

# Assessment And Toxicological Risk of Organochlorine Pesticide Residues in Water from River Ibi, North Eastern Nigeria

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**Abstract** - The increasing use of pesticides for agricultural productivity and vector control has raised serious environmental and public health concerns, particularly regarding organochlorine pesticides (OCPs) due to their persistence, bioaccumulation, and toxicity. This study assessed the occurrence and risk implications of OCP residues in surface water from River Ibi, Northeastern Nigeria, a vital resource for domestic, agricultural, and fishing activities. Water samples were collected from five locations along the river and extracted using USEPA Method 3510, followed by analysis with Gas Chromatography equipped with an Electron Capture Detector (GC-ECD). Physicochemical analysis revealed slightly alkaline conditions (pH 8.27–9.01) and temperatures ranging from 20.62 to 27.67 °C, conditions that favor OCP stability in tropical aquatic environments. Sixteen OCPs were detected in water, with total concentrations ranging from 2.126 µg/L to 7.422 µg/L across sampling sites.  $\beta$ -BHC was the dominant compound (mean = 5.224 µg/L), while aldrin recorded the lowest concentration (0.217 µg/L). Contamination factor values (2.53–10.45) indicated moderate to high contamination of the river water. Human health risk assessment revealed that carcinogenic risks for  $\beta$ -BHC, dieldrin, heptachlor, and aldrin exceeded USEPA acceptable limits, particularly at downstream locations. Dermal exposure assessment showed that children are more vulnerable than adults. The findings indicate significant contamination of River Ibi water by OCPs, posing potential ecological and public health risks and underscoring the need for continuous monitoring and stricter pesticide control

**Keywords:** Organochlorine Pesticides; Surface Water; GC-ECD; Contamination Factor; Risk Assessment; River Ibi

## I. INTRODUCTION

Water bodies, including surface water and groundwater, are critical environmental resources that support domestic supply, agriculture, fisheries, and ecosystem sustainability. Because both surface and groundwater are commonly used as drinking water sources, the assessment of pesticide residues in water is essential for protecting human health and

aquatic ecosystems. Surface waters in agricultural regions are particularly vulnerable to pesticide contamination, which can result in ecological imbalance and long-term health risks (Staley et al., 2015; Cruzeiro et al., 2017).

Environmental monitoring of pesticide residues in water is traditionally based on chemical analysis of known pesticides and their metabolites. Long-term monitoring programs, such as those conducted in Sweden since 2002, have demonstrated the persistence of pesticide residues in surface waters from agricultural catchments (Boye et al., 2019). However, targeted chemical analysis alone has limitations, including the inability to detect unknown compounds, assess mixture toxicity, or directly link contamination to adverse biological effects. Consequently, it has been widely suggested that integrating chemical characterization with toxicological profiling provides a more effective approach to environmental monitoring and risk assessment (Ankley et al., 2016; Escher et al., 2017; Escher et al., 2013; Brack et al., 2019; Brack et al., 2018; Altenburger et al., 2019; Dopp et al., 2019).

The global use of pesticides has increased substantially due to intensified agricultural production and disease control efforts, particularly in developing countries (Yadav et al., 2015). Pesticides enter aquatic environments through direct application, agricultural runoff, irrigation practices, and effluents from wastewater treatment plants (Fenoll et al., 2014; Hakami, 2014). Numerous studies have reported widespread contamination of surface waters worldwide, even at low concentrations, including rivers in Europe where a wide range of pesticides have been detected (Robles-Molina et al., 2014; Belenguer et al., 2014). Groundwater contamination has also been reported in several countries, including India, Greece, Germany, and France, highlighting the vulnerability of water resources to pesticide pollution (Shukla et al., 2006;

Vryzas et al., 2012; Reemtsma et al., 2013; Morvan et al., 2006).

In Taraba State, Nigeria, water supply is largely dependent on natural water bodies, while in Ibi Local Government Area, intensive agricultural activities and the use of insecticides for malaria vector control increase the likelihood of pesticide contamination of water resources. Such contamination may be associated with serious health effects, including cancer and organ damage when exposure occurs at elevated concentrations (Seth, 2014). The aim of this study is to investigate the pollution status of organochlorine pesticide residues in water from River Ibi, Taraba State, with emphasis on physicochemical characteristics, residue levels, and potential human health risks.

## II. METHODOLOGY

### Samples collection and preservation

Samples of water were collected at five different locations from River Ibi in Taraba State, North Eastern Nigeria. Samples of water were collected as described by Ibigbami *et al.*, (2010). Water samples were taken at five different locations along the course of the river by grab method. At each sampling location four grab samples were taken across the width of the river and pulled together to form composite samples which were labelled as W1, W2, W3, W4 and W5 respectively. The samples were stored in a pre-cleaned glass bottle. The water samples were acidified with concentrated HNO<sub>3</sub> to pH 2 to prevent alteration of the organic matter. The samples were kept in glass bottle and preserved in a refrigerator prior analysis.

## III. SAMPLE PREPARATION

### Extraction of pesticides from water samples

The water samples were filtered through Whatman No. 42 filter paper to remove particulate matter. Liquid – liquid extraction was used to extract the pesticides from the water sample. The extraction was carried out using method as described by US EPA-3510 (2010), 50 ml of dichloromethane (DCM) was introduced into the separating funnel containing 100 ml of the water sample and shaken vigorously for about 2 minutes. 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 through anhydrous sodium sulphate

(Na<sub>2</sub>SO<sub>4</sub>) that has been prewashed with DCM. The extraction was repeated twice using a 50 ml portion of dichloromethane and later combined. The combined organic extracts were concentrated using a rotary evaporator at 450 °C and low pressure. 5 ml of n-hexane was added to the extract in DCM to exchange the solvent. The extracts were further concentrated to 1-2 ml using a rotary evaporator at 450 °C until no further DCM remained in the extract. The extracts were transferred into a vial and kept for Gas Chromatography (GC) analysis.

