elements are vital for life (Beasley et al., 2000). Heavy metal contamination is a global hazard that began with the industrial revolution, resulting principally from performing farming practices through application of organic fertilizers, minerals and pesticides to the agricultural soil (Carolin et al., 2017, Hejna et al., 2018) , rapid industrialization and urbanization and the disposal of untreated and/or partially treated effluents from various industries, the pollution level has reached alarming situation in Ethiopia with increasing metal levels and deterioration of agricultural soil quality (Ftsum and Abraha, 2018). The stability of soil and water is impacted by the pollution of heavy metals (Kobielska et al., 2018), resulting in environmental (Bello et al., 2018) and public health problems (Reyes et al., 2016).

Metal toxicity results when our body intake of excess amounts through supplements, food and water (Ibrahim et al., 2006). Heavy metal exhibits specific toxic effects on human beings, damage to kidney, liver, lung, blood cells, mental and central nervous systems (Dorne et al., 2011, Winiarska-Mieczan et al., 2021). Chronic exposure can lead to a gradual increase in neurodegenerative processes, which is related to diseases such as multiple sclerosis and Alzheimer's disease (FAO, 2011, Butt and Sultan, 2011). The heavy metals are toxic even in very small amounts such as arsenic, cadmium , chromium, nickel, and mercury are classified as category one (1) carcinogens, as they increase cancer risk in humans even with mild to moderate exposure (Jaishankar et al., 2014, Kim et al., 2015).

Recent research shows some of our favorite coffee brews can be laced with contaminants and quite a number of studies have been conducted in the whole world to determine the levels of essential and toxic elements in coffee bean (Gure et al., 2017, Feleke et al., 2018, Rubio et al., 2019, Albals et al., 2021, Dubale, 2021). Another researcher have been conducted to determine heavy metal accumulation in beans of cacao (Takrama et al., 2015 ,Bertoldi et al., 2016 ,Aguirre-Forero et al., 2020). Previous studies have also assessed the levels of hazardous components in grains from various countries (Meharg et al., 2013, TatahMentan et al., 2020). Transfer of metals from soil to the coffee beans or other crop products, such as cacao, grains can is absorbed by plants, where they can either store them in the roots or move them into the shoots and grains (Silva et al., 2007). When metals get to the coffee beans, they become the sources of contamination for people, causing harmful health effects such as significantly reduced neurological and hepatic functioning, mutagenesis, and carcinogenesis (Matés et al., 2010).

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Sidama coffee beans are well-known on the global market for their superior quality. Due to this, Sidama coffee bean prices and consumption have increased over the past few years. (Gelaw, 2019).There have been studies before on the determination of metals in coffee bean, but these had different in scope, such as coffee beans samples were taken from farmer's farms and coffee washing industries. To the best of our knowledge, there are no detailed investigations performed on the contents of essential and toxic metals in coffee bean and soil in Dale Woreda, Sidama Regional State. Moreover, the knowledge gap on the contents of essential and toxic metals in coffee bean and soil needs to be filled. Therefore, the aim of this study is to investigate the contents of essential and toxic metals in coffee bean and soil in Dale Woreda, Sidama Regional State, Southern Ethiopia

which were

Materials & Methods

Description of the Study Area

This study was carried out in Dale Woreda, Ethiopia. Geographic location of Woreda is between Latitude 6° 41' 35" north and Longitude 38° 21' 17" east. The capital town of Dale woreda is Yirgalem, which is located 45 km from Hawassa. The southern, western, northern, and eastern borders of Dale are formed by Aleta Wendo and Chuko, Loka Abaya, Boricha, Shebedino, and Wensho. Dale Woreda's elevation along the Lake Abaya shoreline varies from 1200 meters above sea level to around 3200 meters at its westernmost point. Rivers include the Gidabo. Coffee is an important cash crop in Dale, with 17.38 square kilometers planted with this crop, which produced a total of 12.3 million kilograms of beans in 2020/21. Industry in this Woreda includes 51 coffee pulpers (DWFEDO, 2021). Farming chemicals are being utilized in agricultural operations more frequently, possibly to increase yields. The range of the average yearly temperature is between 9.6°C and 29.2°C. There are two rainy seasons in the area, with the first peak being in April–May and the second from August–October. The least amount of rain fell between November and February. The area receives 1102 mm of rain on average yearly. Agroforestry practices appear to be the main features of the land use systems in the region. The main constituents of coffee are caffeine, tannin, fixed oil, carbohydrates, and proteins. It contains 2–3% caffeine, 3–5% tannins, 13% proteins, and 10–15% fixed oils.

Sample collection

For this study, out of the 32 Kebele Administrations in Dale Woreda, only 20% were selected, which included six which was six Kebele . Coffee beans were collected from farmer's farms with its supporting soil from six kebele which are Kege (SS1),Wenenata (SS2), Gane (SS3), Wondo (SS4), Bera (SS5), and Megara(SS6) of Dale woreda using a grab sampling method. In order to get coffee bean samples, eight farmers from one kebele were chosen based on how much coffee they could produce. Following that, a minimum of five coffee plants from a farm with a single farmer were used for sampling. Finally, the entire samples were homogenized to create a single sample of coffee beans that is indicative of a single kebele. The accumulated seize samples have been blended to form a composite sample to end up the representative sample of the bulk. For sampling coffee beans, red cherries harvested during their peak season had been carefully chosen and collected. To make pulping and grading easier, solely ripe crimson cherries have been collected, (i.e. the entire cherry after harvest is first cleaned to separate the unripe, overripe and damaged cherries and to get rid of dirt, soil, twigs and leaves). Using stainless steel forceps, the soil samples were cleansed. The outer layers of the coffee cherry were also removed. Wash the green coffee beans that have been separated from their outer coat with tap water before washing them with deionized water to reduce contamination. The samples were sealed in polythene bags. Coffee washing plant, on the other hand, has been chosen based totally on the following manner: In the chosen six Kebele there were 13 coffee washing plants. One coffee washing plant/ industry was purposively chosen from a single Kebele. For this study a total of six coffee processing plants were selected. All coffee processing industry in Dale Woreda was used wet processing consists of the following steps: Sorting & Cleaning, Pulping, Fermentation, Coffee washing and drying. By submerging them in water, coffee cherries are sorted. The excellent, mature fruit will sink while the bad, unripe fruit will float. Cherry skin and some pulp are removed by pressing the fruit mechanically through a screen in water. There will still be a substantial amount of pulp stuck to the bean that needs to be removed. This is accomplished either by a more recent technique known as machine-assisted wet processing. The remaining pulp is removed in the ferment-and-wash method of wet processing by causing the cellulose to break down while the beans are fermented with bacteria and then thoroughly washed. To obtain samples of coffee beans from washing plants, the washing company left the coffee beans to dry on beds after washing them, and we used those samples for sampling. All the samples were taken in triplicate.

The soil samples had been amassed from the root of the sample coffee plant from which the coffee beans was collected. Soil samples have been collected from the floor 15cm- 25cm under each sampled coffee plant (Csuros and Csuros, 2002). Because the find out about is looking into the uptake of vital and non-essential metals by coffee plants, samples have been taken from the complete place where the plant's root system penetrates. Finally, the samples had been accrued into non-reacting polyethylene bags and carefully blended to make one composite pattern for each Kebele, which was once then delivered to the laboratory.

