Assessment of Some Toxic Heavy Metals in Rice and Beans Sold in Benin City, Nigeria

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Abstract

Rice and beans are staple foods for more than 50% of the world's population. They are prone to heavy metal contamination, with the global rise in heavy metal pollution, which causes harm and danger to the ecosystem and puts people and other living things in major health problems. This study aimed to determine the level of some heavy metals in local and foreign rice and white and brown bean samples obtained from an open market in Benin City. The samples were prepared and analysed using a standard method with the aid of an atomic absorption spectrophotometer (A.A.S.). The results of the analysis show the levels of heavy metals in the beans and rice ranged from 0.013–0.067 mg/kg for Pb, 0.02-0.043 mg/kg for Cr, 0.003-0.367 mg/kg for Mn, 0.263-1.017 mg/kg for Zn, 0.30-0.933 mg/kg for Fe, and 0.01–0.023 mg/kg for Cu, with Cd being the only metal below the detection limit. Statistical analysis using a t-test showed that there was no significant difference between the levels of the selected heavy metals analysed among the bean samples and those analysed among the rice samples. If these heavy metals are used as benchmarks for measuring the product's quality, local rice would be considered to be of higher quality than foreign rice, according to statistical analysis using a correlation matrix that showed a nearly identical heavy metal composition between local and foreign rice. The concentration of all the metals studied was observed to be present at tolerable levels lower than the maximum permissible limit as given by the World Health Organisation (WHO). Based on the research findings, the rice and bean samples studied were safe for human consumption.

Keywords: Staple food, toxic, heavy metals, Oryza sativa, Vigna unguiculata

INTRODUCTION

Rice is a staple food for more than 50% of the world's population, making it the third most produced agricultural crop after maize and sugarcane. With more than one-fifth of all the calories consumed by people worldwide coming from rice, it is the most significant food crop in terms of human nutrition and calorie intake (Mahmud, 2023). This is due to the fact that substantial amounts of maize and sugarcane are used for reasons other than human consumption. Growing rice is one of the most lucrative farming practices in Nigeria. One of Nigeria's most major and widely consumed grains is also the primary crop. The estimated yearly consumption of rice in the country is close to 7 million metric tonnes (Mahmud, 2023). Another important staple food in Nigeria is beans, which are grown all over the world, particularly in underdeveloped nations. Interestingly, beans are Nigeria's fourth-most popular food after rice, yam, and cassava (LIN, 2023). Importantly, using beans in a healthy

diet may promote weight loss. By delaying digestion, the soluble fibre in beans helps people feel full. Consuming enough protein can also help you feel fuller for longer after meals. People consume beans whole or in processed versions, including bean pudding (Moi Moi), bean cake (Akara), and bean flour soup (Gbegiri). Beans can be eaten alone and are also frequently paired with other dishes, including bread, rice, pap, and garri. Beans are unquestionably a favourite food in Nigeria due to their flavour and nutritional value.

