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Evaluation of Metals in Soils used for Cultivation of *Rhamnus prinoides* (Gesho) at Bako Tibe District, Oromiya, Ethiopia

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Abstract

This study was carried out with the objective of determining the quantity of selected essential and non-essential metals; K, Na, Mg, Ca, Cu, Mn, Cr, Cd, Fe and Zn in the soil. Samples were collected from the low and medium altitudes of Bako (9°N latitude and 37.17°E). Wet acid-digestion using a mixture of aqua regia (1:3 HNO_3 to HCl) and H_2O_2 (6:1 mL) was used. K and Na were analyzed using flame photometry, Ca and Mg were determined titrimetrically and the other metals with flame atomic absorption spectrometry (FAAS) after appropriate quality control measures were undertaken to verify and maintain the quality of the data generated. The results of the study showed that the average concentrations of K, Ca, Mg, Na, Cu, Mn, Fe, Zn, Cr and Cd were 2401.38, 8920, 633.19, 628.13, 125.79, 39.66, 38.51, 7.28 and 2.41 mg kg^{-1} and below method detection limit, respectively in the low-altitude; and 3347.38, 10544, 1935.32, 758.13, 113.12, 25.41, 79.94, 50.95 and 3.52 mg kg^{-1} and below method detection limit, respectively in the medium-altitude. The metals such as K, Ca, Mg, Na and Cu were generally found to be in higher concentrations than other metals in both samples.

Keywords: Bako Tibe, Flame atomic absorption spectrophotometer, metals, Soil.

Introduction

Rhamnus prinoides L'Herit, common name dogwood, Amharic name *Gesho*, family Rhamnaceae, is a wide spread plant species in East, Central and South African countries. The African dogwood, *R. prinoides* (Rhamnaceae) is a dense shrub or a tree that grows up to 6 m high. In Ethiopia, the leaves and stems of this plant are used to impart the characteristic bitter flavor to domestically brewed beverages known as *Tella* and *Tej* and it is estimated that well over 5 million people consume these beverages daily (Ararso and Alemayehu, 2013).

Soil is an essential medium for plant growth and for the breakdown and recycling of organic matter. Soil performs this function by supporting plants structurally and supplying elements essential for plant growth. An element is essential to a plant if its deficiency makes it impossible for the plant to complete the vegetative or reproductive stages of its life-cycle, the deficiency is specific to the element in question and can be prevented or corrected by supplying this element and the element is directly involved in the nutrition of the plant. Essential elements are generally divided into major elements (macronutrients) and trace elements (micronutrients). Trace elements are as important as major elements but are required in lower quantities by plants. The trace elements are iron, manganese, zinc, boron, molybdenum, chlorine, cobalt, sodium and silicon. The major elements considered essential for plant growth are carbon, hydrogen, oxygen, nitrogen, phosphorus, potassium, calcium, magnesium and sulphur (EPA, 2002).

Assessing pollutants in different components of the ecosystem has become an important task in preventing risk to natural life and public health (Pujar et al., 2012). Heavy metals contamination has received much attention with regard to accumulation in soils and contamination of aquatic environments (Pandey et al., 2011). In this study the elemental accumulations and distributions of selected major and trace metals (K, Na, Mg, Ca, Cr, Mn, Fe, Zn, Cu and Cd) in soil of low and medium altitudes of Bako Tibe district were investigated and compared with the metals concentration of stem and leaf of *Rhamnus prinoides* cultivated on the same soil in which all the samples were collected at the same time.

The objectives of the study were to: (i) determine the amounts of essential and non-essential metals in the soil, (ii) compare the amounts of essential and non-essential metals in the soil of low and medium altitude, and (iii) compare the amounts of essential and non-essential metals in the soil with the amounts in the stems and leaves of *Rhamnus prinoides*.

Materials and Methods

Description of the study area

Bako Tibe (Figure 1) is one of the districts in the Oromia Region of Ethiopia. Part of the West Shewa Zone, Bako Tibe is found at the Western part of the zone at about 250 km from the regional capital city and national capital, Addis Ababa, and 125 km away from the zonal capital, Ambo and bordered on the south and west by the East Welega Zone, on the north by Horo Gudru Welega Zone, and on the east by Ilu Gelan. The administrative center of this woreda is Bako.

