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Determination of Selected Metals and Nutritional Compositions of Pigeon Pea (*Cajanus cajan*) Cultivated in Wolaita Zone, Ethiopia

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Abstract

This study was aimed to determine the level of selected metals and nutritional composition of pigeon pea seed collected from seven districts of Wolaita zone. A wet digestion procedure involving the use of mixtures of (69% - 72%) HNO_3 and (70%) $HClO_4$ at an optimum temperature and time duration was used to determine metals by using flame atomic absorption spectrometry. Kjeldahl digestion method, Soxhlet extraction and furnace were used to determine nutritional values of pigeon pea, and physicochemical properties of soils were assessed using standard methods. The results showed that the levels of concentration of metals in mg/kg dry weight were ranged 105.17 to 144.07 for K, 8.95 to 12.67 for Mg, 7.74 to 12.27 for Ca, 0.247 to 0.543 for Fe, 0.122 to 0.313 for Zn, 0.061 to 0.432 for Mn, 0.087 to 0.134 for Cu and 0.0011 to 0.00196 for Cr. The proximate composition of pigeon pea was in the range of 19.28% to 25.79% for crude protein, 0.993% to 1.75% for crude fat, 3.75% to 5.31% for ash, 10.65% to 13.73% for moisture, 2.28% to 3.06% for fiber, 54.36% to 60.1% for carbohydrate and 326.8 to 345.23 Kcal for energy. The pH of the soil was in the range from pH 5.09 (strongly acidic) to 6.77 (slightly acidic), EC of the soil ranged from 0.047 to 0.14 dS/m (low), the soil OC level was from 1.6% to 2.42% (moderate), total Nitrogen was from 0.12% to 0.23% (low to moderate), the available Phosphorus content of the soil was from 6.82 to 13.52 mg/kg (low to moderate), CEC value of the soil was from 14.8 to 23.53 meq/100g (moderate). The textural classes of soil were sandy clay loam for all sites except Abela abaya. The study confirmed that pigeon pea was a good source of proteins, carbohydrates, and selected metals such as Mg, K, Ca, Fe, Zn, Mn, Cu, and Cr. The concentration of metals and nutritional compositions of pigeon pea seed were found at a permissible level.

Keywords

Nutritional Value, Pigeon Pea, Selected Metals, Soil

1. Introduction

Pigeon pea (*Cajanus cajan*) domestically known as "Yergib ater", is an important legume grownup all over the tropics and subtropics for its fit for human consumption as a staple food. It is the preferred pulse crop in dryland areas where it is intercropped with cereals or other short-duration annuals. Dry grain, green pods, and fodder are the main products of pigeon pea [1]. It was believed that the origin of pigeon pea is either the North-Eastern part of Africa or India [2]. The cultivation of pigeon pea seed begun at least 3000 years ago. It is now a pan-tropical species particularly fitted to rain-fed agriculture in semi-arid areas because of its deep taproot, heat tolerance, and fast-growing habit [3]. Pigeon pea grows in places with a light-weight frost and in the areas where 20˚C to 40˚C temperature range [4]. It can nurture on soils with pH 5 - 7 and from sands to heavy black clay soils [5].

In Africa, *Cajanus cajan* is a subsistence crop that some countries have been reported to export significant amounts [6]. Africa contributes 9.3% pigeon pea production of the world, which is inadequate compared to the contribution from India alone, which is 74% [7]. This perennial leguminous shrub withstands severe drought better than many legumes, which are because of its deep roots and osmotic adjustment in the leaves [8]. The supplementation of cereals with protein-rich legumes is considered one of the best solutions to alleviate protein-calorie malnutrition in the developing world [9]. Mostly, hunger and malnutrition are increasing as a result of population explosion, shortage of fertile land, and high food prices. Globally, it is the foremost cause of the ailment and the passing of millions of pregnant women and young children. Accordingly, the formulation of nutrient-rich food items from an economic and cheap source like pigeon pea offers an efficient alternative strategy to fight the problem of malnutrition efficiently [10].

In Ethiopia, there is high climate variability and therefore the occurrence of extreme events over recent times. The Ethiopian Institute of agricultural research has been conducted studies on problems of drought resistance, early maturing, and heat-tolerant crop species and varieties. Pigeon pea is one of the grain pulses chosen by the research institute for livelihood improvement to satisfy the present nutrient need of poor and vulnerable people at large [11]. Dryland legumes are believed to offer enormous opportunities for reducing food insecurity and poverty in the semi-arid tropics as a result of their adaptability to such conditions [12]. It also plays a significant role in sustaining the degree of nutrients in soil productivity by fixing atmospheric nitrogen for crop productivity, adding organic matter and micronutrients, and breaking hard plough pan with its long taproots for crop productivity [9]. Pigeon pea has a high tolerance to environmental stresses and has high biomass productivity [13].

Pigeon pea is a good source of essential metals such as Mg, Ca, Fe, K, Na, Mn, Cr, and Zn. Metals like Cu, Cr, Fe, Zn, and Mn are essential for animals and human beings because they play a vital role in different metabolic functions, enzymatic activities, sites for receptors, hormonal functions, and protein transport at specific concentrations [14] [15] [16]. However, excess intake of such elements can cause chronic toxicity [17].

Research and development efforts have supported the release and commercialization of a substantial number of improved varieties of major lowland pulses in Ethiopia. National statistics on area production, and consumption for many decades on pulse crops compared to pigeon pea, whereas pigeon pea has no records since 2014 [18]. There is no documented information on the composition of macro and micronutrient and the nutritional value of pigeon pea grown in the Wolaita zone. Hence, the objective of this study was to determine the distribution pattern of selected metals and nutritional compositions of pigeon pea cultivated in the Wolaita zone, Ethiopia.

