

ORIGINAL RESEARCH

Evaluation of Organochlorine Pesticides (OCPS) and Their Health Risks in Ogegele River, Idah, Kogi State.

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Abstract

Organochlorine pesticides (OCPs) are chemicals that are resistant to degradation in the environments and water bodies; they bioaccumulate and are toxic. In this study, in order to investigate the effect OCP pollution in River Ogegele, a seasonal assessment was conducted. Liquid-liquid extraction (LLE) was employed using methylene chloride, followed by cleanup with silica gel and anhydrous sodium carbonate. The extract was analyzed using gas chromatography according to the United States Environmental Protection Agency (USEPA). The results showed that the concentration of \sum OCPs in the water during wet season ranged from 0.13 to 0.26 ng L⁻¹ while the concentration of \sum OCPs in the water during dry season ranged from 0.01 to 0.07. Most residual OCPs during the wet season were sufficient to pose carcinogenic and non-carcinogenic health risks to humans, whereas levels during the dry season were lower. The results of this study can provide a reference for OCP prevention and control and watershed environmental management.

Keywords: Organochlorine, Pesticides, Pollutants, Persistence, Bioaccumulate

Introduction

Organochlorine pesticides (OCPs) are synthetic pesticides widely used worldwide. They belong to the group of chlorinated hydrocarbon derivatives, which have vast applications in the chemical industry and agriculture. Organochlorine pesticides (OCPs) are known for their high toxicity, slow degradation and have the ability to bio-accumulate in human and animal tissues and organs, because of their hydrophobic and lipophilic properties (Yahaya et al., 2017). OCPs are efficiently

transported into aquatic systems by infiltration, runoff, and atmospheric deposition due to their volatilization (Meyer, 2003; Fatima, 2016). Studies on the toxicokinetics of some common OCPs such as hexachlorocyclohexane, endosulfan and cyclodienes have been linked to several health challenge on people that are frequently exposed to them (Harmouch et al., 2019). Organochlorine pesticides have been linked to numerous health effects in humans such as cardiovascular problem, disruption of endocrine glands and neurotoxic effects (Akor et al., 2024).

OCPs are discharged into the environment by industrial, agricultural, and residential sources. OCPs, can bioaccumulate in the tissues and organs of both humans and animals due to their hydrophobic and lipophilic characteristics (Yahaya et al., 2017). OCPs are transported by leaching through the soil or run-off water in river and streams (Kumar and Mukherji, 2018). Human ingestion exposure can occur through the skin or by inhalation, and it may have toxicological health effects such as immune system dysfunction, endocrine changes, and birth abnormalities (Yahaya et al., 2017a). OCPs have also been found in animal, fish, plant, and water samples. OCPs have also been found in high concentrations in body fluids such as breast milk, urine, and serum from these studies. However, health risk assessment of OCPs is scantily reported (Wanjiku et al., 2022). Most studies carried out on OCPs were based mainly on levels and distributions in environmental samples (Taiwo, 2019). Therefore, this study is aimed at carrying out a seasonal assessment on selected Organochlorine pesticides (OCPs) in Ogegele River in Idah Local Government Area of Kogi State.

MATERIALS AND METHODS

Description of Study Sites

Ogegele River is approximately 1000 km long, with its source in Ichekene, Idah Local Government Area of Kogi State. The river flows through several regions from Ichekene through Oferoba and empties into River Niger. Along its course are several agricultural activities such as poultry farms, rice, potatoes and vegetable farms. Also, domestic activities like washing, bathing and disposal of heaps of refuse. Other human activities operation of diesel reservoir tanks used to power rice mill, operation of engine boats that are used for transportation of food across the river to Aganebode, Edo state. In addition, rice mill factory and carpentry workshops are located along the river. The map and co-ordinates of the four different sampling points (SP1 – SP4) are shown in **Figure 1** and **Table 1** respectively.

Sample collection

Water samples were taken into 1L dark brown bottle at a depth of 1-5 cm from four different sampling points in triplicates, spaced about 100 meters apart, in wet and dry seasons in 2022. They were preserved with 5 mL 0.1M HCl and then stored in ice-chests at 4 °C and transported to the laboratory for analysis (Yahaya et al., 2019a).

