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Comparative profile of glyphosate residues in cowpea grains sold in the municipal and satellite towns of Abuja, Nigeria

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Abstract

The profile of glyphosate residues in cowpea grains sold in the Federal Capital Territory Abuja (FCT), Nigeria was assessed using high performance liquid chromatography.

Methods: Thirty-three cowpea grains samples of red and white morphotype were collected from some selected markets within the FCT, Abuja. Analytical methods on the pulverized cowpea grains included dispersive liquid-liquid microextraction using acetonitrile/water (55:45) as mobile phase, sample clean up and their quantification by HPLC/UV as described by AOAC - QuEChERS method.

Results: The percentage recoveries of the GLY pesticide standard were found to be acceptable at 90.01-101% with limits of detection pesticides standard were 0.011mgkg^{-1} and limits of quantification from 0.022 mgkg^{-1} and regression correlation coefficient (r^2) of 0.987332.

The results showed that the mean concentration of glyphosate in the cowpea grains ranged from 0.11-44.32 ± 0.001 mgkg^{-1} with a mean glyphosate concentration of 6.280 mgkg^{-1} was detected. Six samples representing 18.18% of the samples collected violated WHO/FAO CODEX standard of 15.0 mgkg^{-1}. Comparative studies between municipal and satellite markets revealed that GLY concentration residue was highest and lowest in K'WB (44.32 mg/kg) and K'IB (0.11 mg/kg) respectively while values recorded for Acceptable Daily Intake (ADI) for all the samples were within an acceptable limit of 0.1mgkg^{-1}. Heath risk index values were <1 suggesting that the consumer populations were not at risk.

Conclusion: The high profile of glyphosate residue in cowpea grains from Karimu and Abaji Area Councils of the FCT is of great concern and needed to be further investigated.

Keywords: Cowpea grains; Contamination; Residue; Herbicide; Health hazard; Human exposure; Nigeria

1. Introduction

Glyphosate is a commonly used herbicide in the production of many crops, including beans. There are increasing concerns about the potential health risks associated with glyphosate residues in foods. Currently, more than 1.4 billion pounds of glyphosate are applied to fields per year (Upasani et al., 2019;Beckie et al., 2020; Larsen et al., 2021). Studies have shown that glyphosate residues can be found in a variety of food products and exposure to this herbicide has been linked to several health concerns (Bruce et al., 2016;Kalofiri et al., 2021). Some studies have suggested that glyphosate

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exposure may increase the risk of cancer, while others have linked it to developmental problems and endocrine disruption (Davoren et al., 2018; Shaw, 2021; Antier et al., 2020; Rani et al., 2021).

Glyphosate is the active ingredient of the world's most commonly used herbicide (e.g., Roundup®). It was re-discovered by John Franz of Monsanto in the early-1970s (Dill et al., 2010; David et al., 2010; Benbrook, 2016; Nerozzi et al., 2020). Franz was investigating organophosphorous compounds and noted the plant toxicity of N-(phosphonomethyl) glycine which was later named 'glyphosate' by contraction of its chemical name.(Olajide et al., 2022; USA Patent, 1964). The use of Glyphosate herbicides is highly merited to improve crop yield and quality by reducing or inhibiting the growth of weeds as well as by working as a desiccant for various grain crops including pulses (beans, peas, chickpea, lentils, etc) (Salazar et al., 2020;). Among many herbicides, glyphosate-based herbicides (GBHs) are globally famous and widely used for the control of perennial weeds such as quack grass and thistle as well as by acting as a harvesting aid accelerating crop dry down (Bresnahan et al., 2003; Benbrook, 2016;Richmond, 2018; UNEP,2019).

Studies of glyphosate herbicidal activity revealed that it inhibit the regulatory enzyme 5-enolpyruvylshikimate-3-phosphate synthase (EPSPS) involved in the synthesis of aromatic amino acids in the 'shikimate pathway', resulting in the physiological detriment or death of the plant, fungi or microorganism for which it is applied (Amrhein, et al., 1980; Kishore et al., 1988; Williams et al., 2000; Reynoso et al., 2019; Olajide et al., 2022; Peillex et al., 2022). World Health Organization (WHO), Food and Agricultural organization (FAO) and CODEX Alimentarius Commission and United State Environmental Protection Agency (EPA) regulations set the tolerance levels for the occurrence of glyphosate in food commodities and according to data released by CODEX Alimentarius Commission on pesticides in 2021, the commission prescribed 15 mg/kg as the maximum concentration of GLY in dry bean.