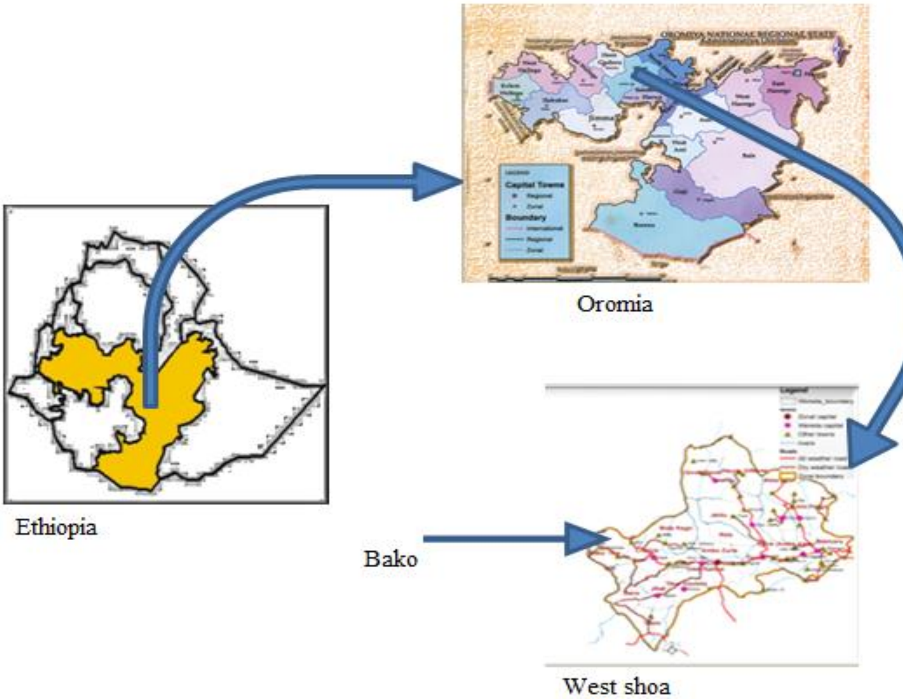

Figure 1: Map of the Study Area

The woreda lies at an altitude of between 1500 and 2870 meters above sea level, of which 1500–1670 masl is considered low-altitude, 1670–2000 masl as medium-altitude and greater than 2000 masl as high-altitude.

Apparatus, chemicals and reagents

Flame atomic absorption spectrophotometer (SL194, Double beam AAS, Elico) and flame photometer (CL 378, Elico) were used. HNO_3 (65–68% Uni-Chem® Chemical reagents, India), extra pure hydrogen peroxide H_2O_2 (30% Uni-Chem® Chemical reagents), aqua-regia (1:3, HNO_3: HCl), HCl (35–38% LR, s.d.fine-cHEM LimTEd, MUMBAI) and sucrose, $C_{12}H_{22}O_{11}$ (HIMEDIA® A.R.), stock standard solutions (1000 ppm) prepared in 20 mL 1:1HNO_3 for Cu metal diluted to 1 L, 17 mL 1:1 HCl for Zn and Fe diluted to 1 L and distilled water were used in this study.

Cleaning of apparatus

All the glassware and materials used during sample collection and experimental work were cleaned before and after use with tap water and detergent, rinsed with distilled water, soaked with 10% (v/v) nitric acid, re-rinsed with distilled water and subjected to total air dry to ensure decontamination.

Stock and working intermediate metal standard preparation

Stock standard solutions of each of the metals of interest were prepared from high purity metals and reagent grade salts using distilled water, nitric acid and hydrochloric acid based on the individual analysis specific instruction of the instruments. The stock solutions were prepared at concentrations of 1000 mg mL^{-1} of the metal.

The working intermediate metal standard solutions (100 µg mL^{-1} each) were prepared by diluting 10 mL of 1000 µg mL^{-1} individual metal stock standard solutions with distilled water to a 100 mL volume.

