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Quantification of Pesticide Residues in Retail Samples of Cowpea - *Vigna unguiculata (L.) Walp*

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Authors' contributions

This work was carried out in collaboration among all authors. Author CSO designed the study, performed the statistical analysis and wrote the protocol. Author CEO wrote the first draft of the manuscript. Authors OJU and CCU managed the analyses of the study. Authors BCN and LUSE managed the literature searches. All authors read and approved the final manuscript.

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Original Research Article

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ABSTRACT

Quantification of pesticide residues in retail samples of food is one way to determine the level of human exposure to these chemicals and hence their potential health hazards. The study was aimed at quantifying the level of some known pesticides in retail samples of *Vigna unguiculata (L.) Walp.* (Cowpea) from two cropping seasons. Five cultivars of cowpea from two different harvest seasons (2016/2017 and 2017/2018) were purchased from Ogige Market, Nsukka, Enugu State, Nigeria. The cowpeas were identified based on city/state where they were cultivated. Two foreign samples were also purchased from London, UK. The pesticide residues were determined using gas chromatography coupled with electron capturing detector (GC-ECD). The results showed that the retail samples of cowpea contained residues of one or more organochlorines and organophosphates. The levels of post-harvest pesticides, 2, 2-dichlorovinyl dimethyl phosphate (DDVP) in 2016/17 season (0.02 µg/g) exceeded the international permissible standards (0.01 µg/g). The levels of the pre-harvest pesticides, glyphosate was low in both seasons (0.01 µg/g) when compared to the international permissible standards (0.1 µg/g). The DDVP was not detected

in the two foreign samples. HCB (Hexachlorobenzene), α -HCH (alpha-Hexachlorocyclohexane), Chlorpyrifos, g-chlordane, t-nonachlor, p-p'-DDT (Dichlorodiphenyltrichloroethane), p-p'-DDE (Dichlorodiphenyldichlo-rowthylene), and p-p'-DDD (Dichlorodiphenyldichloroethane) were detected in the cowpea from two cropping seasons despite being banned from agricultural use. This could be due to the additional application of pesticides during storage of the cowpeas. The findings concludes that the levels of some of the residues exceeded the safety limits while some were below the safety limits, suggesting that some of samples of the cowpea were not safe for human consumption as bioaccumulation, persistence, and toxicity of these residues was likely to pose serious health risks to the consumers. Generally, cowpea from the 2016/17 season contained higher pesticide residues than those from the 2017/18 season.

Keywords: Pesticide residues; GC-ECD; safety limit; cowpea; Nsukka.

ABBREVIATIONS

GC-ECD: chromatography coupled with electron capturing detector: DDVP: 2-dichlorovinvl dimethyl phosphate; a-HCH: alpha-Hexachlorocyclohexane; HCB: Hexachlorobenzene: p-p'-DDT: Dichlorodiphenyltrichloroethane; p-p'-DDE: Dichlorodiphenyldichlo-rowthylene, and р-р'-DDD: Dichlorodiphenyldichloroethane.

1. INTRODUCTION

The loss of crops due to pest, plant disease and competition from weeds is guite very high. To avert these losses, farmers now increasingly deploy pesticides in their agronomic practices. Pesticides are chemical substances used in agricultural practices to aid the production and yield by repelling, preventing, and destroying pests [1]. Pesticide residues above the regulatory standards are regarded as incidental food adulterant which affects the quality of foods commodity including cowpea. Food safety is important for every individual. The interaction of food constituent in our body, the quality of the constituent, safety of the constituent, and a healthy nutrition are important issues that we take into account. An expectation of the society we live in is that the food we eat is wholes safe. That is -- it does not contain harmful bacterial (e.g. Listeria Salmonella, Campylobacter, E. coli 0157) or their toxins e.g. afloxins, botulinum and staphylococcal toxins) that can cause disease- it does not include allergens (e.g peanuts sesame seeds etc) unless they are declared on the packaging. - it does not contain levels of chemical contaminants (e.g. pesticides, PCBs, dioxins, plastics etc,) that are detrimental to health either now or in the future. Therefore, scientists are at the cutting edge of bioscience carrying out ground breaking research on food safety. Our hypothesis was that pesticide

residues would be detected in the retail samples of cowpea and may be above the safety limits.

