

Levels of Selected Essential and Non-Essential Metals in the Soil and Ginger (*Zingiber* officinale) Cultivated in Wolaita Zone, **Ethiopia**

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Abstract

Ginger (Zingiber officinale) is an important spice and medicinal plant used in different parts of the world. The objective of current study was to determine the level of essential and non-essential metals in ginger and its correlation with concentration of metals in the supporting soil. The level of K, Na, Ca, Mg, Mn, Fe, Zn, Cu, Co, Cd and Pb in soil and ginger cultivated in the selected districts of Wolaita zone, Southern Ethiopia were determined using flame atomic absorption spectrometry. A 0.5 g ginger sample was digested using a mixture of 4 ml HNO₃ and 1.5 ml HClO₄ at 210°C for 150 minutes, and a 0.5 g soil sample was digested employing a mixture of 6 ml aqua-regia and 1 ml H₂O₂ at 280°C for 150 minutes. The metal concentrations range in dry weight basis for ginger samples is decreasing in the order: K (1691 - 3487 mg/kg) > Mg (701 - 1583 mg/kg) > Ca (862 - 1476 mg/kg) > Na (398 - 776 mg/kg) > Mn (325 - 672 mg/kg) > Fe (6.14 - 11.92 mg/kg) > Zn (5.30 - 10.09 mg/kg) > (0.12 - 0.23 mg/kg) for Pb. The concentration of Cd, Cu and Co in ginger samples were below the limit of detection. The results revealed that ginger has the ability to accumulate relatively higher amounts of K and Mg among the determined essential metals. The soil samples have been found to be acidic pH, sandy clay loam in texture, a very low electrical conductivity and moderate level of (CEC, organic carbon, available phosphorus and total nitrogen). Although, a positive correlation between the levels of K, Mg, Zn, Mn in ginger and soil samples were observed. All the non-essential metals analyzed in this study were below the permissible ranges set by FAO/WHO.

Keywords

Essential Metals, Flame Atomic Absorption Spectroscopy, Ginger, Non-Essential

Metals, Soil, Organic Carbon, Total Nitrogen, Cation Exchange Capacity, Organic Matter

1. Introduction

Ginger (*Zingiber officinale*) is a herbaceous tropical perennial belonging to the family Zingiberaceae. The Rhizome of ginger has been used as a drug in herbal traditions since antiquity as carminative or antiflatulent, diaphoretic, antispasmodic, expectorant, peripheral circulatory stimulant, astringent, appetite stimulant, anti-inflammatory agent, diuretic, and digestive aid. Moreover, it also imparts flavor and pungency to food and beverages and is particularly consumed as fresh paste, dried powder, slices preserved in syrup, candy, or flavoring tea [1] [2].

Ginger is homegrown to tropical India, South East Asia, Australia, and Japan, with the main center of diversity in Indo-Malaysia [3]. The cultivation of ginger was started in Ethiopia, during the 13th century when Arabs introduced it from India to East Africa [4]. It's the second most generally cultivated spice in Ethiopia, next to chilies. It's limited mostly within the wetter regions of Southern Nations, Nationalities and Peoples Regional State (SNNPRS) and a few parts of western Oromia [5]. Large-scale commercial production of ginger by farmers in SNNPRS is practiced especially in Boloso Bombe, at Wolaita Zone [6].

Plants store and transport metallic elements, both to supply appropriate concentrations of them for later use in metalloproteins or co-factors, and to guard themselves against the toxic effects of excess metals. Growth media including soil, nutrient solution, water, and air are the key sources of metals to vegetables and other crops, which enter by roots or foliage through two main bio-sorption mechanisms: adsorption and/or absorption and accumulated in their tissues [7] [8]. Metal uptake by plants is often suffering from several factors including metal concentrations in soils, soil pH, cation exchange capacity, organic matter content, types and diversities of plants, and age of the plant [9].

Major and minor elements are considered essential nutrients in food. The routine monitoring of the amount of these elements in crops is a common quality control process [10]. However, both deficiency and excesses of those essential trace elements give very serious problems in the human and animal body. Since ginger is a cash crop and one of the widely consumed spice in the study area and all over the world, the assessment of the levels of essential and heavy toxic metals have a particular interest with respect to human health and the quality of its products.

Many kinds of researches were conducted on the determination of essential and non-essential metal levels of ginger in Nigeria, India, Pakistan, and Romania [11] [12] [13] [14]. However, research related to the levels of essential and non-essential metals in ginger cultivated in Wolaita Zone, Southern Ethiopia

was scarce. Therefore, this study was focused on the determination of levels of essential (K, Na, Ca, Mg, Mn, Fe, Zn, Cu, Co) and non-essential (Cd and Pb) metals in ginger and its correlation with the concentration of metals in the supporting soil. It also aimed to assess some physico-chemical properties of the soil. Furthermore, the results of this study may help to identify the difference in mineral content of ginger with the area of cultivation and provide baseline information for researchers who need further investigations in this area.

2. Materials and Methods

2.1. Description of the Study Area

The study was conducted on the five main ginger growing Districts of Wolaita Zone. These include Boloso Bombe, Boloso Sore, Damot Sore, Kindo Didaye and Kindo Koyisha. Wolaita zone is situated between 60°51" to 70°35"N latitude and 37°46" to 38°1"E longitude with an average altitude of 1750 meters and ranges between 501 and 3000 m.a.s.l. It is bounded to the North and the North East by Kambata Tambaro Zone, to the West and Southwest by Dawaro zone, to the south by Gamo Gofa Zone, and to the East by Sidama. There are three agro-ecological zones in the area, out of which Dega accounts 9%, Weynadega 56%, and Kolla 35% [15].

