**The Journal of Animal & Plant Sciences, 27(4): 2017, Page: 1315-1320
ISSN: 1018-7081**

A COMPARATIVE STUDY OF THE INORGANIC NUTRIENTS IN DIFFERENT TYPES OF ZEA MAYS L. USING INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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ABSTRACT

Inductively coupled plasma-mass spectrometry (ICP-MS) was used in this study to perform a quantitative elemental analysis in order to compare the inorganic nutrients in commercial white and noncommercial yellow maize flours. ICP-MS measurements reveals that both white and yellow maize flours contains 20 different elements including toxic elements (Pb, Cd, As, Ni, Cr, Sr, U), essential elements (Ca, Co, Se, Zn, Cu, Fe, Mn, Mo) and probably essential elements (Mg, K, Na, Ba, Al) and their crossponding nutrients values were compared in detail. The ICP-MS analysis revealed that inorganic elements such as Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, U, Zn have concentration of 168.19, 0.17, 2.13, 1327.56, 0.04, 0.12, 9.14, 5.43, 82.03, 34.90, 99.62, 2.83, 0.74, 96.09, 4.5, 9.49, 6.12, 0.03, 6.47 µg/g in white and 200.05, 0.17, 2.53, 1290.27, 0.04, 0.145, 9.85, 11.46, 115.13, 914.98, 1594.14, 21.48, 1.71, 63.89, 6.08, 17.05, 5.23, 0.027, 33.89 µg/g in yellow maize flour, respectively. On the other hand toxic elements such as Cd or Pb in both white and yellow maize flours does not exceed their maximum limit set by the European Legislation or values recommended by the codex alimentarius.

Keywords: inorganic nutrients, white and yellow maize flours, comparative analysis, inductively coupled plasma mass spectrometry

INTRODUCTION

Maize (Zea mays L.) belonging to the family Graminae is one of the most widely grown cereal crop in the world which not only served as the primary staple food in many developing countries but also as a raw material for agriculture-based industries, feed for livestock and poultry (Da Cunha and Do Nascimento 2009);Shah etal.(2009). Maize is widely cultivated throughout the world, United States produces 40% of the world's harvest and other top producing countries include China, Brazil, Mexico, Indonesia, India, France and Argentina. In 2009, the production of maize was 817 million tonnes which was more than more than rice (678 million tonnes) or wheat (682 million tonnes) as reported by Oyekale and Idjesa (2009). Maize or corn can be eaten as cob, parched, boiled, fried, roasted, ground, and fermented for use in breads, porridges, gruel, cakes, and alcoholic beverages while the processed maize used as food thickeners, sweeteners, oils, and nonconsumables. Maize is an inexpensive source of proteins which provides about 15% of the world's protein and 20% of the world's calories (Nuss and Tanumihardjo, 2010). The nutrients or trace elements in the maize or corn are generally classified into three groups from a dietary point of view: essential trace elements (iron, zinc, copper, cobalt, chromium, fluorine, iodine, manganese, molybdenum and selenium); probably essential trace elements (nickel, tin, vanadium, silicon, boron) and the non-essential trace elements (aluminum, arsenic, barium, bismuth, bromine, cadmium, germanium, gold, lead, lithium, mercury, rubidium, silver, strontium, titanium and zirconium) Afzal *et al.*2016); Gwirtz and Garcia-Casal (2014); Major *et al.* (2010); Shuab *et al.* (2016). The nutrients or trace elements of maize shows variation among species and even some subspecies depending on geographical and climatic conditions (Fallico *et al.* 2011); Nehdi (2011). Literature data on nutrients values of the maize are very limited and there have been no reports about the comparison of the nutrients values in the maize flour available in the commercial market and obtained from the locally grown maize. Therefore, the aim of the current research study was to compare the essential trace elements, probably essential trace elements and non-essential trace elements in commercial available white maize flour with the yellow maize flour obtained from the maize grown at University of Agriculture, Faisalabad, Pakistan. The detection of inorganic nutrients in both white and yellow maize flour was performed using inductively coupled plasma-mass spectrometry (ICP-MS). To the best of our knowledge, this is the first study regarding the comparison of the commercially available white maize flour with yellow maize flour grown at University of Agriculture, Faisalabad, Pakistan.

