GC Determination of Herbicides Residues and Health Risk Assessment of Some Crops from Selected Farmlands in Pankshin LGA Plateau State

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Abstract: - The use of herbicides in farming activities has significantly improved agricultural yields as bumper harvest has been recorded. In its usage however, the residues of the herbicides after successive accumulation by the years could be a threat to humans and other non-target organisms after they have performed their primary roles. From oral interview with the farmers it was discovered that glyphosate, paraquat dichloride and 2,4-dichlorophenoxy acetic acid are mostly used within the study area which are hazardous and should be handled with utmost care. Crop samples were obtained alongside soil samples from Bumnan, Bwarak, Larpya and control sites. The samples were pretreated and extractions of the herbicides residues was carried out with the aid of acetone, dichloromethane and hexane as solvents. GC analysis was carried out on the extracts to determine the herbicide residues concentrations and the following results were obtained in mg/kg: Rice from Larpya soil contained 0.002 mg/kg and 0.0124 mg/kg, Potatoes crops collected from Bwarak soil; 0.0021 mg/kg and 0.0012 mg/kg, groundnut from Bumnan soil; 0.0038 mg/kg and 0.0094 mg/kg, potato from control soil; 0.0016 mg/Kg and 0.0009 mg/kg and groundnut also from control soil; 0.0003 mg/Kg and 0.0012 mg/Kg of 4,4- bipyridine and 2,4-diphynoxyacetic acid respectively. A statistical analysis was carried out using one way ANOVA; $p \leq 0.05$ and there was no significant difference among the mean values The bioaccumulation and health risk index for all the crops were below 1 as recommended by EFSA, 2007) and are considered to be of no health hazard to humans and the environment.

Key Words: —*Pesticides, Herbicides, Glyphosate, Paraquat Dichloride, 2, 4-Dichlorophenoxy Acetic, health and Risk.*

I. INTRODUCTION

According to World health organization (WHO) "any substance or mixture of substances in food for man or animals resulting from the use of a pesticide and includes any specified derivatives, such as degradation and conversion products, metabolites, reaction products, and impurities that are considered to be of toxicological significance" are defined as herbicide/ pesticide residues. It was reported that only one percent (1%) of sprayed pesticides applied are often effective while ninety-nine percent (99%) of the pesticides are released to non- target soils, water bodies, and atmosphere and finally absorbed by almost every organism. (Zhang et al., 2011).

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Pesticide residues in food items have been a concern to the environment and consumers of the food and products contaminated with such categories of pesticides (Darko and Acquaah, 2007) The intensive application of herbicides have resulted in the contamination of the atmosphere, ground/waste water and agricultural products which includes; wheat, corn, fruit, vegetables, etc. It also results in the direct pollution of food and food products as well as the biological system (Johnen,1999). It was reported that plant uptake of herbicides and other pesticides post health risk to domestic livestock that forage on crop stubble and consumers of food from these animals (Dem, 2007).

The study determines the residues of herbicides in selected crops widely grown in the study area. The conditions responsible for the accumulation of the residues in the crops will be considered and thereafter recommendations and suggestions will be made to help reduce and if possible eliminate the herbicide residues in edible crops.

II. MATERIALS AND METHODS

A. Sample Collection And Preparations

By September ending when it was established that, crops were ripe for harvest, crops samples were collected across all the farmlands that were treated with herbicides within the study area. These crops include rice from Larpya farmland soil, potato from Bwarak farmlands, Groundnut from Bumnan farmlands and potato and groundnut from control farmlands. Adhering soil were removed by brushing the roots and tuber samples before both were rinsed with distilled water. A global positioning system (GPS) was used to record the coordinate position of places where all the samples were collected and these locations are presented in figure I below;

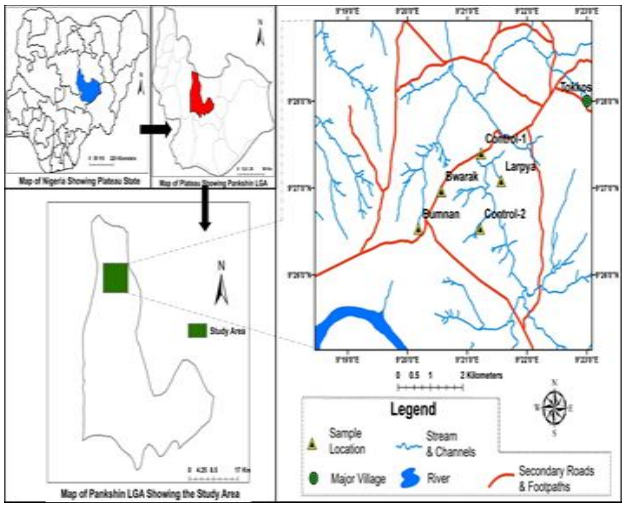

Fig.1. Map of the study area

Each of the crop samples were dried, grounded and sieved prior further analysis.

