

Research Article

Evaluating the Level of Essential and Non-Essential Metals on Papaya (*Carica Papaya*) and Hop (*Rhamnus Prinoides*) Plants in Gummer Woreda Gurage Zone, Central Ethiopia

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Abstract

Unindustrialized countries like Ethiopia; the local plants play major roles to the limited modern health care available. Therefore, the objective of the study was to evaluate essential and non-essential metals; Ca, Mn, Zn, Cu, Fe, Mg, Cd, and Pb of Hop (*Rhamnus Prinoides*) and Papaya (*Carica papaya*) which are commonly used in Gummer woreda central Ethiopia. The level of these metals cultivated were determined using flame atomic absorption spectrometry. The analysis of optimized wet digestion method which a 0.5 g sample using a mixture of 2 ml HNO₃ and 2 ml HClO₄ at 150°C for 210 minutes. The digestion was evaluated by spiking the samples and their percentage recoveries in the range of 89–103.5%. The results showed that both plants under investigation have the ability to accumulate relatively higher amounts of Ca among the determined essential metals. The concentration ranges in dry weight basis in decreasing order for the samples were: Ca (3.27-5.85 mg/kg) > Mn (1.13-3.98 mg/kg) > Zn (1.58-2.96 mg/kg) > Fe (1.17-2.79 mg/kg) > Mg (1.57- 2.54 mg/kg) > Cu (1.09-2.47 mg/kg). The concentration of Pb and Cd in the samples was below the limit of detection. All the non-essential metals analyzed in this study were below the permissible ranges presented by FAO/WHO standards. Hence, the studied plant is safe for dietary and uses with respect to the analyzed metals. Additional studies will be continued on the screening of of the plants based on phytochemical activities.

Keywords

Elemental Inquiry, Flame Atomic Absorption Spectroscopy, Metals, Plants

1. Introduction

World traditional medicines composed of herbs, herbal materials, herbal preparations, and as well as finished herbal products, that contain as active ingredients parts of plants, or other plant materials, or combinations of all. In Africa, up to 80% of the population uses traditional medicine for primary health care. Traditional medicine has maintained its popularity in all regions of the developing world and its use is rapidly

spreading in the industrialized countries [1]. Plants not only serve as complements or substitutes for modern medical treatments, which are often inadequately available, but also enhance the health and security of local people. Evidence obtained from observations of animals shows that even chimpanzees use of plant species for their medicinal value [2]. Thus, these plants play indispensable roles in daily life

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and are deeply connected to diverse social, cultural, and economic events associated with life, illness and death [3]. Historical accounts confirm that traditional medicinal plants were in use as early as 5000 to 4000 B. C in China, and 1600 B. C by Syrians, Babylonians, Hebrews and Egyptians. Local plants in the developing countries play major supplementary roles to the limited modern health care and considered as a rich resources of ingredients. Ten percent of all vascular plants are used as plants in the world [4].

Ethiopia plants have shown very effective contributions for some ailments of human and domestic animals which include *Phytolacca dodencadra* [5], and also many species of *Maytenus* studied by National Cancer Institute [6]. In developed countries this may be partly due to the dissatisfaction with conventional medicines while with the developing countries this is due to lack of medical doctors, shortage of pharmaceutical products and their unaffordable prices.

Some plant species of Ethiopia are reported to have been threatened by the overuse over harvesting for marketing as medicine. A good example is *T. byssinica* whose slender roots are bandaged and small coiled bundles presented for market. Plants like *Moringa oleifera* have been found high levels of essential metals (Na, Ca, Mg, K, Na, Mn, Fe, Zn, Co, Cu, Ni) and level of non-essential metals like Pb and Cd [7]. and *Hibiscus sabsdariffam* plants have been contains level of essential metals like Al, Ca, Mg, K, Na, Mn, Fe, Zn, Co, Se and level of non-essential metals like Pb and Cd [8].