Pesticides are essential agrochemicals used by farmers globally to ensure control of pest attacks on crops, particularly cereals, at both in-field postharvest storage growth and quality management, in the agricultural supply chain system. They aid in ensuring optimum yield as well as minimize storage losses [2]. However, most of these pesticides have been shown to have adverse health implications in both humans and animals upon ingestion. They also affect the organoleptic properties of the stored cereal, thus, reducing the market value as well as consumer acceptance. Cowpea is a staple crop cultivated in developing countries such as Nigeria, Niger Republic, Ghana, Cameroon, Brazil, and China. It is widely consumed as a major source of plantbased protein as well as alternative to animal proteins which are more expensive [3]. Cowpea is, rich in lysine and phenylalanine amino acids, compared to cereal grains. It is also low in fat and high in fibre, contains other health-promoting nutritional components such as vitamins, minerals, and antioxidants which play pivotal roles in preventing diseases [4]. However, one of the major challenges of cowpea production remains the storage of the harvested crops, in line with good agricultural practices, to ensure human and animal health are not predisposed to degenerative conditions, potentially triggered by ingestion and accumulation of harzardous chemicals, pesticides [5-6]. Currently, various pesticides are used for cowpea postharvest include organophosphate, storage which carbamate, and synthetic pyrethroids pesticides [7]. The study was aimed at quantifying the level of some known pesticides in retail samples of Vigna unguiculata (L.) Walp. (Cowpea) from two cropping seasons. Five cultivars of cowpea from two different harvest seasons (2016/2017 and 2017/2018) were purchased from Ogige Market, Nsukka, Enugu State, Nigeria.

2. MATERIALS AND METHODS

2.1 Materials

Nsukka is a town and Local Government Area in Southeast Nigeria in Enugu State. Nsukka is situated at 6.86° North latitude, 7.39° East longitude and 456 meters elevation above the sea level. Nsukka is a big town in Nigeria, about 111, 017 inhabitants (FRNOG, 2007). There are high demand and supply of cowpea in Ogige Market Nsukka due to the University of Nigeria, Nsukka (UNN) community.

2.2 Samples and Sampling

Five cultivars of cowpea from two different harvest seasons (2016/2017 and 2017/2018 cropping seasons) were purchased from Ogige Market. Sampling was conducted in two phases. Firstly, during the nine months post-harvest period at the retail market and during one-week post-harvest. The cowpeas were identified based on city/state where they were cultivated in conjunction with their market name. Two foreign samples were also purchased from London, UK. A total of twelve (12) samples and ten kilograms composites of each sample in sterile poly bags were collected and thus ready for extraction.

2.3 The Experimental Design

The experimental design was based on locations (city/State where cowpea was cultivated). The same treatment was applied to each sample and the same GC-ECD was used for the analysis.

2.4 Sample Preparation

Each of the 12 samples was ground thoroughly using grinding machine and 20 g weighed out, while the remaining were stored in the refrigerator at 4°C as the backup.

2.5 Extraction and Clean-Up of Samples

Each of the 20 g was mixed with 60 g of anhydrous sodium sulphate in the agate mortar to absorb any moisture present and placed the slurry into a 500 ml beaker. The extraction was carried out with 500 ml of nhexane for 24 h. The crude extract was evaporated to dryness using a rotary vacuum evaporator at 40°C.

2.6 Preparation and Analysis

The preparation and analysis of pesticide residues in cowpea samples were carried out in accordance with methods described in the AOAC (1990).

From each sample of cowpea; I ml of the filtered residue was dissolved in 50 ml of chloroform, transferred to a 100 ml volumetric flask, and diluted to the mark. Chloroform was allowed to evaporate at room temperature, 1 ml of the reagent (20 vol. % benzene and 55 % methanol) was added, sealed, and heated at 4°C water bath for 10 minutes. After heating, the organic sample was extracted with hexane and water, so that the final mixture of the reagents, hexane. and water, would be in a proportion of 1:1:1. The mixture was shaken vigorously by hand for 2 minutes and about half of the top hexane phase was transferred to a small test tube for injection. The residues were analyzed using Buck 530 model gas chromatography equipped with an oncolumn (210°C), automatic injector (250°C), Electron capture detector (280°C), HP88 capillary column (100 m x 0.25 ml film thickness) CA, USA. The analytes were identified on differing partition coefficient on the Gas Chromatography column using helium as gas a carrier at a constant temperature, while Electron Capturing Detector (ECD) quantified the analytes through the ionization effect which generates a measurable and steady current of electrons. About 7-10 components and a total of 86 pesticide residues were identified and quantified.