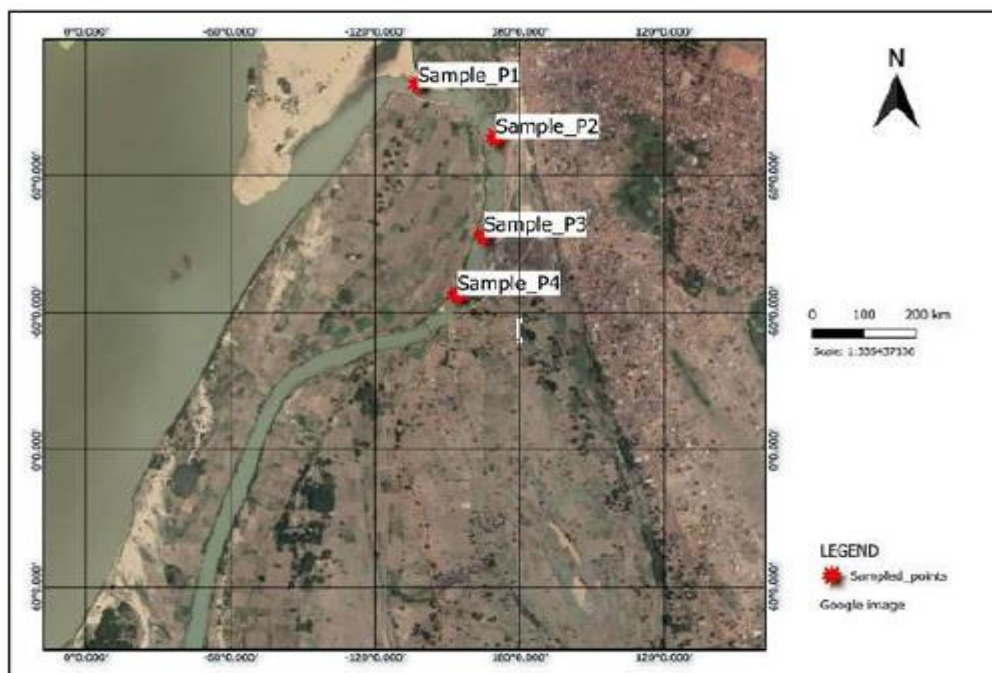


Figure 1: Map of the studied area (sampling site)

Figure 1: Map of the studied area (sampling site)

Table 1: Coordinates of the sampling points.

Sampling points	Latitude	Longitude	Activities
SP1	7° .09' 5" N	6° .7' 26" E	Poultry farm wastes
SP2	7° .09' 7" N	6° .7' 20" E	Repairs and construction of canoe site, engine boat repair, fuel reservoir tanks.
SP3	7° .13' 4" N	6° .7' 13" E	Waste from rice mills, Irrigation sites, Rice farms.
SP4	7° .10' 1" N	6° .7' 07" E	Domestic Waste (washing, bathing) and heaps of refuse dumps.

SP or P: Sampling points

Approximately 400 mL of water samples were extracted three times with 40 mL of dichloromethane (DCM) in a 500 mL separating funnel and then reduced to 5 mL using a rotary evaporator at 37 °C. Similarly, distilled water was treated the same way as sample for quality control. The sample extracts were cleaned-up via a glass column (burette) that were packed with 5g florisil salt and topped with a 2 g layer of anhydrous sodium sulfate. Approximately 10 mL n-hexane was used to pre-elute the column prior to passing the extract through the burette and then eluted with 40 mL n-hexane, condensed to 2 mL in a rotary evaporator and finally transferred into the glass vial and ready for GC-MS analysis (Yahaya et al., 2022a, Adeniji et al., 2019).

Instrumental Analysis

The OCPs determined was analyzed were using a (Hewlett-Pack and 6890 GC) at a Constant flow rate of 3.5ml/min using helium gas a carrier gas (Yahaya et al., 2017). One microliter (1 μ L) each of the sample was injected in Splitless mode at 250 °C into a Hp-5 capillary Column (30m x 0.25m) (Adeniji et al., 2018). The device was Calibrated using working Standard for 13 OCPs ranging from 10-600 ng/L. Analytes in the sample extract were identified by comparing their retention times with those of their standards and quantification was done using the instruments Software (Hiba, 2018).