Calibration metal standard solutions

A blank and five calibration standard solutions of different concentration levels were prepared for each metal from the respective working intermediate standard solutions (100 µg mL^{-1}). The metal concentrations include 1.5, 2.5, 3.5, 4.5, 5.5 µg mL^{-1} for Cr; 0.25, 0.5, 0.75, 1.0 1.25 µg mL^{-1} for Cd; 1.0, 2.0, 3.0, 4.0, 5.0 µg mL^{-1} for Cu; 1.0, 1.75, 2.5, 3.25, 4.0 µg mL^{-1} for Mn; and 0.5, 1.0, 2.0, 4.0, 8.0 µg mL^{-1} for Fe and Zn. These calibration standard concentrations were within the working linear range of the instrument used for analysis. Beginning with the blank and working toward the highest standard, the solutions were aspirated and the readings were recorded.

Spiking metal standard mixture solution

Standard mixture solution containing all the metals of interest at varying concentrations (K and Na = 80, Mn = 40, Cu and Cr = 50, Fe and Zn = 60, Cd = 10 µg mL^{-1}) was prepared from stock standard solutions in a 50 mL volumetric flask. The volume of spike stock solution that should be added to the sample was calculated.

Sample collection and processing

Purposeful sampling technique was used to collect soil samples from the low and medium altitude areas of the study area. Soil samples were specifically collected from around the plant and composited (McDonald et al., 2004), in such a way as to be representative of the surface soil layers from a 20 cm depth. Non-decomposed organic materials were removed prior to sampling (El-Ghawi et al., 2005). The samples collected in January, 2013. The sub-samples were transported in plastic bags to Ambo University chemistry laboratory for further treatment and analysis. The samples were air dried to constant weight for two weeks, grinded using mortar and pestle and sieved through a 1.5 mm stainless steel sieve. The 0.5 g from the sieved sample were digested and analyzed.

Determination of moisture correction factor

The samples were weighed with analytical electronic balance to record the initial weight. It was re-weighed and re-dried until it gives constant mass after oven drying at 105 °C for 12 hrs and the moisture content was determined from the differences and the corresponding moisture correction factor for analytical results or the multiplication factor for the amount of sample to be weighed for analysis was calculated (FAO, 2008).

Determination of soil pH in water

Soil pH was normally measured in soil-water slurry. The determination of the soil pH is a three-step procedure: first, the soil–water slurry in the ratio 1:5 was prepared; and then, the pH meter was calibrated with a buffer solution of pH 4, 7 and 9; and finally, the electrodes were placed into the prepared slurry and the pH was read and recorded (FAO, 2008; Benton, 2001).

Optimization of digestion procedure for soil samples

The measurement of metal concentration in soil was generally by a combination of digestion procedure for dissolution of elements and subsequent measurement of the dissolved elements as described by Gaudino et al., (2007). The conventional aqua-regia digestion procedure as described by Chen and Ma (2001). For digesting soil samples was adopted.

The mixture of aqua-regia (HNO_3 + 3HCl) and H_2O_2 was selected as digestion reagent for the soil samples in this stuidy. The digestion procedures were optimized using different proportions of aqua-regia and H_2O_2 mixtures by varying the digestion time and temperature. The optimum condition for soil samples digestion was found to be a mixture of 6mL aqua-regia (3:1 ratio of HCl to HNO_3) and 1mL H_2O_2, with a digestion temperature of 220^0C and digestion time of 2 hrs.

Quality assurance/control

Calibration and continuing calibration standard

The FAAS was calibrated using a blank and five series of working standard solutions of each metal. The continuing calibration standard of metal standard solution of mid-point calibration concentration was run to test the accuracy of the analytical instrument calibration with each batch samples as described by Csuros and Csuros, (2002) and the deviation from the original value was found to be within ±5%.

The performance of flame photometer for K and Na was checked with the freshly prepared standard solutions of the two respective metals at concentrations of 10, 30, 50, 70, 90 ppm for K and at 1, 5, 10, 20 ppm for Na. The corresponding recovered/ measured values 9.57±1.69, 31.03±1.99, 50.07±0.47, 69.63±0.71 and 89.27±1.27 for K and 0.98±0.10, 5.03±0.15, 10.13±0.31, 15.33±0.76 and 20.67±0.86 for Na were obtained indicating a good performance of the instrument.

