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ASSESSMENT OF PERSISTENT ORGANOCHLORINATED PESTICIDES RESIDUES IN COCOA BEANS FROM SELECTED COCOA FARMS IN EKITI STATE, NIGERIA

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ABSTRACT

With the importance of cocoa beans and its products, it is imperative to know whether the levels of pesticides residues are kept below the recommended levels to minimize the risk to human health. This study investigates the incidence and levels of organochlorinated pesticide residues in cocoa beans from eighteen selected cocoa farms in Ekiti State, Nigeria. Method 3550C of USEPA was employed to extract the pesticides from the samples, while a Gas Chromatography coupled with Electron Capture Detector (GC-ECD) was used for pesticides identification and quantification after careful extraction and clean-up on silica gel. The mean OCPs concentrations ranged from 0.0003 µg/g (α-BHC) to 0.163 µg/g (endosulfan sulphate) with α-BHC as the most frequently found pesticide residue. The concentration levels of lindane, α-BHC, p,p'-DDT, p,p'-DDD, heptachlor, heptachlor-epoxide and endosulfan II were below the maximum residual limit (MRL) in food as reported by European Union, while 0.92%, 2.78%, and 4.6% of endosulfan I, (β-BHC and δ-BHC) and (aldrin and dieldrin) respectively were above the MRL. The detectable levels of OCPs in the beans make it inevitable to conduct regular monitoring so as to ensure that the levels remains below prescribed limits by national and international standards.

1. Introduction

Cocoa farmers in Nigeria have actively used organochlorine pesticides (OCPs) for decades without minding the possible residues on the soils and farm products (Ibigbami *et al.*, 2017). Fourteen of the thirty-six Nigerian state grow cocoa, with the main producing States in the South-western part of the country, where most production areas located in Ondo, Osun, Ekiti, Ogun, Edo and Oyo States. The size of cultivated areas vary across states but an average cocoa farmer in Nigeria has a farm size of 2.5 ha (Oguntade, 2003), while the average delivered per farmer is less than 5 bags per season. Cocoa is the leading cash crop foreign exchange earner in Nigeria contributing over 26% of the Gross Domestic Product (GDP) of the non-oil export in Nigeria, and 19% contribution to the world market (UNCTAD, 2004; Faturoti *et al*., 2012). Pesticides are often employed by farmers because of pests and diseases. Cocoa mirids has been recognized as one of the most serious pest since 1908 due to their devastating effect (Dungeon, 1910). The most common species of mirids in West African countries are *Distantiella theobroma* and *Sahlbergella singularis*. Mirids damage alone, if left unattended to for three years and can reduce yields by as much as 75%.

Pesticides such as copper sulphate, benzene hexachloride, Aldrex 40, diazinon, chlorpyrifos, fenittrothion, Gammalin 20 (lindane), DDT among others have been used by Nigerian cocoa farmers (Asogwa and Dongo 2009; Oyekunle *et al*., 2017, ICCO, 2010),).

Organochlorine pesticides are a class of toxic chemicals containing carbon, hydrogen and chlorine; it is composed of five broad groups namely: dichlorodiphenyltrichloroethane (DDT) and analogues (e.g. diclofor, methoxychlor); the hexachlorocyclohexane or bezene hexachloride and their isomers (e.g. lindane, the ϒ-isomer); the cyclodienes e.g. chlordane, heptachlor, aldrin, dieldrin, endrin, endosulfan; the chlordecones: kelevan, mirex and the toxaphenes (Pope *et al*., 1994). Organochlorines (OCs) pesticides are toxic to biological organisms due to their high lipophilic properties (Lopez *et al*., 2010), resistance to chemical and biological degradation (Afful *et al*., 2010); adsorb on particulate matter due to low water solubility (Yang *et al*., 2005); ability to bioaccumulate and biomagnify (Zhou *et al*., 2006, Malik *et al*., 2009).

The use of OCPs for treatment of pests and diseases by cocoa farmers over the years would no doubt have led to the accumulation of their residues in the cocoa fruits.

