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Assessment of Dietary Exposure to Organochlorine Insecticide in Cabbage (*Brassica oleracea*) from Selected Markets and Stores in South-western Nigeria

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Abstract

Cabbage (*Brassica oleracea*), a ready-to-eat vegetable obtained from open markets and stores was analysed for its organochlorine insecticide (OCI) contamination and potential health risks associated with its regular consumption. The OCI residue levels in the extract from the vegetable were determined using a Gas Chromatograph coupled with Electron Capture Detector (GC-ECD). Health risk estimates were analysed using Estimated Average Daily Intake (EADI) and Hazard Index (HI) for children (16.7 kg) and adults (60 kg) weight categories. The residue analysis showed that the predominant OCI detected in cabbage samples from stores were dieldrin (6.607 ± 4.232 mg kg^{-1}), endrin aldehyde (3.774 ± 0.363 mg kg^{-1}) and methoxychlor (1.404 ± 0.519 mg kg^{-1}), while endrin aldehyde (4.098 ± 0.770 mg kg^{-1}), aldrin (1.583 ± 1.024 mg kg^{-1}) and methoxychlor (1.543 ± 0.460 mg kg^{-1}) recorded the highest concentrations in samples from open markets. However, there was no significant difference in residues detected in cabbage from stores and open markets at $p > 0.05$. The percentage of detected residues above the United Kingdom/European Commission Maximum Residue Limits (MRL) ranged from 13 to 100%. The analysis of health risk estimates revealed that aldrin, dieldrin, endrin aldehyde and heptachlor concentrations were above the reference dose for children, while the quantities of aldrin, dieldrin and endrin aldehyde exceeded the reference dose for adult category. The results revealed that the detected residues exceeded acceptable standard and may present potential systemic risk to the vegetable consumers. Thus, a regular training of farmers on pesticide safety practices, especially on the need to adhere to recommended pre-harvest intervals and routine monitoring of pesticide residues in cabbage and other salad vegetables by regulatory agencies are recommended.

Keywords: Organochlorine; Dietary exposure; Insecticide, Residues; Cabbage; Hazard Index

Introduction

Cabbage (*Brassica oleracea* var. *capitata.* L.) is a cruciferous vegetable that belongs to the family of Brassicaceae. It is a popular exotic leafy vegetable in Nigeria used in homes and events to prepare dishes such as salads, coleslaw, fried rice, jollof rice, shawama, suya and pastries. It provides the richest source of glucosenolates in the human diet (Joao, 2012). The phytonutrients and other phytochemicals present in cabbage aid digestion, and protect humans against stomach ulcer and various types of cancer such as colon, oesophageal, rectum, thyroid, prostate and breast (Brennan *et al*., 2005; USDA, 2005; Fan *et al*., 2006; Wu *et al*., 2010).

Most salad vegetables including cabbage which are marketed in southern parts of Nigeria are usually produced in the rural areas of northern Nigeria particularly in Plateau, Adamawa, Kaduna, Kano, Nasarawa and Benue States (Ogbodo *et al*., 2009; Osondu *et al*., 2014). The production of this vegetable is constrained by many factors including pest and diseases, land tenure insecurity, lack of irrigation facilities and post-harvest losses (Ibeawuchi *et al*., 2015). The main insect pests of cabbage in Nigeria include: diamond back moth (*Plutella xylostella* L.), cabbage looper (*Trichoplusia ni* Hubner), imported cabbage worm (*Pieris rapae* L.) and cabbage maggot *(Delia radicum* L.) (Omokore *et al*., 2010). The activities of these insect pests render the crop unattractive and contribute to their rejection by consumers. In order to meet increasing demand of vegetables in Nigeria, insecticides and other pest management techniques are employed by farmers to control insect pests during cropping season and after harvesting to reduce pest-induced losses and preserve the quality of vegetables harvested (Asogwa and Dongo, 2009). However, most of the farmers misuse the insecticides during the production process. This may result in contamination of harvested vegetables with insecticide residues mainly due to the inability of the farmers to observe the withholding period recommended by manufacturers.