3. RESULTS

3.1 The Concentration of Pesticide Residues in *Vigna unguiculata (L.) Walp.* (Cowpea) Samples from 2016/17 Cropping Season

Table 1 reveals that organochlorines were the most abundant, followed by organophosphates. Glvphosate and DDVP were the organophosphates guantified while others were organochlorines. Glyphosate was the only herbicide quantified. DDVP was the only postharvest (storage) insecticide quantified while others were pre-harvest pesticides. Table 2 also, contains a comparison of the concentration pesticide residues in of cowpea from 2016/17 cropping season to the international permissible standards.

Pesticides	lron µg/g	Potiskum µg/g	Bazza µg/g	Gwarzo µg/g	Brown µg/g	Standards EU/IPS µg/g)
Glyphosate	0.01	0.01	0.00	0.01	0.00	0.1
g-chlordane	0.07	0.01	0.04	0.01	0.06	0.01
t-nonachlor	0.04	0.05	0.05	0.05	0.10	0.01
Chlorplyrifos	0.00	0.00	0.00	0.00	0.00	0.00
α-HCH	0.01	0.00	0.03	0.01	0.03	0.01
DDVP	0.00	0.00	0.02	0.00	0.02	0.01
HCB	0.02	0.02	0.02	0.02	0.02	0.01
p-p'- DDD	0.01	0.01	0.02	0.00	0.02	0.01
<i>p-p'-</i> DDT	0.01	0.00	0.00	0.01	0.00	0.01
<i>p-p</i> '-DDE	0.00	0.00	0.01	0.00	0.01	0.01
Total	0.17	0.12	0.20	0.11	0.30	

Table 1. The concentration of pesticide residues in Vigna unguiculata (L.) walp. (cowpea) samples from 2016/17 cropping season compared to the international permissible

Table 2. The concentration of pesticide residues in *Vigna unguiculata (L.) walp.* (cowpea) Samples from 2017/18 cropping season compared to the international permissible standards

Pesticides	lron μg/g	Potiskum µg/g	Bazza µg/g	Gwarzo µg/g	Brown µg/g	Standards (µg/g/bw, EU/IPS)
Glyphosate	0.00	0.00	0.00	0.01	0.00	0.1
g-chlordane	0.00	0.13	0.01	0.00	0.00	0.01
t-nonachlor	0.00	0.00	0.00	0.00	0.00	0.01
chlorpyrifos	0.00	0.00	0.00	0.00	0.00	0.01
α -HCH	0.00	0.01	0.01	0.00	0.00	0.01
DDVP	0.00	0.01	0.00	0.00	0.00	0.01
HCB	0.03	0.05	0.02	0.00	0.02	0.01
<i>p-p</i> ^DDD	0.01	0.00	0.00	0.01	0.01	0.01
p-p'-DDT	0.00	0.00	0.04	0.00	0.01	0.01
p-p'-DDE	0.00	0.00	0.00	0.00	0.00	0.01
g-HCH	0.00	0.00	0.00	0.00	0.00	0.01
Total	0.00	0.12	0.10	0.04	0.07	

3.2 The Concentration of Pesticide Residues in *Vigna unguiculata* (L.) Walp. (Cowpea) Samples from 2017/18 Cropping Season

Table 2 indicates that a similar trend occurred in the current season (2017/2018) compared to the previous season. The result reveals that organochlorines were the most abundant, followed by organophosphates. Glyphosate, chlorpyrifos, and DDVP were the organophosphate quantified while others were organochlorines. Glyphosate is the only herbicide quantified. DDVP was the only post-harvest (storage) insecticide quantified while others were pre-harvest pesticides. Table 3 also, contains a comparison of the concentration of pesticide residues in cowpea from 2017/18 cropping season to the international permissible standards.

3.3 Comparison of Pesticide Residues in Cowpea from 2016/17 and 2017/18 Cropping Seasons

Table 3 contains a comparison of the total concentration in the cowpea from two cropping seasons (2016/17 and 2017/18). No pesticides were detected in Iron cultivar from 2017/18 cropping season. Same level of residues was quantified in Potiskum cultivar in both seasons. Pesticide residues quantified in Bazza, Gwarzo, and Brown cultivars from 2016/17 cropping season were higher than the same cultivars in 2017/18 cropping season.

