

Assessment of Persistent Organochlorine Pesticide Residues in Commercially Important Fin and Shell Fishes of River Majidun, Lagos, Nigeria

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Authors' contributions

This work was carried out in collaboration among all authors. Author OCE designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors OAA and PNE managed the analyses of the study while, author MOO managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Aim: The pesticide pollution of aquatic ecosystems has developed serious environmental anxiety, provoking a necessity for continuous evaluation of harmful constituents.

Study Design: A quantitative cum descriptive experimental design was used to evaluate the occurrence and concentration of Persistent Organochlorine Pesticides (POPs) in water, sediment, fish (*Tilapia zilli* and *Chrysichthys nigrodigitatus*) and shell fishes (*Macrobrachium vollenhovenii*, *Littorina littorea* and *Callinectes pallidus*) of River Majidun, Lagos, Nigeria.

Place and Duration of Study: Nigerian Institute of Oceanography and Marine Research (NIOMR) between June and December, 2019.

Methodology: Sediment samples were collected by the Rigosha grab sampler and fish samples were purchased from commercial fishermen. Sample preparation was done according to the Environmental Protection Agency (US EPA) 3570 method. POPs were evaluated using Hewlett Packard 5890 series II gas chromatography with electron capture detector.

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Results: Twenty-one organochlorine residues were identified including p'p'DDT, Lindane (γ -HCH), Dieldrin, Heptachlor, Aldrin, Chlordane, Endrin aldehyde, Endrin ketone, Methoxychlor and Endosulphan. Concentrations in water ranged between $0.03 \mu\text{g l}^{-1}$ (Endrin ketone) and $1.97 \mu\text{g l}^{-1}$ (Methoxychlor). In sediment, it is between $4.55 \mu\text{g kg}^{-1}$ (β -HCH) and $128.25 \mu\text{g kg}^{-1}$ (Methoxychlor). In *Macrobrachium vollenhovenii*, Methoxychlor was $123.83 \mu\text{g kg}^{-1}$ and Lindane (γ -HCH) was highest here ($39.35 \mu\text{g kg}^{-1}$). *Callinectes pallidus* had a high concentration of Endrin ketone ($133.13 \mu\text{g kg}^{-1}$). The *Tilapia zilli* highest concentration was $110.35 \mu\text{g kg}^{-1}$ (endrin ketone) and it had the highest pp'DDT which was $41.40 \mu\text{g kg}^{-1}$.

Conclusion: Evidently, there was sequestration of POPs from water into sediment and bioaccumulation in the organisms, due to exposure. The level of POPs in all samples were below the limits of $200 \mu\text{g kg}^{-1}$ fresh weight in fish and sea food set by Codex Alimentarius Commission by FAO/WHO. The attendant environmental/human menace cum inherent danger of the raised levels of POPs, calls for continuous monitoring of River Majidun.

Keywords: River; pesticides; sequestration; bioaccumulation; commercial; shell fish; fin fish.

1. INTRODUCTION

The Persistent Organochlorine Pesticides (POPs) have been used worldwide for several decades. While numerous are barred, a number of countries in Africa still utilize POPs mainly aimed at deterrence of malaria in the forms of insecticides, rodenticides and herbicides. POPs remain categorized by dint of their ability to persist in the environment and bio-accumulate / bio-magnify in organisms of the food chain, through which they ultimately find their way to the human body. Organochlorine compounds are synthetic organic insecticides that contain carbon, hydrogen, chlorine and sometimes oxygen. The active ingredient in organochlorine insecticides is the presence of carbon-chlorine bonds [1]. Generally, they are precursors to either Central Nervous System (CNS) depression or stimulation, contingent upon the type and dose leading to both acute illness (short time after exposure) and chronic illness (after prolonged sub-lethal exposure) [2]. There are mainly 5 groups of POPs including: Dichlorodiphenyltrichloroethane (DDT) and equivalents (eg, dicofol, methoxychlor); Hexachlorocyclohexane (benzene hexachloride) and isomers (lindane, gamma-hexachlorocyclohexane); Cyclodienes (chlordane, heptachlor, aldrin, dieldrin, endrin, endosulfan, isobenzan); Chlordecone, kelevan, and mirex; and Toxaphene. Conspicuously among POPs) is the dichlorodiphenyltrichloroethane (DDT). Organochlorine insecticides had existed as the most utilized pesticide but they have now been replaced with organophosphorus insecticides because of their environmental persistence. Other examples of POPs include aldrin,

chlordane, dieldrin, endrin, heptachlor, hexachloro-benzene (HCB). POPs are not easily degradable compounds and it is known that the interval of degradation of dichlorodiphenyl trichloroethane (DDT) in soil is between 4 to 30 years' period, while other chlorinated compounds remain stable for several years after application [1]. The ecological impotunity of organochlorine insecticides has resulted in their prohibition as agrochemicals to control pests in agriculture and formulation of other pesticide products such as mosquito coils [3]. The forbidden organochlorines include Aldrin, Chlordane, Dichlorodiphenyl trichloroethane (DDT), Dieldrin, Endrin, Heptachlor, Hexachloro-benzene (HCB).

Attributable to the position of man in the food chain he is significantly vulnerable to the consequence of ingesting foodstuffs both from polluted soil or aquatic habitat [4,5]. POPs have been associated universally with a wide variety of negative human health problems including chronic convulsions, procreative catastrophes and birth flaws, resistance structure breakdown and endocrine disorders [6].