Cowpea (*Vigna unguiculata* . Walp) Family Leguminosae is widely grown in tropics and subtropics for human as well as for animal food (Makun et al, 2012; Anjorin et al., 2015). More than 5.4 million tons of dried cowpeas are produced worldwide, with Africa producing nearly 5.2 million. Nigeria, the largest producer and consumer, accounts for 61% of production in Africa and 58% worldwide (FAOSTAT, 2012). Cowpeas cultivars in Nigeria vary in seed size, seed coat texture and colour. Majority of people have preference for brown beans as a pulse. The crop is grown primarily for its seeds locally called beans which are eaten fresh when semi-ripe and as a pulse when dry and mature, or ground into flour. Cowpeas provide a rich source of proteins and calories, as well as minerals and vitamins. A cowpea seed can consist of 25% protein and is low in anti-nutritional factors (Rangel *et al.*, 2003).To provide safe food and ensure food security, there is a need to determine the hazardous compound in food sources such as pesticide residues (Beyer et al., 2008; Carvalho et al., 2017; Kolakowski et al., 2020;Soares et al., 2021).
Quantification of herbicide residues in crop produce and retailed food is one way of monitoring and determining the level of risk and potential health hazards to humans due to exposure to these chemicals. This study aimed at assessing the level of GLY residue in cowpea sold in Abuja, Nigeria and also its human risk assessment in the study area.

2. Material and methods

2.1. The study location

The area of study is the FCT which is the administrative capital of Nigeria and situated in the geographical heartland of the country. It has a land area of 8,000 square kilometers and lies between Lat. 8.25° N and 9.21° N and Long. 6.45° E and 7.39° E and with an estimated population of 1.8 million It has a total area of 713 km^2 (NBS, 2020). The territory's borders are Kaduna State to the North, Kogi State to the South, Nasarawa State to the East, and Niger State to the West (Figure 1). FCT is one of Nigerian leading urbanized centers. Due to its centrality, the FCT is well-connected and accessible from the States and Federal highways. Abuja has savannah vegetation, giving it rich soil for agriculture and a favorable climate that is pleasant year-round and is neither overly hot nor under-cold. The FCT is divided into six area councils; Kuje, Abaji, Bwari, Gwagwalada, Kwali, and Municipal Area Council (AMAC).

2.2. Sampling method

A total of 33 dried cowpea samples morphotype were purchased randomly from several traders in the market from some selected markets located within the six area councils of the FCT for the assessment of GLY residue herbicide and human health risk assessment in 2021 (Table 1). In each market, 5 composite of different varieties of cowpea were collected and bulked together. The collected samples were labeled, placed into sterile polystyrene bags, and immediately transported under complete aseptic conditions in zip lock bags to Chemistry Advanced Research Centre, Sheda Science and Technology Complex Abuja and kept in a -20 ^oC refrigerator pending analytical determination.