3.4 The Concentration of Pesticide Residues in Foreign "A" *Vigna unguiculata (L.) Walp.* (Cowpea) Sample

Table 4 reveals that organochlorines was the most abundant, followed by organophosphates. Glyphosate was the only organophosphate quantified while others were organochlorines. Glyphosate was the only herbicide quantified. DDVP was the only post-harvest (storage) insecticide and was not detected in foreign "A" cowpea sample. Table 5 also, contains a comparison of the concentration of pesticide residues in cowpea from foreign "A" to the international permissible standards.

3.5 The Concentration of Pesticide Residues in Foreign "B" *Vigna unguiculata (L.) Walp.* (Cowpea) Sample

Table 5 reveals that organochlorines was the most abundant, followed by organophosphates. Glyphosate was the only organophosphate quantified while others were organochlorines. Glyphosate was the only herbicide quantified. DDVP was the only post-harvest (storage) insecticide and was not detected in foreign "B" cowpea sample. Table 5 contains a comparison of the concentration pesticide residues in cowpea of from foreign "B" to the international permissible standards.

Pesticides	Iron	Potiskum	Bazza	Gwarzo	Brown
Total from 2016/17	0.17	0.12	0.20	0.11	0.30
Total from 2017/18	0.00	0.121	0.10	0.04	0.07

Table 3. Comparison of the pesticides in cowpea from 2016/17 and 2017/18 cropping seasons

Table 4. The concentration of pesticide residues in foreign "A" cowpea sample compared tothe international permissible standards

Pesticides	Α (μg/g)	Standards EU/IPS (µg/g)
Glyphosate	0.01	0.1
g-chlordane	0.00	0.01
t-nonachlor	0.05	0.01
Chlorpyrifos	0.00	0.01
α - HCH	0.00	0.01
DDVP	0.00	0.01
НСВ	0.02	0.01
p-p ['] DDD	0.01	0.01
<i>p-p</i> 'DDT	0.00	0.01
<i>p-p'-</i> DDE	0.00	0.01
g-HCH	0.00	0.01

Pesticides	Β (μg/g)	Standard EU/IPS (µg/g)
Glyphosate	0.00	0.1
g-chlordane	0.08	0.01
t-nonachlor	0.04	0.01
lpha - HCH	0.00	0.01
DDVP	0.00	0.01
HCB	0.02	0.01
p-p'-DDD	0.00	0.01
<i>p-p'-</i> DDT	0.01	0.01
g-HCH	0.00	0.01

Table 5. The concentration of pesticide residues in foreign "B" cowpea sample compared to the international permissible standards

4. DISCUSSION

Quantification of pesticide residues in retail samples of food is one way to determine the level of human exposure to these chemicals and hence their potential health hazards. synthetic pyrethroids. Carbomates, and organophosphates are the types of pesticides currently allowed for agricultural use, while organochlorines have been banned from agricultural or domestic uses in Europe, North America, and many countries of South America [8-9]. The international permissible standard otherwise known as the Maximum Residue Limit (MRL) of a pesticide is the maximum concentration of its residues that is legally permitted to remain in any food after it has been treated with the pesticide. The MRL is not expected to be exceeded in any foodstuff if the pesticide was applied in accordance with directions for its safe use. If a pesticide residue is found to exceed the MRL in any food, the food commodity is said to be adulterated because it contains an unsafe or illegal amount of the residue [10].

The results of this study showed that the retail samples of Vigna unguiculata (L.) Walp. (Cowpea) contained residues of one or more organochlorines and organophosphates. Carbomates and synthetic pyrethroids were not detected, possibly due to factors such as their concentration below the limits of detection (LOD) or non-availability. Results of this study revealed that organochlorines were the most abundant pesticide, followed by organophosphates. This is probably because cowpea is highly susceptible to infestation by Callosobruchus maculates and consequently often subjected to post-harvest treatment with pesticides to preserve them during storage and avoid economic losses. Incidentally, the present study revealed the widespread use of both pre-harvest and post-harvest pesticides.

