Analysis of Major, Minor and Trace elements Related to Ethiopia Cereal crops using EDXRF Technique

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Abstract— The elemental analysis of cereal crops grown in Ethiopia namely Barley (Hordeum vulgare), Maize (Zea mays), Finger millet (Eleusine coracana), Sorghum (sorghum bicolor) and Wheat (Triticum aestivum) samples were carried out using EDXRF spectrometer. The concentration of 16 elements (Ca, K, S, P, Zn, Cu, Ni, Co, Fe, Mn, Cr, As, Pb, Sr, Rb and Br) were obtained in the above mentioned five selected cereal crops. The results demonstrated that the relative concentrations of obtained elements in these cereal crops are different from one another. Ca is more in millet while it is least in maize. Contrary to this, K is found high in maize and low in wheat but high concentration of P was present in barley and minimum quantity was obtained in sorghum. Significantly in the present work the concentration of heavy metals were found to be with low level concentration besides the absence of P and Mn elements in maize and P in sorghum were noticed. On the other hand high content of calcium, potassium, zinc and Iron micronutrients were found in all cereal species.

Keywords- EDXRF, Cereal, Elemental composition, ppm, Heavy metal, Essential elements

1 INTRODUCTION

For all living organisms, number of nutritional elements is essential for maintaining growth and cell functions; and for completing the life cycle through reproduction. For plants, 14 known essential mineral elements are required, which are mainly acquired from the soil [1]. Majority of the world population nutritional needs is met with the cereals such as rice, maize, wheat, barley, and sorghum [2] that come under Graminaceous category. Seeds or grains that obtain from cereals are one of the main resources for human nutrition and animal feed throughout the world [3]. Around the world, most of the plants seem to have micronutrients with low concentrations, hence it may be considered as a major concern one. Large portions of arable land that suffer from severe yield losses are as a cause of insufficient supply of micronutrients to crops [4]. In addition to reduced yield for farmers, low uptake of micronutrients in plants also results in food and feed products that are poor in minerals. This may be important causes of malnutrition, especially in the populations with a monotonous diet. On the other hand, some areas suffer from excessive uptake of elements, causing toxicity or imbalances in crops or in livestock and humans. The ability to predict and assess the micronutrient status in crops is essential in order to avoid and counteract their deficiencies, toxicity and thereby yield losses. Agriculture sectors employ more than two thirds of Ethiopia's population and are the backbone of the country's economy. Ethiopia is the second largest country in sub-Saharan Africa, with the population of more than 90 million. Currently, over 12.8 million hectares of land are under cultivation causing it the largest producer of food grains in Africa [5]. The major grain crops grown in the country are teff, wheat, maize, barley etc; categorized as primarily cool weather crops and sorghum and millet are categorized as warm weather grain crops. All these crops are predominantly rain fed crops grown all over the country except in some parts of the lowlands. These cereals are predominantly produced by small landholders with not more than 2 hectares (ha) per family. They are consumed for food and their by-products are frequently used as an animal feed. In the present work energy dispersive X-ray fluorescence (EDXRF) technique has been employed for the determination of major, minor and trace element constituents of some of the Ethiopia cereal crops those collected from three different places of Ethiopia. ED-XRF is a simplest, most accurate and more economical analytic technique for the determination of the chemical composition of different types of materials. It can be used for a wide range of elements, from sodium (Z = 11) to uranium (Z = 92), and provides detection limits at the sub-ppm level [6]. This study might help to develop an agricultural management to have yielding(s) with appropriate concentration of nutrients in the cereals during the growing period and to diagnose a suspected nutritional deficiency or toxicity.

2. Materials and methods

2.1. Sample collection and preparation

Barley, Maize, Millet, Sorghum and Wheat samples were collected in the month of September to December 2015 from three different locations of Ethiopia namely

1. Addis Ababa Market (Ehil berenda) (Addis Ababa city located at geographical coordinates of 9^0 1' 48'' N, 38^0 44' 24'' E)
2. Gechi (Gechi is one of the district head quarters in the Oromia region of Ethiopia. Part of the Illubabor Zone, located at 8^0 2' 17''N and 36^0 37' 30''E. Its distance from Addis Ababa to Gechi is 460 km)
3. Shewa Robit (it is a town in north-central Ethiopia, Located in the north Shewa zone of the Amhara region, this town has a longitude and latitude of 10^0 00' N, 39^0 54' *E* coordinates with an elevation of 1280 meters above sea level.

Stones and sediments were removed from the collected grains of the present samples by using stainless steel forceps. All the samples were washed by double distilled deionized water. After oven-drying at 65^0 C for 48 hours, about 150 mg of the washed cereals samples were powdered; homogenized using a mortar and pestle and made into pellets (1*mm* thick and 13*mm* diameter) using a tabletop pelletize machine (Pressure: 100 – 110 kg/cm^2).

2.2. Experimental studies and Method of Validation

Experimental studies of the samples have been carried out at UGC-DAE Consortium for Scientific Research, Kolkata Centre by using a Xenemetrix (erstwhile Jordan Valley) EX 3600 EDXRF spectrometer, which consists of an oil-cooled Rhodium anode X-ray tube (maximum voltage 50 kV, current 1 mA). The measurements were performed in vacuum using different filters (between the source and sample) for optimum detection of elements (table 1). For example, for Na, Si and Al, no filter was used, and a voltage of 6 kV and current of 240 mA were used. A 0.05-mm-thick Ti filter was used in front of the source for K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu and Zn with an applied voltage of 14 kV and a current of 900 mA. For high Z elements such as Pb, Bi, Ag and As, a Fe filter of 0.05 mm thickness was used at a voltage of 37 kV and 45 mA of current. All the spectra of the samples were collected for the duration of 1400 seconds. The X-rays were detected using a liquid-nitrogen cooled 12.5 mm^2 Si (Li) semiconductor detector (resolution 150eV at 5.9KeV). The X-ray fluorescence spectra were quantitatively analyzed by the software NEXT, integrated with the system. Validity of the EDXRF set up was performed by analyzing Standard reference materials (SRM) obtained from National Institute of Standards and Technology (NIST) - Apple leaf (Table 2), SRM1515; Peach leaf (SRM1547) and Oriental Tobacco leaves (CTA-OTL-1) - were used for quantification of the elements and verifying the reliability of the data obtained by the present system.

