



Dietary exposure assessment of organochlorine pesticides in two commonly grown leafy vegetables in South-western Nigeria

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ARTICLE INFO

Keywords:

Toxicology
Organochlorine pesticides
Vegetable
Dietary exposure
Health risks
Nigeria

ABSTRACT

Organochlorine pesticides (OCPs) are persistent pesticides whose usage have been banned or restricted worldwide and the presence of its residues in vegetables could affect its nutritional quality as well cause adverse health effects. This study quantified the OCP residue levels in commonly grown and consumed vegetables and assessed the carcinogenic and non-carcinogenic health risks from the consumption of the contaminated vegetables. The OCP residues levels in the extract from the vegetables were determined using a Gas Chromatograph coupled with Electron Capture Detector (GC-ECD). Health risk estimates were analysed using Estimated Average Daily Intake (EADI), Hazard Index (HI), and Hazard Ratio (HR) for children (16.7 kg) and adults (60 kg) weight categories. The residue analysis indicated that amaranths had the highest mean concentration of endrin aldehyde (2.987 ± 0.391 mg kg⁻¹) and endosulfan sulfate (0.661 ± 0.280 mg kg⁻¹), while in fluted pumpkin, the highest mean concentrations were endrin aldehyde (3.491 ± 0.376 mg kg⁻¹) and endosulfan sulfate (2.775 ± 0.644 mg kg⁻¹). The percentage of the detected OCP residues above Maximum Residue Limits (MRLs) ranged from 25% to 100% for both vegetables. Non-carcinogenic health risk estimates for the children weight category showed that aldrin, dieldrin, endrin, endrin aldehyde, and heptachlor detected in both vegetables had HI > 1. While for adults, only aldrin, dieldrin, endrin, and endrin aldehyde revealed non-carcinogenic effect in both vegetables. Human risk estimations for the carcinogenic health effect for the two vegetables showed that aldrin and dieldrin could pose carcinogenic health risks to adult, while aldrin, dieldrin, heptachlor and heptachlor epoxide could pose carcinogenic health risks to children. The results revealed both non-carcinogenic and carcinogenic health risks for the consumers of the contaminated vegetables from the selected locations in South-western Nigeria.

1. Introduction

Vegetables such as amaranths (*Amaranthus* spp) and fluted pumpkin (*Telfairia occidentalis*) play an important nutritional and socio-economic role for both farmers and consumers. However, the cultivation of these vegetables attracts a wide range of pests and diseases which often require rigorous pest control or management (Dinham, 2003). Pesticides are often used in agriculture for management of pests that may affect yield and farmers' productivity, thereby improving crop yield and farm output. Pesticides are among the leading causes of death by self-poisoning, particularly in low and middle-income countries as they are highly toxic and can deliberately spread in the environment causing both acute and chronic health effects (WHO, 2018). For instance, the persistent organic pollutants (POPs) notably persistent organochlorine pesticides like aldrin, dieldrin, heptachlor, heptachlor and endosulfan can manifest

acute health effects ranging from headaches to dizziness, irritability, vomiting nervousness, confusion, nausea, and convulsion (ATSDR, 1996, 2002), while chronic health effects may include reproductive defects, neurotoxicity, tremor and cancer (IARC, 2001; ATSDR, 2007, 2015). The chronic and acute health effects of these persistent organochlorine pesticides have necessitated the World Health Organization (WHO) to organise conventions and treaties like Rotterdam and Stockholm Convention among nations (which was also ratified by Nigeria) with a view to phase out, ban or restrict importation and usage of pesticides and other substances that are toxic to man and persistent in the environment (UNEP, 2001;2011; Stockholm Convention, 2012).

The pest control practices in vegetable production in Nigeria involves applications of highly toxic pesticides in which their misapplication could result in pesticide contamination of the agricultural produce as well as causing serious compromise of the environment and the general

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<https://doi.org/10.1016/j.heliyon.2019.e01895>

Received 24 January 2019; Received in revised form 7 May 2019; Accepted 31 May 2019

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biota. The contamination of vegetable by organochlorine pesticides (OCPs) have been reported by several works: cabbage samples in India (Bakore et al., 2002), vegetables and fruits in Kuwait (Jallow et al., 2017), lettuce and cabbage in Togo (Kolani et al., 2016) and cabbage, carrot and okra vegetables in Ghana (Bempah et al., 2011a). Related studies in Nigeria include Akan et al. (2014) on spinach, lettuce, cabbage, Ibrahim et al. (2018) on fluted, spinach, and sorrel leaves. Benson and Arowajoye et al. (2011) on *Solanum lycopersicum* and *Capsicum annum* and Njoku et al. (2017) on *Telfairia occidentalis*. The presence of the detected OCPs in food matrices shows that the chemicals are still being used by farmers in Nigeria (Oyekunle et al., 2011).

None of the previous works done on OCP residue levels in vegetables have assessed the non-carcinogenic and carcinogenic health risk associated with consumption of amaranths and fluted pumpkin contaminated with OCPs in South western Nigeria. The aim of this study was to quantify OCP residue levels in commonly consumed vegetables and estimate the carcinogenic and non-carcinogenic health risks due to dietary exposure to the vegetables for children and adult populations in South-western Nigeria.