The result from cowpea harvested in the 2016/2017 cropping season revealed that a number of components of pesticide residues were predominant in Bazza and Brown cultivars when compared to Potiskum, Gwarzo, and Iron cultivars. The sequence of occurrence is Brown $(0.30 \ \mu g/g) > Bazza > (0.20 \ \mu g/g) > Iron (0.17)$ μg/g) > Potiskum (0.12 μg/g) > Gwarzo (0.11 µg/g). The level of DDVP (Dichlorvos or 2,2dichlorovinyl dimethyl phosphate) residues in Bazza (0.02 μ g/g) and Brown (0.02 μ g/g) cowpea were above the international permissible standard (0.01 µg/g). This could be attributed to the application of the insecticides post-harvest at a level likely above the recommended quantity used in preserving stored cowpea to maintain the quality. This corroborates the findings of Yusuf et al. [11], who reported the presence of DDVP residues in cowpea grains, six months after application. This could be attributed to the fact that cowpea from 2016/17 cropping season was purchased nine months after the harvest and may have been therefore, subjected to additional use of the insecticide. 2,2-dichlorovinyl dimethyl phosphate (DDVP) is an organophosphate and was the only post-harvest insecticide detected and quantified in this present study and could be an indication to its effectiveness against a broad spectrum of insect pests in stored products. Levels of DDVP above the safety limits suggests that the cowpea were not safe for human consumption as toxicity of this residue was likely to pose health risks to the consumers. DDVP above the safety limits is a potential hazard ranging from acute to chronic toxicity. Dichlorvos, like other organophosphate insecticides, act on acetylcholinesterase, associated with the nervous systems of insect. Evidence for other modes of action, applicable to higher animals, have also been presented [12]. The level of glyphosate in Gwarzo (0.01 µg/g), Potiskum $(0.01 \ \mu g/g)$, and Iron $(0.01 \ \mu g/g)$ cultivars were

lower than the international permissible standard

 $(0.1 \mu g/g)$. Appropriate dosage used by farmers or decreases in the level with time could be responsible for the observed low level of glyphosate in the cowpea. This is in agreement with the previous findings of Christopher et al. [13] that reported residues of post-harvest insecticide in stored staples foodstuff generally decline rather slowly. Glyphosate (N-(phosphonomethyl)glycine), is а chemical substance that causes serious eye damage and is toxic to aquatic life [14].

Hexachlorobenzene (HCB), g-chlordane, tnonachlor, CH(alphahexachlorocyclohexane), pp-DDD (Dichlorodiphenydichoroethane), p-p-DDT (Dichlorodiphenytrichoroethane), and p-p-DDE (Dichlorodiphenydichoroethylene) were identified in all the cowpeas. This study confirmed the presence of organochlorine insecticide residues in the cowpeas and also confirm that the levels of the residues in the retail samples of cowpea were above their safety limits. Their presence despite the ban as organochlorine pesticides with the characteristics of persistence, bioaccumulation, toxicity, and long range transport, suggests that the foodstuff were not safe for human consumption. The presence of organochlorines could be attributed to the persistence of these chemicals in the soil with high adsorption partition coefficient and their photodegradation ability to resist and biodegradation due the strength of bond between carbon and chlorine atoms in their structure. The result of this study compares to previous findings of Obida et al. [15], which revealed the presence of pesticide residues such as aldrin, endrin, p-p'-DDT, dieldrin, lindane, dazinon, dichlorvos, and carbofuran in bean samples from North-Eastern Nigeria. It also corresponds with the finding of Ogah et al. [10] which revealed the presence of mostly organochlorine pesticide residues in bean samples from Markets in Lagos State. Since they are persistent, their residues may have occurred on food grown in previously treated or contaminated soil. G-chlordane had the highest violation concentration in 2016/17 cropping season with 30% level above the international permissible standard (Table 2). The sequence of violations is as follows: g-chlordane > α -HCH > p-p-DDE > DDVP > HCB. Chlorpyrifos was not detected in seeds from the 2016/17 cropping season either because it was below the limit of detection (LOD) or because it was not used.

The result from 2017/2018 cropping season revealed that different residues were

predominant in Potiskum cultivar. The sequence of occurrence is Potiskum > $(0.12 \mu g/g)$ > Bazza $(0.10 \ \mu g/g) > Brown (0.07 \ \mu g/g) > Gwarzo (0.04$ $\mu g/g$) > Iron (0.00 $\mu g/g$). The levels of DDVP in Potiskum (0.01 μ g/g) and Iron (0.01 μ g/g) cultivars were at the same level as the international permissible standard (0.01 µg/g). The observed result could be attributed to the period of purchase because cowpeas from 2017/18 cropping season were purchased one week after harvest and therefore may not have been subjected to storage insecticides such as DDVP. The fact that DDVP was detected even though at low level agrees with the findings of Stephen et al. [16], who revealed the presence of DDVP in both pre-storage harvest and poststorage harvest samples analyzed.