Table 1: Operating condition of EX 3600 EDXRF spectrometer

Parameters	$e1$	$e2$	$e3$
Filter	None	3-Ti	4-Fe
Emission current(µA)	240	900	45
High voltage (Kv)	6	14	37
Preset time(S)	200	900	300
Atmosphere	vacuum	vacuum	vacuum
Energy Range	10	10	40
Throughput	low	low	low

e1:spectrum1, e2:spectrum2, e3:spectrum3

3. Results and discussion

In the present study five types of cereal crops as mentioned above having different variety (total 18) samples were analyzed in which 16 elements (Ca, K, S, P, Zn, Cu, Ni, Co, Fe, Mn, Cr, As, Pb, Sr, Rb, and Br) were detected in all the samples. The variation of the elemental concentrations in the analyzed cereal samples is shown in the tables 3 to 5. All the samples analyses in this study were carried out in triplicate and the results were reported as mean ± standard deviation.

3.1 Calcium: Calcium (Ca) is an extremely important element in the human body. It is necessary to build healthy bones and teeth. Calcium influences body coagulation, stimulates muscles and nerves; acts as a cofactor for vitamin D and the function of the parathyroid gland. Muscles cannot contract without calcium. Calcium is essential for the regulation of heartbeat, maintains blood pressure and helps control the electrical impulses to the brain [32].

The highest concentration of Ca is found in Millet ranging its value from 5669.8 ± 138.7 to 6939.9 ± 154.9 ppm while

Table 2: Concentrations of elements obtained from NIST (SRM 1515) Apple leaves and Tobacco leaves (CTA-OTL-1) with our experimental set-up

	NIST(SRM 1515)		(CTA-OTL-1)	
Elements	Certified value	Present work	Certified value	Present work
Ca	15260.00	15581.52	*3.17±0.12**	*3.038**
K	16100.00	15878.04	*1.56±0.05**	*1.36 **
S	18000.00	18780.*64*	*0.732±0.081**	*0.684**
P	15900.00	15278.01	2892±134	4723.83
Zn	12.5	14.5	49.9±2.4	46.69
Cu	5.64	7.08	14.1±0.5	12.57
Ni	0.91	0.73	6.32±0.65	6.68
Fe	83.00	71.70	989	1000.34
Mn	54.00	47.98	412±14	421.12
Cr	0.30	1.15	2.59±0.32	2.13
Ba	49.00	67.97	84.2±11.5	82.26
Sr	25.00	29.29	201±20	205.27
Rb	10.20	9.85	9.79±1.27	10.61
Br	1.80	4.26	9.28±1.06	11.78
Se	0.05	0.11	0.153±0.018	0.11

Italic in(%), normal text(ppm)

it is lower in Sorghum (1415.6 ± 69.4-1616.2 ± 21.8 ppm) and Wheat (1457.5 ± 8.6-1543.2 ± 40.7 ppm) relative to all other samples of the present study. The obtained values of Calcium concentration in Maize is (1009.73 to 1782.1 ± 28.5). On the other hand an intermediate range of Ca Concentration value is observed in barley ranging from 1634.5 ± 44.5 to 1744.2 ± 6.1 ppm as shown in the table 3, this result is found to be higher than the earlier reported results [13] and [21]. Higher concentration of Ca has been observed in Millet and Barley belongs to Addis Ababa relative to other regions while higher Ca is observed in Maize, Sorghum and Wheat of other regions relative to Addis Ababa. The observed discrepancy in the value of Ca concentration may be due change in the soil fertility, water used for the crop and climatic too. As the present samples have higher Calcium, these may be more useful for elderly people particularly menopause stage reached women to take barley in the diet as they need calcium. This indicates that Millet can be used widely to develop Calcium rich food items and medicines.

3.2 Potassium: Potassium (K) is extremely important to cells, and without it one could not survive. Potassium exists primarily in intracellular fluids (the fluid inside cells). Potassium stimulates nerve impulses; muscle contractions and is important for the maintenance of osmotic pressure. Potassium regulates the body's acid-alkali balance, stimulates kidney and adrenal functioning and assists in converting glucose to glycogen. Potassium is also important for biosynthesis of protein. Potassium is the third most abundant mineral in the human body [32].

The highest content of K is found in Maize sample with the range of 2311.3 ± 1634.9 to 4222.5 ± 128.6 ppm, the present value has agreement with the earlier reported result [20] and [22] while it is the lowest (821.0 ± 173.7 ppm) in wheat when compared with other cereals. In barley Ca was found in the range of 1226.4 ± 145.6 to 2359.8 ± 102.4, which has fair agreement with the earlier reported data [13]. The recommended average intake of K is 2300 mg/day for adult women and 3100 mg/day for adult men. The Institute of Medicine has not set a tolerable upper intake (UL) for this mineral, but taking large amount of potassium supplements can cause hyperkalemia due to higher quantity of potassium presence in the blood leading to health hazard. The concentration of K in Millet and Sorghum of Addis Ababa is found to be lower than S/Robit region. The result of the present study indicates that the selected Ethiopian cereal crops are found to be rich in potassium. Consequently, diseases like heart stroke, diabetes and hypertension caused by lack of potassium in human body are rare in this country.

