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Assessment and chemical analysis of macro elements, heavy metals, proximate compositions and pesticides contamination on rice cultivated from Kura LGA, Kano, Nigeria

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ABSTRACT

Six rice brands BG-213, Notore, Das, Kwandala, Jeep and Jamila brands were collected from various locations in Kura local government area of Kano, Nigeria. Rice brands were analyzed for proximate compositions, macro elements, heavy metals and pesticides using standard analytical techniques. Results of proximate compositions analyses indicate that the average mean value of moisture content, crude protein, crude fat, ash content and crude fiber in rice brands were; 10.27, 9.17 3.82, 1.93 and 0.34 % respectively. The average mean concentrations of macro elements (Calcium (Ca) and Magnesium (Mg)) are; 53.5 mg/kg and 46 mg/kg, while mean levels of Heavy Metals: Zinc (Zn), Copper (Cu), Nickel (Ni), Chromium (Cr), Cadmium (Cd) and lead (Pb) were; 11.87, 4.04, 0.06, 0.00, 0.044 and 0.00 mg/kg respectively. Pearson Correlation Coefficient analysis performed on rice brands using MATLAB student version VI software shows results of macro elements and heavy metals were at a significant level of $p \geq 0.05$. The GC/MS analysis of organochlorine pesticides in rice brands revealed that the level of pesticides was below the detection limit (BDL) this indicates that brands of rice obtained from the Kura local government area were safe and free from heavy metals and pesticides contamination could be attributed to restriction or regulation for compliance on the application and economy because most of these pesticides are very costly.

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1. Introduction

Rice *(Oryza sativa* L.*)* is one of most popular crops being cultivated in 117 countries across the world. It is one of oldest domesticated crops known to mankind, with farmers having grown it under irrigated conditions for more than 4,000 years.

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It is world's most important food crop and a primary food source for over one third of world's population. Also a means of livelihood for millions of rural households and it plays a vital role in our national food security, henceslogan "Rice is Life' is most appropriate. Rice is vital to more than half the world's populations. Rice is the most important food grain in diets of hundreds of millions of Asians, Africans, and Latin

Americans living in tropics and subtropics. In these areas, population increases are high and will likely remain high at least for decades to come. Rice will continue to be their primary source of food.

Rice is monocot plant of genus *Oryza*and grass family Poaceae (formally Graminae) which includes twenty wild species and two cultivated ones, *Oryza sativa* (Asian rice) and *Oryzaglaberrima* (African rice). *Oryza sativa* is most commonly grown species throughout the world today. Rice has been considered best staple food among all cereals and is staple food for over 3 billion people, constituting overhalf of the world's population (1).Minerals like calcium, magnesium, phosphorus are present along with some traces of iron, copper, zinc and manganese (2). Rice is grown in all ecological and dietary zones of Nigeria, with different varieties possessing adaptation traits for each ecology (3). The two commonly cultivated varieties of rice in Nigeria are *O. sativa* and *O. glabberima* (4,5).

Soils can be contaminated by highly toxic heavy metals (such as As, Cu, Cd, Pb and Hg) from either aerial depositions or irrigation. The heavy metals are likely to induce a corresponding contamination in paddy (6). Rice in or close to contaminated sites can uptake and accumulate these metals, and then exert potential risk to humans and animals (7). Disorder of organs and chronic syndromes may be caused by ingestion of relatively low doses of toxic heavy metals over a long period present in rice. Arsenic is the most toxic heavy metal in rice, therefore, this research highlight contamination level in rice as a representative of heavy metal.

The application of pesticides in most developing countries is becoming an increasingly serious environmental problem due to factors such as water contamination, ecosystem disruption and habitat contamination (8). Pesticides, in general, can be very harmful especially to people coming into contact with them as part of their daily lives. However, the challenges that pests pose on crop production, have resulted in farmers developing more interest in use of pesticides in agriculture fields. In developing countries, most of the farmers are illiterate and do not know how these chemicals should be handled safely. The unsafe application and interaction with these agrochemicals can have negative health impacts upon farmers, chemical applicators on commercial farms and on small-holder farms (8). This practice is resulting in negative health impacts on local.

Therefore, this research is aim at the assessment and chemical analysis of macro elements, heavy metals, proximate composition and pesticides contamination on rice collected from Kura local government area of Kano, Nigeria.