The level of glyphosate in Iron (0.01 μ g/g), Bazza $(0.00 \mu q/q)$, Gwarzo $(0.01 \mu q/q)$, and Brown $(0.01 \mu g/g)$ cultivars were low when compared to the international permissible standard (0.1 μ g/g) and could be due to compliance to regulations and good agricultural practices by farmers. The absence of chlorpyrifos in Iron (0.00 µg/g) and Bazza (0.00 µg/g) cultivars implies that it was not used because it has been banned from agricultural use in some countries. Consuming cowpea laced with chlorpyrifos above the safety level would be an unsafe act which may lead to toxicity. For acute effects, the World Health Organization classifies chlorpyrifos as class II. moderately hazardous toxin [17]. Primarily, other chlorpyrifos and organophosphate pesticides interfere with signalling from the neurotransmitter acetylcholine in the synapse [18]. By irreversibly inhibiting acetylcholinesterase, chlorpyrifos leads to a build-up of acetylcholine between neurons and a stronger, long-lasting signal to the next neuron. Acute symptoms of chlorpyrifos poisoning occur when more than 70% of acetylcholinesterase molecules are inhibited [19].

The level of g-chlordane (0.13 μ g/g) in Potiskum cultivar was high when compared to the international permissible standard (0.01 μ g/g). The level of HCB in Potiskum (0.05 μ g/g), Iron (0.03 μ g/g), Bazza (0.02 μ g/g), and Brown (0.02 μ g/g) cultivar were high when compared to the international permissible standard (0.01 μ g/g) while the level of p-p-DDT (0.04 μ g/g) in Bazza cultivar was also high when compared to the international permissible standard (0.01 μ g/g). The trend in the concentration of all organochlorines detected in both seasons varies across the five locations with some above safety

limits and some below safety limits. G-chlordane also had the highest misuse concentration in 2017/18 cropping season with 65% above the international permissible standard followed by HCB and p-p-DDT. The observed high level of organochlorines such as g-chlordane, HCB, and p-p-DDT could be due to reliability for better post-harvest storage or could also be due to low vapour pressure of organochlorines with the characteristics of accumulation and penetration in the soil. This could be influenced by the condition of the soil including dryness of the soil and soil pH. This corroborates the report of Dinham [20], that the short interval between harvests to market and the likelihood of no testing for pesticide residue in developing countries contributed to frighteningly high residual levels in urban markets and also in agreement with studies of [21], which confirmed the presence of organochlorine insecticide residues in cowpea grains and dried yam chips from markets in Ile-Ife, South-Western Nigeria.

The result from this study revealed that more pesticide residues were present in cowpea from 2016/2017 cropping season when compared to those from 2017/2018 cropping season. The high concentration of organochlorines residues quantified in the 2016/17 cowpea cropping season was a reflection of the persistence, commingling, and past usage which resulted in bioaccumulation or probably arising from the cultivation of the crop on contaminated soils where the application of the insecticides was intense. This could be due to non-compliance with Maximum Residue Limits in 2016/17 cowpea cropping season. The reason for high violation of g-chlordane in both cropping seasons is a reflection of its effectiveness against a wide variety of insects and probably due to availability, cost-effectiveness, and misuse or lack of requisite knowledge on the appropriate dosage needed to be applied whereas the reason for high level of DDVP in the 2016/17 cowpea cropping season could be due to additional use of DDVP for long post-harvest preservation. Considering the level of exceedance of pesticide residues detected in some cowpea from the previous croppina season. manv consumers are expected to be exposed to these substances via cowpea.

The quantification of pesticide residues in the foreign samples was aimed at determining the presence or absence of post-harvest insecticides and compare to the local product. Results from

foreign cowpea samples revealed the presence of pre-harvest pesticide residues in both foreign samples with some above safety limits and some below their safety limits. Results from foreign "A" cowpea sample revealed a high level of tnonachlor (0.05 µg/g) and HCB (0.05 µg/g) and were above the international permissible standard (0.01 µg/g) while the levels of glyphosate (0.01 μ g/g) and α -HCH was low when compared to the international permissible standard (0.01 µg/g). Results from foreign "B" cowpea revealed high level of g-chlordane (0.08 μ g/g) and t-nonachlor (0.04 μ g/g) when compared to the international permissible standard (0.01 ug/g) while the level of glyphosate (0.01 μ g/g), α -HCH (0.01 μ g/g), and p-p-DDD $(0.01 \ \mu g/g)$ was low when compared to the international permissible standard (0.01 µg/g). DDVP was not detected at all in any of the foreign samples. Therefore, the result suggests that packaging would be a good option and a good example of integrated pest management that can prevent the additional use of storage insecticide such as DDVP.