3.3 Phosphorus: Phosphorus (P) is needed to be taken through the food items as it is a critical constituent of all living organisms. Dairy foods, byproducts related to cereals, meat, and fish have rich sources of phosphorus. The phosphorus in plant seeds (beans, peas, cereals, and nuts) is present in a storage form of phosphate called phytic acid or phytate. Only about 50% of the phosphorus from phytate is available to humans because we lack enzymes (phytases) that liberate phosphorus from phytate. Phosphorus is an important constituent of human bones and thus, one cannot imagine about movement of human beings without the adequate amount of this mineral in the body [32]. Apart from providing strength to bones and teeth, other health benefits of phosphorus is important in helping our body perform essential activities for different body parts like brain, kidney, heart and blood.

Among the selected cereal crops the highest concentration of Phosphorus (P) (11973.8 ± 321.2 ppm) is detected in Barley (B102) followed by Wheat (8861.3 ± 1759.5 - 9025.6 ± 4366.1 ppm) of Addis Ababa while it has lowest concentration (315.35 ppm) in sorghum (S405).

No Phosphorus (P) is observed in maize. Though Phosphorus (P) in Sorghum of Addis Ababa with a concentration of 4997.8 ± 892.2 is observed, it is a strange / significant to have no P in the Sorghum samples those collected from other regions. Thus detailed investigation on elemental analysis of soil and irrigated water of Addis Ababa need to be performed to understand causes for presence and absence of P in Sorghum of the present samples. The recommended quantity of Phosphorus (P) is 700 milligrams per day, and the tolerable upper intake level (UL) is 4,000 milligrams per day for adults and if the age is above 70 years, 3,000 milligrams per day is sufficient. In the present study the result are found to be higher than the recommended daily allowance (RDA) and upper intake limit (UL) that proposed by food and nutrition board for barley and wheat samples. These grains can be used as a staple food source for phosphorous. These are also useful for the primary prevention of osteoporosis.

3.4 Zinc: Zinc (Zn) is a very important trace element that essential for many biological factors, which involves over 100 different reactions in the body. Some of these reactions support bodies to construct and Maintain DNA. Zinc is considered as required trace element for growth, repairing tissue, immune system functions and for sexual development [32].

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Zn content in Barley is found to be in the range of 41.5 ± 1.0 -74.3 ± 3.4 as shown in the table 4. The obtained result has consistent and close agreement with the earlier reported data by [11] and [13]. In maize it is found to be in between 26.9 ± 19.0 and 47.8 ± 1.4 ppm exhibiting well agreement with the earlier reported work [22] and [23]. In millet Zn is found to be in the range of 25.6 ± 1.8 to 37.8 ± 1.6 ppm. These results have good agreement with earlier published results [8] and also has disagreement with data reported [9] and [10], this difference might be due to change in the variety, growing area, type of soil, climate, used fertilizer and agricultural practice. Similarly in Sorghum and Wheat we have obtained (20.5 ± 1.4-34.2 ± 0.3 ppm) and (23.1 ± 2.7 - 32.3 ± 2.7 ppm) respectively, which shows good agreement with the results reported earlier [16]. The total accumulation of Zinc is in the order of
barley > maize > millet> wheat > sorghum. The concentration of Zn in all cereal crops is lower than the permissible level (99.4 ppm) set by FAO/WHO (2001) [7]. The RDAs of Zn per day are 4 mg for children of about the age 4–8 years, 8 mg for children of about 9–13 years, 11 mg for male children of about 14–18 years, 11 mg for male adults of about 19–71+ years, 9 mg for female children of about 14–18 years, and 8 mg for female adults of about 19–71+ years of age [30]. It is observed that there is a direct association between Zinc deficiency and cancer [31]. Zinc has played protective role against carcinogenesis and the presence of considerable amounts of Zinc in all these cereal samples can be used for the treatment of cancer.

3.5 Copper: Copper (Cu) is critically important for several functions of body. The health benefits of Copper include proper growth, utilization of iron, enzymatic reactions, connective tissues, hair, eyes, ageing and energy production. Apart from these, heart rhythm, thyroid glands, arthritis, wound healing. RBC formation and cholesterol are other health benefits of copper [32]. As can be seen from Table 4, the level of copper(Cu) ranges from 8.7±3.9 to 14.1±0.2 in barley, 3.3±2.4 to 5.2±1.2 ppm in maize, this result is in good agreement with the result reported by [18, 20] and does not agree with [22].

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Table 3: Concentration of Major elements (*Mean* ± *S D*, *n* = 3, ppm dry weight) in Cereal grain samples collected from Addis Ababa (A.A), Gechi and Shewa Robit.

Cereal	Place	Sample code	Ca	K	P
Barley	A.A 1	B100	1744.2±6.1	2359.8±102.4	8053.3±209.8
	A.A 2	B102	1673.4±54.0	1708.0±391.9	11973.8±321.2
	Gechi	B104	1716.4±62.3	1905.3±214.1	3468.6±417.3
	S/Robit	B106	1634.5±44.5	1226.4±145.6	8718±464.2
Maize	A.A	MZ201	1009.73	2311.3±1634.9	ND
	Gechi1	MZ203	1539.2±374.4	3624.2±28.6	ND
	Gechi2	MZ205	1782.1±28.5	3615.1±55.3	ND
	S/Robit	MZ207	1574.4±397.4	4222.5±128.6	ND
Millet	A.A	MT301	6939.9±154.9	1176.5±129.5	2241.5±1129.0
	Gechi	MT303	6092.0±256.0	956.9±152.1	2534.4±1242.3
	S/Robit	MT307	5669.8±138.7	3086.3±169.8	1066.6±943.9
Sor-ghum	A.A	S401	1515.0±10.8	1144.0±60.3	4997.8±892.2
	Gechi1	S403	1609.7±16.8	1676.7±110.0	ND
	Gechi2	S405	1502.7± 17.7	1176.8±121.0	315.35
	S/Robi1	S407	1616.2±21.8	2454.7±109.0	ND
	S/Robi2	S409	1415.6±69.4	1183.0±512.5	ND
Wheat	A.A	W601	1457.5±8.6	ND	8861.3±1759.5
	Gechi	W603	1543.2±40.7	821.0±173.7	9025.6±4366.1
Minimum			1009.73	821.0±173.7	315.35
Maximum			6939.9±154.9	4222.5±128.6	11973.8±321.2

ND: Not detected

The content of Cu in millet is found in the range of 5.5 ± 0.9 to 12.2 ± 0.8 ppm and (3.8 ± 1.2) to (6.6 ± 2.4 ppm) in sorghum. The level of copper in wheat is found to be in between (3.7 ± 0.5 ppm) to (5.5 ± 0.4 ppm), this result has good agreement with the earlier reported work [16].