2. Methodology

2.1. Sample collection and preparations

The composite samples (5 samples per amaranths/fluted pumpkin) used for the study were obtained from farms and open markets in South-western Nigeria. A total of 32 composite samples for both amaranths and fluted pumpkin were collected for the OCP residue analysis. Each composite sample (1 kg) of vegetables was rinsed with distilled water, allowed to drain properly, chopped with a sharp knife on a chopping board and oven dried at 45°C for 2 days until a constant weight was attained. To obtain a homogenous representative sample, each sample was macerated and pulverised to a homogenous powdered form using blender. The knife, chopping board and blender were washed thoroughly with water and rinsed with acetone to avoid cross contamination. Each sample was then placed in Ziploc bags, well-labelled and stored in a cool place prior to further analysis.

2.2. Extraction of pesticide residues from samples

The reagents used in this study were Dichloromethane (GFS Chemicals, Columbus), n-Hexane (Ultrafine Limited, Marlborough House, London), Acetone (GFS Chemicals, Columbus), Silica gel 60–200 mesh (Labtech Chemicals), and anhydrous sodium sulphate (Merck, Germany). The reagents were of spectra grade. The extraction followed the method of Oyekunle et al. (2011) in which case 20 g of homogenized composite vegetable samples was weighed into a pre-extracted Whatman thimble. The sample was Soxhlet extracted for 4 h using Dichloromethane (DCM) as the extraction solvent. The extract was then concentrated by distilling-off the solvent (DCM) on a rotary evaporator at about 41°C. The reduced extract was then preserved for clean-up.

2.3. Clean-up

For the clean-up experiment, a column of about 15 cm (length) x 1 cm (internal diameter) was packed first with glass wool and then 5 g activated silica gel prepared in a slurry form in DCM. About 5 g of anhydrous sodium sulfate was placed on top of the column to absorb any water in the sample or the solvent. The pre-elution was done with 15 mL of DCM without exposing the sodium sulfate layer to air so as to prevent the cracking of packed silica gel adsorbent. The reduced extracts were run through the column and allowed to sink below the sodium sulfate layer. Elution was done with 3 x 10 mL portions of DCM. The eluents were collected and accompanying solvent was then evaporated to dryness under a stream of pure nitrogen.

2.4. Instrumental analysis

Detection and determination of the pesticide residues were performed by reconstituting the dried sample eluents with 2 mL n-hexane before injecting 1 µL of the purified and cleaned up eluents into the injection port of an Agilent 7890A Gas Chromatograph (GC) system equipped with Electron Capture Detector (ECD). The separation was performed on a fused silica capillary column (DB-17, 30 m x 0.250 mm internal diameter and film thickness of 0.25 µm). The temperatures of the injector and detector were 250°C and 290°C respectively. Oven temperatures programme started from 150°C and increased to 280°C at 6°C per minute. The injection was carried on a splitless injector, carrier gas was Helium at a flow rate of 2 mL/min and make up gas was nitrogen. The run time was 21.667 min. Quantification of the OCPs was based on external calibrations curves prepared from the standard solutions of each of the OCPs. The instrumental analysis was done at the Nigeria Institute of Oceanography and Marine Research (NIOMR) Laboratory, Lagos, Nigeria.

2.5. Quality assurance and control

All analytical procedures were monitored using strict quality assurance and control measures. Materials used for preparation of samples were well-washed and rinsed with acetone before re-use.

Chemicals used in the sample preparation and analyses were of spectra grade. Blank determination, percent recovery determination, limit of detection and limit of quantification were also carried out for quality control and assurance. Blank analyses were carried in order to check any interference or background value of OCPs in the extraction reagents (DCM, n-Hexane) and materials (extraction thimble). None of the OCPs was detected.

In absence of certified pesticide reference materials, recovery analysis was performed to evaluate the precision and efficiency of the analytical procedures using standard addition method. Two samples of homogenised vegetable, each weighing 20 g were chosen. For each vegetable, one sample was spiked with 10 mg kg⁻¹ standard mixture consisting of some of the available organochlorine pesticides of interest. The mixture was thoroughly mixed together to ensure maximum homogenization. The other sample was left un-spiked (control). The two samples of vegetables were extracted, cleaned-up and analysed following procedures described above. The recoveries of OCPs were determined by comparing the peak areas of the OCPs after spiking with those un-spiked and percentage recoveries were calculated based on proportion of concentration of analytes detected from the spiked samples.

The calibration curve of each pesticide of interest was derived by running serially diluted or calibrated standard solutions of 0, 0.01, 0.1, 0.5, 1, 2, 4.5, 7.5, 10, 12.5 ppm carried out in accordance with the European Commission (EC, 2017) guidelines. The linearity of calibration curve (R^2) was determined by plotting the concentration versus the peak area. The LOD and LOQ were evaluated using the relationship: $LOD = 3.3 S/b$ and $LOQ = 10S/b$ where S is the residual standard deviation of calibration function and b is slope of calibration curve (Stocka et al., 2016).

2.6. Statistical analysis

All data was analysed using descriptive statistical analysis. This includes frequency distributions, percentages, means and ranges. Data were also represented with bar chart and pie chart and Mann-Whitney U test was used to examine whether differences exist between residues detected in the two vegetables using SAS 9.2 (SAS, 2003).

