Occurrence and Levels of Organochlorine Pesticide Residues in Maize Samples from Open Markets and Stores in Ile-Ife and Ondo, Southwestern Nigeria

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Abstract

The levels of organochlorine (OC) pesticide residues in maize grains obtained from open markets and stores in Ile-Ife and Ondo were evaluated and compared with established safety limits. The pretreated samples were Soxhlet extracted and the extracts obtained were analysed for their OCPs content using a Gas Chromatograph coupled with an Electron Capture Detector (GC-ECD). A total of 17 OCPs and their residues were detected in most of the samples with the percentage occurrence ranging between 20 and 100%, and the levels found exceeding their Maximum Residue Limits (MRLs). The mean concentration of λ -HCH, Endosulfan II and Endrin aldehyde were 0.118, 0.592 and 1.039 mg kg⁻¹, respectively for maize samples obtained from open markets in Ile-Ife. However, maize samples from Ondo had higher levels of Heptachlor epoxide with a mean concentrations of 13.622 and 18.642 mg kg⁻¹ for open markets and stores, respectively. Amounts of OC pesticide residues detected in the maize samples indicated that samples from stores had higher residue levels than those from open markets. The level of OC pesticides contamination of the analysed maize samples portends both short- and long-term public health concerns, calling for regular monitoring of pesticide residues in maize grains and other food items to ensure higher food quality and safety.

Keywords: Organochlorine pesticides, maize, residues, market, store.

INTRODUCTION

Maize, (*Zea mays* L.) is an important cereal widely cultivated throughout the world in a range of agroecological environments. In Nigeria, maize is mainly produced for local consumption with only small quantities being exported (Cadoni and Angelucci, 2013). The main local dishes produced from maize include pap, tuwo, gwati, and donkunu, with the cereal in cooked, roasted, fried, ground,

pounded or crushed form (Abdulrahman and Kolawole, 2006). It is also one of the important cereals used in complementary food administered to infants after the age of six months and also serves as the main component of poultry and other livestock feed.

Maize production is constrained by high infestation of insect pests and the maize weevil *Sitophilus zeamais* Motsch. which is an important field to store insect pest of maize that attacks the grain both in the field and during storage (Adedire, 2001; Sori and Ayana, 2012).

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Worldwide seed losses ranging from 20 to 90% have been reported for untreated maize due to the maize weevil, *S. zeamais* (De-Lima, 1987; Giga *et al.*, 1991; Boxall, 2002). Synthetic chemical insecticides have been widely used for the control of insect pests of stored grain, particularly *S. zeamais* (Abebe *et al.*, 2009). However, the application of plant protection chemicals, although, highly necessary and effective, can cause the transfer of hazardous substances into the food chain and also have direct effect on those applying or treating the grains (Lozowicka *et al.*, 2014). Also, maize grains used for feeding livestock may be contaminated and consequently, pesticides may be consumed by humans via animal products. According to Akoto *et al.* (2013) human exposure to low doses of pesticides through contaminated food may lead to chronic toxicity. Organochlorine pesticides (OCPs) have become universal contaminants found in all segments of the environment and food chain (Alle *et al.*, 2009) and also they are ubiquitous in the environment because of their persistence, bioaccumulation and long-range atmospheric transport (LRAT) (Wang *et al.*, 2009). The accumulation of organochlorine compounds in foods is still a matter of major concern, although, the use of most OCPs have been banned or restricted in most countries. In Nigeria, the use of OCPs have been banned but there is still recent documented evidence of the compounds in food, fish and edible animal tissues, sediments, water and soil samples (Adeboyejo *et al.*, 2011; Oyekunle *et al.*, 2011; Ogah *et al.*, 2012; Ogunfowokan *et al.*, 2012; Olufade *et al.*, 2014; Oyo-Ita *et al.*, 2014; Anzene *et al.*, 2014; Sosan *et al.*, 2015; Tango and Ezemonye, 2015; Shinggu *et al.*, 2015; Oyekunle *et al.*, 2017; Sosan and Oyekunle, 2017). In other parts of the world, OC pesticides have been detected in cereals and grains, such as wheat and maize which are used as raw materials

for processing cereal-based complementary foods (Bakore *et al.*, 2004; Mawussi *et al.*, 2009; Akoto *et al.*, 2013; Lozowicka *et al.*, 2014; Mekonen *et al.*, 2015; Akoto *et al.*, 2015).

