

Health Risk Assessment of Organochlorine Compounds at a Crude Oil-Impacted Soil in at Okpare-Olomu and Ihwrekreka Communities the Niger Delta

Ogunkeyede Akinyemi Olufemi^{1, *}, Isukuru Efe Jeffery¹, Adebayo Adedoyin Ayorinde¹, Adedosu Taofik Adewale², Tawari-Fufeyin Prekeyi¹

¹Department of Environmental Management and Toxicology, College of Science, Federal University of Petroleum Resources Effurun, Effurun, Nigeria

²Department of Pure and Applied Chemistry, Faculty of Science, Ladoke Akintola University of Technology, Ogbomosho, Nigeria

Email address:

isukuru3@gmail.com (Isukuru E. J.), ogunkeyede.akinyemi@fupre.edu.ng (Ogunkeyede A. O.),

Adebayo.adedoyin@fupre.edu.ng (Adebayo A. A.), taadedosu@lautech.edu.ng (Adedosu T. A.),

tawarifufeyin.prekeyi@fupre.edu.ng (Tawari-Fufeyin P.)

*Corresponding author

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Abstract: Organochlorine compounds (OCCs) are part of molecules that form the complex nature of crude oil. They bioaccumulate in animals and humans to concentrations with the potential to cause non-cancer and cancer-related diseases. OCCs undergo biodegradation to form more toxic complexes in the environmental media. Hence, it is essential to determine the concentration levels of OCCs in crude oil-polluted sites and the health risk they pose within the environmental media in the Okpare-Olomu and Ihwrekreka communities of Delta State, Nigeria. Environmental samples (water, soil, and sediments) were collected from oil spill sites at Okpare-Olomu and Ihwrekreka communities prepared with USEPA Method 8081b in the laboratory for gas chromatography-mass spectrometric (GC-MS) analysis to determine the concentration levels of OCCs. The GC-MS analysis results revealed common OCCs such as Heptachlor epoxide, Endosulfan II, Methoxychlor, Alpha-Lindane, gamma-Lindane and p, p'-DDD. The OCCs observed have two sources, directly from the crude oil spill and the biodegrading effect of the environmental agents. A good correlation was recorded among the OCCs at Ihwrekreka, and Okpare-Olomu according to Pearson's correlation with a moderately positive correlation ($r = 0.514$, $p < 0.991$), a good correlation recorded among the OCCs, which means that any observed health-related challenges within each community are likely to be from similar source; i.e. crude oil spills. The OCCs with high concentrations ranging from 2–140 mg/l were observed for Heptachlor epoxide II, Endosulfan II, Methoxychlor and p, p'-DDD. The presence and concentrations of the OCCs from Ihwrekreka and Okpare-Olomu indicate the potential of OCCs to cause health-related problems. Hence, non-cancer and cancer risk assessments of OCCs in samples were performed on water samples because the river serves as a source of drinking water for the two communities. The non-cancer risk results in both communities revealed that Endosulfan II has the potential to affect all age groups, while Methoxychlor and Heptachlor epoxide (Isomer A) could only affect teenagers. The risk potential of cancer was very high for most of the OCCs ($CR > 10^{-6}$), and compounds such as Heptachlor epoxide (Isomer A), Endosulfan II, p, p'-DDD, and Endosulfan sulfate were already at a state that required protective measures ($CR = 10^{-3}$). Consequently, the study revealed that the water within the two communities could potentially cause both non-cancer and cancer risks to the communities.

Keywords: Organochlorine, Cancer Risk, Heptachlor Epoxide

1. Introduction

Crude oil is a complex compound and comprises different organic substances. Organochlorine compounds (OCCs) are a component of crude oil as the primary source in the environment [1]. OCCs occurring in crude oil could be classified into primary sources during the formation of crude oil [1] and secondary sources during crude oil production, transportation, refining, and general maintenance of production equipment [2-4]. Drilling muds are used for lubricity and viscosity during oil well drilling. Thus, leading to the introduction of OCCs from organo-modified soils components of drilling mud [5].

Ecological, biodiversity, social, economic, and human health risks of crude oil pollution have been reported [6-8]. Crude oil pollution was rampant in the Niger Delta because of excessive, unsustainable resource exploitation, sabotage and vandalism along pipelines (Nwilo and Badejo, 2005 [9]). Omonigho [10] reported an unquantifiable oil spill in the Okpare-Olomu community, which caused enormous devastation to crude pipelines, farmlands, animals, and other properties, as shown in Figure 2. Moreover, Mishra [11] and Badamshin [12] explained that crude oil contains OCCs, which are lipophilic, persist in the environment, bioaccumulate in tissues of animals and humans, with other properties making them cancer-causing substances in

crude oil, causing cardiovascular disorder and other health-related health problem [13-19]. Therefore, there is an urgent need to analyze the crude oil spill site at Okpare-Olomu and Ihwrekreka communities for concentrations of OCCs, and possible health-related risks associated with the people living in the communities.

2. Materials and Methods

2.1. Study Areas

Okpare-Olomu and Ihwrekreka communities in the Niger Delta are located precisely in Ughelli South Local Government Area of Delta State, Nigeria. It lies within latitudes $05^{\circ} 27'N$ and $05^{\circ} 33'N$ and longitude $005^{\circ} 53' E$ and $006^{\circ} 04' E$ of the Niger Delta, Nigeria. The people of Okpare-Olomu are predominantly farmers and fishermen. Okpare-Olomu has a Shell flow station situated in the community, while the Ihwrekreka community has a crude oil pipeline transporting crude oil through the community. The flow of the river Okpare-Olomu suggests the possibility of spilt crude oil finding its way through the next community (Ihwrekreka). Okpare-Olomu is referred to as sample location 1 (L1), and the Ihwrekreka community is referred to as location two (L2), as shown in Figure 1.