Analysis of matrix spike and matrix spike duplicate

Both matrix spike (MS) and matrix spike duplicate (MSD) were prepared for each soil sample by spiking aliquots of 0.5 g of soil with 2.5 mL standards mixture solution equivalent to a concentrations of 4.0 µg mL^{-1} for K and Na, 2.5 µg mL^{-1} for Cu and Cr, 0.5 µg mL^{-1} for Cd and 3.0 µg mL^{-1} for Fe and Zn. They were all carried through the same digestion and analysis steps as an un-spiked sample. The mean recovery values of MS and MSD were used to control overall sample matrix-dependent accuracy of the analytical method. Their relative percent differences (RPD) were calculated and expressed as percent to continuously assess the corresponding method precision (Csuros and Csuros, 2002; Miller and Miller, 2010).

Precision and accuracy

The laboratory precision of the results was assessed by the analysis of laboratory control samples (LCSs, n=3), laboratory control sample duplicates (LCSD), MS (n=3) and MSD. Precision was expressed as the RPD and relative standard deviation (RSD) of replicate results.

The accuracy of the optimized procedure was evaluated by spiking experiments. This included analysis of the MS (n=3), MSD, LCSs (n=3), LCSD and method blanks. Accuracy was expressed as the percent recovery of an analyte that has been spiked to the samples in a known concentration before digestion and subsequent analysis.

Method blank, reagent blank and limit of detection and quantification

The method blank was prepared from sucrose as matrix since there was no clear soil that can serve as the matrix for the soil samples. The blank which was prepared from the sucrose and all reagents was used for the digestion and taken through the entire measurement procedure to detect contamination from reagents, sample handling, and the entire measurement process. Method detection limit (MDL) and limit of quantification for each metal of interest were estimated by digesting and analyzing seven replicates of the method blanks with the optimized procedure for the soil samples. While the instrument was run with reagent blanks/calibration blanks in which no sample was used to determine the background signal and establish the baseline of the instrument.

Analysis of laboratory control samples

Triplicates of LCSs prepared from sucrose spiked with the target analyte of known concentration the same to sample spike were analyzed along with each batch of the soil samples. LCS recoveries and the RSD values of the LCS recoveries values for each metal of interest were calculated and used to control overall analytical method accuracy and precision, respectively which were independent of sample matrix effects (Csuros and Csuros, 2002; Miller and Miller, 2010).

Analysis of metal levels in soil samples

Five replicate analyses were carried out on each sample for the determinations of Na and K with flame photometry and Cu, Mn, Cr, Cd, Fe and Zn with FAAS; and the concentrations of Ca and Mg were determined by complexometric EDTA titration following the FAO procedure (FAO, 2008).

Statistical analysis

The variation in sample mean of the analyte was tested by using T-test of SPSS Version20 Software to test whether the source for variation was from experimental procedure or heterogeneity among the samples. Excel 2007 was used for other calculations.

Results and Discussion

Quality assurance/control

Calibration

Calibration curves for the various concentration ranges showed good correlation coefficients ranged between 0.996 and 0.999 (Table 3), which were all within the required limit (0.995) for trace element analysis (US EPA, 2007). This showed that there was good correlation (relationship) between concentration and absorbance indicating good calibration of the instrument.

Matrix spike and matrix spike duplicate

The highest average recovery obtained was 100.75% (Na) and the lowest 90.5% (Zn) (Table 1) where all were in the range 80–120%, which is recommended for matrix spike recovery of major element analyses by FAAS and Flame spectrophotometer (US EPA, 2008). This indicated that the analytical process has provided the required matrix-dependant accuracy. Therefore, the method was well applicable for all the matrices and all the results obtained were trustable.

RPD values of MS and MSD obtained ranged between 1.631 (Zn) and 13.40 (Na) which were in the acceptance limit (≤15%) (Csuros and Csuros, 2002). This showed that the overall analytical process was less affected by matrix-specific variability and the data generated was in the acceptable quality range.