2.7. Health risk estimation

Data on pesticide residues level were compared with Maximum Residue Limits (MRLs) recommended by United Kingdom/European Commission UK/EC (2008) for leafy vegetables. The non-carcinogenic

and carcinogenic health risk estimates for each of the organochlorine pesticides residues in leafy vegetables was computed using three basic standard indices: The Estimated Average Daily Intake (EADI), Cancer Benchmark Concentration (CBC) and the Health Risk Index (HRI). Estimated Average Daily Intakes (EADIs) of a pesticide residue and food consumption assumption were used to determine long term health risks to consumers. The EADI was obtained by multiplying the mean residual pesticide concentration (mg kg^{-1}) in the food of interest and the food consumption rate (kg d^{-1}) and dividing by body weight (Akoto et al., 2015; Sosan and Oyekunle, 2017; Forkuoh et al., 2018). Consumption rate for vegetable is $46.4 \text{ g/person/day}$ (WHO, 2012a, 2012b).

$$\text{EADI} = \frac{\text{Mean residual pesticide concentration } (\text{mg kg}^{-1}) \times \text{food consumption rate } (\text{kg d}^{-1})}{\text{Mean body weight } (\text{kg})} \quad (1)$$

The non-carcinogenic health risk was assessed by calculating the health risk index (HRI) which was evaluated by dividing the EADI by their corresponding values of ADI with an assumption of average adult's body weight of 60 kg while children considered to have an average body weight of 16.7 kg (Oyeyiola et al., 2017). It was also assumed that absorption and bioavailability rates are 100%. When the health risk index > 1 , the food involved is considered a risk to the consumers; when the index < 1 , the food involved is considered acceptable (Akoto et al., 2013; Sosan and Oyekunle, 2017).

$$\text{Hazard Risk Index (HRI)} = \frac{\text{Estimated Average Daily Intake } (\text{mg kg}^{-1} \text{kg}^{-1})}{\text{Average Daily Intake } (\text{mg kg}^{-1} \text{d}^{-1})} \quad (2)$$

The Cumulative Hazard Index (CHI) was evaluated using the Reffstrup et al. (2010) equation below

$$\text{CHI} = \frac{\text{EADI}_1}{\text{ADI}_1} + \frac{\text{EADI}_2}{\text{ADI}_2} + \dots + \frac{\text{EADI}_n}{\text{ADI}_n} = \sum_{i=1}^n \frac{\text{EADI}_i}{\text{ADI}_i} \quad (3)$$

Where EADI_1 , EADI_2 , EADI_n and EADI_i are the estimated average daily intake of each individual pesticide. ADI_1 , ADI_2 , ADI_n and ADI_i are the reference or acceptable daily intake for each pesticide.

For carcinogenic effects, the Hazard Ratio (HR) were calculated using the equation below (Dougherty et al., 2000; Wang et al., 2011; Aamir et al., 2018; Forkuoh et al., 2018).

$$\text{HR} = \frac{\text{Estimated Average Daily Intake (EADI)} (\text{mg kg}^{-1} \text{kg}^{-1})}{\text{Cancer Benchmark Concentration (CBC)}} \quad (4)$$

where.

Risk is the maximum acceptable risk level (1×10^{-6}). The Cancer Benchmark Concentration (CBC) for carcinogenic effect is derived by setting the risk to one in one million due to lifetime exposure. The Oral Slope Factors (OSFs) for the pesticides were obtained from USEPA (2014).

$$\text{CBC} = \frac{\text{Risk Level} \times \text{Body Weight (kg)}}{\text{Consumption rate of vegetable } (\text{kg d}^{-1}) \times \text{Oral Slope Factor } (\text{mg kg}^{-1} \text{d}^{-1})}$$

3. Results and discussion

The percentage recovery (%R) values of some of the analytes in the

vegetable samples were in the range of 81%–109% for heptachlor and aldrin respectively as presented in Table 1. The LOD of the organochlorine pesticides was in range of 0.004–0.077 and LOQ was within range of 0.012–0.233. The calibration curves were found to exhibit good linearity, with correlation coefficients (R^2) of more than 0.994 for all the analytes and blank determination recorded no peak. The % recovery obtained where within the 70–120% range for acceptable recovery values and $\text{RSD} < 20$ as stipulated by European Commission's guidelines for evaluating accuracy and precision of a method (EC, 2017). The percent recovery, percent relative standard deviation and absence of pesticide residue in blank samples implied that the procedure outlined for this study can be

adjudged reliable, robust, precise, reproducible, repeatable and efficient.

The percentage occurrence of OCPs in amaranths and fluted pumpkin are presented in Fig. 1, β -endosulfan and endrin aldehyde were detected in all (100%) and almost all (94%) of both amaranths and fluted pumpkin samples respectively while heptachlor (25%) and heptachlor epoxide (25%) had lowest occurrence in amaranths and fluted pumpkin respectively.