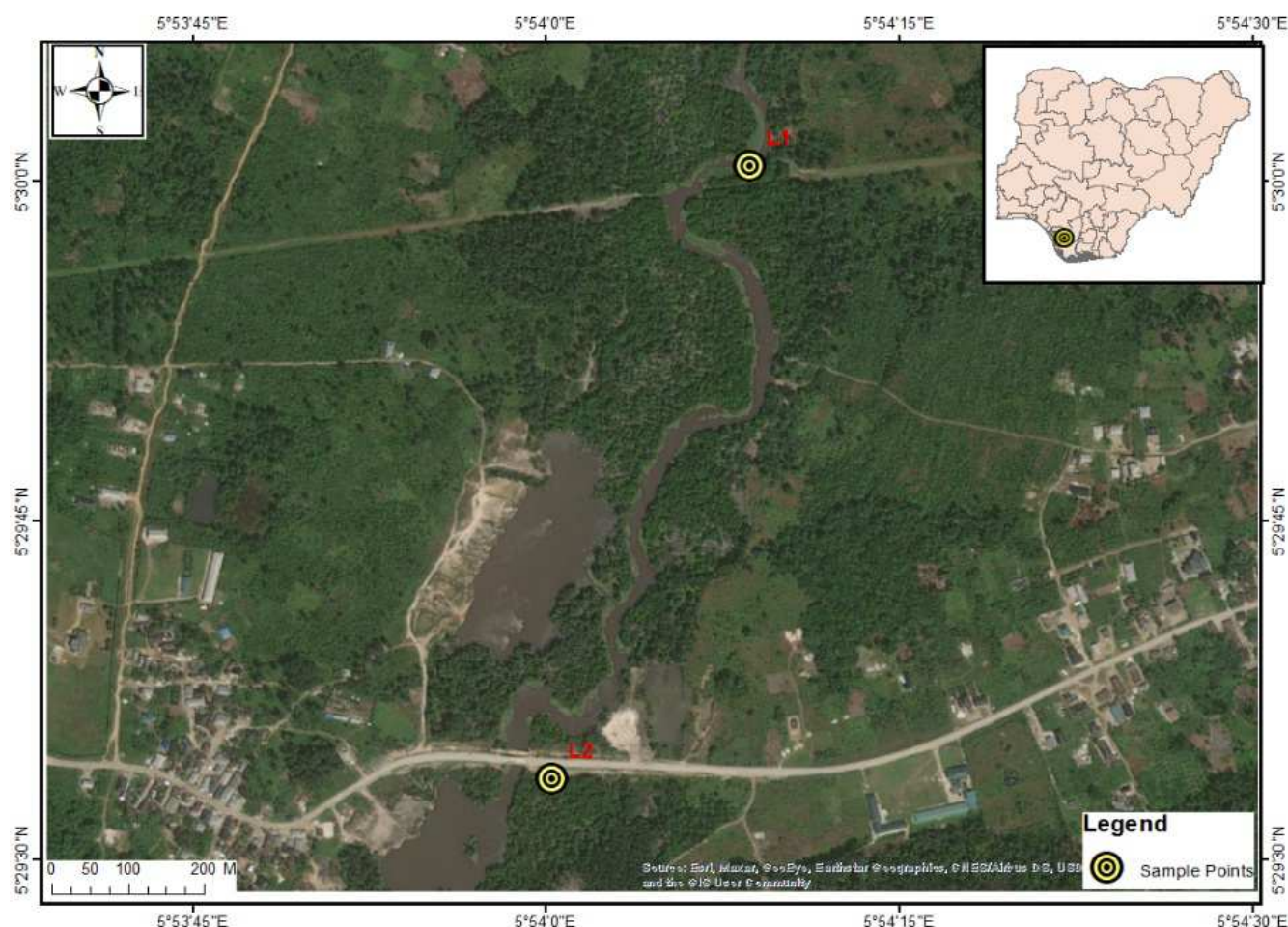


Figure 1. Map of Okpare-Olomu, and Ihwrekreka communities, Delta State of Nigeria showing sample points.



Figure 2. Oil spill incident in Okpare-Olomu river in 2018 [10].

2.2. Sample Collection from Ihwrekreka Community and Okpare-Olomu

Surface soils were collected from Ihwrekreka and Okpare-Olomu communities at depths of 0-15cm with the aid of a sterile soil auger, while sediment samples were collected below surface water level with the aid of a grab sampler. Water samples were collected in amber glass bottles to avoid degradation of OCCs by sunlight. Soil and sediment samples were stored in sterile polyethene bags after collection. Samples collected were stored in an ice chest, then transported to the laboratory and kept below -4°C [20].

2.3. Chemicals

Chemicals used were analytical grade, obtained from Fisher Scientific (USA) and Aldrich Chemical (United Kingdom). The analytical grade acetone and hexane were bought from Kobian Ltd. The purity of the HPLC grade hexane was checked by running its Gas Chromatogram to see any peaks other than that of the solvent. Silica gel and anhydrous sodium sulphate were activated at 200°C before use for the clean-up process [21].

2.4. Sample Extraction and Clean-up Procedure

Collected soil and sediment samples were air-dried, crushed using porcelain mortar and pestle, and sieved through a steel mesh with a 2-mm grid size. The sample extraction procedure before analysis for OCCs was done using USEPA methods 8081b and 1996 with slight modifications [22]. The method of extraction was done using an ultrasonic extractor. Detailed procedures for extraction and clean-up of soil samples are given in Schuster et al. [23]. The 10-ml extract was cleaned up by passing through 100 μL micro syringe columns packed with 15 g of activated silica gel (60-100 mesh size) and topped with 4 g of activated anhydrous sodium sulphate.