2. Materials and Methods

2.1. Description of Sampling Locations

The study was conducted in the Wolaita zone, South Ethiopia. The area is found at South Central Ethiopia between 6.40N - 6.90N latitude and 37.40E - 38.20E longitude and is located at 390 km south of Addis Ababa. The zone has a total area of 4541 km^2 and is composed of 16 districts and 6 registered towns. Its altitude ranges from 700 - 2900 m above sea level. The study area encloses three agro-climatic zones, Kolla (lowland < 1500 m), Woina-Dega (mid-altitude 1500 - 2300 m) and Dega (high land > 2300 m) with most of the area lies within the mid-altitude zone [19].

2.2. Apparatus and Instruments

Polyethylene bag, glass bottles, Electronic miller (Foss Knife tec1095, USA, Digital analytical balance, round bottom flasks, Kjeldahl (UK) apparatus, hot plate, measuring cylinders, pipettes, micropipettes (Dragon med, 1 - 10 μL, 100 - 1000 μL), acid reagents and metal standard solutions. Porcelain crucible, SG-deionizer (Germany, model; SG-2000), Soxhlet apparatus, rotator evaporator, water bath (UK, model; RE200) were used for sample collection and preparations. Flame atomic absorption spectrophotometer (FAAS) was used for the metal analysis. The pH meter to determine pH of the soil and conductivity meter was used to measure electrical conductivity.

2.3. Chemicals and Reagents

HNO_3 (69% - 72%), $HClO_4$ (70%, Analar BDH, England), and 30% H_2O_2 Scharlau, European Union, $LaCl_2 \cdot 6H_2O$ (Aldrich, USA), all the reagents used were of analytical grade. Stock standard solutions containing 1000 mg/l, in 2% HNO_3, of the elements K, Ca, Mg, Fe, Zn, Mn, Cu, Cr, and Cd was used for the preparation of calibration standards and in the spiking experiments. Deionized water was used throughout the experiment. Petroleum ether 40% - 60% was used for fat extraction and Boric acid, NaOH, selenium oxide, methyl red, 0.1N HCl, methyl blue indicator, and K_2SO_4, $CuSO_4$, and SeO_2 catalysts mixtures were used for total nitrogen content analysis in the sample for protein determination. The mixture of HCl, HNO_3 (3:1 ratios), and 30% H_2O_2 was used for the digestion of soil samples in macronutrient and micronutrient determination.

2.4. Sample Collection and Preparation

The pigeon pea seed (*Cajanus cajan*) samples were collected from different localities based on their availability and knowledge of the society regarding their uses. Accordingly, seven sample sites Sodo zuria, Humbo, Abela abaya, Damot woyde, Hobicha from districts, and Tebela and Sodo from town administrations were selected. Triplicate samples of pigeon pea seed from seven sites (3 × 7 = 21) were collected in the Wolaita zone. The collected samples were used for the determination of selected metals and nutritional values of pigeon pea seed.

2.5. Soil Analysis

2.5.1. Soil Sampling and Preparation

Surface soil samples (0 - 20 cm) was collected using auger from different points in a plot of seven different sites of five districts (Abela abaya, Humbo, Hobicha, Sodo zuria, Damot Woyde) and two town administrations (Tebela and Sodo). The soil samples collected from the same plots where pigeon pea seed samples were collected. A total of seven Composite soil samples were collected from the study areas and prepared after thoroughly mixing (homogenizing) the sub-samples of each plot in a plastic bowl. Soils were air-dried ground and mixed thoroughly and passed through a 2 mm sieve for most parameters. Laboratory analysis was conducted to determine the major soil physical and chemical parameters [20].

2.5.2. Physicochemical Properties of Soil

Soil pH was measured potentiometrically in H_2O and 1 M KCl solution at the ratio of 1:2.5 for soil: H_2O and soil: KCl solutions using a combined glass electrode pH meter [21]. Electrical Conductivity (EC) was measured in water as soil to water ratio of 1:5 using a conductivity meter [22]. Soil organic carbon was determined using the Walkley-Black method [23]. Available P was determined by the Olsen method [24]. Total nitrogen (TN) was determined by the Kjeldahl wet digestion and distillation method [25]. The texture of the soil was determined by the hydrometer method after the dispersion of the soil with sodium Hexa Metaphosphate [26]. The cation exchange capacity (CEC) of the soil was determined using the micro-Kjeldahl procedure [25].

2.5.3. Determination of Metal Levels in the Pigeon Pea Samples by FAAS

A wet digestion method was used for metal (Ca, K, Cu, Fe, Mg, Mn, Cd, Zn, and

Cr) analysis. The various acid and flux treatments were carried out at high temperatures in specially designed vessels that help to minimize contamination of the sample with substances in the air, adsorption onto the vessel walls, volatilization, and co-extraction [27].

2.5.4. Methods for Proximate Analysis

The proximate analysis (carbohydrate, fats, protein, moisture, fiber, and ash) of pigeon pea (*Cajanus cajan*) sample was determined by using the AOAC, 2000 method. Carbohydrate was determined by difference [100 − (protein + fat + moisture + ash + fiber)]. The nitrogen value was determined by the Micro-kjeldhal method. The nitrogen value was converted to protein by multiplying to a factor of 6.25. The moisture, ash, and fiber were determined using the weight difference method while the determination of crude fat content of pigeon pea sample was done using the Soxhlet extraction method [28].