In comparison to pathogenic bacteria, mycotoxins, carcinogens, enzymes, and pesticides, heavy metals have become the most difficult to eradicate food contaminants due to their stability, long half-lives, non-biodegradability, bioaccumulation, transferability, and high toxicity at low concentrations (Zhou et al., 2022; Shahjahan et al., 2023). They are known as heavy metals because of their high density (greater than 5 gcm-3), atomic number, atomic weight, and position in the periodic table. These heavy metals are influenced by some physical factors like temperature, air circulation, wind speed, and water direction, which influence their stability in the environment. The outcome is an excessive discharge of heavy metals into natural resources, including soil and marine ecosystems, including cadmium, chromium, arsenic, mercury, lead, nickel, copper, and zinc (Ali et al., 2021). In contrast to anthropogenic sources, which include mining and different types of industrial and agricultural activity, natural sources of heavy metals include the weathering of metal-containing rocks and volcanic eruptions. heavy metals that can accumulate in the soil as a result of leaching processes and dissolve in surface and groundwater can both contaminate it. The accumulation of these heavy metals in the environment, especially in agricultural soil, is causing the general public to express growing worry. The examination of cadmium, nickel, and lead by Hammami et al. (2022) revealed that these heavy metals had detrimental effects on the growth characteristics of common beans, including root and shoot dry weight, shoot-to-root ratio, and pod number. Numerous studies have also shown that dangerous metals like As, Cd, and Pb are not required by human beings but are reported to induce carcinogenicity, which depends on the duration of exposure in the body. There are some other essential metals like Fe, Zn, and Cu that are required by human beings in trace amounts but can induce toxicity at higher concentrations (Sodhi et al., 2022). Heavy metals are usually transported from the soil and stored in rice grains, as well as other plant parts like the husks, leaves, and stems that are either directly or indirectly consumed by humans. According to investigated reports, consuming rice from fields that include a lot of Potentially Toxic Elements (PTEs), or pollutants that are present in proportions greater than the maximum allowable concentrations, can be bad for one's health (Mu et al., 2020; Hussain et al., 2021). Rice is more vulnerable to pollution than other crops, even up to three times that of wheat.

Because of their danger, heavy metals in the environment have been the subject of much research by academics from all over the world. A couple of them are on the list below. Jyothi and Farook (2020) addressed the dangers of mercury exposure as well as its sources. Liu *et al.* studied the buildup of heavy metals and the ecological risk they pose in the soils of the Yellow and Bohai Seas' coastal regions in 2020. Metals like Cd, As, and Pb have been identified as prevalent in cultivated rice (Zakaria *et al.*, 2021). In another vein, heavy metals have been analysed in some beans sold in Kastina State (Yaradua *et al.*, 2017). Based on a study by Ortega *et al.* (2021), cognitive impairment is brought on by lead exposure over time. Shah-Kulkarni *et al.* (2020) analysed heavy metal toxicity and chelating therapy strategies as of 2020, and Kim *et al.* (2019) evaluated prenatal exposure to metal combinations and neurodevelopment in children at 6 months. The current study looks at the specific types of rice and beans sold in the market whether they possess toxic heavy metal.

MATERIALS AND METHODS

Analytical-grade reagents, nitric acid and perchloric acid, were used.

Sample Collection

The samples used for this research were beans: Kano beans (white) and drum beans (brown). Rice: local rice and foreign rice, which were gotten from an open market in Benin City, Edo State (Figure 1), in April 2023. The beans were grown and harvested in Kano. The local rice was grown and harvested in Mokwa town, Niger State. The samples were properly selected and ground with a grinding machine before being used for analysis.



Figure 1: Sample A Raw Samples Sample B: Grounded samples

Determination of heavy metals

The ground samples were placed in an airtight polyethylene bag and taken for digestion. 1 g of each sample was weighed into a boiling flask, and 7.5 mL of a properly combined concentrated solution of nitric acid (HNO₃) and perchloric acid (HClO₄) in a ratio of 2:1 was added and kept overnight for pre-digestion. The flask was then allowed to heat for 1 h 10 min at 80–85 °C. 12 sample solutions and a blank solution were prepared using this procedure. The solutions were cooled, filtered through Whatman No. 42 filter paper, and brought to the mark on the free 50-mL volumetric flask with distilled water. The solutions were then transferred into 100-mL plastic solution bottles and analysed for various metal ions by the AAS.

Statistical analysis

All the data accumulated were subjected to mean, standard deviation, Pearson correlation coefficient, and student T-test analysis using Microsoft Excel 2022.

RESULTS AND DISCUSSION

The results obtained from the study are presented in Table 1.