2.5. Chromatographic Analysis

The instrumental analysis was performed using gas chromatography-mass spectrometry. Two microlitres of each sample were injected in the split-less injection mode. The temperature of the oven in the GC was held at 100°C initially for 2 min, afterwards, it was hiked up at $20^{\circ}\text{C min}^{-1}$ to 140°C (not held), again hiked up at $4^{\circ}\text{C min}^{-1}$ to 200°C and held for 13 min, and finally hiked up at $4^{\circ}\text{C min}^{-1}$ to a final

temperature of 300°C and held for 2 min. The injector temperature was 250°C , the GC interface temperature was 300°C , and the MS source temperature was 250°C . The carrier gas was helium at a flow rate of 1 ml min^{-1} .

2.6. Quality Assurance/Quality Control (QA/QC)

All soil samples were subjected to strict quality control procedures, including analysis of blanks and spiked samples. Analysis was done in triplicates. A batch of seven standards and quality control standards were included at a rate of each set of twenty samples and ten samples, respectively. The limit of detection (LOD) was calculated as three times the standard deviation of the mean blanks, and values below the detection limit were not included. Recoveries ranged from 89 to 130%. All results were blankly corrected. All chemicals used for this research were of analytical grade and were purchased from Merck (Germany). All sorbents (anhydrous sodium sulphate, silica, and alumina) and glassware used were baked at 250°C for 12 h. Milli-Q (Millipore) deionized water was used during the laboratory analysis.

2.7. Statistical Analysis

The correlation study of OCCs for this research was performed with XLSTAT, an add-in to Excel for Windows 16. Principal component analysis (PCA) explains the relationship between measured concentration limits and accelerates the evaluation of potential organochlorine compounds as input sources [24]. Cluster analysis (CA) categorizes or orders the observed concentration limits or variables to pair the common distinctive variables together [25].

2.8. Risk Assessment

Health risk assessment of organochlorine compounds following contact either from dermal or ingestion from the river in Okpare-Olomu and Ihwrekreka communities was done using the guideline recommended by USEPA as reported by Ge et al. [26] and Yahaya et al. [27]. Determinants that can intensify an individual's likelihood of having cancer are age, health conditions, and environments such as a river polluted by organochlorine compounds.

The health risk level of the organochlorine compounds assessed was evaluated using life average daily dose (LADD), cancer risk, and hazard quotient (HQ). Values were evaluated from Equations 1 – 4 in agreement with standard methods set by ECETOC [28] and Hamilton et al. [29]. Hazard quotients were calculated by the formula described in Equation 1 [26, 27].

The following mathematical models were used to evaluate the risk assessment of organochlorine compounds, and the values of the parameters are stated in Tables 1 and 2 and 3.

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

HQ -- Hazard Quotient (Unitless);

ADD -- Intake Exposure Level (mg/kg/day);

RfD -- Reference Dose (mg/kg/day).

$$ADD = \frac{C \times FI \times IR \times EF \times ED}{BW \times AT} \quad (2)$$

$$LADD = \frac{C \times DI \times ED \times CF}{BW \times AT} \quad (3)$$

ADD -- Intake Exposure Level (mg/kg/day);

LADD -- Life Average Daily Dose (mg/kg/body weight);

C -- Average Concentration of the Analyte (organochlorine compounds) (mg/L);

FI -- Fraction Ingested (a whole number with 0–1, however, [27] valued FI as 0.98);

IR -- Daily water contact, possibly through swimming or drinking (ingestion or dermal contact), assessed based on different age categories;

EF -- Exposure Frequency;

ED -- Exposure Duration calculated using different age group;

BW -- Average bodyweight of different age categories;

AT -- Averaging times in days.

However, For LADD, AT -- 70 years \times 365 to give 25,550 days.

Table 1. The parameters used to calculate risk assessment for ADD and LADD.

Unit	0-7	7-17	Adult
FI	0.98	0.98	0.98
IR	0.3	1	1.4
EF	365	365	365
ED	6	11	3
BW	30	46	70
AT	2190	4615	10950
LADD	25550	25550	25550

Rfd is the oral reference dose for a particular organochlorine compound intake in (mg /kg d) as shown in Table 2.

$$\text{Cancer risk (CR)} = LADD \times CSF \quad (4)$$

C -- the concentration of organochlorine compound (mg/L); DI -- Daily Input (L/day); ED -- Exposure Duration (Year); BW -- Body Weight (kg); AT -- Average Life Span (year): 70 years \times 365 = 25,550 days; CSF -- Cancer Slope Factor (mg/kg/day), CF = Conversion Factor.

Table 2. Rfd for organochlorine compounds in environmental samples.

Target Compound	Rfd	Source
alpha-Lindane	0.8	[30]
delta-Lindane	0.8	[30]
beta-Lindane	0.8	[30]
Chlordane	6E-05	[31]
gamma-Lindane	0.3	[30]
Endrin	0.3	[30]
Aldrin	0.03	[30]
Heptachlor	0.5	[30]
Heptachlor Epoxide (Isomer A)	0.013	[30]
trans-Chlordane	6E-05	[31]
p,p'-DDT	0.5	[30]
Endosulfan I	0.006	[31]
Cis-Chlordane	6E-05	[31]
Cis-Nonachlor	6E-05	[31]
p,p'-DDE	0.5	[30]
Endosulfan II	0.006	[31]
trans-Nonachlor	6E-05	[31]
p,p'-DDD	0.5	[30]

Target Compound	Rfd	Source
Endosulfan sulphate	0.006	[31]
Endrin Aldehyde	0.3	[30]
Methoxychlor	0.005	[31]

HQ > 1.0 shows that the organochlorine compounds could pose a threat to individuals in the community or that harmful health effects may result from contact with polluted water. HQ < 1.0 indicates a comparatively low health risk, and a higher value for HQ indicates a greater risk to humans. ADD > 10⁻⁴ indicates the determined lifetime CR. LADD > 10⁻⁶ proposes the highest CR. However, LADD = 10⁻³ indicates that there must be defensive measures in place to prevent contact with polluted water. Also, a CR value > 10⁻⁶ suggests a maximum cancer risk. Values equal to 10⁻³ necessitate preventive measures in place.

