International Journal of Research and Review
Volume 11; Issue: 2; February 2024
Website: www.ijrrjournal.com
Research Paper *E-ISSN: 2349-9788; P-ISSN: 2454-2237*

Distribution, Associated Risks and Sources of Organochlorine Pesticides in Farmland Soils from Ethiope West Area of Delta State, Nigeria

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DOI: https://doi.org/10.52403/ijrr.20240232

ABSTRACT

Organochlorine pesticides (OCPs) usage provides many advantages for agriculture; however, there are also significant concerns to the environment and public health. Since there is little information available on OCPs' distribution, associated risks and sources in Nigerian farmland soils, this study was carried out. Soil samples were collected from farmlands in ten communities. Samples were extracted with hexane/dichloromethane and cleaned up in a column of silica gel and florisil. The OCPs were measured using a gas chromatograph-mass spectrometry (GC-MS). The ∑20 OCPs levels in the soils varied between 47.5 and 109 ng/g. The OCPs homologues distribution in the soils was in the order of ∑DDTs > ∑Drins > ∑Chlordane > ∑BHCs > ∑Endosulfan. The risks assessment result indicated that there was adverse ecological effect on organisms residing in the soils and there is the likelihood that this effect will be frequently observed. Moreover, there was potential non-carcinogenic and carcinogenic risks for persons exposed to OCPs in these farmland soils. The result of the source identification indicated that historical usage was the main source of OCPs in these farmland soils.

Keywords: Soil, Farmland, OCPs, Non-carcinogenic, Carcinogenic, Ethiope West

INTRODUCTION

Organochlorine pesticides (OCPs) are a category of pesticides widely used in agriculture as insecticides, acaricides, and fumigants to manage pests. They are used to avert and remove fungus, weeds, insects, etc in agricultural and public health, as well as management of mosquitos, termites etc.[1-3] In Nigeria, about 125,000 to 130,000 mt of pesticides are applied each year. [4] Moreover, according to FAO [5] data on Nigeria, the amount of pesticides imported increased gradually from $13, 000,000 in 2001 to $28,000,000 in 2003.[6] In 2018, a total of 147, 446 tons of pesticides were brought into Nigeria for agricultural operations [7] while in 2019 and 2020, Nigeria purchased $306,000,000 and $321,000,000 value of pesticides respectively representing about 4.9 % increase in imports.[6] OCPs are a problem for the entire world due to their toxicity, persistence, propensity for bioaccumulation, effects on the environment and human well-being through the food-chain.[8] Many diseases including pancreatic, breast, uterine, liver cancers have been associated to them despite the fact that their harmful health consequences are not completely understood.[9]

Soils are typically the final destination for environmental OCPs. Soils exhibit pollution contribution from various sources. Soil OCPs can be transmitted to air, surface and groundwater through volatilization, leaching and runoff; they can also bioaccumulate in the food-chain, causing negative effects to man and other living organisms.[10] Many variables, including the application method, soil characteristics, application frequency etc influence the destiny of OCPs in soils.[11, 12] Because of their potential to remain in the environment, bioaccumulate, and create hazardous consequences, they were banned in many nations between the 1970s and 1990s. In Nigeria, the use of OCPs was prohibited in 2008 by NAFDAC in 2008. Notwithstanding their prohibition, OCPs are among the most common environmental contaminants, and can be found in a variety of abiotic and environmental media as well as biotic media. Soil is also considered to be a secondary emission source of OCPs after long-term use of OCPs in agriculture. Past OCPs usage may impact OCPs residues in the soil. Ethiope west is a vast agricultural region, located in western Delta State. Thus, the application of OCPs on crops in this area may be significant and possibly affect different environmental media especially the soil. Furthermore, human well-being could possibly be affected through uptake by crops and consequent build-up through the food-web. [6] There is scarcity of data on OCPs in farmland soils in Nigeria in general and Delta State in particular. Thus, the present study aimed at assessing the distribution, risks and sources of OCPs in farmland soils from Ethiope West Area of Delta State, Nigeria. This information is important for creating efficient pollution reduction plans and OCP prediction models.

MATERIALS & METHODS

Description of study area

Ethiope West is a Local Government Area in Delta State, Nigeria. Its headquarters is located in Oghara Town. Ethiope West lies between latitude 5°55'and 5°56'N and longitude 5° 32' and 5° 42'E. It has an area of 536 km² and a population of 203,592 during the 2006 census. The map of the study area showing the sampling towns is shown in Figure 1. The towns include Jesse, Irhodo, Ovade, Mosogar, Idjedaka, Otefe, Ogharefe, Otumara, Ugbenu and Oghareki. The major occupation in the study area is farming using agrochemicals and trading. Yam, cassava and vegetables are some of the major crops farmers cultivates in the area. The area experiences a mean precipitation of 2,700 to 3,000 mm yearly.

Sample Collection

Surface soils from farmlands were collected from ten locations in the study area. Within each location, soils were collected from three farmlands and combined to form a homogenous sample. Soils were collected using a soil auger. The samples were rightly labelled, moved to the laboratory, then dried, sieved to remove pebbles and preserved at -4 °C for analysis.

Chemical Analysis

The protocol for the OCPs extraction from the soils was adapted from the previously published one. [13, 14] Ten gram of soils was extracted ultrasonically with 20 mL of hexane and dichloromethane (DCM) (1:1; v/v) for 30 minutes. The extraction was repeated thrice and the extracts combined. The extract was concentrated and cleaned up in a column of silica gel and Florisil and eluted with 50 mL DCM/hexane (1:4 v/v). Thereafter, the extract was exchanged into 1 mL hexane and transmitted into a container for chemical analysis. A gas chromatograph (Agilent 6890N) combined with a mass spectrometer (Agilent 5975B) and fitted with a column (30m × 320µm × 0.25µm) was used to measure the OCPs in the extracts. The detection and injection temperatures of the instrument were held at 300 °C and 280 °C respectively. The initial oven temperature was kept at 100 °C for 2 minutes before being increased to 180 °C at 15 °C/minute, ramped up to 300 °C at 3 °C/minute, and held for 5 minutes. The mobile gas was 99.9 % pure helium with a stable flowing rate of 0.5

mL/minute. The splitless mode of the GC-MS received a 1L injection of the sample. The mass spectrometer used automatic gain control in conjunction with electron impact ionization (EI) as its mode of operation.