The level of essential metals (Na, Ca, Cu, Fe, Zn, Mn, Cr, Ni, K, Mg, Mn, Co) acceptable by the WHO should not endanger the health of consumers [9]. The World Health Organization cites maximum permissible levels in raw plant materials only for cadmium (0.3 mg kg^{-1}), arsenic (1 mg kg^{-1}) and lead (10 mg kg^{-1}). The continuity of such research endeavor's, in terms of periodical assessment of these and other metal concentration in all the known herbal plants used in plants, would go a long way toward predicting the quality assurance and safer use of herbal products.

Some plants contaminated by metals in the course of cultivation locally consequently determining the content of the metals accumulated in high position. The body of human requires both the metallic and the non-metallic elements within convinced permissible limits for progress and healthiness. Nevertheless, the presence of some heavy metals in massive amounts in the body may have a poisonous effect on the human body. Consequently, toxicity from the active ingredients, the individuals may suffer from trace toxic metal toxicity and hence their normal body function will be affected as trace metals are responsible for most of our body enzymatic activity [10].

Moreover known that the source of mineral nutrients for human being is plant materials consumed in the form of food or medicine. Until the 18th century, the therapeutic properties of many plants, their effect on the human, organism and their method of treatment were known, but the active compound was unknown [11]. In the cause of study area, varies

plants are used to cure a number of diseases by most of individuals the area traditionally in a regular basis. Thus, it is imperative to evaluate the essential metals and non-essential metals in the leaves of plant sample from the plant garden to address the individual intake of mineral nutrients. Currently, there is no documentation which was estimated about the essential and non-essential metals in the leaves of these plants in Gummer worda Central Ethiopia. Subsequently the knowledge of their mineral concentration is the particular interest to propose the maximum dosage of the plants leave for normal body function in terms of essential and non-essential metals content in the study site. Therefore, this research was initiatively conducted to evaluating of essential (Mg, Ca, Cu, Fe, Zn, and Mn) and non-essential metals (Pb, Cd) in Hop (*Rhamnus Prinoides*) and Papaya (*Carica papaya*) plants leaves of the study area.

2. Materials and Method

2.1. Description of the Study Area

Guraghe Zone is one of the zones found in the central parts of Ethiopia. It is bordered on the south by Hadiya on the West, North and East by Oromia Region, Yem on Southwest and on the Southeast by Silte Zone. This study was conducted in Gummer worda, Gurage zone, southern Ethiopia. Arekit is the capital town of the worda located at about 65 Km South East of Wolkite town. According to 2007 population census, the total population of Gummer worda was approximated to 80,163 with the total households of 16,360 [12]. The predictable population for 2012 was 92,481 with 18,874 households by considering 2.9% as natural increase rate of Southern Ethiopia. Similar to other rural Ethiopian ethnic groups, the economy of Gummer Worda households is based on farming. As Gummer's past records reveal that the people conduct farming and animal husbandry for centuries.

2.2. Sample Collection

The leaves of plant samples taken from the farmers of plant plot for Hop (*Rhamnus Prinoides*) and Papaya (*Carica papaya*) which are sited in Bole, Kabul and Jomboro Kebele. Each sample was collected randomly from 6 trees in each sampling sub-sites by using cluster sampling techniques. For both plants a three data point per site for basic test and three triplicates for 2 varieties ($3 \times 2 = 6$) of plant sample was collected by using random sampling technique from the study area. Depending on the availability of the plants, about 100 gm of plant sample from each leaves was collected from garden of plants and packed into polyethylene plastic bags, labeled and transported to the laboratory for further treatment.

2.3. Sample Preparation

The collected leaves of plants sample was wash with a tap water and detergent so as to eliminate dirt, rinsed with distilled water and air dried. Plant samples were crushed and powdered by blending device and specified quantity was taken in an evaporating dish and heated in an oven at 105°C to remove moisture. Then the sample was cooled, ground, sieved and placed in cleaned screw covered polyethylene container. This process was set in a closed system, so the sample decomposition had no contact with external surroundings. Blank solutions were prepared by nitric acid.