B. Extraction of Crop Samples

Method described by Gushit et al., (2013) was adopted for the extraction of samples. 20 g of each of the farm products, which include potatoes, groundnuts and rice collected from the farm in which the herbicides were used for the control of weeds. Each sample weighed was soaked in 50cm3 acetone for 30 minutes. The mixture was then shaken in 100 cm3 of dichloromethane and hexane (2:3) for 45 minutes. The mixture was filtered and the filtrate evaporated using a rotary evaporator to 5cm3. This was finally subjected to column cleansing prior to GC analysis.

C. Health Risk Index (HRI) Analysis

Health risk estimations were done based on pesticide residues detected in crops in the present study. Health risk indices of the pesticide residues via intake of crops were assessed according to the guidelines recommended by the USEPA, where the estimated daily intake (EDI) was compared with the acceptable daily intake (ADI) (Zhang et al., 2011). Estimated Daily Intake (EDI) was found by multiplying the residual pesticide concentration (mg kg-1) by the food consumption rate (kg day-1) and dividing by a body weight of 60 kg for adult population. The average daily crop intakes for adults were considered to be 0.2, 0.02, and 0.4 kg/person/day for rice, groundnut and potato respectively according to the previous report (Wang et al., 2005; Arora et al., 2008). Health risk index (HRI) was calculated using the equation:

Health risk Index (HRI) = EDI/ADI (EFSA, 2007), where, EDI is estimated daily intake and ADI is acceptable daily intake. An index more than 1 is considered as not safe for human health (Darko and Akoto, 2008)

In table.1. are the Maximum Residual Limit and Acceptable Daily Intake for 4, 4–bipyridine and 2, 4 –D for Rice, Potato and Ground nut (Codex, 2006).

Table.1. Maximum Residual Limit and Acceptable Daily Intake for 4, 4 -bipyridine and 2,4 –diphenoxyacetic acid

Herbicide	Crop	MRL (µg/Kg)	ADI (µg/Kg)
4, 4–bipyridine	Rice	100	
	Potato	200	
	Ground nut	200	10
2, 4 –D	Rice		
	Potato	200	
	Ground nut	50	5

III. RESULT AND DISCUSSION

A. Residual Herbicide Concentration of Crop Sample

The herbicide residue concentration in the various crop samples from the Gas chromatography is presented in table.2. below.

Table.2. Concentration of Herbicide residues in crops from selected farmlands in Pankshin LGA, Plateau State.

Crop	Herbicides	Retention time (min)	Conc. (mg/kg) ($\times 10^{-3}$)

Rice,R (Larpya)	4,4 - bipyridine	10.45	02.00 ± 0.01
	2,4 –D	12.79	12.40 ± 0.01
	Glyphosate	ND	BDL
Potato,T (Bwarak)	4,4 - bipyridine	10.45	02.10 ± 0.01
	2,4 –D	12.86	01.20 ± 0.01
	Glyphosate	ND	BDL
Groundnut,Z (Bumnan)	4,4 - bipyridine	10.44	03.80 ± 0.01
	2,4 –D	12.84	09.40 ± 0.01
	Glyphosate	ND	BDL
Potato,Y (Control)	4,4 - bipyridine	10.46	01.60 ± 0.01
	2,4 –D	12.87	00.90 ± 0.01
	Glyphosate	ND	BDL
Groundnut,N (Control)	4,4 - bipyridine	10.45	00.30 ± 0.01
	2,4 –D	12.84	01.20 ± 0.00
	Glyphosate	ND	BDL

BDL = below detection limit, ND = not detected

Values are ± standard deviation

Results of herbicide residues indicated that they were present in the various farm crops, but were found almost below detection limit (BDL). This is when compared to the Maximum residue limit (MRL) of herbicide residues in these various crops as shown in Table.2. Maximum residue limit is defined as the statutory maximum concentration of pesticide residues allowed in the internal or surface of foods or agricultural products, expressed as the micrograms of pesticide residues per kilogram of foods or agricultural products (µg/Kg).

For rice grains, the herbicide residues of 4, 4–bipyridine and 2,4 –diphenoxyacetic acid were 0.002 mg/kg and 0.0124 mg/kg respectively, which are very much below the MRL of both herbicides.