Table 3. The parameters used to calculate cancer risk for this study.

Unit	Unit Value
DI	2
ED	30
BW	60
AT	25550
CSF	0.07
CF	10E-06

3. Results and Discussion

3.1. Organochlorine Compound Concentration in Okpare-Olumu and Ihwrekreka Communities

3.1.1. Soil and Sediment Samples

(i). Okpare-Olumu Community

Concentrations of Heptachlor epoxide, p, p'-DDD, Endosulfan II, alpha, beta, and delta Lindane in sediment and soil samples as shown in Figure 3 and Figure 4 were all lower than concentrations in crude oil samples analyzed by Nelson et al [32]. The results show environmental agents like fungi might have broken down organochlorine compounds in the crude oil spilt. The fungi experiment of D'Annibale et al [32] on aromatic hydrocarbons recorded massive biodegradation of OCCs in the soil and sediment, which suggested a possible cause of biodegraded OCCs observed in the crude oil spill. The degradation of the OCCs causes a lowering of their concentrations compared to crude oil concentrations [33]. The reduction could be related to the photolysis process arising from ultraviolet rays from the Sun on the oil spill, which agrees with a patent work by Matsutani [34] where organochlorine compounds were decomposed with the use of ultraviolet irradiation. Ma et al. [1] experimented with naphtha, kerosene, and light diesel high-value content of OCCs at a concentration range of 302.93, 729.45, and 836.90 mg/L, respectively proved that the lower values of OCCs must have resulted from biodegradation/photolysis. The concentrations of degraded compounds (Heptachlor epoxide, Endosulfan II, and p, p'-DDD) were higher in the results shown in Figures 3 and 4, which confirms the action of environmental agent effects on the crude oil spills [35, 36].

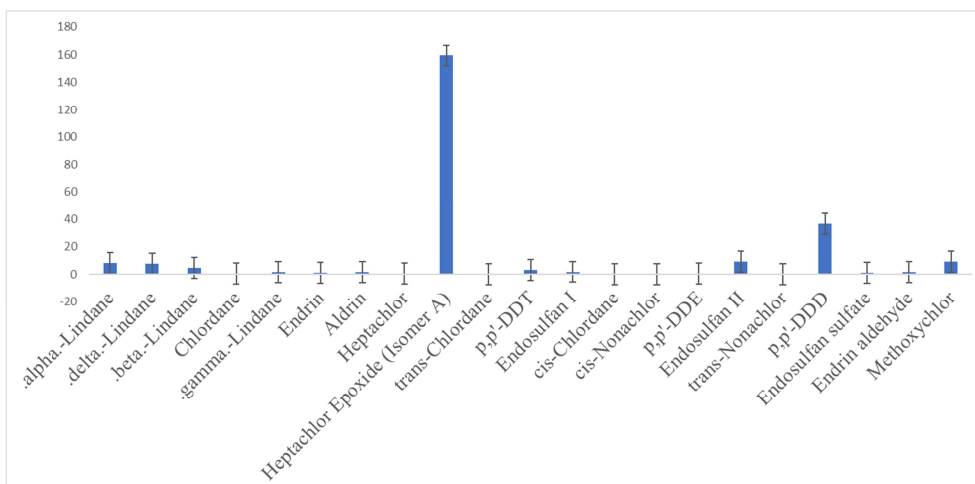


Figure 3. Mean concentrations of organochlorine compounds in sediment samples from Okpare-Olomu (mg/L).

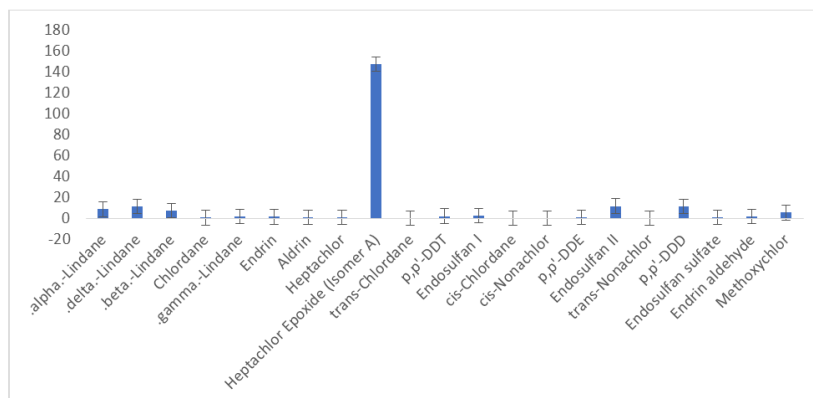


Figure 4. Mean concentrations of organochlorine compounds in soil samples from Okpare-Olomu (mg/L).

(ii). Ihwrekreka Community

Concentrations of organochlorine compounds in soil and sediment samples from the Ihwrekreka community were lower than those of the Okpare-Olomu community. The degradation products such as Isomers of Lindane, Endosulfan II, Heptachlor epoxide, and Methoxychlor had higher concentrations than parent compounds of OCCs, as shown in

Figure 5 and Figure 6. Heptachlor epoxide (isomer A) and Endosulfan II revealed degradation of OCCs in the environmental media in agreement with Fuentus et al [36] that microorganisms are capable of degrading organochlorine compounds. However, their concentrations in the soil and sediment of Okpare-Olomu were higher in values than in Ihwrekreka communities.