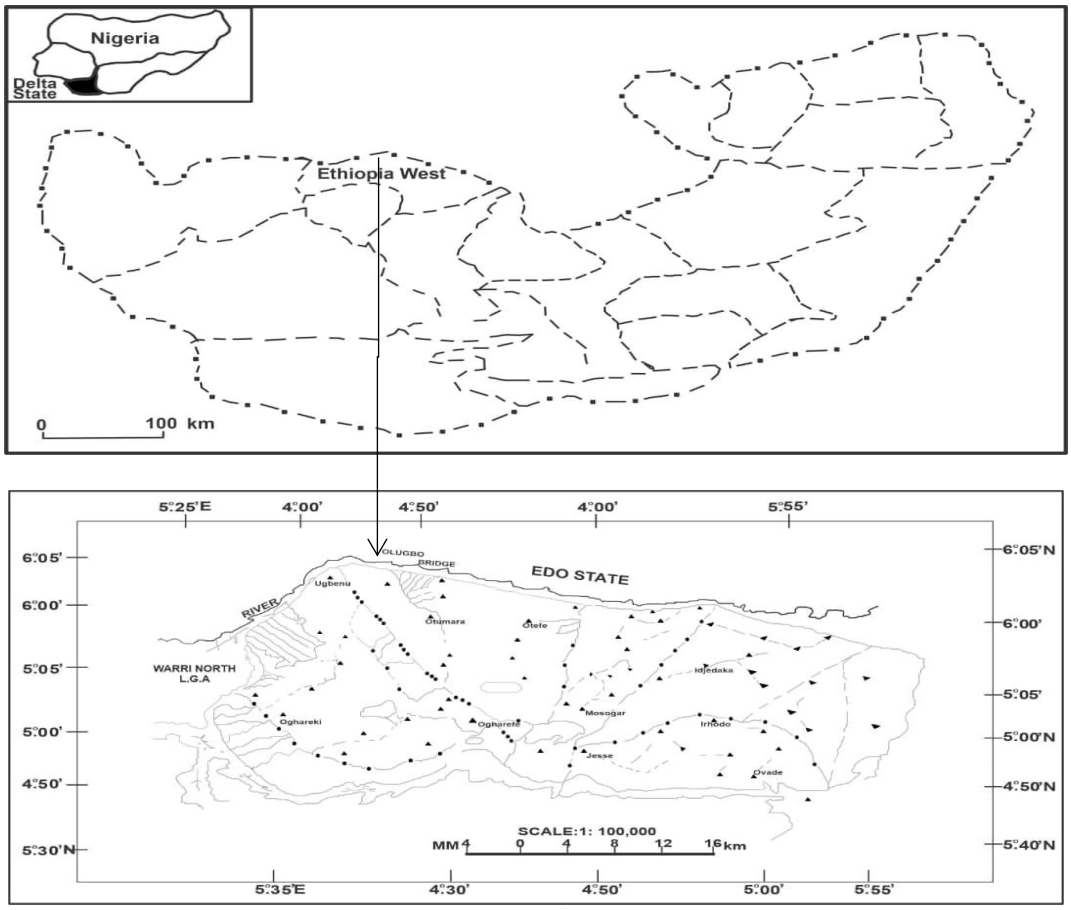

Figure 1: Map of study area

Quality Control and Assurance

Computation of percentage recovery from analysis of matrix spiked samples and blank determinations were employed for quality assurance. Standard solutions of OCP compounds were added to selected fresh portions of soils that were initially analyzed and following all the analytical procedure and the percentage recovery was computed. The percentage of OCPs recovered from the spiked soils varied between 94.8 to 97.9 %. OCPs were not found in the blanks. The levels of OCPs in the soils were measured using external calibration technique. The R^2 of the calibrations obtained varied from 0.9993 to 0.9998.

STATISTICAL ANALYSIS

One-way ANOVA was employed to find out if there was significant discrepancy in the levels of OCPs in the soils. Pearson's correlation and regression plot were employed to evaluate the link between one OCP compound and the other; and between OCPs and soil physicochemical characteristics. Ratio of parent OCP compounds and their metabolites were used to ascertain the OCPs sources. The statistical analyses were done using IBM-SPSS Software 25.

Human Risks Assessment (HRA) of OCPs in the soils

The evaluation of non-carcinogenic and carcinogenic risks arising from OCPs exposure in the soils were carried out with the use of the hazard index (HI) and total cancer risk (TCR) models respectively via the three routes of exposure: ingestion,

inhalation and dermal contact (IID) using equations 1 – 9.[15, 16]

Hazard index (HI) = $\sum HQ = HQ_{Ing}$ + HQ_{Inh} + HQ_{Dermal} (1)

$HQ = \frac{CDInc}{RfD}$ (2)

$CDI_{ing\text{-}nc} = \frac{C \times IngR \times EF \times ED}{BW \times AT_{nc}} \times 10^{-6}$ (3)

$Risk_{inh} = \frac{C \times Inh \times EF \times ED}{PEF \times 24 \times ATca}$ (4)

$CDI_{dermal\text{-}nc} = \frac{C \times SA \times AF \times ABS \times EF \times ED}{BW \times AT_{nc}} \times 10^{-6}$ (5)

Total cancer risk = $Risk_{Ing}$ + $Risk_{Inh}$ + $Risk_{Dermal}$ (6)

$Risk_{ing} = \frac{C \times IngR \times EF \times ED \times CF \times SFO}{BW \times ATca}$ (7)

$Risk_{inh} = \frac{C \times Inh \times EF \times ED \times IUR}{PEF \times 24 \times ATca}$ (8)

$Risk_{derm} = \frac{C \times SA \times AF \times ABS \times EF \times ED \times CF \times SFO \times GIABS}{BW \times ATca}$ (9)