2.2. Chemicals and Reagents

All chemicals and reagents with analytical grade (BDH) were used in this study. HNO₃ (70%) and HClO₄ (70%) (Research-lab Fine Chem Industries, Mumbai, India) were used for the digestion of ginger samples. Aqua-regia, a mixture of 37% HCl (Rediel de-Haen, Germany) and (70%) HNO₃, extra pure 30% H₂O₂ (Scharlau, European Union) solution were used for the digestion of the soil sample. NaHCO₃, NH₄OAc, K₂Cr₂O₇, and H₂SO₄ were used for the physico-chemical analysis of the soil sample. La(NO₃)₃·6H₂O (98%) (Aldrich, USA) was used to avoid refractory interference on the Ca and Mg from their phosphates. Stock standard (BDH Chemicals Ltd Spectrosol[®], Poole, England) solutions containing 1000 mg/L, in 2% HNO₃, of the metals Na, K, Ca, Mg, Cu, Zn, Mn, Fe, Co, Pb, and Cd were used for the preparation of calibration standards and in the spiking experiments. Deionized water was used for dilution of the sample and intermediate metal standard solutions prior to analysis and rinsing glassware and sample bottles.

2.3. Instruments and Apparatus

Polyethylene bags (Moulinex, France) was used during sample collection and preserving the ground and homogenized samples. Teflon knife and chopping board (PTFE, China) were used to cut the ginger rhizome into pieces. A digital pH meter (ELE International PQ qualab) was used to determine the pH of soil samples after stirring by a magnetic stirrer. A hydrometer was used to determine the texture of the soil samples. The conductivity meter was used to measure the

conductivity of the soil solution. A drying oven (Digitheat, J.P. Selecta, Spain) was used for drying ginger sample placed on porcelain crucible. Electronic Blending device (Moulinex, France), ceramic pestle and mortar (Haldenwanger, Germany) were used for grinding and homogenizing the samples. Digital analytical balance (Explorer, Ohaus, Model E11140, Switzerland) with ±0.0001 g was used for weighing the soil and ginger samples. Polyethylene sieve (2 mm) was used to remove large debris, stones, and pebbles from the soil sample. Polyethylene sieve (0.5 mm) was used to remove fine particles from the soil sample. A 100 ml round bottom flasks fitted with a reflux condenser were used in the Kjeldahl apparatus (Gallenhamp, England) for the digestion of samples. Borosilicate volumetric flasks (25, 50, and 100 ml) were used throughout dilution and storage of samples and preparation of metals standard solutions. Pipettes (Pyrex, USA), and micropipettes (Dragonmed, 1 - 10 µL, 100 - 1000 µL, Shangai, China) were used for measuring the volume of reagents and standards. Different sizes of filter papers (Whatman) were used for the filtration of sample solution after digestion during the optimization and sample preparation processes. Buck Scientific Model 210VGP AAS, East Norwalk, USA equipped with a deuterium arc background corrector Flame Atomic Absorption spectrophotometer was used for the analysis of the metals Na, K, Ca, Mg, Fe, Mn, Zn, Cu, Co, Cd and Pb using air acetylene flame.

2.4. Sample Collection

Mature, healthy, and fresh ginger rhizomes and its supporting soil were collected from the farmlands of five districts of Wolaita Zone. These include Boloso Bombe, Boloso Sore, Damot Sore, Kindo Didaye and Kindo Koyisha. The sampling sites were carefully chosen based on ginger production potential. To collect the representative sample, composite samples were taken from each sampling site. The composite samples of fresh ginger and soil (from the surface at a depth of 0 - 20 cm) were collected from each farmland and reserved in clean polyethylene plastic bags for further pre-treatment.

2.5. Sample Preparation

2.5.1. Preparation of Ginger Sample

The collected ginger rhizomes were washed with running tap water to remove adsorbed soil particulates and then rinsed with distilled water. The outer skin of ginger samples was removed by a Teflon knife and chopped into pieces to facilitate drying. The sample was exposed to sunlight for three days to reduce the moisture content and subsequently dried in the drying oven at 80°C for 24 hours to constant weight. The dried sample was powdered using an electronic blender and sieved to prepare a fine powder of ginger for digestion [16].

2.5.2. Preparation of Soil Sample

The soil samples collected from the five sampling areas were air-dried to constant weight for three days and sieved through a 2 mm polyethylene sieve to remove large debris, stones, and pebbles. Then, the samples were grounded using a mortar and pestle, homogenized, and ready for digestion and physicochemical analysis [16].

2.6. Optimization of Digestion Procedure

Obtaining an optimum condition for digestion is the basic requirement for sample preparation for analysis. To select an optimum procedure for digestion parameters like digestion time, reagent volume, a volume ratio of reagents, and digestion temperature were optimized by varying one parameter at a time and keeping the others constant. Parameters giving clear solutions at lower temperatures, requiring minimum reagent volume and digestion time were selected as an optimum procedure for the digestion of ginger and soil samples [17]. Digestions of ginger were carried out using HNO₃ and HClO₄ acid mixture. Soil samples were digested using modified aqua-regia (HNO₃ + HCl + H₂O₂) as recommended by [18].

2.7. Digestion of Ginger Samples

Exactly 0.5 g of the dried and ground ginger sample was accurately weighed on a digital analytical balance and transferred quantitatively into a 250 ml round bottom digestion flask. 5.5 ml of freshly prepared 4:1.5 mixture of concentrated HNO_3 and $HClO_4$ was added to the sample. The sample was swirled gently to homogenize then fitted to a reflux condenser and digested continuously for 2 hours and 30 minutes on a Kjeldahl digestion block. The temperature was adjusted within certain time intervals to give the maximum temperature of 210°C. The digestion gives a clear colorless solution [19].

Digestion of a reagent blank was also performed in parallel with the ginger samples keeping all digestion parameters uniform. To avoid chemical interference in the determination of Mg and Ca in the samples, lanthanum nitrate hydrate is added to the solutions. The clear solution was filtered into 100 ml volumetric flasks through Whatman filter paper. It was diluted with distilled water up to the mark and stored for further analysis [19] [20] [21].