Limits of Quantification (LOQ) and limit of detection were calculated based on Concentration of the blank Sample run.

$$\text{LOD} = 3\text{Sb}/a$$

$$\text{LOD} = 10\text{Sb}/a$$

Where Sb stands for the Standard deviation of the blank.

Statistical Analysis

Data were analysed using graph pad software through one-way analysis of variance (ANOVA).

Values obtained in mean and standard deviation (SD) at significant value of $P < 0.05$.

Risk Assessment

The health implications of OCPs in water were assessed for carcinogenic and non-carcinogenic effects using average daily dose (ADD) in mg/kg/day, hazard quotient (HQ) life average daily dose (LADD) and cancer risk (CR) in equation 1, 2, 3, 4, 5 and 6 correspondingly (USEPA 2001, 2009; Taiwo et al., 2019; Yahaya et al., 2022b).

$$H = \frac{ADD}{RfD} \quad (1)$$

$$R = ADD \times CSF \quad (2)$$

$$DD = \frac{C \times SA \times Kp \times ET \times EF \times ED \times CF}{BW \times AT} \quad (3)$$

$$DD = \frac{C \times SA \times Kp \times ET \times EF \times ED \times CF}{BW \times AT} \quad (4)$$

N.B. AT = 25,550 @ LADD

$$R = LADD \times CSF \quad (5)$$

$$R = ILCR \quad (6)$$

Where C = concentration of OCPs in the sample (mg/L); ADD = average daily dose (mg/kg/day); FI= Ingestion Factor (0.98). IR = Ingestion rate of protein (24.7g/day) EF = exposure frequency (350 days/year), ED = exposure duration (Child: 6years; adult: 30 years); BW = average body weight (adult = 70 kg); AT = average time (child: 2190 days; adult: 10,950 days). RfD = Reference dose (USEPA 2001, 2009; Ulder et al., 2006; Taiwo et al., 2019). CSF = Cancer slope factor (Ekere et al., 2019)

Results

Table 2: The mean concentrations (mg/L) of OCPs along Ogegele River in Wet Seasons (July, 2022)

OCPs	SP1	SP2	SP3	SP4
Alpha.-Lindane	0.001 ± 3.4 E-05	0.0002 ± 1.4E-05	0.005± 5.6 E-06	0.0006 ± 3.1 E-05
Beta.-lindane	0.014 ± 3.2 E-05	0.007±1 .5 E-05	0.003 ± 3.0 E-03	0.004 ± 5.4 E-06
Lindane	0.018 ± 3.0 E-05	0.002± 1.1 E-04	0.004± 2.4 E-04	0.004± 1.1 E-04
Delta.-Lindane	0.017± 8.2E-05	0.02± 5.0 E-04	0.02 ± 2.0 E-04	0.019± 1.1 E-04
Heptachlor	BDL	BDL	BDL	BDL
Aldrin	0.007 ± 4.2 E-04	BDL	BLD	BDL

Heptachlor epoxide	BDL	0.07± 3.3 E-03	0.07 ± 7.6 E-04	0.021± 2.1 E-03
alpha.-Endosulfan	0.0001 ± 5. 6 E-04	BDL	0.0003± 2.0 E-05	BDL
p,p'-DDE	0.14 ± 6.2 E-05	0.08± 1.1 E-03	0.04± 7.1 E-04	0.052 ± 8.1 E-04
Endrin	0.05 ± 1.4 E-05	0.004 ± 6.5 × E-04	0.003± 3.5 E-04	0.02 ± 8.6 E-04
m,p'-DDD	0.02 ± 1.1 E-03	BDL	BDL	0.003± E-04
Endosulfan	0.007 ± 3.5 E-05	BDL	BDL	BDL
Endosulfan sulfate	0.002± 4.1 E-04	0.002± 2.2 E-05	BDL	0.002± 1.1 E-04
∑OCPs	0.2561 ± 5.7E-05	0.1852 ± 5.7E-05	0.1453 ± 5.7E-05	0.1256 ± 5.7E-05

Values are mean ± standard deviation (SD); n = 3
 BDL: Below detection limit; SP: Sampling points

Table 3: The mean concentrations (mg/L) of OCPs along Ogegele River in Dry Season (December, 2022)