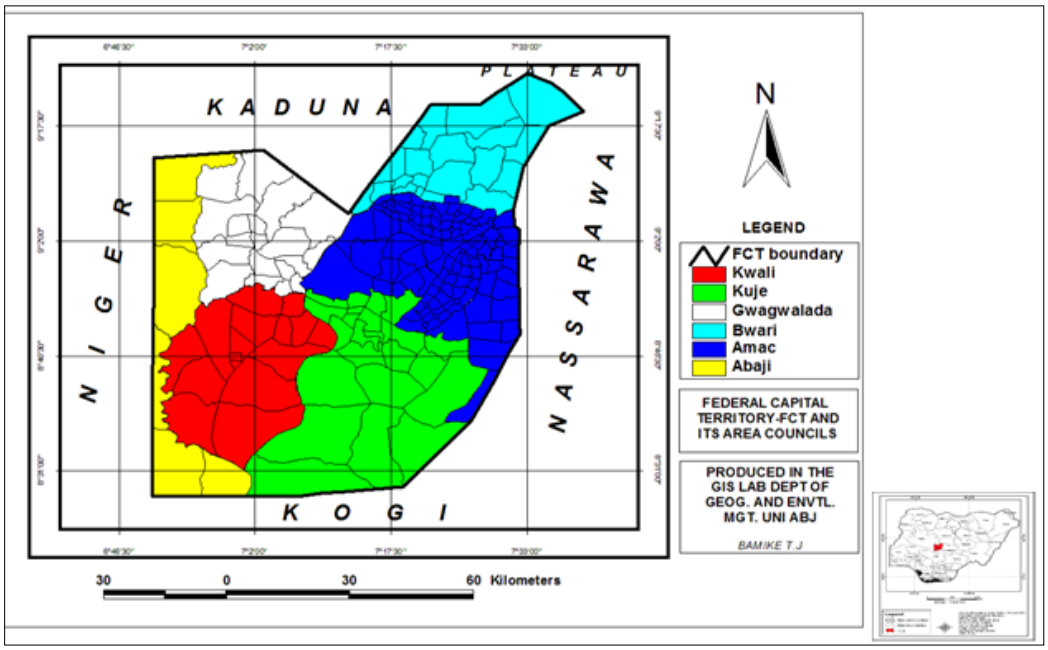

Figure 1 FCTMap displaying the six area councils

2.3. Chemicals and materials

Table 1 Samples of cowpea collected from markets in the six areas councils of the FCT, Abuja

S/N	Area Council	Location/Market	Grain's code
1	Abaji	Abaji	AWB, ARB
2	Kwali	Kwali	KWB, KRB
		Sheda	SWB, SRB
3	Gwagwalada	Gwagwalada	GIB, GRB,GSWB
		Store Opposite teaching hospital	THRB,THWB
4	Bwari	Bwari	BWB, BRB
5	Abuja Municipal	Lugbe Babangida Mkt. Nyanya Wuse	LWB,LRB,LDB RDBN,SWBN WIB,WSWB
		Karmu	K'WB,K'IB,K'SB, K'WSB,K'IB
		Kado fish Mkt	FMWB, FMRB
		Utako	UWB,URB
		Garki village	G'WB,G'DB,G'OB,G'IB
Total number of samples collected			33

RB= red beans, WB=white bean

In this study, the chemicals used were GLY standard, formic acid concentration, acetonenitrile, acetone, Methanol, all solvents are 99.90 % HPLC grade and purchased from Sigma-Aldrich USA. Besides, Sodium sulphate (Na_2SO_4), Magnesium sulphate anhydrous fine powder ($MgSO_4$), graphitized carbon black (GCB), primary secondary amine (PSA), disodium hydrogen citrate sesquihydrate ($C_6H6Na_2O_71.5H_2O$), trisodium citrate dehydrate ($C_6H_2Na_3O_7.2H_2O$), sodium chloride (NaCl) (to remove the remaining water in the solvent), Solid phase extraction tubes (SPE tubes), ceramic discs, purchased from Bioccomma LimitedHong Kong.

2.4. Sample Preparation

Foreign matters such as stone and admixtures were sorted out. And the samples were later pulverized with a laboratory blender (MasterChef) and then extracted and analyzed for the presence of glyphosate residue in bean samples. Quick, Easy, Cheap, Efficient, rapid and safe (QuEChERS) method and dispersive liquid-liquid micro-extraction (DLLME) was used for sample extraction.

2.5. Sample preparation procedure

A QuEChERS-DLLME method previously described by Anastassiades et al., 2003; Abhilash et al., 2009; AOAC Official method, 2007-01; Payá et al., 2007; Bi et al., 2011) were used for extraction of the samples. Ten grams of finely ground sub-sample was placed in a polypropylene centrifuge tube (50 mL) and 10mL water was added. Followed by the addition of 15mL acetonitrile and the mixture vortex vigorously for 5 min. Further, 0.5 g disodium hydrogencitrate sesquehydrate, 1g trisodium citrate dihydrate, 4 g anhydrous magnesium sulphate, and 1 g sodium chloride were added, and the mixture was immediately vortex for another five minutes, then centrifuged at 4500rpm for 5 min. At this stage, an optional low-temperature clean step was performed before dispersive-SPE for the most complex matrices such as bean. For this, an aliquot of the supernatant was transferred into a glass test tube and stored for at least 2 hours in a freezer (−20 ^{o}C). The extract was then separated from the precipitates by simple decantation. An aliquot of the extract was transferred into a polypropylene centrifuge tube containing 100mg anhydrous magnesium sulphate, 75mg graphitized carbon black (GCB) , and 20mg PSA per mL acetonitrile extract. The tube was vortexed for 0.5 min and centrifuged at 4500rpm for 2 min. 1ml of aliquot of the supernatant was transferred into a glass test tube and acidified by adding 15µL of 5 % (v/v) formic acid in acetonitrile per mL of extract and analysed using HPLC.