Where CDI_{ing} and CDI_{Derm} are chronic daily intake for ingestion and dermal contact respectively; $Risk_{ing}$, $Risk_{inh}$ and $Risk_{Derm}$ are risk for IID respectively. The definition of terms and values of all variables are given [10] and [17]. Usually, HI value greater than 1 and TCR value greater than 1 x 10^{-6} indicates the presence of adverse non-cancer and cancer risks respectively.[18]

RESULT AND DISCUSSION

Soils Characteristics

The results of the physicochemical properties are shown in Table 1. The pH, EC and TOC of the soils ranged from 5.19 to 6.38, 19.2 to 20.7 µS/cm and 0.57 to 1.20 % respectively. The values of the soil characteristics of the soils were not significantly different from those earlier documented for soils in the southern part of Nigeria. [19-22]

Table 1: Summary statistics of OCPs concentrations (ng g^{-1}) in the farmland soils

	%DF	MEAN	SD	MEDIAN	MIN	MAX	CV %
pH	100	5.87	0.39	5.91	5.19	6.38	6.57
Electrical conductivity (µS/cm)	100	19.9	0.48	19.8	19.2	20.7	2.40
TOC (%)	100	0.85	0.19	0.82	0.57	1.20	22.6
α-BHC	60	3.23	0.62	2.94	2.69	4.11	19.2
β-BHC	80	4.46	2.28	4.00	1.87	7.94	51.0
γ-BHC	30	4.09	1.21	4.41	2.76	5.11	29.5
δ-BHC	100	4.75	2.73	3.98	1.11	9.01	57.4
∑BHC	**100**	**11.5**	**5.85**	**10.3**	**4.24**	**24.1**	**50.9**
P,p'-DDE	90	5.98	2.92	4.79	3.11	10.6	48.8
P,p'-DDD	80	3.43	0.93	3.38	1.77	4.71	27.1
P,p'-DDT	100	5.23	2.42	5.03	1.95	10.8	46.2
Methoxychlor	70	5.50	3.69	3.81	2.79	13.0	67.1
∑DDT	**100**	**17.2**	**8.01**	**15.2**	**8.63**	**33.6**	**46.6**
α-Chlordane	100	6.03	2.47	6.53	1.61	9.30	40.9
γ-Chlordane	90	3.37	1.25	3.07	1.94	5.03	36.9
Heptachlor	0	ND	ND	ND	ND	ND	ND
Heptachlor Epoxide	90	5.64	1.88	5.73	2.10	8.44	33.4
∑Chlordane	**100**	**14.2**	**3.21**	**12.8**	**9.40**	**19.7**	**22.7**
Endosulfan I	90	4.56	2.93	3.79	1.45	9.94	64.1
Endosulfan II	90	4.94	2.51	4.08	1.96	9.85	50.7
Endosulfan sulfate	90	2.56	2.69	1.87	0.61	9.50	105
∑Endosulfan	**100**	**10.9**	**4.36**	**8.94**	**6.36**	**18.6**	**40.2**
Aldrin	100	4.27	2.18	4.12	1.54	7.72	51.0
Dieldrin	100	1.34	1.05	1.02	0.39	3.34	78.8
Endrin	100	5.04	2.93	4.87	1.36	9.42	58.1
Endrin aldehyde	90	4.20	1.73	5.18	1.78	6.48	41.2
Endrin ketone	0	ND	ND	ND	ND	ND	ND
∑DRINS	**100**	**14.4**	**6.14**	**13.05**	**5.81**	**27.0**	**42.6**
∑20 OCPs	**100**	**68.1**	**18.9**	**62.1**	**47.5**	**109**	**27.7**

DF = Detection frequency

OCPs levels in the soils

The levels of OCPs in the soils are shown in Tables 1. The ∑20 OCPs levels varied between 47.5 and 109 ng/g in the soils. The maximum concentration was found in Ugbenu while the minimum concentration

was found in Jesse. The concentrations of ∑20 OCPs was in the following order: Ugbenu > Oghareki > Otefe > Idjedaka > Mosogar > Otumara > Ovade > Ogharefe > Irhodo > Jesse. ANOVA revealed the presence of significant ($p < 0.05$) discrepancy in the levels of OCPs from these locations. This could have been arised from degradation, multiple sources, soil characteristics among others (Tesi *et al*., 2020a; Emoyan *et al*., 2021). Based on the Chinese environmental quality standards for soils classification, the agricultural soils from Ethiope west area have insignificant OCP pollution i.e. HCHs and DDTs ≤ 50 ng/g.[1, 23] Although, the number of samples studied, number of OCP compounds determined and the method used varies, the results of this study were compared with others in literature. The concentrations of ∑20 OCPs recorded in the present study were higher than the range of 4.04 -10.1 ng/g documented for wetland soils from Central China [24], 13.7-49.1 ng/g in agricultural soils from Cameron highlands, Malaysia [25] and 0.81-16.9 ng/g in agricultural soils along Chao River, China. [26] They were however, comparable to the range of nd-100 ng/g [1], <0.01 – 104 ng/g [27], 3.59-160 ng/g [27], 30.2-159 ng/g.[28] However, higher levels of OCPs have been reported in agricultural soils from Nigeria.[10, 29-31]

OCPs homologues distribution in the soils

The OCPs homologues distribution in the soils was in the order of: ∑DDTs > ∑Drins > ∑Chlordane > ∑BHCs > ∑Endosulfan (Figure 2).

