



Research article

Human health risk assessments of organochlorine pesticides in some food crops from Esa-Oke farm settlement, Osun State, Nigeria

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ABSTRACT

Seasonal levels of organochlorine pesticides (OCPs) in yam, cassava, sweet potato and cocoyam samples collected from Esa-Oke Farm Settlement, Osun State, Nigeria were evaluated. Sampling regiment for three sites lasted four months each during the dry and wet seasons. The dried samples were extracted using Soxhlet extractor with dichloromethane (DCM) as the extraction solvent, while the identification and estimation of OCPs in the crop filtrates, after clean-up, were carried out with Gas Chromatography equipped with Time-of-Flight Mass Spectroscopy Detector (GC-TOFMS). Ten OCPs determined in the crops had the overall seasonal mean levels that ranged from 158 ng/g (dieldrin) to 544 ng/g (heptachlor) and the seasonal mean burden per OCP occurred in the order: heptachlor epoxide (518) > heptachlor (447) > p,p'-DDE (431) > dieldrin (349) > chlordane (327) > aldrin (321) > p,p'-DDD (313) > methoxychlor (303) > endosulfan I (287) > p,p'-DDT (284) for wet season while this order was not the same for dry season of the same crop with heptachlor epoxide (415) > p,p'-DDE (373) > aldrin (305) > heptachlor (307) > methoxychlor (288) > chlordane (274) > p,p'-DDT (263) > p,p'-DDD (263) > endosulfan I (260) > dieldrin (246). For all of the OCPs, the estimated daily intake (EDI) and health risk indices (HRI) were significantly higher than the recommended values. Thus, a regular large-scale consumption of crop products from the farm settlement could result in grave public health concern in the course of time.

1. Introduction

Without a doubt, the discovery of chemical pesticides has greatly aided agricultural output based on crop protection and yield, making pesticides usage nearly unavoidable (Alloway and Ayres, 1997). According to Osibanjo (1994), organochlorine pesticides are still applied in most developing nations, including Nigeria, due to its high effectiveness/usefulness and cheap when compared to alternative pesticides. Pesticides are mostly used as insecticides on both planted and stored crops in these countries (Pope et al., 1994; Anzene et al., 2014).

However, the consequence of pesticides and their residue on non-target environmental components in general continues to raise major concerns, as it appears that the undesirable consequences of pesticide use may offset the largely advantages (Kupfer et al., 2011; Liu, 2005). Pesticides containing organochlorine compounds have been used for a long time in many parts of the world (ATSDR, 2002). There are a group of hazardous chemical compounds (non-polar) that contain hydrogen, chlorine, carbon and can be divided into five categories, namely:

Dichloro-diphenyl-trichloroethane (DDT) and analogues; Hexachlorocyclohexanes (wrongly referred to as Benzene hexachlorides); Cyclodienes; Chlordecones; and Toxaphenes (Cary et al., 2001; Kihampa and Mato, 2009).

Organochlorine pesticides (OCPs) are persistent organic pollutants (POPs) and are non degradable in the environment by biological, chemical, microbiological, or physical processes (Darko and Acquah, 2007). The half-life of organochlorine pesticides varies from months to years, and as well as decades (Cremlyn, 1991). These pesticides are harmful to most marine species and deadly to humans and other animals (Gwary et al., 2012). Even at low concentrations, organochlorine may have significant short-term and long-term effects. Furthermore, the deadly effects of most organochlorines, such as immune system and reproductive organ damage (Fatunsin et al., 2020; Ita, 2017). They accumulate in oily tissues of humans, plants, animals, and are drawn to oily tissues and organs in particular. They build up in large amounts in animals like fish (Bentzen et al., 2008; Ogah et al., 2012).

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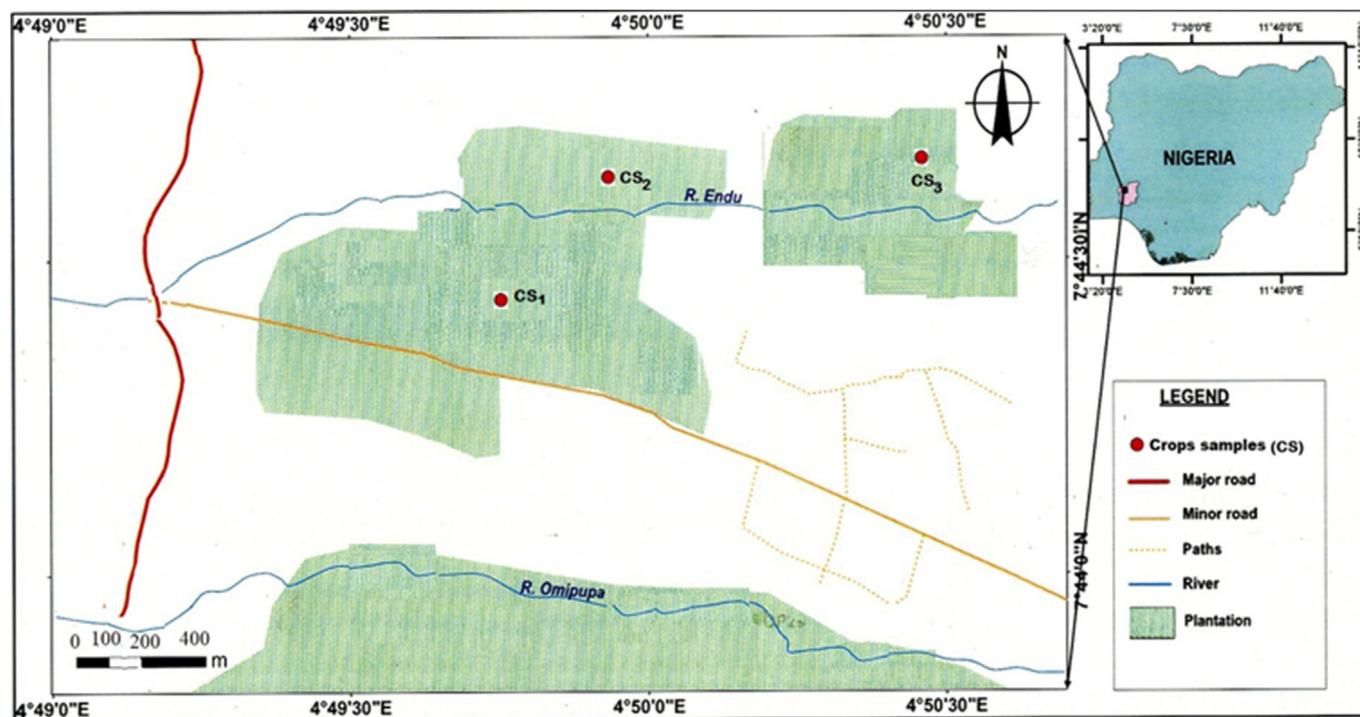