MATERIALS AND METHODS

The maize or corn was grown at research area of the Department of Plant Breeding and Genetics, University of Agriculture, Faisalabad, Pakistan, using randomized complete block design with three replications under normal conditions. During the growth of maize, plant to plant and row to row distances was 20 cm and 40 cm respectively. At maturity, plants were harvested manually and grains were used for the study of proximate chemical composition and detection of inorganic nutrients in maize. The grains of maize were well-grinned and pass through 1mm sieve of millimicro mill (Model Culatti, DFH-48) and it was shaken for 8h at 50^0C whereas white maize flour sample was purchased from the local market in Pakistan. Nitric acid (HNO_3) and hydrogen peroxide (H_2O_2) was purchased from Sigma Aldrich. High purity distilled water obtained from Millipore Milli-Q water purification system was used throughout the work. The samples of white and yellow maize flour were pre-digested in nitric acid (HNO_3) as described in the literature Chung *et al.* (2015). Briefly, 500 mg of the each white and yellow maize flour samples was added to 7 mL of 70% HNO_3 and kept at room temperature for 6 h. After that 1 mL of H_2O_2 was added prior to the digestion, which was carried out using a microwave oven. In the next step, digestion temperature was increased from 30 ˚C to 180 ˚C in 50 min, and the digestion was completed when the digested sample was colorless. Finally, the digested sample volume was adjusted to 50 mL with high purity distilled water. A working standard solution was prepared fresh daily by serial dilution from stock solutions containing 1000 mg/ L (Merck) of the elements. The analytical determination of trace metals was carried out by ICP-MS (Inductively Coupled Plasma-Mass Spectrometer): NexION 300 D (Perkin Elmer, USA). All analyses were performed in triplicate and checked by standard addition. The ICP-MS calibration was carried out by external calibration. The calibration curves of six elements: As, Cd, Cr, Ni, Pb and Zn obtained by the instrument using the blank and four working standards 0, 10, 20, 40 and 100 µg/L and for Al obtained by the instrument using the blank and three working standards 0, 100, 200 and 300 µg/L for all elements, starting from a 1000 mg/L single standard solutions for ICP-MS (Aristar grade , BDH laboratory supplies, England for the trace elements. Correlation coefficient values for all elements were within the range from 0.998 to 0.999.

RESULTS AND DISCUSSION

A photographic comparison of commercial and noncommercial maize grown in the research area of the Department of Plant Breeding and Genetics, University of Agriculture, Faisalabad, Pakistan, is shown in Fig. 1 which shows that commercial available maize flour is white in color, whereas noncommercial maize flour color is yellow. We observed that commercially available white maize flour shows homogenous size distribution, while yellow maize flour grown at University of Agriculture, Faisalabad, Pakistan have small-size debris aggregation with large-size grains along with irregular residues which may be due to non-starch components. ICP-MS was used for the analytical determination of trace elements in both commercially available white maize flour and the maize grown at University of Agriculture, Faisalabad, Pakistan. The quantitation of elements was obtained using external calibration curve method. Three to five point calibration curves, with an appropriate dilution, were used for quantitation, and the concentration ranges for the 20 elemental STDs are shown in Table 1. The results of the present study showed that calibration curves had a good linearity ($R^2 > 0.994$) in the investigated range. The limit of detection (LOD) and limit of quantitation (LOQ) for the 20 elements in maize flour were determined for each calibration curve by using the following equations: LOD = 3*SD/S, LOQ = 10*SD/S, where, SD is the standard deviation of a response, and S is the slope of the calibration curve (Shrivastava and Gupta, 2011). In the current study, the LOD ranged from 0.0017 µg/mL to 0.280 µg/mL and the LOQ from 0.0057 µg/mL to 0.934 µg/mL as shown in the Table 1. In general, the results for most of the elements evaluated indicate the efficiency of ICP-MS and the ability to provide good detection limits and LOQ for maize flour analysis.

