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Trace Elements Profile of High Yielding Varieties of Foxtail Millets *(Setaria Italia L.)* Grown in Bangladesh

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Abstract

Five micro minerals (Zn, Fe, Cu, Co & Cr) and two heavy metals (Pb & Cd) content of the three high yielding varieties (HYVs) of Bangladeshi foxtail millet (*Setaria Italia L.*) (Kaon in Bengali) were estimated by Inductively Coupled Plasma Emission Spectroscope (ICPE-9000). Two different digestion techniques used for the sample preparation were Dry ashing and Wet digestion. Zn (46.83 µ gm/gm), Fe (61.85 µ gm/gm), Cr (0.91 µ gm/ gm) were found in significantly higher levels using wet digestion techniques whereas, Cu (7.25 µ gm/gm), Co (0.012 µ gm/gm) and Pb (0.861 µ gm/gm) contents were estimated greater by dry ashing methods. Bangladeshi HYVs of Kaon were found to rich in Fe, Zn and Cu content. Among the varieties BARI Kaon 1 was the most micro minerals rich variety.

Keywords: Micro-minerals; heavy metals; high yielding varieties; foxtail millet; digestion techniques;

I. Introduction

Foxtail Millet *(Setaria Italia L.)* locally known as Kaon is a minor cereal crop of Bangladesh which is cultivated in marginal low fertile and saline lands. Its annual production is approximately 13 thousand metric tons in Bangladesh[1]. Kaon is regarded as a food for poor people whose malnutrition is highly predominant in these sections of people. Therefore, assessment of Nutritive profile, specially minerals regarded as micro-nutrients, are required to find out a correlation between malnutrition problems with food intake. Generally, micro minerals contribute to smooth physiologic and biochemical functions of human body, though required in minor amounts less than 100 mg/day[2]. However, as each micro mineral like Zn, Fe, Cu, Cr, Co have their individual specific roles in metabolism, biochemical functions, bioavailability and absorption, knowledge of their levels in regularly consumed food is vital to evaluate and control micro nutrient deficiencies.

Among the trace elements Zinc (Zn) plays important roles to fulfill many biochemical functions in human metabolism[3,4]. Micro-nutrient iron (Fe) is a constituent of heme enzymes (hemoglobin, cytochromes, etc) and considered essential for maintaining immune functions[5]. Copper (Cu) serves as constituent of oxidase enzyme and plays vital role in iron absorption[2] and body immune system[6]. Chromium (Cr) as trivalent chromium is a constituent of "glucose tolerance factor" that binds to and potentiates insulin although hexavalent chromium is harmful for health and regarded as a carcinogen.[2]. Cobalt (Co) is required as a constituent of vitamin B_{12}. In contrast to micronutrients, lead (Pb) is a well known toxic trace element to human diet for its multidimensional adverse effects even when present in minute quantity[7]. Cadmium (Cd) is also another toxic trace element which causes renal dysfunction and bone diseases[8].

However, the levels of trace elements content in cereals are known to be affected by crop varieties, soil conditions, weather conditions during growing, fertilizer applications and agricultural practices[9, 10]. As it is hard to compare the nutrient content data of various varieties of cereals and pulses grown in different countries of different geological locations[9], therefore, countries generally have their own Food Composition Table (FCT). The need of this type of information on indigenous and high yielding crop varieties to the interested groups like nutrition researchers, food manufacturers, traders, growers, even consumers are very vital. Besides, sound knowledge on biological and toxic effects of trace elements on human body is also imperative to evaluate a specific variety according to its nutrient content and toxicity.

Moreover, selecting appropriate techniques for determining the trace elements content is also important. No scientific report have yet been found in the literature regarding nutrient quality of high yielding local varieties of Kaon grown in Bangladesh. Therefore, considering all these, five micro minerals (Zn, Fe, Cu, Cr, Co) and two heavy metals (Pb, Cd) content of three HYVs of Kaon grown in Bangladesh were aimed to analyze and evaluate their contents among local varieties of Bangladesh as well as, to compare the performance between two digestion techniques (dry ashing and wet digestion) generally considered for the estimation of different elements.