The aquatic habitat often congregate loads of naturally hazardous wastes and pollutants from both domestic and industrial point and nonpoint sources. Pollution of aquatic habitats by POP residues has been of great anxiety as a consequence of their attendant deleterious effects. The pathways of these chemicals into aquatic environments include leakage from agricultural usages, overflow from sewers, sewage plants, or through nonpoint sources like run offs and abstraction from the atmosphere [7,6,8] thereby increasing POPs absorption and buildup in the food chain through re-suspension.

This promotes fish contamination through ingestion, dermal absorption and respiration.

Hence, this study is geared towards identifying the organochlorine pesticides (POPs) present in River Majidun a freshwater inlet with tidal impacts at its ecotone into the Lagos lagoon, analyzing their concentration in commercially important fish species and evaluating their potential for bio-concentration and bio-magnification in man.

2. MATERIALS AND METHODS

Organochlorine pesticides were analyzed in the water, sediment, fin and shell fish samples using Hewlett Packard 5890 series II gas chromatography with Electron Capture Detector.

2.1 Study Area

This water body is used for domestic purposes, fishing, water transport, and sand dredging, draining its catchment area comprising of residential areas, localized small and medium scale industries. The River Majidun (Fig. 1) is a stretch of freshwater with tidal impacts which covers an area of about 208 km². A greater part of this river is typically not more than 1.5 meters deep [9]. The intersecting rivers are equally not deep and these rivers are known to be locations of vigorous sedimentation and mud deposition.

Majidun River empties into the Atlantic via the Lagos harbor through the Lagos lagoon [9]. The main sea port of Lagos is situated at Apapa off the major strait of the harbor. The western reaches of the river do not have adequate road networks, and several communities there usually depend on water transport. The settlements along river Majidun include Owutu, Falana, Morekete, Abule Igbopa, Ewu, Sarumi, Oripadi, Igbomogun and Oreta. An upsurge in populace plus industrial and economic development of Lagos the commercial center of Nigeria, has given rise to a commensurate generation of numerous categories of wastes and noxious substances into the river.

2.2 Bio-ecology of Studied Species

Most biometric information was obtained from [10]. *Chrysiichthys nigrodigitatus* (Lacepede, 1803) is a catfish of the family Bagridae. It is a tropical (22°C to 28°C) fresh/brackish water specie, preferring a depth between 3 m – 5 m. It is omnivorous (feeding on seeds, insects,

bivalves, detritus). The length at first maturity is 14 cm and could grow up to 65cm. Its fecundity is between 3,086 and 28,086 [11]. The model estimates include Phylogenetic Diversity Index (PD₅₀) has a uniqueness of 0.5 = low to 2.0 = high; Trophic Level = 3.2 ± 0.41 and Resilience showed medium, least recruitment time of 1.4 to 4.4 years [12].

Tilapia zilli (Gervais, 1848) belonging to the family Cichlidae could reach up to 47cm in total length. It is a euryhaline fresh/brackish water specie mainly found inshore within the depth range of 0 to 5m. Its water column position is bottom (benthic) preferring shallow vegetated areas. The Tilapia is an omnivorous specie. The adults are mainly herbivorous while, the juveniles are more carnivorous feeding on zoobenthos. They are demersal, substrate spawners (guarders) within the average price category.

Callinectes pallidus (Rochebrune, 1883) belong to the class Malacostraca, order Decapoda and family Portunidae. They are omnivorous, opportunistic benthic predators with carapace length at first maturity of 4.5 cm and depth range of 2 m to 30 m. Estimates of some properties based on models indicate that their mean preferred temperature is 27°C. They have low vulnerability and very high price category [13].

Littorina littorea (Linnaeus, 1758), the periwinkle, is of the family Littorinidae. Its habitat is on rocky shores, intertidal pools and muddy areas in lagoons and estuaries. It is an omnivorous algal grazer but also feeds on small invertebrates like barnacle larvae and is of high commercial value with a medium price category [13].

Macrobrachium vollenhovenii (Herklots, 1857) is a tropical Palaemonid decapod that is endemic to eastern Atlantic in west Africa from Cape Verde and Senegal to southern Angola. The African river prawn is a catadromous, commercially important, highly priced omnivorous species which feeds on diatoms, rotifer, protozoans and insects [10].

2.3 Sample Collection and Preparation

Surface water samples were collected using 1Litre amber glass bottles. All glass bottles to be used were cleaned with liquid soap, thoroughly rinsed by distilled water, and were oven dried at a temperature of 130°C for thirty (30) minutes to minimize contamination.

