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Variable Uptake and Accumulation of Essential and Heavy Metals in Maize (*Zea mays* L.) Grains of Six Maize Varieties

[1]Ghulam Qadir Shar, [2]Tasneem Gul Kazi, [3]Farman Ali Shah, [4]Abdul Hussain Shar, [2]Fateh M. Soomro

[1]Department of Chemistry, Shah Abdul Latif University, Khairpur (Sindh), Pakistan.
[2]Centre of Excellence in Analytical Chemistry, University of Sindh Jamshoro, 76080, Pakistan.
[3]Department of Chemical Engineering, Mehran University, Jamshoro, Sindh, 76080, Pakistan.
[4]Department of Microbiology, Shah Abdul Latif University, Khairpur (Sindh), Pakistan.

Abstract: Six maize varieties and their soil were analysed for their variable absorption and accumulation of metals in different maize varieties on the basis of their genetic character in the same agricultural land by using atomic absorption spectrometry. Results of the current research showed that the dominants concentration of Na, Ca, and Fe Agaiti-2; Zinc in Golden; K, Mg, Mn and Cu in Sultan among all varieties. The comparative study of eight investigated elements indicate their values in range: K (2687.4-3492.6); Mg (524.96-725.76); Na (230.11-404.07); Zn (16.26-31.16); Fe (6.27-10.73; Mn (3.59-9.33); Ca (3.74-4.13); Cu (1.09-1.97) mg/kg respectively in descending order. The level of K, Zn, Fe were within permissible limit where as Mg, Mn slightly higher; Na, Ca and Cu slightly lower than that of permissible limit given by WHO. Wet digestion method was used during the preparation of samples.

Key words: Maize, Metals, Atomic Absorption Spectrophotometer

INTRODUCTION

Maize (*Zea mays* L.) is one of important crop all over the world and is attracted to all ages of the human. It is only kind of food commodity, which is used for eating in the form of grains with or without heating as well as in bread and bakeries by making countless products. The levels of trace elements are being monitored on a continuous basis by many countries of the world to keep a check on their natural food supply. Surveys by WHO (1980) and FDA (1974-75) have shown that essential and trace elements are usually present in varying concentrations in foods. For the analysis of elements, the Association of Official Analytical Chemists International (AOAC) methodology was used for determination of metals in food and food products of (AOAC,1990). Different elements play different role in the human body; Calcium, magnesium, and zinc are most important minerals for body requirement to maintain health in best way and the calcium is 1-2% of body weight. The requirement of the calcium is for growth and bone formation, besides this it keeps the heart pumping, muscles moving, and nerves communicating. Magnesium activates more than hundred enzymes, helps nerves and muscles function where as Zinc is essential part of more than two hundreds enzymes involved in digestion, metabolism, and reproduction and wound healing. So, zinc is an essential element needed to support the body's immune system. These three elements may help to reduce the likelihood of kidney stones, reduce high blood pressure and other types of heart problems, reduce premenstrual syndrome (PMS) or menstrual cramps, reduce age-related eye diseases, reduce insomnia, reduce anxieties, chronic constipation, hyperactivity, various bone and periodontal diseases, sleep disturbances, mental health/depressive disorders and some forms of cardiovascular disease(Standing Committee,1997). Minerals are widely distributed in all kind of fruits, vegetables, grains and food commodities and are responsible for their growth and colour changes (Belma *et al* 1978). One of the reviews published in connection of the level of the mineral in different food commodities in which there is challenge for both botanist and chemist jointly to enhance mineral concentration for full fill the requirement of the increased population (Michael *et al* 2002). Use of potassium gives good result that could be explained in terms of the better nutrient acquisition, growth and yield parameters recorded (Endris *et al* 2007).Balance minerals in barley give good fertilization and yield as compared to high doses (Černý *et al* 2010).