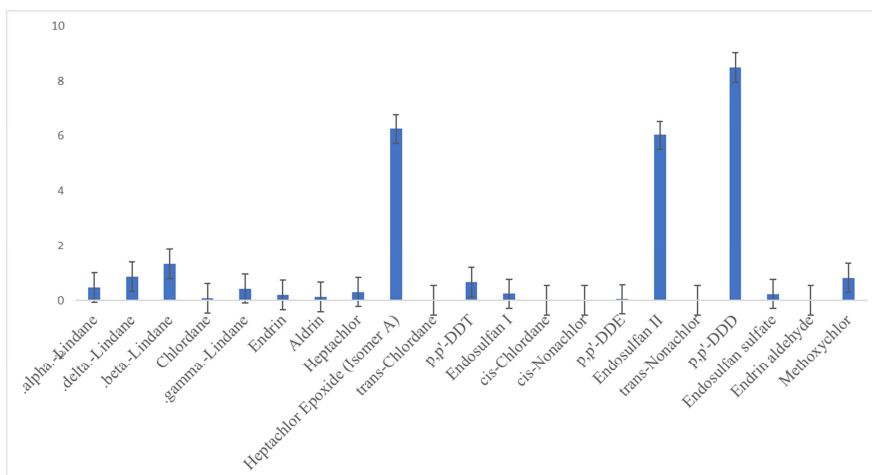


Figure 5. Mean concentrations of organochlorine compounds in Ihwrekreka (mg/L) soil samples.

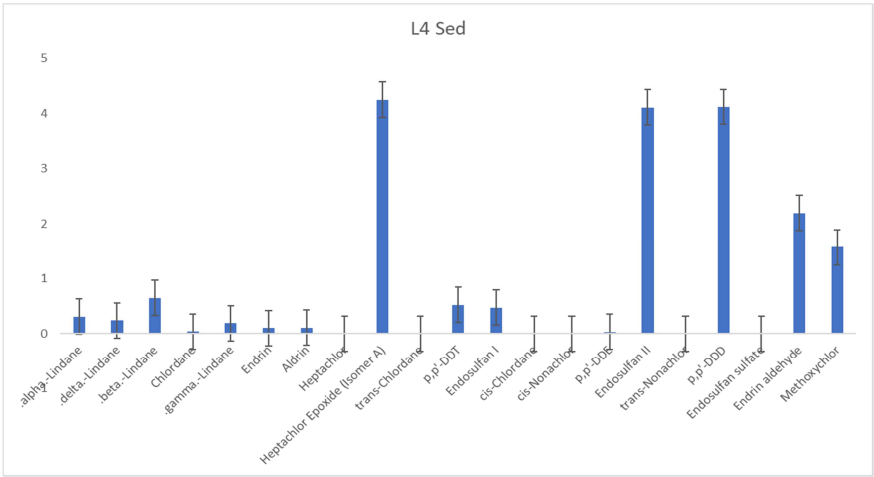


Figure 6. Concentrations of organochlorine compounds in sediment samples (L4 Sed) from Ihwrekrea (mg/L).

3.1.2. Water Samples

Concentrations of organochlorine compounds in surface water in a sample at Okpare-Olomu (Figure 7) were considerably higher in surface water samples when compared to concentrations of organochlorine compounds results from the Ihwrekrea community (Figure 8). Moreover, degradation products such as Isomers of Lindane, Endosulfan II, Heptachlor

epoxide (II), and Methoxychlor at the two sampling locations were higher in concentrations when compared to their parent compound shown in Figures 7 & 8. Although the concentrations were lower compared to soil and sediment results, it still suggests degradation process took place [33, 36] or the settling, and adsorption process into sediments and benthic particles in the water [37] occurred or due to wash-down process [38].

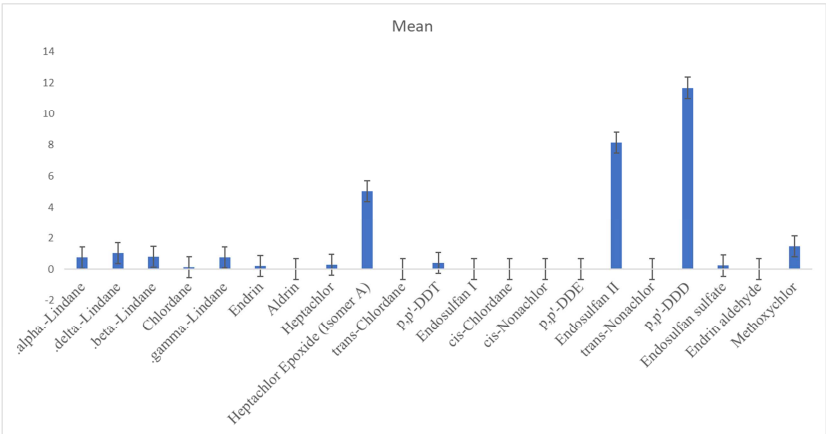


Figure 7. Mean concentrations of organochlorine compounds in water samples from Okpare-Olomu (mg/L).

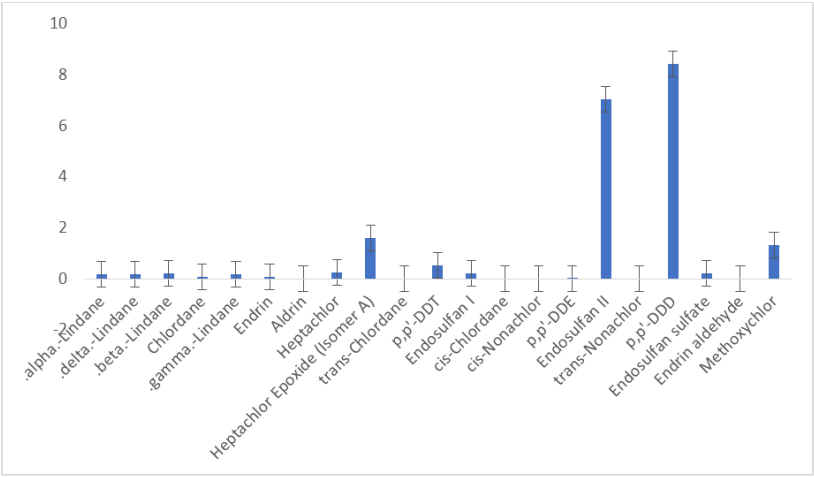


Figure 8. Concentrations of organochlorine compounds in water samples from Ihwrekrea (mg/L).