2.8. Digestion of Soil Samples

In this procedure, 0.5 g of the soil sample was placed in a Kjeldahl flask and 6 ml of aqua-regia (3:1 ratio of HCl to HNO_3) was added first before adding 1 ml of concentrated H_2O_2 . The sample was swirled gently to homogenize then fitted to a reflux condenser and digested continuously for 2 hours and 30 minutes on a Kjeldahl digestion block. The temperature was adjusted within certain time intervals to give the maximum temperature of 280°C. The digestion produces a clear colorless solution. The digest was then cooled and a few drops of water were added before filtering using a Whatman No 42 filter paper. The filtrate was then diluted with de-ionized water to 100 ml and stored for further analysis [18].

2.9. Method Performance and Method Validation

To check the validity of the analytical method, the following method validation parameters such as precision (in terms of repeatability), accuracy (in terms of recovery), method detection limit, matrix spike, and matrix spike duplicate were carried out [22].

2.10. Statistical Analysis

All analyses were carried out in triplicate and the data were presented as means \pm standard deviations. Differences between treatment means were done by using analysis of variance (ANOVA). For comparison of the means of the treatments, the Fisher's least significant difference (LSD) test was used at a = 0.05 significance level. A Pearson Correlation Coefficient was used to check associations of the same metal in the soil with ginger and also to check whether the ions of one kind present in the soil, either facilitate or interfere with the uptake of the other kind of ions. All statistical analyses were done by SPSS 23 and SAS 9.1.3 software for windows [23] [24].

3. Results and Discussions

3.1. Optimization of Digestion Procedure of Ginger and Soil Samples

Different conditions tested for optimization of the digestion procedure for 0.5 g ginger samples were summarized in **Table 1**. From the optimization procedure the acid mixture of 4 ml HNO₃ (70%), and 1.5 ml HClO₄ (70%), digestion time 150 minutes, and digestion temperature 210° C were found to be the optimal condition for the digestion of 0.5 g ginger samples (**Table 1**).

Soil samples were digested using modified aqua-regia (HNO₃ + HCl + H_2O_2) as recommended by [18]. The optimum condition for soil sample digestion was a reagent mixture of 6 ml aqua-regia (3:1 ratio of HCl to HNO₃) and 1 ml H_2O_2 , digestion temperature 280°C, and digestion time 150 minutes for 0.5 g soil sample.

No. of Trials	Reagent volumes (mL) HNO3:HClO4	Digestion temperature (°C)	Digestion time (min)	Observation
1	3:1	120	60	Deep yellow solution
2	2:3	150	90	Deep yellow solution
3	3:2	180	100	Yellowish solution
4	2:4	200	120	Yellowish solution
5	4:1.5*	210*	150*	Clear colorless solution
7	5:2	210	170	Clear colorless solution
8	6:1	240	170	Clear colorless solution
9	5:3	250	200	Clear colorless solution

 Table 1. Optimization of digestion procedure of 0.5 g ginger samples.

*The optimum digestion conditions.

Different conditions tested for optimization of the digestion procedure for 0.5 g soil samples are summarized in Table 2.

3.2. Analytical Method Detection Limits

The detection limit for the methods was calculated by multiplying the standard deviation of seven blank signals each determined in triplicate by three. The calculated Method Detection Limit (MDL) for ginger and soil samples are given in **Table 3**.

3.3. Evaluation of Analytical Method

As shown in **Table 4** and **Table 5**, the percentage recovery for ginger and soil samples lies in the range of 90% - 100.6%, which are within the acceptable range

No. of trials	Reagent volumes (mL) Aqua-regia:H ₂ O ₂	Digestion temperature (°C)	Digestion time (min)	Observation
1	3:2	120	120	Deep Yellow
2	4:1	150	120	Deep Yellow
3	3:3	180	130	Deep Yellow
4	4:2	200	130	Deep Yellow
5	2:4	250	140	Yellow
6	5:1	270	150	Light yellow
7	6:1*	280*	150*	Clear colorless solution
8	5:2	300	180	Clear Colorless
9	6:2	310	200	Clear Colorless

Table 2. Optimization of 0.5 g soil samples.

*The optimum digestion conditions.

Table 3. Instrument and method detection limits of metals in ginger and soil samples.

Metal	Instrument detection limit (mg/L)	Method detection limit for ginger (mg/kg)	Method detection limit for soil (mg/kg)
Na	0.001	0.004	0.006
К	0.010	0.03	0.02
Ca	0.010	0.05	0.07
Mg	0.001	0.004	0.006
Cu	0.020	0.062	0.030
Zn	0.005	0.022	0.007
Mn	0.0010	0.002	0.004
Fe	0.030	0.034	0.022
Co	0.050	0.08	0.08
Cd	0.005	0.01	0.03
РЬ	0.100	0.12	0.150

Metal	Conc. in sample (mg/L)	Amount added (mg/L)	Conc. in spiked sample (mg/L)	Amount recovered (mg/L)	Recovery (%)
Na	590	250	830	240	96
К	2696	500	3199	503	100.60
Ca	1200	500	1690	490	98
Mg	1230	500	1700	470	94
Mn	497	150	642	145	96.70
Fe	9.90	5.00	14.40	4.50	90
Zn	9.30	5.00	14.00	4.70	94
Cu	ND	-	-	-	-
Co	ND	-	-	-	-
Cd	ND	-	-	-	-
Pb	0.16	0.10	0.25	0.09	90

Table 4. Recovery test for the optimized procedure of ginger sample.

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

Metal	Conc. in sample (mg/kg)	Amount added (mg/kg)	Conc. in spiked sample (mg/kg)	Amount recovered (mg/kg)	Recovery (%)
Na	2500	500	2990	490	98
Κ	3345	600	3946	601	100.20
Ca	1670	500	2160	490	98
Mg	2438	500	2933	495	99
Mn	1296	500	1798	502	100.40
Fe	3694	600	4284	590	98.30
Zn	11.90	5.00	16.50	4.60	92
Cu	35.00	15.00	49.0	14.0	93.30
Co	ND	-	-	-	-
Cd	0.20	0.1	0.29	0.09	90
Pb	0.26	0.1	0.35	0.09	90

ND: Concentration values of the studied metals are below method detection limit.

for metals [25]. The results confirm that the method is of good precision and accuracy.