2.4. Instruments and Apparatuses

Digital analytical balance was used for weighing the samples. Round bottom flasks with grounded glass (100 mL) fitted with reflux condenser was employed in digesting the sample on Kjeldahl heating apparatus (Gallenham, England). Stainless steel axe and Teflon (SSAT) knife was used to cut the plant species. Blending device, ceramic pestle and mortar were used for grinding and homogenizing the samples. Borosilicate volumetric flasks (50, 100 and 250 mL) were used during dilution of sample and preparation of metal standard and infusion solutions. Measuring cylinders, pipettes, micropipettes (Dragon med, 1-10 µL, 100-1000 µL) used during measuring different quantities of volumes of sample solution, acid reagents and metal standard solutions. Metals' concentration level was done by flame atomic absorption Spectrophotometer (FAAS) equipped with deuterium background corrector and hollow cathode lamps with air-acetylene flame.

2.5. Chemicals and Reagents

The analytical grade reagents were used for cleaning the glass wares and digesting the leaf samples throughout this work. These are nitric acid 69-72% and 70% HClO₄ was used for the digestion of the plant samples. Stock standard solution of concentration 1000 mg/L in 2% HNO₃ of the metals of reagent grade (Buck Scientific Pure-Graphic) salts of; Mg, Ca, Mn, Fe, Zn, Cr, Cd, and Pb from which 100 mg/L of intermediate standard obtained was for the preparation of the calibration standards of each metal and working standards were prepared from intermediate standards of each metal. For the sample preparation, dilution, and cleaning apparatus prior to analyses deionized water was used [13].

2.6. Experimental Procedures

2.6.1. Cleaning Apparatus

All glass and plastic containers and polyethylene bags were washed with tap water and kept overnight in 10% (v/v) nitric acid solution. After wards, it was cleaned thoroughly with deionizer water and dried in oven and glass ware was kept in clean place, to avoid contamination.

2.6.2. Procedure of Optimization Working

To get a consistent outcome from an analytical experiment; it was prepared a clear and colorless sample solution that is suitable for the analysis using FAAS, different working procedures for the digestion of plant samples were assessed using mixtures of HNO₃ and HClO₄ acids by varying parameters such as volume of the acids mixture, digestion time and digestion temperature. By examining the nature of the final digests obtained by varying the above parameters, the optimized procedure was selected depending up on the clearness of the digests, less digestion time, less reagent volume consumption and simplicity [13].

2.6.3. Sample Digestion

0.5 g of the crushed, powdered and sieved portion of each plant leave samples were accurately weighed on a digital analytical balance and quantitatively transferred into digestion tubes. An optimized amount of freshly prepared mixture, 3 mL of conc. HNO₃ (69-72%) and 3 mL of HClO₄ (70%) were added to each of plant samples, according to optimized digestion procedures of each plant samples. The digested solution was allowed cooling for 40 minutes. To the cooled solutions, a 20 mL portion of distilled deionizer water was added to dissolve the precipitate formed on cooling and gently swirled. The resulting solutions were filtered into a 50 mL volumetric flask with a Watchman filter paper to remove any suspended residues. Subsequent rinsing of the filtrate with 10 mL distilled demonized water was followed until the volume reached the mark. The digestions of the reagent blank samples also were performed in parallel with the plant samples keeping all the digestion parameters the same. The digested and diluted sample solutions were stored in volumetric flask and finally, the digests were kept in refrigerator until analysis.

2.7. Evaluation of Essential and Non-Essential Metals

The intermediate standard solutions were prepared from the stock solutions and a series of dilute solutions of each metal (Na, Ca, Cu, Cr, Zn, Pb, Mn and Cd) under analysis, at different points as the expectations; were prepared from the intermediate standard solutions. For example, the stock solution of calcium was prepared by dissolving appropriately measured grams of calcium salts in distilled water and the working solutions were measured in ppm. Similarly, zinc stock solutions were prepared by dissolving appropriate grams of zinc in distilled water. The diluted working solutions were measured in ppm and the same working solutions were prepared in the concentration range (in ppm) for the other metals. Flame Atomic Absorption Spectroscopy was used for the analysis of the selected level of essential and non-essential metals. After scanning a blank, a standard solution and a sample solution in the programmed wavelength range, the background correction wavelengths were selected manually at appropriate back-

ground positions for each analyze peak. The intensity of essential metals and the absorbance of non-essential metals were obtained from triplicate measurements.