II. Experimental

Materials

Three high yielding varieties (HYV) of Kaon developed by Bangladesh Agricultural Research Institute (BARI), Gazipur were selected for this experiment. The samples were collected from BARI, which were cultivated in their experimental plots according to the standard guidelines. The names of three HYVs were BARI Kaon 1, BARI Kaon 2, and BARI Kaon 3.

Methods

Instrumentation: Simultaneous determination of the trace elements (Zn, Fe, Cu, Co, Cr, Pb, Cd) were carried out by Inductively Coupled Plasma Atomic Emission Spectrometer, ICP-AES (Shimadzu ICPE-9000 multi-type emission spectrometer). However, Fe was also estimated by flame type Atomic Absorption Spectrometer-AAS (HITACHI – E01- 2A) of samples that had been wet digested. Experiments were carried out at Soil Science Division of Bangladesh Rice Research Institute (BRRI).

Moisture and Ash content: The moisture content of the samples were determined by taking 5 gm of grains in metal pots and heated at 130 ± 3ºC for 2 hours[11]. For ash content 2

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- 2.5 gm of dried samples were ashed in a muffle furnace at 800°C for 90 minutes[12].

Dry Ashing Technique[12]: Ashes obtained from the ash content estimation was dissolved with 1 ml of conc. HNO_3 in the crucibles and kept for 10 minutes in the fume hood for dissolving the ashes. The aliquots were then transferred into the volumetric flasks and made up to the mark with deionized water. The prepared solution then transferred to the dry, contamination free plastic bottles through filtration for estimation with ICPE-9000 or AAS.

Wet Digestion Technique [13]: 0.5 gm of dry samples was taken into 25 ml conical flasks where 5 ml of concentrated HNO_3 had been added and kept under a fume hood for over night soaking. The samples were then heated at 110 ± 5ºC for 3 hours until the cessation of red fume evolution and again kept under the fume hood for cooling down to room temperature. After attaining the room temperature 2 ml of conc. $HClO_4$, and 1 ml of conc. H_2SO_4 were added to the digesting samples and heated at 190 ± 5ºC until the volume reduced to 2-3 ml (approximately 1.5 hr). The digested solutions were then made up to the mark in a volumetric flask with deionized water and transferred into plastic bottles through filtration and stored in the refrigerator for further analysis.

Chemicals and reagents: Analytical grade concentrated HNO_3, concentrated $HClO_4$ and concentrated H_2SO_4 from MERCK (Germany) were used in the digestion of samples. De-ionized water used throughout the experiment was collected from deionization plant (E-Pure) having specific resistivity of 18 MΩ-cm. Calibration standards of different concentrations was made from 'ICP Multi Element Standard Solution VIII CertiPUR®.

Detection limits (DL)

The lower detection limits for the measuring elements were calculated by multiplying the three times of standard deviation of the intensity of the blank sample by the "slope" of the calibration curve and shown in Table 1.

Table. 1. Detection limit of the different elements

Elements	Cd	Co	Cr	Cu	Fe	Pb	Zn
DL (ngm/gm)	0.207	0.540	0.194	0.494	0.144	0.054	0.057

Statistical Analysis

Results found in the present study were compared using General Linear Model (GLM) of SPSS 13.0 to perform analysis of variance and Post Hoc Comparison of LSD model[14]. P values with 5% LSD are presented in Table 2– 4.

III. Results

The micro minerals (Zn, Fe, Cu, Co, Cr) and heavy metals (Pb, Cd) content found in the present study are presented in Table 2 & 3. Moisture and ash content results are also presented in Table 4.

Table 2. Comparison between digestion techniques used for estimating different trace elements in Kaon.

Trace elements		N	Digestion techniques (μ gm/gm, dry weight basis)		*P* value
			Dry ashing	Wet digestion	
			Mean ± SEM	Mean ± SEM	
Micro minerals	Zn	6	37.105 ± 2.162	46.827 ± 2.270	.011 *
	Fe	6	31.236 ± 2.218	61.848 ± 2.779	.000 ***
	Cu	6	7.253 ± 0.378	3.324 ± 0.204	.000 ***
	Co	6	0.012 ± 0.003	-	
	Cr	6	-	0.907 ± 0.050	
Heavy metals	Cd	6	-	-	
	Pb	6	0.861 ± 0.025	-	