3.4. Physico-Chemical Properties of Soil

Soil pH and its organic matter content are among those major factors that greatly affect the availability of macro- and micronutrients and even toxic elements in the soils and their uptake by plant roots [26]. The pH and other physico-chemical properties of soils that affect nutrient accumulation in the soil and their availability to the plants were given in Table 6.

The pH of studied soil samples was found to be within the range of 5.02 to

Site		EC (dS/m)	OC (%)	TN	Av. P	CEC	Texture		
	рн			(%)	(ppm)	(Cmol/kg)	% clay	% silt	% sand
BB	6.20	0.02	1.29	0.17	8.73	24.58	26.22	19.65	54.13
BS	5.70	0.02	1.30	0.18	7.05	23.11	25.82	17.69	56.49
КК	5.60	0.07	1.30	0.19	6.65	22.83	24.46	16.50	59.04
DS	6.30	0.02	1.29	0.19	9.91	25.62	27.75	18.78	53.47
KD	5.02	0.05	1.23	0.16	5.84	21.35	20.87	19.51	59.62

Table 6. Average values of physico-chemical characteristics of the soil.

BB = Boloso Bombe, BS = Boloso Sore, KK = Kindo Koysha, DS = Damot Sore, KD = Kindo Didaye.

6.30 in which higher value observed in Damot Sore and a lower value was observed in Kindo Didaye. According to Jones (2003), the pH ranges of the soils in the studied areas are from strongly acidic to slightly acidic in nature [27]. The higher acidity of the soils was mainly owing to the leaching of some basic cations [28] and probably due to poorly managed cultivation, inappropriate use of ammonium-based fertilizers, and accelerated erosions that implied the deterioration of soil quality [29].

The electrical conductivity of the soil was ranged from 0.02 to 0. 07 dS/m. According to Jones (2003), the soils under study were rated as very low EC [27]. The low EC value was a result of the high rainfall of the area leaching much of the salts in the sites. As stated by Singaravel *et al.* (2000), EC value rated as 0.5 dS/m for good soil. Generally, the low EC value was mainly because of the acidic nature of the soil under investigation [30].

The particle size distribution of the soil was found in the ranges 20.87 to 27.75 of % clay, % silt ranges from 16.50 to 19.65, and % sand ranges from 53.47 to 59.62. The textural class of the studied soils was found to be sandy clay loam. Pedologic processes such as erosion, deposition, illuviation, and weathering which are shaped by management practices can alter the texture of soils [26]. Under conditions of high rainfall, clay fractions are likely to be lost through processes of selective erosion and migration down the soil profile which ultimately increases the proportion of sand in surface soils [31].

The cation exchange capacity (CEC) ranged from 21.35 to 25.62 Cmol/kg. The higher value was observed in Damot Sore and a lower value was found in Kindo Didaye. According to Brook (1983), the CEC of the soil was rated as medium in all sites [32]. The relatively lower CEC of the Kindo Didaye District may be due to the lowest clay fraction and the highest sand fractions of the soil. This may be the main reason followed by their low organic matter content. Hence, the depletion of OM as a result of intensive cultivation has reduced the CEC and this is in accord with previous findings [33].

Organic carbon of the soil was found to be in the range of 1.23% to 1.30%. Along with the rating suggested by Tekalign *et al.* (1991), the soil OC contents were in the moderate range [34]. The value obtained in this study was in the same range as the value (0.54% to 1.84%) obtained by [35]. The total nitrogen (TN) of studied soil samples were found to be in the range of 0.16% to 0.19%. According to Havlin *et al.* (1999), the TN content of soils in the study area was categorized under the medium class [36]. The results are in agreement with the findings of Wakene and Heluf (2003) and Tuma (2007) who reported that intensive and continuous cultivation forced oxidation of OC and thus resulted in a reduction of TN [37] [38].

The available phosphorus (P) ranged from 5.84 to 9.91 mg/kg which was in the range with [35] which was found to be 5.65 mg/kg to 39.96 mg/kg. Concerning rating the levels of Olsen extractable P in the soil, the soil understudy could be rated as medium [39]. The lowest available P in Kindo Didaye was may be due to the inherent P deficiency of the soil and P fixation with Fe and Al by the favorable acidic soil reaction [40].

3.5. Distribution of Metals in Ginger Samples

The levels of essential and non-essential metals in the ginger samples determined with FAAS after sample dissolution with the optimized digestion procedure were expressed per dry weight as shown in Table 7 and Figure 1(a).

As shown in **Table 7**, ginger contains a higher amount of essential metal K (1691 - 3487 mg/kg), followed by Mg (701 - 1583 mg/kg) and Ca (862 - 1476 mg/kg). The higher level of K, Ca, and Mg in the ginger was probably due to the fact that nutrient elements such as N, P, K, S, Ca, and Mg are highly mobile in the plant tissue [41] [42] [43]. The other probable reason for the higher concentrations of K, Mg, and Ca is due to the presence of fertilized soil with manure and organic residues which is rich with these metals [44].

The concentration of Mn (325 - 672 mg/kg) in the ginger was higher among

Table 7. Concentration (Mean \pm SD, n = 3 in mg/kg dry wt.) of metals in ginger samples from five sample sites.