2.6. Preparation of glyphosate standard solutions

Individual stock solutions containing 1000mg L^{-1} were prepared by accurately weighing 10mg of GLY standard in 5 ml beaker and dissolved in 5 ml acetonitrile and later transferred quantitatively into 10 ml standard volumetric flask and makeup to the mark with acetonitrile to prepare 1000ppm. An intermediate standard solution containing 200 mg L^{-1} of glyphosate standard was also prepared from the stock solutions by diluting with acetonitrile using the dilution formula. Working standard solutions (ranging from 5 – 40 mg/ml) were prepared from the intermediate standard solution by diluting with deionized water and then used for the optimization of the parameters affecting the QuEChERS-DLLME procedure as well method validation. All solutions were stored under refrigeration below -4 ^{o}C pending analysis (Halim et al., 2013).

2.7. Instruments and equipment

Chromatographic analyses were performed using CECIL 3500 High Performance Liquid Chromatography (HPLC) equipped with a binary pump, and UV-visible wavelength detector (VWD) all purchased from CECIL, England. Chromatographic separation was carried out using Eclipse plus C_{18} column (150 x 4.6 mm I.D., 3.5 µM particle sizes) obtained from CECIL CECIL Technologies. Data acquisition and processing were accomplished with Chemstation software Adept CECIL Technologies. The d-SPE tubes, supel QuE PSA (EN) tubes, containing 150 mgsuperclean PSA, 150 mg. Discoverydsc-18 and 900 mg $MgSO_4$, used for sample clean-up in QuEChERS extraction procedure were purchased from Bioccomma Limited(Hong Kong). The centrifuge used is (England) and vortex mixer scientific industries (USA).

2.8. Analytical Method Validations

2.8.1. Linearity of the Standard Curves

A calibration curve has been produced for quantification. Linearity has been observed all along the area of concentration studied. These ranges of concentrations were selected in function of the sensitivity of the HPLC towards GLY herbicide from the correlation coefficient (r^2) of the linear regression. The calibration curves were obtained by injecting five different concentrations of the GLY herbicide standards in a range of 5, 10, 15, 20 and 25 mg/ml (Santilio et al., 2019).

2.8.2. Limits of Detection and Limits of Quantification

The limits of detection (LOD) and limits of quantification (LOQ) of the method were measured by spiked serial dilution of working standards prepared for calibration curves and calculated by considering a value of 3 and 10 times of background noise, respectively. LOD was determined considering it as 3 times the signal-to-noise ratio, while LOQ was determined as 10 times the signal-to-noise ratio. This means that LOD and LOQ were determined as the lowest concentrations yielding a signal-to-noise (S/N) ratio of 3 and 10, respectively.

2.8.3. Chromatographic conditions

The chromatographic separation of the target analytes was performed based on previous methods (Bi et al., 2011, Bedassa *et al.,* 2015; Martins-Júnior et al., 2009) with minor modifications. An isocratic elution with a binary mobile phase comprising 45 % water (solvent A) and 55 % acetonitrile (solvent B) was used throughout the analysis. Before the subsequent sample/extract injection, the HPLC column was washed by adjusting the mobile phase composition to 5% water (solvent A) and 95 % acetonitrile (solvent B) for 15 min and then was conditioned with the mobile phase (55 % acetonitrile and 45 % water) for additional 20 minutes. Analysis was performed with the mobile phase flow rate of 0.3 mL min^{-1}, column temperature set at 30 ^{o}C, injection volume 10 µL and monitoring wavelength of 254 nm. Chromatograms of each of the samples and Data acquisition were affected by power stream Adept CECIL 4900.

2.9. Identification and Quantification

GLY pesticide residue was identified if the retention times matched those of the standards and the relative abundance was within 10 % bandwidth of those of the standards. Identified GLY pesticide was quantified using the external standard method of comparing sample peak areas with those of the GLY pesticide standards under the same conditions. Each sample was analyzed three times and the mean values were obtained. And the software attached to the data station was used to program individual GLY concentrations of individual bean grains samples based on calibration standards, injection volume, peak area, retention time and bandwidth

