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A study on persistent organochlorine pesticide residues in fish tissues and water from an agricultural fish pond

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Abstract

Organochlorine pesticides (OCPs), (α - BHC, β - BHC, γ - BHC, Heptachlor, Aldrin, Chlordane, p, p' - DDE, o, p' - DDD, p, p' - DDD, Dieldrin, Endrin, Endosulfan and p, p' - DDT) were determined in water and fish samples from the fish pond of Oke-Osun Farm Settlement, Osogbo, Nigeria that receive runoffs from agricultural lands. The aim of the study was to investigate the pollution status of the pond water and fish samples. Qualitative and quantitative analysis of the OCPs after clean-up on silica gel adsorbent were carried out using Gas Chromatography equipped with Electron Capture Detector (GC-ECD). The results showed higher levels of OCPs in the pond water during the rainy season than during the dry season. Higher levels of OCPs were found in the fish samples in the dry season than during the rainy season. Significant positive correlations at $p \leq 0.05$ level were observed for β - BHC and aldrin, chlordane, p, p' - DDE, dieldrin and endrin; γ - BHC and heptachlor, p, p' - DDE, dieldrin and endrin; heptachlor and p, p' - DDD, dieldrin and endrin; heptachlor and p, p' - DDD, dieldrin and endrin; p, p' - DDE and dieldrin and endrin; and dieldrin and endrin. The mean seasonal levels of OCPs in the fish were higher, in most cases, than the recommended WHO Maximum Residue Levels (MRLs) in food items and should give cause for concern. Due to possible toxicity and bioaccumulation tendency of the OCPs by the predators higher in the food chain, the levels of OCPs detected in the fish samples could be a source of future health problems. The OCPs detected are consistent with the agricultural activities of the study area due to pesticide usage.

Key words: Farm settlement, Fish tissues, Organochlorine pesticides, Pond, Water

Introduction

Organochlorine pesticides (OCPs) are synthetic, non-polar, toxic and environmentally persistent dichlorodiphenylethanes, cycodienes or chlorinated benzenes that are used for pests control. Synthetic pesticides were introduced into the Nigerian markets in the 1950s (Adeyeye and Osibanjo, 1990) and farmers have been using them for control of weeds; weevils of cotton, beans and cereals; borers of plant stalks and yams; and disease vectors like tsetse flies and mosquitoes. The persistent nature of the OCPs is advantageous for the control of pests such as termites around buildings. Pesticides applications as enumerated above have brought about increased output of agricultural products and better life quality generally. The use of pesticides and copper fungicides for the treatment of deseases by farmers over the years would no doubt have led to the accumulation of their residues in soils, water and fish of the agricultural areas, as have been reported elsewhere in literature (Merry et al., 1983; Osibanjo and Bamgbose, 1990; Akinnifesi et al., 2006).

However, the challenges of environmental degradation with its associated health problems provoked by the ubiquitous OCPs are daunting owing to their persistent nature and high lipid solubility. In turn, these factors have led to the problems of bioconcentration and biomagnification of the OCPs in animal tissues that live within the environment where the OCPs are found. For example, in the aquatic environment, OCPs are not readily metabolized and excreted by fish hence, they "biomagnify" up the food chain.

When pesticides reach water bodies, they are rapidly absorbed and accumulated by the bottom sediment, plankton, algae, aquatic invertebrates, aquatic vegetation and fish. Greater concentrations

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of organochlorine residues were reported in fish from higher trophic levels even when movement of the residues through a food chain was impossible (Hannon et al., 1970; Amakwe, 1984; Hamelink et al., 1986). Different species of fish vary greatly both in their susceptibility to organochlorine insecticides and in their ability to store residues in their tissues, but it is certain that very large numbers of fish have been killed by these chemicals (Johnson et al., 1973).

Ecological effects of OCPs include interference with reproductive success of organisms high on the food chain, especially fish eating birds such as osprey, pelicans, falcons and eagles. OCPs especially DDT have estrogenic and enzyme inducing properties. The adverse effects of DDT demonstrated in experimental animals include infertility (Jonsson et al., 1975), a decrease in the number of implanted ova (Lundberg, 1974), intrauterine growth retardation (Fabro et al., 1984), cancer (Cabral et al., 1982; Muino et al., 1995), neurologic developmental disorders (Eriksson et al., 1990; Muino et al., 1995) and mortality (Clement and Okey, 1974). Ortho and para isomers of DDT compete with estradiol for binding to estrogen receptors in uterine cytosol thus causing changes in steroid metabolism and alter the ability of birds to mobilize calcium to produce strong egg shells (Close, 1996; Allen and Otis, 1998; Cohn, 1999; Creekmore et al., 1999; O'Shea et al., 2001). This has led to the prescription of tolerances such as maximum residue level (MRL) and no observable adverse effect level (NOAEL) for various pesticides in food and water, especially by the Codex Alimentarius Commission (CODEX, 2004).

Due to their adverse health effects, the use of some of the OCPs such as DDT have been placed under legal restrictions in places like the USA as far back as 1972, but they still continue to enjoy increasing patronage in places like Nigeria and are sold to farmers under different trade names. The high efficacy and lower cost of OCPs compared with alternative pesticides are some of the reasons for their increasing patronage in Nigeria (Adeyemi et al., 2008). Whereas in the developed countries, strategic surveillance programme is put in place to evaluate the OCPs levels in the environment (Luke et al., 1988; MAFF, 1989; Kaphalia et al., 1990), there is a dearth of baseline data on the levels of OCPs particularly in the Nigerian agricultural environments located in remote or not-easily-accessible areas. Past studies were concentrated on city centres and places of easy access in which case there have been reported pollution stresses in such environmental matrices as soil, water, sediments, air and biological materials (Suzuki et al., 1977; Skaare et al., 1990). Osibanjo and Bamgbose (1990) reported the contamination by chlorinated hydrocarbons of Nigerian marine fish and shellfish, based on the analyses of 94 samples of 25 marine fish species during the period 1983 to 1985 and 14 samples of 7 shellfish species in 1987. Ajayi and Osibanjo (1981) noted that rivers and streams in Nigeria within the catchment of major cities and agricultural areas have become grossly contaminated with pesticide residues. Pesticides are among the priority pollutants that has been monitored in a wide variety of matrices such as honey (Muino et al., 1995), waters (Ruiz-Gil et. al., 2008; López-Blanco et. al., 2006), soils (Arias-Este´vez et al., 2008), stream sediments (Gonzalez-Lopez et al., 2005), crops especially leafy vegetables (Rosa et al. 2008) and potato crops (Lopez-Perez et al., 2006) and their levels may represent a serious hazard to human health. In one study on management of pesticides in the United Arab Emirates, Kaakeh et al. (2004), reported that the misuse, overuse and unnecessary use of insecticides have been the most important factor in the growth of interest in pest management and that the application of insecticides represents environmental contamination that constitutes adverse effects on non-target organisms. The greatest potential of unintended adverse effects of pesticides is through the contamination of hydraulic system; hence water is one of the primary media through which pesticides are transported from the application area to other locations and pesticide contamination of ground water is a global issue (Kaakeh et al., 2004; López-Blanco et al., 2005). Of all the various kinds of pesticides used by the farmers in the study area, Gammalin 20 (Lindane) is the most popular (used for protecting kola nut from pest, fishing and also used for formulating local insectides and rodenticides). Others are DDT, DD-force, Weed-Off, Termicot, Atrazin, Glyphosphate, Metaclors-plus, Alaclhlor 2-4 Amcine and aldrin.

The present study focused on the Oke-Osun Farm Settlement, Osogbo, Nigeria, one of the farm settlements established in 1960 where intensive agriculture is practiced till date. In this paper, we report the investigations carried out on the pollution status of the pond water and fish samples from the farm settlement with respect to levels of α - BHC, β - BHC, γ - BHC, Heptachlor, Aldrin, Chlordane, p, p' - DDE, o, p' - DDD, p, p' - DDD, Dieldrin, Endrin, Endosulfan and p, p' - DDT. This study was motivated by the fact that the farm settlement has not, since its establishment, been subjected to a study of this nature and there is evidence that this group of chemicals is still used in agriculture clandestinely under unknown trade names in developing countries such as Nigeria (Sosan et al., 2008; Awofolu and Fatoki, 2003). The dependence of people of the study area and its environs on fish for their protein needs is steadily increasing because fish is relatively cheap and the resulting adverse ecological effects these compounds may have on the aquatic biota and the possible bioaccumulation in food chains, make the monitoring program important.

