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Levels of selected metals in coriander (*Coriandrum sativum* L.) leaves cultivated in four different areas of Ethiopia

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ABSTRACT

Coriander (*Coriandrum sativum* L.) is one of the herbs which is used for medicinal and food purposes. In the present study the levels of selected metals in coriander leaves were determined in the samples collected from four different farmlands (Sebeta, Mekanisa, Holeta and Gefersa) in Ethiopia where its cultivation is common. The levels of metals were determined after digestion of samples with the mixture of 4 mL of HNO_3 and 4 mL of $HClO_4$ at 300 ^oC for 3:00 hours by flame atomic absorption spectrometry. The optimized wet digestion method for coriander leaves analysis was validated through the recovery experiment and a good percentage recovery was obtained (93.2-101%). The levels of metals were found in the range Ca, 2319–3503 mg/kg; Zn, 33.4–54.8 mg/kg and Cr, 5.55-9.86 mg/kg while the trace metals Cu, Ni, Cd and Pb were too low to be detected. The results indicated that Ethiopian coriander is a good source of essential metals and free from the toxic metals Pb and Cd. A statistical analysis of variance (ANOVA) at 95% confidence level indicated that there is significant difference ($p < 0.05$) in the levels of all detected metals between the four sample means. The Pearson correlation was used to predict the dependence of metal levels on one another. The levels of the metals determined in this study compared well with those reported for coriander leaves from some other parts of the world.

Capsule Summary: The levels of selected metals in coriander leaves were determined in the samples collected from four different farmlands in Ethiopia using flame atomic absorption spectrometry.

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INTRODUCTION

Coriander (*Coriandrum sativum* L.), which belongs to the family Apiaceae (Umbelliferae), is a native of Mediterranean region from where it was spread to Europe, Asia, North and South – America and Australia (Purseglove et al., 1981). It is the most important spice crop cultivated throughout the world for its seed and leaf (Mhemdi et al., 2011). Coriander fresh green leaves, commonly known as cilantro or Chinese parsley (Potter, 1996), are widely featured in the cuisines of China, Mexico, South America, India and Southeast Asia. It is grown in more than fifty countries with India at ranking first, both in area and production followed by Mexico, China, former Soviet Union, Central America and South America (Morales-Payan, 2011). The crop grows in tropics and requires a cool but comparatively dry frost-free climate, particularly at flowering and seed formation stages (Sharma and Sharma, 2004). It grows best in dry climates, however it can grow in any type of soil like light, well drained, moist, loamy soil, and light to heavy black soil (Verma et al., 2011). The plant is highly aromatic and has multiple uses in food and in other industries (Dhankhar et al., 2011). It is also used to flavor sausages.

All parts of coriander plant are edible, fresh leaves can be used for garnishing and are common ingredient in many foods. The green herb is also employed for the preparation of either steam-distilled essential oil or the solvent extracted oleoresin (Nadia and Hala, 2012). Fresh juice of coriander is extremely advantageous in curing many deficiencies related to vitamins and iron. All parts of this herb are in use as flavoring agent and/or as traditional remedies for the treatment of different disorders in the folk medicine systems of different civilizations (Sahib et al., 2012). The plant is also used to cure diseases like digestive tract disorders, respiratory tract disorders, urinary tract infections. Coriander has been reported to posses many pharmacological activities like antioxidant (Darughe et al., 2012), anti-diabetic (Eidi et al., 2009), anti-mutagenic (Dima et al., 2013), anti-lipidemic (Sunil et al., 2012) and anti-spasmodic (Gray and Flatt, 1999). Its green foliage, rich in vitamins and other minerals, is used in vegetables and salads while its seeds contain essential oils rich in linalool (Singh et al., 2005).

The coriander oil is used as an antimicrobial agent as it possesses broad spectrum antimicrobial activity (Silva et al., 2011). This oil can be encapsulated in alginates, chitosan, etc. so as to enable isolation, protection, transport and release of its active components like vitamins, flavors, peptides, minerals, fatty acids, polyunsaturated fatty acids, antioxidants, enzymes and living cells. Coriander powder and its essential oil are considered as natural food preservatives including antibacterial, antifungal and antioxidant properties (Politeo et al., 2007). The commercial value of its essential oil depends on its physical properties, chemical composition and aroma quality (Rohit et al., 2011).