Metal	BB	BS	KK	DS	KD	cv	LSD
Na	565 ± 19 ^c	398 ± 25 ^e	512 ± 44^{d}	$634 \pm 32^{\mathrm{b}}$	776 ± 14^{a}	4.99	5.30
К	3487 ± 59^{a}	2825 ± 73^{b}	$2039 \pm 235^{\circ}$	1691 ± 29^{d}	$1820\pm77^{\rm d}$	5.01	216
Ca	$862 \pm 7^{\circ}$	1476 ± 24^{a}	1211 ± 71^{b}	1220 ± 42^{b}	797 ± 11 ^c	5.71	11.57
Mg	701 ± 29^{d}	$1114 \pm 14^{\circ}$	1583 ± 56^{a}	1241 ± 27^{bc}	1371 ± 93^{ba}	11.46	25.08
Mn	$419\pm5^{\rm d}$	$508 \pm 3^{\circ}$	672 ± 3^{a}	578 ± 5^{b}	325 ± 9^{e}	2.18	19.73
Fe	$6.14\pm0.4^{\rm d}$	$9.6\pm0.15^{\rm b}$	11.92 ± 0.61^{a}	11.58 ± 0.00^{a}	$8.86\pm0.15^{\rm c}$	3.53	6.18
Cu	ND	ND	ND	ND	ND	ND	ND
Zn	$5.30\pm0.03^{\rm d}$	$10.09\pm0.16^{\rm a}$	$8.08\pm0.14^{\rm b}$	$6.79\pm0.30^{\rm c}$	$5.63\pm0.15^{\text{d}}$	2.50	3.26
Co	ND	ND	ND	ND	ND	ND	ND
Cd	ND	ND	ND	ND	ND	ND	ND
Pb	$0.15\pm0.04^{\rm c}$	$0.17\pm0.02^{\rm b}$	0.12 ± 0.02^{d}	0.23 ± 0.02^{a}	$0.15\pm0.09^{\rm c}$	26.20	0.75

Means with the same letter in the same row are not significantly different at $\alpha = 0.05$. ND: Concentration of the tested heavy metal below the Method detection limit.

determined essential trace metals. Higher levels of Mn in the ginger may be attributed to the availability of this micronutrient in relatively acidic soils of the farmland. The chemical forms of Mn existing in the soil depend on the soil pH. In acidic soil, an easily absorbed form, Mn^{2+} released from soil by H⁺, which is produced from NH_4^+ [45], can be readily taken up and accumulated in the ginger.

The levels of other essential metals detected in ginger were Na (398 - 776 mg/kg), Fe (6.14 - 11.92 mg/kg), Zn (5.30 - 10.09 mg/kg) and non-essential heavy metals Pb (0.12 - 0.23 mg/kg). The level of Pb was the least among the metals in ginger; however, due to its toxicity deserves special concern.

Generally, potassium and magnesium were the most accumulated essential metals in the ginger samples while Pb was the least with slightly higher amounts in the sample collected from Damot Sore. The observed trend was K > Mg > Ca > Na > Mn > Fe > Zn > Pb and Co, Cu and Cd were below method detection limit in ginger samples. The distribution pattern of specific metals in ginger was discussed in detail as follows:

The concentration of sodium was ranged from 398 to 776 mg/Kg in ginger. The highest mean concentration was found in Kindo Didaye and the lowest concentration was found in Boloso Sore. The value obtained in this study higher than the value of 15 mg/kg reported by [46] and lower than the value (1908.75 mg/kg) reported by [14]. The pattern of concentration of sodium in ginger among different sampling sites was in the order of: Kindo Didaye > Damot Sore > Boloso Bombe > Kindo Koysha > Boloso Sore. One-way analysis of variance showed that the mean concentration of sodium in ginger was significantly different among the studied sites. Fisher's combined probability test using the LSD criterion for significance indicated that the mean concentration of sodium in the ginger sample from Kindo Didaye was significantly higher than other sampling sites at p < 0.001. The possible reasons for higher concentrations of Na in the Kindo Didaye district are probably due to geological differences in the soil and different agricultural practices.

Potassium was the most accumulated metal in ginger with mean concentrations varies from 1691 mg/kg in Damot Sore to 3487 mg/kg in Boloso Bombe. This higher concentration of K in ginger is may be because of its higher concentration in the soil. Weeraratna *et al.* (1977) reported that addition of K fertilizers to the soils rapidly increase the concentration of available K that could be attributed to the mineralization of the organic matter, the solubilization effect of rainwater, and due to increased chemical and biological fixation of potassium in the presence of fertilizers [44]. The concentration of K found in this study was in range with the value of 2442.75 mg/kg reported by [14].

The mean concentration of Calcium was ranged from 862 to 1476 mg/kg in ginger. The highest level of calcium in ginger was observed in Boloso Sore and the lowest concentration was found in Kindo Didaye.

One-way analysis of variance showed that the mean concentration of Ca in the ginger sample from Boloso Sore was significantly higher than other sample sites. The pattern of concentration of calcium in ginger among different sampling sites was in the order of Boloso Sore > Kindo Koysha = Damot Sore > Boloso Bombe = Kindo Didaye. Comparable levels of Ca (1031 mg/kg and 1161 mg/kg) in the ginger were reported from Pakistan and Nigeria respectively [13] [14].

Magnesium was the second most accumulated essential element in ginger next to K. The concentration was ranged from 701 mg/kg in Boloso Bombe to 1583 mg/kg in Kindo Koysha. In the study conducted in Pakistan, the content of Mg was found to be 12 mg/kg in ginger which was lower than the value obtained in this study [13]. The variation may be due to a difference in soil nature and agricultural practices. One-way analysis of variance showed that the mean concentration of Magnesium in ginger from Kindo Koysha was significantly higher than other sites except for Kindo Didaye.

The mean concentration of Fe in ginger was ranged from 6.14 to 11.92 mg/kg. The highest mean concentration was found in Kindo Koysha and the lowest concentration was found in Boloso Bombe. The concentration of Fe found in this study was slightly higher than the value of 2.88 mg/kg reported by [47]. This might be due to geographical and geological differences of the soil and different agricultural practices including the use of different agrochemicals. The permissible limit of iron set by FAO/WHO in edible plants was 20 ppm [48]. Comparing the level with the value obtained in this study it was lower. ANOVA showed that the mean concentration of Fe in ginger is significantly different among the studied sites except in Kindo Koysha and Damot Sore Districts.

The concentration of Manganese in ginger was ranged from 325 to 672 mg/kg. The highest level of Mn was observed in Kindo Koysha and the lowest concentration was found in Kindo Didaye. The value (184 - 401 mg/kg) reported by Yohannes and Chandravanshi (2015) was almost comparable with the value obtained in this study [49]. Higher Mn levels in the studied plant may be attributed to the availability of this metal in relatively acidic soils [50] [51]. The concentration of Mn in ginger obtained from Kindo Koysha was significantly higher than those sampled from the other sites. This may be due to the difference in the type of agricultural practice in Kindo Koysha.