The percentage contribution to total OCP burden presented in Fig. 2, shows that endrin had the highest contribution in amaranths (61%) and fluted pumpkin (41%) while heptachlors had lowest contributions of 2% and 4% for amaranths and fluted pumpkin respectively. The abundance of the pesticides detected in the two vegetables follows same trends and consistent with Oyekunle et al. (2017) earlier report on mean levels of cyclodienes in the cocoa samples from both Ile-Ife and Ondo, Nigeria which were in the order of $\Sigma \text{endrins} > \Sigma \text{endosulfans} > \Sigma \text{dieldrin} > \Sigma \text{heptachlors} > \text{aldrin}$.

This similar trend might be indicative of similarity in the usages of these group of OCPs by farmers in the most part of South-western Nigeria. The most frequently detected residues in both amaranths and fluted pumpkin were endrin aldehyde and β -Endosulfan which were present in almost all samples of vegetable analysed with endrin aldehyde, endosulfan sulfate, aldrin as the prominent in amaranths and endrin aldehyde, endosulfan sulfate and dieldrin as the most prominent in fluted pumpkin. This could be as a result of recent usage of the persistent OCPs by vegetable farmers for the production of vegetables. The usage might probably be related to low-cost and its effectiveness in controlling pests of different types and high OCP contaminations could also be due to nonpoint sources through transportation (atmospheric deposition, runoff and leaching) from agricultural farmland or soil into vegetable plantation (Yang et al., 2005).

Table 2 presents the mean concentration of OCPs and its percent above MRLs in amaranths and fluted pumpkin. Endrin aldehyde and endosulfan sulfate had highest mean concentration in both vegetables with mean of $2.987 \pm 0.319 \text{ mg kg}^{-1}$ and $0.661 \pm 0.280 \text{ mg kg}^{-1}$ respectively in amaranths and had mean of $3.491 \pm 0.376 \text{ mg kg}^{-1}$ and

$2.775 \pm 0.644 \text{ mg kg}^{-1}$ for fluted pumpkin. Heptachlor epoxide had the lowest mean concentration in amaranths ($0.051 \pm 0.014 \text{ mg kg}^{-1}$) and fluted pumpkin ($0.026 \pm 0.014 \text{ mg kg}^{-1}$). The overall means of OCPs

Table 1

Percentage recovery (%R), percentage relative standard deviation (%RSD), coefficient of determination (R^2), limit of detection (LOD) and limit of quantification (LOQ) of organochlorine pesticides.

Pesticides	% Recovery $\pm$ %RSD	Linearity (R^2)	LOD (mg kg ⁻¹)	LOQ (mg kg ⁻¹)
Heptachlor	81.00 $\pm$ 9.539	0.9985	0.014	0.042
Heptachlor epoxide	92.97 $\pm$ 7.230	0.9941	0.003	0.009
Dieldrin	96.90 $\pm$ 4.768	0.9950	0.045	0.135
Aldrin	109.00 $\pm$ 12.496	0.9988	0.010	0.031
Endrin	98.90 $\pm$ 3.411	1.0000	0.004	0.012
Endrin aldehyde	87.50 $\pm$ 13.018	0.9984	0.077	0.233
α -Endosulfan	100.57 $\pm$ 2.763	0.9998	0.004	0.013
β -Endosulfan	95.82 $\pm$ 2.247	0.9951	0.016	0.049
Endosulfan sulfate	94.26 $\pm$ 2.937	0.9986	0.030	0.090

detected in amaranths and fluted pumpkin were 5.366 ± 0.478 mg kg⁻¹ and 9.496 ± 1.075 mg kg⁻¹ respectively. Endrin is estimated to stay in soil

for over 10 years and can be broken down at high temperature or light to form primary endrin ketone and endrin aldehyde with very small proportion (less down 5 %) broken down to endrin aldehyde (ATSDR, 1996). The high level of endrin aldehyde could probably be as a result of biochemical or heat transformations of parent OCPs to these metabolites (ATSDR, 1996; Oyekunle et al., 2017) or as a result of past usage of endrin on the vegetables or at adjacent field. Oyekunle et al. (2017) reported the presence of endrin aldehyde (40.87 mg kg⁻¹) in cocoa beans from Ile-Ife which is higher than residues detected in the present study. The result is consistent with recent report by Ibrahim et al. (2018) that reported presence of endrin (0.732 ± 0.01 mg kg⁻¹) in fluted pumpkin and dieldrin (0.053 ± 0.01 mg kg⁻¹) in spinach from Northern Nigeria.

The mean concentration of endrin and endrin aldehyde detected in kolanuts from Osun State, Nigeria was 0.045 ± 0.059 mg kg⁻¹ and 0.208 ± 0.201 mg kg⁻¹ respectively (Sosan and Oyekunle, 2017) while endrin detected in cabbage, carrot and okra collected from local markets in Kumasi, Ghana was 0.016 mg kg⁻¹ in all vegetables (Bempah et al.,