2. Materials and Methods

2.1 Study Location, Samples Collections and Preservation

The study was conducted in farms from Kano and its environs; Kano is located within Sudan Savannah Zone of Nigeria in West African sub-Saharan region in year 2020. The area is situated between longitude 9^{o} 30′and 12^{o} 30′North, and latitude 9^{o}30′ and 8^{o}42′ East. The climate is characterized by dry and wet seasons. Dry season stretches from October to April, while the wet season is from May to September. The annual rainfall and temperature are between (787 and 1293 mm) and

(14 and 41°C) respectively (9). Brands were collected from Kura LGA at different locations. Sixbrands (N=6) of rice; BG-213, Notore, Das, Kwandala, Jeep and Jamila brands were collected from farms, irrigated farms and markets. The procedure was repeated at an interval of two (2) weeks for six (6) consecutive times for all the rice brands. The brands collected (in a label polyethene bags) were transported to the laboratory and stored (10).

2.2 Samples Preparation for Metal Analysis

About 10 g of each rice brands was weighed into porcelain crucible and evaporated to dryness on a hot plate. The dried rice brands were ashed in muffle furnace at 550°C for 8 h. The ash was dissolved in 10 cm^3 of 1mol dm^{-3} HNO_3 and filtered. The dissolved residue was made up to the mark with distilled water (11).

2.3 Preparation of Standard Stock Solutions

1000 mg L^{-1} Mg stock standard solution was prepared by dissolving 5.0695 g $MgSO_4.7H_2O$ in about 400 mL of a 0.1 mol L^{-1} H_2SO_4 solution and filling the volume up to 500 cm^3 with distilled water. The 1000 mg L^{-1} Ca stock standard solution was prepared by dissolving 1.1488 g $CaCO_3$ in 5 cm^3 of a 1:1 (V/V) hydrochloric acid solution; after gas evolution, the volume was filled up to 500 cm3 with distilled water. Mixed standards were prepared containing Zn, Cu, Ni, Cr, Cd and Pb with concentrations of 0.5 ppm, 1.0 ppm 2 ppm, 4 ppm and 10 ppm. The same procedure was followed for the preparation of standards for each element under the study. Using Lambert-Beer Law, calibration curves for each, elements were drawn from which the concentrations of heavy metals were determined. The final concentration values for all test brands were then derived by taking into account the concentration of the analytes in blank brands and deducting values from the overall concentration in brands. All working standard solutions were stored in plastic bottles.

2.4 Analysis of rice Samples

Flame atomic absorption spectrometer (FAAS) machine (Perkin – Elmer 1110B) was used to measure concentrations of metals and heavy metals present in rice brands, as this is a commonly used technique for determining metals in environmental brands.

Ash, protein, fat, moisture and total solids content were determined according to the method described by Association of Official Analytical Chemists (12). The brands were dried to constant weight, defatted, hydrolysed, evaporated in rotary evaporator and loaded into the Technicon Sequential Multi-Sample Amino Acid Analyser (TSM). The machine model used is DNA O2O9.

Quick, effective, cheap, easy, rugged and safe (QuEChERS) method was to be the method to determine the persistent organic pollutants (POPs) in rice brands and other cereals (13). The extract was centrifuged to remove the fatty matrix, the resulting solution was analysed for pesticides using Gas chromatography/mass spectroscopy (GC/MS). GC/MS is used world-wide as an analytical method for screening, identification, and quantification of various chemicals. GC/MS analysis is particularly suitable for identification and quantification of chemicals used for food materials. Quantification of the residual or migration levels of such chemicals is important for safety assurance and specification testing for national regulatory purposes in many countries.

3. Results

Percentage proximate compositions in rice brands were presented in Fig. 1. The results of mean macro elements and heavy metals concentrations obtained from rice brands were shown in Fig. 2 and 3. The results of Gas chromatography-mass spectrometry (GC/MS) analysis of Persistent Organic Pollutants (POPs) were presented in Fig. 4.