Concentrations of 20 different element having essential, probably essential and toxic trace elements as detected by ICP-MS in both white and yellow maize flour are presented in Table 2. The results of the detected elements are the mean values for three replicates (n = 3) with RSDs and the precision is good and varies from 0.2% (for Na in yellow maize flour) to 7.2% (for Cd also white maize flour) in maize flour samples. For better understanding and detailed analysis, these 20 elements are categorized in three groups toxic elements (Pb, Cd, As, Ni, Cr, Sr, U), essential elements (Ca, Co, Se, Zn, Cu, Fe, Mn, Mo) and probably essential elements (Mg, K, Na, Ba, Al) and the cross-ponding results are shown in Fig. 2-3. As can be seen from the Fig. 2(b) that essential elements (Co, Se, Zn, Cu, Fe, Mn, Mo) are higher in concentration in yellow maize flour except Ca which is higher in white maize flour. The concentration of Zn is 5 times, Mn is 8 times, Cu is 2 times, Mo is 1.6 times, and Fe is 1.5 times higher in yellow maize as compared to white maize flour. Whereas the concentration of Ca is little bit higher in white maize flour as compared to yellow maize flour. Concentrations of the trace essential elements (Ca, Co, Se, Zn, Cu, Fe, Mn, Mo) can be arranged as follows: Co<Mo<Mn<Cu<Zn<Fe <Ca, in

white maize flour, where as it can arranged as: Se<Co<Mo< Cu <Mn <Zn<Fe <Ca in yellow maize flour. Concentrations of Ca, Fe are higher than those obtained by Feil *et al.* (2005); Hassan *et al.* (2009); Ullah *et al* .(2010). The contents of Zn and Cu are significantly less as compared to Ca, Fe, but are comparable to those determined who determined that the Zn contents of maize grains ranged from (37.05-52.4 ppm) whereas Cu concentration is higher than those obtained by Feil *et al.* (2005).

Fig. 3(a) shows the comparison of probably essential elements (Mg, K, Na, Ba, Al) in white and yellow maize flour. The probably essential elements (Mg, K, Al) are higher in concentration in yellow maize flour except Na which is higher in white maize flour and Ba is almost same in concentration in both white and yellow maize flour. The concentration of Mg is 16 times, K is 26 times, Al is 1.2 times higher in yellow maize as compared to white maize flour. Whereas the concentration of Na is 1.5 times higher in white maize flour as compared to yellow maize flour. Concentrations of the probably essential elements (Mg, K, Na, Ba, Al) can be arranged as follows: Ba<K<Na<Mg <Al, in white maize flour, where as it can arranged as: Ba<Na <Al<K <Mg in yellow maize flour. Concentration of Mg in yellow maize flour is higher than those obtained by Feil *et al.* (2005); Hassan *et al.* (2009); Ullah *et al.* (2010) and concentrations of Na and K are significantly less than those obtained by Pfahler and Linskens (1974). The concentration of Al is bit higher than those obtained by Pfahler and Linskens (1974) in maize and then those obtained by Chung *et al.* (2015); Santos *et al.* (2004). The concentration of Ba is relatively low (2.13–2.53lg/g) which is comparable to that obtained by Szymczycha-Madeja (2017) in ryecrisp bread and higher than those obtained by Chung *et al.* (2015) in rice.