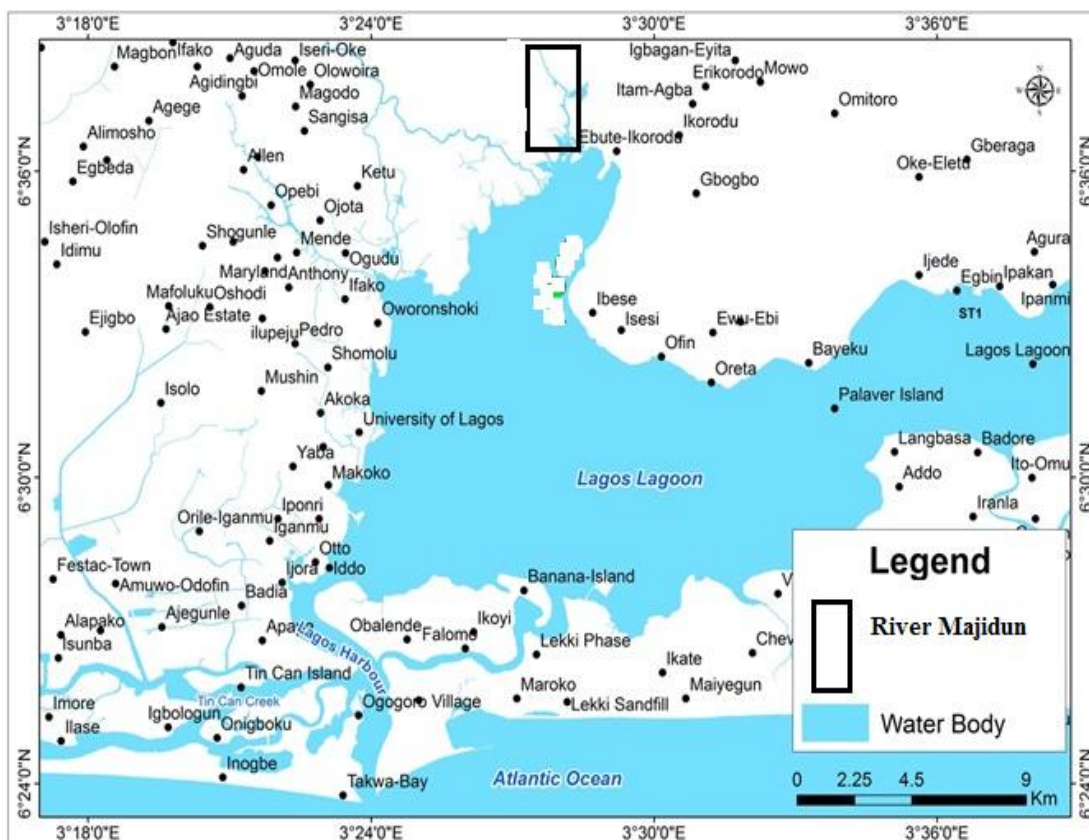


Fig. 1. Showing the Lagos relief map indicating Majidun river

Both water, sediment samples were collected from the upstream, midstream and downstream sections of River Majidun between June and December, 2019. Sediments were collected from the 0 – 3 cm depth using a Rigosha sediment sampler. The sediments were wrapped in aluminum foil and placed in an opaque (black) polyethylene bag. Samples were placed in ice pack chests and kept cool during transportation to the laboratory. The dried sediment samples were sieved through a 2.0 mm stainless steel sieve after which the less than 63 μ m obtained soil samples were prepared with the aid of the 63 μ m stainless steel sieve before analysis.

Six specimen from the sampled fin fish (*Chrysichthys nigrodigitatus* and *Tilapia zilli*) with six each of the shell fishes (*Callinectes pallidus.*, *Macrobrachium vollenhovenii.* and *Littorina littorea*, were bought from commercial fishermen at the fish landing site on River Majidun. The samples were obtained monthly between June and December 2019. The fin fish, and shell fish samples were refrigerated while the water samples were preserved using formalin.

All materials and chemicals used, were carefully prepared for the extraction process.

2.4 Extraction of Water and Sediment

A slightly modified Method 3570 as described by US EPA 2002 was used to extract the pesticide residues in the water samples [14]. 20 ml of dichloromethane (DCM) was introduced into the separating funnel containing 200 ml of water sample from each of the sampled station and shaken vigorously for about 2 minutes at a moderate speed of 200 agitations per minute. Each time after a period of 60 seconds, pressure was released from the outlet. After shaking for about 5 minutes, it was allowed to stand for 10 minutes so that the solvent settles at the bottom of the flask. 30ml of DCM was added to the remaining water sample and shaken vigorously again for 5minutes The sample was allowed to settle for 30 minutes to ensure separation of the phases. After separation, the organic layer was filtered into a 250 ml conical flask that has been prewashed with DCM through anhydrous sodium sulphate (Na_2SO_4). The extractions were

repeated twice using a 50ml portion of dichloromethane and later combined. The combined organic extracts were concentrated using a rotary evaporator at 45°C and low pressure. 5 ml of n-hexane was added to the extract in DCM to exchange the solvent. This was also allowed to stand for complete separation and after 5minutes; the extract was decanted and added to the extract in the round bottom flask. The whole extract was gently mixed together and left to stand for 10minutes. DCM was added to the mixed dense extract and allowed to stand for another 10minutes after which it was filtered using a glass-fiber filter, Gelman type A, to obtain a clear solution (extract).

About 10 g of sediment samples were weighed and moved into an extraction thimble that had been initially washed with n-hexane / acetone and oven dried. The sample was extracted using 100 mL of n-hexane acetone mixture 4:1 v/v for eight hours. The combined organic extract was evaporated using a rotary evaporator at 45°C and low pressure. The extracts were further concentrated to 1-2 ml until no further DCM remained in the extract.

2.5 Reduction of Water Extract Volume

The obtained extract was poured into a conical flask attached to an initially-weighed receiver via a Liebig condenser, which was attached to a rotary evaporator. The bath was filled with water and placed under the attached conical flask, heated for about 10 minutes and maintained at 90° C to reduce the volume of the water extract through evaporation. A little volume of the extract was left in the conical flask (0.5ml from Majidun River sample station).

