Quantitative Study of Multi-residue Levels of Organochlorine Pesticides in Soils of Cocoa Farms in Ekiti State, South Western Nigeria

Ibigbami* O.A, Aiyesanmi A.F, Adeyeye E.I, Adebayo A.O, Aladesanwa R.D

Abstract— Cocoa farmers in Ekiti State of Nigeria have actively used OCPs for decades without minding the possible residues on the farm products and soils. This study aim at investigating the occurrence and the levels of possibly used OCPs in soil of cocoa farms within the state. Soil samples from cocoa farms in Ekiti state, Nigeria were analysed for 14organochlorine pesticides residues using gas chromatograph (GC) coupled with electron-capture detector (ECD) after extraction and clean-up. The reliability of the analytical method was examined by spiking the soils with known concentration of the pesticides and analysed following similar procedures of extraction and clean-up. The percentage pesticides recovered from the spiked samples ranged from 82.2 to 93.2%. The analysed pesticides were predominantly present in the soil samples. The concentration of OCPs in the soil samples during the wet season ranged from below detection limit (BDL) to 487 µg/kg, while the dry season ranged from (BDL) to 894 µg/kg. Correlation analysis showed that the organic matter content of the soil samples appear to influence the retention of the organochlorine pesticides compounds as reflected in the significant positive correlation at ($p < 0.05$) between organic matter content and the mean total organochlorine pesticides in the soil. Analysis of variance (ANOVA) revealed significant seasonal variation ($p < 0.05$) in α- BHC, lindane, δ-BHC, aldrin, endosulfan I, endosulfan II, endosulfan sulphate, *p,p*'-DDD and TOCP.

Keywords- *Organochlorine; pesticides; soil; cocoa farm; gas chromatography*

1 INTRODUCTION

Nigeria, the most popular black African nation, is the world fourth largest producer of cocoa (*Theobroma cacao)* beans behind Cote d 'Voire, Ghana and Indonesia [1]. Out of the thirty six states in Nigeria, fourteen are popularly known for cocoa farming. Ekiti State (an integral part of old Ondo State) contributes over 40% of the total cocoa product from famous old Western region of the country [2]. Cocoa plantations are often susceptible to varieties of pests and diseases which some reports have estimated to account for global production loss of 30% to 40% [3]. For instance, Mirids, one of the most ferocious of these pests is capable of damaging cocoa plants, if left uncurbed, could reduce the global yields by a proportion as high as 75% [3]. In this wake, cocoa farmers have adopted the use of organochlorine pesticides (OCPs), in particular, due to latter's high efficiency for cocoa production. However, the excessive use of these pesticides, coupled by their recalcitrant nature has resulted in the presence of pesticide residues in cocoa farm soils.

- *Corresponding author: Ibigbami O. A. Department of Chemistry, Ekiti State University, PMB 5363, Ado- Ekiti, Nigeria. olayinkaibigbami@yahoo.co.uk
- Aiyesanmi A. F. Department of Chemistry, The Federal University of Technology, PMB 704, Akure Nigeria. demolaktp@yahoo.co.uk
- Adeyeye E. I. Department of Chemistry, Ekiti State University, PMB 5363, Ado- Ekiti, Nigeria. eiadeyeye@yahoo.com
- Adebayo A. O. Department of Chemistry, The Federal University of Technology, PMB 704, Akure Nigeria. aoadebayo@futa.edu.ng
- Aladesanwa R. D. Department of Crop, Soil, and Pest Management, The Federal University of Technology, PMB 704, Akure, Nigeria alarex2003@yahoo.com

In the past century, OCPs have been used for pest and insect control without considering their potential negative impact on the ecosystem and human health [4, 5]. Their agricultural use, particularly dichlorodiphenyltrichloroethane (DDT) and hexachlorocyclohexane (HCH), have been banned worldwide since late 1970 - 1990s. Due to their high refractiveness, these chemicals could linger in the environment for decades before dissipating [6]. OCPs have been monitored in various matrices such as honey [7], waters [8,9], soils and sediments [10-15] and crops (such as leafy vegetables [16]). The levels and contamination of OCPs in water, sediments and fish samples in Nigeria have been investigated [17-23]. Aiyesanmi and Idowu [23] reported the range value of OCPs residues levels from cocoa farm soils in Ondo State as 0.08 (alpha benzenehexachloride) to 350 mg/kg (endosulfan I). However, very few reports are available on similar studies in Ekiti State, a place where OCPs have been profoundly used. Hence, the

present study aims at investigating the levels and distribution of OCPs residues in soils of cocoa farms in the State.

2.0 MATERIALS AND METHODS

2.1 Study area

Ekiti is located between latitude 7^0 25^1 - 8^0 2^1 N and longitude 5^0 00^1 - 6^0 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. The State is mainly an upland zone rising over 250m above sea level. It lies in an area underlain by metamorphic rock and dotted with rugged hills. Ekiti State enjoys tropical climate with two distinct seasons: rainy (April - October) and dry (November - March) seasons with a temperature range of 21^0C and 28^0C, and often with high humidity. Tropical forest exists in the northern peripheries. Ekiti State is buoyant in both agricultural (with cocoa as its leading cash crop) and forest resources (notably timber). Also 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. Fig. 1 shows the map of Ekiti State indicating the Local Government Areas where the samples were collected. This study covers eighteen cocoa-producing communities in Ekiti State: Ijero, Aramoko, Ido-Ile, Ikoro, Igede, Esure, Ise, Emure I, Emure II, Orun, Igbara-Odo, Ilawe, Ilupeju, Ire, Ayedun, Ipawo, Usi and Ifaki.

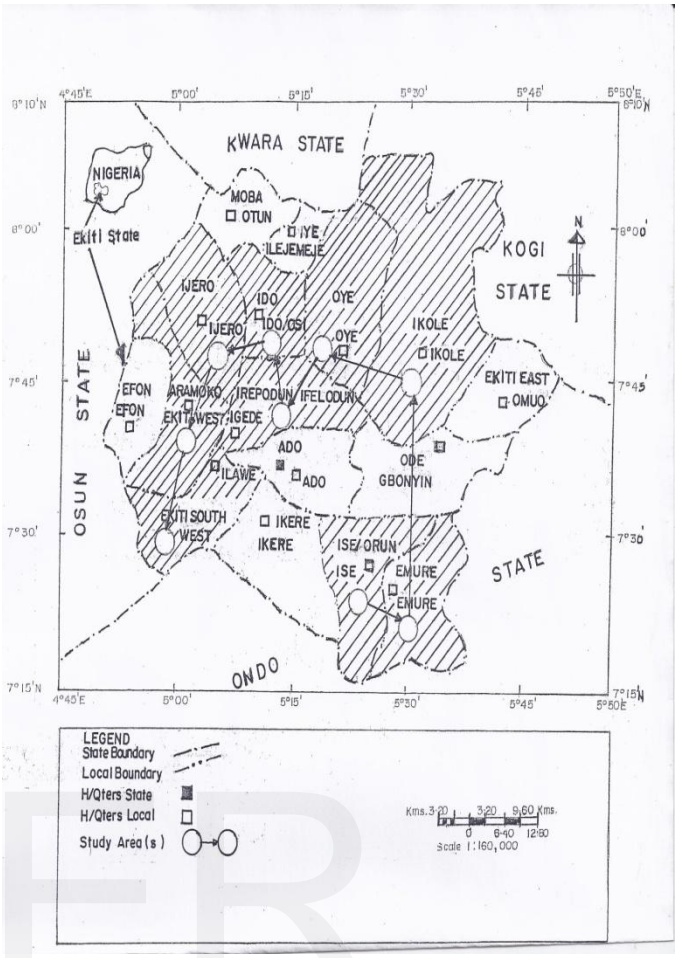

Fig. 1: Map of Ekiti State showing the location of the study areas

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

2.2 Sampling and sample preparation

Two farms were selected in each local government area (LGA), given a total of six soil samples per LGA and fifty-four soil samples in the 18 cocoa farms used for the study. Samples were taken in dry and wet seasons, between 2013 and 2014. The sampling locations were geographically referenced with a Global Positioning System (GPS) Germin (Geko™ 201).