The organochlorine insecticides (OCIs) are compounds characterised by high persistence, low polarity, low aqueous solubility, high lipid solubility, ability to bio-accumulate, long half-life and potential of long range transport (Jayaraj *et al*., 2016). These features have increased the likelihood of their contaminating the environment and food matrices such as vegetables.

Exposure to OCIs over a short period may cause headache, dizziness, nervousness, confusion, nausea, incoordination, vomiting and convulsion (Agency for Toxic Substances and Disease Registry (ATSDR) 2000; 2005), while the long-term exposure to persistent chemicals such as DDT, HCH, endosulfan, and heptachlor have been linked with long term effects which include immune systems defects, neurotoxicity, reproductive toxicity and hepatotoxicity (Sahoo *et al*., 2008; Bano and Bhatt, 2010; Vijaya-Padma *et al*., 2011), alterations in levels of thyroid hormones, neurobehavioral disorders, tremor and death (ATSDR, 2007), Parkinson disease (Hong *et al*., 2014) and as well as causing cancer (Charlier *et al*., 2003; Cohn, 2011; Cohn *et al*., 2015).

Insecticide residues have been reported in cabbage vegetables from other countries such as Ghana (Boateng and Amuzu, 2013; Atieno *et al*., 2014), Togo (Kolani *et al*., 2016), China (Owago *et al*. 2007) and India (Tripathi *et al*., 2010; Bankar *et al*., 2012; Choudhury *et al*., 2013). Related studies carried out on cabbage in Nigeria include Akan *et al*. (2014) on cabbage and other vegetables from Borno State and Ibitomi and Mohammed (2016) on cabbage and other fruits from markets in Kaduna metropolis in Northern Nigeria. However, none of the few studies have evaluated the potential health risk associated with the consumption of the vegetable in order to guarantee that the cabbage marketed in other parts of the country most especially in south-western Nigeria are safe for consumption. Thus, the present study was designed to investigate the occurrence and levels of organochlorine insecticide residues in cabbage sold in some selected locations in Osun and Ekiti States in south-western Nigeria and estimate the potential health risks associated with the detected insecticide residues.

Materials and Methods

Sample Collection and Preparations

The samples used for the study were obtained from selected stores and open markets in Ado-Ekiti (7˚ 37' N and 5 ˚ 13' E) and Ido-Ekiti (7˚ 50' N and 5 ˚ 10' E), Ile-Ife (70˚ 50' N and 4˚ 69' E) and Osogbo (7˚ 46' N and 4˚ 34' E) in South-western Nigeria. The sampling locations in the selected towns were Awedele market, Oja Oba/Oja Bisi market, Olojudo market, Ido daily market, Oluode market, Alekuwodo market, Obafemi Awolowo University Central market, Mayfair market and Ife Central market. A total of 48 cabbage samples (bulked into 16 composite samples) were collected for OCI residue analysis. Each composite sample (1 kg) of cabbage was rinsed with distilled water, allowed to drain properly, chopped with a sharp knife on a chopping board and oven dried at 45^{o}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 Nakai blender (Japan). 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 cool place prior to further analysis.

Extraction of Insecticide Residues from Samples

The extraction followed the method of Oyekunle *et al.* (2011) in which case 20 g of homogenized cabbage sample was weighed into a pre-extracted Whatman thimble. The sample was Soxhlet extracted for 3 hours 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^oC. The reduced extract was then preserved for clean-up.

Clean-up

The clean-up experiment followed the method of Sosan and Oyekunle (2017). The eluents were collected and accompanying solvent was then evaporated to dryness under a stream of pure nitrogen (99.9%).