Preparation of coffee bean samples

On a firm, flat, easy surface, such as raised tables, the accumulated coffee cherries have been dried in direct sunlight. Drying had been used to eliminate moisture from the coffee bean in a slow continuous technique as it takes up to 4 weeks earlier than the cherries were dried to the greatest moisture content, relying on the climate conditions. ''The beans are then removed from the dried husk. After grinding the dried coffee beans, 50 g were used for analysis. Finally, the powdered coffee bean samples were stored in polyethylene plastic luggage and stored in desiccators containing calcium chloride to maintain to constant dry weight until digestion'' (Mitra, 2003). Sample taken from washing plants were also prepared in the same way as the beans from farmland.

Preparation of soil samples

Any visible plant remnants were removed, and the soil samples had been air dried and homogenized. The dried soil samples were ground and sieved via using two mm nylon sieves.

2mm

The total amount of soil samples gathered from a single Kebele furnished over 500 g of sieved soil, of which 50 g have been used for chemical analysis. Before chemical analysis, ''the sieved soil pattern had been further dried in an oven at 50°C for one and 1/2 hour to make its moisture content material uniform. Finally the samples had been saved in sealed polythene and saved in desiccators containing calcium chloride to keep to regular dry weight until digestion'' (Mitra, 2003).

Optimization of digestion conditions

Different microwave digestion techniques were used in an effort to obtain a clear and colorless coffee digest solution that was adequate for FAAS analysis. HNO_3 and H_2O_2 volume, microwave digestion temperature, and digestion duration were the main factors. The three aforementioned factors were changed one at a time to create a total of 20 trails. The best digestion method was chosen based on the following factors: the clarity of the digests (solution free of residue and suspended materials), the smallest reagent volume, the shortest microwave digestion time, and the highest temperature. The developed optimum digesting conditions for coffee bean samples were presented in (**Table 1**).

Digestion of coffee beans

For the evaluation of the concentration of elements using flame atomic absorption spectroscopy and flame emission atomic spectroscopy methods, samples of coffee require to be solubilized. This sample preparation step mostly aims at reducing matrix effects originating from organic compounds and releasing elements in the form of their simple ions (Castro et al., 2009). Literature procedure used for the digestion of coffee powder (Suseela *et al*., 2001) was used with slight modification. 0.3 g of bean powder used to be introduced to a 250 mL spherical bottom flask. The vessels were then put on the turntable of the microwave system after being pre-digested for 10 minutes in a fume hood with 7 mL of HNO_3 68% w/w conc. and 2 mL of H_2O_2 conc. Finally, the sample was digested at the optimum conditions. For each bulk sample, the digestion was done three times. In parallel to the digestion of the samples, the same method was used to digest a reagent blank while maintaining all other digestion settings. Six blanks had been digested for beans samples. The digest used to be allowed cooling at room temperature. 0.1% $LaCl_3.7H_2O$ w/v was once introduced to the digested solution to get rid of the chemical interference of Ca and Na ions. 0.1% $LaCl_3.7H_2O$ w/v was once introduced to the digested solution to get rid of the chemical interference of Ca and Na ions and the answer used to be then stuffed to the mark (25 mL) with deionized water. Triplicate digestions were carried out for each sample. The solutions were stored in the refrigerator until analysis.

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Digestion of soil samples

For digestion of soil samples the EPA 3050B (Epa US, 1996) method used to be applied. ''The system used for the digestion of soil sample was once as follows: at first 1:1 ratio of HNO_3 and H_2O (deionized) were prepared. Of which 10 mL have been added in a digestion vessel containing 500 mg of the dried and sieved soil sample. Finally, after completion of digestion with HNO_3, H_2O_2 and HCl, had been allowed to cool, filtered via Whatman No. 42 filter paper and the ensuing clear light yellow answer were made up to 50 mL with deionized water'' (EPA, 1996). Reagent blanks used to be additionally prepared and digested with the same procedure as that of soil sample. All the solutions were stored in tightly capped polyethylene bottles and stored in a refrigerator until evaluation (EPA, 1996).

Calibration procedure and determination of metals

For the purpose of figuring out the metal concentrations in soil and coffee bean sample solutions, calibration curves were prepared. The calibration curves for each metal were created using diluted stock standard solutions containing 1000 mg/L each of the following metals: Ca, Cd, Co, Cu, Cr, K, Mn, Na, Ni, Pb and Zn in 2% HNO_3.Contents of the metals in coffee bean and soil samples was made by using FAAS and flame emission atomic spectroscopy. To avoid loss through ionization, the concentration of Na and K was determined by emission mode of the instrument. The same analytical approach was used to determine the elements in blank solutions and three replicate determinations for each metal were conducted.

Method validation

Method validation is the process used to confirmation by examination and provision of objective evidence that the particular requirements for a specific intended use are fulfilled. ''Results from method validation can be used to judge the quality, reliability and consistency of analytical results; it is an integral part of any good analytical practice'' (Ajay and Rohit, 2012, Magnusson.B and Örnemark.U, 2014). Since there were no approved standard reference materials available, the approach was validated using spiking. Four flasks containing samples of coffee beans were spiked. In four different flasks, 0.3 g of coffee bean powder sample was taken. 200 mL of 1000 mg/L Ca were spiked into the first flask. The second flask was spiked with 1500 L of the same K concentration as the first flask. 25 L of 10 mg/L Cu, Mn, and Zn were spiked into the third flask. In the fourth flask 15 μL of 10 mg/L of Ni, Co and Cr was spiked. All the spiked samples were digested in triplicate following the optimal digestion procedure developed for coffee bean samples.

Analysis of samples for metals

After the parameters such as burner and lamp alignment, slit width, and wavelength adjustment were optimized for the maximum signal intensity of the instrument, the elements were determined as previously described in Amente Lema (2016), specifically by using flame atomic absorption spectroscopy and flame emission atomic spectroscopy with an external calibration curve. Each metal's hollow cathode lamp was put into the atomic absorption spectrophotometer, which allowed the solution to be inhaled into the flame one at a time. To avoid loss via ionization, the attention of Na and K used to be decided with the aid of flame emission atomic spectroscopy. Calibration curves have been organized to decide the concentration of the metals in coffee bean and soil pattern solutions. Calibration standards are made for each of the following metals using stock standard solutions (Buck Scientific purographics calibration standards, USA) containing 1000 mg/L of each metal. The elements Na, K, Ca, Zn, Mn, Cu, Co, Cr, Ni, Pb, and Cd were among those used. A 10 mg/L intermediate standard was produced from them.

Calculation of Bioaccumulation.