Materials and methods

Description of the sampling location

Oke-Osun farm settlement is located about 3.5 km South of Osun Groove at the outskirt of Osogbo metropolis between the longitudes 007.231 and 007.236°E and latitudes 04.080 and 04.150°N (Figure 1). The location is a rural setting stretching over 220 ha. A large percentage of the total farm land is used mainly for the cultivation of food crops like maize, vegetables and cassava. Crops harvested from this settlement enjoy wide patronage by consumer intermediaries from Osogbo and its environs. The farmers here actively and regularly apply agrochemicals for the control of pests and weeds for the purpose of improving crop yields as deemed necessary without a follow-up assessment of how these agrochemicals (fertilizer, herbicides and germicides) affect the environment of the settlement.

Reagents

The reagents used in this study were of spectra purity. They include analytical grade dichloromethane (DCM) – Rochelle Chemicals, SA; HPLC grade n – hexane – Ultrafine Limited, Marlborough House, London; HNO_3 (AR) – Riedel-deHaën, Germany; Silica gel 60 PF_{254} – MERCK, Germany; anhydrous sodium sulphate - Rochelle Chemicals, SA; and nitrogen (99.999% purity) - Rochelle Chemicals, SA.

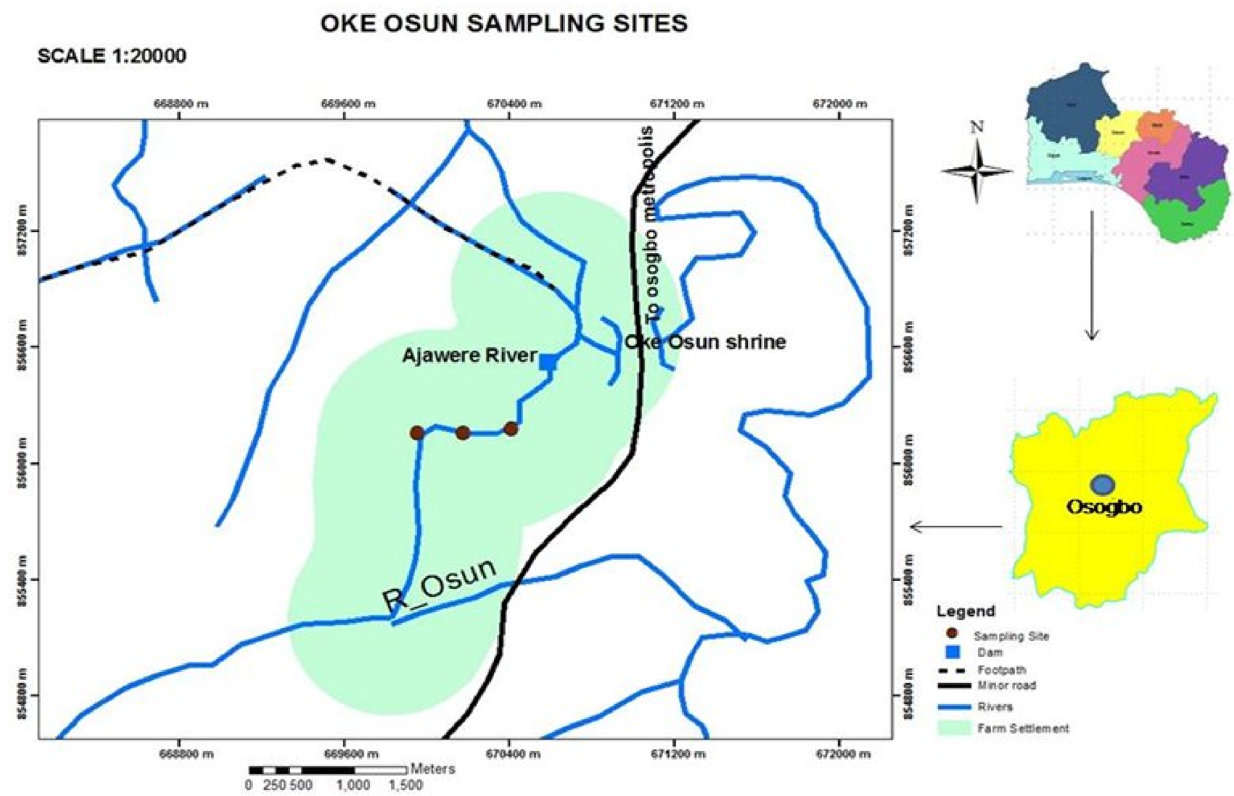

Figure 1. Map showing the sampling sites on the fish pond along Ajawere River.

Sample collection and pretreatment

For each month, water samples from three spots at 20 m apart within the fish pond were collected in pre-treated 2.5 L Winchester glass bottles. Water from the spot of collection was used to rinse the bottles three times before sampling was done. Alteration of the organics due to microbial activities was prevented by acidification of the samples to pH 2 by adding about 5 mL concentrated HNO_3 immediately after collection. The samples were stored in a refrigerator at 4°C prior to analysis (Fatoki and Vernon, 1990; Ogunfowokan et al., 2006). Macrophagous tilapia fish samples (*Tilapia zillii*) for each month were caught from the pond using drag net method with the help of trained personnel from the Department of Fisheries, Osun State Ministry of Agriculture and Natural Resources, Osogbo, Nigeria. The fish samples were wrapped in aluminum foils, kept in an all-glass container and stored in a deep freezer prior to analysis. *T. zillii* is a top to middle feeder fish species (Ize-Iyamu et al., 2007).

Extracting OCPs from water and fish samples

Liquid-liquid extraction method was used to extract OCPs from the 2 L water samples earlier collected. About 500 mL of water sample was put into a 1 L separatory funnel at a time. This was extracted with 10 mL (3 portions) of DCM by vigorous shaking for 30 minutes for each of the triplicate extraction. The extracts were combined, dried with anhydrous sodium sulphate and concentrated to about 2 mL under a stream of nitrogen of 99.999% percentage purity. The reduced extract was preserved for chromatographic clean-up prior to GC-ECD analysis.

The frozen composite whole-body tissue samples were homogenized using an agate mortar and pestle (Leiker et al., 1996; Fatoki and Awofolu, 2003). Approximately 10 g of the properly chopped sample was further mixed with 5 g of anhydrous sodium sulphate. This was soxhlet extracted for 5 hours using DCM/n-hexane mixture. The extract was dried over anhydrous sodium sulphate and concentrated to about 2 mL as described earlier in readiness for the clean-up procedure.

Clean-up procedure

A column of about 15 cm (length) × 1 cm (internal diameter) was packed with about 5 g activated silica gel prepared in a slurry form in n-hexane. About 0.5 cm^3 of anhydrous sodium sulphate was placed at the top of the column to absorb any water in the sample or the solvent. The column was pre-eluted with 15 mL of n-hexane without the exposure of the sodium sulphate layer to air. The reduced extract was placed in the column and allowed to sink below the sodium sulphate layer. Elution was done with 2 × 10 mL portions of the extracting solvent (DCM). The eluate was collected, dried with anhydrous sodium sulphate and then evaporated to dryness under a stream of analytical grade nitrogen (99.999%).

Gas chromatographic (GC) analysis

The dried eluate above was reconstituted with 1mL spectra grade n-hexane and 0.5 mL of 20 ppm hexachlorobenzene was added as an internal standard. A PERKIN ELMER GC Autosystem (XL) available at the Department of Chemistry, University of Botswana, Garborone, Botswana, was used to profile the organochlorine pesticides in the sample using an electron capture detector (ECD). The GC was run under the following conditions: injector temperature: 250°C; detector temperature: 300°C (held for 5 minutes); capillary column: Zebron ZB-1701: 30 m x 0.25 mm i.d. x 0.25 µm f.t.; oven temperature programme: 280°C starting from 50°C for 1minute and continued at 20°C/minute to 150°C and at 5°C/minute to 280°C held for 4 minutes; injected sample volume: 1µL; mode of injection and flow rate**:** splitless mode at the flow rate 19.6 mL/minute; carrier gas: N_2 at 30 mL/min.

Recovery experiment

Since no certified fish and water pesticide reference materials were available to us during the course of this study, recovery analysis was performed in order to ascertain the precision and efficiency of the analytical procedures using standard addition method. 1000 mL aliquot of ultra-pure water, obtained by reverse osmosis using Milli-Q Gradient A10 Water Deionizer, was measured into a 2000 mL beaker and acidified with concentrated HNO_3 to pH 2. This was spiked with 10 mL of 1000 ppm standard mixture consisting of thirteen different organochlorine pesticides (OCPs) purchased. The mixture was thoroughly shaken together to ensure maximum homogenization. This was extracted and cleaned up following the procedures outlined earlier. In addition, 10 mL of the 1000 ppm mixture of the OCPs, in spectra grade n-hexane, was put into a clean oven dried sample bottle. This was dried at ambient temperature by purging with high purity nitrogen gas and redissolved in 1.0 mL n-hexane. 1.0 µL of the mixture was injected into the GC column for GC-ECD analysis. The recoveries of OCPs were determined by comparing the peak areas of the OCPs after spiking with those obtained from the evaporated standard residues and the percentage recovery (%R) was evaluated (Fatoki and Awofolu. 2003).