Instrumental Analysis

Detection and determination of the insecticide 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^oC and 290^oC respectively. Oven temperatures programme started from 150^oC increased to 280^oC at 6^oC 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 minutes. Quantification of the OCIs was based on external calibrations curves prepared from the standard solutions of each of the OCIs. The instrumental analysis was done at the Nigerian Institute of Oceanography and Marine Research (NIOMR) Laboratory, Lagos, Nigeria.

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. Percent recovery determination, response factor (RF) determination and blank determination were also carried out for quality assurance.

Blank Determinations

The background value of OCIs in the DCM was determined by injecting the spectra grade DCM into the GC.

Recovery (%R) Determination

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 insecticides of interest. The mixture was thoroughly mixed together to ensure maximum homogenization. The other sample was left un-spiked. The two samples were extracted and clean up following procedures of Sosan and Oyekunle (2017). With aid of micro syringe, 1 µL of sample was injected into GC column for GC-ECD analysis. The recoveries of OCs were determined by comparing the peak areas of the OCs after spiking with those un-spiked. Percentage recoveries was evaluated based on equation 1

$$\% R = \frac{\text{Peak area of A - Peak area of A'}}{\text{Peak area of OC in standard}} \times 100 \qquad (1)$$

where A = OC in spiked sample and A'= OC in un-spiked sample

Response Factor (RF) Determination

The response factor of the standard OCIs was obtained by the method of Sosan and Oyekunle (2017). This was determined by analyzing 1.0 µL of 1000 ppm stock solution of the standard mixture containing the internal standard (I.S.). The internal standard used for this work was hexachlorobenzene (HCB). The response factor for a sample peak is defined by the expression:

$$RF = \frac{\text{Peak area of OCIs}}{\text{Peak area of internal standard}} \qquad (2)$$

Statistical Analysis

All data was analysed using descriptive statistics (mean, range, standard error and percentage) and student t-test was also carried out using Statistical Analysis System (SAS) 9.1 version.

Health Risk Estimation

Data on insecticide residues level were compared with Maximum Residue Limit (MRLs) recommended by UK/EC (2008) for leafy vegetables. The health risk estimates for each of the organochlorine insecticides residues in leafy vegetables was computed using two basic standard indices: The Estimated Average Daily Intake (EADI) and the Health Risk Index (HRI). Estimated Average Daily Intakes (EADIs) of an insecticide residue and food consumption assumption were used to determine long term health risks to consumers. The EADI was obtained by multiplying the mean residual insecticide concentration (mg kg^{-1}) in the food of interest and the food consumption rate (kg d^{-1}) and dividing by body weight (Darko and Akoto, 2008; Sosan and Oyekunle, 2017). Consumption rate for cabbage in adult is 6.3 g/person/day (WHO, 2012a; 2012b)

$$EADI = \frac{\text{Mean residual insecticide concentration } (\text{mg kg}^{-1}) \text{ x food consumption rate } (\text{kg d}^{-1})}{\text{Mean body weight (kg)}} \qquad (3)$$

The potential health risk was assessed by calculating the health risk index (HRI) which was evaluated by dividing the EADI by their corresponding values of Acceptable Daily Intake (ADI) set by WHO (2003) 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 (USEPA, 2005; 2008). 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; Adeleye *et al*., 2019a).

$$\text{Hazard Risk Index (HRI)} = \frac{\text{Estimated Average Daily Intake } (\text{mg kg}^{-1}\text{ kg}^{-1})}{\text{Average Daily Intake } (\text{mg kg}^{-1}\text{ d}^{-1})} \qquad (4)$$

Results

The percentage recovery (%R) values of some of the analytes in the cabbage samples were in the range of 81% to 109% for heptachlor and aldrin respectively as presented in Table 1. The response factor of the organochlorine insecticides was in the range of 0.902 ± 0.005 (heptachlor) – 1.401 ± 0.100 (endrin). The blank determination records no peak.