Table 1: Heavy metal concentration (mg/kg) in white beans, brown beans, local rice, and foreign rice

Heavy metals	White beans	Brown beans	Local rice	Foreign rice
Pb	0.067 ± 0.031	0.037 ± 0.045	0.013 ± 0.006	0.063 ± 0.012
Cd	BDL	BDL	BDL	BDL
Cr	0.030 ± 0.000	0.043 ± 0.015	0.020 ± 0.010	0.033 ± 0.021
Mn	0.367 ± 0.153	0.300 ± 0.100	0.003 ± 0.069	0.067 ± 0.033
Zn	1.017 ± 0.050	0.897 ± 0.015	0.263 ± 0.015	0.300 ± 0.047
Fe	0.933 ± 0.320	0.300 ± 0.100	0.433 ± 0.058	0.767 ± 0.115
Cu	0.020 ± 0.000	0.023 ± 0.006	0.010 ± 0.000	0.01 ± 0.000
PDI - Palace Datastian Limit				

BDL: Below Detection Limit

In Table 1, the highest level of heavy metal in white bean sample was found with Zn, and the least was found with Cd. The level of heavy metal is therefore in the order Zn>Fe>Mn>Pb>Cr>Cu>Cd.

The brown beans had the highest level of heavy metal found with Zn, and the least was found with Cd. The level of heavy metal is therefore in the order Zn>Fe=Mn>Cr>Pb>Cu>Cd. The local rice had the highest level of heavy metal found with Fe, and the least was found with Cd. The level of heavy metal is therefore in the order Fe>Zn>Cr>Pb>Cu>Mn>Cd. The foreign rice had the highest level of heavy metal found with Fe, and the least was found with Cd. The level of heavy metal is therefore in the order Fe>Zn>Cr>Pb>Cu>Mn>Cd. The level of heavy metal is therefore in the order Fe>Zn>Cr>Pb>Cu>Mn>Cd.

All correlations are strong, as seen in Table 2, except for those of brown beans, local, and foreign rice. Local and foreign rice had the best correlation of 0.9726, meaning that their mineral composition is nearly similar. If these minerals are used as standards for quantifying the quality of the product, it means local rice, in comparison to foreign rice, is of higher quality. There was no significant difference between the two species of beans or the two species of rice analysed in this study, as seen in Table 3.

Table 2: Correlation matrix of the studied heavy metals					
	White Beans	Brown Beans	Local Rice	Foreign Rice	
White Beans	1				
Brown Beans	0.8682	1			
Local Rice	0.8992	0.5957	1		
Foreign Rice	0.8268	0.4442	0.9726	1	

Table 2: Correlation matrix of the studied heavy metals

Table 3:	T-Test Statistical a	nalysis of heav	v metal concentratior	is in rice and beans
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Sample	Pb	Mn	Zn	Cr	Fe	Cu
Beans	0.4012	0.5614	0.0168	0.2051	0.0311	0.3739
Rice	0.0026	0.5185	0.0651	0.7176	0.0111	0

In the present study, the mean Pb content in all the samples was below standard limits according to WHO/FAO, which has a permissible limit value of 0.3 mg/kg for Pb in food (Al-Khatib *et al.*, 2022). Similar results were obtained for studies that reported rice grains cultivated in three major industrial areas of Bangladesh, as well as a study of beans conducted in Kano State, Nigeria, and that conducted for rice and beans cultivated in Yobe State, Nigeria (Alhassan *et al.*, 2019; Usman *et al.*, 2021; Hasan *et al.*, 2022). But differ from a study of rice held in Tangail, the local rice studied by Otitoju *et al.* (2019), and that reported for food crops samples from Kaduna State, Nigeria, with Pb concentrations higher than WHO/FAO limits, which was suspected to be due to widespread application of pesticides with metal contents in the research region (Kormoker *et al.*, 2020; Bawa *et al.*, 2023).

The Cd concentration in this study was not detected in all the samples.

The mean Cr concentration for the white bean sample obtained in this present study was equal to that reported for a study of beans conducted in Kano State (Alhassan *et al.*, 2019). The mean Cr concentration for the brown bean sample obtained in this study, however, is higher than that reported in the aforementioned study. The mean Cr concentration for the local rice sample obtained in this study was in the range of that reported for a study of rice and bean samples cultivated in Yobe State, Nigeria, while the Cr concentration of foreign rice samples obtained in this study was lower than the aforementioned study. The variation observed can be attributed to the nature of the soil condition that affects plant absorption. The mean Cr content in all the samples, however, was below standard limits according to WHO/FAO, which has a permissible limit value of 1.3 mg/kg for Cr in food (Al-Khatib *et al.*, 2022), and the foreign and local rice reported in Indonesia (Wahyuningsih *et al.*, 2023).