Comparative study of 13 metals of different wheat varieties was carried out to check the variation in up

Corresponding Author: Ghulam Qadir Shar, Department of Chemistry, Shah Abdul Latif University, Khairpur (Sindh), Pakistan.

take metals in the same agricultural land (Shar *et al* 2002). The concentration of metals varies variety to variety (Shar *et al*, 2010). Mineral study and composition in cocoa beverages was carried out in Nigeria (Shittu *et al*, 2009). Level of elements of one area cannot match to level other due to geographic variation that effects in plant that of seed grows in soil (Dinusson *et al* 1960). Barley (*Hordeum vulgare* L.) is used mainly for brewing and as animal feed but there is a growing interest in it for human food and industrial uses (Elfverson *et al*, 1999) Essential, trace and toxic elements in barley varieties and its soil of different areas of Pakistan was carried out (Shar *et al*,2007). Elemental analysis by using spectroscopic technique in unpolished rice was studied (Shar, *et al* 2007). Analytical work on different cultivars to check its quality was done (Shar, 2005 and Shar, 2007)

Aims and Objectives:

The purpose of this study was to examine the uptake of essential elements (Na, K, Ca, Mg, Fe, Zn, Mn and Cu) from the soil to seed of various maize varieties, which is commonly used for the human consumption as a food; however soil of the crop was also analyses to check the concentration of these elements present in it.

Experimental:

Procedure:

Representative samples of soil and six varieties of the maize were collected from experimental fields Maize & Millet Research Institute (MMRI) Yusafwala; district Sahiwal (Punjab), Pakistan for the analyses of eight essential metals by using atomic absorption spectrophotometer. The soil was air-dried and seived (<0.5mm) the dried in ovan in the same as maize grains. The experiment was conducted at the above place during normal maize growing season (May, 2001 to August, 2002). Six commercial maize varieties Agaiti-72, Agaiti-75, Akbar, Golden, Sadaf and Sultan were sown and harvested at maturity stage. The grains were separated from their cover, which randomly collected and made the representative samples while as reference samples were obtained from the "Federal Seed Certification and Registration Department of Pakistan".

Six maize varieties and soil samples were dried at 120C^{o} in oven. Five replicate 1g samples of dried soil and 2g of each maize variety were weighed in to 100ml conical flasks and treated with 5ml of nitric acid. 5ml of nitric acid was also added to empty conical flask serving as a blank. The flasks were covered with watch glasses, and their contents were heated to reflux gently on an electric plate. After refluxing for one hour the contents of flasks were treated with 5ml more of nitric, 2ml of 35% hydrogen peroxide was added, and the heating at gentle reflux was continued for another hour. The watch glasses were removed from the flasks, and the heating was continued until the volumes of their contents were reduced to 2-3ml. The contents of flask were cooled, diluted with high purity water, and filtered through whatman # 42 paper in to 25ml volumetric flasks (11). The contents of the flasks were brought to volume with high purity water and examined by atomic absorption spectrometry for determination the concentration of sodium, potassium, calcium, magnesium, iron, zinc, manganese, and copper.

Soil samples:

Composite soil samples (0-15 cm depth) were collected all sites in the maize growing areas. A kg of the soils from each site was taken in the plastic bags. The samples were air dried ground with a wooden pestle in a mortar to a fine powder and stored for analyses of essential and heavy metals. The study on the up take of eight essential macro and micronutrients in maize from the soil and study of the same nutrients was also carried out from the soil.

Instrumentation:

A Hitachi Model 180-50 atomic absorption spectrophotometer was used for the determination of elements such as, sodium, potassium, calcium, magnesium, iron, zinc, manganese, and copper. The hollow-cathode lamps (made by Mtiorika company) of all above elements were operated at lamps current 9.5, 9.5, 7.3, 7.0, 9.5, 9.5, 7.0, and 7.0 mA respectively. The flow-rate for fuel 2.30 1min^{-1} and air 9.40 1min^{-1} was used respectively to obtain a clear yellow flame (reducing condition). The spectrophotometer output was connected to a Hitachi recorder 056 with a range of 5mV. The signals measured were the heights of the absorbance/division peaks. All instrumental parameters are given in table 1.