Table 2 shows the mean concentrations and percentage OCI residues above Maximum Residue Limits (MRLs) in cabbage samples. The results showed that a total of 15 OCI residues were detected in cabbage collected from stores and markets in the selected locations. The total OCI burden detected in cabbage from stores and open markets were 14.257 ± 4.560 mg kg^{-1} and 11.899 ± 2.041 mg kg^{-1} respectively and not significantly different ($p > 0.05$). Among the sub groups of OCIs analysed, cyclodienes, DDT and HCH isomers accounted for 88.2%, 11.6% and 0.2%, respectively of the total organochlorine burden in cabbage obtained from stores whereas in open market samples, 69.5% of the total organochlorine burden detected belongs to cyclodienes group while DDT and HCH isomers accounted for 30.1% and 0.4%, respectively. The mean concentration of HCHs in cabbage from stores and open markets were 0.029 ± 0.011 mg kg^{-1} and 0.046 ± 0.042 mg kg^{-1} respectively.

Table 1: Percentage recovery (R %) and response factor of organochlorine insecticides

OCI	**Response Factor**	**Amount (**mg kg^{-1}) **of OCI used for spiking**	**Mean amount of OCI recovered**	**% Recovery**
HCB	-	10	9.48	94.80
γ-HCH	1.063 ± 0.023	10	10.08	100.80
Aldrin	1.200 ± 0.005	10	10.90	109.00
Dieldrin	1.101 ± 0.007	10	9.69	96.90
Heptachlor	0.920 ± 0.005	10	8.10	81.00
Endrin	1.401± 0.100	10	9.89	98.90
p, *p’*- DDT	1.300 ± 0.003	10	10.50	105.00

Table 2: Mean concentrations and MRLs of organochlorine insecticide residues in cabbage from stores and open markets in South-western Nigeria

		Store (n=8)				Open markets (n=8)			
Insecticides	**UK/EC MRL** (mg kg^{-1})	**Mean ± SE** (mg kg^{-1})	**Range** (mg kg^{-1})	**% above MRLs**	**% group**	**Mean ± SE** (mg kg^{-1})	**Range** (mg kg^{-1})	**% above MRLs**	**% group**
α-HCH	**0.01**	ND	-	ND		ND	-	ND	
β-HCH	**0.01**	ND	-	ND		ND	-	ND	
γ-HCH	**0.01**	0.020 ± 0.010	ND - 0.062	37.5		0.013 ± 0.009	ND - 0.073	25	
δ-HCH	**0.01**	0.009 ± 0.009	ND - 0.073	12.5		0.033 ± 0.033	ND - 0.267	12.5	
Σ HCH		**0.029 ± 0.011**			**0.20**	**0.046 ± 0.042**		**25**	**0.41**
Heptachlor	**0.01**	0.355 ± 0.121	ND - 1.023	75		0.568 ± 0.210	0.116 - 1.864	100	
Heptachlor epoxide	**0.01**	0.006 ± 0.006	ND - 0.047	100		0.031 ± 0.022	ND - 0.171	25	
Aldrin	**0.01**	0.519 ± 0.119	0.106 - 1.097	100		1.583 ± 1.024	0.245 - 8.698	100	
Dieldrin	**0.01**	6.607 ± 4.232	ND - 30.102	75		0.581 ± 0.235	ND - 2.149	87.5	
Endrin	**0.01**	0.159 ± 0.151	ND - 1.215	25		0.109 ± 0.068	ND - 0.561	50	
Endrin aldehyde	**0.01**	3.774 ± 0.363	2.430 - 5.173	100		4.098 ± 0.770	1.977 - 8.635	100	
α-Endosulfan	**0.05**	0.024 ± 0.012	ND - 0.069	37.5		0.032 ± 0.016	ND - 0.110	37.5	
β-Endosulfan	**0.05**	0.784 ± 0.067	0.492 - 1.013	100		0.671 ± 0.144	ND - 1.244	87.5	
Endosulfan sulfate	**0.05**	0.339 ± 0.105	ND - 0.724	62.5		0.287 ± 0.076	ND - 0.678	75	
Σ Cyclodienes		**12.568 ± 4.578**			**88.15**	**7.959 ± 1.899**			**69.51**
p, p' DDD	**0.05**	0.080 ± 0.048	ND - 0.380	37.5		1.065 ± 0.837	ND - 6.742	37.5	
p, p' DDE	**0.05**	0.022 ± 0.013	ND - 0.099	37.5		0.039 ± 0.029	ND - 0.238	37.5	
p, p' DDT	**0.05**	0.154 ± 0.076	ND - 0.446	37.5		0.798 ± 0.599	ND - 4.886	37.5	
Methoxychlor	**0.01**	1.404 ± 0.519	ND - 4.382	75		1.543 ± 0.460	ND - 3.333	75	
Σ DDT		**1.660 ± 0.660**			**11.64**	**3.445 ± 1.294**			**30.08**
Total OCI burden		**14.257 ± 4.560**				**11.899 ± 2.041**			
t-test					**0.696 ns**				