Response factor (RF) and limits of detection determinations

The response factor of the standard OCPs was determined by analyzing 1.0 µL of 1000 ppm stock solution of the standard mixture containing the internal standard (I.S.) on the GC-ECD. The response factors (RF) were obtained from the relationship:

$$RF = \frac{\text{Peak area of OCPs}}{\text{Peak area of I.S.}}$$

(Fatoki and Vernon, 1990; Ogunfowokan et al., 2003 and 2006).

The limits of detection (LOD) were evaluated by the determination of concentrations that give signals equal to the blank signal plus three standard deviations of the blank using the equation $y_C = y_B + 3s_B$; where y_C = analyte signal equivalent to detection limit; y_B = blank signal; and s_B = standard deviation of the blank. From the value of y_C, the analyte concentration corresponding to the detection limit was evaluated for GC-ECD determination of OCPs.

Statistical analysis

Both descriptive and inferential statistical analyses were used to interpret experimental data in this study. Data were analysed using SPSS for Windows, version 16. The matrix correlation coefficients of OCPs in pond water and fish from Oke-Osun Farm settlement was carried out to show if significant correlations at $P < 0.05$ level occurred between individual OCPs in the matrices. Cluster analysis was also used to classify a group of the OCPs into similar classes that are associated.

Results and discussion

The results of recovery experiment are presented in Table 1 as mean percentage recoveries. Based on the percentage recovery values that ranged from 82.11 to 99.27 % in water, the analytical procedures outlined for OCPs assessment in this study are adjudged reliable, reproducible and efficient. The range of response factors of 0.657 to 1.892 showed the separation efficiency of the GC-ECD equipment used for the identification and quantification of OCPs. The LOD values for the OCPs ranged from 0.056 to 2.107µg/L. The percentage relative standard deviation (%RSD) values for the recoveries of OCPs in water ranged from 2.57 to 6.99 %. These values showed that precision was better than 10 % RSD. The gas chromatogram of a mixture of the 13 OCPs plus the internal standard is shown in Figure 2. The 13 pesticides were well resolved and eluted within 25 minutes.

Table 1. Response factors, relative retention times, limits of detection and mean % recovery of OCPs in water from the fish pond of Oke-Osun farm settlement, Osogbo, Nigeria.

OCP	Response Factor	Retention Time (min)	% Recovery[#] in Water	Calculated limits of detection (µg/L)
HCB	-	8.58±0.25	92.31±5.81	0.673
α-BHC	1.772±0.011	9.93±0.21	85.16±5.04	1.087
γ-BHC	1.161±0.022	11.39±0.33	99.27±3.66	0.097
Heptachlor	1.286±0.101	12.26±0.42	92.03±6.42	1.090
Aldrin	1.344±0.021	13.28±0.34	86.72±5.14	2.107
β-BHC	0.672±0.005	14.01±0.44	89.62±4.84	0.100
Chlordane	0.603±0.006	17.29±0.26	91.21±3.76	0.483
p, p'- DDE	0.890±0.010	17.58±0.13	93.44±3.26	0.183
Dieldrin	0.934±0.040	18.21±0.29	83.98±3.18	0.895
o, p' - DDD	1.276±0.059	18.72±0.41	96.67±5.40	1.110
Endrin	1.076±0.021	19.00±0.52	84.59±2.57	0.307
p, p'- DDD	1.892±0.276	20.43±0.36	94.81±4.92	2.003
β-Endosulfan	0.657±0.055	20.72±0.29	82.11±4.77	0.067
p, p'- DDT	0.942±0.019	25.44±0.38	93.18±6.99	0.056

#Values are reported as mean of triplicate analysis ± % RSD.

Table 2. (a-d). Rainy Season Levels of OCPs (μg/L) in Pond Water from Oke-Osun Farm Settlement, Osogbo, Nigeria.

(a) May 2004

	α - BHC	β - BHC	γ - BHC	Heptachlor	Aldrin	Chlordane	p, p' - DDE	o, p' – DDD	p, p' - DDD	Dieldrin	Endrin	Endosulfan	p, p' - DDT	Total burden per sampling site
Pond water 1	4.88 ±1.02	8.46 ± 1.18	9.73 ± 1.93	10.96 ± 0.29	8.40 ± 2.05	6.60 ± 1.25	8.18 ± 1.87	8.27 ± 0.72	3.44 ± 1.04	5.30 ± 1.53	5.94 ± 1.79	7.67 ± 2.04	7.03 ± 3.46	82.18 ±20.17
Pond water 2	1.84 ± 0.21	1.85 ± 0.12	3.21 ± 0.15	1.96 ± 0.11	1.75 ± 0.17	1.29 ± 0.11	4.13 ± 0.01	5.65 ± 0.13	4.59 ± 0.11	2.14 ± 0.10	3.60 ± 0.15	1.22 ± 0.10	8.02 ± 0.17	41.25 ±1.64
Pond water 3	3.88 ±1.04	ND	ND	ND	ND	ND	6.74 ±1.43	6.72 ±0.17	ND	6.39 ±0.71	5.56 ±0.34	10.32 ±0.38	7.06 ±0.37	46.67 ±4.44
Mean ± s.d.	3.53 ±1.55	3.44 ±4.45	4.31 ±4.96	4.31 ±5.85	3.38 ±4.43	2.63 ±3.50	6.35 ±2.05	6.88 ±1.32	2.68 ±2.39	4.61 ±2.21	5.03 ±1.26	6.40 ±4.68	7.37 ±0.56	57.24 ±22.25
Range	1.84-4.88	ND-8.46	ND-9.73	ND-10.96	ND-8.40	ND-6.60	4.13-8.18	5.65-8.27	ND-4.59	2.14-6.39	3.60-5.94	1.22-10.32	7.03-8.02	41.25-82.18

Value = mean of triplicate analysis ± s.d.; ND = Not detected

(b) June 2004

	α - BHC	β - BHC	γ - BHC	Heptachlor	Aldrin	Chlordane	p, p' - DDE	o, p' – DDD	p, p' - DDD	Dieldrin	Endrin	Endosulfan	p, p' - DDT	Total burden per sampling site
Pond water 1	16.69 ± 0.18	18.40 ± 0.12	24.86 ± 0.94	54.29 ± 1.86	64.15 ± 1.42	4.17 ± 0.13	90.14 ± 2.33	100.88 ± 0.97	41.07 ± 1.21	44.47 ± 2.93	38.79 ± 1.62	63.28 ± 1.10	78.60 ± 1.53	629.79 ±16.34
Pond water 2	15.73 ± 0.27	44.69 ± 0.62	42.85 ± 0.70	24.67 ± 0.45	25.11 ± 0.46	9.32 ± 0.53	56.63 ±1.05	61.99 ± 0.93	24.41 ± 0.28	11.35 ± 0.14	34.88 ± 0.92	58.97 ±1.51	59.29 ± 0.81	469.89 ±8.67
Pond water 3	27.76 ± 0.49	ND	31.54 ± 1.14	23.40 ± 0.24	58.54 ± 1.82	6.79 ± 0.37	108.60 ± 2.14	52.63 ± 0.17	54.44 ± 1.96	56.05 ± 1.16	46.61 ± 3.22	83.18 ± 2.10	62.08 ± 1.29	611.62 ±16.10
Mean ± s.d.	20.06 ±6.69	21.03 ±22.46	33.08 ±9.09	34.12 ±17.48	49.27 ±21.11	6.76 ±2.58	85.12 ±26.35	71.83 ±25.59	39.97 ±15.05	37.29 ±23.20	40.09 ±5.97	68.48 ±12.91	66.66 ±10.44	579.28 ±87.54
Range	15.73-27.76	ND-44.69	24.86-42.85	23.40-54.29	25.11-64.15	4.17-9.32	56.63-108.60	52.63-100.88	24.41-54.44	11.35-56.05	34.88-46.61	58.97-83.18	59.29-78.60	469.89-629.79

Value = mean of triplicate analysis ± s.d.