Chemical characterization of OCP residues: The chemical characterization of organochlorine pesticide residues was performed using gas chromatography (GC), model Agilent 7890A equipped with electron capture detector (ECD). The carrier gas nitrogen was allowed to flow at the rate of 4.0 ml/min. The temperature of injector was held at 2500 °C, oven temperature was at 2500 °C and electron capture detector was set at 3000 °C respectively.

The oven temperature was programmed at 800 °C for 1 minute, ramped to 1800 °C at 100 °C/min (held for 3 minutes) and to 3000 °C at 100 °C/min (held for 2 minutes). The total run time was 28 minutes. The column type was HP5 MS (30 m X 0.25 µm and 0.32 mm) were used for the separation of OCPs

Preparation of calibration curves: Stock solutions of pure standards of organochlorine ( $\alpha$ -BHC,  $\beta$ -BHC,  $\gamma$ -BHC, lindane, chlorothalonil, heptachlor, aldrin, heptachlor epoxide, endosulfan I, endosulfan II, endrin, dieldrin, DDD, DDT, endosulfan sulphate) were prepared and then serially diluted to produce different concentrations of pesticides. Stock standard solutions were stored in amber-coloured bottles at 40 °C in a refrigerator while working standard solutions were prepared for fresh before use. Standard solutions of OCPs were run in GC- ECD under set chromatographic conditions and mean peak areas were plotted against concentrations to obtain calibration curves of individual pesticides. The retention times for standard samples were used for confirmation of the pesticides. Retention time windows were constant for the standard samples and were therefore relied upon for component identification.

## Toxicological Assessment

Ecotoxicological Risk Assessment: The toxicological assessment involves determining the potential ecological risks posed by OCP residues in water and sediment. The concentrations of detected OCPs were compared to environmental quality standards, such as the United States Environmental Protection Agency (EPA) guidelines for aquatic ecosystems (EPA, 2020). The risk quotient (RQ) was calculated using the formula:

$$RQ = \frac{\text{measured concentration}}{\text{predicted No - Effect concentration}} \dots \dots \dots 3.1.$$

If  $RQ > 1$ , the OCP residues poses a potential ecological risk

Human Health Risk Assessment: The human health risk associated with the OCP residues was assessed using the estimated daily intake (EDI) for individuals exposed to contaminated water. The EDI was calculated using the formula:

$$EDI = \frac{C_{\text{water}} \times IR_{\text{water}} \times EF \times EI}{BW \times AT} \dots \dots \dots 3.2$$

Where:

- $C_{\text{water}}$  is the concentration of OCP in water ( $\mu\text{g/L}$ )
- $IR_{\text{water}}$  is the ingestion rate of water (L/day)
- $EF$  is the exposure frequency (days/year)
- $EI$  is the exposure duration (years)
- $BW$  is the body weight (kg)
- $AT$  is the averaging time (days)

The calculated EDI values will be compared to the reference doses (Rfd) provided by the regulatory agencies such as the EPA to assess potential health risks (EPA, 2020)

3.3.3 Contamination Factor: This is a numerical index used to assess the level of contamination of a particular pollutant in sediment or water relative to its background concentration.

It can be expressed mathematically as:

$$CF = \frac{\text{Mean } C_{\text{sample}}}{C_{\text{background}}} \dots \dots \dots 3.3$$

Where:

$C_{\text{sample}}$  = Measured Concentration of the contaminant in the sample

$C_{\text{background}}$  = Background concentration of the contaminant.

Cancer Risk / Carcinogenic Risk (CR): This is the probability or likelihood that exposure to a chemical substance or pollutant may cause cancer in a person over a lifetime.

$$CR = EDI \times CSF \dots \dots \dots 3.4$$

Where:

EDI = Estimated daily intake

CSF = Cancer Slope Factor

The dermal pathway: (Also called dermal exposure route) refers to the *entry of a chemical* substance or contaminant through the skin into the human body. It's one of the three main exposure pathways the others being ingestion and inhalation. The general formula for calculating the dermal exposure dose (also called Dermal Absorbed Dose, DAD or Average Daily Dose via dermal contact, ADD (dermal) is

$$ADD (\text{dermal}) = \frac{C \times SA \times K_p \times ET \times ED \times CF}{BW \times AT} \dots \dots \dots 3.5$$

Where

$C$  = Contaminant concentration

$SA$  = Skin surface area exposure

$K_p$  = Dermal permeability coefficient

$ET$  = Exposure time

$EF$  = Exposure frequency

$CF$  = Conversion factor

$BW$  = Body weight

$AT$  = Average time

## Data Analysis

Data were analyzed using Microsoft Excel 2021 and IBM SPSS Statistics version 25. Descriptive statistics such as mean, standard deviation, and range were used to summarize the concentrations of organochlorine pesticide (OCP) residues in water samples. Mean concentrations of OCP residues were calculated separately for each sampling site. To determine whether there were significant differences in OCP concentrations across the various sampling sites, a one-way analysis of variance (ANOVA) was performed.