In the present studies, from over all cereal samples the obtained maximum concentration (14.1±0.2 ppm) of copper is in barley while it is lowest (3.3±2.4 ppm) in maize. The result obtained in the present study is lower than the required maximum limit/ content of Cu in food (73.3 ppm) items that set by FAO/WHO [7]. Adequate intake (AI) levels for copper have been recognized for infants i.e. 0 to 6 months of age and for those between 7 to 12 months of age as 200 and 220μg/day respectively. The RDAs for 1–3 years, 4–8 years, 9–13 years, 14–18 years, and 19–50+ years of age are 340, 440, 700, 890, 900, and 900 mg/day, respectively. The RDAs during pregnancy (14 through 18 years and 19 through 50 years) and lactation (14 through 18 years and 19 through 50 years) are 1000 and 1300 μg/day respectively [28]. Although copper is indispensable to the good health but excessive consumption may result in serious health problems like kidney and liver damage [29]. Because of these possible adverse consequences from high copper ingestion, an endurable upper intake level (UL) of 10 mg/day has been established for adults who are older than 19 years of age. The levels of copper, obtained in the present study carried out in five cereal samples are lower than UL; therefore these cereals crops are very important for proper growth.

3.6 Nickel: Nickel (Ni) helps to provide optimal growth, healthy skin, strengthens the bone structure, and enhances the absorption of Zinc. Nickel is well known as an activator of a number of enzymes like alkaline phosphatase, oxaloacetate, decarboxylase, etc. Nickel deficiency causes depressed growth rate and dermatitis [32]. The highest content of Nickel (8.9 ± 1.3 ppm) is detected in sorghum (S407) while it is lowest (1.0 ± 0.4 ppm) in maize (MZ201) and wheat (W601). The result is found to be lower than the maximum limit (67 ppm) set by FAO/WHO [7]. Therefore taking the grains that are undertaken for the present study may be advantageous for the activation of these enzymes.

Table 4: Concentration of Minor and trace elements (Mean ± *S D*, *n* = 3, ppm dry weight) in Cereal grain samples collected from Addis Ababa (A.A), Gechi and Shewa Robit.

Cereal	Place	Zn	Cu	Ni	Co	Fe	Mn
Barley	A.A 1	44.2±3.6	8.9±1.1	1.2±0.3	0.47	89.8±5.0	13.8±1.4
	A.A 2	41.5±1.0	8.7±3.9	1.9±0.9	0.4±0.1	51.5±2.2	8.4±1.6
	Gechi	74.3±3.4	14.1±0.2	1.2±0.6	0.16	201.3±5.3	19.5±3.0
	S/Robit	54.6±2.6	10.0±1.8	1.5±0.8	0.4±0.1	56.0±3.1	11.8±0.5
Maize	A.A	26.9±19.0	3.3±2.4	1.0±0.4	0.4±0.2	27.3±19.3	ND
	Gechi1	39.9±3.4	4.9±0.4	2.3±0.3	0.4±0.04	102.3±2.7	ND
	Gechi2	47.8±1.4	5.2±1.2	4.3±0.9	0.3±0.2	97.6±4.4	ND
	S/Robit	42.4±2.5	5.1±0.8	2.5±1.8	0.47	81.2±2.2	ND
Millet	A.A	25.6±1.8	5.5±0.9	2.4±1.0	0.46±0.02	233.9±9.0	771.6±15
	Gechi	28.4±1.8	8.5±1.7	2.4±0.8	0.16	52.1±0.6	330.8±2.1
	S/Robit	37.8±1.6	12.2±0.8	1.3±0.8	0.4±0.1	91.2±1.5	774.4±11.2
Sorghum	A.A	20.5±1.4	5.2±0.2	2.0±0.6	0.45	35.4±3.3	8.1±0.4
	Gechi1	24.8±0.9	6.6±2.4	3.1±0.5	0.4±0.1	45.2±0.5	5.8±2.0
	Gechi2	25.6±2.5	6.4±1.2	2.3±0.7	0.16	61.0±2.5	12.7±1.1
	S/Robit1	23.1±3.2	3.8±1.2	8.9±1.3	0.4±0.1	74.5±3.2	17.5±2.5
	S/Robit2	34.2±0.3	4.5±1.9	2.8±1.6	0.3±0.2	135.5±15.7	5.2±0.4
Wheat	A.A	23.1±2.7	3.7±0.5	1.0±0.4	0.467	17.5±5.2	12.4±1.2
	Gechi	32.3±2.7	5.5±0.4	2.7±1.4	0.3±0.2	45.2±3.5	26.0±1.5
Minimum		20.5±1.4	3.3±2.4	1.0±0.4	0.16	17.5±5.2	5.8±2.0
Maximum		74.3±3.4	14.1±0.2	8.9±1.3	0.47	233.9±9.0	774.4±11.2

ND: Not detected

3.7 Cobalt: Cobalt (Co) is another required element for good health. It Forms the core of Vitamin B-12. Without Cobalt, Vitamin B-12 could not exist. Additionally, Vitamin B-12 prevents nerve damage by contributing to the formulation of the protective sheath that insulates nerve cells. An excess intake of cobalt may cause the overproduction of red blood cells (Kalagbor et al., 2014).