Residues of OCPs have been reported in cocoa beans from Nigeria by Oyekunle *et al.* (2017), Aikpokpodion *et al.* (2012a, 2012b), while Owusu-Ansah *et al.* (2012), Frimpong *et al.* (2012), Okoffo *et al*. (2016) reported the levels in Ghana cocoa beans. With the little information on pesticides contamination of cocoa beans from Nigeria, hence, it is important to constantly monitor the residue concentrations of OCPs in cocoa beans given the potential health risk of pesticides. Therefore, the study aim in determining the occurrence and levels of persistent organochlorine pesticides in cocoa beans from Ekiti State to ascertain if their concentrations meet the prescribed limits by international standards.

2. Materials and methods

2.1. Study area

Ekiti is located between latitude 7^{o} 25^{1} – 8^{o} 2^{1} N and longitude 5^{o} 00^{1} – 6^{o} 00^{1} E in the rainforest belt of Southwestern Nigeria and lies south of Kwara and Kogi States, east of Osun State and bounded by Ondo State in the east and south. Figure 1 shows the map of Ekiti State indicating the Local Government Areas where the samples were collected. The State is mainly an upland zone rising over 250 m above sea level. It lies in an area underlain by metamorphic rock and dotted with rugged hills.

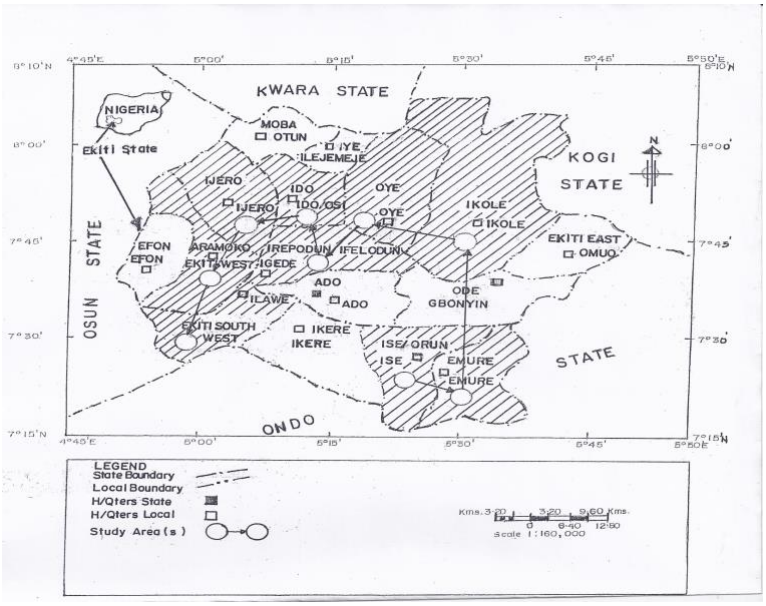

Figure 1. Map of Ekiti State showing the position of the study areas

Source: Min. of Lands, Urban and Regional Planning, Ado-Ekiti/Dept. of Geography and Planning Science, Cartographic Unit, Ekiti State University (EKSU), Ado-Ekiti.

Ekiti State enjoys tropical climate with two distinct seasons: rainy (April - October) and dry (November - March) seasons with a temperature range of 21ºC and 28ºC, and often with high humidity. Ekiti State is buoyant in both agricultural (with cocoa as its leading cash crop) and forest resources (notably timber).

Food crops like yam, cassava, and grains (such as rice and maize) are grown in large quantities. Other notable crops like kolanut and varieties of fruits are also cultivated in commercial quantities. Ekiti State covers about 6,353 km^2 land area.

This study covers eighteen cocoa-growing communities in Ekiti State: Ijero (IJR), Aramoko (ARA), Ido-Ile (IDE), Ikoro (IKO), Igede (IGD), Esure (ESR), Ise (ISE), Emure I (EMR), Emure II (EMU), Orun (ORN), Igbara-Odo (IGR), Ilawe (ILW), Ilupeju (ILJ), Ire (IRE), Ayedun (AYD), Ipawo (IPW), Usi (USI) and Ifaki (IFK).