Bio-concentration factor (BCF);-It has been defined that bio-concentration factor is the ratio of heavy metal concentration in edible part of the plant to heavy metal concentration in soil sample(Rattan et al., 2005, Sharma et al., 2018). Accordingly, heavy metal transfer from soil to plant was calculated as by the formula used by (Kachenko and Singh, 2004) and given in Eq (1).

$$\mathrm{BCF} = \frac{\text{heavy metal content in plant}}{\text{heavy metal content in respective soil}} \quad \ldots\ldots\ldots\ldots\ldots\ \text{Eq (1).}$$

The value of BCF greater than 1 indicates that the plant is a potential accumulator for the metal being considered for analysis(Barman et al., 2000).

Data analysis

An analysis was done using SPSS version 24 ANOVA was used to determine the significant differences in the mean concentration of metal within coffee bean from farmland at the various sampled sites at $p< 0.05$ significant level. Additionally, t-tests had been performed in order to check whether there was difference in metals concentration between coffee beans from farmland and washing industries. Finally, to correlate the effect of one metal concentration on the concentration of the other metal in the coffee beans samples, the Pearson correlation matrices using correlation coefficient (r) for the samples were used.

Results

Metal concentration in soil samples

The highest mean Ni concentration (0.194±0.009 mg kg^{-1}) was recorded in soil sampled from Kege Kebele (**SS1**) and the lowest (0.172±0.002mg kg^{-1}) was recorded in Bera Kebele (**SS5**). (**Table 2**).The highest mean Zn concentration (0.163±0.007mg kg^{-1}) was recorded in soil sampled from SS1 and the lowest (0.141±0.001mg kg^{-1}) was recorded in SS3. The mean Co concentration was reported in two sites: 5.43±0.305mg kg^{-1} in soil samples from SS1 and 4.27±0.20 mg kg^{-1} at SS2. The highest mean Cu concentration (49.96±0.99mg kg^{-1}) was recorded in soil sampled from SS3 and the lowest (22.34±0.25mg kg^{-1}) was recorded in SS4.

Cadmium levels in the soil shown in Table 2, the mean concentration of Cd varied between 2.38 ±0.044 and 3.36±0.1 with the highest in the sample from SS1 and the lowest from SS4. Calcium had the highest concentration (1355±18.02mg kg^{-1}) of macro elements in all soil samples, followed by K (681.43±1.52mg kg^{-1}) and Na (111.63±0.35 mg kg^{-1}).Similarly, Cu (49.96±0.99mg kg^{-1}) as detected in greater abundance among the microelements, followed by Mn (0.62±0.238mg kg^{-1}), and Zn (0.163±0.007mg kg^{-1}). Co>Cd>Ni was assigned to the remaining trace metals (Table 2). In soil samples from six kebeles, metals such as Pb, and Cr were found to be not detected. Kege Kebele soil sample analysis shows that, Ca (1355±18.02mg kg^{-1}) was the highest from the examined metals. K and Na were traced in highest concentration next to Ca with concentration of 673±2.65mg kg^{-1} and 111.63±0.35mg kg^{-1}, respectively.

Out of the analyzed microelements, Cu (42.66±2.52 mg kg^{-1}) was found to be in highest amount followed by Co (5.33±0.305 mg kg^{-1}) and Mn (0.62±0.238mg kg^{-1}). Similarly, the levels of Cd, Ni and Zn were 3.1±0.1mg kg^{-1}, 0.191±0.009 mg kg^{-1} and 0.161±0.007 mg kg^{-1}, respectively. The average metal concentrations in the kege soil were determined to be in the following order: Ca>K>Na>Cu>Co>Cd> Mn>Ni>Zn (**Table 2**).

Pearson's correlation coefficient was used to examine the correlations between the contents of different elements in soil. The analysis revealed that there were significance ($p<0.01$, $p<0.05$) positive correlation between heavy elements; Cd-Zn (r=0.511), Cd-Ca (r=0.507), Cd-Na(r=0.81), Cd-K (r=0.57), Ni-Co (r=0.882), Zn-Co (r=0.469), Cu-Ca (r=0.537), Ca-Na (r=0.652), Na-K (r=0.69); all have positive correlations (**Table 3**). Other's correlations were insignificant, such as Cd with Ni, Co, Cu, Mn, and K ,Ni found to be non-significant with Zn, Cu, Ca, Mn, and K ,Zn also found to be non-significant with Cu, Ca, Mn, Na and K,Cu found to be non-significant with Mn ,Na and Similarly Ca found to be non-significant with Mn and K .Likely Mn found to be non-significant with Na and K indicating that the concentration of one element may not have an impact on the concentrations of other elements in the study area. The positive correlation between Cd with Zn, Ca, Na and K indicates correlation among the metals in coffee beans. The rise in levels of Cd increases the tendency of Zn, Ca, Na and K to increase.

Metals in coffee bean sample from farm land

Potassium (K) was found to have the greatest concentration (99.93±0.04mg kg^{-1}) among the macro elements detected in coffee beans from all sampling farm land sites (Kege, Wenenata, Gane, Wondo, Bera, and Magara). The finding of the present study revealed that Na and Ca were also detected in significant amounts in coffee bean sample from farmers' farms, with concentrations of 22.04 ±0.042 mg kg^{-1} and 17.23± 0.36 mg kg^{-1}, respectively. The highest concentrations observed for Manganese in this study was 0.927±0.004mg kg^{-1} (**Table 4**). The highest concentration of Ni (0.074±0.003 mg kg^{-1}) reported in coffee bean from farmland. Zinc concentration in the samples analyzed ranged between 0.054-0.076mg kg^{-1}.wheras, Copper concentration in the in the present study ranged between 0.14-0.28mg kg^{-1} In coffee beans of the selected study site, Pb ,Co, Cr, and Cd was not found (**Table 5**).

In coffee beans from Kege farmer's farms, Mn was determined to be the most abundant minor element, followed by Cu, Zn and Ni. Likewise the levels of Cu (0.22 ± 0.0026 mg kg^{-1}) and Zn (0.073 ± 0.003 mg kg^{-1}) were higher than that of Ni (0.055 ± 0.004 mg kg^{-1}).Except for Pb, Cd ,Co and Cr, which had not detected in coffee bean, all kinds had equal minor element concentrations. In farmer's coffee beans from Wenenta, Wondo, Gane, Bera, and Magara Kebele, nearly the matching dissemination pattern of elements was detected as in Kege Kebele (**Table 5**).

Bio-concentration factor of trace metals from soil to Coffee bean/ Transfer factor

Mn had the highest bio-concentration factor/transfer factor (1.495) among the elements examined. However, among the examined samples, Cu had the lowest transfer factor (0.0048), which is at the Magara locations (SS6). In Kege Kebele (SS1), the overall transfer pattern for trace metals was Mn > Zn > Ni > Na> K > Ca > Cu (**Table 6**). This demonstrates unequivocally that Mn bioaccumulation factors were higher in coffee samples than for other metals.

Metals in coffee bean sample from washing industry.