A standard stainless steel hand auger was used to obtain the top soil samples, to a depth of 20 cm from three locations within each selected cocoa farm. Soil samples from each location were homogenized, and a representative (composite) sample was obtained and kept appropriately in labelled glass sample bottles. At the laboratory, the soil samples were later air dried for 4 weeks, ground in agate mortar and sieved through 2 mm mesh size. The sieved

samples were later stored in glass bottles for subsequent analysis.

For the physicochemical parameters, soil samples from various sampling locations in each farm were pooled together and composite sample were taken for each farm.

2.3 Physicochemical analysis of soil sample

The pH of the sieved soil samples, after dispersion in water was determined by the method proposed by Hendershot et al [24]. The soil particle size was determined by hydrometer method described by Shedrick and Wang [25], whist wet oxidation method of Walkley and Black described by Schulte [26] was used for the organic matter content determination. The cation exchange capacity was determined by the method provided by Radojevic and Bashkin [27].

2.4 Extraction of organochlorine pesticides residues from the soil samples

The extraction of OCPs from the soil samples was carried out using the EPA 3550C method [28]: For each sample, About 20 g was mixed with 20 g of anhydrous Na_2SO_4in a pre-cleaned 250 cm^3 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 with the same starting soil-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 40 ^{0}C.

2.5 Extract clean-up

The clean-up involved the use of a column of about 15 cm (length) x 1cm (internal diameter) packed with activated silica gel (Silica gel 60 F_{254}) (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).

2.6. 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 ^{0} C; column type: HP5 MS; column dimension: (30 m x 0.25 µm x 0.32 mm; oven program: initial temperature at 80^0 C for 1 minute, first ramping 10 ^{0}C/min for 10 min (180 ^{0}C); maintained for 3 min; second ramping at 10 ^{0} C/min for 12 min (300 ^{0} C); maintained for 2 min; detector: electron capture detector (ECD); detector temperature: 300 ^{0}C; hydrogen pressure: 22 psi; compressed air: 35 psi. The total run time was 28 minutes.

2.7 Quality assurance and quality control

Similar volume of solvents (n-hexane/acetone) and anhydrous sodium sulphate used in the extractions was subjected to similar extraction and clean-up procedures as the examined samples to detect any possible trace of the studied pesticides.

Stock solutions of organochlorine (α-BHC, β- BHC, δ-BHC, lindane, chlorothalonil, heptachlor, aldrin, heptachlor-epoxide, endosulfan I, endosulfan II, dieldrin, *p, p'*-DDD, *p, p'*-DDT and endosulfan sulphate) were prepare and stored in amber coloured bottles at 4^0 C in a refrigerator where working standard solutions were prepared fresh before use. Under the set chromatographic conditions, standard calibration curve was prepared for each OCP. The signatory retention time for each OCPs was used as confirmatory indicator. Calibration curves were produced with four different concentrations (0.1, 0.25, 0.5, 1.0 ng/µl)

To determine the validity of the methodology, a recovery study was performed using standard addition method, where a known amount of pesticide was added to the samples and then analysed for the total amount of OCPs. Three samples were spiked with the mixture of pesticides standard solutions (1, 2 and 5 µg/l). The spiked samples were allowed to stand for some hours and then extracted, cleaned up and analysed as described in the method above. The results showed that the mean recovery values ranged from 82.2 to 93.2%. This indicated that the analytical procedures were reliable, reproducible and efficient. All reagent used were of spectra purity.

2.8 Data analysis

Data generated in the study were subjected to statistical analysis to test for spatial and seasonal variations with analysis of variance (ANOVA), t-test and Pearson correlation as applicable, using SPSS 15.0 package. One level of confidence limit (p = 0.05) was considered in the interpretation of the statistical results.

3.0 RESULTS AND DISCUSSION

3.1 Physico-chemical properties of the soil

The mean values of the physico-chemical properties at the various sampling areas for both seasons are listed in Table 1. The soil pH varied from one location to another within the study area. The pH ranged from moderately acidic to very slightly acidic. The mean values during the wet season ranged from 5.85 ± 0.07 to 6.65 ± 0.71 while the dry season's value ranged from 5.95 ± 0.07 to 6.70 ± 0.07. The highest pH was recorded in ISE and IJR while AYD and IGR showed the least pH value in wet and dry seasons. The marked variation in the pH values is not unexcepted as many dynamic soil reactions utilizing H^+ ions such as oxidation-reduction, complexation-dissociation and sorption-desorption occur to a different extent in different parts of a soil [29].

The organic matter content in soil is the organic fraction derived from living organisms, decomposed plant and animal residue. As a result of decomposition, inorganic nutrients in plant tissues are released into the soil and humus is formed.

Table 1(a): Mean physico-chemical characteristics of soil from the study farms (wet season)

Sampling farm	pH	OM(%)	CEC (cmol/kg)	Sand (%)	Clay (%)	Silt (%)
IJR	6.35±0.07	3.93±0.11	2.47±0.41	48.2±1.14	33.1±0.14	18.9±1.41
IKO	6.30±0.14	3.66±0.93	2.50±0.34	43.6±0.78	34.7±4.38	21.7±5.16
ISE	6.65±0.71	5.43±0.11	1.68±0.89	40.7±0.07	33.2±0.07	25.5±0.71
ORN	6.60±0.14	5.22±0.15	2.21±0.89	40.5±1.13	30.2±0.21	29.7±0.64
ARA	6.25±0.21	3.45±0.04	1.11±0.07	49.75±1.48	33.2±2.89	17.0±1.41
IDE	6.15±0.14	3.34±0.40	1.93±0.15	48.5±3.11	32.2±1.34	20.2±1.76
USI	6.00±0.21	3.62±0.78	1.30±0.10	46.9±5.44	30.8±0.57	22.2±6.01
IFK	5.95±0.07	2.96±0.19	1.35±0.39	50.3±2.47	34.2±8.27	15.4±5.80
IGD	5.95±0.07	3.80±0.01	1.57±0.39	31.4±1.98	48.8±3.39	21.8±2.55
ESR	5.95±0.21	3.64±0.77	1.50±0.25	30.5±3.39	50.5±1.06	22.1±1.56
EMU	6.40±0.00	4.92±0.65	1.34±0.06	40.9±0.14	31.3±0.14	28.2±0.35
AYD	5.85±0.07	5.69±0.62	1.68±0.18	42.3±1.27	33.7±0.71	26.2±1.13
IPW	5.95±0.07	4.80±0.72	1.79±0.31	40.7±0.35	30.5±1.23	30.1±2.33
ILW	6.05±0.35	4.25±1.53	2.25±0.16	50.7±0.07	31.2±0.07	18.5±0.71
IGR	5.95±0.07	4.24±0.20	1.05±0.69	51.7±0.21	29.7±0.14	19.6±0.35
IRE	6.30±0.00	332±0.40	1.60±0.39	48.6±0.14	33.1±0.14	19.0±0.04
ILJ	6.15±0.00	4.80±0.01	1.67±0.89	50.4±2.27	34.1±8.26	15.5±0.11
CTR	6.21±0.21	3.40±0.65	1.50±0.40	42.1±1.24	28.5±0.70	28.3±1.15

Data are presented as mean ± S.D (n) =2
IJR= Ijero; IPW= Ipawo; ISE= Ise; ORN= Orun; ARA=Aramoko; IDE= Ido-Ile; USI= Usi; IFK= Ifaki; IGD= Igede; IKO= Ikoro ESR= Esure; EMR= Emure;AYD=Ayedun; IPH= Ipawo; IRE=Ire; ILJ= Ilupeju; ILW=Ilawe; IGR=Igbara-Odo;. CTR= Control.