Table 1: Mean %R and RPD values of metals from MS and MSD; and %R and RSD values of LCSs analyzed along with real samples for method validation

Metals	LCS (%R, n=3)	LCS (RSD)	MS & MSD (%R, n=2)	MS & MSD (RPD)
K	91.667±3.82	4.17	92.375 ±3.71	5.68
Na	87.5±9.01	10.30	100.75 ±9.55	13.40
Cu	93.21±7.16	7.68	91.10 ±0.27	10.69
Mn	94.57±4.44	4.69	98.2 ±3.96	3.10
Cr	98.56±2.86	2.90	98.77 ±2.61	4.55
Cd	96.58±4.08	4.23	98.4 ±4.81	2.78
Fe	97.56±1.73	1.77	97.73 ±0.43	2.59
Zn	96.78±1.97	2.04	90.5 ±0.17	1.63

LCS= laboratory control samples, %R= percent recovery, RSD= relative standard deviation, MS= matrix spike, MSD= matrix spike duplicate, RPD= relative percent difference

Method precision and accuracy

The calculated RSD of recovery values were under the required limit (Table 1). This is within ≤15% as reported by Csuros and Csuros (2002). This indicated that the analytical method, which covers digestion and instrumental measurement has acceptable repeatability and precision.

The percent recoveries of the sample spiked ranged between the highest 99.25% (Na) and lowest 93.08% (K) (Table 2). All were found to be within the acceptable range (80–120%) for metal analysis (US EPA, 2008). This showed that the analytical method provided results in the required level of accuracy.

Table 2: Recovery and precision test for the optimized procedure from soil sample spikes (n = 3)

Metals	Conc. in sample (µg mL^{-1})	Amount spiked (µg mL^{-1})	Conc. in spiked sample (µg mL^{-1})	Recovery (%)	Precision (%, RSD)
K	24.03±0.84	4.0	27.76±0.91	93.08±2.90	3.11
Na	6.43±0.21	4.0	10.40±0.44	99.25±7.23	7.29
Cu	37.71±2.14	2.5	39.60±2.13	96.65±3.75	5.38
Mn	26.30±0.87	2.0	28.27±0.84	98.38±2.82	2.96
Cr	4.19 ±0.33	2.5	6.56 ±0.39	95.10 ±2.57	5.90
Cd	0.61±0.05	0.5	1.09±0.02	96.33±6.11	1.91
Fe	21.58±1.47	3.0	24.47±1.48	96.18±1.87	6.05
Zn	11±1.52	3.0	13.92±1.38	97.44±4.81	9.89

RSD= Relative standard deviation

Instrument detection, method detection and quantification limits

The reagent blank readings were below the method detection limit indicating that no instrumental variations during the measurements. The method blank analysis results revealed that there were no readings above the method detection limits of the metals. Hence, the analytical method was free from overall laboratory contamination.

The instrument detection limits for both FAAS and FES ranged between 0.06 and 0.72 mg kg^{-1}, indicating good sensitivity of the measuring instrument for analyses. The MDL values lied in the range 0.76 (Cd)–3.9 (K) mg kg^{-1} and method quantification limit values 1.68 (Cd)–6.91 (K) mg kg^{-1} (Table 3). All the values were found to be in the required limit (Temminghoff and Houba, 2004). This indicated that the method was well applied for the determination of the essential and non essential metals.

Table 3: Instrument detection limit (IDL), method detection limit (MDL), method quantification limit (MQL) and correlation coefficients of calibration curves for metals determined in the soil samples

Metals	Correlation coefficient of calibration curves (r^2)	Calibration equation	IDL (mg kg^{-1})	MDL (mg kg^{-1})	MQL (mg kg^{-1})
K	-	-	0.72	3.90	6.91
Na	-	-	0.40	2.66	4.50
Cu	0.999	Y= 0.033X+0.003	0.62	3.12	5.52
Mn	0.996	Y= 0.008X+0.003	0.15	1.89	5.50
Cr	0.999	Y= 0.013X+0.002	0.13	0.77	1.99
Cd	0.999	Y= 0.082X+0.002	0.06	0.76	1.68
Fe	0.998	Y= 0.015X+0.005	0.59	3.36	4.59
Zn	0.997	Y= 0.049X+0.020	0.44	3.30	6.04

Laboratory control sample

The percent recovery values of LCS lied in the range 87.5 (Na)–98.56% (Cr) and their relative standard deviations 1.77 (Fe)–10.30 (Na) (Table 4). And all the values were found under standard control limits 80–120% for LCS recovery, and ≤15% for RSD (Csuros and Csuros, 2002). This showed that the method used for the study has provided the required level of accuracy and precision throughout the analytical process.