Note: ND indicates not detected; SE indicates standard error; ns indicates not significant at $\alpha = 0.05$

Considering the compounds detected in samples from stores, the *γ*-HCH (0.020 ± 0.010 mg kg^{-1}) and δ-HCH (0.009 ± 0.009 mg kg^{-1}) had highest concentration while δ-HCH (0.033 ± 0.033 mg kg^{-1}) and *γ*-HCH (0.013 ± 0.009 mg kg^{-1}) had highest concentration in samples collected from open markets. The mean concentration of cyclodienes in samples collected from stores and open markets were 12.568 ± 4.578 mg kg^{-1} and 7.959 ±1.899 mg kg^{-1} respectively. In cabbage samples collected from stores, dieldrin (6.607 ± 4.232 mg kg^{-1}) and endrin aldehyde (3.774 ± 0.363 mg kg^{-1}) had the highest concentration while in samples collected from open markets, endrin aldehyde (4.098 ± 0.770 mg kg^{-1}) and aldrin (1.583 ± 1.024 mg kg^{-1}) had the highest concentrations. The mean levels of DDTs present in samples from stores and markets were 1.660 ± 0.660 mg kg^{-1} and 3.445 ± 1.294 mg kg^{-1} respectively. In stores, methoxychlor (1.404 ± 0.519 mg kg^{-1}) and *p*, *p*' DDT (0.154 ± 0.076 mg kg^{-1}) had the highest mean concentration while in open markets, the highest residue levels of 1.543 ± 0.460 mg kg^{-1} and 1.065 ± 0.837 mg kg^{-1} were recorded for methoxychlor and *p*, *p*' DDD respectively.

In the analysed cabbage samples from stores and open markets, the percentage of detected residues above MRLs ranged from ND to 37.5 % and ND to 25 % in HCHs with γ-HCH as predominant insecticides in stores (37.5 %) and markets (25%). The percentage above MRLs ranged from 25 to 100% for cyclodienes group detected in samples from both the stores and open markets and the frequently detected insecticides from samples in stores were endrin aldehyde (100%), heptachlor epoxide (100%), aldrin (100%) and β-endosulfan (100%) while endrin aldehyde (100%), heptachlor (100%), and aldrin (100%) were most detected in samples from open markets. The % above MRLs ranged from 37.5 to 75% for DDT and its analogues detected in both the open markets and stores with methoxychlor (75%) as frequently detected insecticide.

The ADIs, EADIs and corresponding Health Risk Index (HRI) as well as the potential health risk associated with detected OCI residues in cabbage are presented in Table 3. For children category. the HRI values showed that dieldrin (13.558), endrin aldehyde (7.424), aldrin (3.965), and heptachlor (1.739) had HRI values > 1, while HRI of other insecticide residues detected were < 1.