As can be seen from table 4, the concentration of Co is found to be in low amount in the selected cereal crops. It ranges from 0.16 to 0.47 ppm in a very narrow range. RDA per day of Co is 1-2 mg for a normal male adult of 22 years of age that established by the Food and Nutrition Board (FNB), National Research Council, 1968.Deficiency of Vitamin B-12 can cause to form red blood cells improperly. Consequently this prevents red blood cells to carry out enough oxygen from lungs to the different parts of bodies of human beings, thus causing a condition called anemia, which is frequently observed in Ethiopia. The present study indicates that Ethiopian cereal crops are poor in cobalt leading to get diseases namely hypothyroidism, goiter, and heart failure in humans due to cobalt deficiency.

3.8 Iron: Certain chemicals in human beings brain are controlled by the presence of Iron (Fe). It is necessary for cell function and blood utilization. The health benefits of Iron mainly include carrying life and giving oxygen to human blood cells. About two-thirds of the bodily iron is found in hemoglobin. It is children and women of the reproductive age who most often suffer iron deficiency. In children, iron deficiency can be caused by improper nutrition and fast growth of the organism. In women, iron deficiency arises from constant loss of blood in the course of menstruation. Iron deficiency is particularly dangerous during pregnancy. Anemia arising from iron deficiency can cause death of the fetus due to shortage of oxygen. Various diseases of the digestive tract (chronic gastritis, enteritis) can also contribute to development of iron deficiency. Excess of iron in the organism is also harmful; it can cause siderosis of lungs and eyes, a disease that arises due to deposition of excess iron compounds in the tissues of those organs. The necessary intake of iron is 10 to 30 mg per day [32]. A dose of 200 mg per day produces a toxic effect.The permissible limit of Fe as set by FAO/WHO (2001) is 425.5 ppm [7].
Iron concentration in five of the selected cereal crops is tabulated in Table 4. The highest content of Fe (233.9 ± 9.0 ppm) is observed in millet, which found to be lower than the earlier data reported [8] while lowest content of Fe is found to be in wheat (17.5 ± 5.2 ppm). RDAs for iron are of 10 mg/day for children of 4–8 years, 11 mg/day for males of 14–18 years, 15 mg/day for females of 14–18 years, 8 mg/day for 19–50 years of male adults, 18 mg/day for 19–50 years of female adults, and 8 mg/day for >50 years of male/female adults [30].
In the present study the concentration of Fe was found to be lower than the permissible limit.

3.9 Manganese: Manganese (Mn) is an essential element for glucose utilization, for lipid synthesis and for its metabolism. Manganese is involved in the normal skeletal growth and also it activates enzyme functions. Health benefits of Mn ensure healthy bone structure, bone metabolism besides its support for building essential enzymes for building bones. It acts as a coenzyme to assist metabolic progression in the human body. Manganese exists in a number of oxidation states, of which Mn (II) is the predominant form in biological systems [32]. Food is the most important source of manganese exposure for the general population. The concentration of Mn in foodstuffs varies considerably, but is mostly below 5 mg/kg. Grain, rice, and nuts, however, may have manganese levels exceeding 10 mg/kg or even 30 mg/kg in some cases. This trace element is connected with synthesis of proteins and nucleic acids also. A certain interrelation is assumed between manganese deficiency and development of lupus erythematosus; these patients condition can be improved by the addition of manganese shorter children consumed on average 40% of manganese less than taller children. Therefore, children need to be feed with millet based diet, which will help to grow fast. Manganese rich food is useful to prevent diseases like diabetes mellitus.
According to the scientific findings, the rate of growth in children largely depends on the manganese consumption. It is established that the highest concentration of Mn is observed in millet (330.8 ± 2.1-774.4 ± 11.2 ppm) compared to others cereals. This value is found to be higher than the earlier result reported by [8]. The lowest content of Mn (5.2 ± 0.4 ppm) in the present work is detected in Sorghum. On the other hand Mn is not detected in maize samples collected from all the selected locations. The concentration of Mn in some samples in the present work is found to be higher than the permissible limit that set by FAO/WHO (2001) [7]. The minimum daily manganese demand of adults is approximately 2 to 3 mg, and the necessary intake is 2 to 9 mg per day.
3.10 Chromium: Chromium (Cr) is a vital component of a molecule that works with insulin to stabilize blood sugar levels. In other words, it helps our bodies absorb energy from the food that people eat and stabilizes the levels of energy, which required feeling throughout the day [32]. Our bodies need sufficient quantities of chromium to make many of the large biological molecules that help us live. The maximum concentration of Chromium (3.6 ± 0.3 ppm) is found in Barley (B102) while the minimum content (0.7 ± 0.2 ppm) is detected in Millet (MT301) as shown in table 5. The present result is found to be higher than the results reported earlier [10, 11, 13, 19, 20, 24] as well as the permissible level of Cr (2.3 ppm) as set by FAO/WHO (2001) [7] for most of the samples except MT303, MT307, S401, S403, S405 and W601. The observed variation may be due to change of cereals variety, growing area, type of soil, climate, used fertilizer, water and agricultural practice.

International Journal of Scientific & Engineering Research, Volume 8, Issue 3, March -2017

3.11 Arsenic: Arsenic (As) and all its compounds are poisonous. The signs of acute toxic exposure to arsenic are vomiting, abdominal pain, diarrhea, and central nervous system depression. Arsenic is a toxic element and is thought of as being carcinogenic for man. It can replace phosphorus in some biological processes. Arsenic promotes chronic anemia and allegories. However, it is established that arsenic deficiency leads to a decrease in the birth rate and also growth inhibition in experimental animals. Deficiency of this element can arise from its insufficient consumption (1 µg/day and less). The arsenic content of the human body is estimated at approximately 18 mg. Chronic intoxication is observed at the intake of 1 to 5 mg per day. In acute poisoning, the symptoms usually arise in 20 to 30 min. FAO and WHO have established the safe weekly dose of 5 µg/kg ofbody mass per day, i.e., 138 µg per day for a person with the mass of 69 kg. The necessary arsenic intake is not scientifically established. The toxic dose is 10 to 50 mg per day [32]. Arsenic (As) is found in a very low level and almost same in all the studied cereal samples (0.2ppm). The level of Arsenic from the cereals in the study area is lower than the maximum allowable concentration (MAC).