Systematic and routine monitoring of pesticide residues in agricultural produce is not carried out in Nigeria and there is also a lack of data on the levels of OC pesticides in stored maize in the country despite recent evidences of their residues in some stored food products. The aim of this study was to ascertain the occurrence and consumption safety level of OC pesticide residues in maize grains from selected markets and stores in Ile-Ife and Ondo, southwestern Nigeria.

MATERIALS AND METHODS

Sample Collection and Preparation

A total of 20 samples of maize grains consisting of five each from open markets and stores were randomly collected from Ile-Ife and Ondo towns. Maize sample collections were made at the wholesale markets popularly patronized and big stores of maize in both locations. The samples (300 g each) were packed in black polyethylene plastic bags, labelled and transported to the laboratory. Foreign matters, including stones, crumbled shafts and other grains were manually removed from the grains before being dried to a constant weight. Each of the samples was thoroughly ground to powdered form using agate mortar and pestle to ease extraction. Each of the powdered samples was then packed in Ziploc bags, labelled and then stored in a refrigerator at 4°C prior to further analysis.

Reagents used and their sources

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). These reagents were procured through various sales representatives of the producing companies' resident in Nigeria. Solvents, such as dichloromethane, n-Hexane and acetone were doubly distilled using all glass distillation kit to obtain higher purity, while silica gel and anhydrous sodium sulphate were heated in an oven at 120°C for 12 h to ensure that no adsorbed water element remained as part of the clean-up materials.

Extraction Procedure

Accurately weighed with an electrical digital balance (Model: Mettler Toledo) capable of reading to four decimal places, a 30 g portion of each ground sample was weighed into a pre-extracted Whatman extraction thimble. Soxhlet extractor was used following the principle described by Oyekunle *et al.* (2011). Using 350 mL of Dichloromethane (DCM) as the extracting solvent, extraction of each sample took an average time of 4 hours. The extract was subjected to distillation for the concentration of the extract to about 4 mL. Further concentration was done to about 2 mL under a steam of high purity nitrogen. The final extract was kept for clean-up before instrumental analysis.

Clean-up procedure

A column of about 15 cm (length) x 1 cm (internal diameter) was packed first with glass wool and then with about 7.5 g activated silica gel prepared in a slurry form in DCM. About 5 g of anhydrous sodium sulphate was placed at the top of the column to absorb any water in the sample or the solvent. Pre-elution was done with 15 mL of DCM, without exposing the sodium sulphate layer to air, so as to prevent the drying up and cracking of the packed silica gel adsorbent. The reduced extract was run through the column and allowed to sink below the sodium sulphate layer. Elution was done

with 3 x 10 mL portions of DCM. The eluate was collected and the accompanying solvent was evaporated to dryness under a stream of analytical grade nitrogen (99.99%). The dried eluate was reconstituted with 1 mL 2, 2, 4-trimethylpentane (isooctane) in readiness for instrumental analysis.

Qualitative identification and quantitative evaluation of the OC pesticides

The dried eluate was reconstituted with 1 mL 2, 2, 4-trimethylpentane (isooctane). With the aid of a micro syringe, 1 µL of the 1.0 mL purified and reconstituted extract was injected into the injection port of a gas chromatograph coupled with a ⁶³Ni electron capture detector (GC-ECD, Hewlett Packard 5890 series II). The column consisted of a DB-5 fused silica capillary column (30 m x 0.32 mm i.d. x 0.25 µm film thickness). The temperatures of the injector and detector were 250°C and 300°C, respectively. The injection was carried out on a splitless injector at 200°C and the purge activation time was 30 s. The carrier gas was N₂ at 30 mL/min; and the splitless flow rate was 19.6 mL/min. The run time was 26 minutes. The individual OC pesticides were identified by comparing the elution time of standard OC pesticides with those in the samples, while each OC pesticide was quantified by comparing the peak areas of the OC pesticides in samples with those in the standard. Gas chromatographic analysis of the samples was carried out at the Nigerian Institute of Oceanography and Marine Research (NIOMR) Central Laboratory, Victoria Island, Lagos, Nigeria.