TABLE 3: Potential health risk estimation of organochlorine insecticide residues in cabbage from selected locations in Ekiti and Osun States, South-western Nigeria

			Children			Adults		
Insecticides	**Mean** (mg kg^{-1})	**ADI** (mg kg^{-1} d^{-1})	**EADI**	**HRI**	**Health risk**	**EADI**	**HRI**	**Health risk**
α- HCH	-	0.005	-	-	No	-	-	No
β- HCH	-	0.005	-	-	No	-	-	No
γ- HCH	0.017	0.005	6.4×10^{-6}	0.0013	No	1.8×10^{-6}	0.0004	No
δ-HCH	0.021	0.005	7.9×10^{-6}	0.0016	No	2.2×10^{-6}	0.0004	No
Heptachlor	0.461	0.0001	1.7×10^{-4}	**1.7391**	**Yes**	4.8×10^{-5}	0.4841	No
Heptachlor epoxide	0.018	0.0001	6.8×10^{-6}	0.0679	No	1.9×10^{-6}	0.0189	No
Aldrin	1.051	0.0001	4.0×10^{-4}	**3.9649**	**Yes**	1.1×10^{-4}	**1.1036**	**Yes**
Dieldrin	3.594	0.0001	1.4×10^{-3}	**13.5582**	**Yes**	3.8×10^{-4}	**3.7737**	**Yes**
Endrin	0.134	0.0002	5.1×10^{-5}	0.2528	No	1.4×10^{-5}	0.0704	No
Endrin aldehyde	3.936	0.0002	1.5×10^{-3}	**7.4242**	**Yes**	4.1×10^{-4}	**2.0664**	**Yes**
α- Endosulfan	0.028	0.006	1.1×10^{-5}	0.0018	No	2.9×10^{-6}	0.0005	No
β- Endosulfan	0.728	0.006	2.7×10^{-4}	0.0458	No	7.6×10^{-5}	0.0127	No
Endosulfan sulphate	0.313	0.006	1.2×10^{-4}	0.0197	No	3.3×10^{-5}	0.0055	No
p, p′ DDD	0.572	0.01	2.2×10^{-4}	0.0216	No	6.0×10^{-5}	0.006	No
p, p′ DDE	0.031	0.01	1.2×10^{-5}	0.0012	No	3.3×10^{-6}	0.0003	No
p, p′ DDT	0.476	0.01	1.8×10^{-4}	0.018	No	5.0×10^{-5}	0.0050	No
Methoxychlor	1.473	0.01	5.6×10^{-4}	0.0556	No	1.5×10^{-4}	0.0155	No

ADI is acceptable Daily Intake set by WHO (WHO, 2003)

In adult category, only dieldrin (3.774), endrin aldehyde (2.066) and aldrin (1.104) had HRI values > 1 in cabbage from stores and open markets while HRI of other detected insecticides were < 1.

Discussion

The % recovery obtained was within the 70-110% range for acceptable recovery values stipulated by European Union's guidelines for evaluating accuracy and precision of a method (EC, 2017). This suggests that the procedure outlined for this study can be adjudged reliable and efficient.