(c) July 2004

	α - BHC	β - BHC	γ - BHC	Heptachlor	Aldrin	Chlordane	p, p' - DDE	o, p' – DDD	p, p' - DDD	Dieldrin	Endrin	Endosulfan	p, p' - DDT	Total burden per sampling site
Pond water 1	29.97 ± 0.55	ND	70.44 ± 2.91	35.76 ± 1.08	ND	31.76 ± 2.10	36.22 ± 0.93	44.45 ± 1.93	24.37 ± 0.44	45.64 ± 1.14	39.90 ± 0.60	51.76 ± 1.06	55.41 ± 1.12	465.68 ±13.86
Pond water 2	30.12 ± 0.46	86.78 ± 0.51	34.69 ± 0.70	63.29 ± 1.88	78.82 ± 1.33	39.72 ± 0.22	63.67 ± 1.32	110.91 ± 1.23	34.34 ± 0.12	99.57 ± 0.39	49.12 ± 0.87	90.19 ± 2.34	69.56 ± 1.09	850.98 ±12.46
Pond water 3	6.48 ± 0.13	3.31 ± 0.09	9.90 ± 0.24	2.04 ± 0.15	8.42 ± 0.91	4.64 ± 0.51	8.44 ± 0.31	3.05 ± 0.06	11.61 ± 0.11	18.05 ± 0.16	13.56 ± 0.10	18.45 ± 0.15	12.35 ± 0.14	120.30 ±3.06
Mean ± s.d.	22.19 ±13.61	30.03 ±49.17	38.34 ±30.43	33.70 ±30.68	29.08 ±43.28	25.34 ±18.38	36.11 ±27.62	52.80 ±54.41	23.44 ±11.39	54.42 ±41.46	34.19 ±18.45	53.47 ±35.90	45.77 ±29.80	478.99 ±365.52
Range	6.48-30.12	ND-86.78	9.90-70.44	2.04-63.29	ND-78.82	4.64-39.72	8.44-63.67	3.05-110.91	11.61-34.34	18.05-99.57	13.56-49.12	18.45-90.19	12.35-69.56	120.30-850.98

Value = mean of triplicate analysis ± s.d.

(d) August 2004

	α - BHC	β - BHC	γ - BHC	Heptachlor	Aldrin	Chlordane	p, p' - DDE	o, p' – DDD	p, p' - DDD	Dieldrin	Endrin	Endosulfan	p, p' - DDT	Total burden per sampling site
Pond water 1	16.19 ± 0.14	5.23 ±0.12	26.54 ± 1.23	14.17 ± 0.62	25.17 ± 0.15	25.35 ± 0.25	21.78 ± 1.26	19.37 ± 1.01	16.16 ± 0.24	12.48 ± 1.10	13.21 ± 0.48	13.71 ± 1.20	15.51 ± 0.20	224.87 ±8.00
Pond water 2	6.65 ± 0.35	11.86 ±0.58	23.84 ± 0.19	15.26 ± 0.31	10.30 ± 0.24	11.93 ± 0.68	17.76 ± 1.38	37.39 ± 0.11	17.87 ± 0.13	5.74 ± 0.20	8.75 ± 0.41	1.35 ± 0.07	25.90 ± 0.86	194.30 ±5.51
Pond water 3	7.57 ± 0.42	ND	22.58 ± 1.50	10.77 ± 0.81	14.54 ± 0.13	7.59 ± 0.26	13.39 ± 1.20	23.94 ± 0.22	19.19 ± 0.57	22.44 ± 0.19	14.67 ± 0.25	8.37 ± 0.15	34.24 ± 0.18	199.29 ±5.88
Mean ±s.d.	10.14 ±5.26	5.60 ±5.79	24.32 ±2.02	13.40 ±2.34	16.67 ±7.66	14.96 ±9.26	17.64 ±4.20	26.90 ±9.37	17.74 ±1.52	13.55 ±8.40	12.21 ±3.08	7.81 ±6.20	25.22 ±9.38	206.15 ±16.40
Range	6.65-16.19	ND-11.56	22.58-26.54	10.77-15.26	10.30-25.17	7.59-25.35	13.39-21.78	19.37-37.39	16.16-19.19	5.74-22.44	8.75--14.67	1.35-13.71	15.51-34.24	194.30-224.87
Rainy Season mean ± s.d.	13.98 ±10.46	15.02 ±25.95	25.02 ±19.28	21.38 ±20.41	24.60 ±27.33	12.42 ±12.75	36.31 ±35.48	39.60 ±36.61	20.96 ±16.14	27.47 ±29.05	22.88 ±17.44	34.04 ±33.13	36.26 ±25.64	330.42 ±240.88
Seasonal range	1.84-30.12	ND-86.78	ND-70.44	ND-63.29	ND-78.82	ND-39.72	4.13 108.60	3.05-110.91	ND-54.44	2.14-99.57	3.60-49.12	1.22-90.19	7.37-66.66	57.24-579.28

Table 3 (a-d). Dry Season Levels of OCPs (µg/L) in Pond Water from Oke-Osun Farm Settlement, Osogbo, Nigeria.

(a) November 2004

	α - BHC	β - BHC	γ - BHC	Heptachlor	Aldrin	Chlordane	p, p' - DDE	o, p' – DDD	p, p' - DDD	Dieldrin	Endrin	Endosulfan	p, p' - DDT	Total burden per sampling site
Pond water 1	4.32 ± 0.02	ND	1.98 ± 0.10	6.22 ± 0.31	8.19 ± 0.40	ND	3.76 ± 0.13	8.90 ± 0.10	ND	4.59 ± 0.21	5.52 ± 0.30	6.84 ± 0.17	3.97 ± 0.14	54.29 ±1.88
Pond water 2	ND	ND	ND	ND	ND	ND	17.92 ± 0.50	ND	4.61 ± 0.56	25.07 ± 1.31	ND	ND	ND	47.60 ±2.37
Pond water 3	4.05 ± 0.09	ND	1.67 ± 0.32	7.68 ± 0.30	11.09 ± 0.71	ND	27.14 ± 0.73	5.98 ± 0.08	3.77 ± 0.31	7.59 ± 0.07	5.26 ± 0.31	6.39 ± 0.14	8.98 ± 0.80	89.50 ±3.86
Mean ± s.d.	2.79 ±2.42	ND	1.22 ±1.07	4.63 ±4.08	6.43 ±5.75	ND	16.27 ±11.78	4.96 ±4.54	2.79 ±2.46	12.42 ±11.06	3.59 ±3.11	4.41 ±3.83	4.32 ±4.50	63.83 ±22.51
Range	ND-4.32	ND	ND-1.98	ND-7.68	ND-11.09	ND	3.76-27.14	ND-8.90	ND-4.61	4.59-25.07	ND-5.52	ND-6.84	ND-8.98	47.60-89.60

Value = mean of triplicate analysis ± s.d.

(b) December 2004

	α - BHC	β - BHC	γ - BHC	Heptachlor	Aldrin	Chlordane	p, p' - DDE	o, p' – DDD	p, p' - DDD	Dieldrin	Endrin	Endosulfan	p, p' - DDT	Total burden per sampling site
Pond water 1	18.47 ± 0.52	3.24 ± 0.03	14.65 ± 0.27	11.87 ± 0.24	20.83 ± 0.30	6.00 ± 0.03	42.82 ± 2.94	13.35 ± 0.13	20.30 ± 0.83	13.39 ± 0.61	18.33 ± 0.60	12.29 ± 0.31	37.20 ± 0.47	232.74 ±7.28
Pond water 2	8.12 ± 0.01	ND	ND	ND	2.08 ± 0.17	4.27 ± 0.07	11.94 ± 0.01	7.39 ± 0.32	5.80 ± 0.40	13.63 ± 0.30	3.06 ± 0.02	10.81 ± 0.43	14.68 ± 0.20	81.78 ±1.93
Pond water 3	ND	ND	ND	ND	ND	ND	ND	ND	5.53 ± 0.27	16.11 ± 0.11	ND	ND	7.61 ± 0.09	29.25 ±0.47
Mean ± s.d.	8.86 ±9.26	1.08 ±1.87	4.88 ±8.46	3.96 ±6.85	7.64 ±11.47	3.42 ±3.09	18.25 ±22.10	6.91 ±6.69	10.54 ±8.45	14.38 ±1.51	7.13 ±9.82	7.70 ±6.71	19.83 ±16.04	114.59 ±105.64
Range	ND - 18.47	ND - 3.24	ND - 14.65	ND - 11.87	ND - 20.83	ND - 6.00	ND - 42.82	ND - 13.35	5.53-20.30	13.39-16.11	ND - 18.33	ND - 12.29	7.61-37.20	29.25-232.74

Value = mean of triplicate analysis ± s.d.