2.2. Sample collection and preparation

Three cocoa trees were randomly selected where two ripe pods were harvested from each of the cocoa trees and combined to make composite samples. Six samples were collected in each farm making a total of 108 cocoa beans samples. The beans were allowed to ferment for 3-5 days before being sun dried and dehulled, grind in agate mortar and later blended with Excella Mixer Blender to fine particles. The samples were then packed in glass sample bottles prior to further analysis.

2.3. Chemicals and reagent used

The reagents used were of spectra purity. They include GC grade n-hexane, acetone and diethyl ether, silica gel 60 F_{254} and anhydrous sodium sulphate.

2.4. Extraction procedure and clean-up

The extraction of OCPs residues from the cocoa beans samples was carried out using the EPA 3550C method (USEPA 2000). For each sample, About 20 g was mixed with 20 g of anhydrous Na_2SO_4 in a pre-cleaned 250 mL conical flask. A 50 mL solvent mixture of acetone and n-hexane (1:1 v/v) was added to the solid mixture. This was followed by sonication in a high frequency ultrasonic bath for 10-15 minutes before allowing to settle on standing.

The extract was then decanted into round bottom flask. The extraction process was repeated twice with the same starting beans-Na_2SO_4 mixture. The sequential extract were combined and concentrated to 2mL using a rotary evaporator. It was re-dissolved in 5 mL n-hexane and later concentrated to 2 mL in a rotary evaporator at 40ºC.

The clean-up involved the use of a column of about 15 cm (length) x 1cm (internal diameter) packed with activated silica gel (2 g) and anhydrous Na_2SO_4 (1 g) on top of the silica gel (adsorbent). The column was conditioned with 15 mL n-hexane prior to clean-up. The extract was introduced into the column and eluted with 20 mL of n-hexane and diethyl ether (1:1 v/v). The eluate was concentrated by drying on the rotary evaporator and recovered into 2 mL n-hexane. The extract was transferred into glass GC vials for subsequent GC analysis. The OCPs in the extracts were determined by a Gas Chromatograph (GC) coupled with electron capture detector (ECD).

2.5. Gas chromatographic condition

The gas chromatography conditions for the analysis of organochlorine were as follows: GC model: Agilent 7890A Autosampler; the carrier gas flow rate was 4.0 mL/min; injector temperature: Split injection: 20:1; carrier gas: nitrogen; inlet temperature: 250 ºC; column type: HP5 MS; column dimension: (30 m x 0.25 µm x 0.32 mm; oven program: initial temperature at 80 ºC for 1 minute, first ramping 10 º C/min for 10 min (180 ºC); maintained for 3 min; second ramping at 10 ºC/min for 12 min (300 ºC); maintained for 2 min; detector: electron capture detector (ECD); detector temperature: 300 ºC; hydrogen pressure: 22 psi; compressed air: 35 psi. The total run time was 28 minutes.

2.6. Identification, quantification and quality control

The limits of detection (LODs) were determined at a signal to noise ratio (S/N) of 3

for each pesticides. A detectable ion should produce a signal that is at least three times the baseline noise, that is, signal-to-noise ratio = 3 and the limit of quantification (LOQ) was based on the signal to noise ratio of 10 as shown in Table 1.

Table 1. Limit of detection (LOD) and limit of quantification (LOQ) (mg/l) for the detection of OCPs

OCPs	**LOD**	**LOQ**
α-BHC	0.007	0.025
β-BHC	0.007	0.023
Lindane	0.006	0.020
δ-BHC	0.007	0.023
Chlorothalonil	0.009	0.029
Heptachlor	0.005	0.016
Aldrin	0.005	0.017
Heptachlor-epoxide	0.006	0.019
Endosulfan I	0.007	0.023
Dieldrin	0.007	0.025
Endosulfan II	0.007	0.022
p,p'-DDD	0.006	0.021
Endosulfan sulphate	0.007	0.022
p,p'-DDT	0.009	0.030

To determine the validity of the methodology, a standard addition method was employed where a known amount of pesticides was added to the samples and then analysed for the total amount of OCPs. The samples were spiked with mixed OCPs standard solutions (1, 2, 5 µg/l). The spiked samples were allowed to stand for some hours and then extracted, clean-up and analysed as described above. Recovery and precision (expressed as relative standard deviation) were calculated for three replicated samples and the data are presented in Table 2. The percent recovered ranged from 81.2% (dieldrin) to 96.9% (β-BHC).