Ethiopia is an ancient country with suitable agro ecologies for various agricultural products at various high-land and low-land areas, making it diversified in spices. Coriander is one of the common spices grown in Ethiopia. The potential areas for the cultivation of coriander are Amhara, Oromiya, Southern Nations, Nationalities, and People's Region (SNNPR) and Gambella regions. In Ethiopia coriander can be found in almost every market, and the main supplies come from Bale and Gondar regions. Coriander is used locally for flavoring purposes in the preparation of red pepper powder, bread and sauces. The seeds of coriander are boiled in water and drunk on an empty stomach to treat stomachache (Jansen, 1981). Since ancient times, coriander has been used to flavor foods and beverages, especially gin, and also medically to treat various diseases, particularly as a carminative (Asfaw and Abegaz, 1998). Ethiopia has been the origin of genetic diversity in coriander (Mengesha et al., 2011).

A study (Reuter et al., 2008) found that coriander leaves are excellent in reducing inflammation naturally. Being an excellent source of omega-3 fatty acids, omega-6 molecules, lipolotion and coriander oil (a compound that helps reduce the inflammatory response in the body). Coriander leaves is very effective in reducing swelling and inflammation in all parts of the body. Coriander leaves contain some very essential nutrients like beta carotene, vitamin C, E, ferulic acid, caffeic acid, kaempferol and quercertin. All of these not only provide nutrition to the body but they also act as very strong antioxidant agents that help to clean up all the free radicals in our body – the ones that are responsible for causing cancer. A study (Wangensteen et al., 2004) found that the extracts from coriander were extremely efficient and very effective in stopping the entire oxidative process–protecting the person from cancer, ageing and wrinkles.

Coriander seed is used primarily as a flavoring agent in the food industry or as a spice in bread, cheese, curry, fish, meat, sauces, soup, pastries and confections. They are used as a flavoring agent in bread and yield essential oil for the manufacturing of soaps and perfumes. As a medicinal plant, coriander has been used to manage diabetes (Swantson-Flatt, 1990), used as an anti-fungal (Basilico and Basilico, 1999), antioxidant (Chithara and Leelamma, 1999), hypolipidemic (Chithara and Leelamma, 2000), antimicrobial (Delaquis et al., 2002), hypocholesterolemic (Chithara and Leelamma, 1997) and anticonvulsant substance (Hosseinzadeh and Madanifard, 2000).

Life on the earth is built from a relatively small number of chemical elements. The most important ones include calcium, magnesium, sodium, potassium, sulfur, chlorine and phosphorus. These are sometimes called the macro-minerals. These are found in the large quantity in our bodies. Although needed in small amounts, trace minerals are absolutely essential for life. They include Fe, Cu, Mn, Zn, Cr, Se, Li, Co, Si, B and probably a dozen of others. The daily allowances of these metals differ from person to person based upon the developmental levels, sex as well as the standards of the different countries they set.

Toxic metals are among the major causes of health problems on earth today. They can cause every imaginable symptom. The problem of heavy metal pollution is increasing throughout the world. Their presence in the atmosphere, soil and water can cause serious problems to all organisms. The toxic metals include lead, mercury, cadmium, arsenic, aluminum, nickel, antimony, beryllium and others.

Recently some studies have been done on the levels of metals in Ethiopian spices (Kitata and Chandravanshi, 2012; Endalamaw and Chandravanshi, 2015; Wagesho and Chandravanshi, 2015; Mekassa and Chandravanshi, 2015; Tefera and Chandravanshi, 2018) and medicinal plants (Derbie and Chandravanshi, 2011; Gebre and Chandravanshi, 2012; Mekebo and Chandravanshi, 2014; Hagos and Chandravanshi, 2016). However, no investigation has been done on the level of metal contents in Ethiopian coriander. Therefore the objective of this study was to determine the levels of essential and non-essential metals in coriander leaves (*Coriandrum sativum* L.) cultivated in Sebeta, Mekanisa, Holeta and Gefersa farmlands of Addis Ababa and

Oromia regions of Ethiopia. The specific objectives were: (i) to develop an optimum working procedure for digestion of coriander leaves samples, (ii) to determine selected metals in coriander leaves by flame atomic absorption spectrophotometry, (iii) to compare the levels of the determined metals in coriander leaves in four different farmlands of Ethiopia, and (iv) to compare the levels of the determined metals in coriander in four different farms of Ethiopia with that of the data in literature.