The level of organic matters in soils influences a number of soil chemical and physical properties. The results obtained in this study showed that organic matter content of the soils ranged from 2.96 ± 0.19% at IFK to 5.69 ± 0.62% at AYD during the wet season while the dry season ranged from 2.24 ± 0.35% at IGD to 5.95 ± 0.09% at ISE. The relative high concentrations of organic matter in some farms could be related to the decomposition and hydrolysis of plants releasing various kinds of organic matter and acids. Soil pH, organic matter and clay contents are known to influence the dynamics and behaviour of both inorganic and organic pollutants in soil [30-32].

The cation exchange capacity (CEC) of the soils ranged from 1.05 ± 0.69cmol/kg at IGR to 2.50 ± 0.34 cmol/kg at IKO during the wet season while the dry season values ranged from 1.55 ± 0.12 cmol/kg at IGR to 3.45 ± 0.15 cmol/kg at IKO. The results showed low levels of CEC. The sand, clay and silt content of the soils during the wet season (%) ranged from 30.5 ± 3.39 - 51.7 ± 0.21, 25.9 ± 0.21 - 50.5 ± 1.06 and 11.6 ± 0.07 - 30.1 ± 2.33 respectively while the dry season value ranged from 39.4 ± 1.30 – 54.3± , 25.9 ± 0.21 -49.1±0.15and 11.6 ± 0.07 - 28.4 ± 1.30 respectively. The soil particles size distribution reveals the textural class of the soils as mainly sandy clay and clay-sandy characteristics of most farms. The dominance of sand fraction might be as s result of high energy level in the farms, giving the deposition area of sandy-clay environment. A variable amount of erosion and deposition in the soil in both seasons is reflected from variable admixture of sand and clay fractions in some samples.

Table 1(b): Mean physico-chemical characteristics of soil from the study farms (dry season)

Sampling farm	pH	OM(%)	CEC (cmol/kg)	Sand (%)	Clay (%)	Silt (%)
IJR	6.55±0.21	3.60±0.07	2.25±0.08	49.3±0.14	28.8±0.07	22.1±0.14
IKO	6.00±0.14	3.85±0.49	3.45±0.20	44.7±0.15	28.8±0.07	26.6±0.15
ISE	6.45±0.07	5.95±0.09	2.65±0.18	42.5±10.3	30.1±2.10	28.4±1.30
ORN	5.90±0.20	5.30±0.00	2.25±2.25	49.1±1.50	34.6±0.40	16.4±1.50
ARA	6.40±0.14	3.45±0.07	2.50±2.30	50.9±1.30	31.2±1.55	18.0±1.40
IDE	6.45±0.11	2.70±0.50	1.70±1.20	48.9±0.12	25.9±0.21	27.7±0.14
USI	5.85±0.00	3.95±0.40	1.75±0.00	51.5±0.07	28.8±0.07	19.8±0.07
IFK	5.99±0.07	2.55±0.06	2.60±0.41	47.6±0.30	27.6±1.20	24.9±2.55
IGD	6.10±0.14	2.24±0.35	1.65±1.80	40.7±1.50	46.8±2.00	12.6±0.15
ESR	5.85±0.21	4.35±0.13	2.35±0.40	39.4±1.30	49.1±0.15	11.6±0.07
EMU	6.20±0.21	3.94±0.01	1.65±0.15	40.3±2.10	46.3±4.30	13.5±3.50
AYD	6.20±0.07	3.09±0.35	2.40±0.00	41.8±1.50	32.7±2.21	25.6±1.47
IPW	5.90±0.21	4.23±0.07	1.60±2.10	43.7±4.15	40.1±3.10	16.3±1.47
ILW	6.25±0.14	3.96±0.06	2.20±0.50	48.1±2.21	31.3±1.50	20.7±1.47
IGR	5.65±0.07	3.04±0.07	1.55±0.12	45.6±0.07	30.1±1.41	24.3±1.47
IRE	6.15±0.71	3.38±0.15	2.15±1.30	43.2±2.20	39.9±1.50	16.9±1.47
ILJ	6.25±0.14	4.20±0.14	2.30±0.70	54.3±3.20	30.8±4.15	14.9±1.47
CTR	6.60±0.00	3.15±0.49	2.30±0.80	42.0±0.07	29.7±1.50	18.3±1.47

Data are presented as mean ± S.D (n) = 2

IJR= Ijero; IPW= Ipawo; ISE= Ise; ORN= Orun; ARA=Aramoko; IDE= Ido-Ile; USI= Usi; IFK= Ifaki; IGD= Igede; IKO= Ikoro ESR= Esure; EMR= Emure;AYD=Ayedun; IPH= Ipawo; IRE=Ire; ILJ= Ilupeju; ILW=Ilawe; IGR=Igbara-Odo;. CTR= Control.

3.2 Occurrence and distribution of OCPs in the soil samples

The range, mean, standard deviation and coefficient of variation (CV) calculated on the overall data are presented in Table 2. The concentration of OCPs in the soil samples ranged from BDL – 487 µg/kg during the wet season while the dry season ranged from BDL – 894 µg/kg. Comparative analysis of the wet and dry seasons result revealed no significant difference ($p>0.05$) in the concentration of heptachlor-epoxide, *p,p*'-DDT, *p,p*'-DDD, dieldrin and endosulfan II as evident in the calculated t-values. Significant variation was also recorded in α-BHC, lindane, δ-BHC, aldrin, endosulfan I, endosulfan II, *p,p*'-DDD, endosulfan sulphate and TOCP among the sampling farms, while δ-BHC, heptachlor, β-BHC, heptachlor-epoxide, dieldrin, endosulfan sulphate and *p,p*'-DDT showed no significant variation. High level of spatial variation was mostly recorded as shown in the calculated coefficient of variation (Table 2). Comparative analysis of the two seasons also revealed no significant differences ($p>0.05$) in the total organochlorine pesticides residues (TOCP) as evident in the calculated t-values. The pattern of contamination of the OCPs in the soil samples (as TOCPs) was in order: EMR > ILW > IKO > IGR > ESR > IRE > ILJ > EMU > ISE > IGD > IJR > IPW > ORN > IFK > AYD > USI >ARA >IDE. The high incidence of OCPs in some soil samples could be as a result of continuous applications, the concentration of the active ingredient, gradient of the farm, frequency and volume of rainfall, nature of the pesticides and age of the farm, etc.

Out of total organochlorine pesticide residues concentrations in the entire soil samples, 30% and 28% of the TOCPs residue in the soil samples contained Σ-BHCs and Σ-endosulfans respectively. About 12%, 11%, 10% and 8% contained Σ-heptachlors, *p,p*'-DDT+*p,p'*-DDD, chlorothalonil, aldrin+dieldrin in that order. The contamination pattern of the entire soil samples from the study areas were Σ-BHCs > Σ-endosulfans > Σ-heptachlors > *p, p*'-DDT+*p, p'*-DDD > chlorothalonil > aldrin+ dieldrin. This implies that the soils from the studied cocoa farms in Ekiti State are more contaminated with the BHCs and endosulfans an indication that cocoa farmers in Ekiti State might have used technical BHC and endosulfan than other OCPs in their cocoa production. The occurrence and levels of these persistent organochlorine pesticides compounds in the soil samples from the study areas are worrisome. Apart from the potential danger they may pose to the soil organisms, there is also the possibility of translocation of these residues from the soil into cocoa fruits through the root system and into crops like vegetables that are commonly intercropped within cocoa farms, thereby constituting serious health risks [35,36,23]. Contamination of surrounding water bodies by pesticides residues through runoff from contaminated farm soils is also likely as reported [37-40].