OCPs Mixture	SP1	SP2	SP3	SP4
Alpha-Lindane	0.0006 ± 5.8E-07	0.002 ± 6. 4E-06	BDL	BDL
Beta-lindane	0.012 ± 4.1E-05	0.019 ± 5.7E-05	BDL	BDL
Lindane	0.006 ± 5.7E-05	0.001 ± 7.5E-06	BDL	BDL
Delta-Lindane	0.016 ± 6.5E-04	BDL	BDL	BDL
Heptachlor	BDL	BDL	BDL	BDL
Aldrin	0.009 ± 5.1E-3	BDL	BDL	BDL
Heptachlor epoxide	BDL	BDL	BDL	BDL
Alpha.-Endosulfan	0.02 ± 5.7E-05	0.015 ± 5.7E-05	0.007 ± 1.1E-05	0.011 ± 2.9E-06

p,p'-DDE	0 BDL	BDL	BDL	BDL
Endrin	BDL	BDL	BDL	BDL
m,p'-DDD	0.004 ± 1.1E-03	0.003 ± 2.9E-06	0.004± 2.3E-07	BDL
Endosulfan	0.003 ± 4.2E-05	BDL	BDL	BDL
Endosulfan sulfate	BDL	BDL	BDL	BDL
Σ OCPs	0.069 ± 1.1E-05	0.048075 ± 2.9E-05	0.011 ± 8.2E-07	0.011 ± 2.9E-06

Values are mean ± standard deviation (SD); n = 3
 BDL: Below detection limit; SP: Sampling points

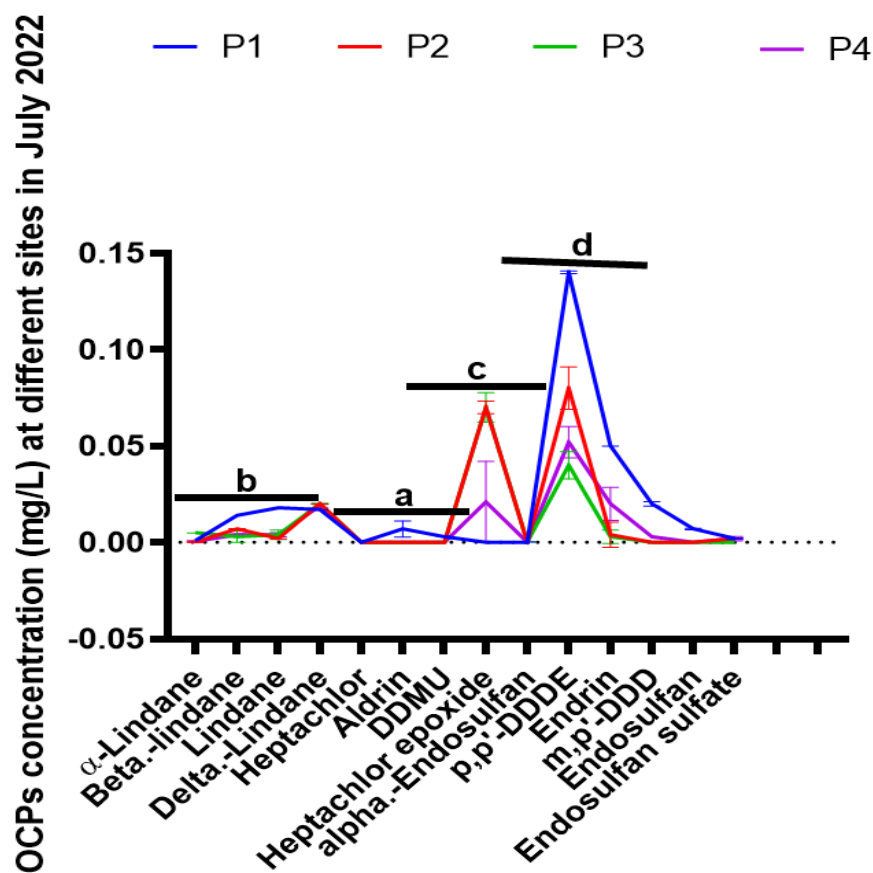


Figure 2: Concentration of OCPs at different sites in wet season (July 2022).