Table 2. Mean percent recovery for the OCPs

OCPs	**Percent recovered**
α-BHC	93.6 ± 1.9
β-BHC	96.9 ± 0.7
Lindane	91.0 ± 3.1
δ-BHC	89.8 ± 2.3
Chlorothalonil	90.9 ± 1.4
Heptachlor	87.4 ± 2.9
Aldrin	90.2 ± 2.5
Heptachlor-epoxide	88.8 ± 4.3
Endosulfan I	89.7 ± 2.7
Dieldrin	81.2 ± 4.4

Endosulfan II	87.7 ± 4.6
p,p'-DDD	91.4 ± 0.9
Endosulfan sulphate	91.6 ± 1.1
p,p'-DDT	89.5 ± 6.8

The mean percent recovery were within the 70 - 110% acceptable range for recovery by EU guidelines for evaluating accuracy and precision of a method (EU 1999), and thus shows that the procedure employed in this method are reproducible, efficient and reliable for OCPs analysis. Standard solutions of OCPs were run in GC-(ECD) under set chromatographic conditions and mean peak areas were plotted against concentrations to obtain calibration curves of individual pesticides. Under the set chromatographic conditions, standard calibration curve was prepared for each OCP. The signatory retention time for each OCP was used as confirmatory indicator. Linearity was determined by plotting calibration curve with standard solution in n-hexane containing four different concentrations (0.1, 0.25, 0.5, 1.0 ng/µL).

2.7. Data analysis

Data generated in the study were subjected to statistical analysis to test for spatial variations with analysis of variance (ANOVA) using SPSS 15.0 package. One level of confidence limit ($p = 0.05$) was considered in the interpretation of the statistical results.

3. Results and Discussion

The study investigated three broad classes of OCPs, namely: chlorinated benzenes, dichlrodiphenylethanes and cyclodienes in cocoa beans from Ekiti State cocoa farms.

The mean concentrations of chlorinated benzenes are shown in Table 3. About 90.7%, 81.5%, 80.6% and 76.8% of the samples contained α-BHC, β-BHC, δ-BHC and lindane respectively with mean concentration of 0.0003(Ayedun) - 0.0134 µg/g (Igbara-Odo), 0.0057 (Esure) - 0.135 µg/g (Ijero), 0.0033 (Ayedun) - 0.143 µg/g (Usi) and 0.0005 (Ayedun) - 0.0205 µg/g (Ilupeju) respectively. Statistical analysis showed significant variation ($p < 0.05$) in BHCs among the sampled farms.

The mean BHCs reported in this study were lower than those reported by Oyekunle et al. (2017) from cocoa stores at Ondo (0.64 ϒ-BHC - 1.13 β-BHC µg/g) and Ile-Ife (0.41 α-BHC - 0.86 δ-BHC µg/g). The mean concentration of lindane fell within the range reported by Frimpong *et al.* (2012) and Okoffo *et al.* (2012), while those reported by Apau and Dodoo (2010) from central region of Ghana (0.411 mg/kg) were higher. Previous studies showed that HCB was a trace contaminant in several pesticides containing chlorine such as lindane, technical HCH, pentachloronitrobenzene (PCNB), pentachlorophenol (PCP), pentachlorophenol-Na (PCP-Na), attrazine, simazine, picloram, chlorothalonil, dimethyl tetrachloroterephalate (DCPA) (USEPA, 1998; Benzon, 1999; Pacyna *et al*., 2003; Barber *et al.*, 2005).