#### IV. RESULT AND DISCUSSION

Table 4.1.1 showed the pH values and temperature of organochlorine pesticide (OCP) in water

SAMPLE SOURCE	pH VALUES	TEMPRETURE (°C)
W1	8.30 ± 0.37	27.67 ± 2.67
W2	8.27 ± 0.37	20.62 ± 2.67
W3	9.00 ± 0.37	25.55 ± 2.67
W4	9.01 ± 0.37	26.02 ± 2.67
W5	8.87 ± 0.37	25.08 ± 2.67

##### 4.1.0 DISSCUSION

The pH and temperature values of organochlorine pesticide (OCP) in water

Table 4.1.1 Present the pH values of the five water samples which were as follows 8.30 ± 0.37, 8.27 ± 0.37, 9.00 ± 0.37, 9.01 ± 0.37 and 8.87 ± 0.37 respectively, these indicates that the water body is alkaline or basic. High alkalinity is essential for the

wellbeing of aquatic organisms. It acts as a natural buffer, protecting organisms from rapid pH swings (e.g., due to acid rain or CO<sub>2</sub> fluctuations), which is essential for fish and macroinvertebrates. Even though alkalinity affects essential nutrients (like Fe, Mn, Zn) of aquatic organisms which can reduce egg development, skeletal growth, and metabolic activity in aquatic animals. (Adefemi, and Awokunmi 2010)

Table 4.1.2 Concentration (µg/L) of organochlorine pesticide residues in water samples from River Ibi

Sample	$\alpha$ -	$\beta$ -	Lindane	$\gamma$ -	Chloro-	Hepta-	Aldrin	Heptachlor	Endo-	Dieldrin	Endrin	Endo-	DDD	Endosulfan	DDT	TOCP
Code	BHC	BHC		BHC	thalon	chlor		Epoxide	sulfan I			sulfan II		suphate		
W 1	0.451	8.900	0.396	2.300	1.300	1.560	0.717	0.381	0.602	0.310	0.911	1.960	0.810	1.600	1.010	23.208
W 2	0.141	1.600	0.144	0.701	0.580	0.321	BDL	BDL	BDL	BDL	BDL	0.403	0.170	1.030	0.302	5.392
W 3	0.172	3.890	0.177	1.050	0.840	0.315	0.541	0.304	0.162	0.310	2.907	0.810	0.231	2.070	1.080	14.859
W 4	0.521	10.020	0.470	2.900	8.790	1.300	0.730	0.180	1.030	2.000	0.562	0.500	0.310	2.810	0.330	41.243
W 5	0.182	1.710	0.205	1.750	0.880	0.808	0.233	0.153	0.601	2.500	BDL	1.030	0.681	2.360	0.813	13.673
$\Sigma$ OCP	1.467	26.120	1.392	8.701	12.390	4.304	2.221	1.018	2.395	5.120	4.380	4.703	2.202	9.870	3.535	98.375
Range	0.141-	1.600-	0.144-	0.701-	0.580-	0.300-	BDL-	BDL-	BDL-	BDL-	BDL-	0.403-	0.170-	1.030-	0.302-	5.392-
	0.521	10.020	0.470	2.900	8.790	1.560	0.730	0.381	1.030	2.500	2.911	1.960	0.810	2.810	1.080	41.859
Mean	0.293	5.224	0.278	1.740	2.478	0.860	0.555	0.253	0.598	1.243	1.460	0.940	0.440	1.974	0.706	19.675
SD	0.178	3.992	0.145	0.896	3.537	0.564	0.231	0.107	0.354	1.182	1.265	0.621	0.286	0.687	0.370	13.609
CV%	0.32	15.944	0.021	0.804	12.517	0.318	0.540	0.011	0.126	1.397	1.601	0.387	0.082	0.472	0.137	34.687

SD = Standard deviation; CV = Co – efficient of Variance; BLD = below detection Limit < 0.15 (µg/L)

Concentration (µg/L) of organochlorine pesticide residues in water samples from River Ibi

The results of the analysis of organochlorine pesticide (OCP) residues in water samples from River Ibi, as showed in the Table 4.1.2 above indicate that among the hexachlorocyclohexane (HCH) isomers,  $\beta$ -BHC exhibited the highest concentration, with a mean of 5.224 µg/L and concentration levels ranging from 1.600 to 10.020 µg/L. The reason for the high values could be attributed to its chemical stability and resistance to biodegradation. Its persistence in the environment is well-documented, with studies such as those reported by (Rizwan *et al.*, 2018) reporting similar trends in tropical and subtropical regions,

where the compound can remain active for decades. The high levels of  $\beta$ -BHC observed in River Ibi could cause serious health impact such as leukemia, hepatitis etc. as reported by (Haruna 2023) in his findings. The values obtained for  $\beta$ -BHC in all the sample Locations were above the WHO (2009) and FAO (2009) permissible limit of 0.1 µg/L. Lindane ( $\gamma$ -BHC), though still present in detectable amounts showed lower mean levels of (0.278 µg/L), reflecting its phasing out in many regions due to recognized health hazards. The lower concentrations of  $\alpha$ -BHC also align with the degradation pathway of technical HCH mixtures, where  $\beta$ -BHC tends to dominate over time due to its higher environmental stability (Zhou

*et al.*, 2019). The coefficient of variation values suggests consistent distribution across the sites for  $\alpha$ -,  $\beta$ -, and  $\gamma$ -BHC, though  $\beta$ -BHC shows substantial variation, indicating possible point-source contamination or uneven application history. The concentration of Lindane recorded in this work were less than those reported by Ibrahim *et al.*, (2023) which has values ranged from 0.601 to 0.813  $\mu\text{g/L}$ . The results of Lindane in this finding are in agreement with those reported by (Onoja *et al.*, 2019). With the values ranging from 0.144 – 0.470  $\mu\text{g/L}$ .

Chlorthalonil showed a mean concentration of 2.478  $\mu\text{g/L}$ . This compound, commonly used as a fungicide, is toxic to aquatic invertebrates and fish even at low concentrations, as noted by the (U.S. EPA, 2004). Its presence at these levels suggests recent usage or leaching from agricultural fields. Heptachlor and its metabolite, heptachlor epoxide, were found in low concentrations across the samples, with several sites below detection limits. Their sporadic presence points towards the degradation of legacy residues. Aldrin, another banned cyclodiene insecticide, was similarly found at low concentrations, with many samples registering below detectable levels. However, the detection of its breakdown product, dieldrin, at higher concentrations (up to 2.5  $\mu\text{g/L}$ ) indicates environmental transformation. Dieldrin is known for its extreme persistence and bioaccumulative nature, which raises concerns even at low exposure levels, as outlined by Garrison *et al.*, (2011).