(c) January 2005

	α - BHC	β - BHC	γ - BHC	Heptachlor	Aldrin	Chlordane	p, p' - DDE	o, p' – DDD	p, p' - DDD	Dieldrin	Endrin	Endosulfan	p, p' - DDT	Total burde per sampling site
Pond water 1	5.82 ± 0.90	ND	8.33 ± 0.15	3.39 ± 0.20	4.73 ± 0.31	2.43 ± 0.30	3.35 ± 0.33	8.46 ± 0.45	5.30 ± 0.44	7.65 ± 0.27	6.75 ± 0.50	12.39 ± 0.75	9.42 ± 0.83	79.02 ±5.43
Pond water 2	5.56 ± 0.04	ND	15.95 ± 0.30	5.75 ± 0.33	14.58 ± 0.66	5.17 ± 0.05	17.23 ± 2.63	15.31 ± 0.36	9.95 ± 1.07	18.77 ± 0.11	16.69 ± 0.46	19.98 ± 0.91	5.19 ± 0.42	150.13 ±7.34
Pond water 3	3.18 ± 0.19	ND	32.89 ± 0.75	14.89 ± 0.36	13.62 ± 0.39	24.63 ± 0.14	ND	23.43 ± 0.52	12.73 ± 0.02	25.42 ± 1.73	22.91 ± 0.75	27.83 ± 1.06	8.98 ± 0.60	210.51 ±6.51
Mean ± s.d.	4.85 ±1.45	ND	19.06 ±12.57	8.01 ±6.07	10.98 ±5.43	10.74 ±12.10	6.86 ±9.14	15.73 ±7.49	9.33 ±3.75	17.28 ±8.98	15.45 ±8.15	20.07 ±7.72	7.86 ±2.33	146.22 ±65.82
Range	3.18-5.82	ND	8.33-32.89	3.39-14.89	4.73-14.58	2.43-24.63	ND-17.23	8.46-23.43	5.30-12.73	7.65-25.42	6.75-22.91	12.39-27.83	5.19-9.42	79.02-210.51

(d) February 2005

	α - BHC	β - BHC	γ - BHC	Heptachlor	Aldrin	Chlordane	p, p' - DDE	o, p' – DDD	p, p' - DDD	Dieldrin	Endrin	Endosulfan	p, p' - DDT	Total burden per sampling site
Pond water 1	7.16 ± 0.63	ND	14.49 ± 0.53	16.23 ± 0.36	9.53 ± 0.29	23.79 ± 0.25	23.52 ± 0.22	17.01 ± 0.67	8.21 ± 0.45	15.10 ± 0.36	18.68 ± 0.17	10.91 ± 0.09	25.30 ± 0.42	190.43 ±4.44
Pond water 2	14.79± 0.48	ND	6.58 ± 0.04	4.85 ± 0.39	23.75 ± 0.61	18.65 ± 0.07	21.6 ± 0.44	12.06 ± 0.41	10.51 ± 0.70	31.99 ± 0.67	34.30 ± 0.52	17.77 ± 1.01	26.73 ± 0.37	223.58 ±5.71
Pond water 3	ND	ND	5.19 ± 0.41	ND	14.14 ± 0.36	3.07 ± 0.14	ND	10.67 ± 1.10	2.41 ± 0.60	27.60 ± 0.06	ND	9.01 ± 0.04	ND	72.09 ±2.71
Mean ± s.d.	7.32 ±7.40	ND	8.75 ±5.02	7.03 ±8.33	15.81 ±7.26	15.17 ±10.79	15.04 ±13.06	13.25 ±3.33	7.04 ±4.17	24.90 ±8.76	17.66 ±17.17	12.56 ±4.61	17.34 ±15.04	162.03 ±79.64
Range	ND-14.79	ND	5.19-14.49	ND-16.23	9.53-23.75	3.07-23.79	ND-23.52	10.67-17.01	2.41-10.51	15.10-31.99	ND-34.30	9.01-17.77	ND-26.73	72.09-223.58
Dry Season mean ±s.d.	5.96 ±5.73	0.27 ±0.90	8.48 ±9.75	5.91 ±5.82	10.21 ±7.70	7.33 ±9.40	14.11 ±13.44	10.21 ±6.74	7.43 ±5.42	17.24 ±8.71	10.96 ±11.02	11.19 ±7.96	12.34 ±7.43	121.67 ±43.31
Seasonal range	ND-18.47	ND-3.24	ND-32.89	ND-16.23	ND-23.75	ND-24.63	ND-42.82	ND-23.43	ND-20.30	4.59-31.99	ND-34.30	ND-27.83	ND-37.20	29.25-232.74

Table 4. Matrix of Correlation Coefficients of OCPs in Pond Water from Oke-Osun Farm Settlement, Osogbo, Nigeria.

	α - BHC	β - BHC	γ - BHC	Heptachlor	Aldrin	Chlordane	p, p' - DDE	o, p' – DDD	p, p' - DDD	Dieldrin	Endrin	Endosulfan	p, p' – DDT
α-BHC	1.00												
β-BHC	0.48*	1.00											
γ-BHC	0.76*	0.28	1.00										
Heptachlor	0.77*	0.69*	0.70*	1.00									
Aldrin	0.69*	0.66*	0.39	0.81*	1.00								
Chlordane	0.65*	0.57*	0.75*	0.64*	0.41*	1.00							
p,p'-DDE	0.78*	0.34	0.48*	0.74*	0.84*	0.26	1.00						
o,p'-DDD	0.73*	0.70*	0.62*	0.97*	0.88*	0.54*	0.77*	1.00					
p,p'-DDD	0.82*	0.37	0.67*	0.77*	0.83*	0.40*	0.93*	0.81*	1.00				
Dieldrin	0.76*	0.73*	0.58*	0.80*	0.81*	0.62*	0.69*	0.83*	0.74*	1.00			
Endrin	0.89*	0.47*	0.74*	0.82*	0.79*	0.67*	0.80*	0.81*	0.85*	0.83*	1.00		
Endosulfan	0.84*	0.58*	0.66*	0.85*	0.85*	0.53*	0.84*	0.87*	0.87*	0.90*	0.91*	1.00	
p,p'-DDT	0.87*	0.48*	0.68*	0.89*	0.80*	0.50*	0.88*	0.89*	0.91*	0.77*	0.89*	0.85*	1.00

*Values are significant at 0.05 level (N = 24).

Table 5. Monthly Mean Levels of OCPs (μg/kg) in Fish from the Pond Water of Oke-Osun Farm Settlement, Osogbo, Nigeria.

	α - BHC	β - BHC	γ - BHC	Heptachlor	Aldrin	Chlordane	p, p' - DDE	o, p' – DDD	p, p' - DDD	Dieldrin	Endrin	Endosulfan	p, p' - DDT	Total Body Burden
May 2004	16.34 ± 0.12	13.52 ± 0.11	2.05 ± 0.06	ND	43.47 ± 0.01	3.81 ± 0.07	24.29 ± 0.15	20.23 ± 0.05	40.77 ± 0.06	20.80 ± 0.01	0.52 ± 0.10	0.57 ± 0.10	70.68 ± 0.21	257.05 ±0.94
June 2004	10.56 ± 0.01	41.02 ± 0.14	1.96 ± 0.22	1.22 ± 0.07	40.39 ± 0.11	ND	30.94 ± 0.03	ND	50.72 ± 0.06	40.36 ± 0.05	ND	1.22 ± 0.08	40.78 ± 0.21	259.39 ±0.77
July 2004	20.54 ± 0.19	15.00 ± 0.04	0.69 ±0.02	1.93 ± 0.17	37.31 ±0.15	ND	49.86 ± 0.09	ND	42.84 ± 0.21	43.33 ± 0.49	ND	6.13 ± 0.15	66.34 ± 0.03	283.97 ±1.54
August 2004	14.03 ± 0.11	33.94 ± 0.10	1.12 ± 0.08	2.27 ± 0.14	51.92 ± 0.21	0.29 ± 0.06	43.58 ± 0.12	14.56 ± 0.15	33.23 ± 0.17	51.97 ± 0.29	0.68 ± 0.05	8.29 ± 0.13	81.78 ± 0.13	337.67 ±1.74
Rainy season mean ± s.d.	15.37 ±4.19	25.87 ±13.73	1.46 ±0.66	1.36 ±1.00	43.27 ±6.29	1.03 ±1.86	37.16 ±11.65	8.70 ±10.31	41.89 ±7.19	39.12 ±13.17	0.30 ±0.35	4.05 ±3.76	64.90 ±17.34	284.47 ±37.52
November 2004	32.85 ± 0.46	25.25 ± 0.15	1.91 ± 0.21	0.96 ± 0.18	35.53 ± 0.14	4.32 ± 0.21	48.09 ± 0.13	23.00 ± 0.08	20.68 ± 0.25	43.74 ± 0.43	2.70 ± 0.26	3.09 ± 0.39	90.60 ± 0.31	332.72 ±3.20
December 2004	41.43 ± 0.12	36.15 ± 0.33	4.66 ± 0.17	2.64 ±0.42	44.88 ± 0.16	4.54 ± 0.09	51.04 ± 0.02	42.65 ± 0.12	31.78 ± 0.10	63.97 ± 0.19	4.38 ± 0.53	2.92 ± 0.17	121.43 ± 0.22	452.47 ±2.64
January 2005	ND	ND	ND	ND	ND	ND	ND	44.94 ± 0.16	ND	ND	ND	5.97 ± 0.19	96.13 ± 0.97	147.04 ±1.32
February 2005	43.68 ± 0.33	39.12 ± 0.37	12.54 ± 0.12	3.94 ± 0.21	35.50 ± 0.23	2.97 ± 2.09	63.84 ± 0.44	52.93 ± 0.24	23.15 ± 0.24	35.20 ± 0.15	13.39 ± 0.64	3.07 ± 0.36	88.70 ± 0.54	418.03 ±4.32
Dry season mean ± s.d.	29.49 ±20.21	25.13 ±17.78	4.73 ±5.52	1.89 ±1.75	28.98 ±19.82	2.96 ±0.75	40.74 ±28.01	40.88 ±12.71	18.90 ±13.47	35.73 ±26.70	5.12 ±5.80	3.76 ±1.47	99.22 ±15.14	337.52 ±135.57
Range	ND-43.68	ND-39.12	ND-12.54	ND-3.94	ND-51.92	ND-4.54	ND-63.84	ND-52.93	ND-50.72	ND-63.97	ND-13.39	0.57-8.29	40.78-121.43	147.04-452.27

Table 6. Bioconcentration factor (BCF) of OCPs in fish from the pond water of Oke-Osun Farm Settlement, Osogbo, Nigeria.

