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Levels of selected metals in commercially available rice in Ethiopia

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Abstract

This study reports the levels of metals in commercially available imported and Ethiopian rice. The levels of thirteen metals (Ca, Mg, K, Na, Fe, Mn, Zn, Cu, Co, Ni, Cr, Cd and Pb) were determined in six varieties of raw rice collected from Addis Ababa supermarkets, Fogera town and Amahara Regional Agricultural Research Institute and in one selected cooked rice by flame atomic absorption spectrometry (FAAS) after digesting the powdered rice samples with HNO_3, $HClO_4$ and H_2O_2 mixture. The validation of optimized digestion procedure was evaluated using spiking method and an acceptable percentage recovery was obtained. The levels of metals found in the imported and Ethiopian rice, respectively, were in the ranges (mg/kg): Ca 75.8-630, 205-427; Mg 90.6-150, 99.5-2250; K 1680-2150, 1100-3020; Na 70.6-78.6, 26.7-80.9; Fe 48.9-117, 41.3-113; Mn 4.1-15.5, 3.7-16.6; Zn 16.4-25.7, 15.6-140; Cu 2.7-4.9, 3.3-15; Co 12.6-14.6, 8.8-10.4; Ni 2.5-75.1, 41.5-69.7; Cr 2.2-3.12, 2.32-4.82; Cd <0.34, 0.45-2.54; Pb 2.1-5.3, 0.8-3.8. Comparison between levels of metals in the imported and Ethiopian rice showed significant differences for most of the metals. The results indicated that Ethiopian rice is comparatively rich in essential metals than imported one. A statistical analysis of variance (ANOVA) at 95% confidence level for metal determination indicated significant difference between the means of each variety of samples. Comparison between levels of metals in cooked and raw rice showed that the difference in the level is not significant.

Introduction

Rice is one of the commonly consumed cereals for more than half of the world's population. It is an important source of energy, vitamins, mineral elements and rare amino acids for human. Rice is one of the most important foods in world supplying as much as half of the daily calories of the world population (Jaisut *et al*., 2008; Zhang, 2009; Abbas *et al*., 2011; Pishgar-Komleh *et al*., 2011). Archaeological and historical evidence points to the foothills of Himalayas in the North and hills in the North-East of India to the mountain ranges of South-East Asia and South-West China as the primary centre of origin of *Oryza sativa*, and the delta of River Niger in Africa for that of *Oryza glaberrima*, the African rice (Jaisut *et al*., 2008). Because the rice plant is highly adaptable to local environment and because human has succeeded in modifying local agro-ecosystem, rice can now be grown in many different locations and under a variety of climates (Mandal *et al*., 2004).

There are 25 species of rice in the genus Oryza. The dominant rice species is *Oryza sativa*, which is believed to have originated somewhere in South-East Asia. In Africa *Oryza sativa* has now almost fully replaced the local species *Oryza glaberrima*, which was grown as a main staple crop in Western Africa before. Other members of the *Oryza* genus are in general not cultivated but some indigenous peoples collect them in times of food scarcity (Jaisut *et al*., 2008). From crosses between African rice *(O. glaberrima)* and Asian rice *(O. sativa)* new varieties called NERICA (NEw RIce for AfriCA) was obtained that led to yield increase by 50% in upland rice ecology of Africa. It contains 2% more protein than their African or Asian parents. They are taller than most rice, making harvesting easier. Pest resistant and tolerant to drought and infertile soils better than Asian varieties (Sarla and Swamy, 2005). The new rice varieties are high-yielding, drought and pest resistant and are uniquely adapted to the growing conditions of West Africa (Sarla and Swamy, 2005).

Rice was introduced in Ethiopia during 1970s and has since been cultivated in small pockets of the country (Gebremeskel, 2010). Even though, rice is not traditional staple food in Ethiopia, it is a high potential emergency and food security crop for the country. Rice production is expanding rapidly and farmers are growing it in many places and over large

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areas and also have developed many Ethiopian recipe using rice including injera, bread (dabo), porridge (genfo), couscous (kinche) and local drink tella and kati kalla (Crawford and Shen, 1998).