About 87.9%, 88.8%, 88.85 and 70.4 % of the total samples contain α-BHC, β-BHC, δ-BHC and lindane respectively. It has been widely recognized that HCH is available in two formulations: technical HCH and lindane. Technical grade HCH contains 10 - 15% gamma-HCH, 60-70% alpha-HCH, 5-12% beta- HCH as well as delta and epsilon forms of HCH. Lindane contains 90% of gamma-HCH. The measured concentrations of the three isomers of BHC (or HCH) are attributable to the use of gamma-isomer (lindane) popularly called Gammalin 20, which is the only BHC isomer with powerful insecticide action. The concentration of α-BHC, β-BHC, δ-BHC and lindane during the wet season ranged from 1.78 - 12.2 µg/kg, 14.6 – 487 µg/kg, 22.2 - 474 µg/kg and BDL -177 µg/kg, while the dry season ranged from BDL - 2.86 µg/kg, BDL - 51.1 µg/kg, BDL - 101µg/kg and BDL - 4.48 µg/kg. The α-BHC, β-BHC, δ-BHC and lindane was below detection limits in soil samples from IKO, ARA and IDE during the dry season while lindane was below detection limits in ILW, IFK, ARA and IDE during the wet season. Although, technical grade HCH and lindane is no longer used as an insecticide in Nigeria, α-BHC, β-BHC, and δ-BHC have been found in the soil and surface water because they persist in the environment [18,22,23]. The range reported for HCH in this study is comparable to that of soils from agriculture area of Delhi region, India (0.01-104 µg/kg) [41] but higher than those reported in other areas of Czeh Republic (soil, 0.49-1.34 ng/g HCH, 2.41 - 7.75 ng/g HCB) [42] and lower in soil from some cocoa farms in Nigeria (ND- 1075 µg/kg δ-BHC) [23].

Table 2: Overall mean concentration (µg/kg) of organochlorine pesticide residues in cocoa farm soil samples

Sample Code		α-BHC	β-BHC	Lindane	Chloro-thalonil	δ-BHC	Hepta-chlor	Aldrin	Heptach-lor-epoxide	Endo-sulfan 1	Dieldrin	Endo-sulfan 1I	P,P¹-DDD	Endo-sulfan sulphate	P,P¹-DDT	TOCP
IJR	Range	BDL-36.7	BDL-487	BDL-35.1	BDL-126	BDL-54.2	BDL-132	BDL-90.3	BDL-74.9	BDL-118	BDL-107	BDL-45.9	BDL-29.3	BDL-113	BDL-53.5	BDL-954
	Mean	12.1	130	9.16	36.5	21.3	35.7	24.7	28.9	32.6	28.7	12.1	7.90	26.3	12.1	416
	SD	15.3	189	14.1	51.4	23.2	53.0	37.6	32.4	46.0	41.5	17.8	11.4	45.5	21.1	452
	CV%	126	146	154	141	110	149	152	112	141	145	147	144	173	174	109
IKO	Range	BDL-122	BDL-152	BDL-37.7	BDL-255	BDL-205	BDL-209	BDL-121	BDL-132	BDL-187	BDL-16.2	BDL-54.7	BDL-63.3	BDL-41.7	BDL-33.5	BDL-1384
	Mean	36.9	61.2	11.7	85.3	76.4	77.2	40.8	36.0	69.1	44.0	18.6	16.1	8.32	6.72	588
	SD	54.5	69.8	17.7	109	96.8	95.7	51.9	56.6	80.8	63.1	25.5	25.9	16.5	13.2	709
	CV%	148	114	151	127	127	124	127	157	117	143	137	161	198	197	120
ISE	Range	0.441-15.9	0.931-219	BDL-6.59	1.28-56.2	0.931-20.0	1.35-63.0	0.468-10.3	0.893-7.07	2.27-24.4	1.33-19.7	2.55-14.7	1.07-5.54	1.84-87.2	1.72-350	85.0-1296
	Mean	7.50	98.1	2.78	22.8	8.92	23.0	4.69	3.63	13.3	9.83	7.05	2.85	169	66.0	439
	SD	7.62	99.9	2.72	24.1	7.15	28.4	4.09	2.38	8.52	7.36	4.67	1.75	345	140	441
	CV%	102	102	97.6	105	80.2	123	87.3	65.6	63.8	74.9	66.2	61.6	204	211	101
ORN	Range	0.426-34.2	517-452	BDL-11.9	1.54-115	0.769-55.6	1.67-121	0.601-17.4	0.840-10.5	1.33-36.3	0.924-35.5	0.987-11.4	0.476-4.45	1.90-86.7	3.28-19.9	76.1-911
	Mean	12.4	167	4.85	37.4	32.9	45.8	7.63	4.55	13.5	12.1	4.39	2.62	38.0	9.98	39.2
	SD	13.9	178	4.70	43.5	34.7	48.8	6.46	3.91	14.5	12.8	4.12	1.51	36.7	7.21	305
	CV%	11.2	106	97.0	116	105	106	84.8	86.0	107	106	93.8	57.6	96.3	72.2	77.7
ARA	Range	BDL-17.6	BDL-229	BDL	BDL-50.9	BDL-26.0	BDL-61.5	BDL-9.94	BDL-6.53	BDL-17.9	BDL-14.5	BDL-6.09	BDL-2.04	BDL-15.8	BDL-2.42	BDL-451
	Mean	8.28	108	-	23.7	13.7	28.9	3.75	2.51	8.77	6.83	2.78	0.92	3.43	1.19	254
	SD	9.09	119	-	26.2	11.8	31.9	4.88	3.19	9.60	7.52	3.07	1.04	6.17	1.31	233
	CV%	110	109	-	111	86.5	111	130	114	109	110	110	110	180	109	91.8
IDE	Range	BDL-23.4	16.3-243	BDL	BDL-54.9	BDL-38.1	BDL-70.8	BDL-9.69	BDL-6.57	BDL-20.8	BDL-18.8	BDL-6.34	BDL-4.54	BDL-3.10	BDL-3.54	BDL-463
	Mean	9.13	47.5	-	23.9	13.1	30.0	4.13	2.74	8.95	7.65	2.76	1.34	1.16	1.41	154
	SD	10.7	96.4	-	27.2	15.9	33.9	4.68	3.08	9.99	8.76	3.08	1.82	1.34	1.61	193
	CV%	117	203	-	113	121	113	113	112	112	114	112	136	115	114	126

Table 2 cont.: Overall mean concentration (µg/kg) of organochlorine pesticide residues in cocoa farm soil samples