Levels of OCPs at different sites in wet season (July, 2022). Data were represented as mean \pm standard deviation of three replicates ($n=3$). A one-way analysis of variance, p -value < 0.05 using Bonferroni Multiple Comparison Test. Superscripts “a, b, c, d” are significantly different.

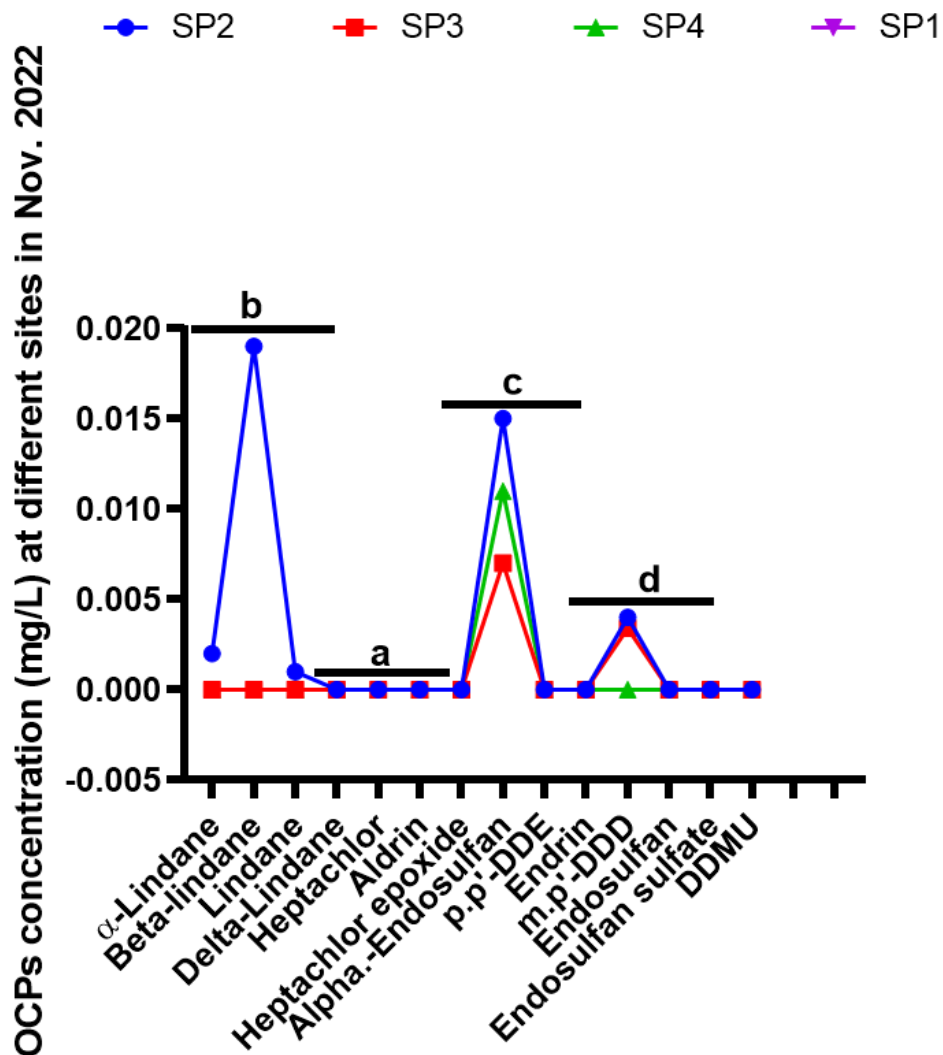


Figure 3: Concentration of OCPs at different sites in dry season (Nov. 2022).

Levels of OCPs at different sites in dry season (Nov. 2022). Data were represented as mean \pm standard deviation of three replicates ($n=3$). A one-way analysis of variance, p -value < 0.05 using Bonferroni Multiple Comparison Test. Superscripts “a, b, c, d” are significantly different.

Evaluation of health risk implication

The time of exposure of living organisms to pollutants need to be taken into consideration for assessment of health risk ECETOC, 2016. The HQ, ADD, LADD and cancer risk value were used for the evaluation of health implication.