The mean Mn concentration in samples obtained in this study was below standard limits according to the WHO/FAO standard permissible limits, which have a value of 500 mg/kg for Mn in food (Al-Khatib *et al.*, 2022). Similar results were obtained for studies that reported imported rice sold in Kaduna, Nigeria, and also in the study that reported bean samples from selected markets in Katsina State, Nigeria (Yaradua *et al.*, 2017; Feka *et al.*, 2022).

In the present study, the mean Zn concentration in the rice samples was lower than that reported in a study of rice sold in Kaduna and much lower than that reported in a study of rice in three major industrial areas of Bangladesh (Feka *et al.*, 2022; Hasan *et al.*, 2022), where rice was analysed with a Zn concentration exceeding the standard limits according to WHO/FAO. However, the Zn concentration in the bean samples of the present study was higher than that reported in a study of bean samples from selected markets in Katsina State, Nigeria (Yaradua *et al.*, 2017). High concentrations of zinc in food have been found to cause little or no harm. Clinical studies revealed that up to 600 mg of zinc sulphate (equivalent to 200 mg of elemental zinc) has been administered daily in divided doses for a period of several months without any reported adverse effects, including effects on blood counts and serum biochemistry; hence, it is safe to say there is a wide margin between nutritionally required amounts of zinc and toxic levels (CAC 2018). The mean Zn concentration in all samples obtained in this study was below standard limits according to the WHO/FAO, which has a permissible limit value of 99.4 mg/kg for Zn in food (Al-Khatib *et al.*, 2022).

The mean Fe concentration in rice samples in this study was lower than that reported in a study in three major industrial areas of Bangladesh (Hasan *et al.*, 2022), where rice was analysed with Fe concentrations less than the standard limits according to WHO/FAO. However, the mean concentration of Fe in white beans in the present study was higher, while that in brown beans was lower than that of the reported study of bean samples from selected markets in Katsina State, Nigeria (Yaradua *et al.*, 2017). The mean Fe concentration in all samples obtained in this study was below standard limits according to the WHO/FAO, which has a permissible limit value of 425 mg/kg for Fe in food (Al-Khatib *et al.*, 2022).

The mean Cu concentration in rice samples in the present study was lower than that reported in a study of rice sold in Kaduna, Nigeria (Feka *et al.*, 2022). Also, the mean Cu content in all the bean samples was below standard limits according to WHO/FAO, as mentioned above. Similar results were obtained for studies that reported bean samples from selected markets in Katsina State, Nigeria (Yaradua *et al.*, 2017). The mean Cu concentration in all the samples, however, was below standard limits according to WHO/FAO, which has a permissible limit value of 73 mg/kg for Cu in food (Al-Khatib *et al.*, 2022).

CONCLUSION

Heavy metal contamination constitutes a major factor in environmental pollution. However, from this study, the concentration of heavy metals in rice and bean species obtained from an open market in Benin City, Edo State, Nigeria, was determined, and the results of this study have shown that the concentration values of Pb, Cd, Cr, Mn, Zn, Fe, and Cu in the samples are generally lower than the WHO/FAO maximum permissive limits, while Cd was not detected in all the samples. The t-test shows that there was no significant difference between the two species of beans or the two species of rice analysed in this study. However, it is imperative to note that chronic exposure to most of these metals, even at low concentrations, should be avoided.