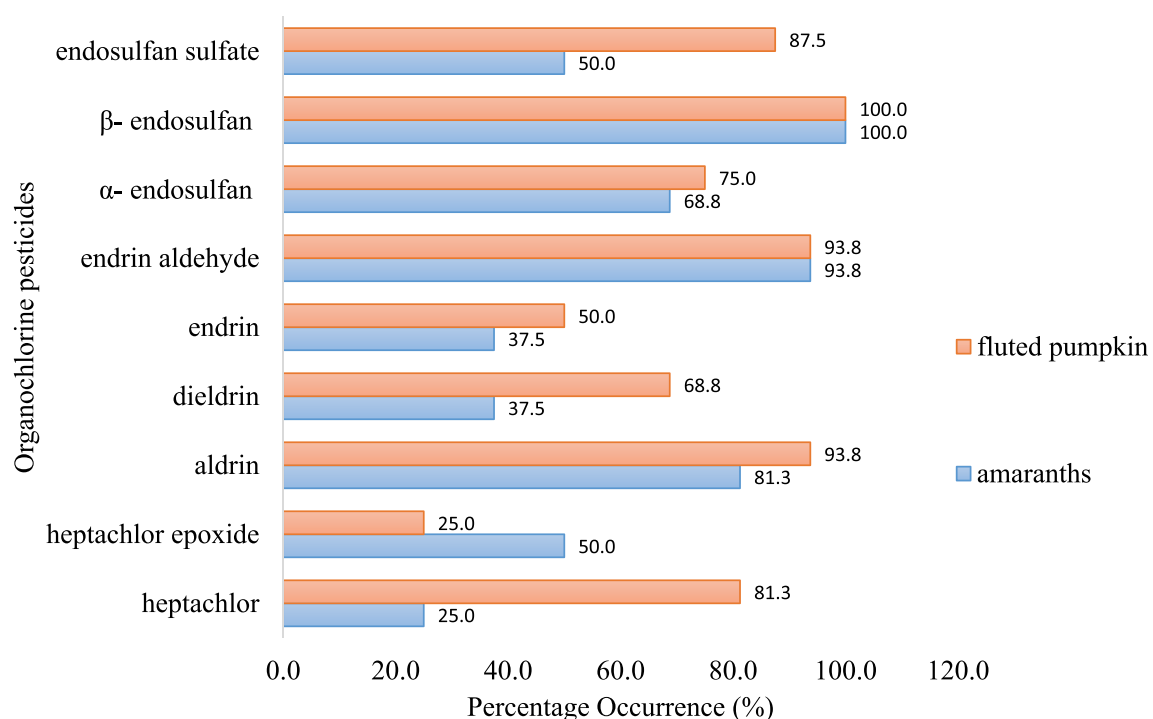


Fig. 1. Percentage occurrence of OCPs in amaranths and fluted pumpkin.

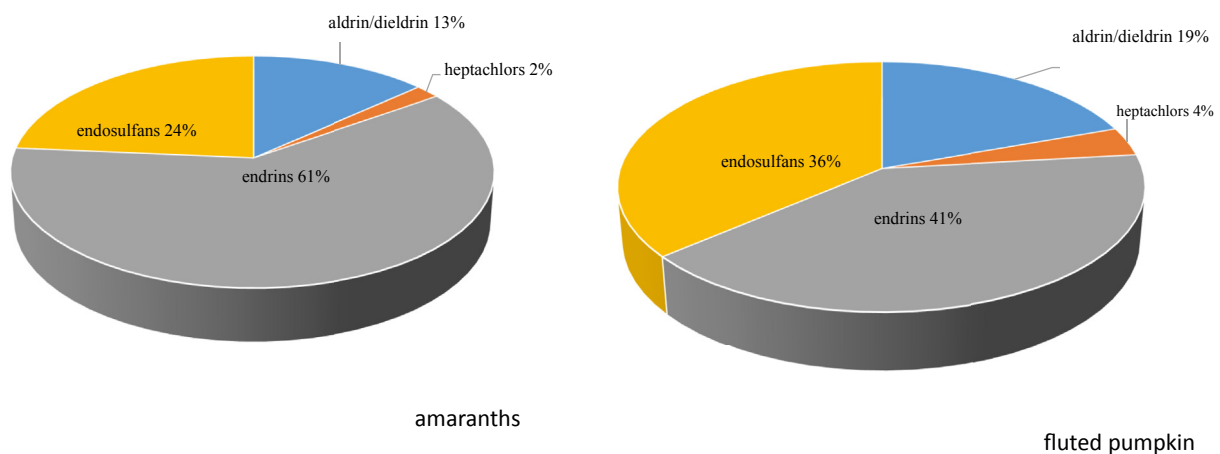


Fig. 2. Proportion of compounds to burden in amaranths and fluted pumpkin.

Table 2

Mean concentrations and MRLs of OCP residues in amaranths and fluted pumpkin from selected locations in South-western Nigeria.