The rice plant can grow to 1-1.8 m tall, occasionally more depending on the variety and soil fertility (Girma, 2010). The traditional method for cultivating rice is flooding the fields while, or after, setting the young seedlings (Ghosh and Bhat, 1998). Rice is the most diversified crop species due to its adaptation to a wide range of geographical, ecological and climatic regions (Skaria *et al*., 2011). Its productivity is severely affected by several biotic and abiotic factors, for example, damage caused by different insect pests and diseases. Rice is affected by more than 100 insects, among which 10-12 pose an economic threat to rice cultivation (Adiroubane and Raja, 2005).

Rice competes closely with wheat as the world most important food crop. Regarding to wheat and maize, rice supplies more than half of all the calories humans consume (Gbabo *et al*., 2009). Rice is a cereal foodstuff which forms an important part of the diet of more than three billion people around the world (Gebremeskel, 2010). It does not only share important relationships with other cereal species and is a model plant for grasses, but it is also the principal mineral element source for over half of the world's population (Zeng *et al*., 2009). Vitamin A, iron and iodine deficiency are the most wide spread and devastating forms of micronutrient malnutrition. The most widely consumed staple crops rice; wheat and maize are not good sources of these nutrients (Prom-u-thai *et al*., 2009).

Rice verities have different qualities that suit different food applications. The rice grain is mostly consumed boiled (or fried) as main staple but it is also widely used for snacks, appetizers, rice soups (congee) and desserts. It is the main constituent of life-saving oral rehydration solutions (ORS), and has been used for this purpose since time immemorial (Storck *et al.*, 2005).

Unfortunately, rice is a poor source of many essential micronutrients and vitamins, and deficiencies in these micronutrients are common in developing countries (Narayanan *et al*., 2007). Rice is a good source of protein, but it is not a complete protein: it does not contain all of the essential amino acids in sufficient amounts for good health, and should be combined with other sources of protein, such as nuts, seeds, beans, fish, or meat (Jaisut *et al*., 2008).

The nutritional value of raw rice per 100 g has 1510 kJ energy, 79 g carbohydrates, 0.6 g fat, 7 g protein, 0.4 g vitamin B_6 and 12 g water. Rice kernels do not contain vitamin A, so people who obtain most of their calories from rice are at risk of vitamin A deficiency. In terms of calories, carbohydrate rich foods should make up around 50% of our total calorific intake (Jafar *et al*., 2008). Rice straw, husks and bran are also a valuable source to fertilizer for the rice field and for composting (Jaisut *et al*., 2008). The complex trait of rice grain quality is the sum of a number of component traits, including appearance, cooking and eating quality, and nutritional quality. The grain quality can be improved genetically through the improvement of grain quality components. Cooking quality is an important character that determines consumer preference (Malini *et al*., 2011).

Chemical forms of metals in soil and soil solution are closely related to the bioavailability and toxicity of metals in plant (Kim *et al.*, 2007). Various anthropogenic activities such as burning fossil fuel, mining and metallurgy, industries and transport sectors redistribute toxic heavy metals into the environment, which persist for a considerable longer period and are translocated to different components in environment affecting living things (Rajaganapathy *et al*., 2011).

There are no reports in the literature about any study on the levels of metals in commercially available imported and Ethiopian rice. Thus the objectives of the present study were to: (i) determine level of major, trace and toxic (Ca, Mg, K, Na, Fe, Mn, Zn, Cu, Co, Ni, Cr, Cd and Pb) metals in commercially available imported and Ethiopian rice, (ii) asses the cooking effect on metal levels, and (iii) compare the levels of metals in commercially available imported and Ethiopian rice with data obtained from other countries. This study reports the levels of major, trace and toxic (Ca, Mg, K, Na, Fe, Mn, Zn, Cu, Co, Ni, Cr, Cd and Pb) metals in commercially available imported and Ethiopian rice and their comparison with data reported from other countries. It also asses the cooking effect in levels of metals in the rice.

Materials and Methods

Instrumentation

Flame atomic absorption spectrometer (Buck Scientific Model 210VGP AAS, East Norwalk, USA) equipped with deuterium arc back ground correctors and hollow cathode lamps with air-acetylene flame was used for the determination of the analyte metals in raw and cooked rice samples. Round bottom flasks with ground glass joint (100 mL) fitted with reflux condenser were employed in digesting the sample on Kjeldahl heating apparatus (Gallenkamp, England).