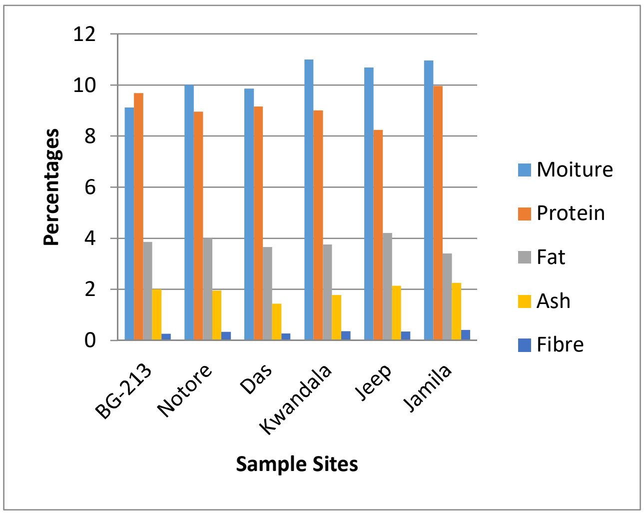

Figure 1. Percentage Mean proximate composition of rice brands

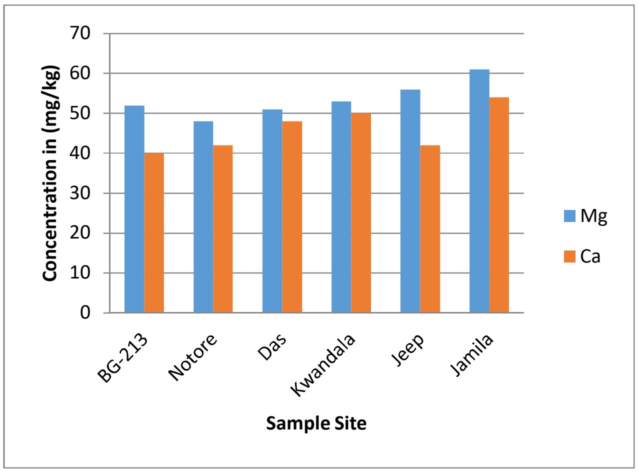

Figure 2: Mean Macro elements Concentrations in Rice Brands in mg/kg

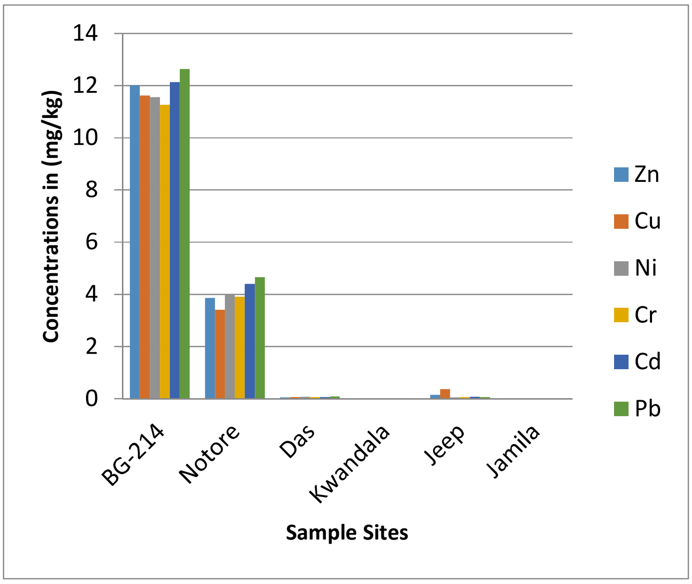

Figure 3. Mean Heavy Metals Concentrations in Rice Brands in mg/kg

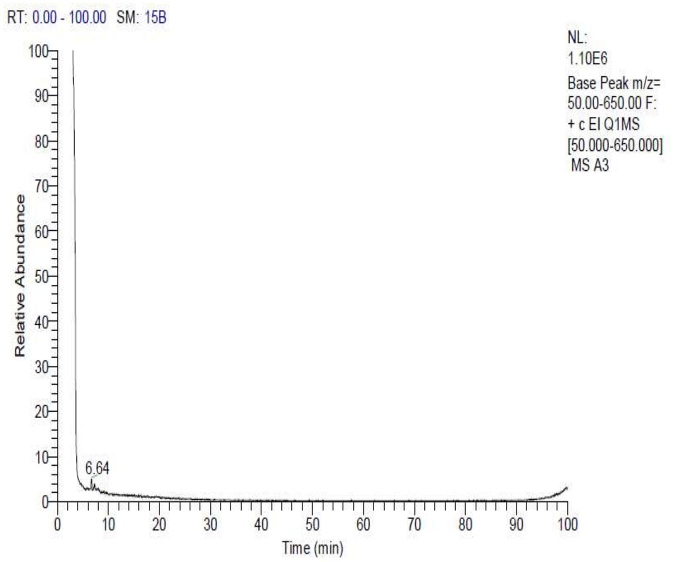

Figure 4. Gas Chromatography Mass Spectrophotometry Analysis of Pesticides in Rice Brands