Analyte Residues Analysed

The samples were analyzed for α, β, γ and δ-HCH, Aldrin, Dieldrin, Heptachlor, Heptachlor epoxide, Endrin, Endrin aldehyde, Endosulfans, Methoxychlor, DDD, DDE, DDT. The average concentration of OC pesticide

residues in maize were compared with the MRLs recommended by European Union (2011).

Data analysis and validation of method

Descriptive statistics (mean, range and standard error) were used to analyze the results obtained using SAS version 9.2 software (SAS Institute, 2003).

Quality Control Measures

Quality control measures were adopted to ensure that the analytical procedures used complied strictly with appropriate standards and specifications and also to further ensure that the results obtained were reliable, valid and of high quality included the determinations of percentage recovery and detection limit.

Percent recovery (%R) determination

Two samples of pulverized maize grains each weighing 20 g were chosen. 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 unspiked. The two samples were extracted and further treated following the procedures of Oyekunle *et al* (2011). Using an injection needle, 1.0 µL of the mixture was injected into the GC column for GC-ECD analysis. The recoveries of OCPs were determined by comparing the peak areas of the OCPs after spiking with those of the unspiked and the percentage recovery (%R) was evaluated based on the expression:

$$\%R = \frac{\text{Peak area of A} - \text{Peak area of A}'}{\text{Peak area of OC in standard}}$$

Where, A = OC in spiked sample and A' = OC in unspiked sample.

Determination of Limit of Detection (LOD)

The limits of detection (LOD) were evaluated by the determination of concentrations that gave signals equal to the blank signal plus three standard deviations of the blank based on the empirical and more specific definition described by Miller and Miller (2000) using the relationship:

$$yC = yB + 3SB$$

where, yC = analyte signal equivalent to detection limit; yB = blank signal; and SB = standard deviation of the blank. From the value of yC, the analyte concentration corresponding to the detection limit was evaluated for GC-ECD determination of OC pesticides.

RESULTS

The percentage recovery (%R) values of some of the analytes in the maize samples in the range of 89.25% (*p*, *p*₂-DDT) and 98.01% (Aldrin) are shown in Table 1. The mean concentration of OC pesticide residues in maize samples from open markets in Ile-Ife and Ondo are presented in Table 2. All the isomers of HCH were detected in all the samples obtained from the two towns except α-HCH which was the only compound not detected from samples from Ondo. The mean concentration of HCH residues in maize samples from Ile-Ife ranged from 0.084±0.034 (β-HCH) to 0.118±0.072 mg kg⁻¹ (γ-HCH), while those of samples from Ondo ranged from 0.064±0.064 (γ-HCH) to 0.656±0.655 mg kg⁻¹ (β-HCH). The percentage occurrence of the OC pesticide ranged between 40 and 60% in Ile-Ife and between 0 [Not Detected (ND)] and 40% in Ondo.

With the Cylodienes group, mean concentration of 1.039±0.985, 0.913±0.913 and 0.827±0.827 mg kg⁻¹ were recorded for Endrin aldehyde, Heptachlor and Endrin, respectively for

all maize samples from Ile-Ife with the lowest concentration ($0.061 \pm 0.037 \text{ mg kg}^{-1}$) recorded for Aldrin. In Ondo, Dieldrin and Endosulfan sulphate were not detected while Heptachlor epoxide and Endosulfan II had mean concentrations of 13.622 ± 6.067 and $0.346 \pm 0.288 \text{ mg kg}^{-1}$, respectively. The frequency of occurrence of these pesticides residues ranged from 20 to 40% and 20 to 60% in samples from Ile-Ife and Ondo, respectively.