2.10. Recovery Studies

Recovery experiments was carried out based on methods proposed by (Fernandes et al., 2013; Liao et al., 2018) this is achieved by using blank samples which were selected for spiking. Pesticide standard solutions were prepared and used for spiking the blank samples. Each standard solution (1.0ml) was added to 10.0g of ground sample to give fortification levels of 2.5, 5.0, 10.0, 15.0 and 20.0 mg/g respectively. Each spiked sample was allowed to stand for six hours and then extracted, cleaned up and analyzed like the test samples as previously described above. The standard solutions were also run on HPLC under the same conditions as the spiked samples. Glyphosphate standards were calculated for both standard solutions and spiked samples. The percent recovery of GLY herbicide was then calculated as follows:

$$\text{Percent recovery} = \frac{\text{Conc in spike sample} - \text{Conc in the unspike sample}}{\text{Amount added}} \times 100$$

2.11. Health Risk Assessment

Health risk estimations were done based on the integration of herbicide analysis data, and exposure assumptions. The assumptions were made based on the United State Environmental Protection Agency's guidelines (EPA, 1996). The Estimated Daily Intakes (EDI) of the herbicide residue and food consumption assumption was used to determine long-term health risks to consumers. The food consumption rate for cereal such as bean is quoted to be 0.1062 kg/person/day with an average body weight of 60 kg for an adult (MoFA, 2010). For each type of exposure, the EDI was obtained as stated in Equation 1 below (Darko and Akoto, 2008). The health risk indices were obtained by dividing the EDI by their corresponding values of ADI (Akomea-Frempong et al., 2017; Forkuoh et al.,2018; FAO/WHO, 2019), assuming an average adult's body weight of 60 kg. When the health risk index >1; the food involved is considered a risk to the consumers. When the health index is < 1, the food involved is considered acceptable (Hamilton and Crossley, 2004; Darko and Akoto, 2008).

$$\text{EDI} = \sum(\text{C} \times \text{IR} \times \text{EF} \times \text{ED})/(BW \times AT) \ldots\ldots \text{eq 1}$$

Where C is the concentration of the herbicide residue in bean grains in mg/kg, IR is the Ingestion rate or consumption rate for an adult (0.027 kg), EF is Exposure frequency (365 days), ED is exposure duration which represents 55.12 years life expectancy rate, BW=Body weight of adult=60kg, AT= Average time of exposure × ED =365X55.12=28121.72. To understand the human health risk factor of contaminated bean, Joint Food and Agriculture Organization of the United Nations FAO/WHO Codex Alimentarius Commission has set the Acceptable daily intake (ADI) 0.1 mg/kg in bean grains respectively (FAO/WHO, 2011). Health Risk Index was computed according to the following formula:

$$(HRI) = \text{EDI}/ADI \times 100 \text{ ----------eq 2}$$

ADI= Acceptable Daily Intake for glyphosate= 0.5 mg/kg

The estimation of non-carcinogenic health hazards from the consumption of bean grains was determined by equation 2 above as provided by the United States Environmental Protection Agency (USEPA), 1989, EPA, 2007, Akande et al., 2020).

3. Results

The percentage recoveries of the GLY pesticide standard were found to be acceptable at 90.01-101% which indicates that the reproducibility of the method was satisfactory. The limits of detection pesticides standard were 0.011mgkg^{-1} and limits of quantification from 0.022 mgkg^{-1}. Calibration curves have been produced for quantification. The calibration curve of the studied analysts shows satisfactory linearity over the selected concentration range with a regression correlation coefficient (r^2) of 0.987332.

The results obtained from each sample's chromatogram as generated by the ADEPT software attached to the data station revealed that all the 33 samples were contaminated with glyphosate residue at various levels of concentrations which represents 100% occurrence of GLY residue in all the samples collected. It was also observed that 6 samples i.e.18.18 % of analyzed samples were contaminated with GLY residue above MARLs of 15 mg/kg. The mean GLY residual concentration was 6.289 mg/kg and with a range of 0.11 – 44.32 mg/kg. Samples K'WB and K'IB have the highest and lowest GLY concentration of 44.32 and 0.11 mg/kg respectively as shown in Table 2.