2.8. Method Validation

Validation method provides that analytical satisfactory for its proposed purpose. The recoveries of metals were studied by spiking known amounts of standard solution to samples. The concentration can be distinguished from fluctuations in a blank, which usually corresponds to average of the blank signal plus three times standard deviation of the blank (Limit of detection = $y_B + 3SD$, where SD = standard Deviation of the blanks) (Miller and Miller, 2005). Method detection limit analyzed that can be measured and reported with 99% confidence that the analyze concentration is greater than zero. In order to determine the method detection limits eight blank samples were digested following the same procedure as the plant samples and each of the blank samples were analyzed for (Mg, Ca, Cu, Fe, Zn, Pb, Mn and Cd) by using FAAS. The recoveries of the spiked samples were calculated using the following formula [13].

$$\text{Percentage of recovery} = (\text{amount after spike} - \text{amount before spike}) / \text{amount added} * 100$$

2.9. Statistical Analysis

One-way variance analysis (ANOVA) and t-test was widely used statistical methods to compare group means. ANOVA uses the F statistics to compare whether the difference between sample means were significant or not. Data entry organization and preliminary.

Summaries done on Microsoft Excel spread sheet. The means, and standard deviations of the data collected was determined using Microsoft Excel. Linear correlations were determined using the Pearson product-moment correlation. The SAS 9.13 for windows version software program was used for statistical analyses.

3. Result and Discussion

3.1. Optimization of Digestion Procedure

Varies conditions tested for optimization of digestion procedure for 0.5 g of plant samples are summarized in Table 1. From the optimization procedure the acid mixture of 2 ml of HNO_3 (70%) and 2 ml of HClO_4 (70%), digestion time of 190 minutes and digestion temperature of 150°C were found to be the optimal conditions for digestion.

Table 1. Optimization of digestion procedure of samples.

No	Wt. (g)	Reagent in volume			Maximum Temp ($^\circ\text{C}$)	Time (min)	Observation
		HNO_3	HClO_4	Total			
1	0.5	6	3	9	310	190	Pale yellow solution
2	0.5	4	3	7	310	190	Clear and colorless
3	0.5	6	1	7	310	190	Brown yellowish
4	0.5	3	3	6	310	190	Clear but pale
5	0.5	5	1	6	310	190	Pale yellow solution
6	0.5	5	2	7	280	160	Pale yellow solution
7	0.5	5	1	6	280	160	Pale yellow solution
8	0.5	3	3	6	280	160	Clear and yellowish
9	0.5*	3*	3*	6*	280*	130*	Clear and colorless
10	0.5	3	3	6	250	190	Brown yellowish

Table 2. Working conditions of the instrument.

Metals	Wavelength (nm)	Lamp current (MA)	Slit width	Instrumental Detection Limit (IDL)	Flame source/color
Ca	423.600	3.00	0.700	0.010	C_2H_2 gas/blue
Mg	287.100	4.00	0.500	0.001	C_2H_2 gas/blue

Metals	Wavelength (nm)	Lamp current (MA)	Slit width	Instrumental Detection Limit (IDL)	Flame source/color
Zn	214.700	2.00	0.700	0.005	C ₂ H ₂ gas/blue
Fe	249.200	7.00	0.300	0.030	C ₂ H ₂ gas/blue
Mn	238.500	6.00	0.200	0.020	C ₂ H ₂ gas/blue
Cu	291.300	5.00	0.400	0.002	C ₂ H ₂ gas/blue
Cd	229.800	2.00	0.600	0.005	C ₂ H ₂ gas/blue
Pb	284.300	5.00	1.00	0.100	C ₂ H ₂ gas/blue

3.2. Evaluation of Analytical Method

As shown in Tables 1 and 2 the proportion recovery for selected two plant samples lie in the range 89-103.5%, which are within the acceptable range for metals [14].