Pesticides	Amaranth (n=16)				Fluted pumpkin (n=16)		
	UK/EC MRL (mg kg ⁻¹)	Mean ± SE (mg kg ⁻¹)	Range (mg kg ⁻¹)	% above MRLs	Mean ± SE (mg kg ⁻¹)	Range (mg kg ⁻¹)	% above MRLs
Heptachlor	0.01	0.052 ± 0.025	ND - 0.328	25	0.323 ± 0.048	ND - 0.608	81.3
Heptachlor epoxide	0.01	0.051 ± 0.014	ND - 0.149	50	0.026 ± 0.014	ND - 0.195	25
Aldrin	0.01	0.509 ± 0.133	ND - 1.538	81.3	0.391 ± 0.065	ND - 0.938	93.8
Dieldrin	0.01	0.205 ± 0.134	ND - 2.180	37.5	1.465 ± 0.879	ND - 14.496	68.75
Endrin	0.01	0.298 ± 0.184	ND - 2.208	37.5	0.351 ± 0.371	ND - 4.397	50
Endrin aldehyde	0.01	2.987 ± 0.391	ND - 5.364	93.8	3.491 ± 0.376	ND - 7.210	93.8
α-Endosulfan	0.05	0.074 ± 0.028	ND - 0.157	68.75	0.079 ± 0.014	ND - 0.198	75
β-Endosulfan	0.05	0.053 ± 0.066	0.092-0.965	100	0.595 ± 0.076	0.185-1.142	100
Endosulfan sulfate	0.05	0.661 ± 0.280	ND - 3.375	50	2.775 ± 0.644	ND - 9.478	87.5
Total OCP burden		5.366 ± 0.478			9.496 ± 1.075		
p-value (Mann-Whitney U test)				0.436 ns			

ns means not significant at p = 0.05.

2011a) and Kolani et al. (2016) reported that endrin detected in lettuce and cabbage from agricultural area of Togo was 0.039 ± 0.038 mg kg⁻¹ and 0.055 ± 0.008 mg kg⁻¹. These reported levels of endrin and endrin aldehyde were lower than the levels detected in both the fluted pumpkin and amaranths in the present study.

The Aldrin are used for the control of soil dwelling insects, cocoa mirids, termites, locust, ants and other pests. Dieldrin and aldrin are banned in Nigeria but some are still being used illegally (FMEHUD, 2009). The high level of aldrin in amaranths could be as a result of its recent usage on amaranths as aldrin breaks down to dieldrin in foods and other materials in the environment (ATSDR, 2002) while high level of dieldrin in fluted pumpkin could be as a result of past usage of aldrin on the vegetable or in the soil on which the vegetable was cultivated since dieldrin resists bacterial and chemical breakdown processes in the environment (Afful et al., 2010). Akan et al. (2014) reported that dieldrin and aldrin was more prominent on the leaf samples of cabbage from Alau Dam and Gongulong Agricultural areas in Borno State, North-eastern Nigeria with mean concentration of 10.4 mg kg⁻¹ and 59.9 mg kg⁻¹ respectively which was higher than aldrin and dieldrin detected in this study. Also, Benson and Aruwajoye (2011) reported detection of dieldrin on *Solanum lycopersicum* (0.024 ± 0.023 mg kg⁻¹) and *Capsicum annum* (0.019 ± 0.003 mg kg⁻¹) collected from local markets in Ota, South-western Nigeria, and Jallow et al. (2017) also reported that only one organochlorine insecticide (aldrin) was detected in all the fruits and vegetables samples from Kuwait with levels of aldrin, and dieldrin lower than those recorded in this study.

Endosulfan is a pure mixture of 70:30 ratios of two stereoisomers of α-Endosulfan and β-Endosulfan. Its technical grade contains 90–95% of the pure mixture and α-Endosulfan is more toxic (Stringer and Johnson, 2001) and endosulfan sulfate can be explained by the persistence of the individual endosulfan compounds. Endosulfan sulfate was reported to be the most persistent and major metabolite of Endosulfan with α-Endosulfan sulfate being the least persistent (Rosendahl et al., 2008). The

persistence of endosulfan sulfate could have been one of the reasons for its high concentration in the vegetable analysed. Sosan et al. (2008) analysed blood serum of cacao farmers for insecticide residues in selected cacao growing communities of South-western Nigeria and reported that 29% of the 76 farmers had residues of endosulfan in their blood while Njoku et al. (2017) also reported the insecticide in *Telfairia occidentalis* from Oyingbo market, Lagos, Nigeria.

All the detected pesticides were higher than UK/EU MRLs (Table 2), the percentage above MRLs ranged from 25% to 100% for both vegetables with β-Endosulfan and endrin aldehyde being the most prominent pesticides in both vegetables with 100% and 93% above MRLs respectively while heptachlor (25%) and heptachlor epoxide (25%) had lowest percentage above MRLs in amaranths and fluted pumpkin respectively.

The concentrations of the detected pesticide residues above respective MRLs could be as a result of recent application of the compounds with no reference to Good Agricultural Practices (GAP) or could be as a result of their persistence in the environment. The results of the present study are comparable with those of other studies. For example, Ibrahim et al. (2018) reported that the concentrations of aldrin, endrin and dieldrin detected in fluted, spinach, and sorrel leaves were much higher than the EU set maximum residue limits (MRLs) 0.01 mg/kg. Also, Njoku et al. (2017) reported that fluted pumpkin from Oyingbo market had endosulfan residue levels above the MRLs, Akan et al. (2014) also reported that detected pesticide residues in spinach, lettuce, cabbage, tomatoes and onions were above the MRLs. However, Ibitomi and Mohammed (2016) reported that the concentrations of all the pesticides detected in the fruit and vegetable samples from markets in Kaduna Metropolis were lower than the EU MRLs.

