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## **Development of Mineral Profiles Including Heavy Metals of Selected, Widely Consuming Rice Varieties (Oryza Sativa L.) In Sri Lanka**

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#### **2. Keywords**

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### **1. Abstract**

Rice is the staple food of most Asian countries with fulfilling the daily nutritional requirements of humans. Therefore, this study was conducted to investigate the levels of concentration of 23 macro and micro elements in 30 selected rice varieties in Sri Lanka for development of minerals profiles including heavy metals. In general, the mean concentration pattern of elements in rice samples was decreased as, P >K >Mg >Ca >Zn >Mn>Fe>Na >B>Al >Cu >Ba >Mo >Cr >Co>Ni>Hg>As. The mean concentration of Sb, Be, Se, Cd, and Pb in rice were lower than the limit of quantification which was 0.05 mg/kg for each element. Mean concentration of Hg in Suduheenati was same as the maximum permissible limit given by WHO/FAO guideline. Moreover, the results of the present study revealed traditional and pigmented rice varieties in Sri Lanka to be a potential source of valuable minerals together with balanced level of other nutrients than branded and non-pigmented rice varieties (p<0.05).

#### **3. Introduction**

Rice is the most important cereal and the back bone of Sri Lankan agriculture since antiquity. Rice grains are a rich source of carbohydrate, fiber, protein, fats, oils, minerals and vitamins [1]. Among all nutritional attributes, minerals play a major role for human growth and development. Minerals can be found in adequate amounts in rice [2]. Even though, in present, rice may contain toxic elements including heavy metals or it may encompass essential elements which can be present more than recommended daily intake for human beings. This happens due to various anthropogenic activities including industrial processes, use of pesticides, chemical fertilizers and atmospheric decomposition. Excessive levels of macro and micro elements can be hazardous to human health and they may cause acute and chronic poisoning. Mainly, heavy metals are potential contaminants which can be accumulated through the food chains and they have a capability to produce different types of detrimental effects on human health [3]. Therefore, this study was conducted to analyze the composition of macro and micro elements of 10 traditional rice varieties and 20 branded and imported rice varieties which were available in

Sri Lanka. For the investigation of mineral levels in rice samples, laboratory validated, reliable analytical approaches were used with sufficient accuracy and precision using Inductively Coupled Plasma – Mass Spectrometer (ICP-MS) and UV-visible spectrophotometer.

According to the past studies, different analytical techniques including dryashing, Atomic Absorption Spectrophotometer (AAS)/ Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES), microwave digestion, AAS/ Inductively Coupled Plasma Mass Spectrometer (ICP-MS), microwave digestion/graphite furnace atomic spectrometer and instrumental neutron activation with k0 standardization were used only for determination of the content of several selected toxic elements in rice [4, 5]. But, when using ICP-MS, it can provide the information about the ratio of elemental isotopes, it has large linear dynamic range, elements can be analyzed with a good precision within a short time (about 1- 2minutes) with lower detection limits [6]. All rice samples were digested in a closed-vessel microwave digestor which is a determinative technique for complete digestion within a shorter time while preventing loss or contamination of the target analytes [7].

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Figure 1: Score plot for the principle compound analysis of mineral composition of traditional and branded rice samples.



**Figure 2:** Biplot for the principle compound analysis of mineral composition of traditional and branded rice samples.

#### **4. Materials and Methodology**

#### **4.1. Reagents and Chemicals**

For determination of metals, ultra-pure nitric acid (≥69%m/v HNO<sub>3</sub>, Merck-Darmstadt, Germany) was used for microwave digestion. Instrument tuning solution (100 µg/L) and internal standard solution (100µg/L) were prepared by diluting ICP-MS stock tuning solution and internal standard solution (10µg/ mL, Agilent technologies, USA). Calibration standard solutions were prepared using multi-element calibration standard 2A, 3 and 4 (10µg/mL, Agilent technologies, USA). Rice samples were



Figure 3: Score plot for the principle compound analysis of mineral composition of pigmented and non- pigmented rice samples.