3. Results and Discussions

3.1. Optimization of the Working Procedure

To prepare a clear and colorless sample solution that was suitable for the analysis using FAAS, different working procedures for the digestion of plant samples assessed using mixtures of HNO_3 and $HClO_4$ acids by varying parameters such as the volume of the acid mixture, digestion time, and digestion temperature [29] [30]. As can be seen in **Table 1** trial No. 5, consumed smaller reagent (acid) volume, smaller digestion time, and a colorless solution with no residue was obtained were chosen as the working conditions.

3.2. Calibration of Instruments

Standard solutions containing 1000 mg/l were used for preparing intermediate standard solutions (10 mg/l) in a 100 mL volumetric flask. As the values were given in **Table 2** appropriate working standards were prepared for each of the metal solutions by serial dilution of the intermediate solutions using deionized water. Calibration curves were plotted with five points for each of the standard

Table 1. Optimization of parameters for wet digestion of pigeon pea samples (Reagent types and volumes, temperature and time attempted during optimization).

Trial No.	Reagent used	Reagent volume (ml)	Temperature (˚C)	Digestion time (h)	Observation
1	HNO_3:$HClO_4$	5:1	150	1:30	Light yellow
2	HNO_3:$HClO_4$	4:2	180	1:50	Deep yellow
3	HNO_3:$HClO_4$	3:3	180	2:10	Clear yellow
4	HNO_3:$HClO_4$	4:1	210	2:30	Pale yellow
5	HNO_3:$HClO_4$*	3:2*	240*	2:50*	Clear colorless
6	HNO_3:$HClO_4$	4:2	270	3:10	Almost clear

*Indicates optimum condition.

of the selected metal using absorbance against concentrations (mg/l) and the correlation coefficients of the calibration curves were >0.997. This confirmed a very good positive correlation between the change in absorbance and concentration.

3.3. Method Detection Limit

The method detection limit for the analysis of metals using FAAS in pigeon pea seed samples was determined using reagent blank. Seven blank samples were digested following the same procedure as the samples and each of the blank samples was analyzed for metal concentrations of Cu, Cd, K, Mg, Ca, Zn, Mn, Fe, and Cr by FAAS. The standard deviation for each element was calculated from blank measurements to determine the method detection limit. Which usually corresponds to three times the standard deviation of the blank (Limit of detection = 3SD, where SD = standard deviation of the blanks) [31]. The result showed that the method detection limit is less than the results of real samples for detected metals and greater than those of not detected metals. From **Table 3**, the method detection limits estimated were greater than the instrument detection limit for all metals in pigeon pea samples.

3.4. Validation of Optimized Procedure (Recovery)

The validity of the analytical procedures and efficiency of the atomic absorption spectrophotometer used for sample treatment and analysis was tested by spiking experiment in a selected sample. For this purpose standard solution of 1000 mg/l

Table 2. Concentration of the standard solutions for FAAS instrument Calibration.

Metals	Concentration of the standards in (mg/l)	Correlation coefficients	Equation for calibration curve (A = mC + b)
Ca	5, 10, 15, 20, 25	0.9997	A = 0.1159 C + 0.0137
Mg	5, 10, 15, 20, 25	0.998	A = 0.177 C + 0.2276
K	0.065, 0.41, 0.785, 1.11, 1.57	0.998	A = 0.1676 C − 0.0858
Fe	1, 2.5, 5, 8, 10	0.9987	A = 0.028 C − 0.0048
Mn	0.5, 1.5, 3, 5, 9	0.998	A = 0.1358 C + 0.0872
Zn	0.25, 0.5, 1.0, 1.5, 2.0	0.999	A = 0.333 C − 0.0126
Cu	0.15, 0.35, 0.61, 0.84, 1.5	0.9999	A = 0.0837 C + 0.0169
Cr	0.05, 0.5, 1.0, 1.5, 2.0	0.9997	A = 0.01 C + 0.0017
Cd	0.5, 1.0, 1.5, 2.0, 2.5	0.997	A = 0.292 C + 0.056

A = Absorbance, C = Concentration in mg/l, m = The slope, b = Intercept.

Table 3. Detection limits for the analysis of pigeon pea samples by FAAS.

Metals	Ca	Mg	K	Fe	Mn	Zn	Cu	Cr	Cd
IDL (ppm)	0.001	0.001	0.001	0.003	0.001	0.005	0.001	0.001	0.001
MDL (mg/Kg)	0.002	0.005	0.003	0.01	0.01	0.007	0.004	0.0011	0.002

IDL = Instrument Detection Limit, MDL= Method Detection Limit.

was used and intermediate standards of 10 mg/l were prepared. The spiked and non-spiked samples were digested and analyzed in similar conditions using an optimized procedure for sample analysis.

As presented in **Table 4**, the results of the percent recoveries for all the metals in the analyzed pigeon pea sample were found within 100 ± 10 percent (90 - 105.8) and the RSD values ranged between 1.3% - 8.2%. This indicates that contamination was not a problem in the digestion procedure and the recovery results were in good agreement with the acceptable values [32].