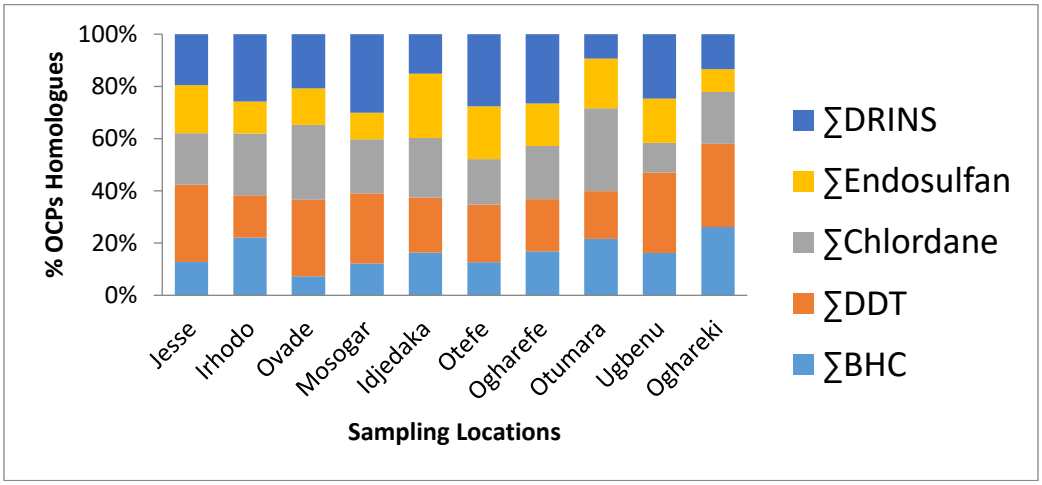

Figure 2: OCPs homologues distribution pattern in the farmland soils

DDTs

The ∑DDTs (p,p'-DDE + p,p'-DDD + p,p'-DDT + Methoxychlor) levels varied between 8.63 ng/g at Irhodo and 33.6 ng/g at Ugbenu. The ∑BHCs accounted for 16.2 to 31.9 % of the total OCPs. The DDTs congeners followed the trend: p,p'-DDE > Methoxychlor > p,p'-DDT > p,p'-DDD. The average ∑DDTs level recorded in these soils was higher than the average ∑DDTs documented by [24, 32, 33] but were in agreement with the range reported by [1, 10]. However, higher ∑DDTs levels has been documented in literature. [31, 34-31]

Drins

The ∑Drins (aldrin + dieldrin + endrin + endrin aldehyde + endrin ketone) levels varied between 5.81 ng/g at Otumara and 27.0 ng/g at Ugbenu and accounted for 9.4 to 30.1 % of the total OCPs. The levels of the individual Drin congeners were in the order of: endrin > aldrin > endrin aldehyde > dieldrin. Endrin ketone was not detected in this study. The ∑Drins obtained in this study was comparable to the range of nd-72.4 ng/g reported by [40] but higher than the range of 0.58 -3.52 ng/g reported by [41].

Chlordanes

The ∑Chlordane (α-chlordane + γ-chlordane + heptachlor + heptachlor epoxide) levels in

the soils varied between 9.40 ng/g at Jesse and 19.7 ng/g at Otumara and accounted for 11.4 to 31.8 % of the total OCPs. The distribution of the chlordanes in the soils followed the order: α-chlordane > heptachlor epoxide > γ-chlordane. Heptachlor was not detected in this study. The ∑chlordanes in the agricultural soils from Ethiope west region were higher than those from Campania Plain, Italy (nd-9.02 ng/g; [40], Rio Negro Basin, Argentina (0.4-0.7 ng/g; [35] and Mexicall Valley, Mexico (0.055-8.2 ng/g; [33]).

BHCs

The ∑BHCs (α- + β- + γ- + δ- BHCs) levels in the soils varied between 4.24 ng/g at Ovade and 24.1 ng/g at Oghareki. The ∑BHCs accounted for 7.3 to 26.3 % of the total OCPs. With respect to concentrations and detection frequency, the BHCs were in the following order: δ-BHC > β-BHC > γ-BHC > α-BHC. The ∑BHCs obtained in here were above the range of OCPs documented for agricultural soils in Argentina [35], Tanzania [32], Iran [42] and Mexico [33] but lower than thoses reported for Nigeria [10, 31], India [43] and Spain [44]. Nevertheless, the levels of ∑BHCs in this study were comparable to others reported in China [1, 8, 34, 45], Romania [39] and Vietnam. [46]

Endosulfans

The ∑Endosulfan (endosulfan I + endosulfan II + endosulfan sulfate) levels in the soils varied between 6.30 at Mosogar and 18.6 ng/g at Ugbenu. The ∑endosulfan accounted for 8.7 to 24.7 % of the total OCPs in the soils. The distribution pattern of the endosulfan compounds was as followed: endosulfan II > endosulfan I > endosulfan sulfate. The ∑endosulfan obtained in our study were comparable to the nd-19.4 ng/g and 0.3-35.2 ng/g reported by [40] and [35] respectively.

Relationship between soil characteristics and OCPs

Because of their hydrophobicity, OCPs can be absorbed by TOC, which is a crucial factor governing their fate in soils. [8, 10]. A rise in soil TOC content gives additional carbon for microorganisms to degrade OCPs. [10] In this current work, significant association was not identified between TOC and Σ20 OCPs (Figure 3) which could be attributed to imbalance in agricultural operations, unending input and multiple sources of OCPs. [10, 47, 48]. Likewise, there was no association between the various OCP compounds and the soil's characteristics (Table 2). This shows that the various OCPs were not significantly absorbed by TOC or affected by other soil characteristics. [10]. Nonetheless, at the 0.01 and 0.05 confidence intervals, a positive association was identified between the OCPs. The positive associations between OCPs pairs imply that they have comparable distribution patterns and the same origin which could be their use in agricultural activities in these locations.