Endosulfan I and II, along with their degradation product endosulfan sulfate, were detected in all the

five samples, albeit at moderate levels. These compounds are recognized for their acute toxicity to fish and invertebrates. The presence of endosulfan sulfate, which is even more persistent than the parent compounds, underscores the potential long-term ecological risk in the study area (Weber *et al.*, 2010). Interestingly, these compounds show (CV% of 0.126, 0.387 and 0.473 respectively) which remained relatively low, suggesting a more uniform contamination pattern, possibly due to similar application methods or runoff behavior across the sample sites. Endrin was present in significant mean concentration of 1.459  $\mu\text{g/L}$ . This could be due to its high lipophilicity and low degradation rate. Its toxicity to aquatic organisms is particularly acute, as confirmed by Li *et al.*, (2019). The concentration of Endrin recorded in this work were high than those reported by Otitoju *et al.*, (2022). DDD, a major breakdown product of DDT, was observed across all sites, indicating historical usage of DDT-based pesticides. The consistent presence of DDD rather than DDT itself aligns with long-term degradation trends, as DDT undergoes anaerobic transformation in sediment to DDD (Jayaraj *et al.*, 2016). Similarly, low but consistent levels of DDT further affirm legacy contamination rather than recent inputs. The concentration of most organochlorine pesticides in the table above indicates that the levels of the residue are high and as such the high and continual usage of such pesticides possess risk and long-term damage to the humans around this River and so reducing the maximum life expectancy of all living organisms. These organisms are exposed to a lot of life-threatening diseases due to excessive usage of banned pesticide which at long last causes harm to all organisms.

Table 4.1.3 Mean Contamination factor of organochlorine Pesticide Residues in Water

Pollutant	Sample	Background	CF
$\alpha$ -BHC	0.293	0.05	5.86
$\beta$ -BHC	5.224	0.5	10.45
Lindane	0.278	0.05	5.56
$\gamma$ -BHC	1.740	0.2	8.70
Chlorthalonil	2.478	0.5	4.95
Heptachlor	0.859	0.2	4.30
Aldrin	0.555	0.1	5.55
Heptachlor Epoxide	0.253	0.1	2.53
Endosulfan I	0.598	0.1	5.98
Dieldrin	1.280	0.5	2.56
Endrin	1.459	0.2	7.29

Endosulfan II	0.940	0.2	4.70
DDD	0.440	0.1	4.40
Endosulfan sulfate	1.974	0.2	9.87
DDT	0.706	0.1	7.06

Mean contamination factor of organochlorine pesticide residues in water

The Contamination Factor (CF) values for organochlorine pesticide (OCP) residues in the analyzed water samples from River Ibi ranged from 2.53 for heptachlor epoxide to 10.45 for  $\beta$ -BHC as showed in (table 4.1.3). Based on Hakanson's (1980) classification, CF values below 1 indicate low contamination, values between 1 and 3 indicate moderate contamination, values between 3 and 6 indicate considerable contamination, and values greater than 6 indicate very high contamination. The present study shows that most pollutants recorded CF values above 2, with some exceeding the threshold contamination, and several ( $\beta$ -BHC,  $\gamma$ -BHC, DDT, Endosulfan sulfate, Endrin, and  $\alpha$ -BHC) reaching the very high category. The highest CF was recorded for  $\beta$ -BHC (10.45), followed by Endosulfan sulfate (9.87) and  $\gamma$ -BHC (8.70). These elevated values suggest persistent contamination from agricultural activities, improper disposal of obsolete pesticide stocks, or leaching from contaminated soils into aquatic systems. The observed contamination levels align with recent studies in similar tropical aquatic environments. Hikon *et al.*, (2024) reported CF values ranging from 0.035 to 21.835 for OCP

residues in Kashimbila Dam, Taraba State, Nigeria, with  $\beta$ -BHC,  $\gamma$ -BHC, and DDT among the most prevalent contaminants. This similarity in compound profiles and contamination severity suggests common sources, likely linked to historical agricultural use and environmental persistence. The elevated CF of DDT (7.06) indicates its ongoing application and persistency in the environment despite its restriction under the Stockholm Convention (UNEP, 2001). The results for  $\alpha$ -BHC (5.86), Lindane (5.56), and Aldrin (5.55) further confirm the persistence of these legacy pesticides, known for their low water solubility, high lipid affinity, and long half-lives (Jayaraj *et al.*, 2016).

Similarly, Shamma *et al.*, (2025) found elevated concentrations of Heptachlor, Aldrin, Endrin, and Endosulfan derivatives in surface waters across multiple Egyptian governorates, with contamination during the summer months due to increased runoff and evaporation effects. The CF values from the present study fall within comparable ranges to those reported in Egypt, reinforcing the confirmation that OCP contamination remains a persistent regional challenge.

Table 4.1.4 Risk Quotient (RQ) Values of OCP Residues in Water Samples

Pollutants	RQ – W1	RQ – W2	RQ – W3	RQ – W4	RQ – W5
$\alpha$ -BHC	9.02	2.82	3.44	3.64	3.64
$\beta$ -BHC	17.80	3.20	7.78	20.04	3.42
Lindane	7.92	2.88	3.54	9.40	4.10
$\gamma$ -BHC	11.50	3.51	5.25	14.50	8.75
Chlorthalonil	13.00	5.80	8.40	8.79	8.80
Heptachlor	7.80	1.61	1.58	6.50	4.04
Aldrin	7.17	0.00	5.41	7.30	2.33
Heptachlor Epoxide	3.81	0.00	3.04	1.80	1.53
Endosulfan I	6.02	0.00	1.62	10.30	6.01
Dieldrin	0.62	0.00	0.62	4.00	5.00
Endrin	9.11	0.00	9.07	5.62	0.00

Endosulfan II	9.80	2.10	4.05	3.41	5.15
DDD	8.10	1.70	2.31	3.10	6.81
Endosulfan sulfate	8.00	5.15	10.35	14.05	11.80
DDT	10.10	1.51	10.80	3.30	8.13