Measuring cylinders (Duran, Germany), pipettes (Pyrex, USA), micropipettes (Dragonmed, 1-10 µL, 100-1000 µL, Shangai, China) were made use during measuring different quantities of volumes of sample solution, acid reagents and metal standard solutions.

Chemicals and reagents

Reagents that were used in the analysis were all analytical grade. (69-72%) HNO_3 (Spectrosol, BDH, England), 70% $HClO_4$ (Aldrich, A.C.S. Reagent, Germany) and H_2O_2 (30%) (BDH Chemicals, England) were used for digestion of rice samples. Lanthanum nitrate hydrate (98%, Aldrich, Muwaukee, USA) was used to avoid refractory interference (for releasing calcium and magnesium from their phosphates). Stock standard solutions containing 1000 mg/L, in 2% HNO_3, of the metals Ca, Mg, K, Na, Fe, Mn, Zn, Cu, Co, Ni, Cr, Cd and Pb (Buck Scientific Puro-Graphic^{tm}) were used for preparation of calibration standards and in the spiking experiments. Deionised water was used throughout the experiment for sample preparation, dilution and rinsing apparatus prior to analysis.

Sampling and pre-treatment

Sample sites were selected according to the areas in which rice is available to the users. Samples were collected from different sites. Basmati, Jasmine, Royal and Ethiopian white rice were collected from supermarkets in Addis Ababa. For Ethiopian red rice Fogera was selected to collect the sample because it is the main rice production area next to Metema found in Ethiopia. The last NERICA (New Rice for Africa) were collected from Amhara Regional Agricultural Research Institute (ARARI), Bahir Dar, Ethiopia. ARARI was selected because this rice variety is present in this institute in pure form but in other place exist with adulterant. 1 kg of each sample was collected from three subsample sites and mixed to form 3 kg bulk sample. 5 L tap water was collected from Addis Ababa in clean plastic polyethylene container (Jerican) for cooking the rice and for the determination of metal levels. 500 mL of tap water sample were filtered and preserved by adding 2% (v/v) nitric acid and kept in a refrigerator for metal determination.

All the raw rice samples were washed with tap water followed by deionised water to avoid any dust materials on the grain and dried until constant weight. The dried rice sample was then ground using a blender in the laboratory and sieved through a 0.457 mm sieve to remove large particles. Rice was cooked using absorption and excess method (Saleh and Meullenet, 2007). To assess the effect of cooking in metal level. About 135 g of Ethiopian white rice sample was cooked in tap water by absorption method which is most commonly practice in Ethiopia. After the cooking process was completed, the cooked rice was allowed drying up to constant weight. The dried sample was ground to obtain the required particle size.

Wet digestion of rice

For digestion purpose, 0.5 g of powdered and homogenized samples were weighed and transferred in to a 100 mL round bottom flask. To this, 2 mL concentrated HNO_3 (69-72%), 1 mL of $HClO_4$ (70%) and 0.5 mL of H_2O_2 (36 %) were added. The mixture was then digested on Kjeldahl digestion apparatus (Gallenkamp, England) fitting the flask to a reflux condenser by setting the temperature at 120^{o}C for 30 min followed by 210^{o}C for 120 min until a clear solution was obtained following the optimized digestion procedure. After a total of 2:20 h, the digested solutions were allowed to cool for 30 min without dismantling the condenser from the flask and for 10 min after removing the condenser. To the cooled solution, 2-5 mL portions of deionized water were added and gently swirled to reduce dissolution of the filter paper by digest residue. The cooled digested samples were filtered into a 50 mL standard volumetric flask with a Whatman filter paper (110 mm) to remove any suspended or turbid matter. Subsequent rinsing of the filtrate with 5 mL deionized water was followed until the volume reached the mark. At this point, the solution was clear and colorless. To each sample 1% 'matrix modifier' lanthanum nitrate hydrate were added so that lanthanum may bind the phosphate and liberate calcium and magnesium in case large phosphate exist in the sample. For each rice samples, triplicate digestions were carried out. Blank solutions were also digested accordingly in triplicate. The digested and diluted sample solutions were then kept in refrigerator until analysis. This digestion process was applied for the metal determination in the raw and cooked rice samples.