3.5. Determination of Physicochemical Properties of Soil

Soil texture

As shown in **Table 5**, the particle size division of the soil types: % clay, % silt, and % sand was ranged from 24.7 - 48.6, 13.1 - 25, and 28.2 - 59.8, respectively. The textural class of the soil was sandy clay loam in all the studied sites except Abela Abaya (AA). The textural class of the soil of AA was clay loam. This soil, therefore, has the potential to hold more water within the particles and suitable for plant growth due to the presence of a relatively high percentage of clay. Sandy soils contain low organic matter and retain little water and, therefore, percolation of water through it is high while clay soil contains high organic matter, capable to resist water and wind erosion of the soil, high cation exchanging capacity and pH buffering capacity [33].

pH

The pH of studied soil samples was found to be in the range of 5.09 to 6.77. The highest pH value (6.77) was obtained in the soils of AA which were slightly acidic compared with the lowest value of soils of Sodo zuria (SZ) (5.09). There were variations in soil pH levels from the soil samples analyzed. The lower pH of SZ was due to the leaching of basic nutrients Ca, Mg from the soil, and replacement of acidic elements such as Al^{3+}, Fe^{2+} [34]. According to Jones (2003), the pH ranges of the soils in studied areas were from strongly acidic to slightly acidic

Table 4. Recovery test results of metals for pigeon pea spike sample.

Metals	Conc. in sample (mg/100g)	Amount added (ppm)	Conc. in spiked sample (mg/100g)	Recovery (%)	RSD (%)
K	123.6 ±2.4	61.8	184.1 ± 3.5	97.8 ± 1.8	1.83
Mg	10.2 ± 0.12	5.1	15.6 ± 0.53	105.8 ± 4.2	3.97
Ca	9.7 ± 0.19	4.85	14.1 ± 1.1	90.7 ± 2.5	2.2
Fe	0.36 ± 0.04	0.18	0.55 ± 0.06	105.6 ± 7.3	6.9
Zn	0.23 ± 0.01	0.11	0.33 ± 0.03	90.9 ± 1.2	1.3
Mn	0.2 ± 0.013	0.1	0.29 ± 0.01	90 ± 6.7	7.4
Cu	0.1 ± 0.005	0.05	0.147 ± 0.08	94 ± 2.9	3.1
Cr	0.002 ± 0.0001	1.0	1.001 ± 0.07	99.9 ± 8.2	8.2
Cd	ND	ND	ND	ND	ND

in nature [35]. The higher acidity of the soils for SZ was mainly due to the leaching of some basic cations [36]. Soil acidity affects the process of other nutrient transformations, solubility, or plant availability of many plant essential nutrients [37].

Soil electrical conductivity

As displayed in Table 5, the electrical conductivity (EC) of the soils were ranged from 0.047 - 0.14 dS/m. Deshmukh (2012) reported that the EC value for good soil rated less than 1 dS/cm. Hence, all soils under investigation were rated as low EC values [38]. The low EC value due to diverse anthropogenic and natural activities including leaching of exchangeable bases, acid rains, organic materials decomposition, use of commercial fertilizers, and other farming practices [33].

Cation exchange capacity

The results in Table 5 confirmed that the cation exchange capacity (CEC) of the soil was in the range of 14.8 to 23.53 cmol/ kg of soil. The uppermost value was observed at AA district whereas, the lowermost was recorded from SZ (14.8 cmol/ kg) districts. According to Landon (1991), the CEC of the soils of the study areas rated as moderate [39]. The CEC of soil is highly influenced by clay content and organic matter of the soil. Soil with higher clay content and organic matter has higher CEC [40]. The relatively low CEC of the Sodo zuria district may be due to the highest sand fraction and the lowest clay fractions of the soil [41].

Soil organic carbon

As depicted in Table 5, the organic carbon (OC) of soil ranged from 1.6 to 2.42. The highest value was found in AA (2.42) and the lowest value was observed in SZ (1.6). According to the rating suggested by Tekalign *et al.* (1991), the soil OC contents of the study area was the moderate range [42]. Soils relatively higher in clay content tend to stabilize and retain more OM than soils with low clay content [43].

Soil total nitrogen (TN)

The TN of the soil sample ranged from 0.12 to 0.23 as shown in Table 5. The highest results were observed for AA (0.23) and the lowest records for SZ (0.12). According to Chowdhury *et al.* (2011), the soil total nitrogen of the study area was ordered from low to moderate [44]. Low total nitrogen was recorded in all four sites except AA (0.23%), Ho (0.21), and DW (0.185) (moderate). The results were in harmony with the findings of Wakene and Heluf (2003) who reported that intensive and continuous cultivation forced oxidation of OC and thus resulted in a reduction of total N [45].

Available Phosphorus

The available P content of the soil revealed in Table 5 was ranged from 6.82 to 13.52 mg/kg. A relatively higher percentage of available phosphorous was observed in the soil of the AA (13.52) district and the lowest available phosphorus was found in SZ (6.82). The low availability of Phosphorus is due to the fact that

Table 5. The physicochemical properties of soil.

Site	pH	% EC	% CEC	% OC	TN	Av. P	Texture of soil			Textural class
							% clay	% Silt	% Sand	
AA	6.77	0.14	23.53	2.42	0.23	13.52	48.6	23.6	28.2	CL
DW	6.09	0.12	19.23	2.05	0.185	8.29	24.7	25	50.3	SCL
HW	5.61	0.07	21.3	2.26	0.15	11.37	25.5	19.1	55.4	SCL
ST	5.25	0.05	17.3	1.77	0.14	7.58	29.3	14.7	56	SCL
SZ	5.09	0.047	14.8	1.6	0.12	6.82	27.1	13.1	59.8	SCL
Ho	6.36	0.116	18.07	1.71	0.21	10.27	28	19.8	52.2	SCL
TT	5.57	0.09	19.6	2.24	0.16	8.2	32	13.4	54.6	SCL

AA = Abela Abaya, DW = Damot Woyde, HW = Humbo Woreda, ST = Sodo Town, SZ = Sodo Zuria, Ho = Hobicha, TT = Tebela Town.

it readily forms insoluble complexes with a cation such as aluminum (Al) and iron (Fe) under acidic soil condition [46]. According to Chowdhury *et al.* (2011), the available phosphorus content of the current study was low to moderate [44]. This may be due to past fertilization, pH, organic matter, texture, and various soil management and agronomic practices and the low availability might be due to leaching, soil erosion, and crop harvest [47] [48].