Sample Code		α-BHC	β-BHC	Lindane	Chloro-thalonil	δ-BHC	Hepta-chlor	Aldrin	Heptach-lor epoxide	Endo-sulfan 1	Dieldrin	Endo-sulfan 1I	P,P¹-DDD	Endo-sulfan sulphate	P,P¹-DDT	TOCP
USI	Range	BDL-20.6	6.43-275	BDL-5.74	BDL-52.7	1.22-31.3	1.50-77.4	0.505-11.9	0.736-7.66	1.21-22.8	1.23-18.6	0.925-6.44	1.67-215	1.96-18.8	2.17-32.9	42.1-541
	Mean	8.98	121	2.54	24.8	12.3	33.3	5.11	3.79	11.3	8.53	3.44	41.6	11.8	10.7	300
	SD	8.73	223	2.49	26.1	13.4	34.8	5.03	3.01	10.8	8.08	2.42	85.3	5.86	11.9	215
	CV%	108	101	97.9	105	109	104	98.3	79.3	95.9	94.8	70.2	205	49.8	111	71.9
IFK	Range	0.542-23.9	13.6-224	BDL-0.638	1.44-49.3	1.62-38.5	2.54-74.9	0.631-10.2	1.21-6.87	1.84-22.4	1.41-15.1	1.25-6.29	0.565-4.40	2.44-127	2.03-118	169-562
	Mean	9.91	119	0.294	22.7	18.1	31.0	4.56	3.35	10.1	8.21	3.69	1.66	66.9	25.6	323
	SD	10.5	120	0.324	23.8	14.0	32.4	4.33	2.49	9.18	7.78	2.24	1.40	61.4	45.6	152
	CV%	106	100	109	105	77.3	104	95.0	74.1	90.7	94.7	60.6	84.4	91.9	178	47.3
IGD	Range	0.426-47.1	8.66-405	BDL-14.8	1.37-149	0.862-61.2	1.67 155	0.412-22.2	0.886-13.9	1.48-42.7	1.07-36.1	1.27-11.8	0.711-11.4	1.29-98.6	1.57-23.7	43.1-1011
	Mean	13.6	138	4.14	39.7	17.4	43.9	6.70	4.96	15.7	11.7	5.41	3.68	30.0	7.37	419
	SD	18.4	161	5.91	58.0	23.7	60.9	8.52	4.87	16.3	13.2	4.15	3.96	37.0	8.41	352
	CV%	135	117	143	146	136	139	127	98.1	104	112	76.6	108	123	114	84.3
ESR	Range	0.421-29.5	4.12-17.2	BDL-4.69	1.26-65.5	0.862-37.8	1.38-98.1	0.590-15.8	1.02-22.3	1.56-45.8	BDL-24.1	BDL-7.08	BDL-5.65	BDL-659	BDL-26.2	88.2-849
	Mean	12.0	131	1.58	29.4	16.0	40.4	6.38	7.72	21.2	9.98	3.76	1.90	158	74.1	485
	SD	13.9	146	1.80	28.8	17.0	46.1	6.78	7.91	17.8	10.9	2.89	2.17	281	115	268
	CV%	13.7	144	1.78	28.5	16.8	45.7	6.71	7.83	17.6	10.8	2.87	2.15	279	114	265
EMU	Range	0.433-30.4	11.4-411	0.524-14.4	BDL-474	0.771-64.2	BDL-125	0.527-21.5	1.05-13.5	1.40-34.0	BDL-27.2	0.955-8.56	0.919-6.71	3.11-111	BDL-25.1	114-1131
	Mean	11.5	148	6.26	103	18.2	46.1	7.25	6.02	16.5	9.38	4.86	3.73	51.6	9.03	442
	SD	14.3.	182	6.56	186	23.9	56.7	9.25	5.45	15.3	11.9	3.24	2.31	45.7	10.5	439
	CV%	124	123	105	181	131	123	127	90.5	92.7	127	66.7	62.1	88.4	116	99.3
EMR	Range	0,548-9.20	4.51-182	0.604-9.16	13.3-68.3	11.9-55.3	1.46-52.6	1.72-60.1	5.00-42.9	29.2-111	4.78-257	7.97-410	4.49-330	BDL-372	BDL-267	256-1400
	Mean	5.28	84.7	5.41	43.2	45.5	27.8	14.9	18.9	63.2	90.1	155	105	101	66.7	810
	SD	4.01	67.5	3.11	19.9	51.8	19.4	22.7	15.6	36.4	100	174	129	160	110	541
	CV%	3.30	55.8	2.57	16.4	42.8	16.0	18.8	12.9	30.1	82.9	144	107	132	90.7	447
AYD	Range	0.522-20.4	10.6-202	0.506-16.9	7.68-68.5	0.936-38.1	1.28-95.9	0.434-24.1	0.729-12.9	13.8-59.6	0.916-16.1	0.975-21.1	0.461-7.18	2.50-151	1.85-5.07	81.5-576
	Mean	6.19	89.4	5.77	30.2	12.6	34.8	6.59	7.11	28.3	9.85	7.55	3.18	46.0	3.36	311
	SD	7.87	90.8	6.72	24.8	13.4	35.5	9.17	6.21	17.2	6.44	7.65	2.50	63.4	1.62	169
	CV%	6.01	69.3	5.13	18.9	10.3	27.1	7.00	4.74	13.1	4.91	5.84	1.90	48.4	8.56	129

Table 2 cont.: Overall mean concentration (µg/kg) of organochlorine pesticide residues in cocoa farm soil samples

Sample Code		α-BHC	β-BHC	Lindane	Chloro-thalonil	δ-BHC	Hepta-chlor	Aldrin	Heptach-lor epoxide	Endo-sulfan 1	Dieldrin	Endo-sulfan 1I	P,P¹-DDD	Endo-sulfan sulphate	P,P¹-DDT	TOCP
IPW	Range	0.463-27.8	12.3-265	0.534-20.4	1.68-131	0.892-53.9	1.27-128	0.450-11.9	0.731-17.9	1.85-74.8	1.02-34.7	3.12-29.4	0.814-53.9	3.14-434	4.06-40.8	50.7-817
	Mean	9.35	86.5	7.45	39.1	18.1	44.5	4.34	6.74	28.9	11.6	12.5	12.9	103	16.3	401
	SD	11.0	113	8.34	50.5	21.1	52.6	4.58	6.74	29.2	12.8	10.4	20.3	174	16.9	26.2
	CV%	118	131	11.2	129	117	118	106	100	101	111	83.1	157	169	104	65.3
ILW	Range	0.516-27.8	4.35-301	BDL-3.80	13.6-210	3.72-101	1.39-164	1.59-28.8	4.38-340	BDL-123	18.0-198	3.06-566	3.56-862	6.03-894	BDL-21.3	582-814
	Mean	11.6	137	2.43	88.2	36.8	65.2	13.3	67.3	35.7	77.4	208	216	243	6.28	685
	SD	11.9	136	1.62	81.9	37.6	68.2	10.2	134	49,5S	79.3	250	331	353	9.20	94.9
	CV%	7.80	89.4	1.06	53.6	24.6	44.6	6.70	87.5	32.3	51.9	163	216	231	6.01	13.8
IGR	Range	0.466 77.1	11.6-230	0.652-16.1	1.73-168	1.05-41.2	1.41-125	0.517-15.4	0.955-18.7	1.69-99.4	1.29-37.1	1.39-102	0.623-153	8.50-334	3.92-58.1	83.8-732
	Mean	33.9	92.9	7.33	67.5	14.9	47.8	6.36	7.61	35.7	14.1	22.9	27.5	93.7	16.3	485
	SD	36.9	102	6.24	73.0	16.7	53.3	6.68	7.41	40.4	14.9	39.1	61.5	128	20.9	281
	CV%	109	110	85.1	113	112	112	105	97.3	113	106	170	223	136	128	57.8
IRE	Range	0.462-124	7.52-252	0.496-177	1.42-100	0.784-71.4	1.16-94.9	0.406-54.7	0.734-56.5	1.22-93.6	0.913-42.8	0.914-35.9	0.402-182	4.44-101	1.35-23.9	56.8-1412
	Mean	24.6	56.2	37.8	41.2	29.5	37.3	21.4	22.6	101	11.1	14.2	39.2	28.1	10.8	475
	SD	48.8	96.3	69.2	41.8	28.7	41.2	23.8	24.7	165	16.6	16.	70.9	36.1	7.31	522
	CV%	199	171	183	101	97.1	110	111	109	163	149	112	118	129	67.9	110
ILJ	Range	0.425-3.43	3.28-227	0.483-96.1	1.25-80.5	0.238-69.8	1.26-81.8	0.410-50.0	0.999-52.0	2.68-121	0.967-64.9	1.50-53.9	0.551-65.9	13.7-74.7	11.1-58.9	50.3-1510
	Mean	1.59	66.4	32.1	24.0	20.5	23.8	17.1	15.4	37.5	116	17.9	20.2	33.0	22.0	448
	SD	1.37	84.6	40.4	31.2	26.3	31.5	20.6	19.8	46.0	261	20.5	26.6	22.4	18.9	548
	CV%	0.73	25.5	21.7	16.8	14.1	16.9	11.1	10.7	24.7	140	11.0	14.3	12.0	10.2	295
CTR	Range	BDL-4.75	BDL-1.90	BDL	BDL	4.70-11.2	BDL-5.60	1.45-6.05	BDL	BDL	BDL-1.40	BDL	1.08-3.30	BDL	BDL	6.15 23.1
	Mean	3.11	0.65	-	-	4.80	2.15	2.70	-	-	0.64	-	2.60	-	-	18.8
	SD	0.68	0.71	-	-	3.10	1.98	1.83	-	-	0.40	-	0.84	-	-	7.16
	CV%	21.8	109	-	-	64.5	92.1	67.8	-	-	6.25	-	32.3	-	-	38.1
t cal		**7.132***	**12.34***	**4.190***	**4.339***	**6.996***	**12.96***	**5.179***	**0.647**	**4.016***	**1.152**	**-1.839**	**-1.581**	**-3.791***	**-1.975**	**-1.304**
F_f cal		**2.125***	**1.361**	**4.739***	**1.331**	**2.830***	**1.673**	**3.816***	**1.414**	**2.558***	**1.562**	**14.289***	**3.153***	**1.425***	**1.586**	**4.673***

n = 6 *BDL= Below detection limit* *Detectable limit of OCPs = 0.15µg/kg* *SD= Standard deviation* *CV=Coefficient of variation*
t = t values calculated for test of sig. difference between dry and wet season *F_f = F values calculated for test of sig. variation between sampling farms* **Significant at $p < 0.05$*