Figures of merit

The analytical wavelengths, the correlation coefficients, and the correlation equations of the calibration curves for the determination of metals in rice samples by FAAS are given in Table 1. The correlation coefficients of all the calibration curves were > 0.999 and these correlation coefficients showed that there was very good correlation (relationship) between concentration and absorbance. The method detection limits were calculated as the concentrations that give signals equal to three times

Table 1. Analytical parameters for the determination of metals in rice samples by FAAS

Metals	Wavelength (nm)	Method detection limit (mg/kg)	Correlation coefficient	Equation for calibration curves
Ca	422.7	0.7	0.9993	$Y = -2.09 \times 10^{-4} + 0.00167X$
Mg	285.2	0.03	0.9999	$Y = 3.44 \times 10^{-3} + 0.10344X$
K	766.5	0.07	0.9998	$Y = -1.18 \times 10^{-4} + 0.0084X$
Na	589	0.05	1.0000	$Y = 9.59 \times 10^{-4} + 1.07957X$
Fe	248.3	0.3	0.9995	$Y = -3.65 \times 10^{-3} + 0.00157X$
Mn	279.5	0.03	0.9999	$Y = 6.52 \times 10^{-1} + 0.0238X$
Zn	213.9	0.2	0.9997	$Y = -6.47 \times 10^{-4} + 0.11418X$
Cu	324.8	0.04	0.9999	$Y = 6.32 \times 10^{-4} + 0.02825X$
Co	240.7	0.2	0.9999	$Y = -1.38 \times 10^{-4} + 0.00913X$
Ni	232.0	0.1	0.9997	$Y = -1.27 \times 10^{-3} + 0.00699X$
Cr	357.9	0.2	0.9999	$Y = -1.93 \times 10^{-4} + 0.00916X$
Cd	228.9	0.3	0.9999	$Y = -1.50 \times 10^{-3} + 0.05516X$
Pb	283.2	1.8	0.9999	$Y = -1.02 \times 10^{-4} + 0.00259X$

the pooled standard deviations of the six blanks (Settle 1997; Fifeld and Kealey, 2000; Huber, 2007) and are given in Table 1. The method detection limits are low enough to detect the metals at trace levels.

Method validation for metal determination

The spiked samples were prepared by adding a small known quantity of metal standard solutions. The method validation of metal analysis was established by spiking experiments. Spiking procedure for raw rice was carried out as follow: from the stock solution 1000 mg/L 25 µL of Mg, 24 µL of Ca, 145 µL of K, and from 100 mg/L stock solution 44 µL of Cu solution were added to round bottomed flask (100 mL) containing 0.5 g rice sample. In the second round bottomed flask (100 mL), from 100 mg/L solution 108 µL of Ni, 111 µL of Na, 25 µL of Pb and from 10 mg/L solution 13 µL of Cd were added. In the third round bottomed flask (100 mL), from 100 mg/L solution 19 µL of Cr, 22 µL of Co, 115 µL of Fe, 15 µL of Mn and 73 µL of Zn solution were added. Similarly, spiking in the cooked rice, from 1000 mg/L stock standard solution 24 µL of Ca, 41 µL of K, 28 µL of Mg and from 100 mg/L stock solution 70 µL of Na were added in to 0.5 g sample present round bottomed flask (100 mL). 10 µL of Cu, 11 µL of Co, 22 µL of Ni, 20 µL of Fe, 16 µL of Cd and 10 µL of Cr from 100 mg/L stock solution added in to another round bottomed flask. 12 µL of Pb, 10 µL of Mn and 27 µL of Zn from 100 mg/L stock solution added into the third round bottomed flask. Then the samples were digested with the optimized procedures. After diluting the digested samples to 50 mL with distilled deionized water, they were analyzed by the same procedure followed for the analysis of rice sample. As used for original samples triplicate spiked samples were prepared and triplicate readings were recorded.