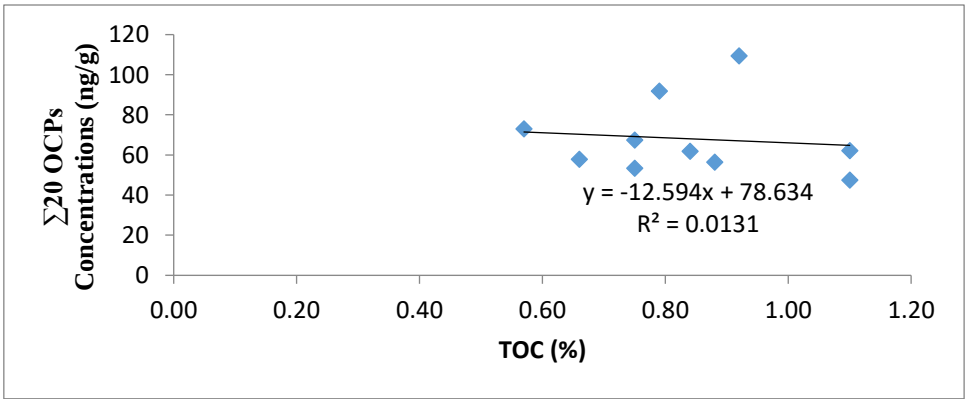

Figure 3: Plot of ∑20 OCPs concentrations with TOC in the soils

Table 2: Pearson correlation coefficient of physicochemical properties and OCPs in the soils

	pH	TOC	EC	α-BHC	β-BHC	γ-BHC	δ-BHC	DDE	DDD	DDT	MC	α-C	γ-C	HCE	Ed1	Ed2	EdS	Ald	Die	End	EndA
pH	1.00																				
TOC	-0.25	1.00																			
EC	-0.46	-0.01	1.00																		
α-BHC	-0.04	-0.14	0.29	1.00																	
β-BHC	-0.59	0.03	0.09	0.27	1.00																
γ-BHC	-0.18	0.18	-0.42	-0.37	0.16	1.00															
δ-BHC	-0.60	0.08	-0.12	-0.27	0.44*	0.53*	1.00														
DDE	-0.47	0.13	-0.21	-0.51	0.44*	0.79**	0.64*	1.00													
DDD	-0.30	0.60*	-0.23	0.03	0.10	0.40*	0.16	0.40*	1.00												
DDT	-0.68	0.67*	0.19	-0.09	0.43*	0.59*	0.45*	0.56*	0.46	1.00											
MC	-0.16	0.13	0.29	-0.27	0.41*	0.08	0.38	0.37	-0.23	0.24	1.00										
α-C	0.00	-0.40	-0.50	-0.17	0.27	0.20	0.08	0.21	-0.28	-0.09	-0.34	1.00									
γ-C	-0.35	0.44*	-0.49	-0.36	0.44*	0.42*	0.56*	0.68*	0.66*	0.37	0.20	0.11	1.00								
HCE	0.04	0.32	0.28	0.73**	0.33	-0.34	-0.47	-0.40	0.21	0.12	0.03	-0.35	-0.14	1.00							
Ed1	0.25	-0.31	-0.34	-0.12	-0.27	0.36	-0.06	0.33	0.10	-0.12	-0.26	0.24	0.02	-0.39	1.00						
Ed2	-0.02	-0.47	0.02	-0.05	0.19	-0.24	-0.02	0.00	-0.04	-0.47	0.01	0.11	0.12	-0.04	-0.36	1.00					
EdS	-0.25	0.28	-0.04	-0.37	0.41*	0.42*	0.54*	0.64*	0.36	0.32	0.73**	-0.34	0.63*	-0.03	-0.25	0.31	1.00				
Ald	0.06	0.17	0.05	-0.44	0.21	0.49*	0.08	0.45*	-0.10	0.40*	0.62*	-0.05	0.05	0.03	-0.19	0.02	0.58*	1.00			
Die	-0.51	0.35	-0.09	-0.50	0.29	0.81**	0.79**	0.85**	0.43*	0.69*	0.44*	-0.12	0.59*	-0.38	0.02	-0.09	0.74**	0.49*	1.00		
End	-0.02	-0.33	0.16	-0.53	-0.21	0.34	0.46*	0.30	-0.41	-0.01	0.44*	-0.11	-0.20	-0.66	0.02	0.11	0.35	0.44*	0.50*	1.00	
EndA	0.49*	0.04	-0.16	-0.32	-0.15	0.02	0.03	0.11	-0.22	-0.21	0.70**	-0.35	0.09	-0.09	0.20	-0.20	0.43*	0.36	0.11	0.32	1.00

EC = Electrical conductivity, TOC = Total Organic Carbon, DDE = p, p'- DDE, DDD = p, p'- DDD, DDT = p, p'- DDT, MC= Methoxychlor, α-C= α-Chlordane, γ-C = γ-Chlordane, HCE = Heptachlor epoxide, Ed1 = Endosulfan I, Ed2 = Endosulfan II, EdS = Endosulfan sulfate, Ald = Aldrin, Die = Dieldrin, End = Endrin, EndA = Endrin Aldehyde

** Pearson's correlation significant at 0.01 level of significance

* Pearson's correlation significant at 0.05 level of significance

Table 3: Hazard index and total cancer risk of OCPs in the farmland soils

	Hazard Index								Total Cancer Risk							
	CHILD				ADULT				CHILD				ADULT			
	HQING	HQINH	HQDERM	HI	HQING	HQINH	HQDERM	HI	RISKING	RISKINH	RISKDERM	Total Cancer Risk	RISKING	RISKINH	RISKDERM	Total Cancer Risk
Jesse	7.20	3.70E-05	1.97	9.17	7.39E-05	4.63E-05	0.35	0.35	1.70E-03	2.69E-10	7.04E-04	2.41E-03	1.17E-04	5.38E-10	4.61E-05	1.64E-04
Irhodo	8.31	6.03E-05	2.29	10.6	1.21E-04	2.22E-05	0.41	0.41	2.03E-03	3.20E-10	8.06E-04	2.83E-03	1.40E-04	6.41E-10	5.51E-05	1.95E-04
Ovade	8.34	1.08E-04	2.26	10.6	2.16E-04	4.03E-06	0.40	0.40	2.02E-03	3.20E-10	6.37E-04	2.66E-03	1.39E-04	6.40E-10	5.43E-05	1.94E-04
Mosogar	11.2	5.33E-05	3.08	14.3	1.07E-04	5.44E-05	0.55	0.55	2.92E-03	4.63E-10	8.35E-04	3.76E-03	2.02E-04	9.26E-10	7.95E-05	2.81E-04
Idjedaka	5.87	1.07E-04	1.59	7.46	2.15E-04	2.62E-05	0.28	0.28	1.48E-03	2.34E-10	5.98E-04	2.08E-03	1.02E-04	4.69E-10	3.98E-05	1.42E-04
Otefe	6.25	1.07E-04	1.64	7.89	2.14E-04	4.03E-05	0.29	0.29	2.32E-03	3.67E-10	3.69E-04	2.68E-03	1.60E-04	7.34E-10	6.13E-05	2.21E-04
Ogharefe	2.27	1.16E-04	0.57	2.84	2.33E-04	4.63E-05	0.10	0.10	1.15E-03	1.83E-10	1.41E-04	1.29E-03	7.94E-05	3.65E-10	3.05E-05	1.10E-04
Otumara	10.6	1.13E-04	2.90	13.5	2.27E-04	2.01E-06	0.52	0.52	2.57E-03	4.07E-10	9.77E-04	3.55E-03	1.77E-04	8.14E-10	6.95E-05	2.47E-04
Ugbenu	9.19	8.30E-05	2.48	11.7	1.66E-04	1.21E-05	0.44	0.44	3.35E-03	5.32E-10	7.04E-04	4.06E-03	2.31E-04	1.06E-09	9.04E-05	3.21E-04
Oghareki	8.9	1.28E-04	2.35	11.2	2.56E-04	3.91E-04	0.42	0.42	2.96E-03	4.69E-10	8.78E-04	3.84E-03	2.04E-04	9.38E-10	7.86E-05	2.83E-04