2.6 Extraction of Fin and Shell Fishes

The fish samples were prepared by the method described by [1] with a slight modification. The samples were put on aluminum foil and the scales of the red belly *Tilapia* fish were neatly removed. To get the fish flesh, the fish samples were dissected and filleted. The fillets were covered in well labeled aluminum foil then weighed with a Mettler Toledo Balance, model JS6002 G/A with a readability of 0.01 g. This process was repeated for the scale less silver catfish samples. Individually, the fish meat was weighed, and homogenized using an agate mortar and pestle. Approximately 20 g of this properly homogenized sample was mixed with 10 g of anhydrous sodium sulphate (Na_2SO_4).

This was extracted for eight hours using dichloromethane: n-hexane (1:1 v/v) 40 ml mixture and concentrated to about 2 ml in a rotary evaporator at 40° C.

The shell fish was placed on an aluminum foil paper and opened up to take out the carapace, which was detached to expose the meaty chunk, weighed and enclosed in labeled aluminum foil. This same procedure was repeated for other shell fish samples.

2.7 Extraction of Fats from Fin and Shell Fish Flesh

A glass wool (filter-like in nature) was inserted into a burette and a spatula was used to fill the burette with the homogenous blend. The burette was then clamped to a retort stand and a beaker was placed under the clamped burette to collect the extract. A combination of acetone and petroleum ether was utilized for fat abstraction. The acetone/petroleum ether (1:1 v/v) combination (30ml) was combined to the homogenized flesh in a burette and the mixture was immersed in the chemical combination. After a time lag ten (10) minutes, extra 70ml of the chemical combination was added. Drop after drop for over one hour, the extract was made to drip into the beaker. This extract was decanted into a flask with round bottom which was linked to an initially weighed container via a Liebig condenser, and drained to approximately 10ml on a water bath sustained at a temperature of 90° C. A rotary evaporator was used to vaporize the residual solvent in the concentrated extract, leaving the fat extract of shell fishes in the container.

2.8 Separation and Clean-Up of Compounds

Separation and cleanup of compounds was as described by [15].

2.9 Determination and Identification of Organochlorine Pesticide (OCP)

POPs were evaluated using Hewlett Packard 5890 series II gas chromatography with electron capture detector. Analytical standards that were > 98% purity were utilized for fortification and standard solutions. Validation of POPs was achieved by means of a gas chromatograph / mass spectrometer (Shimadzu QP2010) and capillary column type HP1MS (30 m × 0.25 µm × 0.25 mm id) under the conditions described by

[15]. Peaks were nil when blanks and solvents were chromatographed, before the samples were screened under same conditions. Known standards, were also chromatographed. The compounds were sorted by signal with automatic injection volume. Identification of compounds in samples was done using retention time.

Calculation

Weight of sample analyzed were: Shrimp = 2g, Water = 200ml, Sediment = 3g, Crab = 2g, Periwinkle = 2g and Tilapia = 2g

Concentration of OCP in Sample Extracts ($\mu\text{g Kg}^{-1}$ or $\mu\text{g L}^{-1}$) = $\frac{\text{Concentration (ppm)} \times 1000}{\text{Weight of sample}}$

2.10 Statistical Analysis

The statistical analysis was carried out with the Statistical Package for Social Sciences (SPSS) model 20.

3. RESULTS

The study on Organochlorine pesticide (OCP) in River Majidun showed a number of results in all of the screened samples. The cumulative total of all POPs in these frequently consumed species was highest in *Macrobrachium vollehenovii* at $792.98 \mu\text{g kg}^{-1}$ (Table 1). The analyzed water sample showed that γ -HCH had the lowest concentration ($0.03 \mu\text{g/l}$), The sequence of concentrations of Lindane (γ -HCH) and its isomers in the Majidun River water are β -HCH > α -HCH > δ -HCH > γ -HCH while methoxichlor was highest at $1.97 \mu\text{g/l}$. The highest DDT metabolite in water was pp'DDD at $0.64 \mu\text{g l}^{-1}$ while p'p' DDE was $0.031 \mu\text{g l}^{-1}$.

Sediment from River Majidun contained various OCPs which included agrochemicals (DDT and Lindane) with their metabolites. The sequence of concentrations of DDT and its metabolites in water was DDD > DDT > DDE The highest concentration observed was ($128.64 \mu\text{g kg}^{-1}$) for methoxychlor and the lowest ($58.6 \mu\text{g kg}^{-1}$) for β -HCH. Sediment showed an evidence of sequestration of all POPs from the water compartment where the overall highest POP recorded was methoxychlor ($128.25 \mu\text{g kg}^{-1}$) and the lowest was β -HCH ($4.55 \mu\text{g kg}^{-1}$). (Fig. 2). The sequence of concentration of HCH and DDT with their metabolites in River Majidun sediment were α -HCH > γ -HCH > δ -HCH > β -HCH and DDD > DDT > DDE respectively.