Fig. 3(b) shows the comparison of toxic elements (Pb, Cd, As, Ni, Cr, Sr, U) in white and yellow maize flour. The toxic elements (Pb, Ni, Cr) are higher in concentration in yellow maize flour except Sr which is higher in white maize flour and (Cd, As, U) almost same in concentration in both white and yellow maize flour. The concentration of Pb is 1.7 times, Ni is 1.4 times, Cr is 1.1 times higher in yellow maize as compared to white maize flour. Whereas the concentration of Sr is 1.2 times higher in white maize flour as compared to yellow maize flour. Concentrations of the toxic elements (Pb, Cd, As, Ni, Cr, Sr, U) can be arranged as follows: U<Cd<As<Ni<Sr<Cr<Pb, in white maize flour, where as it can arranged as: U<Cd<As<Sr<Ni<Cr<Pb, in yellow maize flour. In the case of Pb, its concentrations are 9.49 and 17.04 ug/g for white and yellow maize flour which is comparable to that obtained by Santos *et al.* (2004) and significantly higher than that published in the relevant literature (Cuadrado *et al.* 2000); Demirözü *et al.* (2003); Khouzam *et al.* (2011; Zhao *et al.,* 2013; Szymczycha Madeja, 2017).

The concentrations of Ni, Cr and U as very low as compared to that obtained by Santos *et al.* (2004). The Cd concentrations in both white and yellow maize flours was quite less than those previously reported by Cuadrado *et al*. (2000); Demirözü *et al.* (2003); and Szymczycha-Madeja (2017) . We believe that this change in the concentrations values in the analyzed sample could have several reasons such as source of cereals, geographic area, nature of soil in the place of constituent cultivation and different production processing.

Table 1. Calibration curves, limit of detection (LOD), and limit of quantitation (LOQ) of 20 elements examined in the present study.

Element	Concentration (µg/mL)	Linearity (r^2)	Slope (S)	SD of Response	LOD (µg/mL)	LOQ (µg/mL)
Al	0.01-0.1	0.9984	15273.4	63.0	0.012	0.041
As	0.1-1	0.9995	529.5	49.5	0.280	0.934
Ba	0.01-0.1	0.9997	6614.1	12.0	0.0054	0.0181
Ca	0.01-0.1	0.9980	1312.7	32.0	0.0731	0.243
Cd	0.01-0.1	0.9998	1819.4	13	0.0214	0.0714
Co	0.01-0.1	0.9991	3249.4	13.5	0.0124	0.0415
Cr	0.01-0.1	0.9990	2929.2	27	0.0276	0.0921
Cu	0.01-0.1	0.9992	14530.8	42	0.0086	0.0288
Fe	0.1-1	0.9989	1120.4	30	0.080	0.2677
K	0.01-0.1	0.9971	11946.9	32.96	0.0082	0.0275
Mg	0.01-0.1	0.9991	13907.9	58	0.0125	0.041
Mn	0.01-0.1	0.9991	4358.4	24	0.165	0.055
Mo	0.01-0.1	0.9999	5001.5	11	0.0065	0.0219
Na	0.01-0.1	0.9970	54780.8	50	0.0027	0.0091
Ni	0.01-0.1	0.9981	6790.1	35	0.015	0.0515
Pb	0.01-0.1	0.9995	9601.0	49	0.0153	0.0510

Se	0.1-1	0.9998	770.7	4.7	0.0183	0.0610
Sr	0.01-0.1	0.9997	17985.1	18	0.0030	0.010
U	0.01-0.1	0.9998	17267.9	10	0.0017	0.0057
Zn	0.1-1	0.9991	378.4	1.7	0.0134	0.044

Table 2. Concentration of 20 elements determined by ICP-MS in commercial white and noncommercial yellow maize flour powder grown at research area of the Department of Plant Breeding and Genetics, University of Agriculture, Faisalabad, Pakistan.