OCPs	α-BHC	β-BHC	γ-BHC	Heptachlor	Aldrin	Chlordane	p, p'-DDE	o, p'-DDD	p, p'-DDD	Dieldrin	Endrin	Endosulfan	p, p'-DDT
Rainy season BCF	1.10	1.72	0.06	0.06	1.76	0.08	1.02	0.22	2.00	1.42	0.01	0.12	1.79
Dry season BCF	4.95	93.07	0.56	0.32	2.84	0.40	2.89	4.00	2.54	2.07	0.47	0.34	8.04

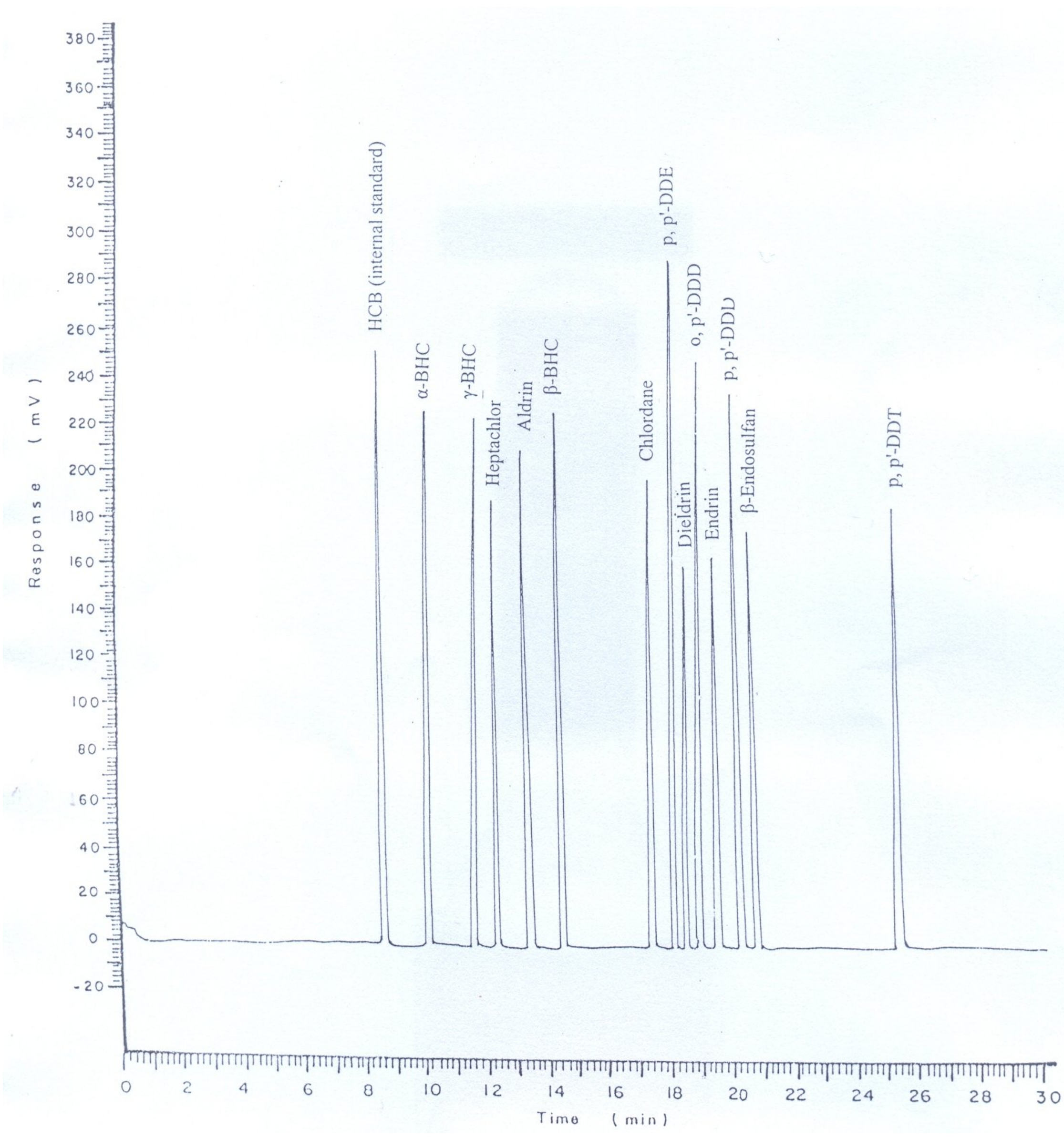

Figure 2. Representative chromatogram of the organochlorine pesticides (OCPs) standards.

Table 7. Matrix of Correlation Coefficients of OCPs in Fish from Oke-Osun Farm Settlement, Osogbo, Nigeria.

	α – BHC	β - BHC	γ – BHC	Heptachlor	Aldrin	Chlordane	p, p'- DDE	o, p'- DDD	p, p'- DDD	Dieldrin	Endrin	Endosulfan	p, p'- DDT
α - BHC	1.00												
β – BHC	0.49	1.00											
γ – BHC	0.50	0.68	1.00										
Heptachlor	0.67	0.34	0.77*	1.00									
Aldrin	0.56	0.86*	0.64	0.46	1.00								
Chlordane	0.23	0.73*	0.42	0.14	0.91*	1.00							
p, p'- DDE	0.62	0.79*	0.89*	0.64	0.58	0.30	1.00						
o, p'- DDD	0.48	-0.07	0.05	0.11	0.08	-0.02	0.07	1.00					
p, p'- DDD	0.64	0.23	0.47	0.84*	0.24	-0.11	0.54	0.04	1.00				
Dieldrin	0.60	0.71*	0.95*	0.81*	0.64	0.34	0.91*	0.12	0.59	1.00			
Endrin	0.56	0.71*	0.98*	0.76*	0.70*	0.45	0.89*	0.20	0.46	0.97*	1.00		
Endosulfan	0.32	-0.41	-0.29	0.17	-0.36	-0.56	-0.15	0.59	0.46	-0.08	-0.19	1.00	
p, p'- DDT	0.46	0.56	0.40	0.12	0.50	0.34	0.45	0.53	-0.14	0.51	0.54	-0.01	1.00

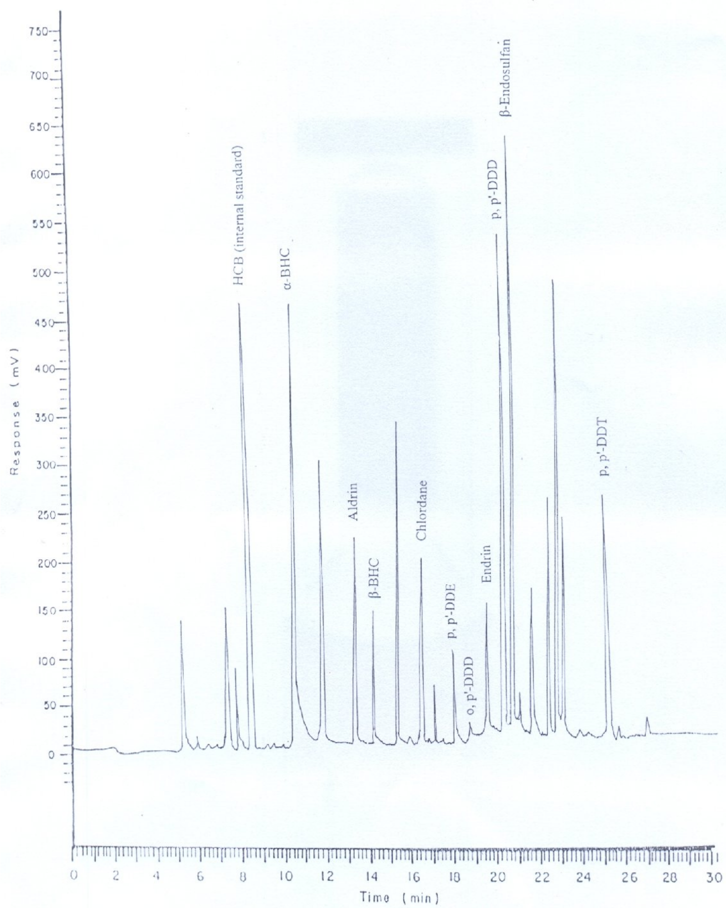

Figure 3. Representative chromatogram of the organochlorine pesticides (OCPs) in pond water.