REFERENCES

- Alhassan, A.J., Muhammad, I.U., Sule, M.S., Dangambo, M.A., Gadanya, A.M., Umar, Y., Misbahu, A., Dangambo, A. and Syed, Md. M. (2019) "Correlation analysis of toxic metals distribution and pollution indices in soil, beans and maize samples of Kano State, Nigeria," *Annual Research & Review in Biology* [Preprint]. https://doi.org/10.9734/arrb/2019/v32i330086.
- Ali, M.M., Hossain, D., Al-Imran, Md., Khan, S., Begum, M., and Osman, M.H. (2021). "Environmental Pollution with Heavy Metals: A Public Health Concern," in *IntechOpen* eBooks. https://doi.org/10.5772/intechopen.96805.
- Al-Khatib, M.A, Qutob, A., Kattan, E., Malassa, H. and Qutob, M. (2022) "Heavy metals concentrations in leafy vegetables in Palestine, case study: Jenin and Bethlehem districts," *Journal of Environmental Protection*, 13 (01), 97–111. https://doi.org/10.4236/jep.2022.131006.
- Bawa, U. (2023) "Heavy metals concentration in food crops irrigated with pesticides and their associated human health risks in Paki, Kaduna State, Nigeria," *Cogent Food & Agriculture*. 9. 5. https://doi.org/10.1080/23311932.2023.2191889.
- Codex Alimentarious Commission (CAC) (2018). Joint FAO/WHO Food Standards Programme Codex Committee On Contaminants in Foods 12th Session Utrecht, The Netherlands. https://www.fao.org/fao-who-codexalimentarius/shproxy/en/?lnk=1&url=https%253A%252F%252Fworkspace.fao.org%252Fsites%252F codex%252FMeetings%252FCX-735-12%252FREPORT%252520%2528FINAL%2529%252FREP18 CFe.pdf
- Feka, D.P., Anhwange, B.A. and Adie, P.A. (2022) "Toxic metals contamination of paddy (*Oryza sativa*) and imported rice sold in Kaduna and its human health risk assessment," *Research Square (Research Square)* [*Preprint*]. https://doi.org/10.21203/rs.3.rs-1953036/v1.
- Hammami, H., Parsa, M., Bayat, H. and Aminifard, M.H. (2022). "The behavior of heavy metals in relation to their influence on the common bean (Phaseolus vulgaris) symbiosis," *Environmental and Experimental Botany*, 193, 104670. https://doi.org/10.1016/j.envexpbot.2021.104670.
- Hasan, G.M.M.A., Das, A.K. and Satter, M.A. (2022) "Accumulation of Heavy Metals in Rice (Oryza sativa. L) Grains Cultivated in Three Major Industrial Areas of Bangladesh," *Journal of Environmental and Public Health*, 2022, pp. 1–8. https://doi.org/10.1155/2022/1836597.
- Hussain, B., Ashraf, M.N., Abbas, A., Li, J., Farooq, M. and Shafeeq-Ur-Rahman. (2021) "Cadmium stress in paddy fields: Effects of soil conditions and remediation strategies," *Science of the Total Environment*, 754, 142188. https://doi.org/10.1016/j.scitotenv.2020.142188.
- Jyothi N.R. and Farook, Md.N.A. (2020). "Heavy Metal Toxicity in Public Health." *Intechopen*. http://dx.doi.org/10.5772/intechopen.90333
- Kim, J.-J., Kim, Y.-S. and Kumar, V. (2019) "Heavy metal toxicity: An update of chelating therapeutic strategies," *Journal of Trace Elements in Medicine and Biology*, 54, 226–231. https://doi.org/10.1016/j.jtemb.2019.05.003.
- Kormoker, T., Proshad, R., Saiful Islam, Md.S., Tusher, T.R., Uddin, M., Khadka, S., Chandra, K. and Sayeed, A. (2020) "Presence of toxic metals in rice with human health hazards in Tangail district of Bangladesh," *International Journal of Environmental Health Research*, 32 (1), 40–60. https://doi.org/10.1080/09603123.2020.1724271.
- Lose It Nigerian (LIN) (2023) "Are Nigerian beans a carb or a protein?" Lose It Nigerian [Preprint]. https://loseitnigerian.com/are-nigerian-beans-a-carb-or-a-protein/.