MATERIAL AND METHODS

Equipment and instrumentation

Electronic blending device (FOSS KNIFETEC 1095, USA) was used for grinding and homogenizing the samples. Electronic series balance (OPTECH, A205EC, Italy) with precision of ±0.0001 g was used for weighing samples. 250 mL round bottom flasks fitted with reflux condenser were used with Kjeldahl (UK) apparatus hot plate to digest the dried and powdered coriander leave samples. Volumetric flasks (25, 50, and 100 mL) were used during dilution and preservation of samples and preparation of metals standard solutions. HTL pipettes with 0.01 mL division with pipette tips and micro pipettes (20-200 µL and 1000-5000 µL) were used for measuring reagents used during optimization, sample preparation, preparation of standard solutions and spike solutions. Refrigerator (SANYO Electric Biomedical Co. Ltd, Japan) was used for sample preservation after digestion and before AAS analysis. Flame atomic absorption spectrophotometer (Analytikjena: Model ZEEnit700P, AAS VGP AAS, Germany) equipped with deuterium arc background correctors and hollow cathode lamps with air-acetylene flame was used for the analysis of the analyte metals.

Reagents and chemicals

HNO_3 (69.5%, Scharlau Chemie S.A. European Union, Spain) and $HClO_4$ (70%, BDH Laboratory Supplies AnalaR®, Poole, England) were used for digestion of coriander leaves samples. $La(NO_3)_3.6H_2O$ (99%, BDH Chemicals Ltd, Poole, England) was used to minimize the precipitation of Ca ion in the form of phosphate and sulfate. Stock standard solutions containing 1000 mg/L of the metals Ca, Cr, Ni, Cu, Zn, Cd and Pb (BDH Chemicals Ltd Spectrosol®, Poole, England) were used for preparation of calibration standards and for the spiking experiments. Deionized water was used for dilution of samples, intermediate and working metal standard solutions prior to analysis and for rinsing glass wares.

Sampling and sample sites description

Sebeta is a town in Alem Gena Woreda of Mirab Shewa in Oromia reginal state. It is the administrative center of the Woreda and a suburb of Addis Ababa. Mekanisa is found in a sub city of Addis Ababa in the south, Ethiopia. Holeta is located in the Oromia Special Zone Surrounding Finfinne, Oromia National Regional State (ONRS) and is bound in the east by Berfata Tokofa and in the south, Wajitu Harbu, in the north Ilala Gojo and Nanogenet in the Welemera Wereda. Gefersa River is found West of Addis Ababa. It is found in Oromia region. The geographical descriptions of sample sites are given in Table 1.

About 0.5 kg of green coriander plant sample was bought from farmers who were selling coriander in the farmlands separately from Sebeta, Mekanisa, Holeta and Gefersa. The samples from each farmland were separately packed in polyethylene plastic bags to get one bulk sample for each farm and brought to the laboratory for analysis. A representative portion of about 200 g samples from each site were packed in the polyethylene plastic bags and were prepared for digestion. Leaves of coriander samples were washed well with the running tap water and deionized water to remove earthy impurities, dried, ground and powdered with acid washed mortar and pestle. The powdered samples were stored in clean polyethylene bags until analysis.

Optimization of digestion procedure

In this study, the coriander leaves samples were made ready for the analysis after wet digestion using Kjeldahl digester heating block. Different digestion procedures were tested by varying the reagent volume, reagent composition, digestion time and temperature. The nature of the final digests was examined, clear and colorless solution was selected and the procedure taken as an optimum. The selection criteria considered were clearness of the digests, short digestion time, low reagent volume, and low temperature. The optimization procedures tested for the sample preparation for the determination of metal contents are given in Tables 2-4.