In soils, sediments and water BHC is broken down to less toxic substances by algae, fungi and bacteria but the process takes a long time. The ratio of α-HCH to gamma-HCH has been used to identify the possible HCH source. The ratio of α-HCH to gamma-HCH between 3 and 7 are indicative of fresh input of technical HCH [43]. In this study, the ratio of α-HCH to gamma-HCH (lindane) (α/gamma ratio) were below three in some cases, while some showed value between 3 and 7 in some farms. This reflects the regular usage of technical usage HCH and lindane in IGR, USI and ILW farms. HCH is very persistent, estimated half life in soil from aerobic and anaerobic degradation ranges from 2.7 to 22.9 years [44].

This persistence combined with a high partition coefficient (log K_w=3.03-6.42) provides the necessary conditions for HCH to bio-concentrate in organisms. A review of the neurological effects of lindane exposure found that lindane can interfere with learning. Acute exposure to lindane may cause seizures of varying degrees (grand mal, petit mal, myoclonus, etc.), memory impairment, hyperactivity, irritability and aggression [45]. Additional studies have shown that exposures to low doses of lindane can interfere with an individual's ability to process new information by altering gamma-aminobutyric acid (GABA). GABA is an amino acid derivative that inhibits pre-synotic transmissions in the central nervous system (CNS) [46].

The concentration of heptachlor and heptachlor-epoxide in the soil samples during the wet season ranged from 13.8 – 209 µg/kg and 2.68 – 132 µg/kg respectively, while the dry season ranged from BDL - 32.0 µg/kg and BDL – 340 µg/kg respectively. This range is comparably lower for heptachlor in soil of Ondo Central Senetorial District of Nigeria (ND - 2493 µg/kg) [23]. About 81.4% and 89.8% of the soil samples contain heptachlor and heptachlor-epoxide respectively. The highest mean concentration of heptachlor and heptachlor-epoxide was obtained in samples from IKO (77.2 ± 95.7 µg/kg) and ILW (67.3 ± 134 µg/kg) respectively while the least was found in ISE (23.0 ± 28.4 µg/kg) and ARA (2.51 ± 3.19 µg/kg) respectively. The levels of heptachlor-epoxide found in the samples may be directly related to the application of heptachlor on the farms since heptachlor is only converted to heptachlor-epoxide in plants and insects tissues. The epoxide is more chemically potent than heptachlor itself [47]. Like other POPs, heptachlor is lipophilic and poorly soluble in water (0.056 mg/l at 25^0 C), thus it tends to accumulate in the body fat of humans and animals. Heptachlor-epoxide is more likely to be found in the environment than its parent compound. The epoxide also dissolves more easily in water than its parent compound and is more persistent. Heptachlor and its epoxide adsorb to soil particles and evaporate [48]. Heptachlor which is still found in soil and water can turn up in food and be passed away in breast milk due to process of bioconcentration. High levels of it seemed to type 2 diabetes risks to about 7% [49].

Aldrin and dieldrin were detected frequently in the soil samples. About 88.9% and 87% of the total soil samples contained aldrin and dieldrin respectively, with varying concentration of BDL – 121 µg/kg (aldrin) and BDL – 257 µg/kg (dieldrin) respectively. Comparing the levels of these pesticides with that of the control samples 1.45 – 6.05 and BDL - 1.40 µg/kg for aldrin and dieldrin respectively, the results reflected the contamination of the cocoa farms. The results obtained from this study showed similar trend with the level of aldrin (ND - 261 µg/kg) reported by Aiyesanmi and Idowu [23] in Ondo Central Senetorial District of Nigeria while dieldrin showed higher level (ND - 551 µg/kg) as compared with Aiyesanmi and Idowu [23]. IKO had the highest level of aldrin while ARA had the least aldrin and dieldrin concentration. Aldrin is readily metabolized to dieldrin by both plants and animals [50]. Aldrin binds strongly to soil particles and is very resistant to leaching into groundwater.

The concentration of chlorothalonil in the soil samples during the wet season ranged from 8.54 – 205 µg/kg, while the dry season ranged from BDL - 68.3 µg/kg. The concentration of chlorothalonil showed no detectable level for the control samples. High level of chlorothalonil was also recorded during the wet season as compared to dry season. Eighty seven percent of the soil samples from the study farms contained chlorothalonil.

The concentration of endosulfan I, endosulfan II and endosulfan sulphate in the soil samples during the wet season ranged from 6.40 - 187 µg/kg, 2.88 - 125 µg/kg and 1.84 - 133 µg/kg respectively, while the concentration during the dry season ranged from BDL - 123 µg/kg, BDL - 566 µg/kg and BDL - 894 µg/kg. The level obtained in this study is significantly lower to those reported in some cocoa farms in

Nigeria (ND - 350 mg/kg) [23] and also lower in most cases than in Indian soil (soil, 0.01 - 7.57 ng/g) [41]. Endosulfan I, endosulfan II and endosulfan sulphate were detected in 88.9%, 87.9% and 88.9% of the total soil samples. The highest mean concentration of endosulfan I, endosulfan II and endosulfan sulphate was obtained in samples from IKO (69.1 ± 15.5 µg/kg), ILW (208 ± 15.1 µg/kg) and ILW (2400 ± 491 µg/kg), while ARA (8.77 ± 15.5 µg/kg), ESR (2.50 ± 15.1 µg/kg) and IDE (1.16 ± 491 µg/kg) had the least. The study reported high level of endosulfan II and endosulfan sulphate during the dry season as compared to wet in most cases. The two conformational isomers of endosulfan, endosulfan I and endosulfan II occurred most frequently and at greater concentration than their metabolite endosulfan sulphate in farms like IJR, IKO, USI and IDE, while IFK, EMR, IPW, AYD, ILW, ESR, IGR showed greater level of endosulfan sulphate than the parent compounds. Much higher concentration of endosulfan I was found in the samples than the corresponding endosulfan II in some farms. The much higher concentration of endosulfan I relative to those of endosulfan II in the samples may be attributed to two reasons. Firstly, the manufactured technical endosulfan normally contains about 67% endosulfan I by mass of the total endosulfan content, while endosulfan II constitute only 32% [51]. It is therefore, not unexpected that more of endosulfan I would be found in the environment wherever the pesticide is applied. Secondly, endosulfan I is thermally stable while endosulfan II is unstable and may be slowly converted to endosulfan I in the environment [52,53].

The concentration of *p,p*'-DDT and *p,p*'-DDD in the soil samples during the dry season ranged from BDL – 1247 µg/kg and BDL - 86.2 µg/kg respectively, while the wet season ranged from BDL - 53.5 µg/kg and BDL - 63.3 µg/kg. The mean concentration of *p,p*'-DDT and *p,p*'-DDD in both seasons ranged from 1.19 ± 1.31 µg/kg (ARA) to 74.1 ± 115 µg/kg (ESR) and 0.92 ± 30.0 µg/kg (ARA) to 216 ± 331 µg/kg (ILW). The range reported for DDT in this study is lower compared to that of soils from agriculture area of Delhi region, India (0.01-2.38 µg/kg) [41]. About 83.3% and 87.9% of the total samples contain *p,p*'-DDT and *p,p*'-DDD. The persistence of DDT in soil can be affected by some factors including method of application, soil type, soil fertility, topography, climate conventions, farming practice, soil pH and organic content [54]. The amount of time for concentrations of DDT to be reduced by 95 percent in soils ranged from 4 to 30 years with an average time of 10 years [55]. The results from this study showed higher levels of *p,p*'-DDD in some farms when compared with the DDT levels, while some farms showed higher level of DDT as compared with the levels of DDD, thus, the DDT concentrations in these farms were from usage of aged technical DDT mixture.