As indicated in **Table 7**, the level of Zn in ginger was ranged from 5.30 to 10.09 mg/kg. The highest mean concentration of Zn in ginger was found in Boloso Sore and the lowest concentration was observed in Boloso Bombe. Comparable levels of Zn in ginger 13.93 mg/kg have been reported by [14]. One-way analysis of variance showed that the mean concentration of Zn in ginger was significantly different among the studied sites except for Kindo Didaye and Boloso Bombe. Fisher's combined probability test using the LSD criterion for significance indicated that the mean concentration of Zn in the ginger sample from Boloso Sore was significantly higher than other sampling sites at p < 0.001. This may be attributed to its higher concentration in the soil. The permissible limit set by FAO/WHO (1984) for edible plants is 27.4 mg/kg which is higher than

that found in the present study [48]. Zinc levels in this study were also below permissible values of 60 mg/kg in vegetables [52] implying that there was no Zn contamination in ginger. The concentration of copper and cobalt in ginger was below the method detection limit in all sample sites.

The concentration of Pb ranged from 0.12 to 0.23 mg/kg in ginger samples. Ginger from Damot Sore had the highest mean concentration which was significantly (p < 0.05) different from the mean value obtained from other sample sites. The mean levels of Pb in ginger were below the permissible values for vegetables (0.3 mg/kg) recommended by the FAO/WHO, implying that there was no lead contamination. The level of lead in ginger samples was also below the permissible limit required in spices (0.3 mg/kg) by the [52].

The permissible limit for Cd set by FAO/WHO (1984) in edible plants was 0.2 mg/kg. However, for medicinal plants, the permissible limit for Cd set by WHO (2005), China, and Thailand was 0.3 mg/kg in finished herbal products [53]. The level of cadmium in ginger in all sampling sites was below the method detection limit implying that there was no Cd contamination.

3.6. Distribution of Metals in Soil Samples

The levels of essential and nonessential metals in the soil samples determined with FAAS after sample dissolution with the optimized digestion procedure were expressed per dry weight as shown in **Table 8** and **Figure 1(b)**.

The soil sample collected from five sampling areas were found to contain detectable metal content of Na, K, Ca, Mg, Mn, Fe, Cu, Zn, Cd, and Pb. There was a significant difference in the concentration of different metals within the soil samples and appreciable differences recognized between the same metals of

Table 8. Concentration (Mean \pm SD, n = 3 in mg/kg dry wt.) of metals in soil samples from five sample sites.

Metals	BB	BS	KK	DS	KD	cv	LSD
Na	2129 ± 796^{cb}	2361 ± 56^{cba}	2969 ± 3^{a}	2640 ± 78^{ba}	$1896 \pm 200^{\circ}$	14.22	67.20
К	3420 ± 42^{b}	3717 ± 158^{a}	3740 ± 80^{a}	$2826 \pm 194^{\rm c}$	2785 ± 8^{c}	3.62	216.4
Ca	$1143 \pm 40^{\circ}$	$1130 \pm 16^{\circ}$	1785 ± 23^{a}	1656 ± 20^{ab}	1230 ± 35^{cb}	0.51	5.10
Mg	$2176 \pm 37^{\circ}$	2023 ± 34^d	3211 ± 12^{a}	$1971\pm0^{\rm d}$	$2520\pm50^{\rm b}$	1.36	58.70
Mn	1240 ± 4^{b}	1265 ± 6^{b}	1174 ± 1°	1317 ± 1^{a}	1000 ± 7^{d}	1.37	29.90
Fe	3673 ± 3^{bc}	3707 ± 3^{ba}	3755 ± 0^{a}	$3602\pm88.0^{\circ}$	3673 ± 3^{bc}	1.07	71.80
Cu	22 ± 4^{c}	$35\pm7^{\mathrm{b}}$	13 ± 4^{d}	48.6 ± 11 $^{\rm a}$	41 ± 5^{ba}	19.56	11.50
Zn	$135\pm7.0^{\mathrm{b}}$	$192.5\pm2^{\rm a}$	112 ± 2^{c}	105 ± 2^d	84.7 ± 2 ^e	2.94	6.73
Co	ND	ND	ND	ND	ND	ND	ND
Cd	0.20 ± 0.01^{a}	$0.19\pm0.03^{\text{a}}$	$0.22\pm0.03^{\text{a}}$	0.19 ± 0^{a}	$0.20\pm0.02^{\text{a}}$	11.33	0.04
Pb	$0.18\pm0.02^{\circ}$	0.25 ± 0.02^{bc}	$0.36\pm0.04^{\rm a}$	0.22 ± 0.04^{bc}	$0.31\pm0.09^{\mathrm{ba}}$	19.83	0.10

Means with the same letter in the same row are not significantly different at α = 0.05. ND: Concentration of the tested heavy metal below the Method detection limit.



Figure 1. Metal concentration in the ginger (a), and in the supporting soil samples (b).

different sample sites.

The concentration of Fe (3602 - 3755 mg/kg) in the soil exceeds much the concentration of other essential elements, this may be due to the presence of an excess amount of hematite (Fe₂O₃) in the soil. This was in good agreement with the analysis conducted by Minaleshewa (2010), soils with low pH contain a high amount of Fe and Al oxides [42].