The detection of organochlorines in cowpea suggests that persistent pesticides may still be in use even though they have been banned in Nigeria and most countries of the world. The reason for their use could be cost-effectiveness and their broader spectrum of activity. Ogah et al. [22], reported that the goal of monitoring of pesticide use in agriculture should, therefore, be directed at ensuring that banned pesticides are no longer manufactured or imported into the country; this is in addition to ensuring appropriate use of recommended products [23,24,25].

Non-compliance with maximum residue limits (international permissible standards) can impact negatively on international trade in agricultural products as each commodity must meet international standards or standards of the receiving. In Nigeria, it is expected that farmers should increase cowpea yield annually for export purposes, but if the trend in violation of pesticides uses in cowpea continues it may jeopardize her effort to export cowpea in the international market and may limit any further agricultural opportunities. Therefore, there is need to suggest the use of Hazard Analysis and Critical Control Points tool as a systematic risk assessment approach that identifies, evaluates, and controls hazards related to food safety throughout the food supply chain. This would further identify critical control points, determine the critical limits for each critical control points,

establish monitoring procedures for critical control points, plan and take corrective action when critical limits are exceeded, and establish verification procedures for the Hazard Analysis and Critical Control Points for the cowpea safety management system. This recommendation could increase the efficiency of the Nigeriacoordinated and national food control programmes to ensure safe and quality cowpea for all.

5. CONCLUSION

Generally, cowpea from the previous season (2016/17) contained higher concentrations of post-harvest and pre-harvest pesticide residues than those from the current season (2017/18). This could be caused by the additional use and over dosing of pesticides during storage. The levels of some of the residues exceeded the safety limits while some were below the safety limits, suggesting that some of the retail samples of cowpea were not safe for human consumption as bioaccumulation, persistence, and toxicity of these residues was likely to pose serious health risks to the consumers. The result also, suggests that proper packaging cowpea could help maintain the quality of cowpea and further prevent the use of storage insecticides.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

 Oguh CE, Musa AD, Orum TG, Iyaji RO, Musa A. Risk Assessment of Heavy Metals Level in soil and Jute Leaves (*Corchorus olitorius*) Treated with Azadirachtin Neem seed Solution and Organochlorine. International Journal of Environment, Agriculture and Biotechnology (IJEAB). 2019;4(3):256-266.

Available:http://dx.doi.org/10.22161/ijeab/4 .3.24.

- Alexandratos N, Bruinsma J. World agriculture towards 2030/2050. The 2012 revision. ESA working paper. Food and Agricultural Organization. Rome; 2012. Available:https://www.fao.org/agriculture/cr ops/themtic-sitemap/theme/pests/code/en
- Ogah CO, Tettey J, Coker HB, Adepoju-Bello AA. Analysis of organochlorine Pesticide residues in beans from markets

in Lagos State, Nigeria. West African Journal of Pharmacy. 2012;23(1): 60-68.