In *M. vollehenovii* there was a glaring evidence of bioaccumulation. While β -HCH was below detection in the African river prawn. Methoxychlor had the highest concentration ($123.83 \mu\text{g/kg}$) and the lowest is endrin aldehyde ($12.2 \mu\text{g kg}^{-1}$). Others, including aldrin ($48.10 \mu\text{g kg}^{-1}$), α chlordane ($28.80 \mu\text{g kg}^{-1}$), α -HCH ($64.05 \mu\text{g kg}^{-1}$), lindane = γ -HCH ($39.35 \mu\text{g kg}^{-1}$) and heptachlor ($66.10 \mu\text{g kg}^{-1}$) were higher in the prawn than other shell fish samples (Fig. 3). Here, the order of concentration of Lindane and DDT with their metabolites were α -HCH > γ -HCH > δ -HCH > β -HCH and DDE > DDT > DDD respectively.

POP residues were observed to be significant in *Littorina littorea* (Periwinkle). Methoxychlor, α -HCH, γ -HCH, Endrin Aldehyde, Dieldrin, p'p' DDT and α -chlordane had the following concentrations of $68.9 \mu\text{g kg}^{-1}$, $54.45 \mu\text{g kg}^{-1}$, $35.90 \mu\text{g kg}^{-1}$, $29.45 \mu\text{g kg}^{-1}$, $26.6 \mu\text{g kg}^{-1}$ and $22.45 \mu\text{g kg}^{-1}$ respectively. The lowest recorded pesticide residue in the periwinkle is β -HCH ($7.95 \mu\text{g kg}^{-1}$). The order of concentration in Lindane and its metabolites was α -HCH > γ -HCH > δ -HCH > β -HCH while that of DDT was DDE > DDT > DDD.

In *Callinectes pallidus*, the concentration of Endrin ketone ($133.93 \mu\text{g kg}^{-1}$), was highest while, the concentration of Methoxychlor and p'p' DDD, reduced in the order of ($94.03 \mu\text{g kg}^{-1}$) and ($62.8 \mu\text{g kg}^{-1}$), respectively. The lowest POP residue in *C. pallidus* was in δ -HCH at ($6.13 \mu\text{g kg}^{-1}$) (Fig. 3). The order of concentration in Lindane and its metabolites was β -HCH > γ -HCH > α -HCH > δ -HCH and that of DDT was DDD > DDE > DDT.

Endrin ketone ($110.35 \mu\text{g kg}^{-1}$) was the highest POP residue in *Tilapia zilli*. Some others reduced in the order of methoxychlor ($84.15 \mu\text{g kg}^{-1}$), endosulphan sulphate ($70.90 \mu\text{g kg}^{-1}$), δ -HCH ($49.60 \mu\text{g kg}^{-1}$), p'p' DDT ($41.40 \mu\text{g kg}^{-1}$) and Endrin Aldehyde ($38.55 \mu\text{g kg}^{-1}$). All POPs were generally higher in *T. zilli* than in *C. nigrodigitatus* except endosulphan II, γ -chlordane and α -HCH. In *C. nigrodigitatus*, Endosulfan II ($75.00 \mu\text{g kg}^{-1}$) was the highest POP closely followed by Endrin ketone ($71.33 \mu\text{g kg}^{-1}$). The lowest value observed was ($5.97 \mu\text{g kg}^{-1}$) for Beta-HCH, (Fig. 4). While the series of concentration of Lindane and DDT with their metabolite in *T. zilli* was δ -HCH > γ -HCH > β -HCH > α -HCH and DDD > DDE > DDT, in *C. nigrodigitatus* it was δ -HCH > α -HCH > γ -HCH > β -HCH and DDT > DDE > DDD.

Table 1. Showing the mean residues of Persistent Organochlorine Pesticides in water, sediment, *Macrobrachium vollenhovenii*, *Litorina Litorea*, *Callinectes pallidus*, *Tilapia zilli* and *Chrysichthys nigrodigitatus* from river Majidun within the period of study

Persistent Organochlorine Pesticides (POPs)	Water ($\mu\text{g L}^{-1}$)	Sediment ($\mu\text{g kg}^{-1}$)	(African River Prawn) <i>Macrobrachium vollenhovenii</i> ($\mu\text{g kg}^{-1}$)	(Periwinkle) <i>Littorina Littorea</i> ($\mu\text{g kg}^{-1}$)	(Crab) <i>Callinectes pallidus</i> ($\mu\text{g kg}^{-1}$)	<i>Tilapia Zilli</i> ($\mu\text{g kg}^{-1}$)	(Silver catfish) <i>Chrysichthys nigrodigitatus</i> ($\mu\text{g kg}^{-1}$)
Aldrin	0.18	28.55	48.10*	19.40**	31.23	32.95	21.03
Alpha (α)- chlordane	0.18	26.95	28.80*	22.45	20.93	21.50	8.20**
Gamma (γ)-chlordane	0.16	17.05	12.80	19.25	21.67*	6.75**	18.60
Alpha (α)-HCH	0.10	37.40	64.05	54.45	14.97	8.95	23.03
Beta (β) HCH	0.14	4.55	BD	7.95	32.80	12.05	5.97
Gamma (γ)- HCH (Lindane)	0.03	31.55	39.35*	35.90	27.20	21.70	8.13**
Delta (δ)-HCH	0.04	27.75	36.95	10.80	6.13**	49.60*	32.30
Dieldrin	0.32	45.65	43.45*	29.05	21.17	32.70	20.97**
Endrin	0.25	22.45	20.60	21.45*	12.13**	18.05	13.97
Endrin Aldehyde	0.34	8.95	12.20**	29.45	20.57	38.55**	14.50
Endrin ketone	0.19	16.90	15.15	19.60	133.13	110.35	71.33
Endosulfan Sulfate	0.20	41.15	34.25	12.90	11.67**	70.90*	22.70
Endosulfan I (endo)	0.23	20.05	41.40*	16.80**	28.50	26.95	18.70
Endosulfan II (exo)	0.29	31.85	31.55	11.80*	45.07	52.60	75.00*
Heptachlor	0.12	10.30	66.10*	16.60	48.40	16.45	12.17
Heptachlor epoxide	0.14	46.85	55.90*	14.50	6.60**	10.80	10.73
p,p' DDD	0.64	58.60	32.90	18.95	62.80	28.20	16.20
p,p' DDE	0.30	48.84*	45.45	21.10	20.50	20.45	14.03**
p,p' DDT	0.05	39.20	39.75	26.60	20.23**	41.40*	25.87
Methoxychlor	1.97	128.25*	123.83	68.90	94.03	84.15	39.37**
Total	7.94	692.64	792.98*	477.90	679.73	705.05	437.60**