Table 2 Glyphosate residue Concentration (mg/kg) in bean grain samples some markets in FCT Abuja, Nigeria

S/N	Sample ID	Glyphosate residue Concentration (mg/kg) in bean samples	S/N	Sample ID	Glyphosate residue Concentration (mg/kg) in bean samples
1	AWB	18.061±0.011	18	SWBN	20.19 ± 0.020
2	ARB	2.300± 0.014	19	WIB	0.533 ±0.011
3	KWB	4.740± 0.023	20	WSWB	5.766±0.012
4	KRB	0.340± 0.013	21	K'WB	44.32 ± 0.031
5	SWB	0.245±0.011	22	K'IB	3.170 ±0.010
6	SRB	3.200 ± 0.021	23	K'SB	18.19 ±0.013
7	GIB	10.44 ± 0.002	24	K'SWB	17.97 ±0.012
8	GRB	0.130±0.012	25	K'IB	0.11- ±0.002
9	GSWB	7.434 ± 0.002	26	FMWB	18.73 ±0.016
10	THRB	0.226±0.020	27	FMRB	2.572 ± 0.010
11	THWB	1.627 ± 0.032	28	UWB	1.234±0.032
12	BWB	3.420± 0.032	29	URB	2.231 ± 0.045
13	BRB	4.300±0.032	30	G'WB	7.435 ± 0.021
14	LWB	3.200 ±0.022	31	G'DB	3.858± 0.012
15	LRB	2.100 ±0.012	32	G'OB	0.7157 ±0.011
16	LDB	0.269± 0.011	33	G'IB	0.200±0.014
17	RDBN	0.3028± 0.040			

A comparative study between the levels of GLY residue in the samples collected from Municipal markets in ascending order as shown in Figure 1 revealed that GLY residue is highest in the white beans collected from Karimun market (K'WB) followed by small white bean collected from Nyanyan market (SWBN) and K'IB recorded the lowest GLY residue value, sample K'SB and FMWB have closely same concentrations.

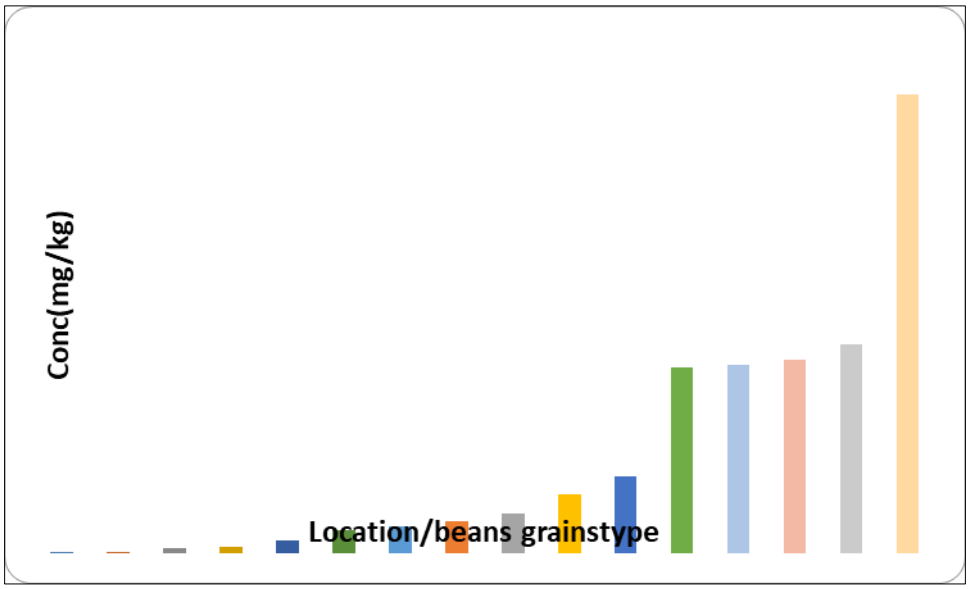

Figure 2 Concentration of GLY residue in cowpea grains from municipal markets FCT, Abuja in ascending order