3.2. Principal Component Analysis (PCA) of Dataset Showing OCCs in Water, Soil, and Sediment Across Okpare-Olumu and Ihwrekreka Communities

The eigenvalues of the principal component analysis of the water, soil, and sediment samples from the Okpare-Olumu community were presented in Table 4. Table 4 revealed that F1 (principal component or factor 1) has significant contributions to the data distribution and correlations observed among the dataset of the 19 organochlorine compounds from the environmental samples analysed. The F1 and F2 influence on the dataset is 99.75%, where 75% contribution is F1. The biplot of the dataset of the Okpare-Olumu community revealed correlations or possible associations among the environmental samples at location one (L1) with majority of the OCC overlaps to form cluster between 0 and -0.1 (Figure 9).

The biplot agrees with the person correlation table for the environmental samples (Table 5). The scattered biplot revealed a stronger correlation between sediment and soil organochlorine components than water components. The F1

strongly influenced the concentration of OCCs in the soil and sediment but moderately influenced the water content. In addition, biplots revealed that the biodegraded contents resulted from parent organochlorine compounds. The biodegraded products have a high concentration that reveals a possibility of a breakdown of the primary organochlorine compounds to form the degraded products [39].

Table 4. Eigenvalues of OCCs in soil, sediment and water in Okpare-Olumu.

	F1	F2	F3
Eigenvalue	2.251	0.742	0.007
Variability (%)	75.045	24.730	0.225
Cumulative %	75.045	99.775	100.000

Table 5. Correlations between variables and factors of OCCs in Okpare-Olumu.

	F1	F2	F3
L1sed	0.978	-0.199	0.059
L1soil	0.949	-0.310	-0.056
L1water	0.627	0.779	-0.007

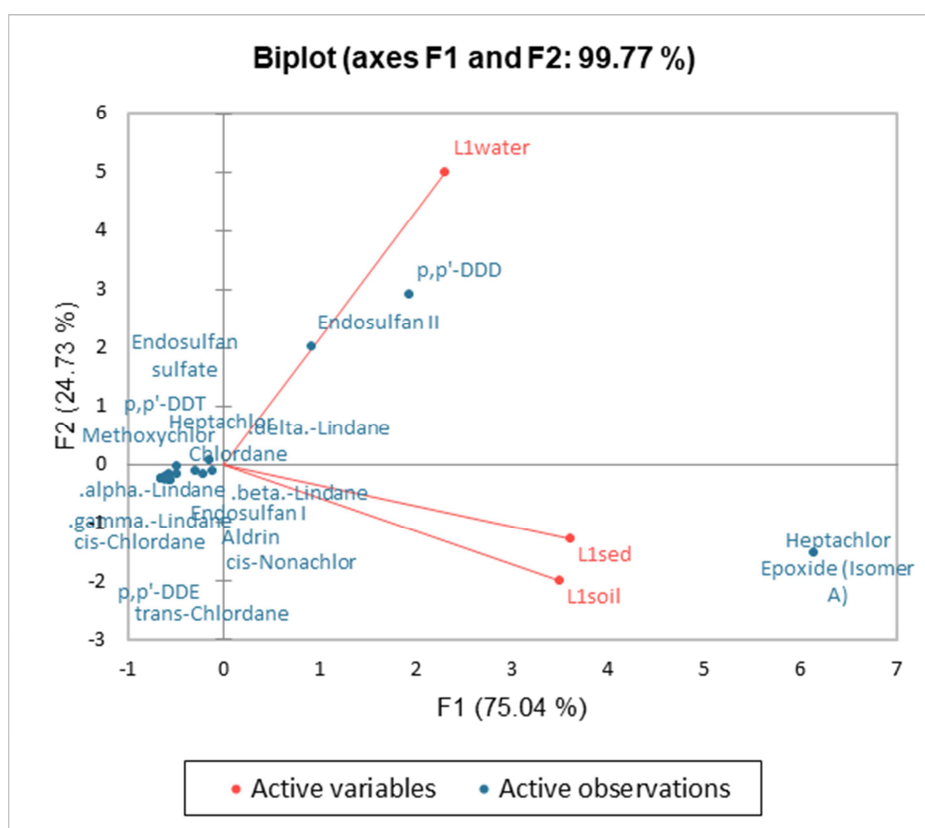


Figure 9. Scatter biplot of organochlorine compounds in soil, sediment and water in Okpare-Olumu.

Ihwrekreka community PCA for OCCs gave similar results to the Okpare-Olumu community because they are majorly influenced by F1. The F1 and F2 contributed 98% to the loading of the dataset of the organochlorines at the Ihwrekreka community (Table 6) and majority of the OCC overlaps to form cluster between 0 and 0.5 in the biplot (Figure 10).

Table 6. Eigenvalues of OCCs in soil, sediment and water in the Ihwrekreka community.

	F1	F2	F3
Eigenvalue	2.750	0.191	0.059
Variability (%)	91.664	6.355	1.981
Cumulative %	91.664	98.019	100.000

They are degradation products from the parent organochlorine compounds from the crude oil spill site products [40].