3.6. Determination of Selected Metals in Pigeon Pea Seed

The pigeon pea samples were analyzed for selected metals (Ca, Mg, K, Fe, Mn, Zn, Cu, Cr, and Cd with FAAS. The results showed that the concentrations of the selected metals (Ca, Mg, K, Fe, Mn, Zn, Cu, and Cr) in pigeon pea seeds of seven sites were detected. The samples had a variable composition of each analyte metals with different concentration ranges among different sites in pigeon pea samples except for Cd which was below the detection limit. Metals were measured in the pigeon pea samples utilizing the FAAS instrument by the external calibration method. The concentration of metals in pigeon pea samples varied in the order of K > Mg > Ca > Fe > Zn > Mn > Cu > Cr (**Table 6**, **Table 7** and **Figure 1**).

Levels of Metals in the Pigeon Pea Samples

Potassium: As depicted in **Table 6**, the potassium concentration was ranged (105.17 - 144.07 mg/Kg). The highest concentration was observed at AA (144.07 mg/Kg) and the least mean concentration was recorded at SZ (105.17 mg/Kg). These could be attributed to different factors such as geographical and climatic variation, differences in physicochemical nature of the soil, and differences in the agricultural practices and inputs used for plant growth [16]. The mean concentration of metal uptake by plants increases as the levels of these metals increase in the soil environment [49]. Nwokolo (2010), reported the mean concentration of potassium in pigeon pea was 125 mg/Kg [50], Rajni and Vikas, 2016 reported 110.4 mg/Kg [51], which were in good agreement with the results

Table 6. The (K, Mg, mean concentration of metals Ca, Fe) with in pigeon pea locations.

Districts	Metals			
	K	Mg	Ca	Fe
AA	144.067^{a} ± 2.32	12.67^{a} ± 0.04	12.27^{a} ± 0.12	0.247^{e} ± 0.03
DW	128.97^{b} ± 3.4	11.37^{b} ± 0.07	11.27^{b} ± 0.5	0.278^{cd} ± 0.09
HW	121.40^{c} ± 2.07	10.54^{c} ± 0.17	8.87^{c} ± 0.08	0.378^{c} ± 0.013
ST	114.87^{d} ± 2.06	9.20^{e} ± 0.08	7.74^{d} ± 0.2	0.465^{b} ± 0.013
SZ	105.17^{e} ± 3.19	8.95^{f} ± 0.03	7.35^{d} ± 0.18	0.543^{a} ± 0.03
Ho	128.07^{b} ± 0.65	11.26^{b} ± 0.21	11.2^{b} ± 0.14	0.283^{ed} ± 0.02
TT	122.87^{c} ± 1.4	10.1^{d} ± 0.02	9.21^{c} ± 0.08	0.314^{d} ± 0.04
LSD	4.08	0..19	0.41	0.04
CV	1.89	1.04	2.38	5.97

*Means with the same letter are not significant, LSD = Least significance difference, CV = Coefficient of Variance, AA = Abela Abaya, DW = Damot Woyde, HW = Humbo Woreda, ST = Sodo Town, SZ = Sodo Zuria, Ho = Hobicha, TT = Tebela Town.

Table 7. The mean concentration of metals (Zn, Mn, Cu, Cr) with in pigeon pea locations.

Districts	Metals				
	Zn	Mn	Cu	Cr	Cd
AA	0.12^{f} ± 0.001	0.06^{d} ± 0.04	0.08^{d} ± 0.002	0.0011^{e} ± 0.0002	ND
DW	0.22^{d} ± 0.004	0.12^{cd} ± 0.08	0.09^{cb} ± 0.002	0.0014^{dc} ± 0.0008	ND
HW	0.23^{d} ± 0.019	0.26^{b} ± 0.02	0.10^{b} ± 0.006	0.0015^{c} ± 0.0001	ND
ST	0.29^{b} ± 0.004	0.30^{b} ± 0.006	0.13^{a} ± 0.02	0.0017^{b} ± 0.0003	ND
SZ	0.31^{a} ± 0.007	0.43^{a} ± 0.01	0.12^{a} ± 0.01	0.0019^{a} ± 0.0002	ND
Ho	0.20 ^{e} ± 0.02	0.13^{c} ± 0.03	0.09^{cb} ± 0.001	0.0016^{bc} ± 0.0003	ND
TT	0.25^{c} ± 0.008	0.15^{c} ± 0.03	0.1^{cb} ± 0.001	0.0013^{d} ± 0.0002	ND
LSD	0.018	0.073	0.013	0.0001	ND
CV	4.41	6.5	7.11	2.004	ND

*Means with the same letter are not significant.