Concentration of Mn (1000 - 1317 mg/kg) in the soil was higher when compared to Zn (84.7 - 192.5 mg/kg) and Cu (13.0 - 48.6 mg/kg). Higher Mn levels in the studied soil may be attributed to the availability of this metal in relatively acidic soils [50] [51]. On the other hand, levels of the toxic heavy metals Cd ranges from 0.19 - 0.22 mg/kg, and Pb ranges from 0.18 - 0.36 mg/kg. In general, the concentration pattern of metals in soil was decreased as Fe > K > Mg > Na > Ca > Mn > Zn > Cu > Pb > Cd. Among the analyzed metals, Co was found to be below the detection limit of the method used in this study. The distribution pattern of specific metals in the soil was discussed comprehensively as follows:

The concentration of sodium was ranged from 1896 to 2969 mg/Kg in the soil sample. The highest mean concentration of Na in the soil samples was found in Kindo Koysha and the lowest concentration was observed in Kindo Didaye. The

pattern of concentration of sodium in the soil among different sampling sites was in the order of Kindo Koysha > Damot Sore > Kindo Didaye = Boloso Bombe = Boloso Sore. One-way analysis of variance showed that the mean concentration of sodium in the soil from Kindo Koysha was significantly higher than other sample sites at p < 0.001. The concentration of Na obtained in this study was higher than the value reported by [54]. The reason for this difference may be due to the use of different methods of farming, geographical, and climatic variation of the sites.

Potassium was the second most accumulated essential metal in the soil next to Fe. The level of K in the soil was ranged from 2785 mg/kg in Kindo Didaye to 3740 mg/kg in Kindo Koysha. Relatively higher K content in the soils may be due to the application of NPKS fertilizers [55]. A Higher concentration of K in the soil was reported by Michael (2006) and a lower level of K was reported by [56].

The mean concentration of Ca was ranged from 1130 to 1785 mg/kg in the soil sample. The highest content of calcium in the soil was observed in Kindo Koysha and the lowest concentration was found in Boloso Sore. This lower concentration of Ca in the soil of Boloso Sore may be due to relatively higher rainfall, which causes the intensive leaching of Ca in the soils. According to Solomon *et al.* (2001), high rainfall in the area causes extensive leaching of Ca and Mg rendering these metals to exist at lower levels [55]. One-way analysis of variance showed that the mean concentration of Ca in the soil was significantly different among the studied sites. Fisher's combined probability test using the LSD criterion for significance indicated that the mean concentration of Ca in the soil sample from Damot Sore was significantly higher than other sampling sites at p< 0.001. The concentration of Ca in the soil (1435 - 1775 mg/kg) reported by Feleke (2010) was in the range with the present study [57].

The level of Magnesium in the soil was ranged from 1971 mg/kg in Damot Sore to 3211 mg/kg in Kindo koysha. One-way analysis of variance showed that the mean concentration of Magnesium in the soil was significantly different among the studied sites except for Boloso Sore and Damot Sore. Fisher's combined probability test using the LSD criterion for significance indicated that the mean concentration of magnesium in the soil from Kindo koysha was significantly higher than other sampling sites at p < 0.001. The concentration (1257 -3306 mg/kg) of Mg in the soil reported by Feleke (2010) was in the range with the concentration obtained in this study.

Iron was the most accumulated metal in the soil under investigation with mean concentration ranged from 3602 to 3755 mg/kg. The highest mean concentration was obtained in Kindo Koysha and the lowest concentration was found in Damot Sore. The soil understudy was a dark reddish-brown color which is indicative of the presence of an excess amount of hematite (Fe_2O_3) [55]. Soils with low pH comprise high amounts of Fe and Al oxides [58]. These may be the reason behind the higher content of Fe metal in these soils. One-way

analysis of variance showed that the mean concentration of iron in the soil was significantly different among the studied sites, at p < 0.001.

The level of manganese in the soil ranged from 1000 to 1317 mg/kg. The soil from Damot Sore had the highest mean level of manganese and the lowest mean concentration was found in Kindo Didaye. One-way analysis of variance showed that the mean concentration of Mn in the soil was significantly different among the studied sites except for Boloso Sore and Boloso Bombe. Comparable level (1030 - 1470 mg/kg) of Mn was reported by [54]. The concentrations of manganese found in this study were lower than the FAO/WHO (2001) recommended limit in the agricultural soil indicating that there was no Mn toxicity.

As shown in **Table 8**, Zn levels in the soil ranged from 84.70 mg/kg to 192.50 mg/kg. The mean concentration of Zn in the soil samples was highest in Boloso Sore which was significantly higher than other sampling sites. This is attributed to farming methods used by farmers in Boloso Sore such as the use of fertilizers and the application of compost manure. Use of agrochemicals such as fertilizers and pesticides has been reported as one source of Zn in the soil [59] while application of compost manure not only results in Zn accumulation in soil but also causes an increase in Zn mobility and enhances Zn leaching [60]. The concentration levels of Zn in this study were in the range with the value (25.50 - 440.30 mg/kg) obtained by [43]. The levels of Zn in this study showed that there was no Zn contamination in the soil since the maximum permissible limit of Zn concentrations in soil is 300 mg/kg [61] [62].

The concentration levels of Cu in the soil ranged from 13.00 to 48.60 mg/kg. The highest mean concentration values were found in Damot Sore which was significantly (p < 0.05) different from mean values obtained in Boloso Bombe, Boloso Sore and Kindo koysha. But the difference was not significant in the soil sample obtained from Kindo Didaye. The difference in Cu levels in the sampling sites could be attributed to the difference in their parent materials. Comparable levels of Cu in soil with a mean value of (43.96 - 71.27 mg/kg) have been reported by [54]. Copper concentration levels reported in this study were below the permissible limits for agricultural land use of 100 mg/kg [52] implying that there was no Cu contamination in the soil. The concentration of cobalt was below the method detection limit in the soil of all sample sites.

As shown in **Table 8**, the levels of lead in soil ranged from 0.18 to 0.36 mg/kg. The highest mean value was recorded in Kindo Koysha and the lowest value was found in Boloso Bombe. The higher level of Pb in Kindo Koysha could be attributed to the addition of artificial fertilizer and pesticides to the soil which leads to an increase of Pb levels in agricultural soil [63]. The values of Pb obtained in this study were lower than Ewers (1991) recommended maximum limit that is 100 mg/kg indicating that there was no Pb contamination in the soil under investigation.