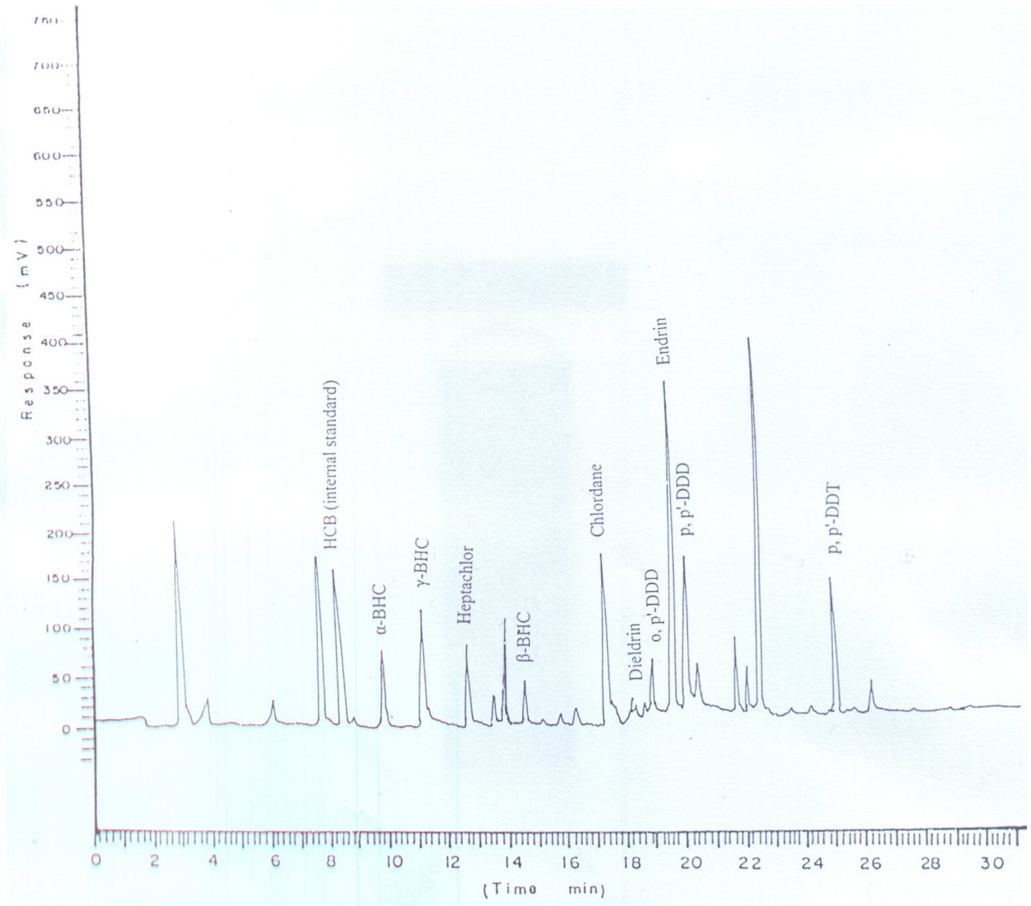

Figure 4. Representative chromatogram of the organochlorine pesticides (OCPs) in fish.

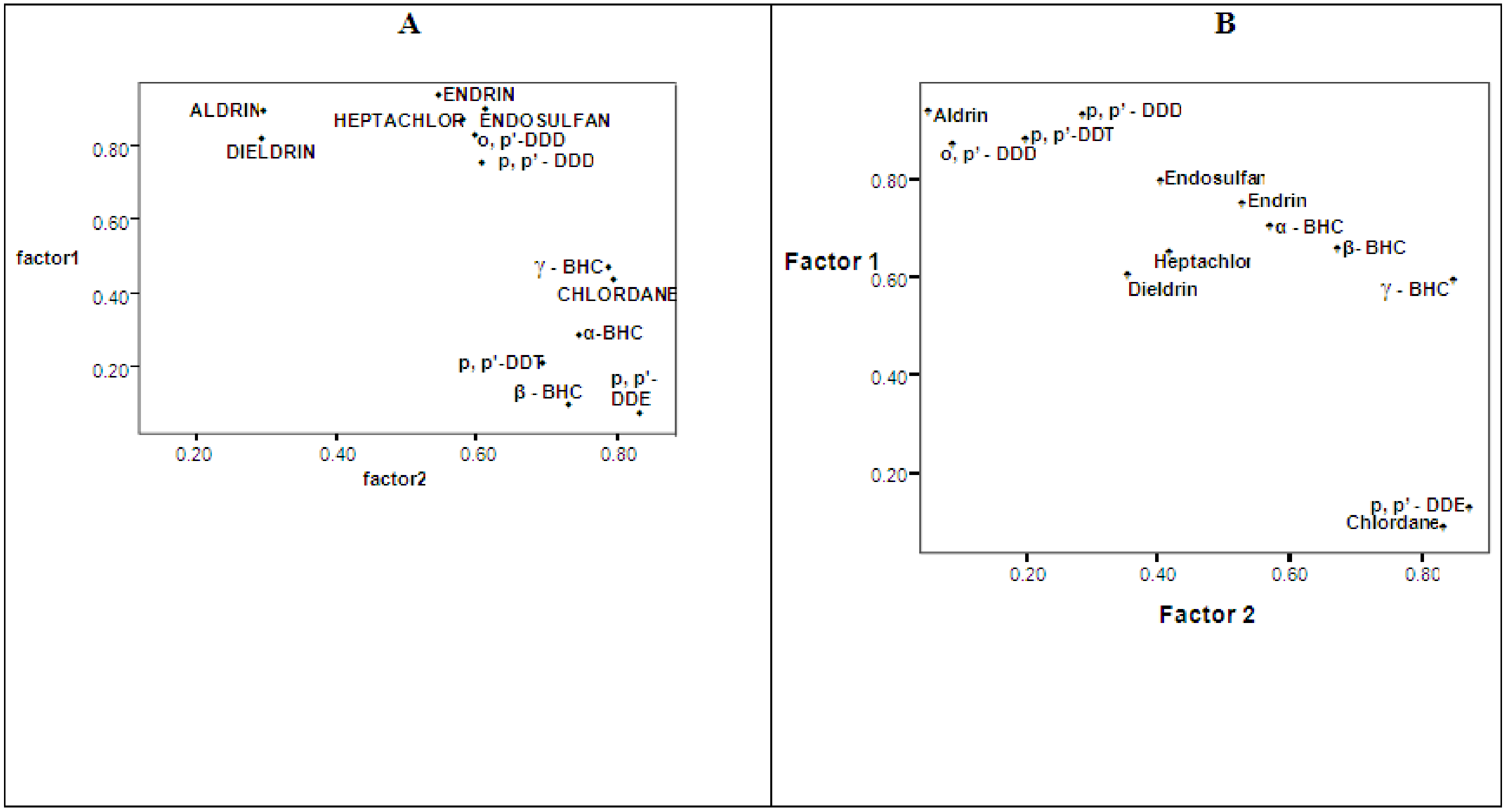

Figure 5. Cluster analyses for OCPs in pond water (A) and Fish sample (B) from Oke Osun farm settlement, Osogbo, Nigeria.

Levels of OCPs in pond water during the rainy season are presented in Tables 2 (a-d). While the monthly mean levels in µg/L ranged from chlordane 2.63 (3.50) in May to p, p'-DDE 85.12 (26.35) in June, the seasonal mean had a range between chlordane 12.42 (12.75) and o, p'- DDD 39.60 (36.61) in the pond water. Agunloye (1984) and Tongo (1985) studied the occurrence and levels (µg/L) of chlorinated hydrocarbons in water of rivers and lakes in Southern Nigeria and obtained for lindane (ND - 167), adlrin (ND - 190), endosulfan (ND - 750), HCB (ND - 9.2) and heptachlor (ND - 96). Ogunlowo (1991) studied the OCPs levels in 9 rivers in Ondo state and obtained a range of ND to 2150 ng/L for lindane, heptachlor, endrin, aldrin and dieldrin. The results obtained in the present study showed that the presence of these pesticides in the pond water occurred at levels comparable to or in some cases higher than those of the earlier workers mentioned above who used similar methods and instrumentation for the analysis of OCPs. The OCPs: α-BHC, p, p'- DDE, o, p'- DDD, dieldrin, endrin, endosulfan and p, p'-DDT occurred in 100% of the pond water samples; γ-BHC, heptachlor, chlordane and p,p'- DDD occurred in 91.7% of the pond water samples while aldrin and β-BHC respectively occurred in 83.3% and 66.7% of the pond water samples studied.