BD = Below Detection; * = Highest; ** = Lowest

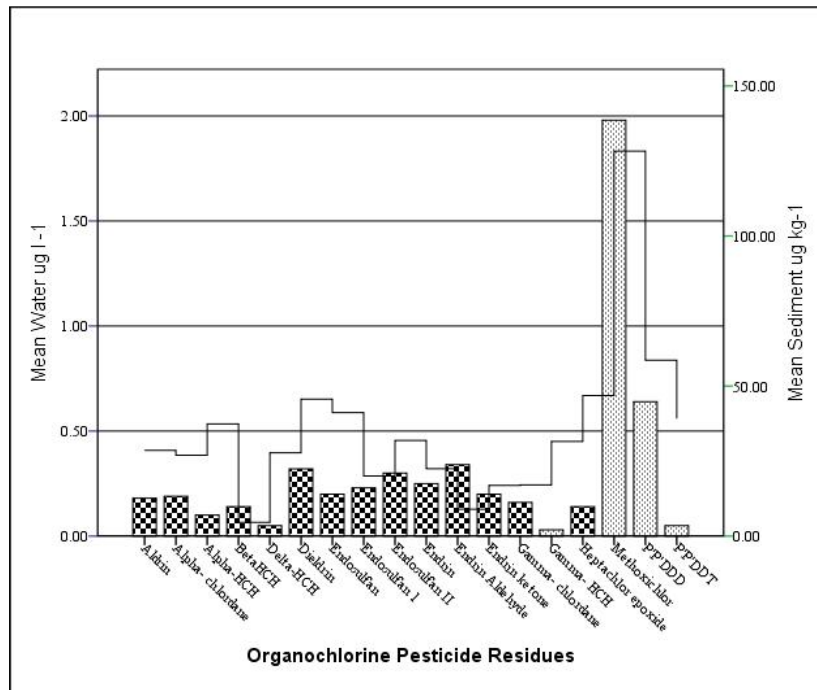


Fig. 2. Showing the mean concentration of persistent organochlorine pesticide residues in water and evidence of sequestration in sediment of River Majidun within the period of study

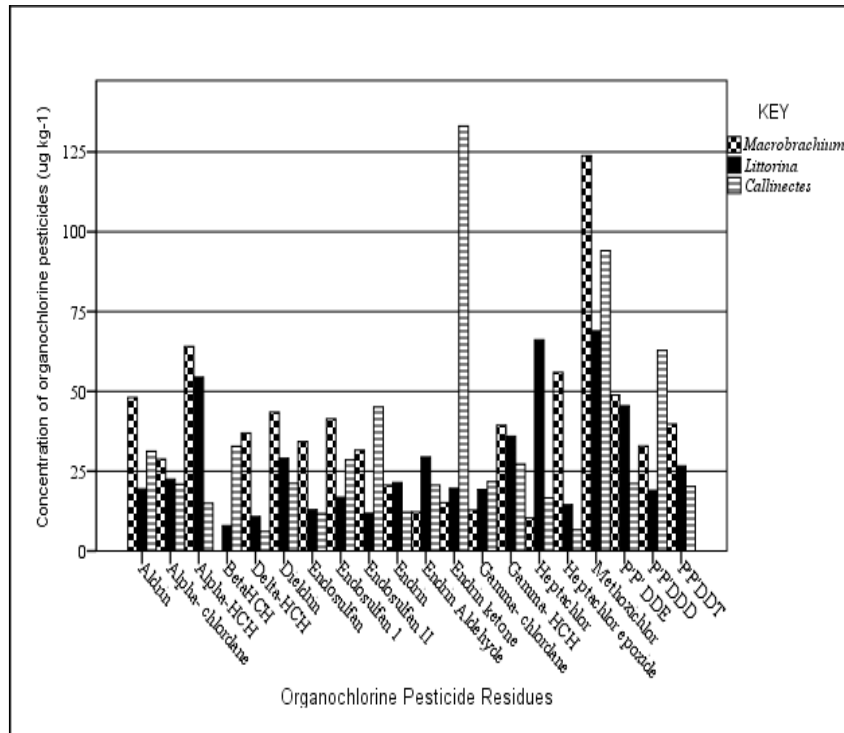


Fig. 3. Showing the relative mean concentration of organochlorine pesticide residues in the three shell fishes (*Macrobrachium vollehoventii*, *Littorina littorea* and *Callinectes pallidus*) of River Majidun within the period of study

