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2025
European Journal of Nutrition & Food Safety
https://ir-library.kabianga.ac.ke/handle/123456789/1211
Kiplangat, Paul, Joyce Kiplimo, Benard A. Ouna, Emily Cheshari, and Job Mapesa. 2025. “Comparative Analysis of Metal Elements in Rice Bran from Selected Regions of Kenya”. European Journal of Nutrition & Food Safety 17 (6):253-62. https://doi.org/10.9734/ejnfs/2025/v17i61754.

European Journal of Nutrition & Food Safety

Volume 17, Issue 6, Page 253-262, 2025; Article no.EJNFS.138549
ISSN: 2347-5641

Comparative Analysis of Metal Elements in Rice Bran from Selected Regions of Kenya

Paul Kiplangat [a], Joyce Kiplimo [a], Benard A. Ouna [b*], Emily Cheshari [b] and Job Mapesa [c]

[a] Department of Physical Sciences, University of Kabianga, Kenya.
[b] Department of Chemistry and Biochemistry, Laikipia University, Kenya.
[c] Department of Public Health, Human nutrition and Dietetics, School of Health Sciences Kenya Methodist University, Kenya.

Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Article Information

DOI: https://doi.org/10.9734/ejnfs/2025/v17i61754

Open Peer Review History:
This journal follows the Advanced Open Peer Review policy. Identity of the Reviewers, Editor(s) and additional Reviewers, peer review comments, different versions of the manuscript, comments of the editors, etc are available here: https://pr.sdiarticle5.com/review-history/138549

Original Research Article

Received: 17/04/2025
Accepted: 19/06/2025
Published: 23/06/2025

ABSTRACT

Aims: Rice bran a by-product of rice milling holds significant nutritional and health value to humans and livestock. However it can accumulate both nutritionally important and toxic metal elements and therefore realization of the nutritional benefits while minimizing potential toxic effects is important. To shed light on this, profiling of metal elements was done.
Study Design: A comparative research design was adopted for this study.
Place and Duration of Study: Rice samples were collected and milled at Lungalunga, Mwea and Ahero in Kenya and analyzed at the Analytical Chemistry laboratory of the Kenya Plant Health Inspectorate Service (KEPHIS) between July 2023 and January 2024.

**Corresponding author: Email: bao.ouna@gmail.com;*

***Cite as:** Kiplangat, Paul, Joyce Kiplimo, Benard A. Ouna, Emily Cheshari, and Job Mapesa. 2025. "Comparative Analysis of Metal Elements in Rice Bran from Selected Regions of Kenya". European Journal of Nutrition & Food Safety 17 (6):253-62. https://doi.org/10.9734/ejnfs/2025/v17i61754.*

Methodology: A total of 18 rice bran samples, six from each of these study regions were analyzed using Inductively Coupled Plasma Optical Emission Spectrometry (ICP- OES).
Results: Rice bran from Lungalunga had the highest amount of Potassium (15148.94mg/Kg), Manganese (290.26mg/Kg), Zinc (76.56mg/Kg), Copper (11.76mg/Kg), Arsenic (0.77mg/Kg) and, the only samples in which Cadmium (0.01mg/Kg) was detected. On the other hand, rice bran from Mwea had the highest amounts of Magnesium (6628.62mg/Kg) and Selenium (2.23mg/Kg) while that from Ahero had the highest amounts of Iron (269.64mg/Kg) and Chromium (2.41mg/Kg). Other than the levels of Magnesium and Zinc from Ahero which were significantly lower than that from the other two regions and; Chromium from Ahero which was significantly higher than that from Mwea, all the others did not vary significantly (p=0.05). Mercury and Lead were not detected in any sample.
Conclusion: Kenyan rice bran contains high amounts of nutritionally important metal elements that can be used to enrich food and feeds. However, levels of Arsenic which is toxic were higher than the Codex limit for husked and polished rice and; for cereal foods. This calls for quality control and surveillance measures that guarantee health benefits and food safety.