- Oguh CE, Uzoefuna CC, Oniwon WO, Ugwu CV, Ahaiwe PT, Okeke CB, Ezikanyi GK. Risk assessment on bioaccumulation of potentially toxic elements on soil and edible vegetables Corchorus olitorius and Amaranthus cruentus grown with water treatment sludge in Chanchaga Minna, Niger State, Nigeria. J. of Res. in Environ. Sci. and Toxicol. 2019;8(2):92-103. DOI:http:/dx.doi.org/10.14303/jrest.2019.0 33.
- USEPA. Multimedia, Multi-pathway and Multi-receptor Risk Assessment (3MRA) Modellling System. U.S Environmental Protection Agency, Office of Research and Development, Washington DC. 2002;1-9.
- Yusuf SR, Lawan SH, Wudil BS, Sule H. Detection of Dichlorvos Residue in cowpea grains, six months after application using High-Performance Liquid Chromatography. Asian Research Journal of Agriculture. 2017;7(4).
- World Health Organization (WHO). World health statistics 2010. Geneva, Switzerland: World Health Organization; 2010.
- Oguh CE, Okpaka CO, Ubani CS, Okekeaji U, Joseph PS, Amadi EU. Natural Pesticides (Biopesticides) and Uses in Pest Management-A critical review, Asian Journal of Biotechnology and Genetic Engineering. 2019;2(3):1-18
- Stockholm convention on persistent organic pollutants (POPs). Geneva, secretariat of the stockholm convention. Available:http://chm.pops.int. Retrieved on February 2018.
- Ogah CO, Tettey J, Coker HB, Adepoju-Bello AA. Analysis of organochlorine Pesticide residues in beans from markets in Lagos State, Nigeria. West African Journal of Pharmacy. 2010;23(1):60-68.
- Yuguda AU, Abubakar ZA, Jibo AU, AbdulHameed A, Nayaya AJ. Assessment of Toxicity of Some Agricultural Pesticides on Earthworm (Lumbricus Terrestris). American-Eurasian Journal of Sustanaible. Agriculture. 2015;9(4):49-59.
- Pancetti F, Olmos C, Dagnino-subiatre A, Rozas C, Morales B. Noncholinesterase effects induced by organophosphate pesticides and their relationship to cognitive processes: Implication for the action of acyl peptide hydrolase. Journal of

Toxicology Environmental and Health. 2007;10:623.

- Christopher ER, Nilda RB, Leopoldo EE, Teal MP. Assessment of new herbicide programmes for cowpea production. Cambridge Core Journals on Weed Technology. 2018;1(2):1-3.
- European Chemicals Agency (ECHA). Glyphosate. The effect of glyphosate. An agency of the European Union; 2017. Available at https://echa.europa.eu.
- Obida MG, Stephen SH, Goni A, Victor OO. Pesticide Residues in bean samples from North-eastern Nigeria. Asian Research Publishing Network (ARPN) Journal of Science and Technology. 2012; 2(2):55-62.
- Stephen SH, Obida MG, Goni A, Victor OO. Pesticide Residues in bean samples from North-eastern Nigeria. Asian Research Publishing Network (ARPN) Journal of Science and Technology. 2012; 2(2):55-62.
- 17. Food and Agriculture Organization of the United Nations and the World Health Organization. The international code of conduct on pesticide management: FAO and WHO, Rome; 2014. Available at https://www.fao.org/agriculture/crops/pest.
- Flaskos J. The developmental neurotoxicity of organophosphorus insecticides: A direct role for the Oxon metabolites. Toxicology letters. 2012; 209(1):86-93.
 Retrieved on 02 April 2018.
- Connors SL, Levitt P, Matthew SG, Slotkin TA, Johnston MV, Kinney MC, et al. Fetal mechanisms in Neurodevelopmental Disorders. Pediatric Neurology. 2008;38(3):163-176.

Retrieved on 02 April 2018.

- Dinham B. Growing vegetables in developing countries for local urban populations and export markets. Problem confronting small scale producers. Pesticide Management and Science. 1993; 59:575-582.
- Olufade YA, Sosan MB, Oyekunle JAO. Levels of organochlorine insecticide residues in cowpea grains and dried yam chips from Markets in Ile-Ife, Southwestern Nigeria. A preliminary survey. Ife Journal of science. 2014;16(2):161-170.
- 22. Devon LJ. Pesticides found to cause transgenerational mental disorders and obesity. Harmful traits are inherited for three generations, Natural News; 2016. Available:http://www.naturalnews.com/pest icides-genetic-expressiontransgenerational-effects. Retrieved on 02 April 2018.
- 23. Langyintuo AS, Lowenberg-Deboer J, Faye M, Lambert D, Ibro G, Mousa B, et al. Cowpea supply and demand in West and Central Africa. Field Crops Research. 2003;82:213-231.
- 24. Sabur SA, Molla AR. Pesticide use, its impact on crop production and evaluation of integrated pest management technologies in Bangladesh. Bangladesh Journal of Agriculture Economic. 2001; XXIV(1 and 2):21-28.
- Singh BB. Recent genetic studies in 25. cowpea. In: Fatokun CA, Tarawali SA, Singh BB, Kormawa PM, Tamo M. (editions). Challenges and Opportunities Sustainable for Enhancing Cowpea Production. International Institute of Tropical Agriculture, Nigeria. lbadan. 2002;3-13.

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