Table 1: Instrumental conditions for the AAS measurement of Na, K, Ca, Mg, Fe, Zn, Mn, and Cu.

Elements	Wave length (nm)	Slit width (nm)	Lamp current (mA)	Fuel flow (acetylene) (l/min)	Flow rate (Air) (l/min)	Burner height (mm)	Oxidant (Air) kg/cm^2	Fuel (Acetylene) kg/cm^2	Signal out put
Na	590	0.4	9.5	2.21	9.4	7.5	1.60	0.25	100%
K	766.8	2.6	9.5	2.3	0	0	0	0.3	0
Ca	422.2	2.6	7.3	2.6	0	12.5	0	0.4	0
Mg	285.5	2.6	7.0	2.0	0	7.5	0	0.2	0
Fe	248.3	0.2	9.5	2.30	0	0	0	0.3	0
Zn	214.0	1.3	9.5	2.0	0	0	0	0.2	0
Mn	279.8	0.4	0	0	0	0	0	0	0
Cu	325.0	1.3	0	0	0	0	0	0	0

Reagents and Calibration:

The supra pure nitric acid (65% w/v) and hydrogen peroxide (35% w/v) reagents (Merck), high-purity water (electrical resistivity〉10mΩ cm) was produced with a Milli-Q system Millipore, MA, USA).

Calibration was obtained with external standards. The standards solutions were prepared by diluting a 1000mg/l multi element solution (ICP Multi element standard iv, Merck, Darmstadt, FRG) with the same acid mixture used for sample dissolution. Glassware were cleaned by soaking with the contact over night in a 10% (w/v) nitric acid solution and then rinsed with deionized water.

Solutions were aspirated into atomic absorption spectrophotometer and absorbance/divisions measurements were made for each element using optimum instrumental conditions for flame atomization mode. Reference standards were also run in parallel for inter calibration of our own standards. Elemental concentration were computed on an IBM compatible PC using a excel computer program.
The statistical calculations for standards are given in table 2.

Table 2: Statistical data for standards of elements

Elements	Concentration range ppm (x)	Absorbance/ Division (y)	Statistical calculation y = m x + c		
			m	c	r^2
Na	0 - 0.25	0 - 0.084*	0.3344	0.0001	0.9996
K	0 - 1	0 - 0.207*	0.2069	0.0006	0.9999
Ca	0 - 5	0 - 0.256*	0.0508	0.0024	0.9993
Mg	0 - 1	0 - 0.885*	0.8856	0.0017	0.9999
Fe	0-1	0 - 0.096*	0.0976	-0.0016	0.9989
Zn	0 - 0.5	0 - 0.138*	0.2761	-0.0004	0.9999
Mn	0 – 1	0 – 0.196*	0.1962	0.0005	0.999
Cu	0 – 1	0 –0.086*	0.0862	0.0004	0.9989

Absorbance*

div. =Divisions

RESULTS AND DISCUSSION

Table 3 shows the level of eight essential major and minor elements in six varieties of the maize that were collected from Maize & Millet Research Institute (MMRI) Yusafwala, district Sahiwal (Punjab), Pakistan and analyzed by using atomic absorption spectrophotometer. In this regard t-test was conducted for collected and certified sample at 99.5% confidence limit for five replicates in each case.