Digestion of the coriander leaves samples

Applying the optimized procedures (Tables 2-4), a 0.5 g of powdered coriander sample was placed in a 250 mL round bottom flask. To this, 4 mL of HNO_3 (69.5%) and 4 mL of $HClO_4$ (70%) were added. The round bottom flask was fitted to a reflux condenser and heated on a Kjeldahl apparatus hot plate for 3 h at a temperature of 300 ^oC. The digest was allowed to cool for 10 min without dismantling the condenser and then further cooled to room temperature for 20 min by dismantling the condenser. The digest was diluted with 20 mL of deionized water and filtered with Whatman filter paper (110 mm, diameter) into a 50 mL volumetric flask. The round bottom flask was further rinsed with 10 mL of deionized water and added to the filtrate. To a 50 mL volumetric flask containing about 0.67 g of $La(NO_3)_3.6H_2O$ the cooled solution was filled to the mark (50 mL) with deionized water. The main reason why $La(NO_3)_3.6H_2O$ was added was to prevent the precipitation of Ca^{+2} with the SO_4^{-2} and PO_4^{-3} if it was present in the samples or the reagents used in the process. For each sample the digestion was done in triplicate. Blank samples, a mixture of 4 mL of HNO_3 and 4 mL of $HClO_4$ were also digested following the same procedure as the samples. Finally, the digests were kept in refrigerator until analysis. The digestion was carried out in triplicates for each bulk sample. Digestion of a reagent blank was also performed

Table 1: Geographical descriptions of sample collection sites

S. No.	Sample site	Approximate geographical locations			
		Latitude	Longitude	Altitude above sea level (m)	Distance in kilometers and directions from Addis Ababa
1	Sebeta	8° 55' 0" North	38° 37' 0" East	2356	23 km, West
2	Mekanisa	9° 44' 0" North	36° 26' 0" East	2306	4.4 km, South
3	Holeta	9° 3' 0" North	38° 30' 0" East	2,391	29 km, West
4	Gefersa	9° 4' 52" North	38° 19' 30" East	1490	18 km, East

Table 2: Optimized reagent volumes for digestion of 0.5 g of coriander leaf samples in HNO_3/$HClO_4$ mixture

Trials	Reagents	Volume ratio (mL)	Observations
1	HNO_3	6	Clear yellow
2	HNO_3:$HClO_4$	5:01	Light yellow
3	HNO_3:$HClO_4$	4:02	Light yellow
4	HNO_3:$HClO_4$	3:03	Clear/suspension
5	HNO_3:$HClO_4$	4:04	Clear (optimized)
6	HNO_3:$HClO_4$	4:02	Yellowish

Table 3: Optimized temperature for digestion of 0.5 g coriander leaf samples in HNO_3/$HClO_4$ mixture

Trials	Temperature (°C)	Observations
1	180	Yellow
2	210	Light yellow
3	240	Clear/suspension
4	270	Clear/suspension
5	300	Clear (optimized)
6	330	Yellowish

Table 4: Optimized time for digestion of 0.5 g coriander leaf samples in HNO_3/$HClO_4$

Trials	Time (h)	Observations
1	2:00	Yellow
2	2:30	Clear/suspension
3	3:00	Clear (optimized)
4	3:30	Clear/suspension
5	4:00	Light yellow

in parallel with the coriander samples keeping all digestion parameters the same. The digested samples were kept in the refrigerator, until the levels of all the metals in the sample were determined.

Analysis of *Coriandrum sativum* L. samples for metal levels

For the analysis of the samples calibration of the instrument with the known concentration of standards were done for each metal of interest. First the intermediate (10 mg/L) standard solutions were prepared from the stock solutions which were 1000 mg/L in concentration. The working standards were prepared based on the sensitivity of the instrument towards the particular metals. These working standards were freshly prepared by diluting the intermediate solutions with deionized water for each metal of interest. The FAAS was calibrated using four series of working standards for each metal of interest. Then Ca, Cd, Zn, Cu, Pb, Ni and Cr were determined with FAAS using calibration curve after the instrumental parameters were optimized for maximum signal intensity. Three replicate determinations were carried out on each sample. All the seven metals were determined by absorption/concentration mode and the instrument readout was recorded for each sample and blank solution. The same analytical procedure was employed for the determination of metals in digested blank solutions. Concentrations of the working standards, value of correlation coefficient of the calibration curve and equations for calibration curves for each metal are listed in Table 5. The correlation coefficients clearly indicate that the change in absorbance with concentration was in good positive correlation and are linearly fit for each metal.