The beans from Megara coffee washing industries, similar coffee beans from farmlands, have the maximum amount of K (77.93±0.115mg kg^{-1}), followed by Na (10.47±0.058mg kg^{-1}) and Ca (3.55±0.114mg kg^{-1}). In the washing industry's beans, Mn (0.92±0.001mg kg^{-1}) was the highest accumulated trace metal, followed by Cu (0.277±0.011 mg kg^{-1}) and Zn (0.094±0.004 mg kg^{-1}). Other critical trace metal concentrations found in coffee beans were Ni (0.074±0.003 mg kg^{-1}). The results show that the concentrations of Co, Cr, Pb and Cd were not detected. The dissemination of elements in coffee beans from all six Kebele's washing plants trails the same trend, as illustrated in (**Table 7**). One-way ANOVA showed, the results of metal concentration showed that significant differences were found ($p > 0.05$) at 95% confidence levels for Ca ,Cu ,Mn and Ni in coffee samples collected from all washing plants. Maximum allowable limits of heavy metals in coffee beans were not found in the literature. As a result, standards for other foods and herbal plants were used to compare (**Table 8**). The results in Table 9 show that the elements content found is more or less analogous to levels published in the literature (**Table 9**).

Except for Ca and K in Kege Kebele, Mn in Bera Kebele, Ca and K in Wenenata, K in Gane, Wodo and Megara Kebele, entirely other measured elements are not significantly different($p> 0.05$) in coffee beans from farmlands and washing plants, according to the findings(**Table 10**).

Discussion

Concentration of Ni (0.194±0.009 mg kg^{-1}) soil sampled of the present study is much lower (8.33 ± 0.55mg kg^{-1}) than that reported in Ethiopian farms where coffee is grown(Dubale, 2021). This difference might be to the use of diverse farming practices, as well as geographical, meteorological and geological differences between the study areas likewise, It may be more common in the Gedeo zone to apply livestock manure to agricultural soil, which could be the cause of the soil's high Ni concentration (Basta et al., 2005, Hejna et al., 2019). Similarly, the finding of the present study was much lower than reported Ni (5.1 ± 3.8mg kg^{-1}) in agricultural land in Kenya (Ndungu et al., 2019) , reported Ni (133.1mg kg^{-1}) in Brazil farm where coffee is grown (Tezottoa et al., 2012) and reported Ni (1.92 ± 1mg kg^{-1}) from Brazilian coffees cultivated area(Santos et al., 2009). .However, the finding of the present study, was much higher (0.05 mg kg^{-1}) than that reported in the Western Ghats,India (Raghavendra and Venkatesha, 2020) . This is owing to the use of diverse farming practices, as well as geographical, meteorological and geological differences between the study areas. Moreover, the application of livestock manure for the agricultural soil is the common practice in the study areas and it could be the possible reason for high Ni concentration in the soil (Basta et al., 2005). The Ni levels analyzed were below permissible limit set by FAO/WHO, 2001 (50.00 mg kg^{-1}) thereby these soil are free of its contamination.

The finding of the present study revealed that the concentration of zinc in soil sampled was lower (52.5 ± 6 mg kg^{-1}) than that reported in Brazil(Santos et al., 2009), reported Zn (83.0 ± 33.5mg kg^{-1}) concentration (Tozottoa et al,. 2012), reported Zn (10.0 ± 3.1mg kg^{-1}) concentration in agricultural land in Kenya (Ndungu et al., 2019) and Zn (47.14 ± 2.51mg kg^{-1}) from Gedeo Zone, Ethiopia (Dubale, 2021). On the other hand, the present study finding much higher than reported Zn was (0.05 mg kg^{-1}) the Western Ghats Region,India (Raghavendra and Venkatesha, 2020). These changes in the concentration of heavy metals could be explained by the regular practice in the study area of applying livestock manures to agricultural soil(Basta et al., 2005, Hejna et al., 2019).The mean concentration of Zn in soils from all sample sites were below permissible limit set by FAO/WHO, 2001 (1000 mg kg^{-1}).this indicates that the soil from all sample sites safe for agriculture with regard to the pollution of zinc.

The highest mean Co concentration of the present study (5.43±0.305mg kg^{-1}), Contrary to other Ethiopian research's findings, the amount of cobalt in the present study was lower than the national average (11.66 ± 0.78 mg kg^{-1}) concentration obtained in Gedeo zone, Ethiopia (Dubale, 2021). However, the finding of the present study was higher than Co (3.57 mg kg^{-1}) concentration reported Kaduna State, Nigeria (Oladeji and Saeed, 2015). This could be due to anthropogenic sources of contamination, such as the widespread use of manure, herbicides, fungicides, and fertilizers, which are high in Co as suggested by (Yasmeen et al., 2010).

Concentration of Cu (49.96±0.99mg kg^{-1}) in soil sampled of the present study, which is much lower (76.9 ± 1.34mg kg^{-1}) than that reported in Ethiopian farms where coffee is grown (Dubale, 2021). However, the concentration of Cu reported by the present study, is much higher (7.10 ± 0.30mg kg^{-1}) than that reported in Brazilian coffees (Santos et al., 2009), reported Cu (36.8 ± 5.9 mg kg^{-1}) concentration in Brazil farm where coffee is grown (Tezottoa et al., 2012), and Cu (0.26 ± 0.17) in agricultural land in Kenya (Ndungu et al., 2019). Numerous variables, such as air deposition from vehicle emissions or heavy traffic along the Hawassa-Moyale road, could be to cause for the heightened Cu concentration (Szwalec et al., 2020). Furthermore, coffee species, geographic origin, coffee variation, usage of fertilizers with various chemical compositions, and other differentiating elements all have a substantial impact on the actual metal content of coffee beans (Kamal et al., 2008). Copper concentration levels reported in this study were below the permissible limits for agricultural land use of 300mg kg^{-1} (FAO/WHO, 2001) implying that there was no Cu contamination in the soil.

In this study, the highest mean Cd concentration was (3.36±0.1mg kg^{-1}), which is much lower (124.3mg kg^{-1}) than reported by previous study (Tezottoa et al., 2012).However, higher than (0.1 ± 0.03mg kg^{-1}) reported in agricultural land of Keniya (Ndungu et al., 2019); Cd (0.001 ± 0.0009 mg kg^{-1}) reported in the Western Ghats Region, India (Raghavendra and Venkatesha, 2020). On the other hand, values reported for Cd (3.49 ±0.26mg kg^{-1}) by previous study (Dubale, 2021) are comparable with the results obtained in the present study. These difference might be due to the difference in the anthropogenic sources like the application of fertilizers (Raymond and Felix, 2011).Cadmium levels reported in the soil are above the levels 3 mg kg^{-1}, the permissible limits for agricultural soil (FAO/WHO, 2001). Therefore, there was Cd contamination in the soil.

Calcium had the highest concentration (1355±18.02 mg kg^{-1}) of macro elements in all soil samples, followed by K (681.43±1.52 mg kg^{-1}) and Na (111.63±0.35 mg kg^{-1}).Similarly, Cu (49.96±0.99 mg kg^{-1}) as detected in greater abundance among the microelements, followed by Mn (0.62±0.238 mg kg^{-1}), and Zn (0.163±0.007 mg kg^{-1}). Co>Cd>Ni was assigned to the remaining trace metals. The three main forms of Ca^{2+} found in soils are as minerals, in solution, and attached to organic matter and clay minerals at exchangeable sites. Soil solution only contains a small portion of the total $Ca^{2+.}$ Only Ca^{2+} can be absorbed by plant roots from soil solutions (Ramírez-Builes et al., 2020). The kind of soil, the mineral composition of the colloids, the pH, the amount of organic carbon, the presence of humid acids, and the cation exchangeable capacities are just a few variables that may affect the amount of Ca^{2+} that is present in the soil solution (Ramírez-Builes et al., 2020).