3.12 Lead: Lead (Pb) is one of the abundant toxic elements. Chronic poisoning arises due to intake of even a small quantity of lead with food and drinking water for a long time. The signs of chronic poisoning are general weakness, skin pallor, and abdominal pain, “lead line” along the margin of the gums, anemia, and kidney dysfunction. Reduced mental capacity, aggressive behavior, and other symptoms are also observed. It is established that chronic intoxication arises from the intake of 1 to 8 mg of lead per day [32]. The Joint FAO/WHO Expert Committee on Food Additives and Contaminants (JECFA) has established the tolerable daily lead intake for a human to be 3 mg. The highest concentration of lead (2.23 ± 0.3 ppm) is found in Barley (B106), on the other hand lowest is detected (0.39 ppm) in sorghum (S409). This result is found to be lower than the tolerable daily intake; therefore the population from the study area may not be exposed to higher levels of toxic elements like lead due to consumption of cereals.

3.13 Strontium: Strontium (Sr) is found to be involved in the utilization of calcium in the body. Moderate dietary levels of strontium helps for absorption or uptake of calcium into bones; but the rachitogenic action takes place at higher dietary levels [32]. The highest concentration of Strontium (32.1 ± 1.1 ppm) is found in millet (MT307) while lowest (6.5 ± 0.1 ppm) is observed in maize (Mz207).

3.14 Rubidium: Rubidium (Rb) has a close physiochemical relationship with potassium and may have the ability to act as a nutritional substitute for it. Although rubidium is not considered as an essential element, some evidence suggests that rubidium may have a role in free radical pathology and serve as a mineral transporter across defective cell membranes, especially in cells associated with aging [32]. The highest concentration of Rb (14.2 ± 2.2 ppm) is observed in sorghum (S407) while lowest (0.5 ppm) is detected in sorghum (S405). Compared to the result reported by earlier studies [15]; (19 ± 7− 96 ± 11), the value of Rb concentration in the present study is found to be much lower. This difference might be due to change in the variety of sorghum, growing area, type of soil, climate, used fertilizer and agricultural practice.

3.15 Bromine: The highest concentration of bromine (Br= 40.9±1.2 ppm) is observed in barley (B100), but the lowest (1.8±0.9 ppm) is detected in sorghum (S405). Bromine is not studied much in respect of its role in living organisms. It is known that Br is a constant component of normal gastric juice, determining together with C1 its acidity.

Bromine compounds suppress the thyroid gland function and enhance hormonal activity of the adrenal cortex. In medicine, they began using bromine to treat insomnia and neurasthenia as far back as ten years after its discovery. Bromine is especially helpful for restoring the excitation–inhibition balance in the brain because concentrates and accumulates in the brain, which aids in “self-regulation”of interrelated processes.

Table 5: Concentration of Minor and trace elements (Mean ± *S D*, *n* = 3, ppm dry weight) in Cereal grain samples collected from Addis Ababa (A.A), Gechi and Shewa Robit (S/Robit)

Cereal	Place	Cr	As	Pb	Sr	Rb	Br
Barley	A.A 1	2.4±0.4	0.086	0.84	8.9±2.5	9.4±0.7	40.9±1.2
	A.A 2	3.6±0.3	0.18	1.67	9.3±0.2	10.9±1.2	21.9±0.5
	Gechi	3.0±0.5	0.17	1.61	7.1±0.6	9.6±0.5	18.7±0.7
	S/Robit	2.4±0.3	0.2±0.0	2.23±0.3	8.7±0.4	1.20.9	9.9±0.9
Maize	A.A	2.2±1.2	0.2±0.02	1.71	6.9±0.6	0.82	6.9±4.1
	Gechi1	2.8±0.5	0.2±0.02	0.9±0.7	6.9±0.5	5.3±0.8	10.7±0.3
	Gechi2	3.0±0.3	0.2±0.02	0.9±0.7	7.2±0.9	8.8±0.8	9.9±0.7
	S/Robit	2.7±0.2	0.2±0.03	1.26	6.5±0.1	5.1±1.5	10.3±1.4
Millet	A.A	2.5±0.3	0.2±0.03	1.31	22.5±0.2	7.7±1.3	10.4±1.3
	Gechi	1.3±0.6	0.2±0.03	1.6±1.1	27.3±1.5	7.6±1.5	9.3±0.9
	S/Robit	0.7±0.2	0.2±0.03	1.8±0.7	32.1±1.1	6.8±0.6	19.1±1.2
Sor-ghum	A.A	2.1	0.2±0.03	0.7	8.2±0.3	4.4±0.6	2.2±0.5
	Gechi1	2.0±0.4	0.2±0.04	2.5±1.8	8.3±0.7	4.5±0.3	2.5±0.4
	Gechi2	2.1±0.9	0.2±0.04	0.94	7.4±0.9	0.5	1.8±0.9
	S/Robi1	2.6±0.2	0.2±0.04	1.3±1.0	7.4±1.0	14.2±2.2	3.3±0.8
	S/Robi2	2.4±0.5	0.1±0.04	0.39	7.9±0.9	2.4±0.8	18.1±2.2
Wheat	A.A	2.2±0.2	0.2±0.04	1.02	8.2±1.8	1.0±0.7	4.2±0.5
	Gechi	2.5±0.2	0.2±0.05	0.52	7.6±0.8	1.6±0.2	5.2±0.8
Minimum		0.7±0.2	0.086	0.39	6.5±0.1	0.5	1.8±0.9
Maximum		3.6±0.3	0.2±0.05	2.23±0.3	32.1±1.1	14.2±2.2	40.9±1.2

The action of bromine on the central nervous system is associated with its ability to accumulate in the lipid part of brain cells, thus activating membrane enzymes. Being a competitor of iodine, bromine regulates the work of the thyroid thyroid gland and thus inhibits the increase in the iodine level in the thyroid gland, which aids in preventing goiter. The bromine content of the human body is 260 mg. The necessary intake value has not been determined so far. The toxic effect occurs at a dose of 3 gm per day [32]. The Present study indicates that barley is a good source of bromine.