The occurrence of the BHC isomers in the cocoa beans could be as a result of the contaminant in several pesticides containing chlorine. The result indicated that HCB residues were also likely from the historical application of technical HCH and lindane. The level of lindane recorded in this study were below maximum residue limits (MRLs) set by European Union (1.0 mg/kg) in food and cocoa fruits. About 2.78% of the total samples were above FAO/WHO food standards for β-BHC and δ-BHC (0.2 µg/g) in food (Codex Alimentarius Maximum Residue Limits (Codex, 2004).

Table 3. Mean concentration (µg/g) of chlorinated benzene in the cocoa beans samples

Sampling farm	**α-BHC**	**β-BHC**	**Lindane**	**δ-BHC**	**TOCP**
ARA	0.0082±0.010	0.0185±0.009	0.0049±0.051	0.0207±0.027	0.0604±0.055
AYD	0.0003±0.004	0.0077±0.014	0.0005±0.001	0.0033±0.003	0.0128±0.019
EMR	0.0025±0.009	0.0303±0.024	0.0037±0.001	0.0083±0.007	0.0449±0.033
EMU	0.0006±0.007	0.0175±0.028	0.0013±0.002	0.0076±0.007	0.0271±0.038
ESR	0.0019±0.003	0.0057±0.008	0.0027±0.004	0.0079±0.009	0.0178±0.024
IDE	0.0072±0.008	0.0088±0.114	0.0111±0.014	0.0242±0.025	0.130±0.161
IFK	0.0019±0.002	0.0355±0.036	0.0040±0.004	0.0619±0.070	0.103±0.112
IGD	0.0056±0.009	0.0169±0.020	0.0904± 0.012	0.0203±0.027	0.0519±0.068
IGR	0.0134±0.005	0.093±0.083	0.0160±0.014	0.0392±0.029	0.1630±0.132
IJR	0.0013±0.002	0.1350±0.042	0.0052±0.007	0.0196±0.022	0.0721±0.064
IKO	0.0042±0.005	0.0289±0.020	0.0124±0.016	0.0230±0.021	0.0685±0.063
ILJ	0.0121±0.017	0.0667±0.137	0.0205±0.027	0.0171±0.020	0.116±0.201
ILW	0.0065±0.004	0.0507±0.059	0.0092±0.004	0.0209±0.007	0.0873±0.729
IPW	0.0127±0.008	0.0916±0.067	0.0151±0.080	0.0514±0.038	0.171±0.121
IRE	0.0108±0.007	0.0635±0.028	0.0116±0.013	0.0532±0.023	0.139±0.707
ISE	0.0026±0.003	0.0501±0.063	0.0028±0.003	0.0101±0.009	0.0656±0.078
ORN	0.0024±0.005	0.0420±0.071	0.0036±0.007	0.0154±0.014	0.0634±0.096
USI	0.0067±0.005	0.1060±0.116	0.0073±0.008	0.1430±0.193	0.2630±0.032

Table 4. Mean concentration (µg/g) of dichlorodiphenylethanes in the cocoa beans samples

Sampling farm	***p,p'*-DDD**	***p,p'*-DDT**	**TOCP**
ARA	0.0535±0.027	0.0382±0.025	0.0917±0.052
AYD	0.0008±0.001	0.0016±0.003	0.0024±0.004
EMR	0.0092±0.011	0.0163±0.021	0.0255±0.031
EMU	0.0016±0.002	0.0031±0.006	0.0047±0.008
ESR	0.0078±0.012	0.0618±0.069	0.0697±0.082
IDE	0.1920±0.031	0.0636±0.068	0.0829±0.099
IFK	0.0077±0.006	0.0191±0.025	0.0268±0.031
IGD	0.0082±0.012	0.0041±0.006	0.0124±0.019
IGR	0.0195±0.013	0.0271±0.012	0.0466±0.025
IJR	0.0067±0.008	0.0118±0.019	0.0176±0.119
IKO	0.0179±0.020	0.0036±0.060	0.0544±0.077
ILJ	0.0197±0.029	0.0132±0.014	0.0329±0.042
ILW	0.0219±0.022	0.0484±0.032	0.0704±0.056
IPW	0.0417±0.029	0.0268±0.021	0.0685±0.051
IRE	0.0405±0.049	0.0297±0.030	0.0702±0.078
ISE	0.0004±0.100	0.0076±0.009	0.0080±0.009
ORN	0.0045±0.073	0.0062±0.007	0.0107±0.015
USI	0.0102±0.078	0.0226±0.035	0.0328±0.043