Figure 1. Map showing sites locations with Esa-Oke farm settlement, Osun State, Nigeria.

Increased organochlorine concentrations along the food chain have been documented, with bioaccumulation and biomagnification occurring in higher species, including humans (Asia and Egwakhide, 2007). Each year, around 3 million pesticide poisoning cases occur worldwide as a result of ingesting large amounts of contaminated agricultural goods containing pesticide residues or their breakdown products, with about 95 percent of deadly toxic cases taking place in developing countries (Oyekunle et al., 2010). In spite of the fact that most noxious organochlorine compounds are banned, they are nonetheless illegally used in most developed countries, both domestically and on agricultural products (Fatoki and Awofolu, 2003). Hitherto, farming is being practiced in Nigeria at largely subsistence and, to lesser extent, at mechanized levels almost year-round with chemicals applied to boost crops production depending on the category of crop and farmland locations (Caldas et al., 1999). Consistent food residue inspection is essentially non-existent in Nigeria which is because of high expense of pesticide residue studies (Adekunle et al., 2018). Farmers have little or no desire to change their current practices, despite efforts to teach farmers about the risks of pesticide use, because authorities lack the resources to pursue them (Hall, 1999). Organochlorine pesticides have remained a source of universal worry due to their general usage and long-distance distribution via ocean currents, surface runoff, and atmospheric transport (Bentzen et al., 2008).

The current research was expected to identify the levels and types of OCPs associated with some food items cultivated within Esa-Oke farm settlement and that were available in both seasons. This was with a view to assessing the health risks associated with large-scale consumption of such food items.

2. Materials and methods

2.1. Description and suitability of the study area

The study area, Esa-Oke farm settlement, was established in the 1960s along with Ago-Owu and Oyere farm settlements (OSSADEC, 2003). Esa-Oke farm settlement is located between latitudes $07^{\circ}44.070'N$ and $07^{\circ}44.585'N$ and longitudes $004^{\circ}50.515'E$ and $004^{\circ}49.566'E$ (Figure 1). Of the ten farm settlements currently in Osun State, namely: Ago-Owu, Esa-Oke, Oyere,

Igbaye, Ifon-Orolu, Oluponna, Mokore, Iwo, Ila-Orangun and Oke-Osun (OSSADEC, 2003), Esa-Oke farm settlement has the largest farmland area of over 2,113 Ha. The farm settlement has infrastructure such as primary school, hospital, and road networks which allow access and movement of farm produce in and out of the settlement with relative ease. Major food crops cultivated at Esa-Oke farm settlement include cocoyam, cassava, yam, maize, vegetables and sweet potato, while cocoa and palm trees are the main cash crops. Farm produce from the farm settlement attracts patronage from many towns and cities within Osun and neighboring States.

2.2. Sampling sites and sample collection

Crop samples from Esa-Oke Farm Settlement, Osun State, Nigeria were collected randomly at three sampling locations as shown in Figure 1. The crop samples collected included yam, cassava, cocoyam and sweet potatoes within the farm settlement during the sampling regime covering February, March, April and May (2018) for wet season, and July, August, September and October (2018) for dry season. The sum of 48 crops was collected for each crop samples. These crop types were selected because they were readily available throughout the sampling period and form part of the staple food items of the settlers.

2.3. Sample preservation, preparation and storage

The crop samples were wrapped in aluminum foil which is labeled appropriately for further laboratory preparation. The crop samples were washed using distilled water, cut into pieces and sun-dried to constant weight within 2 weeks to reduce the moisture content and also to reduce biological or chemical changes. The dried crop samples were manually ground to powdery form and sieved through a 2 mm wire net using an agate mortar and pestle. The homogenized samples were stored inside aluminum foil, kept in labeled zip-lock bags and stored at about $4^{\circ}C$ prior extraction.

2.4. Reagents and materials

The chemicals used were analytical grade. Chemical such as dichloromethane (DCM) from Mallinckrodt Baker (Phillipsburg, NJ,

USA); *n*-hexane was purchased from Tedia (Fairfield, OH, USA); Silica gel 60 PF₂₅₄ (MERCK, Germany); anhydrous sodium sulfate (Rochelle Chemicals, USA). Prior to use, all glass-ware and sample bottles for trace or organic analysis were washed in a liquid detergent solution, rinsed with a pure acetone and *n*-hexane mixture, and then heated in an oven at 120 °C for 12 h (Isioma and Lawrence, 2015). Sigma-Aldrich provided reference grade pesticide standards with purity ranging from 98.5 to 99.5 percent (CRM47426 Johannesburg, South Africa).

2.5. Extraction of OCPs from the crop samples

In a pre-extracted Whatman extraction thimble, a 20 g quantity of each powdered dried crop sample was selected by coning and quartering process was weighed. Extraction of sample was carried-out in the Soxhlet extractor for 5 h using DCM as the extracting solvent, as described by Oyekunle et al. (2010). Using a vacuum rotary evaporator, the extract was concentrated to 3 mL. The extract was allowed to cool to room temperature before being concentrated to about 2 mL under a stream of high purity nitrogen (99.99%). The reduced extracts were kept in vials and put in a freezer for subsequent chromatographic clean-up and OCPs analysis was done using gas chromatography coupled with time-of-flight mass spectrometry (GC-TOFMS). Crop samples from each study site were analyzed three times in total.