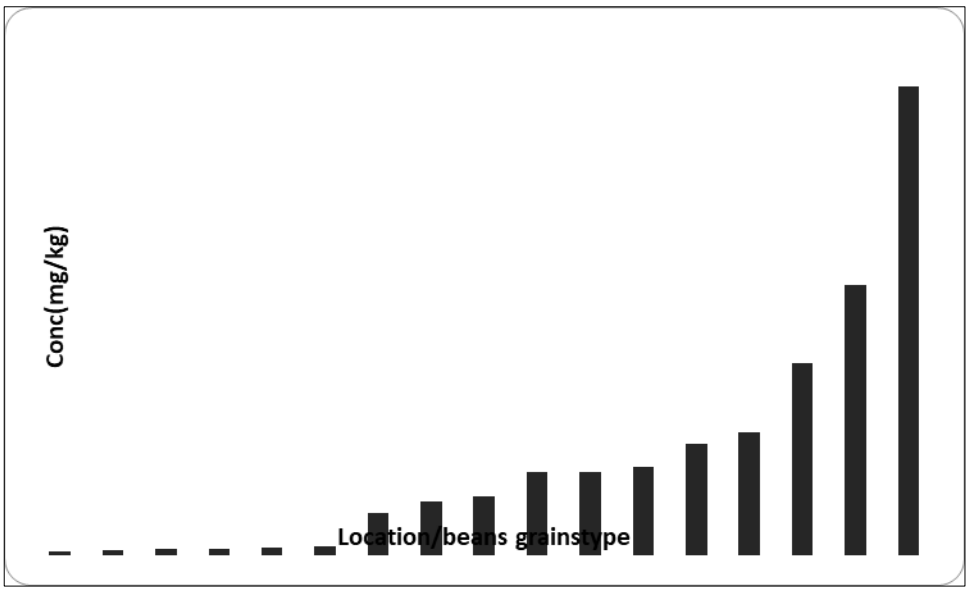

Figure 3 Concentration of GLY residue in cowpea grains from satellite markets FCT, Abuja in ascending order

Contamination of GLY residue in the markets located in satellite towns were also compared graphically as seen in Figure 3 in ascending order and it was revealed that the white beans (AWB) collected from Abaji has the highest concentration GLY residue followed by iron beans (GIB) collected from Gwagwalada market while red beans sample collected from the same market has the lowest concentration, SRB and BWB have similar concentration values. These graphical illustrations revealed different contamination patterns between samples collected from markets located at municipal council and satellites town's markets.

The health risk assessment of the sampled cowpea grains is shown in Table 3. The average daily intake (ADI) i.e. 0.1 mg/kg is the amount of GLY active ingredient that can be consumed daily over a lifetime without harm expressed in mg/kg body weight of the consumer. It was indicated that the EDI of glyphosate ranges from 1.36 x10-5 to 9.086 x10^{-3} $mgkg^{-1}$. Table 3 also revealed that that no health risk associated with the parameter consider. Consumer exposure is of concern if the Estimated Dietary Exposure to a pesticide exceeds the ADI (Maigari et al., 2022). The ADI is the estimated amount of a chemical in food ($mgkg^{-1}$ body weight/day) that can be ingested daily over a lifetime without appreciable health risk to the consumer (Darko and Akoto, 2008; FAO/CODEX, 2011b).

Table 3 Health Risk Assessment of bean grain sold in Abuja, Nigeria

Sample ID	Estimated Dietary Exposure (EDI) mg/kg	Hazard Risk Index (HRI)	Health Risk Status	Sample ID	Estimated Dietary Exposure (EDI) mg/kg	Hazard Risk Index(HRI)	Health Risk Status
AWB	0.00812745	0.0162549	No Risk	SWBN	0.0090855	0.018171	No Risk
ARB	0.001035	0.00207	..	WSWB	0.0199.44	0.039800	..
KWB	0.002133	0.004266	..	K'WB	0.0014265	0.002853	..
KRB	0.000153	0.000306	..	K'IB	0.0081855	0.016371	
SWB	0.00011025	0.0002205	..	K'SB	`0.0081855	0.016371	..
SRB	0.00144	0.00288	..	K'SWB	0.0080865	0.016173	..
GIB	0.004698	0.009396	..	K'IB	0.0000495	0.000099	..
GRB	0.0000585	0.000117	..	FMWB	0.00842849	0.01685698	..
GSWB	0.0033453	0.0066906	..	FMRB	0.0011574	0.0023148	..
THRB	0.00073215	0.0014643	..	UWB	0.0005553	0.0011106	..
THWB	0.00073215	0.0014643	..	URB	0.00100395	0.0020079	..
BWB	0.001539	0.003078	..	G'WB	0.00334575	0.0066915	..
BRB	0.001935	0.00288	..	G'DB	0.0017361	0.0034722	..
LWB	0.00144	0.00189	..	G'OB	0.00032207	0.00064414	..
LRB	0.000945	0.00027252	..	G'IB	0.000090	0.00018	..
LDB	0.00013626	0.000234	..	GIB	0.004698	0.009396	..
RDBN	0.000013626	0.000027252	..	GRB	0.0000585	0.000117	..
WIB	0.00002398	0.00004796	''	-	-	-	..