Figure 4: Biplot for the principle compound analysis of mineral composition of pigmented and non- pigmented rice samples.

spiked using certified reference materials (CRMs – containing Al, Ba, Be, Ca, Mg, Na, K, Sb and B, 1000 mg/L, Sigma –Aldrich, Switzerland). For determination of phosphorous, potassium dihydrogen orthophosphate (99% m/m, BDH laboratory reagents, India) was used to prepare phosphate stock solution (1000 mg/L). Ammonium-meta-vanadate (99%m/m, Riedel-dehaen) and ammonium heptamolybdatetetrahydrate (99% m/m, Merck, Germany) were used for the colorimetric reaction. Nitric acid (69.0-72.0% m/v  $\text{HNO}_3$ , Research – Lab Fine Chem, Mumbai) and Hydrochloric acid (37% m/v HCl, ARISTAR, VMR) were used for acid digestion of the samples.



#### **Table 1:** Variation of physical properties of selected rice varieties in Sri Lanka

#### **4.2. Instruments**

All determinations of metals were carried out by Inductively Coupled Plasma – Mass Spectrometer (ICP-MS Agilent 7900, Japan). Phosphorous content in rice samples were determined by using UV- visible spectro photometer (UV-1800, Shimadzu). Samples were digested using a microwave digester (CEM MARS Xpress, model 240/50). Analytical balance (DENVER TP 214) was



**Table 2:** ICP- MS operating conditions.

used to weigh the samples with an accuracy of 0.0001 g.

#### **4.3. Sample Preparation for Determination of Elements in Rice**

30 rice samples were randomly selected from a local market in Sri Lanka for the analysis. For determination of metals, rice samples (about 0.5000 g) were digested in the microwave digester at 180°C for 30 minutes using nitric acid (10.0 mL). The digested solution was transferred to a volumetric flask (25.0 mL). Metal content of the samples were determined by ICP-MS. Details of the instrumental settings are given in (Table 1). For determination of phosphorous, the rice sample (about 2.0000 g) was ashed at 480˚C for 6 hours. Water (100.0 mL) was addedand was boiled. Conc. HCl (10.0 mL) and Conc.  $HNO<sub>3</sub>$  (10.0 mL) were added to the boiling solution. The solution was transferred to a volumetric flask (100.0 mL). Vanadomolybdate reagent was added and, absorbance was measured at 420 nmusing cell with a 1cm pathlength.

In present study, statistical analysis and graphical presentation were done using Microsoft Excel (version 2013) and Minitab software (version 16) respectively. The data were subjected for analysis of variance at 95% confidence level (ANOVA, p<0.05) with excel and

principal component analysis was carried out in order to determine relationships between traditional and branded rice varieties as well as pigmented and non-pigmented rice varieties.

#### **5. Results and Discussion**

Concentrations of selected macro and micro elements of thirty rice samples were given in the (Table 2). Reliable and accurate data were generated using the validated test methods. Recovery percentages for each element were within the range from 78.5% to 108%.

According to the results of the study, P, K and Mg were available in higher amounts compared to other elements considered during analysis of selected rice varieties. Phosphorous (P) was the most abundant element found in all rice varieties, which ranged from 0.130±0.015 % to 0.630± 0.075%. Basmathi contained the lowest P level while Dikwee comprised the highest amount of P. Godaheenati contained the highest K and Mg levels which were 0.430± 0.021 % and 0.108± 0.007 % respectively. Madathawalu contained the lowest K level which was 0.073±0.004% and Basmathi contained the lowest Mg level whichwas 0.014±0.001%.

All the traditional rice varieties contained Na in considerable levels. The lowest Na level of 2.52±0.15 mg/kg was found in Keeri samba 2 while the highest Na level of 5.95± 0.36 mg/kg was found in Godaheenati. The highest Ca level found was 192.90±11.57 mg/ kgin Red Samba and the lowest of 108.31±6.50 mg/kgwas found inNadu 4.

The highest B level detected was 7.90± 0.76 mg/kg in Nadu 4 and the lowest boron level detected was 0.40±0.04 mg/kg in Pachchaperumal. Madathawalu contained the highest Al level which was 4.10±0.36 mg/kg. Zn, Mn and Fe were the micro elements present at the highest levels in selected rice samples. The lowest Zn level of 11.60±0.56 mg/kg was found in red raw rice while the highest level of 46.30±2.22 mg/kg was found in Rathuheenati. The concentration range for Mn was from 2.10±0.10 to 39.60±1.78 mg/kg. The highest Mn content was found in Rathuheenati while the lowest Mn content was found in Keeri samba 2. The concentration range for Fe of selected rice samples was from 0.70±0.02 to 29.40±1.76 mg/kg. Rathuheenati contained the highest concentration of Fe while Nadu 1 contained the lowest concentration of Fe.