2.6. Clean-up of the extracts

A 15 cm (length) x 1 cm (internal diameter) column was filled with 5 g activated silica gel made in a slurry form in DCM, and 1 g of anhydrous sodium sulphate (Na₂SO₄) was placed on top of the silica gel to absorb any water in the sample or the solvent for the clean-up experiment. Prior to clean-up the column was conditioned with 15 mL DCM. The crop extract was transferred into the column in small amounts and eluted with 20 mL of DCM. At 45 °C and a gentle stream of nitrogen gas, the eluate was concentrated to dryness on the rotary evaporator. The extract was dissolved in 2 mL *n*-hexane and was transferred into glass GC vial for analysis using GC-TOMS.

2.7. Quality assurance and quality control

2.7.1. Blank and replicate determinations

In order to determine whether any of the studied pesticides were present in the reagents, the same quantities of DCM and anhydrous sodium sulphate used in the extractions were subjected to the same extraction and clean-up protocols adopted for analysis of samples. By analyzing the samples in triplicates, precision was determined.

2.7.2. Preparation of working standard solutions and calibration curves

From the stock solutions of organochlorine pesticides (α -BHC, β -BHC, δ -BHC, lindane, heptachlor, aldrin, heptachlor epoxide, endosulfan I, endosulfan II, dieldrin, *p,p'*-DDD, *p,p'*-DDT and methoxychlor) standard solutions were prepared, placed in amber coloured bottles and stored at 4 °C in a refrigerator. From these, working standard solutions were developed and used for the production of standard calibration curves for each OCP under set chromatographic conditions. The signatory retention time for each OCP was used as confirmatory indicator. Calibration curves were produced with seven different concentrations (0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 ng/g).

2.7.3. Recovery analysis

To test the validity (precision and efficiency) of the analytical processes, a recovery study was done using the standard addition method, in which a predetermined quantity of pesticide was added into the samples and then evaluated for the total quantity of OCPs. This was necessary because no certified pesticide reference materials were accessible during this research. About 20-gram sample of crushed crops was separated into two equal parts. One component was injected with a standard 10 ppm

Table 1. Retention times, response factor, limit of detection and quantification and % recovery for OCPs in crops.

Compounds	RT (min)	RF	% Recovery	LOD	LOQ
Heptachlor	5.58	0.812	89.83	0.45	10.20
Aldrin	6.16	1.937	90.54	1.81	3.94
Heptachlor epoxide	8.12	0.621	91.35	1.04	7.98
Chlordane	9.89	1.286	86.56	2.11	10.64
Endosulfan I	11.18	1.982	92.46	1.57	6.73
<i>p,p'</i> -DDE	12.28	0.721	88.81	3.03	10.69
Dieldrin	12.58	1.873	87.57	1.73	7.22
<i>p,p'</i> -DDD	14.06	0.322	94.43	3.51	10.51
<i>p,p'</i> -DDT	15.05	0.639	98.74	0.92	9.96
Methoxychlor	17.75	0.716	93.45	1.62	8.01

RT = Retention time, RF = Response factor, LOD = Limit of detection, LOQ = Limit of quantification.

mixture that included aldrin, dieldrin, *p,p'*-DDE, *p,p'*-DDT, *p,p'*-DDD, chlordane, heptachlor, endosulfan I, heptachlor epoxide, and methoxychlor. These were mixed extensively, while the other fraction (control) was left unspiked. According to Oyekunle et al. (2010) and other researchers procedure, the samples were subjected to the same extraction and clean-up protocols. In addition, an uncontaminated, oven dried sample container was filled with 10 mL of the standard 1000 g/L OCP mixture in spectrum grade *n*-hexane. For GC-TOFMS analysis, 1.0 μ L of each of the injected, uninjected (control) and standard mixture was introduced into the GC column with the help of a microsyringe. Comparing the peak areas of the OCPs after spiking with those obtained from evaporated standard residues, the recoveries of OCPs were determined. The percentage recovery was evaluated from Eq. (1):

$$\% R = \frac{A1 - A2}{B} \times 100 \quad (1)$$

A1 = the quantity of OCP in the spiked sample, A2 = the quantity of OCP in the unspiked sample and B = the quantity of OCP in the spiked sample.

2.7.4. Determination of limits of quantification and detection

The sensitivity of the instrument was measured by measuring the limits of detection (LOD) and the limits of quantification (LOQ) (Table 1) were obtained using Eq. (2):

$$LOD / LOQ = \frac{F \times SD}{b} \quad (2)$$

Where:

F = Factor of 3 and 10 for DL and QL, respectively; SD = Standard deviation of the blank, standard deviation of the ordinate intercept; *b* = Slope of the regression line (Shrivastava and Gupta, 2011).

2.7.5. Response factor (RF) determination

The response factor (RF) was calculated using Ogunfowokan et al. (2012) technique for some of the available standard OCP. This was calculated by examining 1.0 μ L of 1000 ppm stock solution of the standard mixture containing the internal standard (IS) (CLP Organochlorine Pesticide Mix, 1X1ML) into the gas chromatograph. The IS used for this research was CLP Organochlorine Pesticide Mix, 1X1ML. The RF for each of the available samples peak was obtained using Eq. (3):

$$RF = \frac{\text{Peak area of OCP}}{\text{Peak area of I.S.}} \quad (3)$$

2.8. Gas chromatographic analysis of OCP extracts

The GC-TOFMS instrumentation and quantification were carried out by gas chromatography (Agilent Model 7890B) coupled with Pegasus 4D

Table 2. Seasonal mean levels (ng/g) of OCPs in crop samples.