4. Discussion

It was found from this study that the concentration of glyphosate in cowpea grains ranged between 0.11- 20.19 mg/kg. This is higher than the concentration of 0.0164 and 0.0508 mg/kg obtained in the grains from Gombe State, Nigeria (Maigari *et al*., 2022). Vicini et al. (2021) reported Glyphosate contamination in soybeans samples at different concentrations (0.1, 1.6, and1.8 mg/kg). From a pesticide testing of foods related to infants conducted by USDA Pesticide data Program 2020, glyphosate was detected in 90% of the 300 soybeans samples with a mean glyphosate concentration of 1.94 mg/kg, and a maximum concentration of 18.53 mg/kg. Besides, Kolakowski et al. (2020) tested 631 samples of non-staple grains foods in Canada, and 156 contained measurable but compliant glyphosate residue while 35 were found to be non-compliant. Kuan et al. (2023) also found GLY residue in soya bean ranging from 0.04-0.09 mg/kg. Glyphosate residue was recently reported to have caused the deaths of fish at a concentration of 0.004 ml/L in Kano, Nigeria (NAN, 2018).

Herbicide residue in food is usually monitored with reference to Maximum Residue Limits (MRLs) and Average Daily Intakes (ADIs). Codex Alimentarius Commission and EU set 15 mg/kg as the Maximum Residual Limit (MRL) of glyphosate in cowpea (FAO/WHO, 2021). The MRL is an index that represents the highest concentration (expressed in mg kg^{-1}) of the herbicide residue that is legally permitted in food or animal feeds after pesticides application (FAO, 2002). Consumer exposure is of concern if the Estimated Dietary Exposure to a pesticide exceeds the ADI (Maigari et al., 2022). The ADI is the estimated amount of a chemical in food (mgkg^{-1} body weight/day) that can be ingested daily over a lifetime without appreciable health risk to the consumer (Darko and Akoto, 2008; FAO/CODEX, 2011b). Based on the toxicological evaluation, the calculated EDIs for this study are all below the CODEX/FAO/WHO maximum permissible limit of 0.1 mg/kg for GLY. This indicated that the consumers in the study area have no health risks from consuming the

cowpea grains samples (FAO/WHO, 2013; Fucic et al., 2021). The results of the Health Index (HI) also showed that the HI < 1 and according to (Bwatanglang et al., 2019; EPA, 2019, Maggi et al., 2021), if the HI < 1 signifies no associated risk; meaning the exposed population is not likely to pose any significant adverse health risk. The result agrees with those of Bai et al., (2016) on glyphosate on human health via food contamination (Oyeyiola et al., 2017) and (Fedrick et al., 2018) both on dietary exposures to GLY herbicide where they obtained HI < 1. The concern, however, is that the HI values are very close to the maximum value for the hazard index of 1. The effect of the consumed food items with the glyphosate residues may be additive or synergistic. This means that even pesticides that were detected at safe levels may eventually pose health hazards to humans due to combined and accumulated effects in the body (Maigari et al., 2022). Concerns remain about the potential health risks of even low levels of exposure. In addition, there is ongoing debate about the effectiveness of current regulatory frameworks for monitoring and managing glyphosate residues in food. To minimize the potential health risks associated with glyphosate residues in beans and other food products, it is important to follow good agricultural practices, such as using glyphosate at recommended rates and adhering to pre-harvest intervals and good agriculture practices (GAPs). Consumers can also take steps to reduce their exposure to glyphosate residues by washing produce thoroughly and choosing organic or non-GMO options when available. Overall, the potential health effects of glyphosate residues in beans and other food products remain an area of active research and debate, and ongoing monitoring and research are needed to fully understand the risks associated with this herbicide.

5. Conclusion

It was found from this study that the incidence of glyphosate residue contamination in cowpea grains sold in Abuja, Nigeria is higher in the municipal than the satellite markets. However, the residual concentration in the samples was not above MRLs and ADI as set by CODEX. This indicates that the grains do not pose a health risk due to GLY contamination. Regular assessment of food products for pesticides residue should be carried out to ensure sufficient data for regulatory bodies and policy makers in Nigeria. Farmers are however advised to embrace Good Agricultural Practices (GAPs) at all stages of cowpea grains production and processing to guarantee a continuous supply of safe food commodities to the markets.

Compliance with ethical standards

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Disclosure of conflict of interest

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

Authors' contributions

A.A. F proposed the research idea, collected the samples, shared in laboratory analysis of the samples and involved in manuscript writing; D.M.S. approved the study design and revised the manuscript; T.S.A. analysed and interpreted the data and involved in the manuscript writing. All authors read and approved the final manuscript.

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