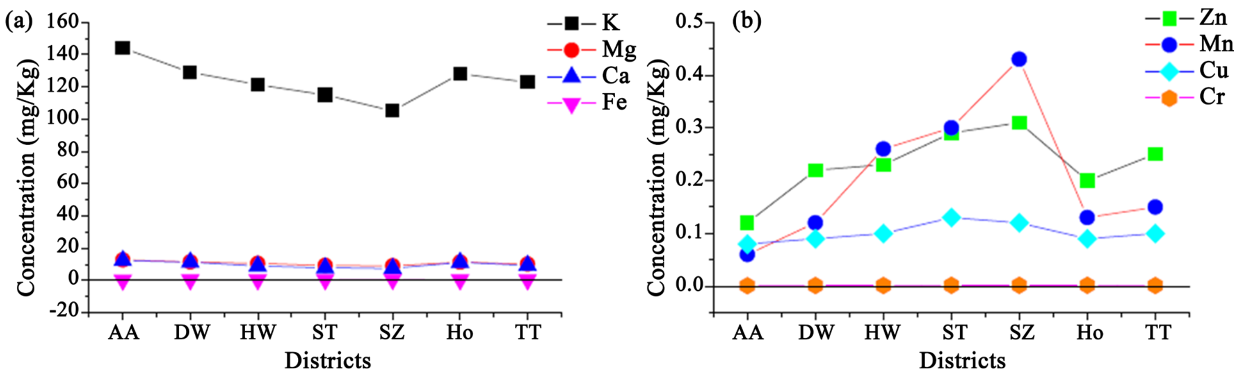

Figure 1. Distribution of metals in pigeon pea from various districts (a) macronutrients (b) micronutrients.

of K in different sites. The reported level of potassium acceptable limit set by FAO, (2012) was 110 mg/Kg [52]. This was in agreement with the present study result.

Calcium: As shown in **Table 6**, the concentration of calcium in pigeon pea seed of different locations was ranged from 7.35 - 12.27 mg/Kg. The highest level of calcium was observed in the AA (12.27 mg/Kg) whereas the least amount was found in SZ. Singh *et al.* (2018) reported that the mean concentration of pigeon pea ranged in 89.5 mg/100g - 118.6 mg/100g [53]. Kunyanga *et al.* (2013) reported (80.5 mg/100g) [54], Foodnet (2002) reported (120.8 mg/Kg) [55]. which were in good agreement with the results of this study but Nwokolo, 2010 reported (150 mg/Kg) [50], was higher than the results of pigeon pea collected from different locations. The variations in concentration and order of accumulated metals were different in the samples probably influenced by the difference in locations in relation to soil pH [56]. The FAO (2012) limit set was 55 mg/100g [52], this is slightly lower than the results of the study area.

Magnesium: The mean concentration level of Mg varies from 8.95 to 12.67 mg/Kg dry weight pigeon pea samples in various locations. Significantly different magnesium concentrations were observed in pigeon pea samples with various treatments. The highest concentration was found in pigeon pea collected from AA whereas the least amount observed in SZ. From literatures, [51] [52] [54] [55] [57] were reported the mean concentration of pigeon pea seed 14.1, 9.0, 10.8, 12.2 and 7.9 respectively. According to USDA (2016), the National Nutrient database, the report level of Mg 18.3 mg/Kg, was higher than the results of the present study [58]. The Permissible limit set by FAO, (2012) was 9.6 mg/Kg [52] that is in agreement with the values of the present study.

Iron: In the study area, the iron content of pigeon pea samples ranged from 0.247 to 0.543 mg/Kg dry weight. The mean concentration of iron was found to be highest at SZ (0.543 mg/Kg) and a low amount of iron was found in AA (0.247 mg/Kg). The reason behind this was related to the increase in acidity of the soil. The literature values in pigeon pea from different workers: Abiola *et al.* (2019) were reported 1.02 mg/100g [57], Kunyanga *et al.* (2013) (5.6 mg/100g) [54], Singh *et al.* (2018) reported 5 mg/100g [53], Nwokolo (2010) (3.9 mg/100g) [50] and Foodnet (2002) (2.9 mg/100g) [55]. These were similar to the records of the current study. The permissible limit set by FAO (2012) in edible plants was 5.23 mg/100g [52], which was in agreement with the present study.

Zinc: The concentration of zinc determined in pigeon pea samples (**Table 7**, **Figure 1**) was from 0.122 to 0.313 mg/Kg dry weight. The highest level of zinc was observed in SZ (0.313 mg/Kg) samples and the lowest level of zinc was determined in AA (0.122 mg/Kg). The reason may be due to the higher leaching of base-forming cations and increasing acidity of the soil. As reported by [59] [60], the mean concentration of Zn was ranged from 0.08 mg/Kg to 0.36 mg/Kg; Kunynga *et al.* (2013) reported 0.27 mg/Kg of Zn in pigeon pea [54]. Similar study by Foodnet (2002) reported 0.24 mg/Kg mean concentration of Zn in pigeon pea

[55]. These were in good agreement with the recorded value of the present study. Abiola *et al.* (2019) was reported (0.48 mg/Kg) [57]; which was slightly higher than this study. The permissible limit of zinc in edible plants set by FAO, (2012) and USDA, (2016) was 0.274 mg/Kg and 0.276 mg/Kg respectively [52] [58], which was similar to the current study.