Pearson correlation analysis carried out to examine the relationship between the soil physico-chemical properties and the levels of organochlorine pesticides residues in the soil samples are showed in Table 3. The results showed that there was a negative correlation between the concentration of the total organochlorine compounds and the pH and silt, while the CEC, clay and sand showed positive but not significant ($p < 0.05$) correlation. This implies that these soil parameters have little influence on the OCPs level. The organic matter content of the soil samples appear to influence the retention of the organochlorine pesticides compounds as reflected in the significant positive correlation (($p < 0.05$) between organic matter content and the total organochlorine pesticides in the soil. This suggested that the organochlorine compounds have high tendency of binding to organic carbons in soil, similar to fats or lipids of plants and animals [33,34].

Table 3: Correlation matrix between the soil physico-chemical properties and mean concentration of total OCPs

Group of parameters compared	Pearson correlation
pH/ MTOCP	-0.085
O.M/ MTOCP	0.339*
CEC/ MTOCP	0.165
Clay/ MTOCP	0.159
Sand/ MTOCP	0.009
Silt/ MTOCP	-0.150

2-tailed test of significance used * Correlation is at the 0.05 level.

4 CONCLUSION

The results showed that the studied cocoa farm soils were contaminated with the persistent organochlorine pesticides. This is evidence of past usage by the farmers in the area. The high concentrations of some of these contaminants pose a great concern. Apart from the potential danger they may pose

to the soil organisms, their possible translocation into edible parts of crops particularly cocoa beans and vegetables which are commonly incorporated in cocoa farms in Nigeria. Runoff or emission into available water surface and river is also very possible. Due to lack of a similar survey for same study area, the data obtained in this research can serve as a reference data on the levels of pesticides residues in soil of cocoa farms in south western Nigeria.

ACKNOWLEDGEMENT

The authors wish to acknowledge the technical assistance rendered by the Chemical Laboratory of the National Food and Drug Administration and Control, Oshodi, Nigeria.

REFERENCES

[1] Cocoa a guide to trade practices: International trade centre product and market development UNCTAD/WTO, Geneva: ITC, 2001, pp. 9-14.

[2] Guide to NEDEP on OLOP opportunities in Nigeria: volume 1 produced by Small and Medium Enterprises Development Agency of Nigeria (SMEDAN) February, 2014.

[3] ICCO (International Cocoa Organisation). Pests and diseases. http://www.icco.orgaccessed on 20th June, 2010.

[4] T. Colborn, F.S. VomSaal, and A.M Soto, "Developmental effects of endocrine-disrupting chemicals in wildlife and humans," *Environ. Health Perspec,* vol. 101, no. 5, pp. 378-384, 1993.

[5] M. Patlak, "Estrogens may link pesticides, breast cancer," *Environ. Sci. Tech,* vol. 30, pp. 210- 211, 1996.

[6] J.Y. Guo, E.Y. Zeng, F.C. Wu, X.Z. Meng, B.X. Mai, and X.J. Luo, "Organochlorine pesticides in seafood products from Southern China and health risk assessment*," Environ. Toxicol. Chem,* 2007, vol. 26, pp. 1109-1115, 2007.

[7] M.A.F, Muino, M.T. Sancho, J.S Gandara, J.M.C. Vidal, J.F. Huidobro, and J.S. Lozano, "Organochlorine pesticide residues in Galician (NW Spain) honeys," *Apidologie*, vol. 26, pp. 33-38, 1995.

[8] L. Ruiz - Gil, R. Romero – Gonzalez, A.G. Frenich, and J.L.M, Vidal, "Determination of pesticides in water sample by solid phase extraction and gas chromatography tandem mass spectrometry," *J. Sep. Sci,* vol. 31, pp. 151- 161, 2008.

[9] C. Lopez-Blanco, S. Gomez-A Ivarez, M. Rey- Garrote, B. Chancho-Grande, and J. Simal-Gandra, "Determination of pesticides by solid phase extraction followed by gas chromatography with nitrogen-phosphorus detection in natural water and comparison with solvent drop microextraction," *Analy. Bioanaly. Chem,* vol. 384, pp. 1002-1006, 2006.

[10] M.C. Kennicutt, S.J. Mc Donald, J.L. Sericano, P. Boothe, J. Oliver, S. Safe, B.J. Presley, H. Liu, D. Wolfe, T.L. Wade, and A. Crockett,"Bockus, D. Human contamination of the marine-environment – Arthur Harbor and Mcmurdo Sound, Antarctica," *Environ. Sci. Tech,* vol 29, pp. 1279-1287, 1995

[11] R. Fuoco, M.P. Colombini, A. Ceccarini, and C. Abete, "Polychlorobiphenyls in Antarctica," *Micro-chem. J.* vol. 54, pp. 384-390, 1992.

[12] J. Aislabie, M. Balks, N. Astori, G. Stevenson, and R. Symons, "Polycyclic aromatic hydrocarbons in fuel-oil contaminated soils, Antarctica," *Chemosphere,* vol.39, pp. 2201-2207, 1999.

[13] T.C. Negoita, A. Covaci, A. Gheorghe, and P. Schepens, P, "Distribution of polychlorinated sbiphenyls (PCBs) and organochlorine pesticides in soils from the East Antarctica coast," *J. Environ. Monitor,* vol. *5,* pp. 281-529, 2003.

[14] N. Gonzalez - Lopez, R. Rial – Otero, B. Cancho – Grande, J. Simal - Gandara, and B. Soto – Gonzalez, "Occurrence of organochlorine pesticides in stream sediments from industrial area," *Arch. Environ. Contam. Toxicol,* vol. 48, no. 4, pp. 296 – 302, 2005.

[15] Arias – Este'vez, E. Lopez - Periago, E. Marti'nez - Carballo, J. Simal - Ga'ndara, J. Mejuto, and L. Garci-a-Rio, "The mobility and degradation of pesticides in soils and the pollution of groundwater resources," *Agric. Ecosystem Env,* vol. 123, pp. 247-260, 2008.

[16] M. Rosa, Gonzalez-Rodriguez, R. Rial-Otero, B. Cancho-Grande, and Simal-Gandara, "Determination of 23 pesticides residues in leafy vegetables using gas chromatography-ion

trap mass spectrometry and analyte protestants;" *J. Chromatography A*, vol. 1196-1197, pp. 100-109, 2008.

[17] O, Osibanjo, and E. Bamgbose, "Review of chlorinated substances in Marine fish and shellfish in Nigeria," *Mar. pollut. Bull,* vol. 21, pp. 581-586, 1990.

[18] O.K. Ize-Iyamu, I.O Asia, and P.A. Egwakhide, "Concentration of residues from organochlorine pesticide in water and fish from some rivers in Edo State, Nigeria." *International J. Physical Sci,* vol. 2, no. 9, pp. 237–241, 2007.

[19] D. Adeyemi, C. Anyakora, G. Ukpo, A. Adedayo, and Darko, G,"Evaluation of the levels of organochlorine pesticide residues in water samples of Lagos lagoon using solid phase extraction method," *Environ. Chem. Ecotoxico,s,* vol. 3, no. 6, pp. 160-166, 2011.

[20] A.O. Ogunfowokan, J.A.O. Oyekunle, N. Torto, and M.S Akanni, "A study on persistent organochlorine pesticide residues in fish tissues and water from an agricultural fish pond," *Emir. J. Food Agric,* Vol. 24, no. 2, pp. 165-184, 2012.