For Potatoes crops collected from Bwarak, the herbicide residues of 4, 4–bipyridine and 2, 4 –diphenoxyacetic acid were 0.0021 mg/kg and 0.0012 mg/kg respectively, while for those collected from the control location, the herbicide residues of 4, 4–bipyridine and 2, 4–diphenoxyacetic acid were 0.0016 mg/Kg and 0.0009 mg/Kg respectively, which are also below the MRL of both herbicides. The herbicide residue in the potato crop collected from the control locations appeared to be lower than those from the farmland.

For the Ground nut crops collected from Bumnan, the herbicide residues of 4,4–bipyridine and 2,4 –diphenoxyacetic acid were 0.0038 mg/Kg and 0.0094 mg/Kg respectively, while for those collected from the control location. The herbicide residues of 4,4–bipyridine and 2,4 –diphenoxyacetic acid where 0.0003 mg/Kg and 0.0012 mg/Kg respectively, which are also below the MRL of both herbicides. The herbicide residue in the ground nut crop collected from the control locations were also noted to be lower than those from the farmland.

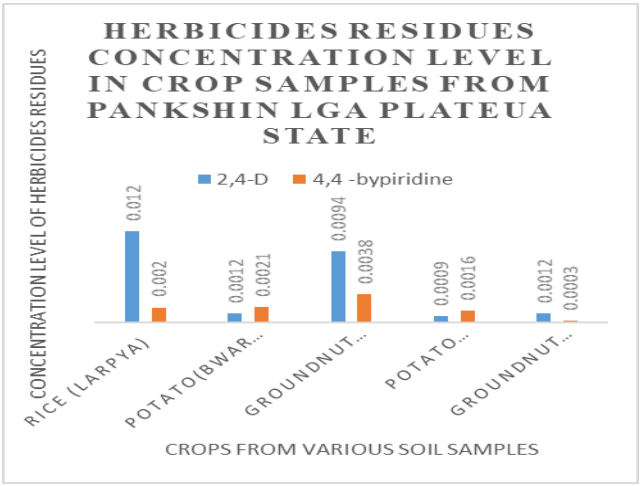

Fig.2. A chart showing the herbicides residues concentration in crops

From figure.2. above it can be observed that 2,4 – D residues has the higher values in the crops that were analyzed compared to the values obtained for 4,4 –bypiridine as observed in Rice sample from Larpya (0.0124 mg/kg), groundnut sample from Bumnan (0.0094 mg/kg) and groundnut sample from the control soil (0.0012 mg/kg). This could be attributed to the corresponding values of herbicide residues obtained from the soil samples from which the crops were obtained. Yet it is also worthy of note that the trend that was observed from the herbicide residues of soil samples is not the case for the crops as 4,4 – bypiridine has a higher value than 2,4 –D in potato sample (0.0021 mg/kg and 0.0012 mg/kg respectively) from Bumnan and potato sample from control soil with values of 0.0016 mg/kg and 0.0009 mg/kg of 4,4- bibyridine and 2,4 – D respectively. It could also be attributed to the method of application or disparity in the rate of absorption of these herbicides by the crops as this occurrence was observed only in potatoes for this research. (Junaki et al., 2017 and sohdia, 2009)

have reported paraquat in potato tubers at 0.01 mg/kg and 0.005 mg/kg respectively.

(Gushit *et al.*, 2012) reported that root crops including potatoes were observed to contained considerably high concentration of herbicides residues with their derivatives which included 2,4 – D (0.02 mg/kg) and antrazine (0.10 mg/kg) and they attributed this to the farming practices which is mostly characterized with mixed cropping. In this case, the herbicides are used to control weeds when the tubers of these crops are already formed and almost matured for harvest leading to adsorption of the herbicides. This is aside the residue accumulation in the crops already ripped for harvest.

However, (Nikhuhat et al., 2020) reported an analysis carried out to determine herbicide residues of paraquat and oxyfluorfen. It was found that the residue of both the herbicides was below detectable limit (0.001 mg kg^{-1} for oxyflourfen and 0.01mg kg^{-1} for paraquat) in potato tubers; however the oxyfluorfen residue was detected in potato leaves and was found to be 0.0035 mg kg^{-1}. Therefor the low concentration of herbicide residues observed for potatoes could be as the result of the fact that most of the residues were absorbed by the potato leaves.

The result of both herbicide residues was also subjected to statistical analysis using one way ANOVA at 95 % confidence level and the mean values were not significantly different. And observing the values they are all below the maximum residual limit (MRL) as given by (CODEX, 2006) presented in table 2 above.

B. Health Risk Assessment

Some health risk parameters of 4,4 – bypyridine and 2,4- D that were calculated for various crop samples are presented in table 3 and 4 below respectively.