Table 4: Percent recoveries and RSD values of laboratory control soil samples analyzed along with real samples (n = 3)

Metals	Amount spiked (mg L^{-1})	Conc. in spiked sample (mg L^{-1})	Accuracy (Recovery, %)	Precision (RSD, %)
K	4.0	3.67 ±0.15	91.67 ±3.82	4.17
Na	4.0	3.5 ±0.36	87.5 ±9.01	10.30
Cu	2.5	1.9 ±0.13	93.21 ±7.16	7.68
Mn	2.0	1.89 ±0.09	94.57 ±4.44	4.69
Cr	2.5	2.46 ±0.07	98.56 ±2.86	2.9
Cd	0.5	0.48 ±0.02	96.58 ±4.08	4.23
Fe	3.0	2.93 ±0.05	97.56 ±1.73	1.77
Zn	3.0	2.9 ±0.06	96.78 ±1.97	2.04

Soil pH and metals in the soil samples

The pH of the low altitude soil was 6.82 ± 0.22 and that of the medium altitude was 7.21±0.26. The low altitude soil was slightly acidic while the medium altitude soil can be described as being moderately alkaline.(FAO, 2008).

The moisture content of the two soil samples were 2.55 and 1.26% with moisture correction factor (mcf) of 1.03 and 1.01 respectively for both medium and low altitude areas. These correction factors were used for the calculation of the metal concentrations.

The total concentrations of the metals in the soil samples are presented in Table 5. The mean concentrations of all metals were higher in both the medium altitude and lower altitude soil samples except chromium. However, in the lowland altitude all metal concentrations were found to be lower when compared to that of the medium altitude, with the exception of manganese which recorded a higher value (39.66 mg kg^{-1}) in the lower altitude. T-test showed significant differences ($P < 0.05$, at 95% CL) among the analyzed soil samples for the mean concentrations of all metals except for Cu. The concentrations of all metals except Cr in the analyzed soil samples were under the EPA maximum permissible limit of typical concentration in soil dry matter 1,000–30,000 mg kg^{-1} for K, 5,000–30,000 mg kg^{-1} for Ca, 1,000–15,000 mg kg^{-1} for Mg, 10,000–50,000 mg kg^{-1} for Fe, 20-30 mg kg^{-1} for Mn, 2–100 mg kg^{-1} for Cu, 10–200 mg kg^{-1} for Zn, 0.1–1 mg kg^{-1} for Cd (EPA, 2002) and the minimum reporting limit 1 mg kg^{-1} for Cr in the soil (US EPA, 2012).

The distribution of the selected essential and non-essential metals in each soil samples were in the order of: Ca > K > Mg > Na > Cu > Mn > Fe > Zn > Cr > Cd (BMDL) in the low altitude soil samples and Ca > K > Mg > Na > Cu > Fe > Zn > Mn > Cr > Cd (BMDL) in the medium altitude soil samples.

Table 5: Average concentration (mg kg^{-1} air dry weight) of metals in low and medium altitude soil samples

Sample type	Average concentrations (mg kg^{-1} air dry weight)									
	K	Na	Ca	Mg	Cu	Cr	Mn	Cd	Fe	Zn
Low altitude soil	2401.38 ±95.03	628.13 ±27.39	8920 ±126.49	633.19 ±60.96	125.79 ±4.98	2.41 ±0.24	39.66 ±0.99	BMDL	38.51 ±10.11	7.28 ±2.95
Medium altitude soil	3347.38 ±263.82	758.13 ±45.83	10544 ±121.98	1935.32 ±105.89	113.12 ±14.92	3.52 ±0.57	25.407 ±0.19	BMDL	79.94 ±9.91	50.95 ±9.34

BMDL= below method detection limit,

The analyzed selected metal levels in low altitude soil sample when compared with that of stem and leaf of the *Rhamnus prinoides* showed that they were significantly varied (Ararsa and Alemayehu, 2013). The concentration of K was highest in leaf and lowest in soil. Na, Mg, Cu, Fe and Cr levels were highest in soil, lowest in leaf; Ca and Mn were higher in soil, lower in the stem; Zn levels were found to be lower in the leaf and higher in the stem samples; however, Cadmium levels were below method detection limits in all samples(Table 6).