[21] G.A. Idowu, A.F. Aiyesanmi, and B.J. Owolabi, "Organochlorine pesticide residue levels in river water sediment from cocoa-producing areas of Ondo State central senatorial district, Nigeria," *J. Environ. Chem. EcotoxicoL*, vol. 5, no. 9, pp. 242-249, 2013.

[22] O.A. Ibigbami, A.F. Aiyesanmi, E.I. Adeyeye, A.O, Adebayo, and R.D. Aladesanwa, "Assessment of organochlorine and organophosporus pesticides resolve in water and sediments from Ero River in South West, Nigeria," *J. Chem. Biol. Phy. Sci.* vol. 5, no.4, pp. 4679 – 4690, 2015.

[23] A.F. Aiyesanmi, and G.A. Idowu, "Organochlorine pesticides residues in soil of cocoa farms in Ondo State central district, Nigeria," *Env. Natur. Resour. Resea,* vol 2, no. 2, pp. 65-72, 2012.

[24] W.H. Hendershot, H. Lalande, and M. Duquette, "Soil reaction and exchangeable acidity. In (M.R. Carter Ed.) Soil sampling and methods of analysis for Canadian Society of Soil Science, London: Lewis, 1993, pp 141-145.

[25] B.H. Shedrick, and C. Wang, "*Particle size distribution,"* In (M.R. Carter, Ed) Soil sampling and methods of analysis for Canadian Society of Soil Science, London: Lewis, 1993. pp 449-511.

[26] E.E. Schulte, "*Recommended soil organic matter test"* In Recommended soil testing procedures for the North-eastern United State 2nd ed. 1995.

[27] M. Radojevic, and V.N. Bashkin, "Practical Environmental analysis," Published by the Royal Society of Chemistry, Uk, pp. 350-354, 1999.

[28] US Environmental Protection Agency SW-846, test methods for evaluating solid waste, 3rd edn. Update IVB' Chapter 4, organic analytes. US EPA, Washington, DC. 2000.

[29] D.I. Sparks, Environmental Soil Chemistry. 2nd Edition, San Diego: Academic Press, 2003.

[30] DPR. Environmental guidelines and standards for petroleum Industry in Nigeria (Revised edition), Department of Petroleum Resources, Ministry of Petroleum and Mineral Resource, 2002.

[31] N.L. Gale, C.D. Adams, B.G. Wixson, K.A. Loftin, and Y. Huang, "Lead, zinc, copper and cadmium in fish and sediments from the Rig River and Flat River creek of Missouri's old lead belt," *Environ. Geochem. Health,* vol. 26, pp. 37-49, 2004.

[32] A.F. Aiyesanmi, W.B. Tomori, and B.J. Owolabi, "Relative partitioning of some heavy metals in dumpsite soil using chemical speciation technique," *International J. Chem. Sci,* vol. 1, no.1, pp. 96-104, 2008.

[33] D. Swackhamer, and R.A Hites, "Occurrence and bioaccumulation of organochlorine compounds in fish from Siskiwitlake, Isle Royale, Lake Superior," *Environ. Sci. Technol,* vol. 22, pp. 543-548, 1988.

[34] T.W. Bentzen, E.H. Follman, S.C. Amstrup, G.S. York, M.J. Woller, D.C.G. Muir, and T.M. O' Hara, "Dietary biomagnifications of organochlorine contaminants in Alaskan polar bears," *Canadian J. Zoo,* vol. 86,pp. 177-191, 2008.

[35] L.R. Townsend, and H.B. Specht, "Organophosphorus and organochlorine pesticide residues in soils and uptake by tobacco plants," *Canadian J. Plant Sci,* vol. 55, pp. 835-842, 1975.

[36] A. Quintero, M.J. Caselles, G. Ettiene, N.G. De Colmenares, T. Rami' rez, and D. Medina, "Monitoring of organophosphorus pesticide residues in vegetables of agricultural area in Venezula," *Bull. Environ. Conta. Toxicol,* vol. 81, pp. 393-396, 2008.

[37] J.A.A. Castilho, N. Fenzl, S.M. Guillen, and F.S. Nascimento,"Organochlorine and organophosphorus pesticide residues in the Atoya river basin, Chinandega, Nicaragua," *Environ. Poll.* vol. 110, pp. 523-533.

[38] L.K. Konstantinou, D.G. Hela, and T.A. Albanis, "The status of pesticide pollution in surface waters (rivers and lakes) of Greece. Part 1. Review on occurrence and levels,"*Environ. Poll.* vol. 141, no. 3, pp. 555-570, 2006.

[39] E. Pazou, P. Lalaye, M. Boko, C.A.M van Gestel, H. Ahissou, S. Akpona, B. van Hattum, K. Swart, N.M. and van Straalen, "Contamination of fish by organochlorine pesticide residues in the Queme River Catchment in the republic of Benin" *Env. International*, vol. 32, pp. 594-5699.

[40] S.K. Sarkar, B.D. Bhattacharya, A. Bhattacharya, M. Chatterjee, A. Alam, K.K. Satpathy, and M.P. Jonathan, "Occurrence, distribution and possible sources of organochlorine pesticide residues in tropical coastal environment of India: an overview," *Env. International*, vol. 34, no. 7, pp. 1062-1071, 2008.

[41] A. Bhupander, "Residues of Pesticides and Herbicides in Soils from Agriculture Areas of Delhi Region, India," *J. Environ. Earth Sci,* vol. 1, no. 2, pp. 1-8, 2011.

[42] J. Klanova, N. Matykiewiczova, Z. Macka, P. Prosek, P. Laska, K. Laska, and P. Klan, "Persistent organic pollutants in soils and sediments from James Ross Island, Antarctica," *Environ. Pollu,* pp. 1-8, 2007.

[43] R.Q. Yang, A.H. Lv, J.B. Shi, G.B. Jaing, "The level and distribution of organochlorine pesticides (OCPs) in sediments from the Haihe River, China," *Chemosphere,* vol. 61, PP. 347-354.

[44] Environment Canada. Hexachlorobenzene: Priority substance list assessment report ministry of supply and services, Cat No En 40-215/75, 1993.

[45] A. Duffard, and R. Duffard, "Behavioral toxicology, risk assessment, and chlorinated hydrocarbons," *Environ. Health Perspec,* vol. 104, no. 2, pp. 353-360, 1996. .

[46] T. Narahashi, Nerve membrane ion channels as the target site of insecticides. Mini Reviews in Modern Chemistry, vol. 2, pp. 19-432, 2002.

[47] R.J. Cremlyn, Agrochemicals preparation and mode of action, New York, N.Y: John wiley & sons, 1991.

[48] ATSDR. Heptachlor and heptachlor-epoxide- Fact sheet. 2007.

[49] K. Harmon, New mass- screening method. Finds Additional Environmental Risks for Diabetes. (Scientific American, May, 2010).

[50] WHO. Aldrin and Dieldrin. Environmental Health Criteria 91. World Health Organization, Geneva, 1989.

[51] Wealth Health Organization (WHO). Chemistry and specifications of pesticides, Thirteenth report of the WHO expert committee on vector biology and control, Geneva WHO, 1990.

[52] C.J. Hapeman, W.F. Schmidt, and C.P Rice, "Structural and thermodynamic considerations in the isomeric conversion of endosulfan I. 213th National Meeting of the American Chemical Society, San Francisco, California, USA, April 13-17". *Abstracts of papers: American Chem. Socie.* vol. 213, pp. 1-3, 1997.

[53] C.P. Rice, C.J. Haperman and S.M. Chernyak, "Experimental evidence for the inter-conversion of endosulfan isomers, In: 213th National Meeting of the American Chemical Society, San Francisco, California, USA, April 13-s17, 1997.

[54] EPA (Environmental Protection Agency) DDT: A review of scientific and economic aspects of the decision to ban its use as a pesticide, EPA-540/1-75 022. Washington, 1975.

[55] C.A. Edwards, "Insecticide residues in soils, "*Residue Rev,* vol. 13, pp. 83-132, 1996.