Table 3. Recovery test for the papaya sample.

Metal	Conc. in sample (mg/L)	Amount added (mg/L)	Conc. in spiked sample (mg/L)	Recovery (%)
Ca	3.87	2	5.72	92.5
Mg	2.06	2	3.86	90
Mn	1.79	2	3.62	91.5
Fe	1.91	2	3.81	95
Zn	2.54	2	4.57	103.5
Cu	2.25	2	4.19	97
Cd	ND	-	-	-
Pb	ND	-	-	-

Table 4. Recovery test for the Hop sample.

Metal	Conc. in sample (mg/L)	Amount added (mg/L)	Conc. in spiked sample (mg/L)	Recovery (%)
Ca	5.83	2	7.83	100
Mg	2.17	2	4.27	105
Mn	2.99	2	5	100.5
Fe	1.63	2	3.43	89
Zn	2.1	2	4	95
Cu	1.75	2	3.56	90.5
Cd	ND	-	-	-
Pb	ND	-	-	-

3.3. Evaluation of Metals in Plant Samples

The evaluation of essential and non-essential metals in the two plant samples determined with FAAS after sample dissolution with the optimized digestion procedure were expressed per dry weight as shown in Table 5.

Table 5. Concentration (mean \pm SD, $n = 3$ in mg/kg dry wt) of metals in plant samples from three sample sites.

Sites	Plants	Metals							
		Ca	Mg	Cu	Zn	Mn	Fe	Cd	Pb
Wosh wocha	Papaya	3.95 \pm 0.07 ^g	2.21 \pm 0.31 ^{dc}	2.10 \pm 0.13 ^{cbd}	2.34 \pm 0.00 ^{ba}	1.93 \pm 0.12 ^{gf}	2.79 \pm 0.05 ^c	ND	ND
Dekeya	Hop	5.91 \pm 0.09 ^a	2.21 \pm 0.24 ^{dc}	1.90 \pm 0.13 ^{ced}	2.07 \pm 0.06 ^{fed}	2.98 \pm 0.06 ^{cd}	1.74 \pm 0.05 ^d	ND	ND
Kabul	Papaya	5.11 \pm 0.11 ^d	2.54 \pm 0.06 ^a	1.09 \pm 0.26 ^{hg}	2.96 \pm 0.21 ^a	1.49 \pm 0.10 ^h	1.62 \pm 0.01 ^{edf}	ND	ND
	Hop	5.64 \pm 0.19 ^{bc}	1.90 \pm 0.09 ^{fe}	1.62 \pm 0.15 ^{fe}	1.58 \pm 0.06 ^g	1.13 \pm 0.15 ⁱ	1.63 \pm 0.00 ^{ed}	ND	ND
Bole	Papaya	5.18 \pm 0.15 ^d	2.18 \pm 0.16 ^{dc}	1.96 \pm 0.10 ^{ced}	2.96 \pm 0.00 ^a	1.89 \pm 0.12 ^g	1.17 \pm 0.05 ^g	ND	ND
	Hop	5.85 \pm 0.06 ^{bc}	1.57 \pm 0.11 ^{fe}	2.47 \pm 0.16 ^{cb}	1.88 \pm 0.01 ^f	3.98 \pm 0.06 ^d	1.72 \pm 0.10 ^d	ND	ND
CV		2.68	7.68	9.53	6.89	4.23	7.16	-	-
LSD		0.23	0.27	0.29	0.26	0.19	0.21	-	-

Means with the same letter in the same row are not significantly different at $\alpha=0.05$. CV: Coefficient of Variance

ND: Concentration of the tested heavy metal below the Method detection limit. LSD: Least Significant Difference

The exception of Pb and Cd, all the metals under investigation (Ca, Mg, Fe, Mn, Cu and Zn) were detected above Table 5. The ranks of metals however differ significantly among plants and accordingly sampling sites. The result revealed that, calcium is the most accumulated essential metal in both plants. This is in line with the study of Ayenew *et al.* 2014, which the higher level of Ca in plants 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. The other probable reason for higher concentration of Ca is due to different agricultural practice as the present of fertilized soil with manure and organic residues which is rich with these metals [15]. Particularly also it was approved in the study site that the Jomborokebele uses manure and organic residue on their agricultural lands.