Table 4: Ratios of parent OCPs and their metabolites and their interpretations in relations to the sources of OCPs in the farmland

Isomeric ratios	Values	Sources	Agricultural soils
α-HCH/γ-HCH	> 3	Inputs from technical HCH and long-range transportation	-
	< 3	Fresh/Recent input of lindane	Oghareki
γ-HCH/∑HCH	> 1	Historical/aged input	-
	< 1	Inputs from technical HCH and long-range transportation	Otefe, Ugbenu, Oghareki
β-HCH/γ-HCH	> 1	Historical/aged input	Ugbenu, Oghareki
	< 1	Fresh/Recent input	-
p, p'- DDD/ p, p'- DDE	> 1	DDD is the dominant degradation product of DDTs	Jesse
	< 1	DDE is the dominant degradation product of DDTs	Ovade, Idjedaka, Otefe, Otumara, Ugbenu, Oghareki
(p, p'- DDD+ p, p'- DDE)/ p, p'- DDT	> 1	Historical/aged input	Jesse, Idjedaka, Otefe, Otumara, Ugbenu, Oghareki
	< 1	Fresh/Recent input	-
(p, p'- DDD+ p, p'- DDE)/∑DDT	> 0.5	Long term weathering of historical/aged DDTs	Ovade, Idjedaka, Ugbenu, Oghareki
	< 0.5	Fresh/Recent input	-
p, p'- DDT/∑DDT	> 0.5	Fresh/Recent input	Ugbenu, Oghareki
	< 0.5	Historical/aged input	All locations except Ugbenu and Oghareki
α-Chlordane/β-Chlordane	> 1	Historical/aged input	All locations except Jesse and Ugbenu
	< 1	Fresh/Recent input	Jesse and Ugbenu
Endosulfan I/Endosulfan II	< 2.33	Historical/aged input	All except Otumara and Oghareki
	> 2.33	Fresh/Recent input	-
Endrin/Dieldrin	> 1	Degradation process	All locations
	< 1	Fresh input of dieldrin	-
Dieldrin/Aldrin	> 1	Fresh input of dieldrin	-
	< 1	Degradation process	All locations

HHRA of OCPs in the soils

The results of HHRA of the OCPs in the soils for child and adult exposure are shown in Table 3. The HQs were in the following order: $HQ_{Ing} > HQ_{Derm} > HQ_{Inh}$ for both child and adult. The HQ_{Ing} and HQ_{Derm} values for child were greater than for adult while the HQ_{Inh} values for adult were greater than for child. These observations were due to pica attitude and smaller body weight of a child; and the longer exposure duration for adult. [10, 17] The HI values ranged from 2.84 to 14.3 for child and 0.10 to 0.55 for adult. The average HI value for child was more than for adult 27 times. This suggests that children were more vulnerable to risks from OCPs in the soils. The HI values for child were above 1 and indicate the existence of non-cancer risk for a child exposed to OCPs in the soils. Whereas the HI values for adult were < 1 and indicate the non-existence of non-cancer risk for an adult exposed to OCPs in the soils.

The risk levels of OCPs followed the same order as the HQs. The TCR values varied from 1.29×10^{-3} to 4.06×10^{-3} for child and 1.10×10^{-4} to 3.21×10^{-4} for adult. The average TCR for child was about fourteen times higher than that of adult. This too indicates that children are at a greater risk from the OCPs than adults. The TCR values were above 1×10^{-6} and designate the presence of carcinogenic risk to both child and adult from OCPs in the soils.

OCPs source apportionment

The ratios of parent OCPs and their metabolites have been utilized to classified the sources of OCPs into fresh or historical usage [34, 45, 49, 50]. The ratios used and their interpretations in relation to the sources of OCPs in the present study are shown in Tables 4. Table 4 clearly indicated that the main source of OCPs was historical usage.

CONCLUSION

This study showed that the farmland soils from Ethiope west area of Delta State, Nigeria have insignificant OCP pollution. The OCPs homologues distribution in the soils was in the order of ∑DDTs > ∑Drins > ∑Chlordane > ∑BHCs > ∑Endosulfan. There was no association between the various OCP compounds and the soil's characteristics. The ecological risk assessment result indicated that there was adverse ecological effect on organisms residing in the soils and there is the likelihood that this effect will be frequently observed. The HI and TCR values indicated that there are potential non-cancer and cancer risks from OCPs exposure in the soils. The source apportionment suggested that the OCPs in the soils were from past usage.

Declaration by Authors

Acknowledgement: The authors are grateful to TETFUND, Nigeria for funding this study (Project Reference Number: TETF/CE/DR&D/COE/MOSOGAR/IBR/2022). The authors are also grateful to Mrs Helen Sanubi for her assistance during sampling and analysis.