OCPs	Seasons	Yam	Cocoyam	Sweet Potato	Cassava	Mean Burden per OCP	OCP maximum permissible limit (WHO/FAO 2013)
Aldrin	Wet	328 ± 45	294 ± 61	269 ± 23	392 ± 43	321 ± 53	30
	Dry	316 ± 21	303 ± 61	252 ± 23	351 ± 43	308 ± 42	
Dieldrin	Wet	380 ± 42	326 ± 20	277 ± 37	414 ± 41	349 ± 60	30
	Dry	276 ± 52	232 ± 22	158 ± 10	317 ± 31	246 ± 68	
p,p'-DDT	Wet	288 ± 25	255 ± 19	226 ± 20	366 ± 31	284 ± 60	200
	Dry	288 ± 13	230 ± 29	225 ± 27	309 ± 22	263 ± 41	
p,p'-DDD	Wet	317 ± 72	311 ± 25	273 ± 11	349 ± 21	313 ± 30	200
	Dry	299 ± 21	236 ± 19	212 ± 29	304 ± 15	263 ± 45	
p,p'-DDE	Wet	446 ± 26	425 ± 49	382 ± 44	469 ± 61	431 ± 36	200
	Dry	378 ± 36	330 ± 57	319 ± 73	465 ± 26	373 ± 66	
Endosulfan I	Wet	290 ± 19	287 ± 35	232 ± 22	338 ± 17	287 ± 43	300
	Dry	281 ± 24	243 ± 33	217 ± 45	299 ± 28	260 ± 36	
Chlordane	Wet	333 ± 18	325 ± 26	309 ± 27	340 ± 21	327 ± 13	20
	Dry	269 ± 51	252 ± 23	245 ± 15	329 ± 35	274 ± 37	
Heptachlor	Wet	460 ± 17	449 ± 41	333 ± 29	544 ± 34	447 ± 86	30
	Dry	321 ± 17	312 ± 21	215 ± 18	380 ± 42	307 ± 68	
Heptachlor Epoxide	Wet	528 ± 16	510 ± 17	492 ± 15	541 ± 18	518 ± 21	30
	Dry	432 ± 19	415 ± 28	330 ± 26	481 ± 18	415 ± 63	
Methoxychlor	Wet	342 ± 43	259 ± 24	250 ± 14	362 ± 33	303 ± 57	200
	Dry	299 ± 21	263 ± 18	249 ± 41	339 ± 19	288 ± 40	
Range	Wet	288–528	255–510	226–492	338–544	284–518	
	Dry	269–432	230–415	158–330	299–481	246–415	
Mean ± s.d	Wet	371 ± 80	344 ± 86	304 ± 81	412 ± 76	358 ± 79	
	Dry	316 ± 51	282 ± 58	242 ± 51	357 ± 65	300 ± 54	
CV	Wet	21.56	25.00	26.65	18.45	22.07	
	Dry	16.14	20.57	21.07	18.21	18.00	

sd = Standard deviation; CV = Coefficient of variation.

TOFMS (LECO) with a capillary GC column (RestekRtx-CL pesticides 2) 30 m × 0.25 mm id × 0.25 μm film thickness. The GC operating conditions were: splitless injection, injector temperature 250 °C, helium carrier gas (99.99% purity) at a flow rate of 0.9 mLmin⁻¹ with column head pressure 7.4 psi, oven temperature from 70 °C (2 min hold), then raised to 130 °C at the rate of 25 °C min⁻¹, afterwards raised to 220 °C at 2 °C min⁻¹, and then raised to 280 °C at 10 °C min⁻¹, and eventually 4.6 min hold. The sample (1 μL) was injected in splitless modes. The TOFMS was routinely set in selective ion monitoring (SIM) mode and each compound was quantified based on peak area using one target and one or two qualifier ion. The mass spectrometer parameters were set as follows: electron impact ionization mode with 70 eV electron energy, scan mass range 100–400 at 0.62 s/cycle, ion source temperature 230 °C, MS quad temperature 150 °C, EM voltage 1450 and solvent delay 4 min (Table 1).

2.9. Risk assessment

In the present research, based on pesticide residues found in crops health risk assessments were determined. The indices of pesticide residue health risk by dietary intake of crops were evaluated in accordance with the USEPA's (USEPA, 2005) regulations, where the estimated daily intake (EDI) was compared to the acceptable daily intake (ADI) (Sosan et al., 2015). Risk Assessment was done by calculating the health risk index (HRI) using Eq. (4):

$$HRI = \frac{EDI}{ADI} \quad (4)$$

This was achieved based on the residue levels of OCPs present in the crop samples. The estimated daily intake (EDI) was calculated and compared with the established acceptable daily intake (ADI, 2017). By

multiplying the residual pesticide concentration (ngg⁻¹) by the crop consumption rate (gday⁻¹) and dividing by body weight, the estimated daily intake (EDI) was found (Lamaire et al., 2004). For adults and children (age 2–5 years), calculations were conducted. The mean body weight of adults was considered to be 60 kg, while the mean body weight of children was considered to be 16.7 kg (CEFH, 2008). Values for EDI were obtained from the Eq. (5):

$$EDI = \frac{F \times Cr}{\text{mean body weight}} \quad (5)$$

where F = crop consumption data (165.9 g/day) (WHO, 2017), and Cr = concentration of OCPs in crop sample.

2.10. Statistical analysis of the data

The various data acquired was subjected to descriptive and inferential statistics. This was necessary in order to have a clearer picture of the parameters evaluated, and hence, interpret their effects in a more scientifically acceptable manner.

3. Results and discussion

3.1. Method validation

The accuracy and precision of the results were appraised by recovery studies (%R) ranging between 86.56 and 98.74 (Table 1). The samples were analyzed in triplicates to justify the accuracy of the results. Calculating the limits of detection (LOD = 0.45–3.51) and limits of quantification (LOQ = 3.94–10.69) of the instrument revealed that the analytical

Table 3a. Health risk assessment based on acceptable daily intake (ADI) of Pesticide Residues in Studied Crops for Children in Wet Season.