Cu and Mo content of rice varieties did not elicit a great variation except Dikwee, Godaheenati and Masuran. Godaheenati, Rathuheenati, Pachchaperumal and Suwandel contained As

**Table 3.** Concentrations of selected elements in analyzed rice samples.

Name	${\bf P}$					B		Sb		
of the	(as P2O5)	K $(\%)$	Mg $(\%)$	Na (mg/kg)	Ca (mg/kg)	(mg/kg)	Al (mg/kg)	(mg)	Be (mg/kg)	Ba (mg/kg)
variety	$(\%)$							kg)		
Dikwee	$0.630 \pm 0.075$	$0.288 \pm$	$0.072 +$	$4.93 \pm$	$116.21 \pm$	$1.50+$	$2.70+$	N.D.	$N. D. \le 0.05$	$0.40+$
		0.014	0.004	0.30	6.97	0.14	0.24	< 0.05		0.04
Goda heenati	$0.580 \pm 0.069$	$0.430 \pm$	$0.108 +$	$5.95\pm$	154.16±	$4.60 \pm$	$1.30+$	N.D.	$N. D. \le 0.05$	$0.70 +$
		0.021	0.007	0.36	9.25	0.44	0.11	< 0.05		0.06
Rathu heenati	$0.388 \pm 0.046$	$0.270 \pm$	$0.066 \pm$	$5.50+$	$129.65 \pm$	$5.50+$	$0.30+$	N.D.	N. D.	$0.30 \pm$
		0.013	0.004	0.33	7.78	0.53	0.03	< 0.05		0.03
	Sudu heenati $0.416 \pm 0.050$	$0.248 \pm$	$0.056\pm$	$5.58 +$	$150.21 \pm$	$4.20 +$	$2.30+$	N. D.	$N. D. \le 0.05$	$1.80 +$
		0.012	0.003	0.33	9.01	0.4	0.2	< 0.05		0.16
Pachcha-	$0.430 \pm 0.051$	$0.292 +$	$0.069 \pm$	$5.05 \pm$	$125.70 \pm$	$0.40+$	$1.50+$	N.D.	$N. D. \le 0.05$	$0.20 \pm$
perumal		0.014	0.004	0.30	7.54	0.04	0.13	< 0.05		0.02
Suwandel	$0.191 \pm 0.023$	$0.114\pm$	$0.014\pm$	$4.67 +$	148.62±	$5.00 \pm$	N. D.	N.D.	$N. D. \leq 0.05$	$0.60 \pm$
		0.005	0.001	0.28	8.92	0.48	< 0.5	< 0.05		0.05
Masuran	$0.380 \pm 0.045$	$0.215+$	$0.060 \pm$	$3.94 \pm$	154.16±	$4.57+$	$1.28 +$	N.D.	$N. D. \leq 0.05$	$0.67\pm$
		0.010	0.004	0.24	9.25	0.44	0.11	< 0.05		0.06
Herath banda	$0.420 \pm 0.050$	$0.124 +$	$0.037\pm$	$4.05 \pm$	$150.21 \pm$	$2.64 \pm$	$2.96 \pm$	N.D.	$N. D. \le 0.05$	$1.78 +$
		0.006	0.002	0.24	9.01	0.25	0.26	< 0.05		0.16
Mada-thawalu	$0.640 \pm 0.076$	$0.073\pm$	$0.043\pm$	$3.92 +$	144.67±	$6.11 \pm$	$4.10+$	N.D.	N. D. < 0.05	$0.36 +$
		0.004	0.003	0.24	8.68	0.59	0.36	< 0.05		0.03
Sulai	$0.420 \pm 0.050$	$0.087 +$	$0.041 \pm$	$2.56 \pm$	169.97±	$5.60 \pm$	$3.75 \pm$	N.D.	$N. D. \le 0.05$	$1.36 \pm$
		0.004	0.003	0.15	110.20	0.54	0.33	< 0.05		0.12
Red raw rice	$0.295 \pm 0.035$	$0.146 \pm$	$0.033\pm$	$4.11 \pm$	144.67±	$7.60 +$	$1.80 \pm$	N.D.	$N. D. \leq 0.05$	$0.30 \pm$