N = no. of replicate, - = Not detected, SEM = standard error of mean, *** = significant at p< 0.001, * = significant at p< 0.05

Effects of digestion technique on level of trace elements in millet: Table-2, showed that there had been significant differences in the Zn, Fe and Cu content in Kaon when samples were digested by two different digestion techniques used in this study. Wet digested Kaon showed significantly higher Zn and Fe content with values 26% and 98% higher than respective dry ashing results. In contrast, significantly higher level of Cu (7 μ gm/gm) was found by dry ashing technique which was 2 times higher than the level observed by wet digestion. Co and Pb were undetected by wet digestion method and however, Cr was undetected by dry ashing techniques. Moreover, Cd content was lower than the detection limit of ICP-AES using for both the digestion techniques.

Dependence of trace elements level on HYVs and digestion techniques: Zn showed signifi-cant (P= 0.000) variations among the three HYVs of Kaon (Table -3), whereas, the estimated levels for other trace elements were non-significant (except Cu). The level of Zn found in the Kaon varieties ranged from 32.66 – 53.15 μ gm/gm (dry weight basis). Highest level of Zn was identified in BARI Kaon -1 (53.15 μ gm/gm) compared to the other varieties using wet digestion technique. However, this value was 21 % higher than the result obtained for BARI Kaon 1 by dry ashing (43.73 μ gm/gm). Consequently, comparison among 3 HYVs showed that Zn level was identified significantly higher in Kaon 1 irrespective to digestion techniques used in this study.

Interaction between variety vs digestion techniques again highlighted that Zn was estimated 21% to 33% higher levels i.e. better levels using wet digestion than dry ashing. In case of Fe, like Zn, significantly higher response was noticed from wet digestion than dry ashing. However, a range of 72% to 2.2 times differences was observed comparing Fe content in 3 varieties using 2 different digestion techniques. Similar to Fe & Zn, Cu levels also significantly differ for each type of Kaon variety when estimated using two different techniques. However, in contrast to Fe & Zn, Cu was identified in significantly higher levels when dry asing technique was used than wet digestion. Table 3 also showed that BARI Kaon 1 contain significantly better Cu content (7.9 µ gm/gm) than other 2 varieties used in this study.

Table. 3. Dependence of HYV and digestion techniques on trace elements content (µ gm/gm, dry weight basis) for different varieties of Kaon digested by dry ashing or wet digestion technique.

Trace elements		Digestion techniques	Different varieties of Kaon (mean from N= 2) (µ gm/gm, dry weight basis)			P Value, 5% LSD
			BARI Kaon -1	BARI Kaon -2	BARI Kaon -3	
Micro minerals	Zn	Dry ashing	43.739 a	32.660 b	34.916 b	0.000***,
		Wet digestion	53.153 c	40.860 d	46.467 e	2.480
	Fe	Dry ashing	37.582 a	25.957 a	30.169 a	0.002**,
		Wet digestion	64.695 b	58.641 b	62.209 b	14.254
	Cu	Dry ashing	7.983 a	6.255 b	7.521 ab	0.001***,
		Wet digestion	3.407 c	3.287 c	3.278 c	1.523
	Co	Dry ashing	0.020	0.005	0.013	0.191, NS
		Wet digestion	-	-	-	
	Cr	Dry ashing	-	-	-	0.168, NS
		Wet digestion	0.988 ± 0.088	0.776	0.958	
Heavy metals	Cd	Dry ashing	-	-	-	
		Wet digestion	-	-	-	
	Pb	Dry ashing	0.905 ± 0.023	0.839	0.839	0.571, NS
		Wet digestion	-	-	-	

N = no of replicate, - = Not detected, NS= Not significant, *** = significant at P<0.001, ** = significant at P<0.01, values with a different letter are significantly different with in a food item based on 5% LSD

There was no significant difference observed for Co, Cr, and Pb levels among the three HYVs although in BARI Kaon 1 Pb was found in highest level.

Moisture and ash content showed no significant differences among the HYVs of Kaon (Table -4). Grand mean (for 3 varieties) of moisture & ash content observed were 12.84 % and 3.52% respectively.

Table 4. Moisture and Ash content of the high yielding varieties of Kaon.