Wet season	Yam				Cocoyam			Sweet Potato			Cassava		
	Conc mg/kg	EDI (mg/kg/day)	ADI (mg/kg/day)	HRI	Conc mg/kg	EDI (mg/kg/day)	HRI	Conc mg/kg	EDI (mg/kg/day)	HRI	Conc mg/kg	EDI (mg/kg/day)	HRI
Aldrin	0.00033	0.00326	0.0001	32.584	0.00029	0.0029	29.206	0.00027	0.0027	26.723	0.00039	0.0039	38.942
Dieldrin	0.00038	0.00377	0.0005	7.545	0.00033	0.0032	6.477	0.00028	0.0028	5.504	0.00041	0.0041	8.226
p,p'-DDT	0.00029	0.00286	0.0020	1.431	0.00026	0.0025	1.267	0.00023	0.0022	1.123	0.00037	0.0036	1.818
p,p'-DDD	0.00032	0.00315	0.0020	1.575	0.00031	0.0031	1.545	0.00027	0.0027	1.356	0.00035	0.0035	1.734
p,p'-DDE	0.00045	0.00443	0.0020	2.215	0.00043	0.0042	2.111	0.00038	0.0038	1.897	0.00047	0.0047	2.330
Endosulfan I	0.00029	0.00288	0.0300	0.096	0.00029	0.0029	0.095	0.00023	0.0023	0.077	0.00034	0.0034	0.112
Chlordane	0.00033	0.00331	0.0005	6.612	0.00033	0.0032	6.457	0.00031	0.0031	6.139	0.00034	0.0034	6.755
Heptachlor	0.00046	0.00457	0.0005	9.139	0.00045	0.0045	8.921	0.00033	0.0033	6.616	0.00054	0.0054	10.808
Heptachlor epoxide	0.00053	0.00525	0.0005	10.490	0.00051	0.0051	10.133	0.00049	0.0049	9.775	0.00054	0.0054	10.748
Methoxychlor	0.00034	0.0034	0.1000	0.034	0.00026	0.0026	0.026	0.00025	0.0025	0.024	0.00036	0.0036	0.036

procedures were reliable, reproducible, and efficient, especially with R% values falling within the EC (2000) recommendation of 70–110 R% values as acceptable for efficient analytical procedures.

3.2. Levels of OCPs in crops collected from Esa-Oke Farm Settlement

The results of seasonal mean levels of the ten OCPs found in the 96 analyzed crop samples and their maximum acceptable limits are presented in Table 2. During the wet season, seasonal mean levels of OCPs had the following ranges: 288 ng/g p,p'-DDT to 528 ng/g heptachlor in yam, 255 ng/g p,p'-DDT to 510 ng/g heptachlor in cocoyam, 226 ng/g p,p'-DDT to 492 ng/g heptachlor in sweet potato and 338.47 ng/g endosulfan I to 541 ng/g heptachlor epoxide in cassava, while in dry season, the ranges were 269 ng/g chlordane to 432 ng/g heptachlor epoxide in yam, 230 ng/g p,p'-DDT to 415 ng/g heptachlor epoxide in cocoyam, 158 ng/g dieldrin to 330 ng/g heptachlor epoxide in sweet potato, 299 ng/g endosulfan I to 481 ng/g heptachlor epoxide in cassava.

Both the wet and dry seasonal mean values of the OCPs in crop samples gave similar overall patterns: sweet potato (304, 242) < cocoyam (344, 282) < yam (371, 316) < cassava (412, 357) respectively without significantly different values at $0 \leq 0.05$. From Table 2, most of the OCPs detected were above the recommended WHO MRLs values of between 20 and 300 (ng/g) in agricultural products (WHO, 2013). Differences in the plant families involved may be one of the factors responsible for the observed discrepancy, and thus their systemic capacity to store the pesticides probably varied. Other reasons that may account for the variations in pesticides found in the crop species are the quality of the soil, planting season, the quantity of pesticides used and the type of pesticide applied (Ahmed et al., 2006; NCEH, 2005).

A further comparison of the individual OCPs detected in crop samples (Table 2) revealed that during the wet season, heptachlor epoxide (518) > heptachlor (447) > p,p'-DDE (431) > dieldrin (349) > chlordane (327) > aldrin (321) > p,p'-DDD (313) > methoxychlor (303) > endosulfan I (287) > p,p'-DDT (284). This order was, however, not the same for the dry season, where the seasonal mean burden variations were heptachlor epoxide (415) > p,p'-DDE (373) > aldrin (305) > heptachlor (307) > methoxychlor (288) > chlordane (274) > p,p'-DDT (263) > p,p'-DDD (263) > endosulfan I (260) > dieldrin (246). The average concentrations of aldrin, DDT, dieldrin, endosulfan and endrin residues in beans in another study in Lagos, Nigeria, was 9.8, 35.1, 5.8, 22.5 and 7.8 ng/g, respectively (NCEH, 2005).

Based on this research and other research done in Nigeria on the levels of OCPs in foods, OCP concentrations were lower than those stated from other parts of the world. Moreover, the OCP levels observed in this research were higher than those recorded in Nigeria's previous studies (Aiyesanmi and Idowu, 2012; Ogunfowokan et al., 2012). The higher level might be a result of noncompliance with the usage directive or due to frequent use of organochlorine pesticides within the farmland. In

Nigeria, the list of widely used pesticides is mostly dominated by carbamates and organochlorines and just a handful of organophosphate pesticides (Han et al., 1998). The present study and others like it previously conducted showed that farmers are still using organochlorine pesticides at will (Chen et al., 2011).

Coefficient of variation (CV) values that were not less than 18.45 for cassava and were as high as 26.65 for sweet potato during wet season (Table 2) which were markedly different from one another. This indicated, more or less, a sudden rate of input of OCP into the crop samples either as a result of leaching from the site of contamination. In other words, the factors responsible for the presence of these OCP in crop samples might be sudden change in anthropogenic activities or weather elements. For dry season, the CV values range from 16.14 for yam to 21.07 for sweet potato. The discrepancies were signs of highly difference rate of addition of the pesticides investigated.