Table 1: Response Factor, Percent Recovery and Limit of Detection for OCPs

OCPs	RF	%Recovery	LOD ($\mu\text{g/g}$)
HCB	—	95.21	0.089
Aldrin	1.439	98.01	0.029
Dieldrin	1.092	97.27	0.068
Heptachlor	1.345	90.09	0.086
Endrin	1.393	93.56	0.101
<i>p, p'</i> -DDT	0.958	89.25	0.081

The observed levels of diphenyls were 0.065 ± 0.042 , 0.046 ± 0.028 and $0.059 \pm 0.036 \text{ mg kg}^{-1}$ for *p, p'*-DDT, *p, p'*-DDE and *p, p'*-DDD, respectively in Ile-Ife. However, in Ondo, Methoxychlor had the highest mean concentration of $9.613 \pm 5.930 \text{ mg kg}^{-1}$, followed by DDT ($0.392 \pm 0.089 \text{ mg kg}^{-1}$). The percentage occurrence of the different compounds was 40% for all samples from Ile-Ife and from 40 to 100% in Ondo. The OC pesticide burden shows that Cyclodiene group had the highest concentrations in Ile-Ife ($3.985 \pm 3.848 \text{ mg kg}^{-1}$) and in Ondo ($14.708 \pm 6.950 \text{ mg kg}^{-1}$). The levels of all the OC pesticides detected were above the recommended MRL for each of the compounds.

Table 3 shows the levels of OC pesticide residues detected in maize samples from stores in Ile-Ife and Ondo. All the OC pesticides screened were detected in most of the samples from Ile-Ife with the percentage occurrence ranging from 20 to 100%. Among the HCH

Table 2: Mean Concentrations of Organochlorine Pesticide residues in Maize samples from Open markets in Ile-Ife and Ondo, Southwestern Nigeria

Pesticide	Mean $\pm$ SE	Ile-Ife			MRL	Ondo		
		% Occurrence	% above MRL			% Occurrence	% above MRL	
α -HCH	0.114 ± 0.070	40	100	0.01	ND	ND	ND	
β -HCH	0.084 ± 0.034	60	100	0.01	0.656 ± 0.655	20	100	
γ -HCH	0.118 ± 0.072	40	100	0.01	0.064 ± 0.064	20	100	
δ -HCH	0.087 ± 0.036	60	100	0.01	0.097 ± 0.043	40	100	
ΣHCH	0.403 ± 0.212				0.817 ± 0.762			
Aldrin	0.061 ± 0.037	40	100	0.01	0.112 ± 0.069	40	100	
Dieldrin	0.098 ± 0.098	20	100	0.01	ND	ND	ND	
Endosulfan I	0.063 ± 0.063	20	100	0.05	0.009 ± 0.009	20	100	
Endosulfan II	0.592 ± 0.591	20	100	0.05	0.346 ± 0.288	40	100	
Endosulfan sulphate	0.329 ± 0.296	40	100	0.05	ND	ND	ND	
Endrin	0.827 ± 0.827	20	100	0.01	0.208 ± 0.106	60	100	
Endrin aldehyde	1.039 ± 0.985	40	100	0.01	0.127 ± 0.127	20	100	
Heptachlor	0.913 ± 0.913	20	100	0.01	0.284 ± 0.284	20	100	
Heptachlor epoxide	0.063 ± 0.038	40	100	0.01	13.622 ± 6.067	60	100	
ΣCyclodienes	3.985 ± 3.848				14.708 ± 6.950			
<i>p, p'</i> -DDD	0.059 ± 0.036	40	100	0.05	0.090 ± 0.057	40	100	
<i>p, p'</i> -DDE	0.046 ± 0.028	40	100	0.05	0.107 ± 0.078	40	100	
<i>p, p'</i> -DDT	0.065 ± 0.042	40	100	0.05	0.392 ± 0.089	100	100	
Methoxychlor	0.076 ± 0.048	40	100	0.05	9.613 ± 5.930	60	100	
ΣDiphenyls	0.246 ± 0.154				10.202 ± 6.154			

n = 5 for each town
ND = Not Detected

SE = Standard Error of Mean
MRL = Maximum Residue Limit

Table 3: Mean Concentrations of Organochlorine Pesticide residues in Maize samples from Stores in Ile-Ife and Ondo, Southwestern Nigeria