Keywords: Rice bran; food; feed; toxic; metal elements; nutritionally important.

1. INTRODUCTION

Rice is cultivated in several parts of Kenya including Mwea, Ahero, Bura, Lungalunga, Bunyala, and Migori—mainly through irrigation. It is also grown under rain-fed conditions in regions like Kakamega (Atera et al., 2018). Harvested rice is normally milled producing husks and brown rice which is further polished generating white rice and rice bran (Lantin, 1999). The chemical composition of rice and its by-products is influenced by bioaccumulation, which depends on factors such as the quality of irrigation water, fertilizers, industrial and human activities, and soil geology (Hasan et al., 2022) (Scutarașu & Trincă, 2023) (Arunrat et al., 2024).

Studies on both white and brown rice in countries like the US, Thailand, Italy, and India have reported the presence of various metals, including Arsenic (As), Lead (Pb), Cadmium (Cd), Manganese (Mn), Copper (Cu), Zinc (Zn), Iron (Fe), Magnesium (Mg), Calcium (Ca), and Potassium (K), The ranges in concentrations of these metals on brown rice which habour rice bran was: As- 139-403µg/Kg, Pb- 1.4–34µg/Kg, Cd- 7.7-65µg/Kg, Zn- 15-23mg/Kg, Cu- 2.24-4.77mg/Kg, Mn- 18-35mg/Kg, Fe- 7-16mg/Kg, Mg- 937-1410mg/Kg, Ca- 64-116mg/Kg and K-1981-3003mg/Kg (TatahMentan et al., 2020). Similarly in rice bran, K (14850.0mg/Kg), Mg (7810.0mg/Kg), Mn (142.1mg/Kg), Zn (60.4mg/Kg), Fe (185.4mg/Kg), and Se (0.156mg/Kg) have been reported (Sapwarobol et al., 2021). In addition, As (<5µg/Kg), Cd (<50µg/Kg), Pb (<500µg/Kg) and; Cr (30µg/Kg) were reported in rice bran in Bangladesh (Haque et al., 2021). Earlier studies on rice bran sampled from Kenya and USA reported Fe at 75mg/Kg (Mwea) and 97mg/Kg (RiBran USA); Zn at 46mg/Kg (Mwea) and 53mg/Kg RiBran USA); As at 0.12mg/Kg (Mwea) 0.86mg/Kg (RiBran USA); Cd and Pb each at <0.1mg/Kg (Mwea and RiBranUSA) (Kinyuru et al., 2015). Some of these metals such as Mg, Ca, Cu, Mn, Zn and Fe among others are required for structural stability or as cofactors by metalloproteins which carry out important physiological processes including catalysis and regulation of gene expression (Permyakov, 2021) (Ouna, 2025). Though such metals are nutritionally and medically important (Muhande et al., 2024); however excessive intake can be toxic (Jomova et al., 2022). Therefore a balance between nutritious and toxic effects is important. This underscores the need to monitor their concentrations in food and animal feed ingredients.

On the others hand, heavy metals such as Hg, Cd, Cr, As and Pb among others, are known to be highly toxic when consumed above safety limits or for long (Scutarașu & Trincă, 2023) (Wei et al., 2023). Their toxicity damages the mammalian nervous system (Hg, Pb and As); kidney (Hg, Cr and Cd), liver (Hg, Pb, Cd and As), lungs (Pb and Cd), skin (As and Cr) and gastrointestinal tract (Hg, Pb, Cr, Cd and As) among others (Balali-Mood et al., 2021) (Permyakov, 2021) (Jomova et al., 2022) (Scutarașu & Trincă, 2023). Consequently, to minimize these detrimental health effects, Codex Alimentarius set maximum safety limits for rice as follows: As- 200µg/Kg for polished and 350µg/Kg for husked rice; Cd- 400µg/Kg for polished and unpolished rice and; Pb- 20µg/Kg for cereal foods (CODEX, n.d.). It's therefore important to know the content of toxic metals in human food and animal feeds. Though several studies determining metal profiles of rice have been done in several countries (Wei et al., 2023)

(TatahMentan et al., 2020), similar studies on rice bran are still few.