Precision and accuracy

The most common terms related to analytical quality procedures to express the extent of errors in analytical measurements are accuracy and precision. Most of the common statistical methods applied in analytical chemistry are the standard deviation, relative standard deviation and range of series of measurements (Skoog *et al.*, 1996). In this particular study the results of the measurements are expressed as the mean of the measurements together with the standard deviation of the triplicate samples with triplicate measurements of each sample.

Validation of optimized procedure

The validity of the optimized procedure was assessed by spiking experiments. For this purpose standard solution of 1000 mg/L (from BDH Chemicals Ltd Specrtrosol®, Poole, England) was used and intermediate standards of 100 mg/L and 10 mg/L were prepared. The spiking was done by classifying the metals in to two triplicate groups. In the first group 8 μL of 1000 mg/L of Cr, 33 μL of 1000 mg/L of Zn, 80 μL of 1000 mg/L of Pb, 25 μL of 1000 mg/L of Cd, 150 μL of 1000 mg/L of Ni and 60 μL of 1000 mg/L of Cu were spiked in a flask containing 0.5 g sample. In the second group 58 μL of 1000 mg/L of Ca was spiked in a flask containing 0.5 g sample. The spiked and non-spiked samples were digested and analyzed in similar conditions using optimized procedure before sample analysis. The percentage recoveries of the analyte were calculated. The results of recovery analysis are given in Table 6. The percentage recovery lies within the range 93.2-101%. The percentage recovery for coriander leave samples were between 90 and 110% (100 ± 10), which were within the acceptable range for all metals.

RESULTS AND DISCUSSION

Metals in coriander leave

The determination of the levels of metals in the coriander leaves samples was carried out by FAAS. The mean values were determined from triplicate analysis of each sample and triplicate samples were analyzed from each sampling area. The results are reported in terms of mean ± SD, for all the metals in this study.

Results of determined metals from each sampling sites are listed as (mg/kg) mean ± SD in Table 7. Cr was detected in only one sample while Cd, Pb, Cu and Ni were not detected in any of the coriander leaves samples, because their concentrations were below detection limits.

Distribution patterns of metals in the coriander leaves

The uptake of metals by plants takes place through different and complex biochemical processes. The uptaking processes vary based on the ability of the plants to absorb metals from the soil, the availability of the minerals in the soluble and usable forms, the abundance of particular minerals at the particular areas, the degree of contamination of the soil with heavy metals, etc. The differences in the levels of metals in soil arise mainly due to pollution of the biosphere resulting from the rapid industrialization and modern large scale agricultural activities, i.e. use of different types of fertilizers, pesticides, herbicides and other chemicals. The use of sewage sludge, pesticides, herbicides, irrigation with polluted water and fertilizers on agricultural lands highly affect the quality of food products for humans and animals.

The distribution and accumulation of metals in coriander leaves are the reflections of the mineral composition of the soil and the degree of mineral pollution of the environment in which the coriander plant grows. Therefore, the actual metal concentration of coriander leaves vary considerably according to the geographic origin, the use of fertilizers with different chemical compositions and other characterizing features such as quality of water for irrigation and also the storage conditions of the products.