The concentrations of the OCIs in samples from both stores and markets follow same trends of ΣHCH < ΣDDT < Σcyclodienes suggesting possibility of same source for cabbage sold by the traders. The prominence of γ-HCH and δ-HCH in cabbage from both stores and open markets could be possibly as a result of usage of technical Lindane that contained γ-HCH and δ-HCH for production of cabbage in Northern Nigeria. The higher concentration of γ-HCH with respect to α-HCH and β-HCH isomers suggests that Lindane (γ-HCH) is recently used for the cabbage production in Northern Nigeria as it has not degraded to its metabolites, α-HCH and β-HCH. In similar study in Northern Nigeria, Akan *et al*. (2014) reported that γ-HCH, dieldrin, α-HCH, aldrin and endosulfan were detected in leaf cabbage sampled from Alau Dam and Gongulong area with a mean concentration of 132.4 ± 7.34 mg kg^{-1}, 59.87 ± 1.34 mg kg^{-1}, 53.5 ± 7.19 mg kg^{-1}, 23.45 ± 3.45 mg kg^{-1} and 10.44 ± 0.11 mg kg^{-1} respectively which was much higher than the detected levels in this present study. In a recent study in south western Nigeria, Adeleye *et al*. (2019b) reported that δ-HCH detected in amaranths and fluted pumpkin from markets were 0.168 ± 0.068 mg kg^{-1} and 0.467 ± 0.147 mg kg^{-1} respectively. This is higher than the residues levels recorded in cabbage samples from both the stores and markets. In cabbage collected from India, Choudhury *et al.* (2013) reported the detection of α-HCH with mean concentration of 0.003 mg kg^{-1} and Bankar *et al.* (2012) reported the detection of α-HCH, β- HCH, γ-HCH and δ-HCH in range of 10.87 - 12.65 mg kg^{-1}, 4.43 - 3.23 mg kg^{-1}, 3.23 - 4.54 mg kg^{-1} and 5.43 - 5.96 mg kg^{-1} respectively which were also higher than HCHs detected in this present study. In contrast, Kolani *et al.* (2016) reported the total HCHs detected in cabbage from Togo to be 0.0151 mg kg^{-1} which is lower than (0.029 mg kg^{-1} and 0.046 mg kg^{-1}) in the present study.

Aldrin is used for control of soil dwelling insects (termites, ants), locust, cocoa mirids, and other pests and is reported to being used illegally in Nigeria (Federal Ministry of Environment (FMEHUD), 2009). The high level of aldrin in cabbage from open markets could be as a result of its recent usage in cultivation of cabbage while high level of dieldrin in samples from stores could be as a result of past usage on crops or degradation of aldrin used on the vegetable or in the soil on which the vegetable was cultivated as aldrin breaks down to dieldrin in foods

and other materials in the environment (ATSDR, 2002). The prominence of endrin aldehyde could be as a result of past usage on crops or probably be as a result of biochemical transformations of parent OCIs to these metabolites (Oyekunle *et al*., 2017). The mean concentration of aldrin and endrin aldehyde detected in cocoa beans (Oyekunle *et al*., 2017) from Ile-Ife, Osun State was 3.31 mg kg^{-1} and 40.87 mg kg^{-1} respectively which were higher than levels detected in present study locations. The aldrin and endrin aldehyde detected in this study is comparable with residues detected in amaranths and fluted pumpkin in selected locations in south western Nigeria by Adeleye *et al*. (2019a) while aldrin detected in cabbage from stores and markets was found to be higher than 0.00107 $mgkg^{-1}$ detected from cabbage in selected markets in Lagos by Oyeyiola *et al*. (2017).
The higher levels of methoxychlor and DDT were detected in cabbage obtained in the stores and markets and this revealed a similar trend which points to the fact that insecticide with methoxychlor and DDT as active ingredients are still being used by cabbage farmers in the Northern part of the country where the cabbage was produced since the marketers claimed not to spray chemicals on the crops at storage. In the present study, samples from stores had mean levels of DDT greater than both DDD and DDE which is an indication that DDT was recently used in the areas where cabbage is produced as it has not weathered or degraded. Boateng and Amuzu (2013) reported that concentrations of organochlorines in cabbage from Ghana were α-HCH (0.02 mg kg^{-1}), DDD (0.02 mg kg^{-1}) *p, p'* DDE (0.23 mg kg^{-1}), *p, p'* DDT (0.21 mg kg^{-1}), α-endosulfan (0.020 mg kg^{-1}) which are comparable with the levels recorded in the present study. However, Bolor *et al.* (2018) reported that OCI residues detected in cabbage from Ayigya, Ghana were methoxychlor (0.184 ± 0.0121 mg kg^{-1}) and *p, p'*-DDT, (0.00567 ± 0.00044mg kg^{-1}) while Kolani *et al.* (2016) reported DDTs detected in cabbage from Togo was between 0.000003 - 0.000215 mg kg^{-1} which is lower than the residue detected in both stores and open market in the present study.