Rice bran is mainly used in the production of animal feeds. Several recent studies have found stabilized rice bran to be nutritious and of health benefit (Kinyuru et al., 2015) (Sapwarobol et al., 2021) (Zambrana et al., 2021) (Manzoor et al., 2023) and as such efforts aiming at integrating it in human diet are underway (Saji et al., 2020) (El-Rahman, 2023) (Odingo et al., 2025). Successful extraction of rice bran oil and other biomolecules for human and industrial use have also been reported (Pal & Pratap, 2017) (Nidhishree et al., 2024) (Future markets, n.d.). Though these initial studies have demonstrated a high potential for rice bran value addition, key to its realization, is research on its nutritional value and safety. This study therefore evaluated the content of toxic heavy metal elements: Cr, As, Cd, Hg and Pb and; nutritionally important metal elements: Mg, K, Mn, Fe, Cu, Zn and Se in Kenyan rice bran from Mwea, Ahero and Lungalunga using Inductively Coupled Plasma Optical Emission Spectrometry (ICP- OES).

2. MATERIALS AND METHODS

2.1 Sampling

Paddy rice samples were obtained from Mwea, coordinate- 37° 21' 14" East and 0° 42' 55" South; Ahero, coordinate- 34° 55' 0" East and 0° 11' 0" South and; Lungalunga, coordinate- 39° 7' 0" East and 4° 33' 0" South. Convenient sampling of farmers at an interval of 2-5km was done on the basis of their availability and willingness to sale 5Kg of their paddy rice. A total of 6 samples (3 from Thiba North and 3 from Thiba South) were picked from Mwea. An equal number (3 from Muhoroni and 3 from Nyando) was picked from Ahero while another 6 samples were picked from (Jego, Kiwengu and Tsuini) Lungalunga bringing the total to 18 samples. Each sample was labeled and milled in a single local mill capable of separating rice mill products. To avoid cross- contamination, the mill was cleaned before milling of each sample and the resultant rice bran was collected directly into a new Kraft paper. Rice bran samples were labeled with the same field codes. All samples were then shipped to the Analytical Chemistry laboratory of the Kenya Plant Health Inspectorate Service (KEPHIS) Nairobi Kenya where they were stored at ambient room temperature before analysis on a private contract. The whole study was done between July 2023 and January 2024.

2.2 Sample Processing

Sample digestion was done as described by Runge et al., (2019). Briefly, 0.5g of each rice bran sample was weighed and digested using nitric acid at 200°C for two hours in a High Performance Microwave digestion system. Digested samples were covered and let to stand for about 12 hours. The extract was put in a 250 ml volumetric flask and diluted to the mark using grade 2 de-ionized water.

Standards for each metal were sourced from Merck kGaA Darmstadt EMD Millipore Corporation Germany and prepared in 5% nitric acid. Fresh standards of 10, 5 and 1mg/Kg, 500, 100, 10 and 1µg/Kg were prepared by serial dilution of a 10mg/Kg stock solution of each metal standard and used to calibrate the ICP OES instrument. Spiked samples of 100µg/Kg and 10mg/Kg for every test metal were prepared in a similar manner.

2.3 Detection and Quantitation of Metal Elements

Detection and quantitation of metal elements was done using Thermoscientific iCap 7000 ICP-OES (Germany) (Runge et al., 2019) using a standard procedure from the manufacture. Optical emission data was acquired using the following Qtegra software parameters: Purge gas flow was set at trickle, auxiliary gas flow at 0.5 L/min, coolant gas flow at 12 L/min and nebulizer gas pressure at 460 kPa.