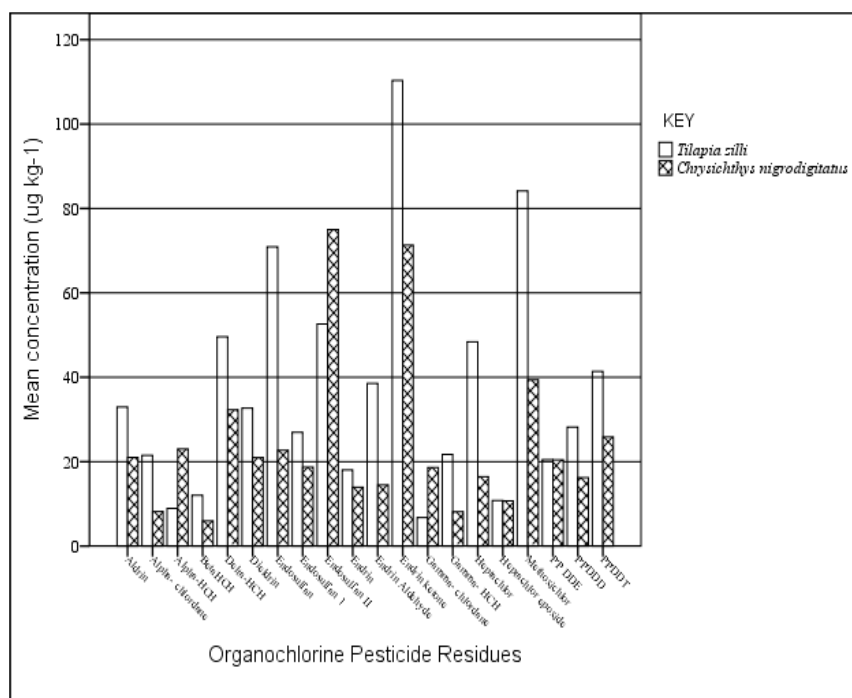


Fig. 4. Showing the relative mean concentration of organochlorine pesticides residues in *Tilapia zilli* and *Chrysichthys nigrodigitatus* of River Majidun within the period of study

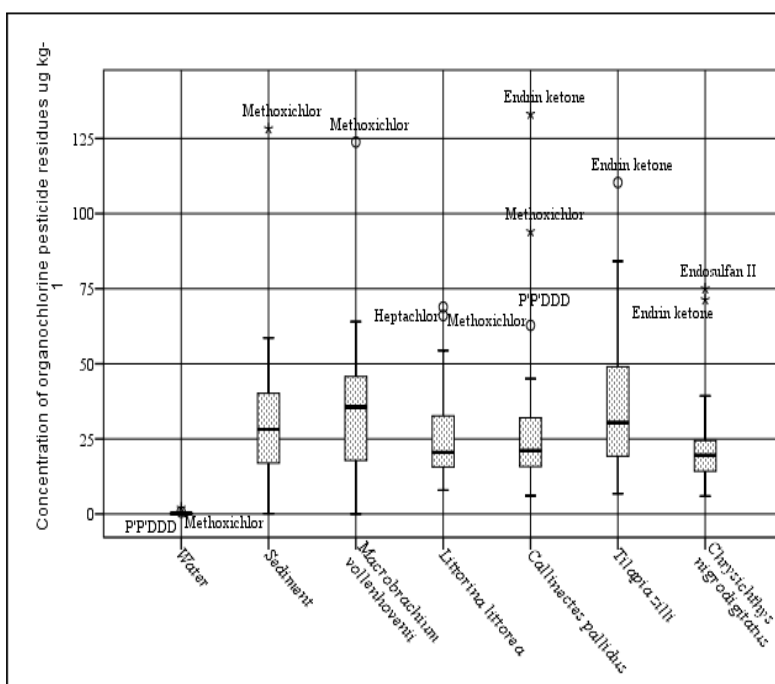


Fig. 5. The boxplot of organochlorine pesticide residues in water, sediment, *Macrobrachium vollenhovenii*, *Littorina littorea*, *Callinectes pallidus*, *Tilapia zilli* and *Chrysichthys nigrodigitatus*, showing the principal pesticide residues and order of decreasing concentrations in River Majidun, within the period of study

The box plot (Fig. 5) clearly exhibited the low level of POPs in water compared to the sequestered concentration in the sediment of River Majidun. It evinced that Methoxychlor, Endrin ketone, Endosulphan II and p'p'DDD were the principal pesticide residues in River Majidun and the total concentration of pesticides decreased in the order of *Macrobrachium vollenhovenii* (Prawn), *Tilapia zilli*, *Callinectes pallidus* (Crab), *Littorina littorea* (Periwinkle) and *Chrysichthys nigrodigitatus* (Silver catfish). While the total concentration in water was the lowest of all, the total quantity in sediment was higher than the quantity in crab, periwinkle and silver catfish.

4. DISCUSSION

Analyses of the water, shell fish, fin fish and sediment in River Majidun showed that Methoxychlor and Endrin ketone, were higher and it may be due to the farming, fishing, sand dredging activities and the discharge of household wastes. The analyzed water and its resources indicated that OCPs such as, DDT, DDE, DDD and Beta-HCH had the smallest values in River Majidun. The α/γ -HCH ratios are known to distinguish the possible HCH source. A ratio greater than 3 denotes a long distance transport cum atmospheric deposition. While a ratio close to or less than one (<1) is an indication of point source Lindane origins [15]. In River Majidun water sample, the α/γ -HCH ratio (3.3) indicated a long distance transport cum atmospheric deposition, all others were on either side of one (1) except *Chrysichthys nigrodigitatus* (2.8). The increased agricultural and medium scale localization of commercial activities around River Majidun could be accountable for the high application of POPs in the area and consequent accumulation in the biota.