Results and Discussion

Recovery results of metal determination

The percentage recovery for raw and cooked rice samples were obtained with in the acceptable range (100 ± 10%) for all the metals except for Co and Pb in raw rice sample, for which recovery of 87% and 88%, respectively, were obtained. Similarly, for cooked rice sample, Co and Pb recoveries obtained were 89% and 86%, respectively. The lower recovery for the above elements may be attributed to the matrix analyte interaction which might be high and that is why their recovery values decreased.

Level of metals in raw rice samples

The levels of metals in raw rice samples are given in Table 2. From the whole rice analysed for metal level determination K was highest in concentration followed by Mg while Cd was lowest in concentration in the samples. This is because of metals such as K and Mg are mobile in to plant tissue (Marschner, 1995). As shown in Table 2 except in Royal and Jasmine variety of rice samples in all other

Table 2. Average level (mean ± SD, n = 9, mg/ kg dry weight) of metals in rice samples

Metal	Basmati rice	Jasmine rice	Royal rice	Ethiopian white rice	Ethiopian red rice	NERICA rice (New rice for Africa)
Ca	75.8±7.5	79.6±6.5	630±27	210±2	205±6	427±3
Mg	137±6	90.6±6	150±4	99.5±0.7	971±44	2,250±202
K	1,830±88	1,680±87	2,150±100	1,100±103	3,020±207	2,550±173
Na	73.8±3.1	78.6±1.3	70.6±1.3	74.6±0.7	26.7±1.4	80.9±4
Fe	49.5±3.9	48.9±4.8	117±1.8	108±8	113±10	41.3±1.7
Mn	4.7±0.4	4.11±0.2	15.5±0.8	3.7±0.3	16.6±0.5	16.1±0.8
Zn	25.7±2.1	20.9±0.3	16.4±0.4	51.6±0.2	16.7±0.2	140±9
Cu	3±0.2	2.7±0.09	4.9±0.3	15±1.3	3.3±0.02	3.6±0.01
Co	12.6±1.1	14.6±1.2	12.7±1.2	8.8±0.7	8.9±0.7	10.4±0.7
Ni	75.1±1.7	2.5±0.1	10.5±0.9	69.7±1.6	41.5±2.3	ND
Cr	3.12±0.05	2.2±0.05	ND	4.82±0.09	2.32±0.04	3.9±0.2
Cd	0.34±0.01	ND	ND	0.54±0.02	0.45±0.01	2.54±0.2
Pb	5.3±0.7	4.2±0.4	2.1±0.1	3.3±0.2	0.8±0.07	3.8±0.3

ND: Not detected, concentration of the tested metal was below the method detection limit

rice's toxic metals such as Cd and Pb was detected. A comparison done on the mean Pb and Cd content of the different types of rice showed that genetic makeup of the rice plant is an important factor in the absorption of the metals (Bakhtiarian *et al*., 2001). Pb and Cd cause accumulation and in the long term cause an insufficiency in different tissues and organs. The use of contaminated water in the rice fields causes an increase in the Pb and Cd content of the grains of rice and the consumption of this rice causes it to enter the body (Bakhtiarian *et al*., 2001).

Metals detected were found in Basmati rice in the order of K > Mg > Ca > Ni > Na > Fe > Zn > Co > Pb > Mn > Cr > Cu > Cd. The results showed that the sample contains the highest level of K with identified concentration 1,830 mg/kg followed by magnesium with a value of 137 mg/kg. The lowest concentration was found for toxic metal Cd which was 0.34 mg/kg. The trend in other rice samples also showed in the order as follows: Jasmine rice K > Mg > Ca > Na > Fe > Zn > Co > Pb > Mn > Cu > Ni > Cr. Ethiopia red rice K > Mg > Ca > Fe > Ni > Na > Zn > Mn > Co > Cu > Cr > Pb > Cd. NERICA rice K > Mg > Ca > Zn > Na > Fe > Mn > Co > Cr > Pb > Cu > Cd. In rice samples mentioned above from the trend of the metals the highest level was K followed by Mg and Ca. Their respective concentration were (1,680, 3,020, 2,550) mg/kg for K, (90.6, 970, 2,250) mg/kg for Mg and (79.6, 205, 427) mg/kg for Ca in Jasmine, Ethiopian red and NERICA rice, respectively. The lowest concentration in Ethiopian red rice and NERICA rice was Cd and the value obtained as 0.45 mg/kg and 2.54 mg/kg respectively. However, the lowest concentration in Jasmine rice was Cr with the value of 2.2 mg/kg and Cd was not detected that it gives value below the method detection limit. Similarly in NARICA rice Ni was below the method detection limit. In Royal and Ethiopian white rice concentration of metals are ranked in order of K > Ca > Mg > Fe > Na > Zn > Mn > Co > Ni > Cu > Pb and K > Ca > Fe > Mg > Na > Ni > Zn > Cu > Co > Cr > Mn > Pb > Cd, respectively. The highest level of metal in Royal and Ethiopian white rice was K followed by Ca with the value of (2,150, 1,100) mg/kg for K and (630, 210) mg/kg for Ca, respectively. The lowest concentration found in Royal rice was Pb 2.1 mg/kg. In this rice type Cr and Cd was not detected they were below the method detection limit. Cd provides the lowest concentration in Ethiopian white rice 0.54 mg/kg.