2.4 Data Analysis

Obtained data was exported into Microsoft Excel (Microsoft Corporation, USA) which was used to organize data and compute descriptive statistics, including mean concentrations, standard deviations, and ranges for each metal element across the three study regions and; generation of bar graphs. To determine whether the differences in the mean concentrations of metal elements among the three regions were statistically significant, a one-way Analysis of Variance (ANOVA) was conducted using the IBM SPSS Statistics version 26 (IBM Corp., Armonk, NY, USA).

3. RESULTS AND DISCUSSION

To detect and quantify metal elements in rice bran, six samples from each region were analyzed using ICP OES. Instrument calibration using standards for each metal element revealed accurate measurement as depicted in the representative calibration curves presented in Fig. 1.

All tested nutritionally important metal elements (K, Mg, Mn, Fe, Cu, Zn and Se) were detected at various concentrations in various samples. Potassium was detected in all samples (Table 1) at between 11889.57-19220.69mg/Kg (Lunga-lunga), 13646.77-15074.65mg/Kg (Mwea) and 9091.32-19518.76mg/Kg (Ahero) and; was the most abundant metal element in all regions with the highest mean (Fig. 2a) value of 15148.94±3048.08mg/Kg (Lungalunga) followed by 14489.01±525.78mg/Kg (Mwea) and 11750.38±3898.92mg/Kg (Ahero), though this variation was not significant (p=0.05) across the three regions. Magnesium was also detected in all samples (Table 1) at between 5479-7096.05mg/Kg (Lungalunga), 6065.54-8040.05-mg/Kg (Mwea) and 3970.93-4756.27mg/Kg (Ahero) and was the second most abundant metal (Fig. 2a). Its highest mean level of 6628.62±721.75mg/Kg (Fig. 2a), was detected in rice bran from Mwea followed by 6185.80-±693.43mg/Kg (Lungalunga) and 4355.38±285.00mg/Kg (Ahero), which was significantly lower (p=0.05) than the other two.

Manganese was also detected in all samples from all regions (Table 1) at 138.23-398.44mg/Kg (Lungalunga), 129.7-545.81mg/Kg (Mwea) and 161.45-372.79mg/Kg (Ahero). It was the next most abundant metal with a highest mean (Fig. 2b) value of 290.26±86.97mg/Kg (Lungalunga) followed by 251.40±89.04mg/Kg (Ahero) and 243.56±162.02mg/Kg (Mwea). There was no significant difference (p=0.05) among these means. Iron which was the next most abundant metal was also detected in all samples from all regions (Table 1) at concentration ranging from: 174.42-472.56mg/Kg (Ahero), 115.13-545.81mg/Kg (Mwea) and 81.19-106.72mg/Kg (Lungalunga). Rice bran from Ahero had the highest mean (Fig. 2b) value of 269.64±111.02mg/Kg, followed by 232.63±168.14mg/Kg and 95.37±11.64mg/Kg in rice bran from Mwea and Lungalunga respectively. These variation in means was not significant (p=0.05) across these regions.