Source of Funding: TETFUND, Nigeria.

Conflict of Interest: The authors declare no conflict of interest.

REFERENCES

1. Gereslassie T, Workineh A, Atieno OJ, et al. Determination of occurrences, distribution, health impacts of organochlorine pesticides in soils of Central China. International Journal of Environmental Research and Public Health. 2019; 16: 146
2. Sakan S, Ostojić B, Đorđević D. Persistent organic pollutants (POPs) in sediments from river and artificial lakes in Serbia. Journal of Geochemical Exploration. 2017; 180: 91–100
3. Jayaraj R, Megha P, Sreedev P. Organochlorine pesticides, their toxic effects on living organisms and their fate in the environment. Interdisciplinary Toxicology. 2016; 9: 90–100
4. Asogwa EU, Dongo LN. Problems associated with pesticides usage and applications in Nigeria cocoa production: A review. African Journal of Agricultural Research. 2009; 4: 675–683.
5. FAO. AOSTAT Statistical Database. Food and Agricultural Organization, Rome. 2005.

6. Tesi GO, Obi-Iyeke GE, Ossai JC, et al. Human exposure to organochlorine pesticides in vegetables from major cities in south-south Nigeria. Chemosphere. 2022; 303(Part 3): 135296
7. FAOSTAT. Statistics of production crops and pesticide trade for all area of the world. 2020; Available at: http://www.fao.org/0e3121c5-b1bf-4689-9efb-c431428f61a8. (Accessed 15 May 2022).
8. Yang D, Qi SH, Zhang J, et al. Residues of organochlorine pesticides (OCPs) in agricultural soils of Zhangzhou City, China. Pedosphere. 2012; 22: 178–79.
9. Botella B, Crespo J, Rivas A, et al. Exposure of women to organochlorine pesticides in Southern Spain. Environmental Research. 2004; 96(1): 34-40.
10. Tesi JN, Tesi GO, Ossai JC et al. Organochlorine pesticides (OCPs) in agricultural soils of southern Nigeria: Spatial distribution, source identification, ecotoxicological and human health risks assessment. Environmental Forensic. 2020; https://doi.org/10.1080/15275922.2020.1850570
11. Lupi L, Bedmar F, Wunderlin DA, et al. Organochlorine pesticides in agricultural soils and associated biota. Environmental Earth Sciences. 2016; 75: 519
12. Pose-Juan E, Sánchez-Martín MJ, Andrades MS, et al. Pesticide residues in vineyard soils from Spain: Spatial and temporal distributions. Science of the Total Environment. 2015; 514: 351–358
13. Yao S, Huang J, Zhou H, et al. Levels, distribution and health risk assessment of organochlorine pesticides in agricultural soils from the Pearl River Delta of China. International Journal Environmental Research & Public Health. 2022; 19: 13171.
14. Sun JT, Pan LL, Zhan Y, et al. Contamination of phthalate esters, organochlorine pesticides and polybrominated diphenyl ethers in agricultural soils from the Yangtze River Delta of China. Science of the Total Environment. 2016; 544: 670–676
15. USEPA. Risk assessment guidance for Superfund, Vol. I: Human health evaluation manual. Office of Solid Waste and Emergency Response EPA/540/1-89/002. 1989
16. USEPA. Risk assessment guidance for superfund. Volume 1: Human Health Evaluation Manual (F, supplemental guidance for Inhalation Risk Assessment) EPA/540/R/070/002, Office of Superfund Remediation and Technology Innovation, Washington, DC. 2009
17. Emoyan OO, Peretiemo-Clarke BO, Tesi GO et al. Occurrence, origin, ecological and human health risks of organochlorine pesticides in soils from selected urban, suburban and rural storm water reservoirs. Soil and Sediment Contamination: An International Journal. 2021; https://doi.org/10.1080/15320383.2021.1913993
18. USEPA. Regional screening levels (RSL) summary tables. 2010; http://www.epa.gov/risk/risk-based-screening-table-generic-tables (accessed 21 January, 2020).
19. Aziza AE, Iwegbue CMA, Tesi GO et al. Concentrations, sources, and exposure risk of polychlorinated biphenyls in soil profiles of the floodplain of the lower reaches of the River Niger, Nigeria. Environmental Monitoring and Assessment. 2021; 193(9): 579
20. Emoyan OO, Onocha E, Tesi GO. Concentration assessment and source evaluation of 16 priority polycyclic aromatic hydrocarbons in selected vehicle-park soils southern Nigeria. Scientific African 2020; 7: e00296
21. Tesi GO, Ojegu JO, Akporido SO. Distribution and risk of metals in soils of refuse dumpsites in some urban towns in Delta State, Nigeria. African Scientist. 2020; 21(1): 211-224
22. Osakwe SA, Okolie LP. Physicochemical characteristics and heavy metals contents in soils and cassava plants from farmlands along a major highway in Delta State, Nigeria. Journal of Applied Science and Environmental Management. 2015; 19(4): 695-704
23. Syed JH, Malik RN, Li J, et al. Status, distribution and ecological risk of organochlorines (OCs) in the surface sediments from the Ravi River, Pakistan. Science of the Total Environment. 2014; 472, 204.
24. Xing X, Hu T, Qi S, et al. Spatial distribution, possible sources and health risks of PAHs

and OCPs in surface soils from Dajiuhu sub-alpine wetland, central China. Journal of Geochemical Exploration. 2020; 208: 106393