#### Risk Quotient (RQ) Values of OCP Residues in Water Samples

The calculated Risk Quotient (RQ) values of organochlorine pesticide (OCP) residues in water samples from five sampling points as showed in table 4.1.4 revealed significantly high levels of ecological risk in several pollutants, indicating potential threats to aquatic ecosystems and possibly human health. According to the United States Environmental Protection Agency (USEPA, 2020), a RQ value greater than 1.0 signifies a high ecological risk. Therefore,  $\alpha$ -BHC has RQ values ranging from 2.82 to 9.02, indicating a consistently high ecological risk across all stations. Similar findings were reported by Olutona *et al.*, (2019) in the Osun River, Nigeria, where  $\alpha$ -BHC posed high ecological risks in water bodies situated near agricultural settlements. This study is in agreement with such observation, suggesting that agricultural runoff remains a significant pathway for BHC contamination in water bodies.

$\beta$ -BHC had the highest RQ values, with a maximum of 20.04 in and a minimum of 3.20. This aligns with the findings of Adeyemi *et al.*, (2017), who recorded  $\beta$ -BHC RQ values exceeding 10.0 in sediments of the Lagos lagoon. The magnitude of these values in both our study and theirs indicates bioaccumulation tendencies and persistent exposure scenarios that may lead to chronic toxic effects in aquatic organisms. Lindane a well-documented persistent organic pollutant showed RQ values between 2.88 and 9.40. These values are reflective of USEPA's sediment quality guidelines, which classify Lindane as a priority pollutant with a probable effect concentration (PEC) of 0.33  $\mu\text{g/L}$  (USEPA, 2020). The elevated RQ observed in this study were consistent with Obida *et al.*, (2020), who identified Lindane as a dominant risk factor in water bodies within agricultural zones of Northern Nigeria.

$\gamma$ -BHC (Gamma-Hexachlorocyclohexane) presented similarly elevated RQ, ranging from 3.51 to 14.50 the finding of this study aligns with Musa *et al.*, (2018) who reported RQ values exceeding 10.0 in irrigation water sources in the Benue Valley, Nigeria.

Chlorthalonil also shows RQ values, from 13.00 to 8.80. Although not as extensively reported in Nigerian literature, international studies, such as Cerejeira *et al.* (2003) in Portugal, demonstrated Chlorthalonil RQ exceeding 5.0, highlighting its toxicity to non-target aquatic organisms like crustaceans and fish.

Heptachlor and its epoxide derivative presented varying RQ; Heptachlor ranged from 1.58 to 7.80, while Heptachlor Epoxide ranged from 1.53 to 3.81. These findings are in tandem with Akan *et al.* (2014), who reported Heptachlor RQ exceeding 3.0 in water bodies near industrial effluent zones in Kano State, Nigeria. The presence of Heptachlor Epoxide a more stable metabolite further signifies long-term contamination trends in the sampled water bodies. Aldrin, although recording RQ of 0.00 and 7.30 showed irregular distribution is indicative of point-source contamination, as observed in the work of Akpan *et al.*, (2018), where Aldrin concentrations were sporadic but significantly toxic where present.

Endosulfan I and II, along with Endosulfan sulfate displayed high-risk profiles. Endosulfan sulfate was notably high with RQ values ranging from 5.15 to 14.05, exceeding standard acceptable limits. Kah *et al.*, (2007) documented similar findings in rivers receiving agricultural runoff, where sulfate metabolites of Endosulfan presented higher toxicity potentials than the parent compound. Dieldrin and Endrin showed variable patterns. Dieldrin recorded low RQ at (0.62 but high at 4.00 and 5.00 respectively), signifying localized contamination events. Darko and Akoto, (2008) who reported Endrin RQ below 5.0 in Ghanaian rivers. DDD and DDT both breakdown products and parent compounds of the infamous DDT family, exhibited RQ values above 1.0 across nearly all sampling sites, with DDT reaching 10.80 This persistent occurrence of DDT residues supports global reports by WHO (2019), which stress that although DDT has been restricted in many countries, its residues are still found at ecologically risk levels in developing nations due to illegal usage or historic persistence.

Table 4.1.5 Estimated Daily Intake (EDI) of organochlorine Pesticide (OCP) Residues in Water Samples for Adults (mg/kg/day) in River Ibi

Pollutants	EDI –W1	EDI –W2	EDI –W3	EDI –W4	EDI –W5
$\alpha$ -BHC	1.29E-05	4.03E-06	4.91E-06	1.49E-05	5.20E-06
$\beta$ -BHC	2.54E-04	4.57E-05	1.11E-04	2.86E-04	4.89E-05
Lindane	1.13E-05	4.11E-06	5.06E-06	1.34E-05	5.86E-06
$\gamma$ -BHC	6.60E-05	2.00E-05	3.00E-05	8.29E-05	05.00E-05
Chlorthalonil	3.71E-05	1.66E-05	2.40E-05	2.54E-05	2.51E-05
Heptachlor	4.46E-05	9.17E-05	9.00E-06	3.71E-05	2.31E-05
Aldrin	2.05E-05	0.00E + 00	1.55E-05	2.09E-05	6.66E-06
Heptachlor Epoxide	1.09E-05	0.00E + 00	8.69E-06	5.14E-06	4.37E-06
Endosulfan I	1.72E-05	0.00E + 00	4.63E-06	2.95E-05	1.72E-05
Dieldrin	8.86E-06	0.00E + 00	08.86E-06	5.71E-05	1.66E-05
Endrin	2.60E-05	4.86E-06	2.31E-05	1.61E-05	0.00E + 00
Endosulfan II	5.60E-05	1.15E-05	8.31E-05	1.43E-05	2.95E-05
DDD	2.32E-05	4.86E-06	6.60E-06	8.86E-06	1.86E-05
Endosulfan sulfate	4.57E-05	8.63E-06	5.91E-05	7.99E-05	6.74E-05
DDT	2.89E-05	8.63E-06	3.00E-05	9.43E-06	2.32E-05

Estimated Daily Intake (EDI) of organochlorine Pesticide (OCP) Residues in Water Samples for Adults (mg/kg/day) in River Ibi

The Estimated Daily Intake (EDI) values of organochlorine pesticide (OCP) residues in the analyzed water samples provide insight into the potential chronic exposure risk to human health. EDIs are essential for evaluating the extent of chemical intake in relation to the Acceptable Daily Intake (ADI) set by international regulatory bodies such as the World Health Organization (WHO 2021) and Food and Agriculture Organization (FAO 2021).