The positive relationship exhibited in their water concentrations indicates the transfer of Heptachlor epoxide from sediment to water, probably due to perturbation in the water body [39].

The correlation of the factors (principal components) with the variables at OCCs in Ihwrekreka showed very strong correlations influenced by F1. A strong positive correlation

has been observed in the biplots corresponding to Table 7, suggesting that p, p'-DDD, Endosulfan II and Heptachlor epoxide in soil, sediment in soil, sediment, and sediment sediment-water have similar sources.

Table 7. Correlations between variables and factors of OCCs in Ihwrekreka.

	F1	F2	F3
L4 soil	0.980	-0.025	-0.196
L4 water	0.943	0.322	0.089
L4 Sed	0.949	-0.294	0.114

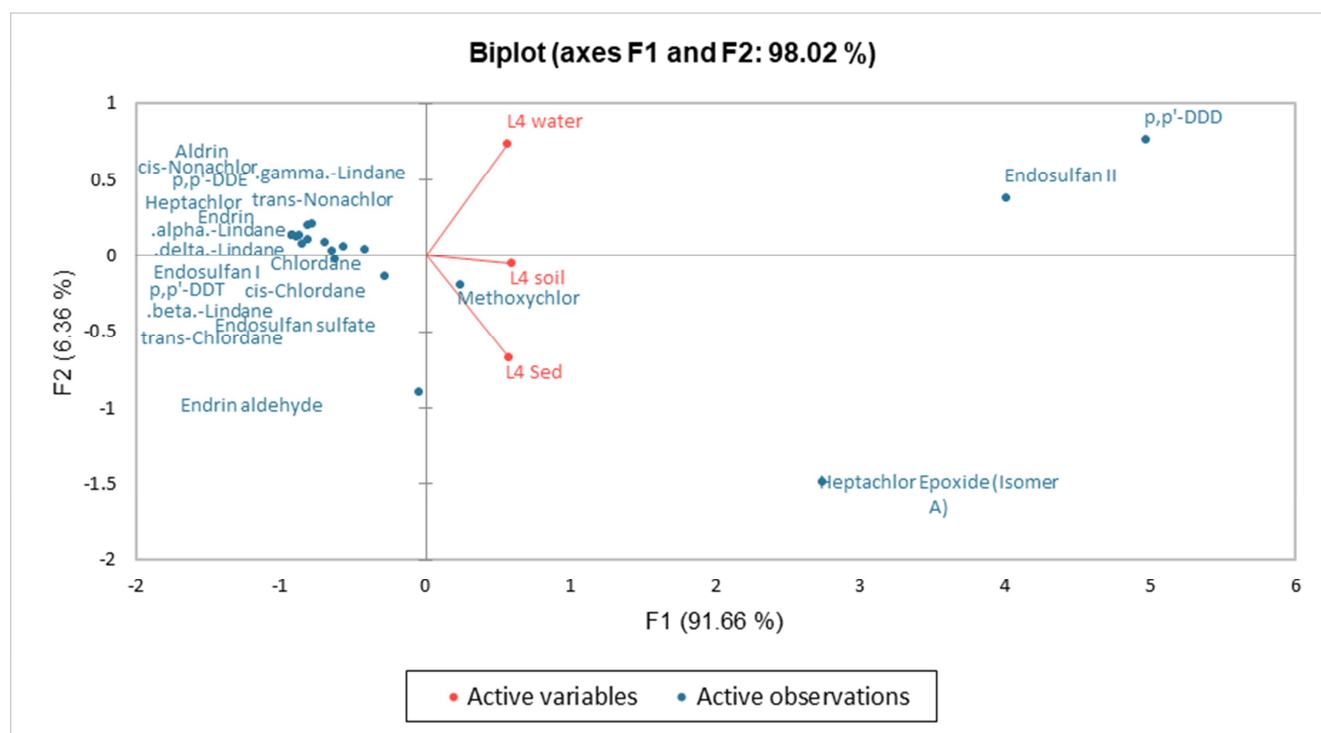


Figure 10. Scatter biplot of organochlorine compounds in soil, sediment, and water in Ihwrekreka.

Table 8. Hazard Quotient (HQ) of the OCCs for different ages for water at L1.

Target compounds	HQ 0-7yrs	HQ 7-17yrs	HQ adult
.alpha.-Lindane	8.88E-03	1.93E-02	1.78E-03
.delta.-Lindane	1.27E-02	2.76E-02	2.54E-03
.beta.-Lindane	9.68E-03	2.10E-02	1.94E-03
.gamma.-Lindane	2.45E-02	5.33E-02	4.90E-03
Endrin	6.04E-03	1.31E-02	1.21E-03
Heptachlor	5.59E-03	1.21E-02	1.12E-03
Heptachlor Epoxide (Isomer A)	3.80E+00	8.25E+00	7.59E-01
p,p'-DDT	7.84E-03	1.70E-02	1.57E-03
p,p'-DDE	2.45E-04	5.33E-04	4.90E-05
Endosulfan II	1.33E+01	2.88E+01	2.65E+00
p,p'-DDD	2.29E-01	4.97E-01	4.58E-02
Endosulfan sulfate	3.51E-01	7.63E-01	7.02E-02
Methoxychlor	2.82E+00	6.14E+00	5.64E-01

3.3. Risk Assessment of Organochlorine Compound in Okpare-Olumu and Ihwrekreka Communities

The health risks associated with the organochlorine compounds in the water samples at the Okpare-Olumu community were assessed for non-cancer and cancer risk potential, using an established USEPA. The mathematical

models in Equations 1-4 above [27, 28]. The non-cancer risk results for all the organochlorine compounds assessed at Okpare-Olumu were presented in Table 9. The assessment cut across children, teenagers and adults that could be affected. The results revealed that most of them had hazard quotient values of less than one except Endosulfan II, heptachlor epoxide (Isomer A) and Methoxychlor. Moreover, Heptachlor Epoxide (Isomer A) and Methoxychlor pose a non-cancer risk health threat among children and teenagers. Only Endosulfan II could potentially cause hazardous health problems to all ages who drink the water.