Variety Name	Moisture content (mean ± SEM) (%, wet basis), N=3	*P* value	Ash content (mean ± SEM) (%, dry basis), N=4	*P* value
BARI Kaon -1	12.590 ± .061		3.661 ±.169	
BARI Kaon -2	13.217 ± .024	0.912, NS	3.341 ±.020	0.172, NS
BARI Kaon -3	12.709 ± .081		3.550 ±.089	

NS= Not significant, SEM= Standard Error of Mean.

IV. Discussion

Among the micro minerals the level of Zn, Fe and Cu found in the three HYVs of Kaon (*Setaria Italia L.)* grown in Bangladesh were ranged from 40.86 - 53.15, 58.64 - 64.69 and 6.25 - 7.98 µ gm/gm respectively. These values supported the data of Ragaee *et al*, 2006, 65.9 µgm/gm of Zn and 199.8 µgm/gm of Fe and 3.4 µgm/gm of Cu in pearl millet *(Pennisetum glaucum L.)* from UAE[15]. However, by comparison Zn and Fe levels of this study is higher than those reported in the USDA[16] (16.8 and 30.1 µgm/gm respectively) and Canadian nutrient data base[17] (16.8 and 30.1 µgm/gm respectively) for millet (*Panicum miliaceum L.)*. But the level of Cu obtained was in agreement with those published database. Similarly, the comparison of the present data with those published by Ekholm *et al*, 2007 showed the higher level of Zn and Fe but similar level of Cu in millets reported from Finland[10]. The level of Fe obtained for Bangladeshi millet supported the results of millet grown in Mali[9] and reported by Barikmo *et al*, 2007 although the level of Zn content was lower. For Co and Cr the levels identified in the HYVs of Bangladeshi millets were 0.005 - 0.02 µgm/gm, and 0.77 - 0.98 µgm/gm respectively. These results were similar to those found in Indian millets[18] *(P. pyphodes)* studied by Sing and Garg, 2006. Whereas, Ekholm et al, 2007 reported 0.06, 0.03 and 0.22 µgm/gm of Co, Cd and Pb respectively in millets from Finland[10], the levels of Pb was found higher in all the three varieties examined in this study compared to the respective data. Overall, according to trace elements profile identified, Kaon grown in Bangladesh showed standard value of Cu content which plays vital role for iron absorption, since, Fe can not be absorbed sufficiently from food grain without the presence of Cu[2]. In addition to that, the presence of both Cu

and Cr has beneficial effects on HDL-Cholesterol and plasma triglyceride concentrations that are not observed with these minerals individually[6].

In the present study two different digestion techniques, commonly used for trace elements analysis selected through reviewing the literature, were dry ashing at 800 °C and wet digestion using tri-acid (HNO_3, $HClO_4$ and H_2SO_4). The obtained results highlighted significant variations in estimated trace elements levels, very specific for particular elements. It seems Zn, Fe and Cr from Kaon could be better extracted using wet digestion techniques. In contrast, for Cu, Co and Pb dry ashing technique could be preferred. For instance, these finding supported the reports by Santos *et al,* 2004[19] Conti *et al*, 2000[20] who used dry ashing method for estimating Cu, Co and Pb although they did not compare between these digestion techniques. However, Ekholm *et al*, 2007[10] and Hussein and Bruggemann, 1997[21] used tri-acids for wet digestion of Co, Cu, Fe, Zn, Cd & Pb.

The reason behind the lower estimated levels of Zn, Fe, Cr from Kaon using dry ashing could be incomplete dissolution of these elements from the ash, whereas, the lower levels of Cu, Co and Pb shown using wet digestion techniques might be due to the nature of the matrix. In general, it seems that trace elements could be better extracted using specific digestion techniques. However, further investigations are worthwhile to confirm the correlation of important trace elements in food matrixes with various digestion techniques.

V. Conclusion

Assessing the observed trace elements levels from this study on HYVs of Kaon grown in Bangladesh showed that, these cereal grains are rich in Fe, Zn, Cu and Cr. By comparing the obtained levels among the varieties, BARI Kaon 1 could be graded as quality grain for micro minerals. However, it seems that particular trace elements could be better estimated by using specific digestion technique since significant variation in micro minerals levels were noticed when two digestion techniques were compared.

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