		0.007	0.002	0.25	8.68	0.73	0.16	< 0.05		0.03
Tempered Red samba	$0.356 \pm 0.042$	$0.156 \pm$	$0.039\pm$	$4.09 +$	169.97±	$6.90 +$	$0.60 \pm$	N.D.	$N. D. \leq 0.05$	$1.30 +$
		0.007	0.002	0.25	10.2	0.66	0.05	< 0.05		0.11
Red Nadu	$0.374 \pm 0.045$	$0.168 \pm$	$0.037 +$	$3.90 \pm$	$146.25 \pm$	$4.30+$	$3.70+$	N.D.	$N. D. \leq 0.05$	$0.50 \pm$
		0.008	0.002	0.23	8.78	0.41	0.33	< 0.05		0.04
Red samba	$0.422 \pm 0.050$	$0.160 \pm$	$0.041 \pm$	$5.92 +$	192.90±	$3.80 +$	N. D.	N.D.	$N. D. \leq 0.05$	$0.40 \pm$
		0.008	0.003	0.42	11.57	0.36	< 0.5	< 0.05		0.04
Rathu kekulu	$0.460 \pm 0.055$	$0.180 +$	$0.044\pm$	$4.84 +$	157.32±	$7.40+$	N.D.	N.D.	$N. D. \leq 0.05$	$0.80 +$
		0.009	0.003	0.29	9.44	0.71	< 0.5	< 0.05		0.07
Basmathi	$0.133 \pm 0.016$	$0.086 \pm$	$0.009\pm$	$5.23 \pm$	181.83±	$6.90 \pm$	N.D.	N.D.	$N. D. \leq 0.05$	$0.05 \pm 0$
		0.004	0.001	0.31	10.91	0.66	< 0.5	< 0.05		
White raw rice	$0.187 \pm 0.022$	$0.128 \pm$	$0.018\pm$	$3.12+$	134.39±	$4.60 \pm$	$1.00 \pm$	N.D.	$N. D. \le 0.05$	$0.40+$
		0.006	0.001	0.19	8.06	0.44	0.09	< 0.05		0.04
White sambaraw	$0.227 \pm 0.027$	$0.116 \pm$	$0.016\pm$	$3.21 \pm$	$176.29 \pm$	$2.10+$	N. D.	N.D.	N. D. < 0.05	$0.20 \pm$
		0.006	0.001	0.19	10.58	0.2	< 0.5	< 0.05		$0.02\,$
Nadu 1	$0.168 \pm 0.020$	$0.186 \pm$	$0.011 \pm$	$4.60 \pm$	$152.58 \pm$	$4.90 \pm$	$0.70+$	N. D.	$N. D. \leq 0.05$	$0.30\pm$
		0.009	0.001	0.28	9.15	0.47	0.06	< 0.05		0.03
Nadu 2	$0.249 \pm 0.030$	$0.182 +$	$0.025\pm$	$4.16\pm$	$171.55 \pm$	$5.60 \pm$	$1.40 \pm$	N.D.	$N. D. \leq 0.05$	$0.30+$
		0.009	0.002	0.25	10.29	0.54	0.12	< 0.05		0.03
Nadu 3	$0.183 \pm 0.022$	$0.180 \pm$	$0.010\pm$	$3.33\pm$	$114.63 \pm$	$7.50 \pm$	$0.80 +$	N. D.	$N. D. \leq 0.05$	$0.30\pm$
		0.009	0.001	0.2	6.88	0.72	0.07	< 0.05		0.03
Nadu 4	$0.130 \pm 0.015$	$0.172+$	$0.009\pm$	$3.58 \pm$	$108.31\pm$	$7.90 \pm$	N.D.	N. D.	$N. D. \leq 0.05$	$0.20 \pm$
		0.08	0.001	0.21	6.5	0.76	< 0.5	< 0.05		$0.02\,$
Nadu 5	$0.215 \pm 0.026$	$0.180 \pm$	$0.011\pm$	$3.05 \pm$	119.37±	$1.40 \pm$	N.D.	N. D.	$N. D. \leq 0.05$	$0.40+$
		0.009	0.001	0.18	7.16	0.13	< 0.05	< 0.05		0.04
Samba 1	$0.152 \pm 0.018$	$0.132 +$	$0.010 \pm$	$4.17 +$	$146.25 \pm$	$5.20 \pm$	N.D.	N.D.	$N. D. \leq 0.05$	$0.30\pm$
		0.006	0.001	0.25	8.78	0.5	< 0.5	< 0.05		0.03