Table 4: The ADD and LADD for Child and adult in Dry Season along Ogegele River

<u>OCPs</u>	<u>ADD6yrs</u>	<u>ADDad</u>	<u>LADD6yrs</u>	<u>LADDad</u>	<u>Cancer Risk (All ages)</u>
Alpha.-Lindane	2.55E-05	5.10E-05	2.47E-05	2.886E-05	8.06E-15
Beta.-lindane	3.08E-04	6.16E-04	2.99E-05	3.4877E-04	9.741E-14
Lindane	6.86E-05	1.37E-04	6.65E-06	7.77E-05	2.17E-14
Delta.-Lindane	1.57E-04	3.14E-04	1.52E-05	1.776E-04	4.96E-14
Heptachlor	0	0	0	0	0
Aldrin	6.86E-05	1.37E-05	6.65E-05	7.77E-05	2.17E-14
Heptachlor epoxide	5.19E-04	1.04E-03	5.04E-05	5.88E-04	1.64E-13
alpha.-Endosulfan	0	0	0	0	0
p,p'-DDE	0	0	0	0	0
Endrin	1.12E-04	2.2344E-04	1.08E-05	1.27E-04	3.53 E-14
m,p'-DDD	2.94E-05	5.88E-05	2.85E-06	3.33E-05	9.30E-15
Endosulfan	0	0	0	0	0
Endosulfan sulfate	0	0	0	0	0

Child: 0-6year; Adult: ad

The health risk evaluations of OCPs in dry seasons, ADD, LADD and cancer risk (Table 4.) were between 0 – 2.94E-05, 0 - 6.65 E-06 and 0 - 1.37E-05, 0 - 3.33 E-05 as well as 0 - 9.30E-15 for child, adult and all ages correspondingly. Similarly, in table 5, ADD, LADD and cancer risk values

for wet season, ranged from 0 - 3.92E-06, 0 - 6.65E-06 and 0 - 7.84E-06, 0 - 6.65E-06 and also 0 - 9.30E-15 for child, adult and all ages individually.

The ADD of some analytes were greater than 10^{-4} . It is an indication of lifetime cancer risk. Alpha-lindane, lindane, aldrin and m,p'-DDD were 10^{-5} . All analytes for LADDs were below 10^{-6} except lindane and endrin (in child) that were greater than 10^{-6} which means highest cancer risk. Furthermore, the LADD for Heptachlor epoxide is equal to 10^{-3} , meaning it requires a protective measure (USEPA-IRIS, 2007; Taiwo et al., 2018). However, the cancer risk values were in all analytes lower than cancer risk permissible limit, therefore, there is possibly no harmful effects to the dwellers along this river.

Table 5: The ADD and LADD for Child and adult in Wet Season along Ogegele River

OCPs	ADD6yrs	ADDad	LADD6yrs	LADDad	Cancer Risk (All ages)
Alpha.-Lindane	6.66E-05	1.33E-04	6.46E-06	6.46E-06	2.11E-14
Beta.-lindane	2.74E-04	5.49E-04	2.66E-05	2.66E-05	8.68E-14
Lindane	2.74E-04	5.49E-04	2.66E-05	2.66E-05	8.68E-14
Delta.-Lindane	7.45E-04	1.49E-03	7.22E-05	7.22E-05	2.36E-13
Heptachlor	0	0	0	0	0
Aldrin	6.86E-05	1.37E-05	6.65E-06	6.65E-06	2.17E-14
DDMU	0	0	0	0	0
Heptachlor epoxide	1.578E-03	3.16E-03	1.53E-04	1.53E-04	4.99E-13
alpha.-Endosulfan	3.92E-06	7.84E-06	3.8E-07	3.8E-07	5

p,p'-DDE	3.058E-03	6.115E-03	2.96E-05	2.96E-04	9.67E-13
Endrin	7.55E-04	1.509E-03	7.32E-05	7.32E-05	2.39E-13
m,p'-DDD	2.94E-05	5.88E-05	2.85E-06	2.85E-06	9.30E-15
Endosulfan	6.86E-05	1.37E-04	6.65E-06	6.65E-06	2.17E-14
Endosulfan sulfate	5.88E-05	1.18E-04	5.70E-06	5.70E-06	1.86E-14

Child: 0-6year; Adult:

Table 6: Hazard quotient (HQ) and hazard index (HI) in wet and dry seasons in Ogegele River