4. Discussion

Figure 1 indicates mean proximate composition of rice brands collected from Kura farms of 10.27, 9.17, 3.82, 1.93 and 0.34% for moisture content, crude protein, crude fat, ash content and crude fiber respectively. The moisture content value ranged from 9.12 to 11.00%, the highest value was observed in Kwandala brand and lowest value was obtained in BG-213 brand, highest value of moisture discovered in kwandala brand may cause it not be stored for a very long time because least moisture content in foods helps in long term storage. This may be as a result of hydrological status or agronomic potentials (14). Increased moisture content may also likely affect the milling characteristics and palatability of cooked rice. The highest content of crude protein of 9.96% was obtained in Jamila brand while the lowest value of 8.25% was in Jeep brand. The high cost of Jamila brand may be attributed to the rich value of protein in it. Other rice brands have varying proportions of protein which can be favourably compared with those reported by Eggum et al (15). The variation may be as a result of genotype and environmental differences. Also worthy to note that amino acids balance of rice brands protein is exceptionally good (16). Crude fat content was ranged from 3.66 to 4.21%, like moisture value in the rice brands the highest content was obtained in Jamila brand (4.21%) and the lowest was in Das rice brand (3.66%). The overall fat content of rice brands were considered to be very low in comparison with those reported by Ibukun (17) in some brands of white rice. The effect of excess intake of dietary fat has some well established health implications especially for overweight. The consumption of excess of saturated fat has been recognized as the most important dietary factor aiding increased level of cholesterol. Besides the cholesterol implications due to high fat intake, obesity is a factor in the causation of disease (18). In this research BG - 213 brand could be better preferred in terms of low fat content. Moreover, rice fats, commonly referred to as oil (rice bran oil) due to its character at room temperature, are characterized by a high nutritional value. High proportion of unsaturated fatty acids, accounting for up to 80%, causes the liquid consistency of the oil. Because of its high level of unsaturation, rice bran oil is known to have blood cholesterol lowering effects (19). The highest ash content was observed in Jamila brand (2.26%) while the lowest value was obtained in Das rice brans (1.44%). Percentage ash content of rice brands has a direct bearing on the macro mineral content of the rice. Edeogu et al (14) reported that the ash content of a food sample gives an idea of the macro elements present in the food sample. More so, since greater amount of rice bran are removed from the grain during milling and polishing, more minerals are lost (20). The crude fiber content in rice brands were range from 0.26 to 0.42%, the lowest value was obtained from Das rice brand (0.26 %) and the highest fiber content was observed in Jamila brand (0.42%). The high fiber content in rice signifies the good quality trait because rice is a good source of insoluble fiber. Insoluble fiber reduces risk of bowel disorders and fights constipation (21). Diet low in fiber can lead to a wide range of ailments and conditions, especially among urban dwellers that consume more refined foods.

Fig.2 present the mean macro elements concentrations in rice brands collected from Kura farms of 53.5 and 46 mg/kg for magnesium (Mg) and calcium (Ca). The highest magnesium concentrations were obtained in Jamila rice (61 mg/kg) and the lowest in Notore rice brand (48 mg/kg). Concentrations of calcium ranged from 40 to 54 mg/kg, highest concentration were obtained from Jamila brand (54 mg/kg) and the lowest in Notore brand of (40 mg/kg). The level of macro elements rice brands may be ascribed to genetic factor or mineral content of the soil (20). Concentrations of macro elements in this study are slightly higher than those reported by Ibukun (17). The rate of fertilizer application and the native fertility of paddy fields have been shown to affect the macro elements levels (22). In this regards the high and low values of macro elements might be attributed to these factors. Pearson correlation analysis indicates a significant correlation between Calcium and Magnesium in the rice brands at a significant value of $p \geq 0.05$.