Correlation Coefficient for all the observed major and minor elements has been evaluated and are presented in the tables 6, 7 and 8 for Addis Ababa, Gechi and Shewa Robit respectively. Correlations might indicate a common uptake mechanism, or a common source, and a lack of metabolic regulation.

For cereals those collected from Addis Ababa, the highest positive and significant correlation has been determined between the content of Ca and Fe (r=0.967), Ca-Mn (r=0.994), Ca-Ni (r=0.707), Ca-Cr (r=0.702). Calcium concentrations have a meaningful relation with only Fe, Mn, Ni and Cr, changing the concentration of Ca also depends on the concentration of these elements. Increasing the uptake of ca will enhance the content of chromium which plays a role in insulin signal amplification, activates insulin receptor kinase activity and prevent diseases characterized by insufficient production of insulin such as diabetes mellitus.

The content of Potassium is in positive correlation with Zn (r=0.618), these elements are important nutrient for

International Journal of Scientific & Engineering Research, Volume 8, Issue 3, March -2017

growth, increasing the content of k enhance Zn level, but taking large amount of these elements may leads for varies health related problems.

The content of P is in moderate positive correlation with Zn (r=0.550) and positive and significant correlation with Cu (r=0.640). Due to the positive correlation they have, using phosphorous fertilizer may increase the content of P as well as Cu. The concentration of Zn showed strong positive and significant relation with the content of Cu (r= 0.882). The highest positive and significant correlation is observed between Fe-Mn (r=0.952), Fe-Cr (r=0.779) as shown in the table 6. Manganese toxicity is usually caused by chronic exposure of workers in iron and steel factories; this indicates higher intake of Fe increases the level of Mn.

Table 6: Correlation of major, minor and trace elements for cereal samples collected from A.A

Properties	Ca	K	P	Zn	Cu	Ni	Co	Fe	Mn	Cr
Ca	1	-0.159	-0.324	-0.164	0.018	0.707*	0.322	0.967**	0.994**	0.702*
K		1	-0.232	0.618*	0.443	-0.104	0.451	0.050	-0.157	0.095
P			1	0.550	0.640*	-0.041	0.075	-0.300	-0.405	-0.437
Zn				1	0.882**	-0.118	-0.172	0.039	-0.225	0.011
Cu					1	0.267	0.019	0.196	-0.070	-0.003
Ni						1	0.040	0.666*	0.673*	0.114
Co							1	0.339	0.294	0.617
Fe								1	0.952**	0.779*
Mn									1	0.705*
Cr										1

*,** Level of significance p<0.05, p<0.01

Table 7: Correlation of major, minor and trace elements for cereal samples collected from Gechi

Properties	Ca	K	P	Zn	Cu	Ni	Co	Fe	Mn	Cr
Ca	1	-0.347	0.035	-0.225	0.184	-0.08	-0.442	-0.237	0.993**	-0.738*
K		1	-0.563	0.372	-0.264	0.381	0.508	0.379	-0.434	0.663*
P			1	0.087	0.153	-0.253	-0.184	-0.060	0.115	0.025
Zn				1	0.706*	-0.364	-0.251	0.968**	-0.253	0.718*
Cu					1	-0.705	-0.614*	0.742*	0.196	0.075
Ni						1	0.467	-0.495	-0.141	0.051
Co							1	-0.279	-0.474	0.264
Fe								1	-0.263	0.665*
Mn									1	-0.768*
Cr										1

*,** Level of significance p<0.05, p<0.01

Table 8: Correlation of major, minor and trace elements for cereal samples collected from Shewa Robit.

Prop-erties	Ca	K	P	Zn	Cu	Ni	Co	Fe	Mn	Cr
Ca	1	0.294	-0.107	-0.018	0.771*	-0.363	0.089	0.020	0.999**	0.983**
K		1	-0.501	-0.132	-0.029	0.010	0.800*	-0.203	0.274	-0.133
P			1	0.800*	0.535	-0.393	0.063	-0.603	-0.130	0.042
Zn				1	0.564	-0.793*	0.250	-0.395	-0.040	-0.021
Cu					1	-0.66	0.132	-0.319	0.759*	-0.800*
Ni						1	-0.005	-0.112	-0.360	0.424
Co							1	-0.727*	0.052	0.068
Fe								1	0.058	-0.107
Mn									1	-0.988**
Cr										1

*,**Level of significance p<0.05, p<0.01

Table 8 shows that the linear correlation of major, minor and trace elements of cereal samples those collected from Shewa Robit, the highest positive and significant correlation is determined between content of Ca-Mn (r=0.999) at level of significance 0.01 and Ca content is in positive correlation with Cu (r=0.771). Positive correlation is obtained between Ca content and Cr(r=0.983), they do not block the action of one on the other. . Phosphorous is found to have a positive correlation with Zn (r=0.800) and a moderate positive and significant correlation with Cu (r=0.535), on the other hand negative correlation is obtained between P and Fe (r=0.603). Changing the concentration of P also depends on the concentration of Zn, Cu and Fe. Zn has a positive correlation with Cu(r=0.564) and negative correlation with Ni(r=0.793). The content of Cu shows positive correlation with the concentration of Mn (r=0.759) where as it is showing negative correlation with Ni content (r=0.66) and Cr(r=0.800). Positive correlation and negative correlation have been obtained for Fe content in association with Co(r=0.727). The correlation of Mn and Cr (r=0.988) pair shows negative having the significant level of 0.01.