In a related study of the distributions of essential and non-essential metal levels in the medium-altitude soil of Bako Tibe , the concentrations of metals in the stem and leaf of *Rhamnus prinoides* were also found to vary significantly (Ararso and Alemayehu, 2013). The concentration of K and Ca were higher in leaf and lowest in soil. Na, Fe, Zn and Cu levels were higher in soil and lower in leaf. Ca was found to be lower in stem when compared to the leaf and that of the concentration in soil. Moreover, the concentrations of Mg, Mn and Cr were higher in soil and lower in the stem. Cadmium levels were below method detection limits in all the samples (soil and plant) (Table 6).

Thus, from this study, most of the accumulation of metals in the stem and leaf of *Rhamnus prinoides* could be attributed to their presence in the soils on which the plant was being cultivated in addition to other factors such as soil pH and the use of manure. Generally, concentrations were found to be higher in the medium altitude compared to the lower altitude areas. This could be attributed to higher rainfall, more vegetation and level of organic matter decomposition in addition to the soil pH.

Table 6: Comparison of average concentration (mean ± SD, n = 5, mg kg^{-1} oven dry weight) of metals in stem and leaf of *R. prinoides* and soil samples

Metals	Leaf (mg kg^{-1} oven dry weight)		Stem (mg kg^{-1} oven dry weight)		Soil (mg kg^{-1} oven dry weight)	
	Low altitude	Medium altitude	Low altitude	Medium altitude	Low altitude	Medium altitude
K	12927.3 ± 346.92	11651.3 ± 333.44	10239.54 ± 386.23	8855.54 ± 269.94	2401.38 ± 95.03	3347.38 ± 263.82
Na	226.21±19.24	320.21 ±10.37	308.66 ±7.91	413.66±7.91	628.13 ± 27.39	758.13 ±45.83
Ca	7424 ±159	11120 ±126.49	6144 ± 191	7416 ± 153.88	8920 ±126.49	10544 ±121.98
Mg	352.34 ±13.14	1526.81 ±122.98	413.62 ± 12.64	1210.21 ±103.08	633.19 ± 60.96	1935.32 ±105.89
Cu	29.1 ± 3.46	36.98 ±6.43	46.34 ± 4.75	49.91 ± 5.83	125.79 ± 4.98	113.12 ±14.92
Mn	13.11 ± 0.28	7.36 ±1.98	9.41 ± 0.26	3.36 ± 0.2	39.66 ±1.0	25.41 ± 0.19
Cr	1.71 ± 0.34	1.71 ±0.19	2.17 ± 0.3	2.37 ± 0.24	2.41 ± 0.24	3.52 ± 0.57
Cd	BMDL	BMDL	BMDL	BMDL	BMDL	BMDL
Fe	8.58 ±1.23	10.71 ±3.98	9.39 ± 3.37	10.73 ± 0.1	38.51 ±10.11	79.94 ± 9.91
Zn	3.48 ±1.54	7.91 ±4.99	16.33 ± 3.04	18.36 ± 6.12	7.28 ±2.95	50.95 ± 9.34

BMDL = below method detection limit

Conclusion

A wet acid-digestion method using the mixture of aqua-regia (HCl and HNO_3) and H_2O_2 for preparation of soil samples were optimized, validated and used. The determinations of essential and non-essential metal levels (K, Na, Ca, Mg, Cr, Cu, Zn, Fe, Mn and Cd) in the samples were by flame photometer, flame atomic absorption spectrophotometer and complexometric titration with EDTA. The quality of the analytical data generated and general laboratory performance were continuously monitored and verified through the quality control parameters including CCS, LCSs, MS, MSD, method blank and laboratory solvent/reagent blanks. The laboratory procedures were all within acceptable limits/ guidelines.

Elements such as K, Ca, Mg, Na and Cu were generally found in higher concentrations than the other metals of interest in both samples. There was variations in metal concentrations in the soil which may be ascribed to: the physical and chemical nature of the soil (cation exchange capacity, organic matter content and soil pH); atmospheric deposition of the metals (which may be influenced by innumerable environmental factors such as temperature, moisture and pH) (Kalra, 1998).

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