Table 4 showed the mean concentrations (mg/kg) of dichlrodiphenylethanes in the cocoa beans samples. About 71.2% and 72.2% of the samples contained *p,p'*-DDT and *p,p'*-DDD with mean concentration ranged of 0.0016 (Ayedun) - 0.0636 µg/g (Ido-Ile) and 0.0008 (Ayedun) - 0.0535 µg/g (Aramoko) respectively. Significant variation was recorded in *p,p*'-DDD, while *p,p*'-DDT showed no significant variation ($p > 0.05$) among the sampling farms. The high incidence of DDT in some of the samples could be as a result of continuous applications in spite of the ban on its usage.Studies in Africa have found large amount of DDT residue in breast milk, fish, soil and cow's milk (Ejobi *et al*., 1996, 1998; Nyangababo *et al*., 2005; Ogwok 2009). DDT concentrations in cocoa beans have been reported by Aikpokpodion *et al*. (2012a) in Ondo, Cross river and Ogun States, Nigeria. Their results showed that 70% of the cocoa beans analysed from Ondo State had DDT residue, while 10% from Cross River and Ogun States had DDT residue. The mean concentration (57.8 ± 81.5 and 82.2 ± 54.4 µg/g) reported by Oyekunle *et al.* (2017) for *p,p*'-DDT in Ile-Ife and Ondo were higher than those reported in this study, while those reported by Frimpong *et al.* (2012) from Ghana were within the same range with the present study. The level of *p,p*'-DDT and its metabolite (*p,p*'-DDD) from all the study areas were below EU set standards of 0.5 µg/g for DDT (EU, 2005). The occurrence of DDT in the farms confirmed the usage in Ekiti State in the past, as most of the sampled farms were over 50 years. DDT and its metabolites can magnify through the food chain due to their chemical and physical nature. They are lipophilic and are stored mainly in body fat. Report of Darko and Acquaah (2007) confirmed the lipophilic nature of DDT and its metabolites that were concentrated in beef fat than the tissue (meat). The detection of DDT in cow milk at high concentration was also an indication of the ability of the pesticide to associate with animal tissue (Clerknevik, 2000). Through their persistence and lipohilicity, pesticide may concentrate in the adaptive tissues and in the blood serum of human. This was confirmed by the findings of Sosan *et al.* (2008) who reported the detection of organochlorine residue in the serum of 42 out of 76 cocoa farmers in South-western Nigeria.

The mean concentrations (µg/g) of cyclodienes in the samples are shown in Table 5. Many of the cyclodienes species analysed are breakdown products of the parent pesticide. Seven cyclodienes pesticides were evaluated in the study. About 90.7% of the beans samples contained dieldrin; 76.8% had endosulfan II; 75.9% contained endosulfan I and heptachlor; aldrin was found in 75%; endosulfan sulphate in 71.2%; while 73.1% contained heptachlor-epoxide.