Level of metals in cooked rice and tap water used for cooking

Uptake of heavy metals by plants from soil and contamination of food by heavy metals during harvesting, transportation, storage, marketing and processing stages are major sources of heavy metals in foods (Othman, 2011). All selected thirteen metals

Table 3. Average concentration (mean ± SD, n = 9, mg/kg dry weight) of metals in cooked rice sample and tap water

Metals	Ethiopian white rice (cooked)	Tap water
Ca	240 ± 20	33.6 ± 2.8
Mg	130 ± 4	39 ± 2.8
K	1,010 ± 90	1.5 ± 0.6
Na	84.3 ± 4.7	12.3 ± 0.8
Fe	111 ± 3	14.8 ± 0.2
Mn	4.2 ± 0.3	1.22 ± 0.01
Zn	54.3 ± 4.9	6.5 ± 0.5
Cu	16.3 ± 1.1	2.2 ± 0.08
Co	7.7 ± 0.7	1.47 ± 0.02
Ni	70.1 ± 3.3	1.5 ± 0.06
Cr	4.06 ± 0.4	0.7 ± 0.04
Cd	0.6 ± 0.04	1.2 ± 0.05
Pb	3.6 ± 0.2	1.1 ± 0.1

Table 4. Range of concentration of imported and Ethiopian rice

Metals	Imported rice (mg/kg)	Ethiopian rice (mg/kg)
Ca	75.8-630	205-427
Mg	90.6-150	99.5-2,250
K	1,680-2,150	1,100-3,020
Na	70.6-78.6	26.7-80.9
Fe	48.9-117	41.3-113
Mn	4.1-15.5	3.7-16.6
Zn	16.4-25.7	15.6-140
Cu	2.7-4.9	3.3-15
Co	12.6-14.6	8.8-10.4
Ni	2.5-75.1	41.5-69.7
Cr	2.2-3.12	2.32-4.82
Cd	< 0.34	0.45-2.54
Pb	2.1-5.3	0.8-3.8

were detected by the same procedure as the raw rice. As shown in Table 3 the level of metals in decreasing order in cooked rice observed as K > Ca > Mg > Fe > Na > Ni >Zn > Cu > Co > Mn > Cr > Pb > Cd. However, the trend in raw rice were K > Ca > Fe > Mg > Na > Ni > Zn > Cu > Co > Cr > Mn > Pb > Cd. The trend in raw and cooked rice is not the same. The order of Mg and Fe and Mn and Cr in raw rice is interchanged in cooked rice. Moreover, the determination indicates that the level of the metal shows some increment except in K, Co and Cr. In general the difference between raw and cooked rice is not significant.

In tap water used to cook rice for their metal determination, metals which are major, trace and toxic (Ca, Mg, K, Na, Fe, Mn, Zn, Cu, Co, Ni, Cr, Cd and Pb) were also determined in it. Frequent use of heavy metal contaminated water in the agricultural fields leads to soil pollution and gradually enriched the soil with heavy metals (Bhaskar et al., 2010). The investigation of this study provide results in Table 3 which indicate that the pattern of concentration of metals in tap water were Mg > Ca > Fe > Na > Zn > Cu > Ni > K > Co > Mn > Ca > Pb > Cr.