All the detected organochlorine insecticides were above MRLs for the vegetable. The results of the present study are comparable with those of other studies. For example, Akan *et al*. (2014) reported that the concentrations of the pesticides detected in the vegetable samples (spinach, lettuce, cabbage, tomatoes and onions) were observed to be at high levels much higher than the maximum residue limits (MRLs) and acceptable daily intake values (ADIs) set for the vegetables. In another study, Adeleye *et al*. (2019a) reported that the concentrations of all detected pesticides in amaranths and fluted pumpkin from selected markets and farms in south western Nigeria were greater than EU MRLs which ranged between 25 and 100%. In a similar study in Ghana, Boateng and Amuzu (2013) reported that concentration of organochlorine in cabbage from

Ghana exceeded the MRL while in Togo, Kolani *et al*. (2016) reported that 36.4% of HCHs detected in cabbage samples exceeded EU MRLs. This falls within range of results of the residues detected in this present study. However, in a study in Nigeria, Ibitomi and Mohammed (2016*)* reported that the concentrations of all the pesticides detected in the fruit and vegetable samples from the four markets within Kaduna Metropolis were found to be much lower than the European Union (EU) set maximum residue limits (MRLs). Owago *et al*. (2007) reported that the organochlorine residues detected in vegetables in China was below the Chinese Extraneous Maximum Residue Limit of 0.05 mg/kg^{-1} and 0.01 mg/kg^{-1}.

The HI was > 1 for dieldrin, aldrin, and endrin aldehyde means it posed risk to both adult and children while heptachlor posed risk to only children consumers of cabbage which suggest that the insecticides could cause systemic toxicity for the consumers of cabbage in the study area. The hazard index value <1 implies that the OCIs do not pose threat or risk to consumers of the vegetable. The compounds with <1 may also indicate that the OCIs residues found in vegetable in the present study pose minimal human health risk. The results obtained from the present study were lower when compared with the analysis of health risk estimates of organochlorine pesticide reported by Sosan and Oyekunle (2017) in kolanut samples obtained from selected markets in Osun State with HI values of > 1 for γ-HCH, aldrin, endrin, endrin aldehyde and heptachlor. In contrast to the present study, Oyeyiola *et al.* (2017) reported that none of the vegetables (notably cabbage and lettuce) collected from selected markets in Lagos posed no risk to children and adult consumers of the vegetables with HRI < 1 while Bolor *et al.* (2018) reported that the combined health risks estimated for adults and children for the consumption of cabbage in selected locations in Ghana were < 1.

Although HCHs, DDTs and endosulfans posed minimal risk in the present study, it does not imply full safety as the mean levels of recorded residues were above their respective EC/UK MRLs. Although, cabbage is classified as elite food but occasionally consumed by a large group of people as salad, the excessive consumption of the vegetable with detected residues can results into bioaccumulation over a period of time which could have adverse chronic effects on children and adult consumers. Thus, there exists the likelihood of increase in potential risks for systemic health effects associated with insecticides used in production of cabbage in Nigeria if not regulated.

Conclusions

The findings from this study indicated the presence of organochlorine insecticide residues in cabbage sold in the study locations in south-western Nigeria with their level of contamination above their respective UK/EC MRLs which were probably due to recent applications of the detected insecticides or past usage. Prolong and regular consumption of the cabbage from study locations by children and adults could present chronic health risks. To fully utilize the health benefits associated with consumption of cabbage vegetables, the routine evaluation of pesticide residues in the vegetables and enforcement of laws on importation and usage of toxic and banned pesticides by regulatory agency are recommended.

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