Essential metals in coriander leaves

Metals absorbed by plants from different sources are accumulated in different parts of the plant's body, like roots, stems, leaves, seeds and other parts. The amount of metals accumulated in the plants' body parts is variable, i.e. some of them are higher in the roots, some others in the seeds and others in leaves and other parts of the plants. Since the focus of this study is on the level of metals in leaves of coriander plant, the common edible part of the coriander plant by human beings let us have a look on the contents of the metals analyzed in coriander leaves, collected from different sample sites. The concentration of Ca was highest of all the metals under consideration. It was within the range 2212 – 3522 mg/kg dry weight. Among the sample sites the highest concentration of Ca was determined in a sample from Gefersa (3503±0.3 mg/kg dry weight) followed by Holeta (3024±0.5 mg/kg), Sebeta is 2918±1 mg/kg and Mekanisa 3024±0.5 mg/kg. In this study the concentration of Ca determined by sample sites decreased in the order: Gefersa > Holeta > Sebeta > Mekanisa. As shown in Table 7, Zn was (29.7 – 55.2 mg/kg dry weight) in coriander leaves sample. The concentration of Zn in coriander leaves collected from the four sample sites is in the order: Mekanisa > Holeta > Gefersa > Sebeta.

The amount of Ca that a person can get from coriander leaves is lower than the daily recommended values (200 g); this indicates that coriander leaves alone cannot be a good source of Ca needed for the daily requirement. Therefore the person must get supplementary Ca from other sources. The amount Zn that a person can get is also below the required amount. Hence supplementary diet is needed for Zn metal too. The amount of Cr is very sufficient since it is toxic it is within the recommended range (0.03–0.25 μg/day).

Table 5: Working standard concentration, correlation coefficient and equation of the calibration curves for determination of metals using FAAS

Metal	Wavelength (nm)	Concentration of working standards (mg/L)	Correlation coefficient (R)	Equation for calibration curves
Ca	422.7	0.15, 0.25, 0.5, 1	0.9997	A = 0.038C – 0.002
Cr	228.8	0.5, 0.75, 1, 1.25	0.9956	A = 0.012C – 0.000
Ni	232.0	0.5, 1.5, 3 , 6	0.9950	A = 0.001C –0.000
Cu	324.8	0.4, 0.6, 0.8, 1	0.9994	A = 0.022C – 0.000
Zn	213.9	0.25, 0.5, 0.75, 1	0.999	A = 0.16966C + 0.0024
Cd	357.9	0.15, 0.25, 0.45, 0.65	0.9953	A = 0.001C – 0.000
Pb	283.3	0.4, 0.8, 1.2, 1.6	0.9984	A = 0.003C + 7 x 10^{-05}

Table 6: Recovery test for the optimized procedure of coriander leave samples

Metal	Conc. of metal in unspiked sample (mg/kg)	Amount spiked (mg/kg)	Mean conc. of metal in spiked sample (mg/kg)	Amount recovered (mg/kg)	(% R)±SD
Ca	2918±44	58.4	2977	59.0	101±4.0
Cr	7.73±0.15	8.0	15.6	7.87	91.2±7.5
Ni	ND	150	150	150	105±5.0
Cu	ND	60	57.2	57.2	108±1
Zn	33.1±0.02	6.63	39.8	6.70	101±2
Cd	ND	25	24.3	24.3	96.0±4.0
Pb	ND	80	78.9	78.9	107±4

ND = not detected, % R = percent recovered

Table 7: Levels of metals in mg/kg in coriander leaves from Sebeta, Mekanisa, Holeta and Gefersa

Metal	Concentration (mg/kg) (mean ± SD) of metals in samples from				Range of metal in samples from four sites (mg/kg)
	Sebeta	Mekanisa	Holeta	Gefersa	
Ca	2918±1	2319±2	3024±0.5	3503±0.3	2319–3503
Cr	8.0±0.02	ND	ND	ND	ND–8.0
Zn	33.1±0.05	54.8±0.006	42.1±0.08	40.3±0.05	33.1–54.8
Ni	ND	ND	ND	ND	ND
Cu	ND	ND	ND	ND	ND
Cd	ND	ND	ND	ND	ND
Pb	ND	ND	ND	ND	ND