<u>OCPs</u>	<u>Wet Season</u>		<u>Dry Season</u>	
	<u>HQ6yr</u>	<u>HQad</u>	<u>HQ6yrs</u>	<u>HQad</u>
<u>Lindane</u>	<u>5.48E-05</u>	<u>1.10E-04</u>	<u>1.4 E-03</u>	<u>2.74 E-05</u>
<u>Aldrin</u>	<u>2.286E-03</u>	<u>4.57E-03</u>	<u>2.33E-01</u>	<u>4.6 E-03</u>
<u>Heptachlor epoxide</u>	<u>1.21E-01</u>	<u>6.31E-03</u>	<u>0</u>	<u>0</u>
<u>Endrin</u>	<u>2.52E-03</u>	<u>0.05</u>	<u>0</u>	<u>0</u>

Child: 0-6year; Adult: ad

The OCPs HQ and HI values (**Table 6**) in wet and dry seasons for child and adult were within 1.21 E-01 - 5.48 E-05, 0.05 - 1.10 E-04 and 0 - 1.4 E-03; 0 - 2.74 E-05 disparately. The analytes evaluated were based on the availability of their RfD. The HQ in wet and dry season were below unity (1) for child and adult independently. This implies relatively low ecological risk (USEPA-IRIS, 2007; Taiwo et al., 2018; Haruna et al., 2023)

Discussion

The mean OCPs concentrations in the water sample taken from four Sampling Points (SP1 – SP4) was presented in **Table 3**. 8 OCPs were revealed in all. Alpha lindane (0.0005).beta lindane

(0.0124), lindane (0.004) Aldrin (0.00999), alpha Er (0.00204), m, p¹ DDE (0,004J, Endosulf (0.0027) were detected. SP1 revealed 5 OCPs, alpha lindane (0.0018), beta lindane (10.877) Lindane (10034) alpha E'r (010144) and m, p' DDE (0.0034) were detected. SP2 revealed 2 OCPs, alpha Er (0.0072) and M, P¹ DDE (0·0034) and Only alpha Er (0.0107) was detected in sample point 4 (SP4).

The results indicated the presence of eight OCPs—lindane, beta-lindane, delta-lindane, aldrin, endosulfan, m,p'-DDE, and alpha-endosulfan—in trace amounts. The low pesticide concentrations in SP2–SP4 could result from limited pesticide use for controlling soil-borne insects. During the dry season, OCPs concentration was very low, as a result of less agricultural activities like spraying of herbicides, pesticides and other insect repellents. It could also be as a result of high level of volatilizations due to high temperature, slow rate of degradation of OCPs in sludge under anaerobic conditions as documented by Buser and Muller (1995). The results compared favorably with that of Yahaya et al. (2017), Li et al. (2021) and Xu et al. (2023) but could not agree with the one documented by Haruna et al. (2023). During the wet season, Alpa-lindane to Delta- lindane were detected in SP1 – SP4, Heptachlor to Endosulphate were below detection limit in some sampling points. The presence of OCPs during wet season could be as a result of increased agricultural activities such as use of herbicides and pesticides.

The health risk evaluations of OCPs in dry seasons, ADD, LADD and cancer risk (Table 4) were between 0 – 2.94E-05, 0 - 6.65 E-06 and 0 - 1.37E-05, 0 - 3.33 E-05 as well as 0 - 9.30E-15 for child, adult and all ages correspondingly. Alpha-lindane, lindane, aldrin and m,p'-DDD were 10^{-5} below 10^{-6} except lindane and endrin (in child) that were greater than 10^{-6} . Furthermore, the ADD and LADD for children and adult as shown in **Table 5** were below the recommended limit (Pawelezyk, 2013; USEPA, 2015). The HQ were lower than 1 which indicates low ecological risk.

Conclusion

Water samples were extracted using the liquid-liquid extraction (LLE) method and analyzed for OCP priority pollutants during wet and dry seasons using GC-MS. The level of OCPs recorded in wet season were above maximum permissible limit, which implies the water is polluted, while in dry season, most of the analytes were not detected. Furthermore, ADD, LADD, and HQ values were below USEPA thresholds, indicating very low ecological risk. Therefore, there is need to monitor the water bodies in order to provide safe water for dwellers along the river side especially during the wet season.

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