Tables 3 (a - d) represents the dry season levels of OCPs in the pond water. The lowest monthly mean level in µg/L, ND, was recorded for β-BHC in November, January and February and chlordane in November while the highest monthly mean level of 24.90 (8.76) µg/L was recorded for dieldrin in February. For the dry season mean level, the OCPs levels ranged between β - BHC 0.27 (0.90) and dieldrin 17.24 (8.71) µg/L. The results showed higher values in comparison to the values of α - and β - BHC (1 - 302 ng/L), lindane (7 - 297 ng/L), aldrin (ND - 19 ng/L), heptachlor (4 - 202 ng/L) and total DDT (ND - 1266 ng/L) reported by Nwankwoala and Osibanjo (1992) for surface waters in Ibadan. The values obtained in this study, however, were quite higher than the values obtained in one of the earliest studies on River Nile (El-Sebae and Abu-Elamayen, 1979) in which the levels of lindane, heptachlor, o,p'- DDT and p,p'-DDT ranged between 100 and 950 ng/L in all the water samples. The concentration levels of OCPs in the pond water suggested the use of the pesticides in the recent past despite the fact that some of the OCPs detected such as DDT had been outlawed since 1990 (FEPA, 1991).

The matrix of correlation coefficients of the OCPs in the pond water at 0.05 levels in Table 4 showed positive significance of 92.2% for all the correlated items. The pesticides with significant positive correlations likely shared common sources and were probably affected by related factors in the aquatic environment. Table 5 contains a list of the mean levels of OCPs (in µg/kg) in fish samples on a monthly basis. The rainy season monthly mean values of OCPs (µg/kg) in fish ranged from endrin 0.30 ± 0.35 to p, p'- DDT 64.90 ± 17.34 with a total mean body burden of 284.47 ± 37.52 µg/kg. On the other hand, during the dry season, the monthly mean values of OCPs (µg/kg) in fish ranged between 1.89 ± 1.75 of heptachlor to 99.22 ± 15.14 of p, p'- DDT with a total OCPs body burden of 337.52 ± 135.57 µg/kg. α-BHC, endosulfan and p, p'-DDT were found in all (100%) of the fish samples; β-BHC, γ-BHC, aldrin, p, p'-DDE, p, p'-DDD and dieldrin in 87.5% of the samples; heptachlor and o, p'-DDD in 75.0% of the samples; and chlordane and endrin in 62.5% of the samples.

The levels of OCPs detected in the fish samples of the present study, were in most cases relatively higher than the values obtained by Amakwe (1984) in freshwater fish samples collected from various locations in Oyo and Ogun states of Nigeria in which lindane (7 - 106.0); p, p' - DDE (2.0 - 30.0); p, p' - DDD (2.0 - 60.0); p, p'-DDT (3.0 - 18); total DDT (3.3 - 161); heptachlor (1.0 - 300); endosulfan (3 to 904); and α - HCH (0.2 - 5.0) were detected at ng/kg levels. However, the results of the present study for levels of OCPs in fish compared well with those of Fayomi (1987): α - HCH (1.0); aldrin (ND - 14.9); p,p'-DDE (ND - 4.2); DDD (ND - 8) µg/kg; Osibanjo and Bamgbose (1990): HCB (0.04 - 9.48); lindane (ND - 5.30); endosulfan (ND - 4.95); DDT (0.15 - 18.6); aldrin (ND - 54.60) µg/kg; and those of Manirakiza *et al.* (2002): HCB (5.4 - 81.5), heptachlor (ND - 13.1), aldrin (ND - 0.2), p, p' - DDE (6.7-197.5), o, p' - DDD (ND - 12.1), p, p' - DDT (ND - 31.6), dieldrin (ND - 7.1), endrin (ND - 14.4) and endosulfans (1.5 - 49.7) µg/kg. Figures 3 and 4 are representative chromatograms for OCPs detected in the raw pond water and fish samples respectively. The bioconcentration factors (BCF) of OCPs for fish in the two seasons are listed in Table 6. The values ranged from 0.01 (endrin) to 2.00 (p, p' - DDD) in rainy season and from 0.32 (heptachlor) to 93.07 (β - BHC) in dry season. Although the levels of OCPs in the pond water were higher during the rainy season, the BCF was higher in all the cases considered during the dry season. This, by implication, means that the fish samples were more contaminated with OCPs during the dry season than in the rainy season. The higher dry season levels of

OCPs in fish (Table 5) generally might be due to their feeding more on insect larvae, coarse vegetable matters and sediment-associated particles that had accumulated the OCPs overtime. The mean seasonal levels of OCPs in the fish were higher, in most cases, than the recommended WHO Maximum Residue Levels (MRLs) in food items. For example, γ-BHC (lindane) and dieldrin with WHO MRLs of 6.0 μg/kg (Darko and Acquaah, 2007) occurred in this study at 25.02 and 27.47 μg/kg levels respectively during the rainy season and at 8.48 and 17.24 μg/kg levels respectively during the dry season. However, the levels of DDT in the fish samples were generally lower than the 500 μg/kg WHO MRLs (Darko and Acquaah, 2007).

The matrix of correlation coefficients of OCPs in fish samples (Table 7) showed significant positive correlations at 0.05 level for β - BHC and aldrin, chlordane, p, p' - DDE, dieldrin and endrin; γ - BHC and heptachlor, p, p' - DDE, dieldrin and endrin; heptachlor and p, p' - DDD, dieldrin and endrin; heptachlor and p, p' - DDD, dieldrin and endrin; p, p' - DDE and dieldrin and Endrin; and dieldrin and endrin.

Cluster analysis, a method for dividing a group of objects into classes so that similar objects are in the same class (Miller and Miller, 2000), was applied in this study to see the possible association of the OCPs. Three clusters of OCPs were found (Figure 5 A) in the pond water: aldrin, o,p'- DDD, p,p'-DDT and p,p'-DDD; endosulfan, endrin, α-BHC, β-BHC, γ-BHC, heptachlor and dieldrin; and p,p'-DDE and chlordane, which shows that each of the three classes of compounds are associated. Their presence in the samples may be due to factors such as transportation of applied OCPs by surface run-off from the nearby agricultural soils into the pond, formation of the metabolites of OCPs and careless handling and disposal of materials contaminated with the OCPs e.g. washing of empty OCPs containers into the pond water after application by the farmers. For the fish, feeding directly on contaminated food items within the pond or drinking of contaminated water and metabolite formation within and outside the body tissue of fish are considered to be the likely factors responsible for the presence of the three clusters of OCPs observed (Figure 5 B). The observed clusters in fish are: aldrin and dieldrin; endrin, heptachlor, endosulfan, o,p'-DDD, and p,p'-DDD; γ-BHC, chlordane, p,p'-DDT, α-BHC, β-BHC and p,p'-DDE. The occurrence of OCPs in water and fish from the pond of Oke Osun Farm settlement is consistent with the agricultural activities of the study area due to pesticide usage by the farmers for the control of weeds and pests. Some of the pesticides found in the matrices like chlordane, endosulfan, DDE and DDT have been implicated to have endocrine disrupting properties which may greatly impact on the bio-diversity of the aquatic ecosystem.

Conclusion

In conclusion, this study has shown that pond water and fish samples from Oke Osun farm settlement are contaminated with OCPs in varied degrees in both dry and wet seasons.

Higher levels of OCPs were recorded in the pond water during the rainy season with a mean range of 12.42 ± 12.75 μg/L chlordane – 39.60 ± 36.61 μg/L o,p'-DDD than the dry season with a mean range of 0.27 ± 0.90 μg/L β-BHC – 17.24 ± 8.71 μg/L dieldrin. Conversely, however, higher levels of OCPs were found in the fish samples in the dry season than during the rainy season due to possible greater bioaccumulation tendency in the fish species during the dry season. Generally, the mean seasonal levels of OCPs in the fish were higher, in most cases, than the recommended WHO Maximum Residue Levels (MRLs) in food items and should give cause for concern. Occurrence of the OPCs in fish and water from the pond is consistent with the agricultural activities of the study area due to pesticide usage by the farmers. Further work on pesticide residues in blood serum of the farmers and municipal water sources of the study area is recommended.

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