In soil samples from six kebeles, metals such as Pb, and Cr were found to be not detected. Kege Kebele soil sample analysis shows that, Ca (1355±18.02 mg kg^{-1}) was the highest of all the detected metals. K and Na were found in highest amount next to Ca with values of 673±2.65 mg kg^{-1} and 111.63±0.35 mg kg^{-1}, respectively. Out of the analyzed microelements, Cu (42.66±2.52 mg kg^{-1}) was found to be in highest amount followed by Co (5.33±0.305 mg kg^{-1}) and Mn (0.62±0.238 mg kg^{-1}). Likewise, the concentrations of Cd, Ni and Zn were found to be 3.1±0.1 mg kg^{-1}, 0.191±0.009 mg kg^{-1} and 0.161±0.007 mg kg^{-1}, respectively. The average metal concentrations in the kege soil were determined to be in the following order: Ca>K>Na>Cu>Co>Cd> Mn>Ni>Zn.

According to Sharma and Raju (2013), a high correlation coefficient (near +1 or -1) indicates a good relationship between two variables, whereas a concentration around zero indicates no relationship at a significant level of 0.05 **%** level. If r > 0.7, it is strongly correlated, whereas r values between 0.5 and 0.7 indicate moderate correlation between two different parameters. This study revealed that there is a positive correlation between Cd with Zn, Ca, Na and K indicates the linear relationship between the metals. The rise in levels of Cd increases the tendency of Zn, Ca, Na and K to increase. This is in line with previously reported data reported by Dubale (2021) found that Mg, Ca, Cr, Mn, Zn and Co in farmland soils in Gedeo, Ethiopia may have a similar origin determined by a correlation study of soil heavy metals.

Potassium (K) was found to have the greatest concentration (99.93±0.037mg kg^{-1}) among the macro elements detected in coffee beans from all sampling farm land sites. As suggested by (Weis and Weis, 2004), ‘’the highest concentrations of K in coffee beans are probable to be attributable to the truth that nutrient like K,N, P, S, and Mg are particularly cell in plant tissues and can be trans placed from ancient to younger plant tissues’’. According to (Çalişkan and Çalişkan, 2017), another reason for increased K concentrations is because this element is among the most important nutrients for plants and with the exception of N, potassium is the element that plants absorb the most compared to other elements.

The concentration of K in coffee bean from farmland reported by the present study (99.93±0.037mg kg^{-1}), which is much lower (18,634.66±538.67mg kg^{-1}) than that reported in poland (Janda et al., 2020) and reported K (15042.8 ± 53.29mg kg^{-1}) concentration from Gedeo Zone, Ethiopia (Dubale, 2021). On the other hand, values reported for K (21.31-427.84mg kg^{-1}) by (Omer et al., 2019) are comparable with the results obtained in the present study. The studied coffee beans were above the permissible limit set by FAO/WHO which is 32500 mg kg^{-1} in plants. K is essential because it lowers the risk of stroke, supports healthy nerve and brain function, and has diuretic qualities and also it helps control the water and acid-base balance in the blood and tissues and It has apparently been demonstrated that patients with high blood pressure can lower their blood pressure by eating a high potassium diet (He and MacGregor, 2008).

The finding of the present study revealed that Na and Ca were also detected in significant amounts in coffee bean sample from farmers' farms, with concentrations of 22.04 ±0.042 mg kg^{-1} and 17.23± 0.36 mg kg^{-1}, respectively. This result is consistent with Na concentration (6.84-564.74) and Ca concentration (6.76-32.09mg kg^{-1}) reported in Saudi Arebia (Omer et al., 2019) and reported by (Adler et al., 2019) Na concentration (18.6±11.31mg kg^{-1}) in green coffee bean. However ,the finding of Ca concentration (17.23± 0.36 mg kg^{-1}) in the present study was much lower (1252.93 ± 30.17 mg kg^{-1}) than that reported in Gedeo Zone (Dubale, 2021) The finding of Na (22.04 ±0.042 mg kg^{-1}) concentration in the present study, which was much higher (1.8–9.3 mg kg^{-1}) than that reported in green coffee bean (Martín et al., 1998) and Such great differences in Na(6.1 ± 2.3 mg kg^{-1}) concentration were also reported by previous study (Grembecka et al., 2007). This variation might be due to the type of soil where the coffee was cultivated (Santos and Oliveira, 2001).

The highest concentrations observed for Manganese in coffee bean for the present study was 0.927±0.004 mg kg^{-1}. When we compare the present experimental value with different country earlier reported. The finding of the present study was much lower (8.63±10.14mg kg^{-1}) than reported previous study (Omer et al., 2019) and reported Mn (23.60 ± 1.30 mg kg^{-1}) concentration in Gedeo Zone ,Ethiopia (Dubale, 2021). However, fairly agrees with this range (0.48-28.69mg kg^{-1}) reported by (Omer et al., 2019). The soil plant system is highly specific for different, elements; plant species and environmental conditions (Gure et al., 2017). As a result, coffee species, geographic origin, coffee kind, the application of fertilizers with varying chemical compositions, and other distinguishing characteristics all have a significant impact on the actual metal content of coffee beans(Kamal et al., 2008).Mn has a high solubility at low pH, its concentration in acidic soil is likely to be high(Wood, 1985) The permissible limit set by FAO (1993) for edible plants is 2mg kg^{-1}.

The highest concentration of Ni (0.074±0.003 mg kg^{-1}) reported by the present study, which is in good agreement with Ni (0.05–0.39mg kg^{-1}) reported in coffee bean (Grembecka et al., 2007) and Ni (0.07±0.11mg kg^{-1}) reported in coffee bean (Omer et al., 2019).However, the results presented in the present study are generally lower (0.415 ±0.04 mg kg^{-1}) than reported previous study (Adler et al., 2019) and reported Ni (2.43 ± 0.14 mg kg^{-1}) conceration in coffee bean (Dubale, 2021). The steps used in the production of natural or soluble coffees, the variety and type of coffee, the methods used in the preparation and storage of coffee, as well as the origin (particularly the type of soil where coffee plants are grown), all have a significant impact on the concentration of Ni elements (Santos and Oliveira, 2001, Grembecka et al., 2007). The maximum permissible limit for Ni set by FAO (1993) for edible plants is 1.63mg kg^{-1}.

Zinc concentration in the samples analyzed ranged between 0.054-0.076mg kg^{-1}, which was much lower than Zinc concentration (Zn) ranged between (3.74 to 46.89 mg kg^{-1}) reported in Yemeni green coffee beans (Nogaim et al., 2014), reported Brazil (Silva et al., 2017) Zn (5.53 to 55.83 mg kg^{-1}) , reported Zn (3.09-4.04 mg kg^{-1}) in green coffee bean (Adler et al., 2019), and reported Zn (8.74-12.75 mg kg^{-1}) concentration (Dubale, 2021).However, this result is consistent with Zn concentration (0.0-4.59 mg kg^{-1}) reported in Saudi Arabia (Omer et al., 2019). Zinc concentrations vary greatly depending on a number of factors, including the coffee's origin, variety, and type coffee confection and storage (Ashu and Chandravanshi, 2011).