Elements	White Maize Flour(µg/g)	Yellow Maize Flour(µg/g)
Al	168.196(0.6)	200.052(1.3)
As	0.166(1.9)	0.173(4.1)
Ba	2.138(1.2)	2.53(1.2)
Ca	1327.563(1.1)	1290.272(1.0)
Cd	0.04(5.9)	0.04(7.2)
Co	0.118(4.3)	0.148(2.7)
Cr	9.144(0.8)	9.854(1.0)
Cu	5.431(1.3)	11.465(0.7)
Fe	82.032(1.2)	115.13(1.2)
K	34.907(0.3)	914.984(0.9)
Mg	99.617(1.2)	1594.137(0.7)
Mn	2.829(2.4)	21.481(1.9)
Mo	0.738(2.4)	1.171(1.4)
Na	96.086(1.4)	63.887(0.2)
Ni	4.349(1.6)	6.083(0.8)
Pb	9.497(0.5)	17.047(0.3)
Se	<LOD	0.062(6.9)
Sr	6.121(0.5)	5.231(0.9)
U	0.031(0.8)	0.027(1.3)
Zn	6.47(1.6)	33.898(0.6)

Figure1. Photograph of commercial white and noncommercial yellow maize flour powder grown at research area of the Department of Plant Breeding and Genetics, University of Agriculture, Faisalabad, Pakistan.

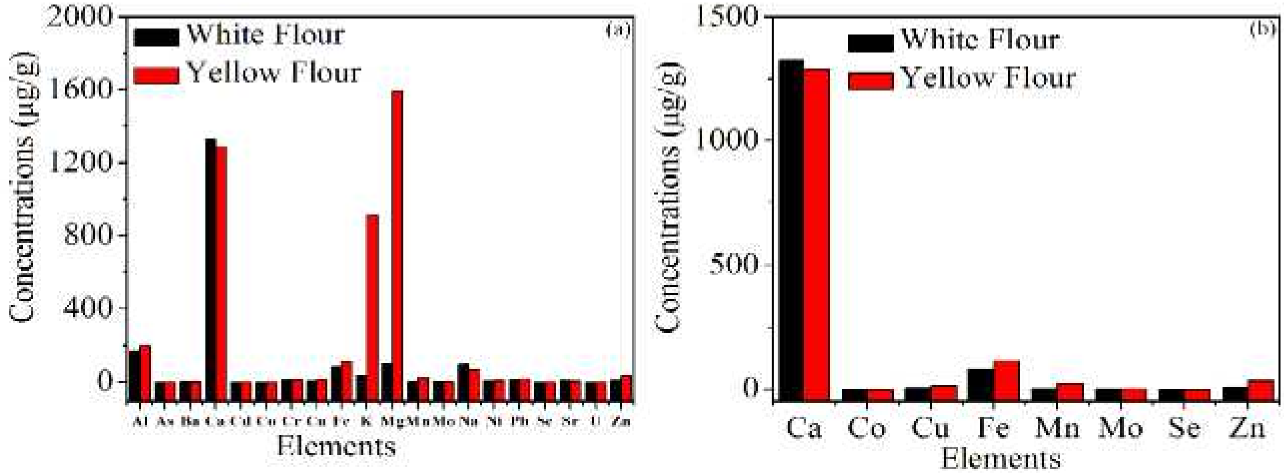

Figure2. (a) Overall comparison of the concentration of 20 elements determined by ICP-MS in commercial white and noncommercial yellow maize flour powder grown at research area of the Department of Plant Breeding and Genetics, University of Agriculture, Faisalabad, Pakistan (b) Comparison of the concentration of essential elements determined by ICP-MS in commercial white and noncommercial yellow maize flour powder grown at research area of the Department of Plant Breeding and Genetics, University of Agriculture, Faisalabad, Pakistan.