Pesticide	Ile-Ife			MRL	Ondo		
	Mean±SE	% Occurrence	% above MRL		Mean±SE	% Occurrence	% above MRL
α -HCH	0.168±0.014	100	100	0.01	0.065±0.065	20	100
β -HCH	0.110±0.028	80	100	0.01	0.032±0.032	20	100
γ -HCH	0.130±0.034	80	100	0.01	0.105±0.105	20	100
δ -HCH	0.167±0.017	100	100	0.01	ND	ND	ND
ΣHCH	0.575±0.093				0.202±0.202		
Aldrin	0.120±0.031	80	100	0.01	ND	ND	100
Dieldrin	0.310±0.209	60	100	0.01	0.139±0.086	40	100
Endosulfan I	0.082±0.051	40	100	0.05	0.117±0.117	20	100
Endosulfan II	0.322±0.165	60	100	0.05	0.091±0.057	40	100
Endosulfan sulphate	0.046±0.046	20	100	0.05	0.080±0.050	40	100
Endrin	ND	ND	ND	0.01	0.250±0.250	20	100
Endrin aldehyde	0.629±0.500	60	100	0.01	ND	ND	ND
Heptachlor	0.152±0.072	60	100	0.01	2.151±2.151	20	100
Heptachlor epoxide	32.647±32.200	80	100	0.01	18.642±12.233	40	100
ΣCyclodienes	34.308±33.274				21.47±14.944		
<i>p, p'</i> -DDD	0.102±0.026	80	100	0.05	0.292±0.025	100	100
<i>p, p'</i> -DDE	0.186±0.036	100	100	0.05	0.042±0.042	20	100
<i>p, p'</i> -DDT	0.341±0.175	60	100	0.05	0.031±0.031	20	100
Methoxychlor	0.108±0.044	60	100	0.05	21.124±3.684	100	100
ΣDiphenyls	0.737±0.281				21.489±4.007		

n = 5 for each town

SE = Standard Error of Mean

ND = Not Detected

MRL = Maximum Residue Limit

group, was the predominant isomers were α -HCH and (γ -HCH) with a mean concentrations of 0.168±0.014 and 0.105±0.105 mg kg⁻¹ from samples taken from stores in Ile-Ife and Ondo, respectively. However, in the Cyclodienes group, Heptachlor epoxide was the predominant residues in both towns as it occurred at the mean concentration of 32.647±32.200 and 18.642±12.233 mg kg⁻¹ from Ile-Ife and Ondo, respectively. Aldrin and Endrin aldehyde residues had mean concentrations of 0.120±0.031 and 0.629±0.500 mg kg⁻¹, respectively from stores in Ile-Ife, however, these two compounds were detected from maize samples from stores in Ondo. Level of Endrin residues was 0.250±0.250 mg kg⁻¹ in Ondo, but it was not detected

in samples in Ile-Ife. High Endosulfan II residues were recorded in Ile-Ife (0.322±0.165 mg kg⁻¹) and in Ondo (0.091±0.057 mg kg⁻¹). The levels of Methoxychlor was excessively higher in samples from Ondo (21.124±3.684 mg kg⁻¹) compared to Ile-Ife (0.108±0.044 mg kg⁻¹).

Also, in the samples from Ile-Ife, the concentration of *p, p'*-DDT was higher (0.341±0.175 mg kg⁻¹) than its metabolites, *p, p'*-DDD (0.102±0.026 mg kg⁻¹) and *p, p'*-DDE (0.186±0.036 mg kg⁻¹). However, in Ondo, *p, p'*-DDT had the least detected residue.