Manganese: As shown in **Table 7**, manganese content ranged from 0.061 mg/Kg to 0.432 mg/Kg. The highest manganese content was observed in SZ (0.432 mg/kg) and the lowest content was found in AA (0.061 mg/Kg) due to the increase in pH of soil. As reported by Foodnet (2002) the manganese mean concentration was 0.92 mg/Kg [55]; Singh (2018) reported 0.5mg/Kg [53]. These were higher than the results obtained in this study. Abiola *et al.* (2019) were reported 0.138 mg/Kg [57]; Rajni and Vikas (2016) reported (0.069) [51]. This was satisfactorily agreed with this study.

Copper: The mean concentration of copper (**Table 7**, **Figure 1**) in this study was ranged from 0.08 to 0.13 mg/Kg dry weights in Pigeon pea samples. The relatively highest level of copper was found in ST (0.13 mg/Kg) samples and the least was for that of AA (0.08 mg/Kg) samples due to the variation in acidity and a textural class of soil. From the literature, Foodnet (2002) reported (0.13 mg/Kg) [55]; Rajni and Vikas (2016) reported (0.12 mg/Kg) [51], and Saxena (2010) reported 0.13 mg/Kg [59]. These were similar to the results recorded in different locations. The permissible limit set by FAO (2012) in edible plants was 1.2 mg/100g [52].

Chromium: The chromium content of pigeon pea samples in this study was 0.0011 to 0.0019 mg/Kg dry weight in the pigeon pea sample. From the result, the highest level of chromium was recorded in SZ (0.0019 mg/Kg) and the lowest was found at AA (0.0011 mg/Kg). The difference between samples based on locations was very small. This may be due to the availability of chromium metals in various soil types and characteristics [61]. As reported by Rajni and Vikas (2016), the chromium concentration was 0.001 mg/Kg [51]. According to Jabeen *et al.* (2010), the chromium content in pigeon pea seed was 0.19 µg/g [62]. Pigeon pea seed contains minute amounts of chromium which is required in very small amounts in the body for the regulation of blood sugar and transport of glucose into the cells [63].

3.7. Determination of Proximate Composition in Pigeon Pea Sample

The proximate contents such as protein, fats, carbohydrates, moisture, ash, crude fiber, and energy values were given in **Table 8** and **Table 9** as gm/Kg of seeds.

Crude protein content

As shown in **Table 8**, the average protein content of pigeon pea was ranged from (19.28% - 25.79%). The highest crude protein was found to be 25.79% at AA, and the lowest mean concentration was observed at ST (19.28%). The level of crude protein in pigeon pea of AA was significantly different ($p < 0.05$) from ST and SZ. This may be attributable to agroecology, soil type, and fertilizer

Table 8. The mean concentration (mean ± SD) of proximate composition of pigeon pea samples.

Districts	Crude Protein	Crude fat	carbohydrate	Moisture
AA	25.79^{a} ± 1.2	0.993^{d} ± 0.05	54.36^{d} ± 0.47	13.05^{bac} ± 0.65
DW	22.5^{c} ± 0.33	1.6^{ac} ± 0.02	57.35^{bc} ± 0.24	12.6^{bc} ± 0.26
HW	21.59^{d} ± 0.63	1.62^{bac} ± 0.04	58.53^{b} ± 0.25	12.3^{c} ± 0.2
ST	19.28^{f} ± 0.67	1.72^{ba} ± 0.09	57.54^{bc} ± 0.27	13.73^{a} ± 0.31
SZ	20.3^{e} ± 0.1	1.56^{c} ± 0.05	57.43^{bc} ± 0.2	13.3^{ba} ± 0.53
Ho	21.27^{d} ± 0.13	1.75^{a} ± 0.2	60.1^{a} ± 0.23	10.65^{d} ± 0.73
TT	23.21^{b} ± 0.72	1.57^{bc} ± 0.03	57.04^{c} ± 0.32	12.33^{bc} ± 0.31
CV	2.87	5.71	4.97	3.71
LSD	1.135	0.154	0.941	0.82

*Means with the same letter are not significant, CV = coefficient of variance, LSD = least significant difference.

application difference depending on farmers [64]. According to Vasave (2003), Aparna (2004), Pawar *et al.* (2009) and Oke (2014), the reported level was ranged from 17.97% - 26.38% [65] [66] [67] [68]. These were relatively similar to those recorded in the present study. According to John (2005), the percent crude protein of commonly grown pigeon pea was in the range between 18% - 26% [69]. Similarly, Sharma *et al.* (2011) reported (2% - 22%) [64], and Kachare *et al.* (2017) reported (17.62% - 25.45%) [70], these were all in good agreement with the results obtained in the present study. The permissible level of crude protein in pigeon pea recommended by FAO, 2016 was 22.3%.

Crude fat content

As depicted in **Table 8**, the crude fat ranged from 0.993% to 1.75%. From the result, maximum crude fat was found in Ho and the least average content of fat was recorded at AA (0.993%). The percent crude fat of pigeon pea of this study was comparatively lower than the fat percentage (2.77%, 2.74%, 4.78%, 3.68%) reported by [54] [68] [71] [72] respectively. Eltayeb *et al.* (2010), and Sharma *et al.* (2011) reported 12%, and 1.7% crude fat respectively [73] [64], and John (2005) reported the crude fat content in ranges between 1.2% - 8.1% [69]. (USDA, 2016) database report was 1.49% [58]. These were similar to the results of the present study.