Persistent organic pollutants (POPs), such as OCPs, are notorious for their bioaccumulative tendencies, hence even EDI values below ADI thresholds should not be dismissed casually, especially in regions where water bodies are continuously exposed to agricultural runoff.

Among all the detected organochlorine pesticide residues in the water samples,  $\beta$ -BHC (Beta-Hexachlorocyclohexane) exhibited the highest Estimated Daily Intake (EDI) value of 2.86E-04



mg/kg/day at site W4, indicating greater exposure potential compared to other compounds. This value is close to the WHO/FAO Joint Meeting on Pesticide Residues (JMPR) Acceptable Daily Intake (ADI) of  $3.00\text{E-}04$  mg/kg/day, the elevated  $\beta$ -BHC concentration implies persistence in the aquatic environment, likely due to historical agricultural use and slow degradation. This observation agrees with Adeyemi *et al.*, (2021), who also reported significant  $\beta$ -BHC contamination in surface waters of Southwestern Nigeria, attributing it to residual agrochemical presence from past farming practices. Similarly,  $\gamma$ -BHC (Lindane) demonstrated relatively high EDI values across sampling sites, ranging from  $2.00\text{E-}05$  at W2 to  $8.29\text{E-}05$  mg/kg/day at W4. Although these values remain below the WHO/FAO ADI of  $3.00\text{E-}04$  mg/kg/day, they indicate continued environmental input and persistence of the compound in the water system. Comparable EDI levels were observed by Wang *et al.*, (2019) in agricultural watersheds in China, where Lindane residues persisted long after its prohibition, confirming the compound's environmental stability and bioaccumulative tendency. Chlorthalonil and Heptachlor Chlorthalonil, often overshadowed by the more notorious OCPs, presented EDI values between  $1.66\text{E-}05$  and  $3.71\text{E-}05$  which are below the WHO's ADI of 0.03 (WHO, 2020). However, its classification as a probable human carcinogen (USEPA, 2019) necessitates a precautionary approach. Díaz-Torres *et al.*, (2022) reported similar low EDI levels in water bodies in Latin America but emphasized its chronic risk due to long-term exposure, even at minimal concentrations. Heptachlor showed sporadic EDI levels, at  $9.17\text{E-}05$ . Given the WHO ADI of 0.0001 for Heptachlor (FAO/WHO, 2021), these values are significant, particularly when viewed through the lens of cumulative exposure. Akan *et al.*, (2020) highlighted similar patterns in rural Nigerian water bodies, where Heptachlor levels fluctuated drastically depending on proximity to agricultural fields.

The detection of Aldrin, Dieldrin and Heptachlor Epoxide at varying EDI levels is indicative of residual contamination from historical pesticide applications. Although Aldrin and Dieldrin EDIs at  $5.71\text{E-}05$  are below their respective ADIs of 0.0001 (WHO, 2019), the persistent nature of these compounds and their known tendency to biomagnify through food chains cannot be overlooked. Darko and Akoto (2018) emphasized that even sub-threshold exposure to these compounds can culminate in significant health risks over extended periods, particularly in vulnerable populations.

Endosulfan I and II, along with Endosulfan sulfate, displayed moderate EDI values, with Endosulfan sulfate reaching up to  $7.99\text{E-}05$ . These values fall well below the WHO ADI of 0.006 (FAO/WHO, 2021). Nevertheless, Pawar and Rao (2020) documented endocrine-disrupting effects of Endosulfan derivatives at levels previously deemed non-threatening, underscoring the need for a re-evaluation of acceptable limits, especially in developing countries where regulation enforcement is often lacking.

Endrin showed EDI values up to  $2.60\text{E-}05$  which, though lower than the ADI of 0.0002 (WHO, 2019), is troubling given the compound's persistence and bioaccumulative properties. Likewise, DDD and DDT recorded EDI values ranging from  $4.86\text{E-}06$  to  $3.00\text{E-}05$  mg/kg/day. Studies by Kumar *et al.*, (2022) in the Ganges River, India, showed similar residual DDT contamination despite long-standing restriction, highlighting the global challenge posed by these legacy pollutants. The enduring presence of DDT and its metabolites (DDD, DDE) in water bodies, as observed in this study, is not uncommon in tropical regions where climatic factors favor the slow degradation of such compounds. Santos *et al.*, (2021), investigating water bodies in Brazil, observed that DDT residues were still prevalent decades after their official prohibition, echoing the findings of this study.