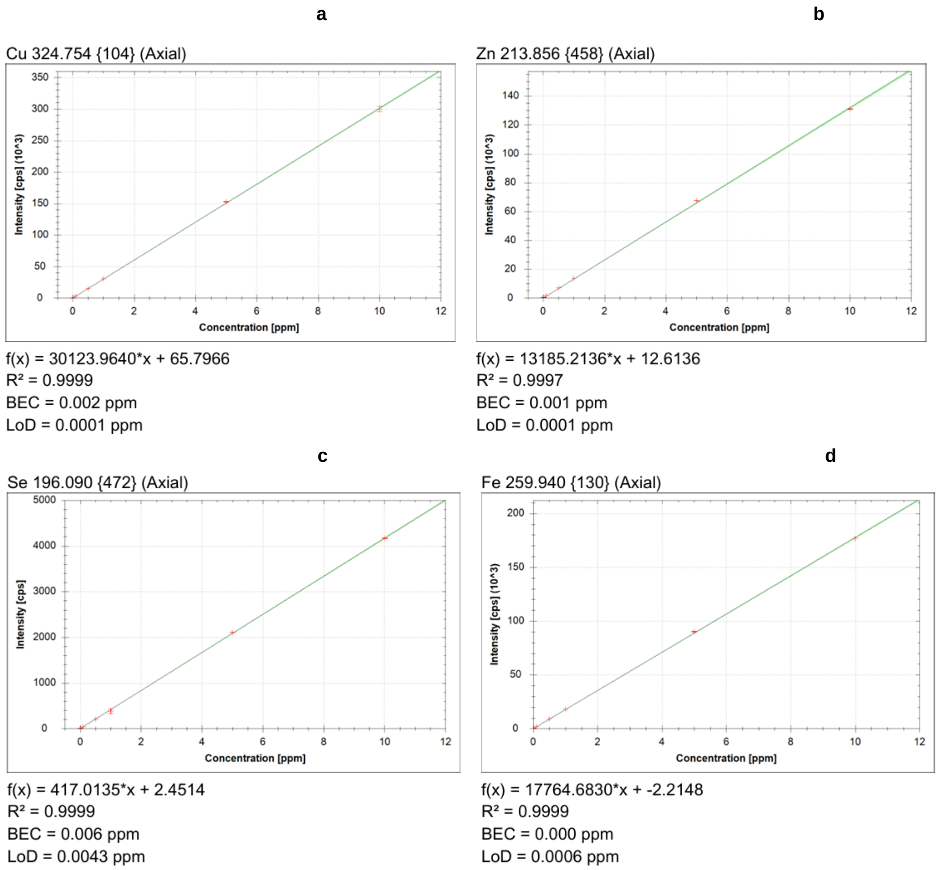

Fig. 1. ICP OES calibration curves. a) calibration curve for copper, b) calibration curve for zinc, c) calibration curve for selenium and d) calibration curve for iron