Generally, it was observed that the wet season total average burden values were relatively higher than the dry season mean values. This could be due to the fact that large amount of these pesticides was used during the wet season than the dry season, and hence, more pesticides were readily absorbed by crops.

Levels of p,p'-DDT in the crop samples were lower than that of its metabolites (p,p'-DDD, p,p'-DDE and p,p'-methoxychlor) suggesting that p,p'-DDT was one of the components of pesticides that had been used in the farm settlement over time (Osibanjo, 1994; Sosan et al., 2018). Also, higher levels of heptachlor epoxide than heptachlor suggested that most of the heptachlor had probably been transformed to heptachlor epoxide and this signified higher stability of the derivatives and confirmed the fact that heptachlor epoxide could be resistant to degradation in the environment than the parent compound. Heptachlor should have been phased-out of agrochemical stores among the insecticides that have been banned in Nigeria. However, it is alleged that it is either marketed under various names or labels or added to other pesticides currently in use by Nigerian farmers as one of the active ingredients (Sosan et al., 2020).

Farmers and consumers in developing countries are exposed to harmful chemicals that are prohibited or regulated in other nations, putting them at great risk (Ahmed et al., 2006), but are still being used in developing nations. Some pesticides found in crops, such as p,p'-DDE, chlordane, heptachlor epoxide, and endosulfan I, have been linked to endocrine and estrogenic disruption, which can have a significant impact on ecosystem biodiversity (Cremllyn, 1991; Yu et al., 2011) since they are tenacious and accumulate in the crops slowly and easily (Alloway and Ayres, 1997).

3.3. Daily intake and health risk assessment of the OCPs in crops

In order to provide advice on how to safeguard customers' health from pesticide exposure through food consumption, it is necessary to evaluate the hazards related with pesticide exposure through food consumption

Table 3b. Health risk assessment based on acceptable daily intake (ADI) of Pesticide Residues in Studied Crops for adult in Wet season.

Wet season	Yam				Cocoyam			Sweet Potato			Cassava		
	OCP	Conc mg/kg	EDI (mg/kg/day)	ADI (mg/kg/day)	HRI	Conc mg/kg	EDI (mg/kg/day)	HRI	Conc mg/kg	EDI (mg/kg/day)	HRI	Conc mg/kg	EDI (mg/kg/day)
Aldrin	0.000328	0.00091	0.0001	9.069	0.00029	0.0008	8.129	0.00027	0.00074	7.440	0.00039	0.0011	10.800
Dieldrin	0.000380	0.00105	0.0005	2.101	0.00033	0.0009	1.803	0.00028	0.00077	1.532	0.00041	0.0011	2.280
p,p'-DDT	0.000288	0.00080	0.002	0.398	0.00026	0.0007	0.353	0.00023	0.00063	0.313	0.00037	0.0010	0.505
p,p'-DDD	0.000317	0.00088	0.002	0.438	0.00031	0.0009	0.430	0.00027	0.00076	0.378	0.00035	0.0010	0.480
p,p'-DDE	0.000446	0.00123	0.002	0.617	0.00043	0.0012	0.588	0.00038	0.00106	0.528	0.00047	0.0013	0.650
Endosulfan I	0.000290	0.00080	0.03	0.027	0.00029	0.0008	0.027	0.00023	0.00064	0.021	0.00034	0.0009	0.031
Chlordane	0.000333	0.00092	0.0005	1.841	0.00033	0.0009	1.797	0.00031	0.00085	1.708	0.00034	0.0009	1.880
Heptachlor	0.000460	0.00127	0.0005	2.544	0.00045	0.0012	2.483	0.00033	0.00092	1.842	0.00054	0.0015	3.000
Heptachlor epoxide	0.000528	0.00146	0.0005	2.920	0.00051	0.0014	2.820	0.00049	0.00136	2.720	0.00054	0.0015	3.000
Methoxychlor	0.000342	0.00095	0.100-	0.009	0.00026	0.0007	0.007	0.00025	0.00069	0.007	0.00036	0.0010	0.010

Table 4a. Health risk assessment based on acceptable daily intake (ADI) of Pesticide Residues in Studied Crops for Children in Dry Season.

Dry season	Yam				Cocoyam			Sweet Potato			Cassava		
	OCP	Conc mg/kg	EDI (mg/kg/day)	ADI (mg/kg/day)	HRI	Conc mg/kg	EDI (mg/kg/day)	HRI	Conc mg/kg	EDI (mg/kg/day)	HRI	Conc mg/kg	EDI (mg/kg/day)
Aldrin	0.000316	0.003139	0.0001	31.392	0.0003	0.00301	30.100	0.00025	0.0025	25.034	0.00035	0.00349	34.869
Dieldrin	0.000276	0.002742	0.0005	5.484	0.00023	0.0023	4.609	0.00016	0.00157	3.139	0.00032	0.00315	6.298
p,p'-DDT	0.000288	0.002861	0.002	1.431	0.00023	0.00228	1.142	0.00023	0.00224	1.118	0.00031	0.00307	1.535
p,p'-DDD	0.000299	0.00297	0.002	1.485	0.00024	0.00234	1.172	0.00021	0.00211	1.053	0.0003	0.00302	1.510
p,p'-DDE	0.000378	0.003755	0.002	1.878	0.00033	0.00328	1.639	0.00032	0.00317	1.585	0.00047	0.00462	2.310
Endosulfan I	0.000281	0.002791	0.030	0.093	0.00024	0.00241	0.081	0.00022	0.00216	0.072	0.0003	0.00297	0.099
Chlordane	0.000269	0.002672	0.001	5.345	0.00025	0.0025	5.007	0.00025	0.00243	4.867	0.00033	0.00327	6.537
Heptachlor	0.000321	0.003189	0.001	6.378	0.00031	0.0031	6.199	0.00022	0.00214	4.272	0.00038	0.00377	7.550
Heptachlor epoxide	0.000432	0.004292	0.001	8.583	0.00042	0.00412	8.245	0.00033	0.00328	6.557	0.00048	0.00478	9.557
Methoxychlor	0.000299	0.00297	0.100	0.030	0.00026	0.00261	0.0261	0.00025	0.00247	0.025	0.00034	0.00337	0.034

Table 4b. Health risk assessment based on acceptable daily intake (ADI) of Pesticide Residues in Studied Crops for adult in Dry Season.