Table 5. Mean concentration (µg/g) of cyclodienes in the cocoa beans samples

Sampling farm	Heptachlor	Heptachlor-epoxide	Aldrin	Dieldrin	Endosulfan I	Endosulfan II	Endosulfan-sulphate	TOCP
ARA	0.0207±0.027	0.0125±0.012	0.0098±0.010	0.0210±0.024	0.0372±0.047	0.0165±0.030	0.1630±0.115	0.281±0.266
AYD	0.0032±0.04	0.0005±0.001	0.0013 ±0.002	0.0002±0.006	0.0024±0.038	0.0012±0.002	0.0038±0.007	0.0127±0.021
EMR	0.0086±0.006	0.0031±0.002	0.0043±0.003	0.0175±0.026	0.0081±0.012	0.0116±0.011	0.044±0.117	0.147±0.117
EMU	0.0064±0.09	0.0013±0.002	0.0026±0.003	0.0034±0.005	0.0023±0.003	0.0024±0.003	0.0763±0.015	0.026±0.042
ESR	0.0089±0.014	0.0153±0.0031	0.0051±0.007	0.0182±0.027	0.0094±0.013	0.0022±0.004	0.0014±0.002	0.0606±0.097
IDE	0.0279±0.030	0.0129±0.003	0.0061±0.004	0.0233±0.023	0.0119±0.011	0.0174±0.013	0.1550±0.208	0.174±0.097
IFK	0.0090±0.008	0.0026±0.003	0.0055±0.004	0.0039±0.004	0.0083±0.007	0.0033±0.004	0.0923±0.133	0.125±0.164
IGD	0.0282±0.039	0.0126±0.018	0.0155±0.021	0.0107±0.018	0.0291±0.004	0.0201±0.022	0.0072±0.011	0.123±0.172
IGR	0.0633±0.035	0.0276±0.023	0.0422±0.035	0.0197±0.013	0.0430±0.034	0.0413±0.027	0.0811±0.047	0.318±0.214
IJR	0.0084±0.009	0.0132±0.015	0.0092±0.012	0.0080±0.009	0.0059±0.007	0.0306±0.011	0.0151±0.022	0.112±0.117
IKO	0.007±0.008	0.0103±0.011	0.0057±0.008	0.0106±0.008	0.0249±0.028	0.0155±0.012	0.1080±0.199	0.183±0.278
ILJ	0.0353±0.048	0.0104±0.016	0.0209±0.029	0.0073±0.014	0.0319±0.031	0.0121±0.019	0.0205±0.038	0.138±0.195
ILW	0.0215±0.010	0.0076±0.062	0.0117±0.006	0.0114±0.005	0.0320±0.007	0.0327±0.045	0.1570±0.148	0.274±0.229
IPW	0.0021±0.004	0.0243±0.013	0.0139±0.005	0.0231±0.013	0.0329±0.024	0.0259±0.031	0.0392±0.031	0.171±0.121
IRE	0.0152±0.009	0.0289±0.025	0.0138±0.022	0.0642±0.057	0.0101±0.016	0.0616±0.010	0.0866±0.096	0.280±0.332
ISE	0.0094±0.012	0.0057±0.008	0.0050±0.006	0.0045±0.007	0.0253±0.022	0.0151±0.011	0.0301±0.054	0.0914±0.120
ORN	0.0140±0.022	0.0045±0.008	0.0067±0.008	0.0025±0.006	0.0051±0.006	0.0075±0.010	0.0175±0.028	0.0279±0.092
USI	0.0257±0.032	0.0096±0.010	0.0365±0.010	0.0083±0.007	0.0205±0.024	0.0199±0.021	0.0538±0.047	0.174±0.168

Analysis of variance showed no significant variation ($p > 0.05$) in endosulfan II, dieldrin and heptachlor-epoxide, while heptachlor, aldrin, endosulfan I, endosulfan sulphate and TOCP showed significant variation among the sampled farms. The mean concentration of heptachlor and heptachlor-epoxide in the beans samples ranged from 0.0032 (Ayedun) - 0.0633 µg/g (Igbara-Odo) and 0.0002 (Ayedun) - 0.0289 µg/g (Ire) respectively. Samples from Ipawo, Ire, Esure, Ijero and Ikoro showed higher level of heptachlor-epoxide than heptachlor (the parent compound). The heptachlor and is metabolite level obtained in this study were lower in most cases than those reported by Oyekunle et al. (2017) where 0.63 – 2.27 µg/g and 0.59 – 3.96 µg/g in Ondo and 0.02 – 3.96 µg/g and ND – 6.13 µg/g in Ile-Ife were reported for heptachlor and heptachlor-epoxide. The level of the heptachlor-epoxide in the beans samples was directly related to the heptachlor application on the farms since heptachlor-epoxide is a metabolite of heptachlor. None of the beans samples exceeded the EU MRL of 0.2 µg/g for heptachlor and heptachlor-epoxide in food.