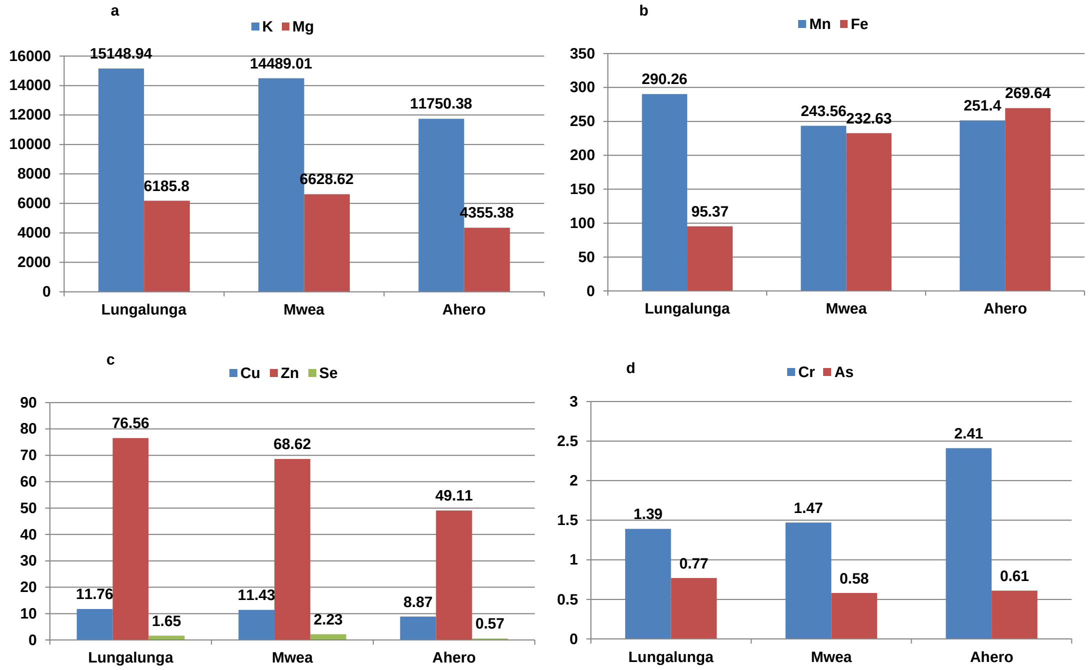

Fig. 2. Regional variation of metals in rice bran. a) variation of Potassium and Magnesium, b) variation of Manganese and Iron, c) variation of copper, zinc and selenium d) variation of chromium and arsenic

The concentration of Zinc which was also detected in all samples (Table 1) ranged from 71.08-81.45mg/Kg (Lungalunga), 56.86-77.78mg/Kg (Mwea) and 40.73-56.36 (Ahero). It had the next highest concentration with the highest mean (Fig. 2c) of 76.56±3.77mg/Kg in rice bran from Lungalunga followed by 68.62±6.75mg/Kg (Mwea) and 49.11±5.85mg/Kg (Ahero). The mean levels in rice bran from Ahero were significantly lower (p=0.05) than that in the other two regions. On the other hand, Copper which was also detected in all samples (Table 1) from all regions had its levels ranging from: 8.67-14.49mg/Kg (Mwea), 8.36-14.52mg/Kg (Lungalunga) and 7.46-10.33mg/Kg (Ahero). It was the next most abundant with the highest mean of 11.76±2.16mg/Kg (Fig. 2c) in rice bran from Lungalunga with no significant difference (p=0.05) compared to 11.43±2.58mg/Kg and 8.87±1.11mg/Kg in rice bran from Mwea and Ahero respectively. Selenium which was the least abundant metal in this category (Fig. 2c) was detected in the range of 0.8-11.52mg/Kg, 0.22-6.2mg/Kg, 0.8-11.52mg/Kg respectively in 50%, (n=6), 83.3%, (n=6) and 100%, (n=6) of samples from Mwea, Lungalunga and Ahero. Again there was no significant difference (p=0.05) among the means of 2.23±4.58, 1.65±2.31 and 0.57±0.46mg/Kg in rice bran from Mwea, Lungalunga and Ahero (Fig. 2c) respectively.

Analysis of toxic metal elements (Cr, As, Cd, Hg and Pb) detected Chromium and Arsenic in all tested rice bran samples from all studied regions (Table 2). Chromium was the most abundant (Fig. 2d) with sample concentrations (Table 2) ranging from 1.58-3.79mg/Kg, 1.13-1.85mg/Kg and 1.14-1.58mg/Kg in samples from Ahero, Mwea and Lungalunga respectively. The highest mean was 2.41±0.84mg/Kg (Fig. 2d) in rice bran from Ahero followed by 1.47±0.25mg/Kg and 1.39±0.20mg/Kg in rice bran from Mea and Lungalunga respectively. The variation between mean concentrations in samples from Ahero and Mwea was statistically significant (p=0.05). The levels of Arsenic (Table 2) ranged from 0.64-0.92mg/Kg, 0.50-0.83mg/Kg and 0.43-0.72mg/Kg in samples from Lungalunga, Ahero and Mwea respectively. The highest mean level of 0.77±0.10mg/Kg (Fig. 2d) was detected in rice bran from Lungalunga followed by 0.61±0.13mg/Kg and 0.58±0.11mg/Kg from Ahero and Mwea respectively. The difference among these means was not significant (p=0.05). Cadmium was detected (Table 2) at an average of 0.01±0.02mg/Kg in a few samples, (33.3%, n=6) from Lungalunga at between 0.02-0.04mg/Kg. None was detected in samples from Ahero (n=6) and Mwea (n=6). Mercury and Lead were not detected in any of the analyzed samples.