Dry season	Yam				Cocoyam			Sweet Potato			Cassava		
	OCP	Conc mg/kg	EDI (mg/kg/day)	ADI (mg/kg/day)	HRI	Conc mg/kg	EDI (mg/kg/day)	HRI	Conc mg/kg	EDI (mg/kg/day)	HRI	Conc mg/kg	EDI (mg/kg/day)
Aldrin	0.00032	0.00087	0.0001	8.737	0.00030	0.0008	8.378	0.00025	0.00070	6.970	0.00035	0.0010	9.700
Dieldrin	0.00028	0.00076	0.0005	1.526	0.00023	0.0006	1.283	0.00016	0.00044	0.874	0.00032	0.0009	1.760
p,p'-DDT	0.00029	0.00080	0.002	0.398	0.00023	0.0006	0.318	0.00023	0.00062	0.311	0.00031	0.0009	0.425
p,p'-DDD	0.0003	0.00083	0.002	0.413	0.00024	0.0007	0.326	0.00021	0.00059	0.293	0.00030	0.0008	0.420
p,p'-DDE	0.00038	0.00105	0.002	0.523	0.00033	0.0009	0.456	0.00032	0.00088	0.441	0.00047	0.0013	0.645
Endosulfan I	0.00028	0.00078	0.030	0.026	0.00024	0.0007	0.022	0.00022	0.00060	0.020	0.00030	0.0008	0.028
Chlordane	0.00027	0.00074	0.0005	1.488	0.00025	0.0007	1.394	0.00025	0.00068	1.354	0.00033	0.0009	1.820
Heptachlor	0.00032	0.00089	0.0005	1.775	0.00031	0.0009	1.725	0.00022	0.00059	1.188	0.00038	0.0011	2.100
Heptachlor epoxide	0.00043	0.00119	0.0005	2.389	0.00042	0.0011	2.295	0.00033	0.00091	1.824	0.00048	0.0013	2.660
Methoxychlor	0.0003	0.00083	0.1000	0.008	0.00026	0.0007	0.007	0.00025	0.00069	0.007	0.00034	0.0009	0.009

(Oyekunle et al., 2017). Since maximum residual limits are not toxicological limits, the amounts of OCP exposure obtained in this study were compared to the WHO's food standard program Joint Meeting on Pesticide Residue and the Australian Pesticide and Veterinary Medicines Authority's acceptable daily intake (ADI) (WHO, 2017; FAO/WHO, 2017) to estimate the human health risk from consumption of foodstuffs. Health risk index (HRI) was obtained by the ration of estimated daily intake (EDI) (mg/kg/day) and their corresponding values of acceptable daily intakes (ADI) for agricultural and veterinary chemicals (Shoiful et al., 2013).

ADI, EDI and HRI of pesticide residues for children and adults during wet and dry seasons are presented in Tables 3a, 3b, 4a and 4b. An index of >1 specifies that consumption is dangerous for human wellbeing

(Hossain et al., 2015). The health indices follow similar trend for both seasons. For children category in wet season, Table 3a shows the health risk estimations, aldrin (32.584), heptachlor epoxide (10.490), heptachlor (9.139), dieldrin (7.550), chlordane (6.616), p,p'-DDE (2.215), p,p'-DDD (1.575) and p,p'-DDT (1.431); aldrin (29.206), heptachlor epoxide (10.133), heptachlor (8.921), dieldrin (6.477), chlordane (6.455), p,p'-DDE (2.111), p,p'-DDD (1.545) and p,p'-DDT (1.267); aldrin (26.723), heptachlor epoxide (9.775), heptachlor (6.616), chlordane (6.139), dieldrin (5.504), p,p'-DDE (1.897), p,p'-DDD (1.356) and p,p'-DDT (1.123); aldrin (38.941), heptachlor (10.808), heptachlor epoxide (10.749), dieldrin (8.226), chlordane (6.755), p,p'-DDE (2.330), p,p'-DDT (1.818) and p,p'-DDD (1.734) had HI values > 1 in yam, cocoyam, sweet potato and cassava respectively and could pose

Table 5. Pearson correlation coefficient of OCP in crop samples.

	Aldrin	Dieldrin	p,p'-DDT	p,p'-DDD	p,p'-DDE	Endosulfan I	Chlordane	Heptachlor	HeptaEpoxide	Methoxychlor
Aldrin	1.000									
Dieldrin	0.668*	1.000								
p,p'-DDT	0.156	0.348	1.000							
p,p'-DDD	0.739*	-0.279	-0.440	1.000						
p,p'-DDE	0.468	0.587	0.411	-0.155	1.000					
Endosulfan I	0.373	0.001	-0.365	-0.158	0.488	1.000				
Chlordane	-0.683	-0.503	-0.612	0.843**	-0.504	-0.137	1.000			
Heptachlor	0.747*	0.778*	0.274	-0.454	0.826*	0.553	-0.671	1.000		
Hepta Epoxide	0.921**	0.773*	0.237	-0.580	0.756*	0.504	-0.699	0.933**	1.000	
Methoxychlor	-0.035	0.130	-0.278	0.404	0.072	0.083	0.444	0.094	0.043	1.000

** Correlation is significant at the 0.01 level (2-tailed).

* Correlation is significant at the 0.05 level (2-tailed).