- Mahmud, A. (2023) "First, Let's Talk About Rice and its Production in Nigeria." *Economic Confidential* [Preprint]. https://economicconfidential.com/2023/04/rice-production-nigeria-mahmud/.
- Mu, T., Zhou, T., Li, Z., Hu, P., Luo, Y., Christie, P. and Wu, L. (2020). "Prediction models for rice cadmium accumulation in Chinese paddy fields and the implications in deducing soil thresholds based on food safety standards," *Environmental Pollution*, 258, 113879. https://doi.org/10.1016/j.envpol.2019.113879.
- Ortega, D.R., González Esquivel, D.F., Ayala, T.B., Pineda, B., Manzo, S.G., Quino, J.M., Mora, P.C. and Pérez de la Cruz, V. (2021) "Cognitive Impairment Induced by Lead Exposure during Lifespan: Mechanisms of Lead Neurotoxicity," *Toxics*, 9(2), p. 23. https://doi.org/10.3390/toxics9020023.
- Otitoju., G. T. O., Otitoju, O., Ezenwa, C. P., Omale, B. B. E., Abdussalaam, R. O. and Ali, J. (2019). "Heavy Metal Levels in Locally Produced Rice in the South West Region of Nigeria". Acta Scientific Nutritional Health 3 (2), 120-124.
- Shahjahan Md., Emon, F.J., Rohani, Md.F., Sumaiya, N., Jannat, F.T., Akter, Y., Kari, Z.A., Tahiluddin, A.B. and Goh, K.W. (2023) "Bioaccumulation and Bioremediation of Heavy Metals in Fishes—A review," *Toxics*, 11 (6), 510. https://doi.org/10.3390/toxics11060510.
- Shah-Kulkarni, S., Lee, S., Jeong, K.S., Hong, Y.C., Park, H., Ha, M., Kim, Y. and Ha, E.H. (2020). "Prenatal exposure to mixtures of heavy metals and neurodevelopment in infants at 6 months," *Environmental Research*, 182, 109122. https://doi.org/10.1016/j.envres.2020.109122.
- Sodhi, K. K., Mishra, L. C., Singh, C. K. and Kumar, M. (2019). "Perspective on the heavy metal pollution and recent remediation strategies". *Current Research in Microbial Sciences*, 3, 100166. https://doi.org/10.1016/j.crmicr.2022.100166.
- Yaradua, A.I., Alhassan, A.J., Shagumba, A.A., Nasir, A., Idi, A., Muhammad, I.U. and Kanadi, A.M. (2017) "Evaluation of heavy metals in beans and some beans product from some selected markets in Katsina State Nigeria," *Bayero Journal of Pure and Applied Sciences [Preprint]*. https://doi.org/10.4314/bajopas.v10i1.68s.
- Wahyuningsih, N. E., Setiawan, H., Nabiha, P. I., Kartasurya, M. I. and Azam, M. (2023).
 "Heavy Metals Contamination of Local and Imported Rice in Semarang, Central Java, Indonesia". Journal of Ecological Engineering, 24(7), 49–60, https://doi.org/10.12911/22998993/163308.
- Zakaria, Z., Zulkafflee, N. S., Redzuan, N. A. M., Selamat, J., Ismail, M. R., Praveena, S. M., Tóth, G. and Razis, A. F. A. (2021). "Understanding Potential Heavy Metal Contamination, Absorption, Translocation and Accumulation in Rice and Human Health Risks" *Plants*, 10, 1070. https://doi.org/10.3390/plants10061070.
- Zhou, Y., Jiang, D., Ding, D., Wu, Y., Wei, J., Kong, L., Long, T, Fan, T. and Deng, S. (2022). "Ecological-health risks assessment and source apportionment of heavy metals in agricultural soils around a super-sized lead-zinc smelter with a long production history, in China," *Environmental Pollution*, 307, 119487. https://doi.org/10.1016/j.envpol.2022.119487.