Calcium

The mean concentration of Calcium was ranged from 3.95 to 5.85 mg/kg. The top level of calcium was observed in Hop collected from Jomboro and the lowest concentration was found in Papaya sample collected from Wosh wocha Dekeya. One –way analysis of variance showed that the mean concentration of Ca in Hop sample was significantly higher than papaya plants. The pattern of concentration of calcium among different sampling site was in order of; Bole > Kabul > Wosh wocha Dekeya. The distribution calcium pattern between two plants in order: Hop > Papaya. However, the result of this study indicated that the concentration of calcium was smaller than the study reported in Nigeria which the levels of Ca stated to be 248.6 μ g/g and in Ethiopia it was reported 170- 320 μ g/g in medicinal plants [16]. This might be recognized to different plant species had varying concentration pattern abilities to take up and accumulate metals [17].

Magnesium

The concentration of magnesium was ranged from 1.57 mg/kg in Hop from Bole to 2.54 mg/kg in Papaya sample collected from Kabul. One –way analysis of variance showed that the mean concentration of Mg in Papaya sample was significantly higher than Hop plants. The pattern of concentration of magnesium among different sampling was in order of; Kabul > Jomboro > Bole. In the plants; Papaya > Hop. Similarly, the study conducted by [18] the content of Mg in papaya which was higher than the value obtained in this study. The variation may be due to difference in soil nature and the different agricultural land practices.

Copper

The concentration of copper was ranged from 1.09 to 2.47 mg/Kg. The highest mean concentration was found in Hop sample collected from Bole and the lowest concentration was found in Papaya from Kabul. The concentration of copper sampling site was in order of; Bole > Jomboro > Kabul. The distribution pattern of copper in both plants was in order; Hop > Papaya. Fisher's combined probability test using the LSD criterion for significance indicated that the mean concentration of copper in both plants sample from Bole was significantly higher than other sampling sites at $\alpha = 0.05$. The outcomes showed that concentration of copper in both plants was below the accepted limit set by FAO/WHO and allowable limit of copper set by China and Singapore in medicinal plants, which were 20 mg/kg and 150 mg/kg respectively [10]. The possible reason for higher concentrations in Cu was probably due to geological differences of the soil and similarly different agricultural practices.

Zinc

As indicated in Table 5, the level of Zn in plants was ranged from 1.58 to 2.96 mg/kg. The highest and lowest mean concentration of Zn was found in papaya, 2.96 mg/kg from Kabul. The concentration of zinc among different sam-

pling site was in order of; Kabul> Bole> Wosh wocha Dekeya. Similar level of Zn in Hop 3.48 mg/kg has been reported by [19]. This may be attributed to its higher concentration in the soil. After evaluation, metal limit in the studied both plants with those suggested by FAO/WHO, was found that Zn is below this limit for comestible plants. According to [20] limits were not established for zinc.

Manganese

The concentration of Mn was ranged from 1.13 to 3.98 mg/kg in the samples. The highest level of Mn was observed by hop plant in Jomboro and the lowest concentration was found in Kabul. However, for medicinal plants the [20] limit is not thus far recognized for manganese. Report of [21] that the range of manganese in their study was between 44.6 to 339 mg/kg in selected medicinal plants of Egypt. [22] reported that the range of manganese in his study was 157 ± 7.5 mg/kg to 421 ± 9.0 mg/kg in Croton leaves of Ethiopian medicinal plant. Higher Mn levels in the studied plant may be attributed to the availability of this metal in relatively acidic soils.