carcinogenic health risk to children while for adult category, aldrin (9.069), heptachlor epoxide (2.920), heptachlor (2.544), dieldrin (2.101) and chlordane (1.841); aldrin (8.129), heptachlor epoxide (2.820), heptachlor (2.483), dieldrin (1.802) and chlordane (1.797); aldrin (7.440), heptachlor epoxide (2.720), heptachlor (1.842), chlordane (1.708) and dieldrin (1.532); aldrin (10.800), heptachlor epoxide and heptachlor (3.000), dieldrin (2.280) and chlordane (1.880) had HI values >1 in yam, cocoyam, sweet potato and cassava respectively (Table 3b) signifying that they could cause systemic health effect for adult consumers of the crops. Also, children's low body weight may contribute to their high risk index for crop consumption; as a result, rigorous monitoring of this residue in food crops ingested by children is required. During dry season, Table 4a shows the health risk estimations for children category, aldrin (31.392), heptachlor epoxide (8.583), heptachlor (6.378), chlordane (5.345), dieldrin (5.484), p,p'-DDE (1.878), p,p'-DDD (1.485) and p,p'-DDT (1.431); aldrin (30.100), heptachlor epoxide (8.245), heptachlor (6.199), chlordane (5.007), dieldrin (4.609), p,p'-DDE (1.639), p,p'-DDD (1.172) and p,p'-DDT (1.142); aldrin (25.034), heptachlor epoxide (6.557), chlordane (4.868), heptachlor (4.272), dieldrin (3.139), p,p'-DDE (1.585), p,p'-DDT (1.118) and p,p'-DDD (1.053); aldrin (34.869), heptachlor epoxide (9.557), heptachlor (7.550), chlordane (6.537), dieldrin (6.298), p,p'-DDE (2.310), p,p'-DDD (1.535) and p,p'-DDT (1.510) had HI values > 1 in yam, cocoyam, sweet potato and cassava respectively, while for adult category, aldrin (8.737), heptachlor epoxide (2.389), heptachlor (1.775), dieldrin (1.526) and chlordane (1.488); aldrin (8.378), heptachlor epoxide (2.295), heptachlor (1.725), chlordane (1.725) and dieldrin (1.283); aldrin (6.970), heptachlor epoxide (1.824), chlordane (1.354) and heptachlor (1.188); aldrin (9.700), heptachlor epoxide (2.660), heptachlor (2.100), chlordane (1.820) and dieldrin (1.760) in yam, cocoyam, sweet potato and cassava respectively (Table 4b) suggesting that both the children and adults might be at danger of consuming crops from the research area. However, for children category, health indices of endosulfan I and methoxychlor were <1 all food crops in both seasons while for adult, health indices of p,p'-DDT, p,p'-DDD, p,p'-DDE, endosulfan I and methoxychlor were <1 in yam, cocoyam, sweet potato and cassava respectively in both seasons.

Consumption of the tainted pesticide has the potential to cause cancer in children and adults who consume food crops grown in the research area, with risks exceeding one in a million people while aldrin, dieldrin, chlordane, p,p'-DDT, p,p'-DDD, p,p'-DDE, heptachlor and heptachlor epoxide could have a cancerous influence on the health of children who consume food crops. The HR > 1 indicates that OCP residues in crops constituted a long-term harm to human health, particularly cancer (Isioma and Lawrence, 2015). The Stockholm Convention identified aldrin, dieldrin, heptachlor, and heptachlor epoxide as hazardous chemicals in 2001, and endosulfan was added in 2011, indicating that all of the chemicals are harmful to human health and the environment and should not be used in crop production. Dieldrin, aldrin, heptachlor, and

heptachlor epoxide are similarly categorized as group 2B probably carcinogenic to humans by the International Agency for Research on Cancer (IARC) and the United States Environmental Protection Agency (USEPA) (IARC, 2001; ATSDR, 2002, 2007). Due to their lifetime exposure to OCP residues in food crops, persons (including children and adults) are at risk of acquiring cancer. Incidentally, cassava, cocoyam and yam are often part of the highly desired food crops of several people in Nigeria. Thus, applications of recalcitrant and highly toxic pesticides on farmlands where these crops are planted should be done with utmost caution (Ibigbami et al., 2017).

3.4. Statistical analysis

Table 5 showed Pearson correlation coefficient of the OCP in the crop samples where a total of 10 positive significant correlations out of 55 pairs of correlation at both 0.01 and 0.05 significant levels amounting to 18.18%. The OCP that showed positive correlations were either from the same source or similarities applied (in terms of concentration) or were similarly affected by similar environmental factors.

4. Conclusion

Seasonal levels of OCPs in some staple food items collected from Esa-Oke Farm Settlement, Osun State, Nigeria had been evaluated. The crop samples were found to be generally contaminated with aldrin, dieldrin, p,p'-DDD, p,p'-DDE, p,p'-DDT, endosulfan I, chlordane, heptachlor, heptachlor epoxide and o, p methoxychlor at levels generally higher than their corresponding FAO/WHO maximum permissible values. The HRIs in several cases were above 1, signifying that OCPs in crops produced from Esa-Oke farm settlement posed high risk over continuous and regular consumption. This survey has further strengthened the argument that OCPs are still in use in Nigeria especially for plants and pests control. It is therefore recommended that routine monitoring programs and risk assessment studies for xenobiotics, such as OCPs in crops from various farm settlements are needed to prevent, control and reduce the pollution of food crops from such settlements and minimize the associated health risks. Also, the of non-chemical insect pest control such as biocontrol (use of natural enemies) and the practice of organic farming (no synthetic pesticides and fertilizers) should be encouraged among farmers in the southwestern part of the country and in Nigeria at large.

Declarations

Author contribution statement

J.A. Oyinloye: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

J.A.O. Oyekunle, A.O. Ogunfowokan: Conceived and designed the experiments.

T. Msagati, A.S. Adekunle, S.S. Nety: Contributed reagents, materials, analysis tools or data.

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Data availability statement

Data will be made available on request.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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