ND = Not detected

Non-essential (toxic) metals in coriander leaves

According to World Health Organization the dietary exposure to Cd is estimated to be about 1.2 x 10^{-4} to 4.9 x 10^{-4} mg/kg of body weight daily. Intake of dietary Cd should not exceed 0.007 mg/kg of body weight, per week. For a healthy male of about 80 kg of body weight, that is only 0.65 mg per week, a very small amount is needed. Cd is retained in the kidneys and liver (50 to 70% of accumulated Cd is deposited in these organs); excessive exposure can lead to kidney disease and serious liver damage. Pb is a major chemical pollutant of the environment, and highly toxic to man. Pb can cause brain and kidney damage, decrease in hemoglobin production and male fertility. It enters human body by inhalation and ingestion, absorbed and carried by the blood. There is evidence that Pb pollution can include aggressive behavior in animals which can also occur in humans (Juberg *et al*., 1997). However, the levels of Cd, Pb and Ni were not detected in the coriander leaves. Therefore using coriander leaves from these farmlands is safe for human consumption and safe for human health problems due to the accumulation of Cd, Pb and Ni in coriander. The concentration of Cr (8.0±0.02 mg/kg dry weight) in coriander leaves sample is not safe to humans because it is above the WHO/FAO (2.3 mg/kg) level.

Analysis of variance (ANOVA)

Table 8: Analysis of variance (ANOVA) between and within coriander leaves samples at 95% confidence level

Metal	Comparison	Df	F_{cal}	F_{cri}	p-value	Remarks
Ca	Between samples	3	63.7	4.06	$6.3x10^{-6}$	Significant difference among the sample means
	Within samples	8				
	Total	11				
Zn	Between samples	3	9.16	4.06	0.0057	Significant difference among sample means
	Within samples	8				
	total	11				

SD = standard deviation, Df = degree of freedom, F_{cal} = F calculated, F_{cri} = F critical

Table 9: Pearson's correlations of the detected metals in coriander leave samples

	Ca	Cr	Zn
Ca	1.000		
Cr	-0.031	1.000	
Zn	-0.661	-0.699	1.000

The variations in sample means of the metals were tested by the help of ANOVA, whether the sources for variations were from experimental procedure or heterogeneity among the samples (i.e. difference in mineral contents of soil, pH of soil, water, atmosphere; variation in application of agrochemicals like fertilizers, pesticides, herbicides etc or other variations in cultivation procedures).

The results in Table 8, shows the significance of the results between samples and within samples. From the table one can see that, there is significant difference at 95% confidence level in mean concentrations of all the metals. The source for this significant difference between sample means may be the difference in mineral compositions of the soil or pH of soil which predict the degree of mineral absorption by plants. As one can see from Table 8, the F-calculated exceeds F-critical value in the sample means are significantly different in the case of Ca and Zn.

Pearson correlation of metals within coriander leaves

In this particular study, to correlate the effect of the concentration of one metal over the other metals the Pearson correlation coefficients were employed. The correlations of the metals in the four farmlands of the coriander leave samples are shown in Table 9.

The values of Pearson correlation coefficient in Table 9 revealed that there is weak negative correlation between metals with each other. The weak correlation indicating that the presence or absence of one metal do not affects the other metal. The metals which are not detected have no correlation.

CONCLUSIONS

An efficient digestion procedure for the determination of metals in the coriander leaves samples were optimized and validated through spiking method and a good percentage recovery was obtained (100±10%) for all the metals of interest. The levels of metals in coriander leaves determined in this study can be expressed in the following order: Ca (2918–3503 mg/kg) > Zn (33.1–54.8 mg/kg) > Cr (5.55–9.86 mg/kg). The non-essential toxic heavy metals, Cd, Pb and Ni were found to be below the detection limits of the instrument. From the results of this work it is possible to conclude that coriander leaves from the selected sites accumulated relatively larger amounts of Ca and Zn among the selected metals, respectively. A relatively lower amount of Cr (e.g. 5.55–9.86 mg/kg from Sebeta sample) was recorded. The ANOVA results at 95% confidence level suggests that there were significant difference in the mean concentration of Ca and Zn metals except for Cr (single mean value). These differences could be attributed to the difference in mineral contents of soil or pH of soil which predict the extent of mineral absorption by Coriander. The results indicated that Ethiopian coriander is a good source of essential metals and free from the toxic metals Pb and Cd.

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