Table 1. Levels of nutritionally important metal elements in rice bran from different regions of Kenya

Region	**Nutritious metals Min-Max in mg/Kg (%; n)**						
Metal	**K**	**Mg**	**Mn**	**Fe**	**Cu**	**Zn**	**Se**
Lungalunga	11889.57-19220.69 (100; 6)	5479-7096.05 (100; 6)	138.23-398.44 (100; 6)	81.19-106.72 (100; 6)	8.36-14.52 (100; 6)	71.08-81.45 (100; 6)	0.22- 6.2 (83.3; 6)
Mwea	13646.77-15074.65 (100; 6)	6065.54- 8040.05 (100; 6)	129.7- 545.81 (100; 6)	115.13- 545.81 (100; 6)	8.67- 14.49 (100; 6)	56.86- 77.78 (100; 6)	0.8-11.52 (50;6)
Ahero	9091.32-19518.76 (100; 6)	3970.93- 4756.27 (100; 6)	161.45- 372.79 (100; 6)	174.42- 472.56 (100; 6)	7.46- 10.33 (100; 6)	40.73- 56.36 (100; 6)	0.31- 1.49 (100; 6)

NB: % is the percentage of samples in which a metal element was detected; n is the total number of tested samples in that region.

Table 2. Levels of toxic metal elements in rice bran from different regions of Kenya

Region	Toxic metals Min- Max in mg/Kg (%; n)				
Metal	**Cr**	**As**	**Cd**	**Hg**	**Pb**
Lungalunga	1.14 - 1.58 (100; 6)	0.64 - 0.92 (100; 6)	0.02– 0.04 (33.33; 6)	nd (0; 6)	nd (0; 6)
Mwea	1.13 – 1.85 (100; 6)	0.43 – 0.72 (100; 6)	nd (0; 6)	nd (0; 6)	nd (0; 6)
Ahero	1.58 – 3.79 (100; 6)	(0.50 – 0.83 (100; 6)	nd (0; 6)	nd (0; 6)	nd (0; 6)

NB: % is the percentage of samples in which a metal element was detected; n is the total number of tested samples in that region and; nd is not detected

The mean levels of tested nutritionally important metal elements were far higher than those in reports. The mean levels of Iron (95.37-269.64mg/Kg) were higher than 75mg/Kg and 97mg/Kg reported in rice bran from Mwea and RiBran USA respectively (Kinyuru et al., 2015) but within the 185.4mg/Kg reported by Sapwarobol et al. (2021). Similarly, detected levels (49.11-75.56mg/Kg) of Zinc were higher than 46 and 53mg/Kg reported from rice bran from Mwea and RiBran USA (Kinyuru et al., 2015). Again in contrast, these means compares well with a value of 60.5mg/Kg for this metal element in rice bran (Sapwarobol et al., 2021). In same vein, the mean levels of Potassium (11750.38-15148.94mg/Kg), reported in this study are in agreement with the 14850.0mg/Kg, reported by Sapwarobol et al. (2021). However levels of Magnesium (4355.38-6628.62mg/Kg) were lower than the 7810.0mg/Kg (Sapwarobol et al., 2021) while means for Manganese (255.3-284.8) and Selenium (0.7-3.1mg/Kg) were respectively higher than 142.1mg/Kg and 0.156mg/Kg in reports (Sapwarobol et al., 2021). Again the levels of Cu (8.9- 11.7mg/Kg in this study are higher than 2.24-4.77mg/Kg reported for brown rice (TatahMentan et al., 2020). Various nutritionally important metals are widely used as food and feed supplement and management of various health conditions among others (Jomova et al., 2022) (Muhande et al., 2024). Therefore their detection in rice bran in high amounts offers an opportunity for its utilization in food and feed supplementation. However, since excessive intake of any metal element can cause toxicity (Jomova et al., 2022), determination and recommendation of dietary intake is important.