Comparison of metals level in imported and Ethiopian rice

From the general view as shown in Table 4 most of metals range in imported rice included in the range of Ethiopian rice. The difference observed in the range of the metals between imported and Ethiopian rice indicates mainly that the species difference may causes such a difference. Since rice imported from abroad belonged to the species *Oryza sativa* but rice from Ethiopia belonged to species *Oryza glaberrima*.

Comparison of metals levels in this study with literature values

As the comparison in the Table 5 showed most of the values reported in the literature are comparable with the present study. Ca level in the literature (Zhang, 2009) is higher to some extent than the present study. Similarly in Mg metal (Zhang, 2009). Fe level in the present study was higher than reported in the literature (Mehdi *et al*., 2003; Yap *et al*., 2009). Mn (Mehdi *et al.*, 2003; Yap *et al*., 2009), Zn (Mehdi *et al*., 2003; Lin *et al*., 2004), Ni (Mehdi *et al*., 2003; Lin *et al.*, 2004), and Co (Fu *et al*., 2008) are relatively lower than the present study. However, Na in the literature (Zhang, 2009) is higher than the present study. Cr is higher (Lin *et al*., 2004; Frega, 2005) to some extent than result of the present study. Toxic metals Pb and Cd are higher in rice varieties in the present study than reported in the literature (Mehdi *et al*., 2003; Lin *et al*., 2004; Yap *et al*., 2009). This implies that the variety and the environmental condition are also the reason for the difference.

Analysis of variance

Variations in the mean levels of metals between the samples were tested whether it was from a random error or treatment. ANOVA use the F statistic

Table 5. Comparison of metals levels of the rice sample with values reported in literature

Metals	Rice variety	Concentration (mg/kg)	Origin	Reference
Ca	Basmati rice	800	United state	(Zhang, 2009)
	Basmati rice	500	India	(Zhang, 2009)
	Jasmine rice	200	United state	(Zhang, 2009)
	Black sweet rice	1,200	China	(Zhang, 2009)
	Ethiopian rice	198-427	Ethiopia	Present study
	Imported rice	76-630	Thailand & Pakistan	Present study
Mg	Basmati rice	10,000	United state	(Zhang, 2009)
	Basmati rice	2,000	India	(Zhang, 2009)
	Jasmine rice	900	United state	(Zhang, 2009)
	Black sweet rice	8,000	China	(Zhang, 2009)
	Ethiopian rice	99.5-2,249	Ethiopia	Present study
	Imported rice	90.6-149.5	Thailand & Pakistan	Present study
K	Basmati rice	10,000	United state	(Zhang, 2009)
	Basmati rice	11,000	India	(Zhang, 2009)
	Jasmine rice	12,000	United state	(Zhang, 2009)
	Black sweet rice	3,000	China	(Zhang, 2009)
	Ethiopian rice	1,101-3,025	Ethiopia	Present study
	Imported rice	1,679-2,145	Thailand & Pakistan	Present study
	Basmati rice	1,600	United state	(Zhang, 2009)
	Basmati rice	1,400	India	(Zhang, 2009)
Na	Jasmine rice	1,200	United state	(Zhang, 2009)
	Black sweet rice	2,200	China	(Zhang, 2009)
	Ethiopian rice	27.1-81	Ethiopia	Present study
	Imported rice	70-80	Thailand & Pakistan	Present study
Fe	Sabah rice	2.88	Malaysia	(Yap *et al*., 2009)
	Super Basmati rice	3.16	Pakistan	(Mehdi *et al*., 2003)
	Shahee Basmati rice	3.38	Pakistan	(Mehdi *et al*., 2003)
	Ethiopian rice	41-113	Ethiopia	Present study
	Imported rice	49-117	Thailand & Pakistan	Present study
Mn	Super Basmati rice	1.88	Pakistan	(Mehdi *et al*., 2003)
	Shahee Basmati rice	1.86	Pakistan	(Mehdi *et al*., 2003)
	Sabah rice	1.53	Malaysia	(Yap *et al*., 2009)
	Ethiopian rice	4-17	Ethiopia	Present study
	Imported rice	4-15.5	Thailand & Pakistan	Present study
Zn	Sabah rice	0.69	Malaysia	(Yap *et al*., 2009)
	Super Basmati rice	1.68	Pakistan	(Mehdi *et al*., 2003)
	Shahee Basmati rice	1.6	Pakistan	(Mehdi *et al*., 2003)
	Taiwan rice	13.1	Taiwan	(Fu *et al*., 2008)
	Ethiopian rice	17-140	Ethiopia	Present study
	Imported rice	16-21	Thailand & Pakistan	Present study
Cu	Sabah rice	0.312	Malaysia	(Yap *et al*., 2009)
	Taiwan rice	2.22	Taiwan	(Lin *et al*., 2004)
	Super Basmati rice	0.93	Pakistan	(Mehdi *et al*., 2003)
	Shahee Basmati rice	1.08	Pakistan	(Mehdi *et al*., 2003)
	Ethiopian rice	3.3-15	Ethiopia	Present study
	Imported rice	2.7-5	Thailand & Pakistan	Present study
Co	Taizhou rice	0.46	Taizhou	(Fu *et al*., 2008)
	Black sweet rice	0.29	China	(Fu *et al*., 2008)
	Ethiopian rice	9-78.9	Ethiopia	Present study
	Imported rice	13-15	Thailand & Pakistan	Present study
Ni	Taiwan rice	0.29	Taiwan	(Lin *et al*., 2004)
	Super Basmati rice	0.13	Pakistan	(Mehdi *et al*., 2003)