River water samples from Majidun showed that the highest concentration of OCP residues were low relative to that found in the sediment. Banned substances like Methoxychlor, p, p' DDT, β -HCH were observed to surpass numerous doubles of the maximum allowable limits (10 ng l^{-1} in water) aimed at securing freshwater organisms in Canada [16]. This indicates an increased rate of contamination agreeing with [17-20] that there is an over-all pollution of inland aquatic habitats by a wide variety of Persistent Organochlorine Pesticides (POPs).

All the major POPs were detected except Hexachlorobenzene. This study agrees with [6] that showed pesticide concentration to be high in

the riparian sediment. They postulated that POPs have a tendency to cling with soil constituent parts at the benthos that serves as their ultimate sink and bio-accumulate in the tissues of shell fish (*Callinectes* specie). Feeding on polluted shell fish for an appreciable interval of time could become lethal to humans.

The various uses of River Majidun which include fishing, domestic water transportation and sand mining are all pathways of POPs contamination. Other conduits of POPs into the river consist of local sewage disposal cum aerosol usage against mosquitoes for malaria prevention, household pests, weeds and leaching from riverbank agricultural farmlands. River Majidun has several rivers draining into it including River Ogun, River Ipakodo and River Owutu which also brings in effluents from upstream. The catchment area is largely residential with low industrialization. It is known that aerial and ground spraying of these POPs especially Dieldrin, DDT, Heptachlor, Endosulfan and HCH are applied for health and control of human and livestock diseases.

The results here are similar to level of DDT and the α -HCH values reported for some major rivers in United Kingdom [21]. This investigation agrees with [16] that bulk of the inland waters in Africa have γ -HCH (Lindane) concentration below $10 \mu\text{g/L}$ remaining within the recommended guideline for the protection of freshwater aquatic life in Canada. Conversely, only the water and *C. nigrodigitatus* samples fell into this category at $0.03 \mu\text{g kg}^{-1}$ and $8.13 \mu\text{g kg}^{-1}$ respectively. All other samples in this study were higher than $10 \mu\text{g kg}^{-1}$.

Also, the results are several folds higher than the 4 ng l^{-1} standard fixed for freshwater organisms in Canada. Besides a limited number of flashpoints as a consequence of localized point source pollution glitches, sediments of inland aquatic habitats in Africa are comparatively untainted by synthetic organochlorine pesticides and the concentrations found were more often lesser than concentrations conveyed for industrialized nations [22], Although these assertions are outdated.

Levels of chlorinated hydrocarbon substances in fish are similar to results obtained by [23], apart from a limited circumstance nearby pollution flashpoints. concentrations observed were higher than the acceptable boundaries for pesticides in sea food for anthropoid ingestion [24].

Persistent Organochlorine pesticides (POPs) have been investigated for seven different environmental compartments (i.e. water, sediment, 3 shell fishes and 2 fin fishes) in River Majidun, Lagos State, Nigeria. River Majidun contains significantly lower concentration of these chemicals that is far below $10 \mu\text{g l}^{-1}$ which is the endorsed standard aimed at safeguarding the life expectancy of organisms, especially of the upper trophic level in Canada [16]. River Majidun is considered by this, study, to be significantly polluted with POPs and therefore poses an ecological threat. Results showed that there was sequestration of POPs from water into sediment and bioaccumulation in the organisms, due to exposure. The levels of POPs were observed to be considerably greater in both the fin and shell fishes than in the water and only the concentration in Prawn and Tilapia were higher than that of sediment. The level of concentration of all POPs residues in all samples were below the residue limits of $200 \mu\text{g kg}^{-1}$ fresh weight in fish and sea food set by Codex Alimentarius Commission by [24]. Some banned organochlorines detected in River Majidun include Aldrin, Chlordane, Dichlorodiphenyltrichloroethane (DDT), Dieldrin, Endrin, and Heptachlor. [25], Affirmed that by using a multi-parametric approach, a better understanding of response mechanisms to pollution in fish may be achieved in order to improve the ecological status of river ecosystems.

Here, a slightly modified Method 3570 as described by US EPA 2002 was the extraction process utilized to achieve an understanding of the pesticide pollution status in the Majidun riparian ecosystem [14].

5. CONCLUSION

Owing to the ecological threat and impending peril of the high levels of POPs in River Majidun and the very clear and present hazard of subsequent sequestration in sediment and bioaccumulation by these commercially important medium to highly priced fin and shell fish species, the organisms have become potentially hazardous for human consumption and use, therefore, it needs urgent monitoring and more research works to be carried out in view of controlling the pollution in this water body. The study area needs continuous checking of these non-easily degradable chlorinated hydrocarbons with a view to

inhibiting extensive ecological health dangers and stimulating maintenance and wellbeing of the riparian resource. Further study should include Pathology and Epidemiology to ascertain the structural / functional deviation from norms of body systems (organs cum body fluids) and the incidence, distribution and possible control of certain related pesticide-bioaccumulation-ailments in the local consumers.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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