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In the present study, Co and Cr were not found in coffee samples from farmlands. This finding is consistent with the previous study reported by Getachew and Worku (2014) for raw and roasted coffee bean and reported; Santos and Oliveira (2001) in Brazilian soluble coffee. However, the previous study has reported Co (2.6-8.4mg kg^{-1}), and Cr (0.21-0.28mg kg^{-1}) concentration in the Ethiopian green coffee beans (Abera Gure et al. 2017). Similarly, another study has reported Co (2.47- 2.86 mg kg^{-1}), and Cr (1.04-1.92mg kg^{-1}) concentration in the Ethiopian green coffee beans (Dubale 2021). Co and Cr are mostly polluted by mining, manufacturing, fertilizers, pesticides, and rock weathering(Zhou et al., 2020). The negligent application of fertilizers, wastewater discharge, burning of coal and motor fuels, and increased mining of cobalt ore have all contributed to an increase in the concentration of naturally occurring Cobalt (Saaltink et al., 2014). The maximum permissible limit for Chromium set by FAO (1993) for edible plants is 0.02mg kg^{-1}.However; there was no maximum permissible limit for Cobalt set by FAO (1993) for edible plants.

Copper concentration in the in the present study ranged between 0.14-0.28mg kg^{-1}, Which is much lower (12-13mg kg^{-1}) than the previous study reported by Getachew and Worku (2014) ; Abera Gure *et al.* (2017) Cu(11-23mg kg^{-1}) for raw coffee bean; Adler *et al.* (2019) Cu (9.4-18.5 mg kg^{-1}) for green coffee; and Dubale (2021) have reported Cu (23.39-28.5mg kg^{-1}) coffee from farm land. However, the finding of the present study is closely resembles the 0.13-10 mg kg^{-1} range reported by (Omer et al., 2019). The Cu was found low concentration in samples of coffee from farmland. The reason for this low concentration is that the soil where coffee plant grow and environmental conditions which effect the concentration (Ayele et al., 2015). The concentration is affected by a variety of factors, including the type of coffee used, the fertilizer used, and fertilized ground where crops were grown (Suseela et al., 2001). FAO/WHO (1993) defined an acceptable level of 3.00 mg kg^{-1} in edible plants. After comparing the metal limit in the investigated coffee beans to the FAO/WHO (1993) recommendations, it was discovered that all coffee bean collect Cu below this level. However, the WHO (2005) limits for Cu have not yet been determined for medicinal plants. Cu acceptable limits in medicinal plants were determined by China and Singapore at 20 mg kg^{-1} and 150 mg kg^{-1}, respectively (WHO, 2005).

In coffee beans of the selected study site, Pb and Cd were not found. This finding is consistent with the previous study reported by Getachew and Worku (2014) for raw and roasted coffee bean; Abera Gure *et al.* (2017) for raw coffee bean and Dubale (2021) for coffee bean sample form farm land. However, Adler *et al.* (2019) have observed higher values for Pb(0.076±0.0956 mg kg^{-1}) in Bosnia green coffee and reported by (Nogaim et al., 2014) Pb (0.599–7.989 mg kg^{-1}) in Yemeni green coffee beans. This indicates that coffee beans' chemical composition differs depending on the region in which they are grown. These hazardous metals were not detected in the present study might be due to no environmental degradation due to industrial operations or chemical contamination from sources such as vehicles and pesticides in Dale Woreda, .Furthermore, the absence of commercial fertilizers and pesticides for coffee plantations in Ethiopia may be evidenced by the low amounts of hazardous metals (Gure et al., 2017). Pb and Cd have no nutritional worth for humans, regardless of their very low concentration. As a result, consumers will not be exposed to any health risks as a result of these hazardous substances in dale Woreda coffee beans. The maximum permissible limit for lead and cadmium set by FAO (1993) for edible plants is 0.43mg kg^{-1} and 0.21mg kg^{-1} respectively.

The amount of trace metals taken up by plants was calculated to determine the Bio-concentration factor (BCF) of trace metals from soil to plant (Welde Amanuel and Berhanu Kassegne, 2022). The principal pathway for potentially hazardous metals to enter the food chain is by the movement and deposition of heavy metals from soil to edible parts of plants (Sharma et al., 2018). Bio-concentration factor is a significant measurement for the pollution assessment of soils with the highest level of trace metals (Welde Amanuel and Berhanu Kassegne, 2022). When BCF is larger than 1, it means that the plant has the potential to store the metal under consideration for examination (Barman *et al*., 2000). The amount and types of heavy metals present, plant species, soil physicochemical properties, and other factors all affect how quickly heavy metals are transferred to and accumulated by plants at different rates (Sharma et al., 2018, Fonge et al., 2021).

Mn had the highest bio-concentration factor/transfer factor (1.495) among the elements examined. This demonstrates that there is a possibility that the trace metal is derived from natural sources, is available for uptake, and has a low rate of metal retention in soil (EU, 2002). The higher transfer factor of Mn in coffee bean can create a chance for higher human consumption. Mn influenced plant function in addition to being harmful to human health. Suresh *et al*. (1987) observed that excess soil Mn disrupted stomata function in plant(Suresh et al., 1987). Mn also caused human lung injury like cough, bronchitis, pneumonitis along with damages lung (Boojar and Goodarzi, 2002).

In the analysed samples, Cu had the lowest transfer factor (0.0048), which is at the Magara locations (SS6).It was apparent that TF of some metals (Cu) decreased when the plants were grown in the soil with a higher contamination (Mirecki.et al.2017).It might become more tightly bound to the soil and alter the composition of the soil. This shows that the plant tissue absorbed most of the soil's trace metal concentration. The general pattern of trace metal transfer in Kege Kebele (SS1) was Mn> Zn> Ni > Na> K> Ca > Cu. This clearly shows that Mn bioaccumulation factors in coffee samples were higher than for other metals.

The beans from Megara coffee washing industries, like coffee beans from farmer's farms, have the maximum amount of K (77.93±0.115 mg kg^{-1}), followed by Na (10.47±0.058 mg kg^{-1}) and Ca (3.55±0.114 mg kg^{-1}). In the washing industry's beans, Mn (0.92±0.001 mg kg^{-1}) was the highest accumulated trace metal, followed by Cu (0.277±0.011 mg kg^{-1}) and Zn (0.094±0.004 mg kg^{-1}). Other critical trace metal concentrations found in coffee beans were Ni (0.074±0.003 mg kg^{-1}). The results show that the concentrations of Co, Cr, Pb and Cd were not detected.

Conclusions

Mean metal concentrations in the soil were determined to be in the following order: Ca>K>Na>Cu>Co>Cd>Mn>Ni>Zn. except Cd, all metals analyzed were below permissible limit set by FAO/WHO. Cadmium levels reported in the soil are above the levels 3 mg kg^{-1}, the permissible limits for agricultural soil (FAO/WHO, 2001). Therefore, there was Cd contamination in the soil.