	Shahee Basmati rice	0.09	Pakistan	(Mehdi *et al*., 2003)
	Ethiopian rice	42-70	Ethiopia	Present study
	Imported rice	2.5-75	Thailand & Pakistan	Present study
Cr	Sabah rice	1.34	Malaysia	(Yap *et al*., 2009)
	Taiwan rice	0.1	Taiwan	(Lin *et al*., 2004)
	Ethiopian rice	2.3-4.8	Ethiopia	Present study
	Imported rice	2.2-3.12	Thailand & Pakistan	Present study
Cd	Sabah rice	0.18	Malaysia	(Yap *et al*., 2009)
	Taiwan rice	0.01	Taiwan	(Lin *et al*., 2004)
	Super Basmati rice	0.18	Pakistan	(Mehdi *et al*., 2003)
	Shahee Basmati rice	0.13	Pakistan	(Mehdi *et al*., 2003)
	Iranian rice	0.41	Iran	(Maleki *et al*., 2007)
	Ethiopian rice	0.25-0.45	Ethiopia	Present study
	Imported rice	< 0.34	Thailand & Pakistan	Present study
Pb	Sabah rice	ND	Malaysia	(Yap *et al*., 2009)
	Taiwan rice	0.01	Taiwan	(Lin *et al*., 2004)
	Super Basmati rice	2.95	Pakistan	(Mehdi *et al*., 2003)
	Shahee Basmati rice	2.89	Pakistan	(Mehdi *et al*., 2003)
	Ethiopian rice	0.8-3.8	Ethiopia	Present study
	Imported rice	2.1-5.3	Thailand & Pakistan	Present study

to compare whether the difference between sample means are significant or not (Miller and Miller, 2005). The result showed that for all metals, at the 95% confident level, the means were significantly different ($p < 0.05$). The source for this significant difference between sample means may be the difference in mineral contents of soil, pH of soil, pesticides and insecticides used during cultivation.

Conclusion

The levels of metals (Ca, Mg, K, Na, Fe, Mn, Zn, Cu, Co, Ni, Cr, Cd, and Pb) in three imported and three Ethiopian varieties of commercially available rice were determined. The wet digestion method and the determination of selected metals at trace levels in rice by flame atomic absorption method were found to be efficient, precise and accurate. The efficiency of sample preparation and instrument were tested by assessing standard deviation and conducting recovery experiments. K was highly accumulated in rice samples and toxic metal Cd was found to be the lowest. Comparison between levels of metals in the imported and Ethiopian rice showed significant differences for most of the metals. Analysis of variance showed that there was significant difference at 95% confidence level in the means of metal levels in the six rice samples. Comparison between levels of metals in cooked and raw rice showed that the difference in the level is not significant.

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