Table.3. Some Health Risk parameters of 4, 4 - bypyridine residue in some of the farm crops.

Crops	BAC	EDI (µg/kg)	HRI
Rice (Larpya soil)	0.40	0.0067	0.0007
Potato (Bwarak soil)	0.53	0.0140	0.0014
Groundnut (Bumnan soil)	0.25	0.0013	0.0001
Potato (control soil)	0.80	0.0667	0.0067
Groundnut (control soil)	0.15	0.0000	0.0000

BAC = bioaccumulation coefficient, EDI = estimated daily intake and HRI = health risk Index

Table 4. Some Health Risk parameters of 2, 4 - D residue in some of the farm crops.

Crops	BAC	EDI (µg/kg)	HRI
Rice (Larpya soil)	0.40	0.0413	0.0083
Potato (Bwarak soil)	0.53	0.0080	0.0016
Groundnut (Bumnan soil)	0.25	0.0031	0.0006
Potato (control soil)	0.80	0.0060	0.0012
Groundnut (control soil)	0.15	0.0004	0.0001

BAC = bioaccumulation coefficient, EDI = estimated daily intake and HRI = health risk Index

Estimated health risk index (HRI) were obtained by dividing the EDI (mg kg^{-1} day^{-1}) by their corresponding values of acceptable daily intakes (ADI). Table 10 and 11 expresses the estimated daily intake values and the corresponding health risk index for 4,4–bipyridine and 2,4 –diphenoxyacetic respectively. The HRI values ranges between 0.0001 and 0.0083 for 2,4- D, 0.0000 and 0.0067 for 4,4 –bypyridine respectively. The values obtained indicated that the health risk for both herbicide residues was low. Results were below the cut-off value of 1 which indicate that there is no potential health risk. However, there is need for farmers to control and ensure proper application of these herbicides so as to avoid future risk.

IV. CONCLUSION

Though 4,4 –bypridine and 2,4 –D residues were present in both the soil samples and crop samples at various concentrations, there was no significant difference among the values obtained for both the herbicides residues. The concentrations of both herbicides residues in all the samples were below the maximum residual limit given by CODEX (2006) and they pose no threat to health as the health risk index calculated was below the value of one. Never the less it is important that the farmers within the locality are educated on the hazard of this chemicals and how to properly use them to avoid future Risk

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REFERENCES

[1]. Darko, O. and Acquaah, S. O., (2007) Level of organochlorines pesticide residues in meet. Int. J. Environ. Sci. Tech., 4 (4): 521-524.

[2]. Darko, G. and Akoto, O., (2008). Dietary intake of organophosphorus pesticide residues through vegetables from Kumasi, Ghana. Food and Chemical Toxicology 46: 3703-3706.

[3]. Dem, S.B., (2007) Pesticide Residues in Soil and Water from Four Cotton Growing Areas of Mali, West Africa. Agricultural, Food and Environmental Sciences. Vol. 1. Issue 1. 1-12.

[4]. EFSA (European Food Safety Authority). (2007). The EFSA's 7th scientific colloquium summary report – cumulative risk assessment of pesticides to human health: The Way Forward. EFSA, November 2006, Parma, Italy.

[5]. Gushit S.J, Eno .O. E, Harami M. A, and Ovi J. A., (2012). The persistence of herbicides residue in fadama and upland soils in Plateau state, Nigeria.

[6]. Gushit S.J., Eno .O. E, Harami M. A, and Chindo I. Y., (2013). Analysis of herbicides residue and organic priority pollutants in selected root and leafy vegetable crops in plateau state Nigeria.

[7]. Johnen, B.G., (1999) Herbicides and food quality a misfit? In Proceedings of Brighton Conference, weeds. Vol 3. British Crop Protection Council UK. 875-882. .

[8]. Janaki P, Archana M, Sathya P. R, Nithya C, Chinnusamy C, Prabhakaran N. K., (2017).

[9]. Effect of herbicides on potato and their persistence in acid soil under semiarid tropical condition. Advance Plants Agric Research. 7(3):272–277.

[10]. Nikhat K., Ghazala Y., Tahreem H., and Madiha T., (2020) Assessment of Health Risk due to Pesticide Residues in Fruits, Vegetables, Soil, and Water Journal of Chemistry Volume 2020.

[11]. Sondhia S. (2009). Persistence of oxyfluorfen in soil and detection of its residues in rice crop. Toxicological & Environmental Chemistry.; 91(3):425– 43.

[12]. Zhang, W., Jiang, F. and Ou J. (2011) Global Pesticide consumption and Pollution: with China as a focus. Preceding of the International Academy of Ecology and Environmental Sciences. 1 (2): 125-144.