Metal levels in coffee bean samples from farmers' farms are in the following order: K>Na>Ca >Mn>Cu> Ni>Zn. Metal levels were found to be K>Na>Ca >Mn>Cu> Zn>Ni in coffee beans from the washing plants. In both coffee, the levels of toxic metals (Pb and Cd) were not determined, and trace heavy metal levels were below the FAO/WHO maximum permissible limits. As a result, there is no health risk linked with the use of Dale Woreda coffee beans due to harmful and trace heavy metals. Mn had the highest bio-concentration factor/transfer factor among the elements examined. However, Cu had the lowest transfer factor. The general pattern of trace metal transfer in Kege Kebele (SS1) was Mn > Zn > Ni > Na>K > Ca > Cu. According to the findings of this study, there are permitted levels of macro and trace elements in coffee beans from farmlands and washing plants. As a result, metal pollutants have no effect on the coffee grown in Dale Woreda. As a result, concerned bodies should make more marketing and raise awareness to increase and spread the recognition and consumption of Dale Woreda coffee beans in the national and international coffee market.

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Table 1 (on next page)

Mean metal concentrations in soil samples

Table 1 Optimum microwave digestion conditions of coffee bean samples.

step	1	2	3
Temperature ^{0}c	150	200	45
Time in minutes	5	10	10
Power-w	80	85	0

Table 2 (on next page)

Correlation Analysis of Heavy Metals of Soil in the selected Kebele of Dale Woreda

Table 2 Mean metal concentrations in soil samples (mean standard deviation)

	Ca	Cd	Co	Cu	K	Mn	Na	Ni	Zn
SS1	1355±18.02	3.36±0.10	5.43±0.31	42.46±2.52	673±2.65	0.62±0.24	111.63±0.35	0.194±0.01	0.163±0.01
SS2	1538.67±3.20	2.53±0.06	4.27±0.20	47.48±0.58	403.47±1.53	0.5±0.001	26.52±0.04	0.181±0.001	0.146±0.002
SS3	445±0.99	2.67±0.06	ND	49.96±0.99	603±0.10	0.467±0.02	26.77±0.02	0.191±0.001	0.141±0.001
SS4	346.67±2.51	2.38 ±0.04	ND	22.34±0.25	604.61±0.58	0.48±0.002	13.37±0.032	0.181±0.001	0.155±0.005
SS5	1352.67±2.50	2.93±0.02	ND	47.7±1.15	681.43±1.52	0.49±0.001	112±0.10	0.172±0.002	0.153±0.002
SS6	1401±1.10	3.01±0.006	ND	45.26±1.52	680.43±0.57	0.50±0.001	110.3±0.10	0.178±0.001	0.146±0.005
MPL	-	3.0	50.0	300.0	-	-	-	50.0	1000.0

ND =not detected, MPL=Maximum Permissible Limit for Agricultural soils according to FAO 2001

Table 3(on next page)

Concentration of non-toxic metal concentration in coffee bean sample from farm land in Dale Woreda, Ethiopia, 2021

Table 3.Correlation Analysis of Metals of Soil in the selected Kebele of Dale Woreda

	Cd	**Ni**	**Zn**	**Cu**	**Ca**	**Mn**	**Na**	**K**
Cd	1							
Ni	0.337	1						
Zn	**0.511***	0.241	1					
Co	0.359	**0.482***	**0.469***					
Cu	0.363	0.035	-0.421	1				
Ca	**0.507***	-0.285	0.144	**0.537***	1			
Mn	0.135	0.155	0.334	-0.014	0.266	1		
Na	**0.81****	-0.161	0.396	0.369	**0.65****	0.325	1	
K	**0.57***	0.012	0.379	-0.075	-0.096	0.151	**0.69****	1

* Correlation is significant at the 0.05 level (2-tailed). ** Correlation is significant at the 0.01 level

Table 4(on next page)

Concentration of toxic metal concentration in coffee bean sample from farmer's farms in Dale Woreda, Ethiopia, 2021

Table 4 Concentration of essentials metal concentration (mean ± SD, n = 3, mg kg-1) in coffee bean sample from farm land in Dale Woreda, Ethiopia, 2021

		K	Ca	Na	Mn
Kege		99.93±0.037	15.15±0.614	22.04±0.042	0.927±0.004
wenenata		69.06±0.047	17.23±0.36	5.73±0.049	0.105±0.003
Gane		80.587±0.08	3.05±0.04	6.927±0.038	0.082±0.003
Wondo		78.10±1.081	3.96±0.063	3.10±0.10	0.088±0.003
Bera		69.36±0.55	16.11±0.11	5.73±0.049	0.105±0.003
Magara		99.27±0.714	15.33±0.189	21.077±0.99	0.093±0.004
MPL	Medicinal plant	32500	-	-	-
	Edible plant	-	-	-	2

MPL=Maximum Permissible Limit for medicinal and edible plants according to FAO 1993

Table 5(on next page)

Bio-concentration factor (BFC) of heavy metals analyzed in coffee bean grown by Dale Woreda and its farm land

Table 5 Concentration of toxic metal concentration in coffee bean sample from farmer's farms in Dale Woreda, Ethiopia, 2021

		Ni	Zn	Co	Cu	Cr	Pb	Cd
Kege		0.055±0.004	0.073±0.003	ND	0.22±0.0026	ND	ND	ND
Wenenata		0.053±0.003	0.065±0.004	ND	0.24±0.002	ND	ND	ND
Gane		0.074±0.003	0.055±0.002	ND	0.28±0.0037	ND	ND	ND
Wondo		0.052±0.005	0.07±0.0017	ND	0.14±0.0020	ND	ND	ND
Bera		0.057±0.003	0.067±0.002	ND	0.234±0.01	ND	ND	ND
Magara		0.057±0.008	0.07±0.001	ND	0.22±0.0005	ND	ND	ND
MPL	Medicinal plant	1.63	No MPL	No MPL	20	2	10	0.3
	Edible plant	No MPL	27.4	No MPL	3	0.02	0.43	0.21

ND =Not detected, MPL =Maximum Permissible Limit for medicinal and edible plants according to FAO 1993

Table 6(on next page)

Mean concentration (mean ± SD, n = 3, ppm) of elements in coffee bean sample from washing industry in Dale Woreda, Ethiopia, 2021

Table 6 Bio-concentration factor (BFC) of heavy metals analyzed in coffee bean grown by Dale Woreda and its farm land

Sampling area	**Transfer of trace metals**						
	K	Ca	Na	Mn	Ni	Zn	Cu
Kege	0.149	0.011	0.197	**1.495**	0.284	0.448	0.0052
wenenata	0.171	0.011	0.216	0.21	0.293	0.445	0.0051
gane	0.134	0.0068	0.258	0.176	0.387	0.390	0.0056
wondo	0.129	0.0114	0.232	0.183	0.287	0.452	0.0063
Bera	0.102	0.0119	0.051	0.214	0.331	0.438	0.0049
Megara	0.146	0.0109	0.191	0.186	0.320	0.479	0.0048