Five of the elements i.e., Sodium, potassium, calcium and magnesium, among eight are macronutrient elements and possesses higher concentration as compared to four minor elements i.e., iron, zinc, manganese and copper. However, the value of calcium was found lower as compared to the majority of the minor elements, this may be due to their genetic character. Variable data of nutrients shows that the distribution of the essential nutrient elements was not uniform in all varieties of maize in same location. Precision and accuracy of results were checked by running the five replicates and each replicate was run three times. The values of table 3 indicates that maximum concentration of sodium was observed (404.07±27.01) in Agaiti-75 and its minimum concentration (230.11±23.72) mg/kg in Sultan variety. Potassium is one of the most important elements, which can play key role in majority of the biological process, including electrolysis, therefore its high concentration needed to all living organism. Maize is one of the important food commodities that contain large quantity of potassium in all varieties ranges (2687.4 ±131.16 to 3492.6±325.83mg/kg). Magnesium possess second one highest position in all tabulated metals and its value lies (524.96±26.35 to 725.76±37.38) mg/kg in all maize varieties that is slightly higher level than the permissible limit of WHO. Calcium is also one of the important macro elements and its lower level (2.36±0.23 to 4.13±1.40) mg/kg was detected in almost all maize varieties when compared with other macro elements available in maize as well as recommended value of WHO.

The heavy metals/essential trace metals plays vital role in most of the metabolic process during growth

and development of biological tissues, when available within permissible level but below and above the recommended value have adverse effect for life. Among four essential microelements; the highest concentration of Zn was detected, which vary variety to variety in the same agriculture plot in range of 16.26±0.67 to 31.16±2.73 mg/kg. Maximum concentration of iron was observed (10.73±0.40) in Agaiti-75 and its minimum concentration (4.40±0.34) mg/kg in Akbar variety where as the concentration of manganese was detected in the range of 3.59±0.38 to 9.33±0.71 mg/kg, which shows that over all uptake of iron and manganese in all varieties are more or less same with the exception of Agaiti-75 and Sultan varieties that have significant difference. Copper is the only element that possesses lowest level (1.09±0.17 to 1.91±0.40 mg/kg) among all maize varieties and elements. The representative samples of soil of same agricultural land indicates that the deposition of Na, K, Ca, Mg, Fe, Zn, Mn, and Cu were analysed 3968.0±456.09, 13426.7±412.7, 3504.5±383.5, 36295.4±2639.5, 4413.5±517.3, 66.30±7.22, 522.09±47.21, 16.18±2.05 mg/kg respectively. These analytical values of soil tells that the soil of this specific land is rich of these elements, which possesses many folds higher concentration of mentioned eight elements absorbed by the plant and deposited in maize grains.

Table 3: Determination the level of eight essential elements present in six maize varieties (mg/kg)

Elements	Maize Varieties					
	Agaiti-72	Agaiti-75	Akbar	Golden	Sadaf	Sultan
Na	265.69±32.92	404.07±27.01	392.2±37.65	273.60±28.67	400.11±25.83	230.11±23.72
K	2827.4±116.5	2687.4±131.16	3317.5±179.14	3230.0±218.93	3072.5±166.53	3492.6±325.83
Ca	3.74±0.49	4.13±1.40	2.36±0.23	3.20±0.39	3.74±0.38	3.05±0.14
Mg	620.88±28.59	524.96±26.35	550.95±11.10	606.53±20.57	666.57±39.33	725.76±37.38
Fe	8.86±0.86	10.73±0.40	4.40±0.34	8.24±0.71	6.37±0.71	6.27±0.86
Zn	24.37±2.55	24.06±2.10	16.26±0.67	31.16±2.73	30.36±1.96	28.10±1.54
Mn	8.70±0.32	4.65±0.77	3.59±0.38	7.10±0.94	6.58±0.48	9.33±0.71
Cu	1.50±0.15	1.32±0.15	1.09±0.17	1.86±0.30	1.64±0.31	1.91±0.40

Conclusion:

It has been concluded that the highest concentration of sodium, calcium, iron were found in Agaiti-75; Potassium, magnesium, manganese and copper in Sultan and zinc in Golden varieties where as lowest concentration of sodium was detected in Sultan; Potassium and magnesium in Agaiti-75; Calcium, iron, zinc, manganese and copper in Akbar varieties.

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