Iron

The mean concentration of Fe in plants was ranged from 1.17 to 2.79 mg/kg. The highest mean concentration was found in papaya collected from Jomboro and the lowest concentration was found in also papaya Bole. Fisher's combined probability test using the LSD criterion for significance indicated that the mean concentration of Fe in plants sample from Jomboro was significantly higher than other sampling sites at $\alpha = 0.05$. This might be due to geographical and geological differences of the soil and different agricultural practices including the use of different agro-chemicals. The acceptable limit recommended by FAO/WHO in edible plants was 20 ppm [2]. However, the level of iron in this study values, it was in some amount higher than permissible level of iron in edible plants.

Lead

Lead was not detected in both samples from all sampling sites. Since Pb was below method detection limits in this study there was no lead contamination. The study contrasts reported by [13] the concentration of lead was in small amount in *Foeniculum vulgare*, *Artemisia afra*, *Hagenia abyssinica* and *Echinops kebericho* with concentrations of 0.11 ± 0.02 , 0.11 ± 0.08 , 0.11 ± 0.02 , 0.08 ± 0.05 mg/kg, respectively.

Cadmium

The permissible limit for Cd set by [9] in edible plants was 0.2 mg/kg. However, for plants the permissible limit for Cd set by [20], China and Thailand was 0.3 mg/kg in finished herbal products. The level of cadmium in the given plants in all sampling site was below the method detection limit implying that there was no Cd contamination.

3.4. Correlation of Metals Among Samples

For the correlate, the effect of one metal concentration

on the concentration of the other metal, Pearson correlation matrices using correlation coefficient (r) for the samples were used and presented in table 6 below. The values of Pearson correlation coefficient showed that there is weak and/or moderate positive or negative correlation of metals with each other except for some metals. The weak negative or positive correlation indicating that the presence or absence of one metal affect in lesser extent to the other. Relatively high negative correlation between Mg and Cu indicate that large absorption of Mg may affect the absorption of Cu.

Table 6. Pearson correlation of Metals.

	Ca	Mg	Cu	Zn	Mn	Fe
Ca	1					
Mg	-0.133	1				
Cu	-0.026	-0.509**	1			
Zn	-0.349*	0.240	0.125	1		
Mn	0.322*	-0.132	0.022	-0.115	1	
Fe	0.091	0.264	-0.343*	-0.226	0.354*	1

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

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

4. Conclusion and Recommendation

Based on the finding, the optimized wet digestion method was used and evaluated by spiking samples and their percentage recoveries were in the range of 89-103.5% which was in the acceptable range.

1. The result indicated that both plants accumulate relatively higher amounts Ca among the evaluated essential metals.
2. The evaluation of metals in the both plants could be put in the following order $Ca > Mg > Mn > Zn > Fe > Mg > Cu$; Pb and Cd were below method detection limit.
3. Non-essential metals evaluated in this study were below the permissible ranges presented by FAO/WHO standards. Henceforth, the plants were safe for nutritional and uses with the respect to analyzed metals.
4. Mn and Fe show positive correlation indicating that more level of Mn enhance the availability of Fe. Some other metals like Ca and Zn, Ca and Mn show negative correlation.
5. For the further; based on the results, monitoring of non-essential metals in plants needed to minimize the risk of bioaccumulation in human.