Table 4.1.6 Estimated Daily Intake (EDI) of organochlorine Pesticide (OCP) Residues in Water Samples for Children (mg/kg/day) in River Ibi

Pollutants	EDI –W1	EDI –W2	EDI –W3	EDI –W4	EDI –W5
$\alpha$ -BHC	$3.01\text{E-}05$	$9.40\text{E-}06$	$1.11\text{E-}05$	$3.48\text{E-}05$	$1.21\text{E-}05$
$\beta$ -BHC	$5.93\text{E-}04$	$1.07\text{E-}04$	$2.59\text{E-}04$	$6.68\text{E-}04$	$1.14\text{E-}04$

Lindane	2.64E-05	9.60E-06	1.18E-05	3.10E-05	1.37E-05
$\gamma$ -BHC	1.53E-04	4.67E-05	7.00E-05	1.93E-04	1.17EE-04
Chlorthalonil	8.67E-05	3.87E-05	5.60E-05	5.93E-05	5.87E-05
Heptachlor	1.04E-04	2.13E-05	2.10E-05	8.67E-05	5.37E-05
Aldrin	4.78E-05	0.00E + 00	3.58E-05	4.87E-05	1.56E-05
Heptachlor Epoxide	2.54E-05	0.00E + 00	2.02E-05	1.23E-05	1.02E-05
Endosulfan I	4.01E-05	0.00E + 00	1.08E	6.87E-05	4.01E-05
Dieldrin	2.06E-05	0.00E + 00	2.06E-05	1.33E-04	3.89E-05
Endrin	6.10E-05	1.08E-05	5.40E-05	3.73E-05	0.00E + 00
Endosulfan II	1.31E-05	2.67E-05	1.94E-04	3.27E-05	6.87E-05
DDD	5.40E-05	1.13E-05	1.54E-05	2.06E-05	4.53E-05
Endosulfan sulfate	1.07E-04	2.01E-05	1.38E-04	1.87E-04	1.57E-04
DDT	6.73E-0.5	2.01E-05	6.98E-05	2.21E-05	5.42E-05

Estimated Daily Intake (EDI) of organochlorine Pesticide (OCP) Residues in Water Samples for Children (mg/kg/day) in River Ibi

The EDI values for  $\alpha$ -BHC ranged from 9.40E-06 to 3.48E-05 mg/kg/day. According to FAO/WHO (2009), the Acceptable Daily Intake (ADI) for  $\alpha$ -BHC is 0.0003 mg/kg/day. The EDI values are below the ADI, but chronic exposure, even at low levels, poses risks of neurotoxicity and endocrine disruption (Kumar *et al.*, 2022). Similar levels were observed in the findings of Adeyemi *et al.*, (2020) in the Ogun River, Nigeria, suggesting persistent environmental contamination.  $\beta$ -BHC recorded significantly higher EDI values, ranging from 1.07E-04 to 6.68E-04 mg/kg/day. The values exceeded FAO/WHO's ADI of 0.0003 mg/kg/day, indicating a potential non-carcinogenic health risk. This aligns with findings from Olutona and Aderemi (2019), where  $\beta$ -BHC concentrations in Osun River surpassed safety thresholds, attributed to historical pesticide application in agriculture.

Lindane, another isomer of BHC, had EDI values ranging between 9.60E-06 and 3.10E-05 mg/kg/day. These are below the WHO's ADI of 0.0003 mg/kg/day (WHO, 2020). However, given lindane's high bioaccumulation potential, chronic low-dose exposure still warrants concern, especially in children (Asogwa and Dongo, 2018). Studies in India's

Ganges River showed similar lindane contamination (Gupta *et al.*, 2021).

EDI values spanned from 4.67E-05 to 1.93E-04 mg/kg/day, remaining below the ADI but alarmingly close at W4.  $\gamma$ -BHC is notorious for its persistence and bioaccumulative nature, posing risks to the central nervous system (Li *et al.*, 2023). This trend mirrors findings in Lake Victoria by Wandiga *et al.*, (2022), highlighting that  $\gamma$ -BHC remains a contaminant of concern in African freshwater systems.

Chlorthalonil, was detected with EDI values between 3.87E-05 and 8.67E-05 mg/kg/day. The USEPA (2018) lists its chronic oral reference dose (RfD) at 0.015 mg/kg/day, making current levels non-threatening in isolation. However, cumulative exposure to multiple pesticides amplifies risks a phenomenon observed in cumulative risk assessments (Khumalo *et al.*, 2023).

Heptachlor's EDI show at 1.04E-04 mg/kg/day, while Heptachlor epoxide was detected up to 2.54E-05 mg/kg/day. Both are below WHO's ADI of 0.0001 mg/kg/day, but proximity to the threshold is concerning. Heptachlor is restricted in many countries, yet residues persist due to its stability (UNEP, 2019). Similar residue levels were reported

in the Niger Delta region (Oyekunle et al., 2022). Aldrin (showed up to 4.87E-05 mg/kg/day) and Dieldrin (at 1.33E-04 mg/kg/day) are notorious OCPs banned globally. WHO's ADI for Dieldrin is 0.00005 mg/kg/day, this suggests a potential non-cancer hazard quotient > 1, as shown in studies of water bodies in southwestern Nigeria (Olatunde et al., 2021).

Endosulfan I, II, and its sulfate metabolite had EDI values between 1.31E-05 and 1.87E-04 mg/kg/day. The highest concentration was observed for Endosulfan sulfate at (W4). WHO's ADI for Endosulfan is 0.006 mg/kg/day. Though within limits, persistent exposure is linked to developmental and reproductive toxicity (Gbaruko and Friday,

2022). The observed levels are consistent with those in Cross River Basin by Essien et al., (2022).

Endrin's EDI reached up to 6.10E-05 mg/kg/day, while DDD (a DDT metabolite) ranged from 1.13E-05 to 5.40E-05 mg/kg/day. WHO's ADI for Endrin is 0.0002 mg/kg/day, meaning these values, though below ADI, still require attention due to bioaccumulation risks. Similar detections in River Benue have been linked to outdated stockpiles (Chukwuma et al., 2021).

DDT the EDI values for DDT ranged between 2.01E-05 and 6.73E-05 mg/kg/day. These are within the WHO's ADI of 0.0001 mg/kg/day. However, considering DDT's endocrine-disrupting properties and its detection in mothers' breast milk in Nigeria (Adeyeye et al., 2023).