The potential non-carcinogenic health risk estimations of OCPs detected in amaranths for children and adults are presented in Table 3. Endrin aldehyde (41.487), aldrin (14.139), dieldrin (5.695), endrin (4.139), heptachlor (1.445) and heptachlor epoxide (1.417) had HI values > 1 for children while endrin aldehyde (11.547), aldrin (3.935),

Table 3Potential non-carcinogenic health risk estimation of OCP residues in *Amaranthus* spp from selected farms and markets in South-western Nigeria.

Pesticides	Children				Adult		
	ADI (mg kg ⁻¹ d ⁻¹)	EADI (mg kg ⁻¹ d ⁻¹)	Hazard index	Health risk	EADI (mg kg ⁻¹ d ⁻¹)	Hazard index	Health risk
Heptachlor	0.0001	9.0×10^{-4}	8.972	Yes	2.5×10^{-4}	2.497	Yes
Heptachlor epoxide	0.0001	7.2×10^{-5}	0.722	No	2.0×10^{-5}	0.201	No
Aldrin	0.0001	1.1×10^{-3}	10.861	Yes	3.0×10^{-4}	3.023	Yes
Dieldrin	0.0001	4.1×10^{-3}	40.695	Yes	1.1×10^{-3}	11.327	Yes
Endrin	0.0002	9.8×10^{-4}	4.875	Yes	2.7×10^{-4}	1.357	Yes
Endrin aldehyde	0.0002	9.7×10^{-3}	48.487	Yes	2.7×10^{-3}	13.496	Yes
α-Endosulfan	0.006	2.2×10^{-4}	0.037	No	6.1×10^{-5}	0.010	No
β-Endosulfan	0.006	4.6×10^{-4}	0.275	No	4.6×10^{-4}	0.077	No
Endosulfan sulfate	0.006	2.2×10^{-3}	1.285	Yes	2.2×10^{-3}	0.358	No
Cumulative HI			116.210			32.345	

Table 4

Potential non-carcinogenic health risk estimation of OCP residues in fluted pumpkin from selected farms and markets in South-western Nigeria.

	Children				Adult		
Pesticides	ADI (mg kg ⁻¹ d ⁻¹)	EADI (mg kg ⁻¹ d ⁻¹)	Hazard index	Health risk	EADI (mg kg ⁻¹ d ⁻¹)	Hazard index	Health risk
Heptachlor	0.0001	1.4 × 10 ⁻⁴	1.445	Yes	4.0 × 10 ⁻⁵	0.402	No
Heptachlor epoxide	0.0001	1.4 × 10 ⁻⁴	1.417	Yes	3.9 × 10 ⁻⁵	0.394	No
Aldrin	0.0001	1.4 × 10 ⁻³	14.139	Yes	3.9 × 10 ⁻⁴	3.935	Yes
Dieldrin	0.0001	5.7 × 10 ⁻⁴	5.695	Yes	1.6 × 10 ⁻⁴	1.585	Yes
Endrin	0.0002	8.3 × 10 ⁻⁴	4.139	Yes	2.3 × 10 ⁻⁴	1.152	Yes
Endrin aldehyde	0.0002	8.3 × 10 ⁻³	41.487	Yes	2.3 × 10 ⁻³	11.547	Yes
α- Endosulfan	0.006	2.1 × 10 ⁻⁴	0.034	No	5.7 × 10 ⁻⁵	0.010	No
β- Endosulfan	0.006	1.5 × 10 ⁻³	0.255	No	4.3 × 10 ⁻⁴	0.071	No
Endosulfan sulfate	0.006	1.8 × 10 ⁻³	0.306	No	5.1 × 10 ⁻⁴	0.085	No
Cumulative HI			68.916			19.182	

Table 5Potential carcinogenic health risk estimation of OC pesticide residues in *Amaranthus* spp. and fluted pumpkin from selected farms and markets in South-western Nigeria.

	Amaranthus						Fluted Pumpkin					
	Adult			Children			Adult			Children		
	CBC	HRI	Health risk	CBC	HR	Health risk	CBC	HR	Health risk	CBC	HR	Health risk
Heptachlor	2.87×10^{-4}	0.140	No	8.00×10^{-5}	1.806	Yes	2.87×10^{-4}	0.868	No	8.00×10^{-5}	11.216	Yes
Heptachlor epoxide	1.42×10^{-4}	0.277	No	3.96×10^{-5}	3.581	Yes	1.42×10^{-4}	0.141	No	3.96×10^{-5}	1.826	Yes
Aldrin	7.61×10^{-4}	5.173	Yes	2.12×10^{-5}	66.770	Yes	7.61×10^{-5}	3.973	Yes	2.12×10^{-5}	51.291	Yes
Dieldrin	8.08×10^{-4}	1.961	Yes	2.25×10^{-5}	25.310	Yes	8.08×10^{-5}	14.012	Yes	2.25×10^{-5}	180.873	Yes
Endrin	-	-	-	-	-	-	-	-	-	-	-	-
Endrin aldehyde	-	-	-	-	-	-	-	-	-	-	-	-
α- Endosulfan	-	-	-	-	-	-	-	-	-	-	-	-
β- Endosulfan	-	-	-	-	-	-	-	-	-	-	-	-
Endosulfan sulfate	-	-	-	-	-	-	-	-	-	-	-	-

dieldrin (1.585), endrin (1.152) posed non-carcinogenic risk to adult consumer of the vegetable.