The mean concentration of OC pesticides residues detected in maize samples from open markets and stores are presented in Table 4. The percentage occurrence ranged from 10 to

Table 4: Mean concentrations of Organochlorine Pesticide residues in Maize samples from Open markets and Stores in Ile-Ife and Ondo, Southwestern Nigeria

Pesticide	Open Markets (n=10)			MRL	Stores (n=10)		
	Mean±SE	% Occurrence	% above MRL		Mean±SE	% Occurrence	% above MRL
α -HCH	0.057±0.038	20	100	0.01	0.117±0.036	60	100
β -HCH	0.370±0.008	40	100	0.01	0.071±0.024	50	100
γ -HCH	0.091±0.046	40	100	0.01	0.118±0.052	50	100
δ -HCH	0.078±0.027	50	100	0.01	0.092±0.029	50	100
ΣHCH	0.596±0.119				0.398±0.141		
Aldrin	0.086±0.038	40	100	0.01	0.060±0.025	40	100
Dieldrin	0.049±0.049	10	100	0.01	0.225±0.110	50	100
Endosulfan I	0.036±0.031	20	100	0.05	0.100±0.060	30	100
Endosulfan II	0.469±0.313	30	100	0.05	0.207±0.090	50	100
Endosulfan sulphate	0.164±0.150	20	100	0.05	0.063±0.032	30	100
Endrin	0.517±0.406	40	100	0.01	0.125±0.125	10	100
Endrin aldehyde	0.583±0.492	30	100	0.01	0.315±0.258	30	100
Heptachlor	0.598±0.463	20	100	0.01	1.151±1.068	40	100
Heptachlor epoxide	6.842±3.645	50	100	0.01	25.645±16.528	70	100
ΣCyclodienes	9.344±5.587				27.891±18.296		
<i>p, p'</i> -DDD	0.074±0.032	40	100	0.05	0.197±0.036	90	100
<i>p, p'</i> -DDE	0.076±0.040	40	100	0.05	0.114±0.035	60	100
<i>p, p'</i> -DDT	0.228±0.071	70	100	0.05	0.186±0.098	40	100
Methoxychlor	4.845±3.216	50	100	0.05	10.616±3.910	80	100
ΣDiphenyls	5.223±3.359				11.113±4.079		

ND = Not Detected

MRL = Maximum Residue Limit

SE = Standard Error of Mean

70% and from 10 to 90% in open market and in store samples, respectively. The mean concentration of γ -HCH was 0.118 ± 0.052 and 0.091 ± 0.046 mg kg⁻¹ in stores and open market, respectively. The predominant pesticide from the Cyclodienes group was Heptachlor epoxide with very higher residue level of 25.645 ± 16.528 mg kg⁻¹ recorded in the store samples than the open markets samples (6.842 ± 3.645 mg kg⁻¹). This was followed by Heptachlor (1.151 ± 1.068 mg kg⁻¹) in samples from stores. Concentration of all other Cyclodienes did not exceed 1 mg kg⁻¹ in both store and open markets samples. Generally, residues of diphenyl compounds were higher in the stores than in open markets, with exception of

p, p'-DDT. The levels of Methoxychlor were very high in stores (10.616 ± 3.910 mg kg⁻¹) than in the open market (4.845 ± 3.216 mg kg⁻¹). The least frequently detected pesticides were Endosulfan I (0.036 ± 0.031 mg kg⁻¹) in open market and Aldrin (0.060 ± 0.025 mg kg⁻¹) from the stores. All the pesticide residues detected samples were above their respective MRLs.

Figure 1 shows the proportion of OC pesticide burden in maize samples from open markets and stores in Ile-Ife and Ondo. Of the total OC pesticides detected, the percentage burden of HCH and DDT isomers detected in maize samples from open markets were higher than those from the stores, while the percentage of the

Figure 1: Proportion of Organochlorine pesticide (OCP) residues in maize samples from Open Markets and Stores in Ile-Ife and Ondo, Southwestern Nigeria

detected Cyclodienes group of the total OCP was higher in Ondo samples compared to the open markets.