References

- [1] Kassaye, Amberbir, Getachew and Mussema, 2006. A historical overview of traditional medicine practices and policy in Ethiopia, *The Ethiopian Journal of Health Development* Vol. 20 (2) 2006: 127-134.
- [2] Farnsworth, N. R., 1994. *Ethnopharmacology and drug development in ethnobotany and search for new drugs*; Ciba foundation symposium 185 Chichester, UK, John Wiley and Sons, pp. 42-59.
- [3] JAICAF, 2008. Medicinal plants associated with life in Cultural, and economic events, vol. 3, pp. 1673.
- [4] Bassam., 2012 "Microbial profile of Tella and the role of Gesho (*Rhamnusprinoidea*) as bittering and antimicrobial agents in traditional Tella (Beer) production," *International Food Research Journal*, vol. 21, no. 1, pp. 357-365.
- [5] Aklilu, L., 1974, Studies on the molluscicidal properties of Endod (*Phytolaca dodecandra*). Toxicity of various molluscicides to fish and snails. *Ethiop Med J* 1974; 12: 109-116.
- [6] Kupchan, 1972;. Standardization of herbal medicines-A review. *Int. J. Biodivers. Conserv*, 4, Lesniewicz, Jaworska, and Zyrnicki. 2006. Macro- and micronutrients and their bioavailability in polish herbal medicaments. *Food Chem.* 99, 670-679.
- [7] Fakankun, OA; Babayemi, JO; Akosile, SO (2012). Evaluation of fish gills as potential target organ for accumulation of heavy metals. *Afi. J. Animal & Biomedical Sci.* 7(1): 15-18.
- [8] Muhammad, Afewerk and Chandravanshi, 2012 "Levels of essential and nonessential metals in *Rhamnusprinoidea* (Gesho) cultivated in Ethiopia," *Bulletin of the Chemical Society of Ethiopia*, vol. 26, no. 3, pp. 329-342.
- [9] FAO/WHO., 1984. Contaminants. In *Codex, Alimentarius*, vol. XVII, Edition 1. FAO/WHO, Codex Alimentarius Commission, Rome.
- [10] Khan S., Cao Q., Zheng Y. M., Huang Y. Z., Zhu Y. G. Health risks of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China, *Environ Pollut*, 152 (2008), pp. 686-692.
- [11] Khan, S., Waqas, M., Ding, F., Shamshad, I. and Arpd, H. 2015. The influence of various biochars on the bio accessibility and bioaccumulation of PAHs and potentially toxic elements to turnips (*Brassica rapa* L.). *J. Hazard. Mater*, 300: 243-253.
- [12] Federal Democratic Republic of Ethiopia Population Census commission (FDRECC) (2008) Summary and Statistical Report of the 2007 Population and Housing Census, December 2008, 76-83.
- [13] Alemayehu H., and Mesfin B. 2019. "Determination of level of some metals in selected plants in Gurage zone, southern Ethiopia", *International Journal of Current Research*, 11, (03), 1839-1844.
- [14] Hight, 1998. Flame atomic absorption spectrometric determination of lead and cadmium extracted from ceramic food ware. Food and drug administration, division of field science, Rockville, MD. Food and Drug Administration. Laboratory Information Bulletin; no. 4126.
- [15] Weeraratna C, Watson M, Wettasingha D 1977: Effect of mineralization of tea pruning on some soil characteristics. *Plant Soil*, 46, 93-99.
- [16] Oloyede, O. 2005. Chemical Profile of Unripe Pulp of Carica papaya. *Pakistan Journal of Nutrition*, 4: 379-381.
- [17] Remon, E., Bouchardon, J., Cornier, L., Guy, B., Leclere, B. and Faure, O. 2005. Soil Characteristics, Heavy Metal Availability and Vegetation Recovery at a Former Metallurgical Landfill: Implications in Risk Assessment 1843 *International Journal of Current Research*, Vol. 11, Issue, 03, pp. 1839-1844, March, 2019 and Site Restoration. *Environmental Pollution*, 137, 316-323.
- [18] Tessema, D. and Belete, Y. 2015: Spectroscopic Investigation of Metal Level in Aloe Vera Plant, and the Soil Where the Aloe Vera Grows: Arba Minch, Southern Ethiopia.
- [19] Nagari and Mengistie, 2014, Concentration levels of Essential and Non-essential Metals in Ethiopian Khat (*Catha edulis* Forsk). *Bio. Trace. Elements*.
- [20] World Health Organization (WHO), 2005, *Quality Control Methods for Plant Materials*, World Health Organization, Geneva, Switzerland.
- [21] Sheded GM, Pulford ID, Hamed IA (2006). Presence of major and trace elements in seven medicinal plants growing in South Eastern Desert, Egypt *J. Arid. Env.* 66: 210-217.
- [22] Divrikli U, Horzum N, Soylak M, Elci L (2006). Trace heavy metal contents of some spices and herbal plants from western Anatolia, Turkey. *Int. J. Food Sci. Tech.* 41: 712-716.