A comparison between these results and published data and Codex limits on toxic metal elements revealed that the mean levels of detected Chromium which ranged from 1.39-2.41mg/Kg were higher than the 30µg/Kg reported in rice bran from Bangladesh (Haque et al., 2021). The means for Arsenic which ranged between 0.58-0.77mg/Kg were far much higher than: 0.12mg/Kg in rice bran from Mwea (Kinyuru et al., 2015); <5µg/Kg reported in rice bran from Bangladesh (Haque et al., 2021); brown rice 139-403µg/Kg (TatahMentan et al., 2020) and Codex limits for both polished (200µg/Kg) and husked rice (350µg/Kg) (CODEX, n.d.). However these values were less than 0.86mg/Kg reported in RiBran rice bran from USA (Kinyuru et al., 2015). Excessive consumption of Arsenic can lead to neurological, hepatological and dermatological dysfunction among others (Balali-Mood et al., 2021). Therefore, these high levels of Arsenic call for caution during food and feed formulation. On the other hand, levels of Cadmium in rice bran from Lungalunga (0.01mg/Kg) was within <0.1mg/Kg and <50µg/Kg reported in rice bran from Mwea and RiBran from USA (Kinyuru et al., 2015) and Bangladesh (Haque et al., 2021) respectively. This value was also within the Codex limit of 400µg/Kg (CODEX, n.d.) for polished and unpolished rice and 100µg/Kg for cereal grains.

Detection of higher values for both nutritionally important and toxic metal elements than previously reported could have been influenced by factors such as: differences in geological composition and agrochemicals used (Hasan et al., 2022) (Arunrat et al., 2024) in sampled locations; mixing of rice milling components such as husks (Lantin, 1999) and; variation in the detection limit of measuring equipment. Future studies evaluating levels of these metal elements in other rice mill components; soil and water used for irrigation and; industrial activities and agronomic practices within and upstream of the rice growing region can provide definite answers and inform corrective measures. In this study the use of ICP OES was successful in detecting several abundant metal elements but was not successful in the detection of Cadmium, Mercury and Lead. While it's possible that some of these metal elements were absent in the studied rice bran, however the validity of this postulation requires further tests using a larger sample size and more sensitive instruments such as the Inductively Coupled Plasma Mass Spectrometry (ICP MS).

4. CONCLUSION

From the foregoing results, Rice bran from Lungalunga had the highest amount of potassium, Manganese, Zinc and Copper. On the other hand, rice bran from Mwea had the highest amounts of Magnesium and Selenium while that from Ahero had the highest amount of iron. In general other than iron and Manganese, rice bran from Ahero had the least amounts of the other studied nutritionally important metal elements compared to the other regions. This study also revealed the concentration of toxic metal elements: Chromium, Arsenic and Cadmium, in the studied rice bran samples. Rice bran from Ahero had the highest amounts of Chromium while rice bran from Lungalunga had the highest amounts of Arsenic. The detected values of Arsenic across the study regions were higher than the Codex limit for husked and polished rice and; for cereal foods respectively while the detected levels of Cadmium (Lungalunga) were within these limits. Therefore in order to tap nutritious benefits in the reported metal elements while minimizing risks, quality control measures aimed at reducing levels of toxic metals to acceptable limits during food and feed formulation are required. These findings offer baseline data; though broader studies targeting other rice mill products, more rice growing regions, larger sample sizes, soil and water among others are needed for more conclusive insights.

ETHICAL APPROVAL

This study was reviewed and approved by the Kenya Methodist University, Approval no. KeMU/ISERC/INT/01/2022.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Authors hereby declare that No generative AI technologies such as Large Language Models (ChatGPT, COPILOP, etc.) and text- to- image generators have been used during the writing or editing of this manuscript.

ACKNOWLEDGEMENT

We thank all farmers who contributed to the success of this study.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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