Table 4.1.7 Cancer Risk (CR) Values for OCP residues in water samples from River Ibi

Pollutant	CSF (mg/kg/day)	CR W1	CR W2	CR W3	CR W4	CR W5
$\alpha$ -BHC	6.30	8.127E-05	2.539E-05	3.093E-05	9.387E-05	3.276E-05
$\beta$ -BHC	1.80	4.572E-04	8.226E-05	1.998E-04	5.148E-04	8.802E-05
Lindane	1.30	1.469E-05	5.343E-06	6.578E-06	1.742E-05	7.618E-06
$\gamma$ -BHC	1.30	8.580E-05	2.600E-05	3.900E-05	1.078E-04	6.500E-05
Chlorthalonil	0.011	4.580E-07	1.826E-07	2.640E-07	2.794E-07	2.761E-07
Heptachlor	4.50	2.007E-04	4.127E-04	4.050E-05	1.669E-04	1.039E-04
Aldrin	17.0	3.485E-04	0.000E+00	2.635E-04	3.553E-04	1.132E-04
Heptachlor Epoxide	9.10	9.919E-05	0.000E+00	7.908E-05	4.677E-05	3.977E-05
Endosulfan I	N/A	N/A	N/A	N/A	N/A	N/A
Dieldrin	16.0	1.418E-04	0.000E+00	1.418E-04	9.136E-04	2.656E-04
Endrin	N/A	N/A	N/A	N/A	N/A	N/A
Endosulfan II	N/A	N/A	N/A	N/A	N/A	N/A
DDD	0.24	5.568E-06	1.166E-06	1.584E-06	2.126E-06	4.464E-06
Endosulfan sulfate	N/A	N/A	N/A	N/A	N/A	N/A
DDT	0.34	9.826E-06	2.934E-06	1.020E-05	3.206E-06	7.888E-06

Cancer Risk (CR) Values of OCP residues in water samples from River Ibi.

The cancer risk (CR) assessment of organochlorine pesticides (OCPs) in water revealed notable variations across pollutants and exposure scenarios (W1–W5). Among the compounds analyzed, aldrin ( $3.55 \times 10^{-4}$ ), dieldrin ( $9.13 \times 10^{-4}$ ), heptachlor ( $4.13$

$\times 10^{-4}$ ) and  $\alpha$ -BHC ( $9.39 \times 10^{-5}$ ) exhibited the highest cancer risks, while DDT ( $3.21 \times 10^{-6}$ ), DDD ( $1.17 \times 10^{-6}$ ) and chlorthalonil ( $1.83 \times 10^{-7}$ ) recorded the lowest values. The Cancer Slope Factor (CSF) values indicate the potency of each compound as a carcinogen, with aldrin (17.0 mg/kg/day) and dieldrin (16.0 mg/kg/day) ranking as the most toxic. The

results of this findings are in agreement with Li *et al.*, (2021) who reported aldrin and dieldrin as dominant carcinogenic contributors in water from the Yangtze River, China, with CR values ranging from  $10^{-5}$  to  $10^{-3}$ . Likewise, Rahman *et al.*, (2023) in Bangladesh who found these compounds to pose the greatest carcinogenic risks among all OCPs analyzed in water. Based on CR magnitude, the order of potential cancer risk followed the trend: Aldrin > Dieldrin > Heptachlor >  $\alpha$ -BHC >  $\beta$ -BHC > Lindane > DDT > DDD > Chlorthalonil. Aldrin and dieldrin showed the highest CR values of  $9.13 \times 10^{-4}$  in W4, suggesting they were the major contributors to lifetime cancer risk in the studied area. This ranking pattern aligns with the known persistence, lipophilicity, and carcinogenic potency of these compounds (Ali *et al.*, 2023; Li *et al.*, 2021). The moderate cancer risks associated with heptachlor and BHC isomers ( $\alpha$ - and  $\beta$ -BHC) in this study are consistent with results by López-Benítez *et al.*, (2024), who also observed similar patterns in riverine sediments in Mexico, reporting CR values of  $10^{-5}$ – $10^{-4}$ .

Chlorthalonil, DDD, and DDT displayed relatively low CR values ( $< 10^{-5}$ ), which are below the threshold ( $1 \times 10^{-6}$ – $1 \times 10^{-4}$ ) often considered acceptable for lifetime cancer risk by the U.S. EPA (2023). These results suggest that, although DDT is persistent, its carcinogenic potency is lower than that of aldrin or dieldrin. Several studies have similarly indicated that DDT and its derivatives contribute less to carcinogenic risk compared to more potent OCPs. For example, Aigberua and Izah (2020) both observed CR values for DDT and DDE in the  $10^{-6}$  range, supporting the present observation that these compounds fall within acceptable risk limits. Endosulfan and endrin in their risk estimation (Ali *et al.*, 2023; Rahman *et al.*, 2023), the present findings list these compounds as “N/A,” indicating concentrations below detection limits.

## V. CONCLUSION

This study has demonstrated that River Ibi is moderately to highly contaminated with multiple organochlorine pesticide residues in water. Sixteen compounds were detected, with  $\beta$ -BHC,  $\gamma$ -BHC, chlorthalonil, and endosulfan sulfate emerging as the dominant pollutants. The results show that W4 and W3 are the most impacted sampling locations, both in terms of concentration and toxicological risk, while W1 recorded the lowest contamination levels.

The slightly alkaline pH (8.27–9.01) and moderate temperatures (20.62–27.67°C) further support the persistence of these pesticides, as degradation rates tend to be lower under such conditions.

Toxicological risk assessment revealed significant potential for human exposure through (EDI) with children facing greater vulnerability than adults. The estimated daily intake and cancer risk (CR) values exceeded the United States Environmental Protection Agency (USEPA) acceptable risk threshold ( $1 \times 10^{-6}$ ) at W3 and W4 for  $\beta$ -BHC and DDT, implying potential carcinogenic and chronic health effects from prolonged contact with contaminated water. The persistence of banned organochlorine compounds, such as DDT and its metabolites, strongly suggests ongoing illegal usage or remobilization from agricultural soils into the river system during runoff.

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