25. Farina Y, Abdullah MP, Bibi N, et al. Pesticides residues in agricultural soils and its health assessment for humans in Cameron Highlands, Malaysia. Malaysian Journal of Analytical Sciences. 2016; 20(6): 1346 – 1358
26. Yu Y, Li Y, Shen Z, et al. Occurrence and possible sources of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) along the Chao River, China. Chemosphere. 2014; 114:136-43.
27. Bhupander K. Residues of pesticides and herbicides in soils from agriculture areas of Delhi Region, India. Journal of Environment and Earth Science. 2011; 1(2): 1-8
28. Wang F, Jiang X, Bian YT, et al. Organochlorine pesticides in soils under different land usage in the Taihu Lake region, China. Journal of Environmental Science. 2007; 19(5): 584–590
29. Oyekunle JAO, Ogunfowokan AO, Torto N, et al. Determination of organochlorine pesticides in the agricultural soil of Oke-Osun farm settlement, Osogbo, Nigeria. Environmental Monitoring & Assessment. 2011; 177: 51–61
30. Aiyesanmi AF, Idowu GA. Organochlorine pesticides residues in soil of cocoa farms in Ondo State Central District, Nigeria. Environment and Natural Resources Research. 2012; 2: 65-76.
31. Osesua BA, Tsafe AI, Birnin-Yauri UA, et al. Profile of organochlorine pesticide degradation in soil of Wurno irrigation farm areas in Sokoto State, Nigeria. International Journal of Advanced Academic Research in Sciences, Technology & Engineering. 2018; 4(1): 2-19
32. Mwevura H, Kylin H, Vogt T, et al. Dynamics of organochlorine and organophosphate pesticide residues in soil, water, and sediment from the Rufiji River Delta, Tanzania. Regional Studies in Marine Science. 2021; 41(101607): 1–9.
33. Sanchez-Osorio JL, Macías-Zamora JV, Ramírez-Alvarez N, et al. Organochlorine pesticides in residential soils and sediments within two main agricultural areas of northwest Mexico: concentrations, enantiomer compositions and potential sources. Chemosphere 2017; 173: 275-287
34. Yu HY, Li FB, Yu WM, et al. Assessment of organochlorine pesticide contamination in relation to soil properties in the Pearl River Delta, China. Science of the Total Environment. 2013; 447:160–168
35. Miglioranza KSB, Moreno JEA, Moreno VJ. Dynamics of organochlorine pesticides in soils from a southeastern region of Argentina. Environmental Toxicology & Chemistry. 2003; 22: 712–717
36. Zhang A, Chen Z, Ahrens L, et al. Concentrations of DDTs and enantiomeric fractions of chiral DDTs in agricultural soils from Zhejiang Province, China, and correlations with total organic carbon and pH. Journal of Agriculture & Food Chemistry. 2012; 60: 8294–8301.
37. Zhang A, Fang L, Wang J, et al. Residues of currently and never used organochlorine pesticides in agricultural soils from Zhejiang Province, China. Journal of Agriculture & Food Chemistry. 2012; 60: 2982–2988.
38. Tao S, Liu W, Li Y, et al. Organochlorine pesticides contaminated surface soil as reemission source in the Haihe Plain, China. Environmental Science & Technology. 2008; 42: 8395–8400.
39. Dragan D, Cucu-Man S, Mocanu R, et al. Accelerated solvent extraction method for the determination of polychlorinated biphenyls and organochlorine pesticides in soils. Rev Roum Chim. 2007; 52(6): 597–601
40. Qu C, Albanese S, Lima A, et al. Residues of hexachlorobenzene and chlorinated cyclodiene pesticides in the soils of the Campanian Plain, southern Italy. Environmental Pollution. 2017; 231: 1497-1506
41. Aiyesanmi F, Ademefun AE, Ibigbami OA et al. Polycyclic aromatic hydrocarbons and organochlorine pesticides in floodplain soils: A case study of Onuku River in Okitipupa, Nigeria. Environmental Challenges. 2021; 5: 100351
42. Kafaei R, Arfaeinia H, Savari A, et al. Organochlorine pesticides contamination in agricultural soils of southern Iran. Chemosphere. 2020; 240: 124983
43. Mishra K, Sharma RC, Kumar S. Ecotoxicolgy and environmental safety contamination levels and spatial distribution of organochlorine pesticides in soils from India. Ecotoxicology & Environmental Safety. 2012; 76: 215–225

44. Calvelo-Pereira R, Monterroso-Martínez MC, Martínez-Cortízas A, et al. Analysis of composition, distribution and origin of hexachlorocyclohexane residues in agricultural soils from NW Spain. Science of the Total Environment. 2010; 408: 5583–5591
45. Qu C, Qi S, Yang DS, et al. Risk assessment and influence factors of organochlorine pesticides (OCPs) in agricultural soils of the hill region: a case study from Ningde, southeast China. Journal Geochemical Exploration. 2014; 149: 43–51
46. Toan V, Thao V, Walder J, et al. Contamination by selected organochlorine pesticides (OCPs) in surface soils in Hanoi, Vietnam. Bulletin of Environmental Contamination & Toxicology. 2007; 78:195–200
47. Tesi GO, Iwegbue CMA, Emuh FN, et al. Ladgo Dam floods disaster of 2012: An assessment of the concentrations, sources and risks of polycyclic aromatic hydrocarbons in floodplain soils of the lower reaches of River Niger, Nigeria. Journal of Environmental Quality. 2016; 45: 305-314
48. Dirbaba NB, Li S, Wu H, et al. Organochlorine pesticides, polybrominated diphenyl ethers and polychlorinated biphenyls in surficial sediments of the Awash River Basin, Ethiopia. PLoSONE. 2018; 13(10): e0205026.
49. Bai J, Lu Q, Zhao Q et al. Organochlorine pesticides (OCPs) in wetland soils under different land uses along a 100-year chronosequence of reclamation in a Chinese estuary. Scientific Report. 2015; 5: 17624
50. Tang J, Feng J, Li G, et al. Occurrence and possible sources of organochlorine pesticides in soils of Ningbo, East China. Earth and Environmental Science Transactions of the Royal Society of Edinburgh. 2018; 1–6, https://doi.org/10.1017/S1755691018000506

How to cite this article: Moses O. Omayuli, Omotekoro S. Emakunu, Oghenewairhe Emefe, Juliet N. Tesi. Distribution, associated risks and sources of organochlorine pesticides in farmland soils from Ethiope West Area of Delta State, Nigeria. *International Journal of Research and Review*. 2024; 11(2): 304-315. DOI: *https://doi.org/10.52403/ijrr.20240232*

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