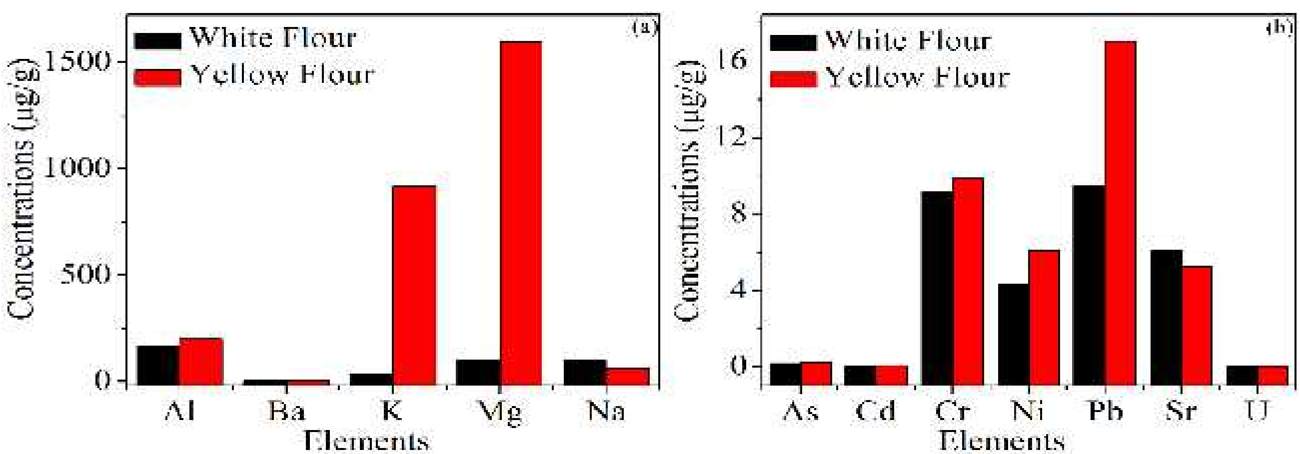

Figure3. (a) Comparison of the concentration probably essential elements determined by ICP-MS in commercial white and noncommercial yellow maize flour powder grown at research area of the Department of Plant Breeding and Genetics, University of Agriculture, Faisalabad, Pakistan (b) Comparison of the concentration of toxic elements determined by ICP-MS in commercial white and noncommercial yellow maize flour powder grown at research area of the Department of Plant Breeding and Genetics, University of Agriculture, Faisalabad, Pakistan.

Conclusion: The comparison of the nutrients present in both commercial white and noncommercial yellow maize flour was performed using inductively coupled plasma mass spectroscopy (ICM-MS) technique. The results shows that concentration of essential elements such as Zn, Mn, Cu, Mo and Fe is 8, 2, 1.6 and 1.5 times higher in white maize flour as compared to yellow maize flour. On the other hand yellow maize flour contain Mg, K, Al, are 16, 26 and 1.2 times higher as compared to white maize flour respectively, whereas the concentration of Na is 1.5 times higher in white maize flour as compared to yellow maize flour.

REFERENCES

Afzal, S., N. Akbar, R. Ahmad, and M. Hameed (2016). Performance of Maize, Wheat and Riceunder Various Cropping Systems under Agro-Climatic Conditions of Faisalabad. Transylvanian Review.

Chung, I.-M., J.-K. Kim, J.-K. Lee, and S.-H. Kim (2015). Discrimination of geographical origin of rice (Oryzasativa L.) by multi elementan alysis using inductively coupled plasma atomic emission spectroscopy and multi variate analysis. J. Cereal Science, 65: 252-259.

Cuadrado, C., J. Kumpulainen, A. Carbajal and O. Moreiras (2000). Cereals contribution to the total dietary intake of heavy metals in Madrid, Spain. J. Food Composition and Analysis, 13(4): 495-503.

Da Cunha, K.P.V and C.W.A. Do Nascimento (2009). Silicon effects on metal tolerance and structural changes in maize (Zea mays L.)grown on acadmium and zincen riched soil. Water, air, and soil pollution, 197 (1-4):323-330.