Cadmium content in the soil was ranged from 0.19 mg/kg to 0.22 mg/kg (Table 8). The higher concentration of Cd observed in Kindo Koysha and the

lowest value was observed in Boloso Sore. But the difference was not significant among all sampling sites. The possible source of cadmium might be the application of phosphate fertilizer in which cadmium exists as an impurity [64]. The amount of cadmium determined in this study was lower than Ewers (1991) recommended maximum limit for soil that is 3 mg/kg.

3.6. Correlation of Metal levels between Ginger and Soil Samples

For most metals, the levels in some sampling area of ginger were varied not proportionally to levels of the same metals in the corresponding soil. This inequivalent variation in the level of metals in ginger and soil may result from the difference in availability of the absorbable form of metals in soil due to differences in soil acidity or the presence of competing ligands [65]. The level of metals in ginger was less than the level of metals in the soil from all sampling sites. Hence, ginger is said to be a non-hyper accumulator/non-phytoremediator [66]. The higher concentration of metals in the soil than ginger indicates most metals in the soil were not in the bio-available form. To correlate the effect of one metal on the concentration of the other metal, the Pearson correlation matrices using correlation coefficient (r) for the samples were used and presented in **Table 9**.

As shown in **Table 9**, metals K, Mg, Zn, and Mn showed a positive correlation in soil and ginger indicating that the more level of each metal in the soil, the more the accumulation of corresponding metals in the ginger. This verifies that the dependence of metal concentration in the plant on the metal concentration of respective soil. Na in soil with Na in ginger, Ca in soil with Ca in ginger, Fe in soil with Fe in ginger, and Pb in soil with Pb in ginger have a negligible relationship. This poor correlation can lead to the probable conclusion that the concentration of metals in the soil measured by the total metal determination method cannot be used as a predictor of metal concentration in ginger. This may be due to the fact that total metal contents of soil contains all exchangeable metals, carbonate bound metals, oxides bound metals, organic matter bound metals and residues, while metals which are bioavailable for plant uptakes are found in

	Ta	Ы	.e 9),]	Pearson	correlation	coefficient	for	metals	in	ginger	with	soil	samr	ole
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Metals	Na in ginger	K in ginger	Mg in ginger	Ca in ginger	Fe in ginger	Zn in ginger	Mn in ginger	Pb in ginger
Na in soil	-0.39	-0.26	0.47	0.39	0.63*	0.36	0.83**	-0.06
K in soil	-0.88**	0.53*	-0.05	0.51*	0.02	0.64*	0.47	-0.43
Mg in soil	0.06	-0.29	0.65*	-0.14	0.36	0.01	0.36	-0.56*
Ca in soil	-0.16	0.63*	-0.37	042	-0.55*	-0.37	0.01	-0.49
Fe in soil	-0.45	0.19	0.26	0.18	0.08	0.41	0.24	-0.55
Zn in soil	-0.87**	0.64*	-0.40	0.66*	-0.19	0.73*	0.14	0.01
Mn in soil	-0.62*	0.29	-0.41	0.61*	0.15	0.37	0.55*	0.36
Pb in soil	0.09	-0.51*	0.67*	0.05	0.48	0.24	0.27	0.06

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

the exchangeable metals [67].

Sodium in ginger showed a negative correlation with K, Zn, and Mn in the soil. Potassium in ginger showed a positive correlation with Ca and Zn whereas a negative correlation with Pb in the soil. Magnesium in ginger showed a positive correlation with Pb in the soil. Calcium in ginger showed a positive correlation with Zn and Mn in the soil.

3.7. Correlation of Metals within Ginger Sample

As shown in **Table 10**, there was a negative correlation for Na with (K, Zn, and Mn) and K with (Mg and Fe). Positive correlation for Mg with (Fe), Ca with (Fe, Mn, and Zn), Fe with (Mn) and Zn with (Mn) was observed. Metals interact with other metals in the uptake process by the plants. This is because some metals have similar chemical properties. For example, Mn shows properties of both the alkaline earth cations such as Mg²⁺ and Ca²⁺ and the heavy metals (Zn, Fe) [67]. This could be the probable reason for high positive correlation for Mg with (Fe), Ca with (Fe, Mn, and Zn), Fe with (Mn) and Zn with (Mn) which may arise from common anthropogenic or natural sources as well as from similarity in chemical properties.

The high negative correlation for Na with (K, Zn and Mn) and K with (Mg and Fe) indicate the large absorption of one metal may affect the absorption of another metal in the ginger plant. The other metals have a weak negative or positive correlation indicating that the presence or absence of one metal has an effect to a lesser extent on the other. According to Kraus (2002) and Santos (2009), with increasing application of potassium, the content of Fe and Cu decreases in plant tissues [68] [69]. Therefore, the interaction of K with Fe and Cu is antagonistic. This could be the reason behind the negative correlation of K with Fe in ginger.

	Na	K	Mg	Ca	Fe	Zn	Mn	Pb
Na	1							
К	-0.517*	1						
Mg	0.180	-0.773**	1					
Ca	-0.780**	-0.034	0.213	1				
Fe	-0.120	-0.750**	0.787**	0.588*	1			
Zn	-0.794**	0.011	0.274	0.921**	0.490	1		
Mn	-0.542*	-0.243	0.408	0.667**	0.755**	0.537*	1	
Pb	0.137	-0.218	-0.140	0.131	0.145	0.001	0.001	1

Table 10. Pearson Correlation matrices for metals in ginger sample.

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

4. Conclusion

The optimized wet digestion method was used and evaluated by spiking ginger

and soil samples and their percentage recoveries were within the range of 90% - 100.6% which was within the acceptable range. The result showed that ginger accumulates relatively higher amounts of K, Mg, and Ca among the determined essential metals. Non-essential metals analyzed in this study were below the permissible ranges presented by FAO/WHO standards. Hence, the plant is safe for dietary and medicinal uses with reference to analyzed metals. A positive correlation between metals in the ginger and soil was obtained for Mg, Zn, K, and Mn indicating that the more level of metals in the soil, the more accumulation of corresponding metals in the ginger. The studied soil was found to be acidic in nature, sandy clay loam in texture, very low electrical conductivity and a moderate level of (CEC, organic carbon, available phosphorus, and total nitrogen).

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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