On their roles in biological systems, heavy metals are classified as essential and nonessential. Essential heavy metals are important for living organisms and may be required in the body in quite low concentrations. Nonessential heavy metals have little known biological role in living organisms. In this study essential heavy metals are zinc and copper andnon-essential heavy metals were Nickel (Ni), Chromium (Cr), Cadmium (Cd) and Lead (Pb) which were regarded as toxic. Figure 3 shows the mean heavy metal concentrations of Zinc (Zn), Copper (Cu), Nickel (Ni), Chromium (Cr), Cadmium (Cd) and Lead (Pb) of 11.87, 4.04, 0.06, not detected (nd), 0.044 and not detected (ND) respectively. The highest concentrations of zinc were observed in Jamila brand (12.64 mg/kg) while the lowest values were obtained in Kwandala brand (11.26 mg/kg). The copper concentrations in rice brands ranges between 3.41 to 4.66 mg/kg, the highest concentrations were observed in Jamila brand (4.66 mg/kg) and the lowest in Notore brand (3.41 mg/kg). Zinc and copper are essential for growth and stress resistance as well as for biosynthesis and functions of different biomolecules such as carbohydrates, chlorophyll, nucleic acids, growth chemicals, and secondary metabolites (23). Both deficiency and excess of an essential heavy metals leads to diseases or abnormal conditions. However, the lists of essential heavy metals may be different for different groups of organisms such as plants, animals, and microorganisms. It means a heavy metal may be essential for a given group of organisms but nonessential for another one. The interactions of heavy metals with different organism groups are much complex (24). The nickel concentrations ranges between 0.04 to 0.08 mg/kg, the lowest concentration were obtained from in BG-213 brand (0.04 mg/kg) while the highest values were observed in Jamila brand (0.08 mg/kg). The concentrations of cadmium ranges from 0.044 to 0.36 mg/kg, the highest value of cadmium were obtained in Notore brand (0.36 mg/kg) while the lowest value was obtained in Das brand (0.044 mg/kg). The chromium and lead concentrations were conspicuously not observed from all the rice brands. Contamination of rice fields with toxic heavy metals leads to bioaccumulation of these elements in the rice plant. The translocation of heavy metals from roots of the rice plant to stem, leaves, and rice grains is of human health concern. Rice crop is especially susceptible to heavy metal contamination because it needs water during most of its growth period. Heavy metals Nickel (Ni), Chromium (Cr), Cadmium (Cd) and Lead (Pb) were ubiquitous in the environment with harmful effects on human health. Their presence in rice as a public health concern, lead is on top followed by Cadmium (25). Human intake of Cd has been reported to be highest through consumption of rice (26). Contamination of rice with toxic heavy metals is a necessary health concern in developing countries (27).

Figure 4 shows results of gas chromatography–mass spectrometry (GC/MS) analysis of organochlorine pesticides (OCPs) in the brands, it reveals none of the target pesticides (α-HCH, β-HCH, γ-HCH, δ-HCH, aldrin, dieldrin, endosulfan, p,p-DDE, o,p-DDT, p,p-DDD and p,p-DDT) were found in the rice brands. This indicates that the pesticides in the rice brands were Below the Detection Limit (<BDL). These results indicated that there was limited usage of the pesticides in the area either for regulation compliance or economic reasons because most of these pesticides are always easy to find.

5. Conclusion

Proximate composition, macro elements, heavy metals and organochlorine pesticides investigated in the six (6) brands of rice were found to be within the acceptable levels of National Environmental Standards Regulations Enforcement Agency (NESREA). This result of macro elements and heavy metals analysis implies that the rice brands cultivated from Kura were of good quality and nutritional values and safe for human consumption. Results of gas chromatography–mass spectrometry (GC/MS) analysis of organochlorine pesticides (OCPs) reveals that none of the target pesticides were found in the rice brands. It indicates that the pesticides in the rice brands were Below the Detection Limit (<BDL). The results indicated that there was limited usage of the pesticides either for regulation compliance or economics reasons because most of pesticides are not readily available.

Proximate compositions values for rice brands such as fat, protein, moisture, ash and fiber were also determined in the brands and it was observed that this compositions like other parameters in the study were greatly influenced by several factors such as genetic, environmental, type of fertilizer, hydrological status, agronomic level use in the farms. The fat level of rice brands followed this trend Kwandala> Jamila > Jeep >Notore > Das > BG - 213; indicating that BG - 213 rice brand contain less fat compared to other rice brand in this study.

Pearson correlation coefficient (r) analysis between the macro elements, heavy metals and proximate composition indicated there was a strong positive correlation between macro elements and proximate composition and a moderate and weak correlation exists between the heavy metals and macro elements. All values were determined at a significant level of $p \geq 0.05$. This implies that macro elements in rice brands have a direct bearing on values of proximate compositions.

Conflict of interest

Authors declare that there is no conflict of interest.

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