Demirözü, B., I. Saldamli, B. Gürsel, A. Uçak, F. Çetinyokuş and N. Yüzbaşi (2003). Determination of some metals which are important for food quality control in bread. J. Cereal Science, 37(2): 171-177.

Fallico, B., G. Ballistreri, E. Arena and Ö. Tokusoglu (2011). Nut Bioactives: Phyto chemicals and Lipid-Based Components of Brazil Nuts, Cashews, Macadamias, Pecans, and Pine Nuts. Fruit and Cereal Bioactives: Sources, Chemistry, and Applications, 213.

Feil, B., S. Moser, S. Jampatong and P.Stamp (2005). Mineral composition of the grains of tropical maize varieties as affected by pre-anthesis drought and rate of nitrogen fertilization. Crop Science, 45(2): 516-523.

Gwirtz, J. A. and M. N. Garcia-Casal (2014). rocessing maize flour and corn meal food products. Annals of the New York Academy of Sciences,1312(1): 66-75.

Hassan, A. B., G. A. Osman, M. A. Rushdi, M. M. Eltayeb and E. Diab (2009). Effect of gamma irradiation on the nutritional quality of maize cultivars (zea mays) and sorghum (sorghum bicolor) grains. Pak J Nutr, 8(2): 167-171.

Khouzam, R. B., R. Lobinski and P. Pohl (2011). Multi-element analysis of bread, cheese, fruit and vegetables by double-focusing sector-field inductively coupled plasma mass spectrometry. Analytical Methods, 3(9): 2115-2120.

Major, J., M. Rondon, D. Molina, S. J. Riha and J. Lehmann (2010). Maize yield and nutrition during 4 years after biochar application to a colombian savanna oxisol. Plant and soil, 333(1-2): 117-128.

Nehdi, I. (2011). Characteristics, chemical composition and utilisation of albizia julibrissin seed oil. Industrial crops and products, 33(1): 30-34.

Nuss, E. T. and S. A. Tanumihardjo (2010). A paramount staple crop in the context of global nutrition. Comprehensive reviews in food science and food safety, 9(4): 417-436.

Oyekale, A. and E. Idjesa (2009). Adoption of improved maize seeds and production efficiency in rivers state, nigeria. Academic J. Plant Sciences, 2(1): 44-50.

Pfahler, P., and H. Linskens (1974). Ash percentage and mineral content of maize (zea mays l.) pollen and style. Theoretical and applied genetics, 45(1): 32-36.

Santos, E., D. Lauria and C. P. Da Silveira (2004). Assessment of daily intake of trace elements due to consumption of foodstuffs by adult inhabitants of rio de janeiro city. Science of the Total Environment, 327(1): 69-79.

Shah, S. T. H., M. S. I. Zamir, M. Waseem, A. Ali, M. Tahir, W. B. Khalid, S. Shah, M. Zamir, M. Waseem, and A.Ali (2009). Growth and yield response of maize (zea mays L.) to organic and inorganic sources of nitrogen. Pakistan J. Life Soc. Sci, 7(2): 108-111.

Shuab, R., R. Lone and K. Koul (2016). Influence of arbuscular mycorrhizal fungi on storage metabolites, mineral nutrition and nitrogen assimilating enzymes in potato (solanum tuberosum L.) plant. J. Plant Nutrition (just-accepted).

Szymczycha-Madeja, A. (2017). Rapid method of element determination in ryecrisp bread by ICPOES. Arabian J. Chemistry, 10:3913-3919.

Ullah, I., M. Ali and A. Farooqi (2010). Chemical and nutritional properties of somemaize (Zea mays L.) varieties grown in NWFP, Pakistan. Pakistan J. Nutrition, 9(11): 1113-1117.

Zhao, H., B. Guo, Y. Wei, and B. Zhang (2013). Multi-element composition of wheat grain and provenance soil and their potentialities as fingerprints of geographical origin. J. Cereal Science, 57(3): 391-397.