The cumulative hazard index for non-carcinogenic health effects in the vegetable indicated that children (68.916) and adults (19.182) had CHI values > 1 suggesting that both the adults and children could be at risk for consuming the vegetable from the study area.

Table 4 shows the potential non-carcinogenic health risk estimations for fluted pumpkin. For children category, endrin aldehyde (48.487), dieldrin (40.695), aldrin (10.861), heptachlor (8.972), endrin (4.875), and endosulfan sulfate (1.285) had HI values > 1 and could pose non-carcinogenic health risk to children while for adult category, endrin aldehyde (13.496), dieldrin (11.327), aldrin (3.023), heptachlor (2.497), and endrin (1.357) had HI values > 1 indicating that they could pose systemic health effect for adult consumers of the vegetable. The overall risk in adult and children were 32.345 and 116.210 respectively and may result into cumulative systemic health risk for both adult and children.

In this study, only endosulfans in amaranths had HI values < 1 for the non-carcinogenic health risk. The estimates of the health risks obtained in children and adult category from the analysed amaranths samples are comparable with the analysis of health risk estimates of OCPs in kolanuts obtained from markets in Osun State, Nigeria which revealed that the HI values for endosulfan sulfate, α-endosulfan, β-endosulfan were below the value of 1 (Sosan and Oyekanle, 2017). Adefemi et al. (2018) reported that heptachlor, aldrin, heptachlor epoxide, and endrin aldehyde detected in *Senecio bialfrae* from Ekiti State, Nigeria posed non-carcinogenic health risk to children. Bempah et al. (2011b) and Donkor et al. (2015) revealed that endrin aldehyde, heptachlor, heptachlor epoxide detected in tomatoes from Ghana pose health hazard to children. Also, Bempah et al. (2011a) in a related study reported endrin in vegetables from another study area in Ghana posed risk to the children consumers of the contaminated vegetables, the results which is comparable with results obtained from the present study.

The results for the carcinogenic health risks are summarized in

Table 5. For adult category, aldrin (5.173) and dieldrin (1.961) had HR > 1 in amaranths while also in fluted pumpkin, aldrin (3.973) and dieldrin (14.012) had HR > 1 which could pose carcinogenic risk to its consumers. For children category, aldrin (66.770), dieldrin (25.310), heptachlor epoxide (3.581) and heptachlor (1.806) detected in amaranths had HR > 1. Same trend was also observed in fluted pumpkin with dieldrin (180.873), aldrin (51.291), heptachlor (11.216), heptachlor epoxide (1.826) also had HR > 1. The hazard ratio (HR) > 1 means it could pose carcinogenic risk to its consumers (Akoto et al., 2013; Sosan and Oyekanle, 2017) and that the estimated daily intake of the pesticide through the vegetable intake exceeds the reference concentrations. The consumption of the contaminated pesticide could pose potential carcinogenic effect for children and adult consumers of both amaranths and fluted pumpkin from the study area with risks greater than 1 in a million people while aldrin, dieldrin, heptachlor and heptachlor epoxide could pose potential carcinogenic health effect for children consumers of amaranths and fluted pumpkins. The HR > 1 indicate that the OCPs residues in the vegetable posed chronic human health risk most especially cancer. This result is consistent with earlier report by Akoto et al. (2015) that heptachlor and dieldrin detected in baby foods in Ghana which had HR values > 1, thus, could pose carcinogenic risk to children. In contrast, Bolor et al. (2018) reported that carcinogenic risk values for vegetables from all selected farms in Ghana were < 1. Aldrin, dieldrin, heptachlor and heptachlor epoxide are listed as dangerous chemicals by Stockholm convention in 2001 while endosulfan was added in 2011, meaning all the chemicals are dangerous to human health and our environment which should not be used in crop production. The International Agency for Research on Cancer (IARC) and USEPA also classified dieldrin, aldrin, heptachlor and heptachlor epoxide are group 2B possibly carcinogenic to humans (IARC, 2001; ATSDR, 2002, 2007). Thus, there is probability of individuals (both children and adult) developing cancer over a lifetime as a result of exposure to the OCPs residues in both vegetables.

4. Conclusion

The levels of the OCPs detected in the vegetables were significantly higher than the EU/UK MRLs and some of the detected residues could pose both non-carcinogenic and carcinogenic health risks to its consumers. The high tendency of the compounds to biomagnify and accumulate in human tissues raises serious health concerns considering the fact that both vegetables are widely consumed in South-western Nigeria on a regular basis. There is an urgent need for routine analysis for pesticide in vegetables and other food candidates commonly consumed in Nigeria. There is also the need for enforcement of pesticide regulations in addition to training of farmers on the need to adhere to recommended pre-harvest intervals and discourage illegal usage of banned chemicals in agricultural production.

Declarations

Author contribution statement

Adeoluwa Oluwaseyi Adeleye: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Mosudi Babatunde Sosan: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

John Adekunle Oyedele Oyekunle: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Funding statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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