Carbohydrate content

The total carbohydrate content of pigeon pea under investigation was ranged between 54.36 mg/100 g to 60.10 mg/100g. The maximum carbohydrate content was observed in the Ho (60.10 mg/100g) and the lowermost value was found at AA (54.36 mg/100g). The Mean carbohydrate content in pigeon pea from Ho was significantly ($p < 0.05$) higher than the rest. This may be related to the soil pH textural class, and change in the agroecology of study areas. Saxena (2010) reported 57.6 mg/100g [59], Oke (2014), Olalekan and Bosede (2010), Adamu and Oyetunde (2013), Kunyanga *et al.* (2013) were reported between 51.4% -

58.8% [54] [68] [71] [72]. These were in good agreement with the results of this study. The permissible level of carbohydrate in pigeon pea recommended by FAO was 60.4%. These were in good agreement with the results obtained by the current study.

Moisture content

The data (**Table 8**) revealed that moisture contents varied from 10.65% to 13.73% in various locations. The highest moisture content (13.73%) was found at ST and least at Ho (10.65%). Analysis of variance showed that the level of moisture content was significantly different among districts, ($p < 0.05$). Oke, (2014) and Eltayeb *et al.* (2010) were reported 11.2% and 11.7% respectively [68] [73]. These were in good agreement with those recorded in the present study. Olalekan and Bosede, (2010) reported 8.45% moisture contents in pigeon pea [71]. This was comparatively lower than the results recorded in this study. The permissible level of moisture in pigeon pea recommended by FAO, (2012) was 10.8% [52].

Ash contents

Ash contents of pigeon pea of the study area were ranged between (3.75% - 5.31%). Maximum Ash content was found in ST (5.31%) and minimum content in AA (3.75%). Oke, (2014), Adamu and Oyantunde, (2013) reported 8.22%, and 9.93% respectively [68] [72]. These were relatively higher than those recorded in the present study. However, [54] [71] [73] reported 3.58%, 4.58%, and 3.2% ash content of pigeon pea respectively. The permissible level of ash in pigeon pea recommended by FAO was 3.8%. It was in agreement with the current investigation.

Crude fiber

The results presented in **Table 9** revealed that the crude fiber content of pigeon pea was ranged from 2.28% to 3.06% in the study districts. The highest value was found in AA (3.06%) and the smallest was recorded in SZ (2.26%). The content of crude fiber in pigeon pea seed was significantly different ($p < 0.05$).

Table 9. The mean concentration (mean ± SD) of proximate composition of pigeon pea samples.

Districts	Ash	Fiber	Energy
AA	$3.75^{d} \pm 0.39$	$3.06^{a} \pm 0.06$	$330.54^{d} \pm 1.56$
DW	$4.39^{bc} \pm 0.29$	$2.91^{b} \pm 0.02$	$332.4^{c} \pm 1.24$
HW	$4.23^{bcd} \pm 0.33$	$2.73^{c} \pm 0.05$	$335.06^{b} \pm 2.6$
ST	$5.31^{a} \pm 0.26$	$2.41^{e} \pm 0.02$	$326.8^{f} \pm 0.89$
SZ	$4.77^{ba} \pm 0.32$	$2.26^{f} \pm 0.012$	$328.48^{e} \pm 0.9$
Ho	$3.95^{cd} \pm 0.08$	$2.28^{f} \pm 0.02$	$345.23^{a} \pm 1.1$
TT	$4.2^{bcd} \pm 0.54$	$2.65^{d} \pm 0.01$	$335.13^{b} \pm 2.3$
CV	5.81	2.08	4.7
LSD	0.597	0.059	0.487

*Means with the same letter are not significant.

Kunyunga *et al.* (2013), Adamu and Oyentunde, (2013) and Saxena, (2010) were reported higher content (6.98%, 6.6% and 5.54% respectively) of fiber in pigeon pea [54] [59] [72]. John (2005), Oke (2014), and Eltayeb *et al.* (2010) were reported the Crude fiber content between (1.2% - 8.1%) in pigeon pea [68] [69] [73]. These were similar results and in good agreement with the current study. The permissible level of crude fiber in pigeon pea recommended by FAO, (2008) was 1.5% [74].

Energy content

As presented in **Table 9**, the average energy content of pigeon pea in the study districts was in the range of 326.8 - 345.23 Kcal/g. The highest energy content was found in Ho (345.23 Kcal) district and the least mean energy content was obtained at ST (326.8 Kcal/g). According to the report by [57] [68] [75], the mean energy content in pigeon pea was 298.25, 334.3, and 304.3 Kcal/g respectively. These were in good agreement with the current study. FAO (2016) recommended the level of energy was 358.8 Kcal/g [4].

4. Conclusion

The study revealed that the concentrations of selected metals (K, Mg, Ca, Fe, Zn, Mn, Cu, and Cr) were determined in pigeon pea seed and the metal Cd was found to be below the method detection limit in all districts. The highest concentration of K, Ca, and Mg were found in pigeon pea seed at Abela abaya (AA) and lowest at Sodo zuria (SZ) due to higher soil pH and a textural class of soils of AA while the concentration of Fe, Zn, Mn, Cu, and Cr were high in the pigeon pea at SZ. The proximate analysis result indicated that pigeon pea was a good source of protein, carbohydrate, energy but low-fat content. The ANOVA at a 95% confidence level suggested that there was a significant difference in the mean concentration of selected metals and nutritional values in different locations. Physicochemical properties in various locations elucidate the soils of the study area are suitable for the production of pigeon pea. The results of this study suggest that these cereal plants are safe to be utilized as a staple food since the concentration of metals and nutritional values are within the recommended limits of FAO and WHO guidelines.

Availability of Data and Materials

We declare that the data and materials presented in this manuscript can be made available as per the editorial policy of the journal.

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Conflicts of Interest

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

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