Table 7 (on next page)

Comparison of current results for coffee beans from farms and the washing industry with FAO

Table 7 Mean concentration (mean ± SD, n = 3, ppm) of elements in coffee bean sample from washing industry in Dale Woreda, Ethiopia, 2021

	Ca	Cd	Co	Cu	K	Mn	Na	Ni	Zn
SS1	3.733±0.03^{a}	ND	ND	0.243±0.003^{a}	75.81±0.026^{a}	0.92±0.001^{a}	10.30±0.10^{b}	0.074±0.003^{a}	0.054±0.004^{d}
SS2	2.816±0.021^{a}	ND	ND	0.191±0.001^{a}	61.39±0.026^{c}	0.08±0.003^{a}	15.04±0.04^{a}	0.074±0.003^{a}	0.063±0.004^{c}
SS3	3.71±0.015^{a}	ND	ND	0.254±0.004^{a}	71.07±0.049^{a}	0.09±0.004^{a}	3.43±0.043^{c}	0.054±0.004^{a}	0.075±0.002^{b}
SS4	4.33±0.035^{a}	ND	ND	0.146±0.004^{a}	68.30±0.093^{b}	0.09±0.003^{a}	1.43±0.035d	0.073±0.002^{a}	0.094±0.004^{a}
SS5	2.81±0.017^{a}	ND	ND	0.191±0.001^{a}	61.59±0.356^{c}	0.08±0.005^{a}	15.04±0.041^{a}	0.052±0.001^{a}	0.067±0.004^{c}
SS6	3.55±0.114^{a}	ND	ND	0.277±0.011^{a}	77.93±0.115^{a}	0.09±0.001^{a}	10.47±0.058^{b}	0.071±0.001^{a}	0.053±0.002^{d}

Table 8(on next page)

Metal Concentrations in Coffee Beans Compared to some of the Literature Values

Table 8 Comparison of current results for coffee beans from farms and the washing industry with FAO/WHO, different organizations, and nations' maximum permissible values for metals.

Elements	Present study		MPL (ppm)	Type of plant	Refrences
	CBFF	CBWI			
Ni	0.05-0.08	0.05-0.08	1.63	Edible plant	(FAO/WHO, 1993)
			No MPL	Medicinal plant	(WHO, 2005)
Zn	0.054-0.076	0.051-0.09	50	Grain	(USAD, 2000)
			No MPL	Medicinal plant	(WHO, 2005)
			100	Beans	(USAD, 2000)
			27.4	Edible plant	(FAO/WHO, 1993)
Co	ND	ND	No MPL	Medicinal plant	(WHO, 2005)
Cu	0.14-0.29	0.14-0.28	40	In food	(FAO/WHO, 1993)
			3	Edible plant	(FAO/WHO, 1993)
			20	Medicinal plant	(WHO, 2005) set by Singapore
			150	Medicinal plant	(WHO, 2005) set by china
Cr	ND	ND	2	Medicinal plant	(WHO, 2005)
			0.02	Edible plant	(FAO/WHO, 1993)
Ca	3.0-17.27	2.80-4.37	-	-	
Mn	0.08-0.11	0.07-0.10	No MPL	Medicinal plant	(WHO, 2005)
			2	Edible plant	(FAO/WHO, 1993)
Na	3.0-22.1	1.40-15.09	-	-	
K	69.0-99.97	61.4-78	32500	Medicinal plant	FAO/WHO, 1993)
Pb	ND	ND	0.43	Edible plant	(FAO/WHO, 1993)
			10	Medicinal plant	(WHO, 2005)
Cd	ND	ND	0.21	Edible plant	(FAO/WHO, 1993)
			0.3	Medicinal plant	(WHO, 2005)

CBFF= coffee beans from farms, CBWI= Coffee beans washing industry, ND=Not detected, MPL =Maximum Permissible Limit

Table 9(on next page)

T –test among coffee beans from farmer's farms and washing industries

Table 9 Metal Concentrations in Coffee Beans Compared to some of the Literature Values

	(Onianwa et al., 1999) Coffee beverage	(Suseela *et al.*, 2001) coffee powders	(Silva *et al.*, 2017) roasted and ground coffee	(Gure *et al.*, 2017) in green coffee	(Adler *et al.*, 2019) in green coffee	(Omer et al., 2019) in green coffee	(Dubale, 2021) in Ethiopia		**Present study**	
							CBFF	CBWI	CBFF	CBWI
Ni	0.04-2.58	NR	0.03-1.95	<0.04-2.5	0.415±0.04	0.0-0.25	1.66-2.43	1.56-2.32	0.05-0.08	0.05-0.08
Zn	4-14	2-9	5.53-55.8	4-21	3.6 ±0.67	0.0-4.59	8.74-12.7	9.41-13.0	0.054-0.076	0.051-0.09
Co	0.1-14	NR	NR	2.6-8.4	NR	NR	2.47-2.86	2.31-2.75	ND	ND
Cu	2-9	0.4-16	0.7-17.18	11-23	14 ±6.43	NR	23.4-28.5	23.1-28.2	0.14-0.29	0.14-0.28
Cr	0.89-6.98	0.4-1.00	0.03-0.10	0.21-0.28	NR	NR	1.04-1.92	0.94-1.90	ND	ND
Ca	NR	869-1171	NR	710-1250	789 ±132.23	6.76-32.1	1037-1253	1090-1270	3.0-17.27	2.80-4.37
Mn	NR	7-13	9.81-39.8	13-19	NR	0.48-28.7	17.3-23.6	17.2-22.6	0.08-0.11	0.07-0.10
Na	NR	NR	NR	NR	18.6±11.31	6.8-564.7	NR	NR	3.0-22.1	1.40-15.09
K	NR	14000-29000	NR	13010-17000	19898±445.48	21.31-427.84	14631-15043	14602-14980	69.0-99.97	61.4-78
Pb	0.09-0.91	NR	0.03-1.58	<0.05	0.076 ±0.0956	0.0-23.88	ND	ND	ND	ND
Cd	0.02-0.31	NR	0.03-0.10	ND	0.015 ±0.0005	0.00-8.01	ND	ND	ND	ND

Table 10(on next page)

Table 10

test among coffee beans from farmer's farms and washing industries

1 Table 10 T –test among coffee beans from farmer's farms and washing industries

	t	Sig.	Mean Diff.	Std. Error Diff	95% CI	
					Lower	Upper
Ni	-1.91	0.064	-0.00594	0.003109	-0.01226	0.000373
Zn	-0.39	0.694	-0.00149	0.003757	-0.00912	0.006146
Cu	0.58	0.567	0.008444	0.014612	-0.02125	0.03814
Ca	5.77	**0.01**	8.310556	1.44024	5.383635	11.23748
Mn	2.28	**0.029**	0.006111	0.002682	0.00066	0.011562
Na	0.66	0.517	1.482222	2.264297	-3.11938	6.083828
K	3.89	**0.01**	13.36944	3.43744	6.383726	20.35516

2 CI=Confidence interval