DISCUSSION

This study established the presence of OC pesticides residues in maize samples from open markets and stores in the selected towns in southwestern Nigeria with percentage occurrence in the samples ranging from 20 to 100%. This observation is similar to the findings of Ogah *et al.* (2011) who reported that 96% of the maize samples from Lagos markets contained residues of one or more organochlorine pesticides. The predominance of HCH isomers in open markets indicated that the OCs were widely used in the protection of the maize against insects. For example, the detection of the γ -HCH, the commonly used all-purpose insecticide indicated that this insecticide were still available in the market as this insecticide have been frequently detected in food items in southwestern Nigeria (Adeyeye and Osibanjo, 1999; Ogah *et al.*, 2011; Ogah

et al., 2012; Sosan *et al.*, 2015; Sosan and Oyekunle, 2017). The types and frequency of Cyclodienes group of the OCs detected in open markets in Ile-Ife might be due to the high production of maize in the town and its environs and a high demand for the grains by the residents for processing into various local dishes. These factors may have necessitated the high usage of pesticides which resulted in the detection of the compounds in the samples. The predominance and high concentrations of Endosulfans in Ile-Ife also attested to the fact that these compounds are still much in use despite its ban. Olufade *et al.* (2014) earlier reported the presence of this insecticide in yam chips and cowpea grains in markets in Ile-Ife, while Reksha-Naik and Prasad (2006) stated that endosulfan residues in wheat were reported in all market samples in India. In Cameroon, Sonchieu *et al.* (2010) reported Lindane and Endosulfan in maize samples with mean concentrations higher than the EU-MRL for the insecticides. However, the detection of high levels of Heptachlor epoxide and Methoxychlor from open markets in Ondo town might be as a

reflection of the past usage which resulted in bioaccumulation or probably arising from the cultivation of the crop on contaminated soils where application of insecticides were intense. Methoxychlor is a component of DDT. Although, the usage of OC pesticides most especially Lindane (γ -HCH) and DDTs in agriculture had been banned in Nigeria but nothing is known about its illegal use through smuggling and possibly through another trade name by which it was being sold in the market. Ondo, a town in Ondo State, is known for high cultivation of cash crops, such as cocoa, which requires large volume of pesticides. This, along with the long establishment of farm settlements in the state, might have been responsible for the detection of high levels of these pesticides in maize samples.

Generally, the results indicated that maize samples from stores contained substantially more OC pesticide residues than those from the open markets. The high rate of occurrence and levels of OC pesticide in store samples most especially in Ile-Ife indicated that more of these chemicals were used for storage of maize. The predominance and high levels of Heptachlor and Heptachlor epoxide from the two towns and Methoxychlor from Ondo further suggest that these compounds must have been active ingredients of common insecticides likely to have been used in the protection of maize against insects in storage. This is likely to happen because most farmers used any available types of insecticide for the control of both the field and storage insect pests. More worrisome is that fact that the agrochemical retailers who the farmers rely upon, to give adequate guidance on various types and proper usage of pesticides are not trained or have limited information on proper handling of pesticides. Hence, they cannot provide adequate guidance to their customers as reported by Sosan *et al.* (2013). In Ghana, Heptachlor was detected at mean levels of 0.005 ± 0.005 mg

kg^{-1} in maize while Methoxychlor concentrations in maize and cowpea were 0.002 ± 0.001 mg kg^{-1} and 0.003 ± 0.001 mg kg^{-1} (Akoto *et al.*, 2013). These levels are far lower than what were detected in samples in the present study. Heptachlor, DDT and its metabolites have been detected in rice and wheat from India (Toteja *et al.*, 2003). Also, in India, Bakore *et al.* (2004) reported that all of the wheat samples from India were contaminated with various organochlorine pesticide residues of DDTs and its metabolites, HCH and its isomers, Heptachlor and its Epoxide and Aldrin.