in a considerable level of concentration which did not exceed the maximum permissible limit in rice which is 0.2 mg/kg given by WHO/FAO guideline of As in rice [8]. The maximum concentration of Hg of analyzed rice samples was same to the maximum permissible limit in rice given by WHO/FAO guideline of Hg in rice which was 0.1 mg/kg. Concentrations of Be, Sb, Cd, Se and Pb were lower than the Limit of Quantification (LoQ) of the test method which was 0.05 mg/kg for each element.

Significant differences (p<0.05) were observed in the content of P as  $P_2O_5$ , Na, Mg, Ba, Mn, Fe, Zn of traditional and branded rice varieties. There were no any significant differences (p<0.05) the content of K, Ca, B and Cu of traditional and branded rice varieties. As the same way, there were significant differences (p<0.05) between the content of P as  $P_2O_5$ , Na, Mg, Ba, Mn, Fe, Zn of pigmented and non-pigmented rice varieties. There were no any significant differences (p<0.05) the content of K, Ca, B and Cu of pigmented and non-pigmented rice varieties.

In the (Figure 1 and 2), it is noted that the most of the traditional rice varieties and minerals are mapped on the area with positive loading in the first component (PC1). In other words, traditional rice varieties are associated with higher mineral concentrations than the branded rice varieties. In the (Figure 3 and 4), it is noted that the most of the pigmented rice varieties and minerals are mapped on the area with positive loading in the first component (PC1). In other words, pigmented rice varieties are associated with higher mineral concentrations than the non-pigmented rice varieties.

The levels of micronutrients in rice including Fe, Mn and Zn can be decreased due to usage of different steps in the post production of rice such as milling or polishing, and parboiling [9]. Fe, Mn and Zn are localized in different parts of rice grains being concentrated in the aleurone, embryo and endosperm. With the removal of aleurone and embryo during milling or polishing process, Fe,

Mn and Zn contents in rice grains are reduced [10]. Fe and Zn deficiencies are the most common micronutrient deficiencies in humans around the world. Rice is used as the main staple food in the most of Asian countries, improving iron and zinc content and bioavailability in rice grains is the most effective way to solve this problem. As reported data in United States Department of Agriculture (USDA), white, long-grain, raw rice contains 8 mg/kg of Fe. Through bio-fortification including conventional breeding or genetic engineering, International Rice Research Institute (IRRI) developed rice lines with an average iron content ranging from 12–15 mg/kg in the milled rice grains and 40–45 mg/kg of Zn.

According to this study, concentrations of iron in Sri Lankan traditional rice varieties were in high levels which were more than two times richer when comparing with the rice lines developed by IRRI. Therefore, without performing the bio-fortification, Sri Lankan traditional rice varieties can be used as a rich iron source to fulfill the daily nutritional requirement of iron. These traditional rice varieties may also be used as a good source for bio-fortification or genetic engineering to increase the grain iron level to minimize iron deficiency.

There are several reasons for increased iron levels in rice grains. They may be usage of inorganic fertilizers in high levels, accumulation of iron in rice grains due to long growing period (long – duration varieties) before harvesting or naturally these varieties can absorb and utilize a high amount of iron under acidic or saline soil conditions.

#### **6. Conclusion**

The mean concentration pattern of elements in studied rice samples was decreased as, P >K >Mg >Ca >Zn >Mn>Fe >Na >B >Al >Cu >Ba >Mo >Cr >Co >Ni >Hg >As. The mean concentration of Sb, Be, Se, Cd, and Pb in rice samples were lower than the limit of quantification which was 0.05 mg/kg for each element. Traditional

rice varieties were richer in minerals including P as  $P_2O_5$ , Na, Mg, Ba, Mn, Fe and Zn than branded rice varieties. Therefore, traditional rice varieties are good sources of most of the daily mineral requirement of human than branded rice varieties in Sri Lanka. Pigmented rice has more nutritional value than nonpigmented rice according to generated results. Widely consuming rice cultivars in Sri Lanka are quite safe from heavy metals contamination.

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