The mean aldrin concentration ranged from 0.0013 (Ayedun) - 0.0422 µg/g (Igbara-Odo), while that of dieldrin ranged from 0.0002 (Ayedun) - 0.0642 µg/g (Ire). The mean concentration of aldrin (0.13 – 10.2 µg/g) and dieldrin (ND – 14.5 µg/g) reported by Oyekunle *et al.* (2017) were comparatively similar in some cases, while most showed higher level than those reported in this study.

About 4.6% of the beans samples showed concentrations above FAO/WHO (0.05 µg/g) for aldrin and dieldrin in food. The mean concentration (µg/g) of endosulfan I, endosulfan II and endosulfan sulphate ranged from 0.0023 (Emure I) - 0.0430 µg/g (Igbara-Odo), 0.0012 (Ayedun) - 0.0616 µg/g (Ire) and 0.0014 (Esure) - 0.163 µg/g (Aramoko), respectively. The notable differences in the amounts of these pesticides were perhaps due to the farming systems adopted by the cocoa farmers, the age of the farms, the active ingredient concentration as prepared by the farmers among other factors. Due to few reports on endosulfan in cocoa beans, few comparable data are available. It was reported that 28 out of 45 (64%) of the cocoa beans samples in Ghana had endosulfan I, while endosulfan II was detected in 23 out of 45 (52%) with concentration range of ND – 0.10 mg/kg (Frimpong *et al.*, 2012). This was comparable to some samples reported in this study. Aikpokpodion *et al.* (2012) reported ND – 0.74 mg/kg for endosulfan 1 with an average value of 0.55 µg/g in Ondo State, the value which is comparatively higher than the average value of 0.0012 - 0.163 µg/g for samples collected in this study. Endosulfan I and endosulfan II were lower in most cases than what Oyekunle *et al.* (2017) reported for Ondo and Ile-Ife, while endosulfan sulphate was comparable in some farms from the study areas.

About 0.72% and 15.7% of the samples exceeded the maximum residue limit (0.1 µg/g) set by the (Codex, 2004; EU, 2005) for endosulfan and endosulfan sulphate, while none of the endosulfan II exceeded the EU-MRLs standards in food. The level of the enodsulfans obtained in the samples were mostly within the range reported by Scholten *et al.* (2010) in 139 cocoa beans obtained from fifteen cocoa producing countries. The high level of endosulfan in some cases suggests extensive usage of endosulfan in Ekiti cocoa farms. The cultivation activities of cocoa farmers, persistent frequent and indiscriminate applications of pesticide as reported by Aikpokpodion *et al.* (2012) were said to been responsible for the higher level of endosulfans in some Nigeria farms.

4. Conclusions

Residues of OCPs were found in cocoa beans of the selected cocoa farms with α-BHC as the most frequently found pesticide residue. The concentration levels of lindane, α-BHC, *p,p*'-DDT, *p,p*'-DDD, heptachlor, heptachlor-epoxide and endosulfan II were all below the maximum residual limit (MRL) in food, while 0.92%, 2.78%, 4.6% and 15.7% of endosulfan I, (β-BHC and δ-BHC), (aldrin and dieldrin) and endosulfan sulphate respectively were above the MRL. The high proportion of samples with detectable amounts of the pesticide residues

points to previous use in the studied areas. The study therefore, recommends the need for continuous survey and monitoring of pesticides residue in cocoa farms and products in order to ensure that the residual levels remain below prescribed limits by the national and international standards. There is also need for an intense awareness among farmers on reasons why they should stop the use of banned pesticides on cocoa and other food products.

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