In a similar study conducted in Turkey, Methoxychlor, DDT and its metabolites, Aldrin, Heptachlor, β and γ -HCH were found to be the highest OC pesticide residues in wheat (Guler *et al.*, 2010). Mawussi *et al.* (2009) also detected γ -HCH, Heptachlor, DDT and its metabolites, α and β -Endosulfan in maize and cowpea in Togo. Aldrin and Dieldrin, the metabolites of Aldrin were reported in maize samples in Korhogo and Sinématiali in Cote D'Ivoire (Alle *et al.*, 2009). Also, Mahugija *et al.* (2017) reported high levels of pesticide residues in maize grains, which are among the sources of poultry feeds in Tanzania.

The Cyclodienes group of the OC pesticides analysed recorded the highest occurrence when compared with HCH and its isomers or diphenyls. This could be attributed to the ban on Lindane marketed as Gamalin 20EC[®] in the HCH group and DDT which have been only recommended for restricted use for malaria control in some African countries by World Health Organization (WHO). Lozowicka *et al.* (2014) reported that over 60% of total organochlorine contamination in cereal grains was due to DDTs components in Kazakhstan. In Nigeria, however, there is no official usage of this insecticide. Endosulfan which belongs to the Cyclodienes group is now a popular insecticide available in market which are now been used as a replacement for Lindane.

Although, Endosulfan has also been banned but they are still available in agrochemical shops in Nigeria.

The residue load above MRL in samples analysed in this study pointed to the fact that there could be illegal use of OC pesticide in the study areas for agricultural purposes either on the field or in storage most especially for protection against maize weevils. The mean concentrations of OC pesticides detected in maize samples from Lagos markets ranged from 7.9-52.0 µg/kg and maximum residue limits (MRLs) of some pesticides were exceeded in up to 7% of samples (Ogah *et al.*, 2011) while Oyekunle *et al* (2011) also reported high levels of OC pesticides in top soils of some agricultural farmlands in Oke-Osun farm settlement in Nigeria after many years of their applications. Maximum Residue Limits for β -HCH, β -Endosulfan, *p*, *p'*-DDE and *p*, *p'*-DDD were found to be exceeded in both maize and cowpea samples in Ghana (Akoto *et al.*, 2013).

Maize as a major component of livestock feed are only crushed and mixed with other livestock feed ingredients without any further processing for consumption by the birds. According to Udeaan and Bindra (1973) most of the pesticides in cereal grains are contained in outer layers of the grain and therefore, milling and similar processing techniques remove the residues to varied extent. However, the level of concentration and frequency of application of the harmful chemicals may be another factor for consideration in the rate at which processing will reduce the level of pesticide residues. Apart from the regular application of pesticide for protection against field and storage insect pests of maize, the outbreak of occasional insect pests such as armyworm may lead to an increase in application of pesticide which residues could be high in Nigerian staple foods like maize.

According to Zhao *et al* (2013), Poultry feeds may contain chemical contaminants such as pesticides and can be sources of contamination of poultry products including eggs (Windal *et al.*, 2009). A recent study by Mahugija *et al* (2018) revealed high levels of OC pesticides, such as Aldrin, Dieldrin, DDT, Endosulfan and HCH have been reported in poultry feed, raw and cooked eggs with chicken feeds found to be the most contaminated followed by raw eggs and finally cooked eggs.

The occurrence of the OC pesticides above MRLs in the maize samples in the present study is an indication of some form of misuse and/or abuse of these chemicals which may have health implications for both humans and livestock. Although the maize samples from stores contained substantially higher amounts of OC pesticide residues than maize samples from markets, it is, however, not possible to draw conclusions that more of the OC pesticides are being used on maize for storage due to the fact that store owners purchase maize from different locations within the region.

CONCLUSION

This study revealed that maize samples from open markets and stores in Ile-Ife and Ondo, southwestern Nigeria were contaminated with OC pesticide residues above the Maximum Residue Limits (MRLs). This level of contamination may pose a danger to humans since food contamination is the main route of exposure to OC pesticides. Further monitoring studies on pesticide residues levels of OC pesticides and other pesticides used for maize grain protection in storage and the dietary intakes estimates from the pesticide levels should be evaluated to give an insight into likely health risks to livestock and humans.

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