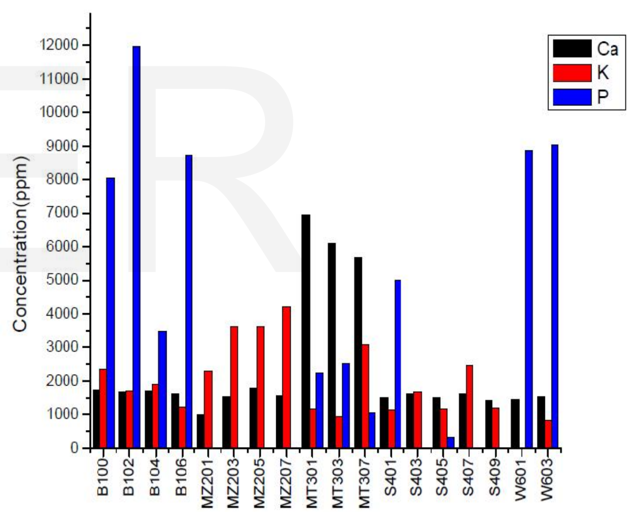

Fig 1: concentration of major element in Barley, Maize, Millet, Sorghum and Wheat collected from Addis Ababa (A.A), Shewa Robit and Gechi

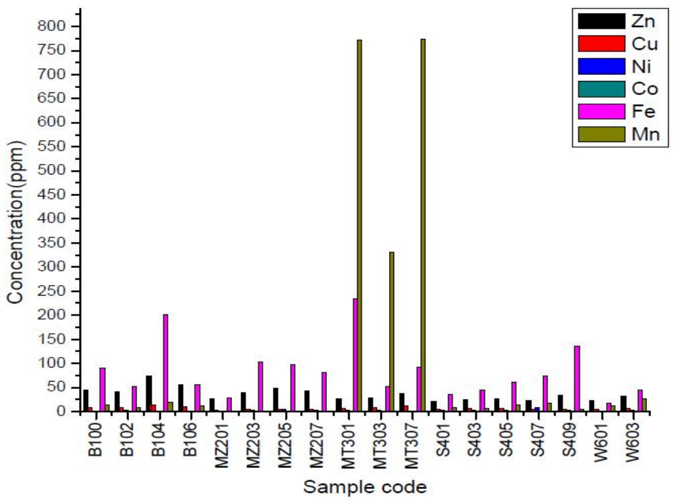

Fig 2: concentration of minor and trace elements in Barley, Maize, Millet, Sorghum and Wheat collected from Addis Ababa(A.A), Shewa Robit and Gechi

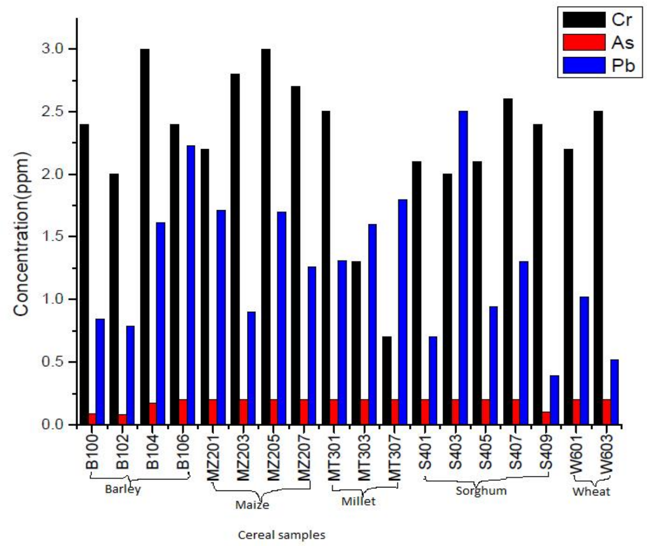

Fig 3: Concentration of heavy metals Cr, AS and Pb in Barley, Maize, Millet, Sorghum and Wheat collected from Addis Ababa (A.A), Shewa Robit and Gechi

4 Conclusion

The determination of the concentrations of major, minor and trace elements in Cereal grains has provided a very valuable and comprehensive baseline information and data on the pollution status of the study area. The present investigations revealed that the cereals are one of the good sources of essential elements. The mean values of the elements that present in the samples those purchased in Addis Ababa (ehil berenda) markets and the sample that collected directly from gechi and shewa robit agricultural locations are found to have no much significant deviation. The concentration of 15 elements (Ca, K, P, Zn, Cu, Ni, Co, Fe, Mn, Cr, As, Pb, Sr, Rb, and Br) were analyzed in five selected cereal crops. After the analysis, the selected cereals were found to have heavy metals namely Copper (Cu), Zinc (Zn), Iron (Fe), Arsenic (As) and Lead (Pb) in each of the samples. Cadmium (Cd) was not present in all the analyzed cereals. However, the concentrations of these metals in the cereals analyzed were below the safe limit set by FAO/WHO (2001) [7]. Therefore, these cereal samples should be considered as safe for consumption and also may serve as sources of trace elements to the people. The obtained data allows for understanding the grains which are poor or rich in essential elements. This is an important feature to choose foods for a balanced diet. Results showed that cereals grown in the selected areas of the present study are not contaminated and the levels of toxic elements are also very low. Significantly, daily intake of food items related to the Ethiopian cereals revealed that consumption of them does not reach to the risk of health. Daily intake of toxic elements due to consumption of the cereals that collected from the studied areas were less than the permissible limit of these elements, thus no risk was detected from the present study. We concluded that population from the study areas may not expose to higher levels of toxic elements, however, more studies need to be performed for assessment of total daily intake of toxic elements due to consumption of different types of food items to have complete sight of Ethiopia situation, and also to estimate the risk of these elements amongst Ethiopian population. This data can serve as a guideline for researchers and environmental managers to identify future anthropogenic impacts at the studied areas with respect to the measured elements. Better assessment needed for remediation of bio-accumulation by monitoring the changes in the concentration of the elements from the existing levels.

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