The HQ results for OCCs from Ihwrekreka communities were presented in Table 8. The OCCs have the potential to bioaccumulate over time, which could lead to health risks. Endosulfan II could potentially have health risks for all ages because the values were HQ>1. But Methoxychlor and Heptachlor epoxide (Isomer A) will only potentially affect children and teenagers. The Okpare-Olumu and Ihwrekreka communities' model results for the non-cancer risk of their water revealed that similar OCCs could cause potential hazards. There is a need to purify the water before it can be

fit for drinking. The average daily intake and lifespan average daily intake calculated in mg/kg/body weight [27] was essential for modelling the cancer risk potential of the OCCs. The cancer slope factor revealed the per cent increase in the risk of having cancer associated with a dose of a toxin every day for a lifetime; when multiple with the LADD, it gives the cancer risk value of each OCCs present in the water samples. If the cancer risk values were $>10^{-6}$, that is the

highest cancer risk, while values equal to 10^{-3} require protective measures [27]. The potential cancer risk was calculated for children, teenagers and adults within the Okpare-Olomu community, as shown in Table 10. The organochlorine compound with the least potential to cause cancer was p, p'-DDE. Most of the other compounds have the potential to cause carcinogenic problems in humans within the community.

Table 9. Hazard Quotient (HQ) of the OCCs in water at L2 for different age group samples.

Target compounds	HQ 0-7yrs	HQ 7-17yrs	HQ adult
.alpha.-Lindane	2.02E-03	4.39E-03	4.04E-04
.delta.-Lindane	2.21E-03	4.79E-03	4.41E-04
.beta.-Lindane	2.45E-03	5.33E-03	4.90E-04
.gamma.-Lindane	5.55E-03	1.21E-02	1.11E-03
Endrin	2.78E-03	6.04E-03	5.55E-04
Heptachlor	4.90E-03	1.07E-02	9.80E-04
Heptachlor Epoxide (Isomer A)	1.21E+00	2.63E+00	2.42E-01
p,p'-DDT	1.03E-02	2.24E-02	2.06E-03
Endosulfan I	3.59E-01	7.81E-01	7.19E-02
p,p'-DDE	2.94E-04	6.39E-04	5.88E-05
Endosulfan II	1.15E+01	2.51E+01	2.31E+00
p,p'-DDD	1.65E-01	3.59E-01	3.30E-02
Endosulfan sulfate	3.68E-01	7.99E-01	7.35E-02
Methoxychlor	2.59E+00	5.62E+00	5.17E-01

However, Heptachlor epoxide (Isomer A), Endosulfan II and p, p'-DDD have reached protective measures for teenagers within the community. Hence, the ingestion of the water or derm contact of the water while summing could initiate cancer-related illness within the populace.

Table 10. The cancer risk results of OCCs in the Okpare-Olomu community.

OCCs	LADD	LADD	LADD Adult	CR	CR	CR
	0-6 yrs	7-17 yrs		children	Teenager	Adults
.alpha.-Lindane	6.09E-04	2.43E-03	6.09E-04	4.26E-05	1.70E-04	4.26E-05
.delta.-Lindane	8.69E-04	3.47E-03	8.69E-04	6.08E-05	2.43E-04	6.08E-05
.beta.-Lindane	6.64E-04	2.64E-03	6.64E-04	4.65E-05	1.85E-04	4.65E-05
Chlordane	8.82E-05	3.52E-04	8.82E-05	6.17E-06	2.46E-05	6.17E-06
.gamma.-Lindane	6.30E-04	2.51E-03	6.30E-04	4.41E-05	1.76E-04	4.41E-05
Endrin	1.55E-04	6.19E-04	1.55E-04	1.09E-05	4.33E-05	1.09E-05
Heptachlor	2.39E-04	9.54E-04	2.39E-04	1.67E-05	6.68E-05	1.67E-05
Heptachlor Epoxide (Isomer A)	4.23E-03	1.69E-02	4.23E-03	2.96E-04	1.18E-03	2.96E-04
p,p'-DDT	3.36E-04	1.34E-03	3.36E-04	2.35E-05	9.38E-05	2.35E-05
p,p'-DDE	1.05E-05	4.18E-05	1.05E-05	7.35E-07	2.93E-06	7.35E-07
Endosulfan II	6.83E-03	2.72E-02	6.83E-03	4.78E-04	1.90E-03	4.78E-04
p,p'-DDD	9.81E-03	3.91E-02	9.81E-03	6.87E-04	2.74E-03	6.87E-04
Endosulfan sulfate	1.81E-04	7.20E-04	1.81E-04	1.27E-05	5.04E-05	1.27E-05
Methoxychlor	1.21E-03	4.82E-03	1.21E-03	8.47E-05	3.37E-04	8.47E-05

The cancer risk analysis of the Ihwrekreka community was analyzed as shown in Table 11. Although most of the OCCs have the potential to cause cancer-related disease, p,p'-DDD and Endosulfan sulfate were already at the protective measure stage for teenagers.

The cancer risk results from the two communities showed that the water analyzed can cause non-cancer and cancer risk related health problems to the populace. There is a need to purify the water to make it fit for drinking and swimming.

Table 11. The cancer risk results of OCCs at the Ihwrekreka community.

OCCs	LADD	LADD	LADD	CR	CR	CR
	Children	Teenagers	Adults	children	Teenager	Adults
.alpha.-Lindane	1.39E-04	5.52E-04	1.39E-04	9.73E-06	3.86E-05	9.73E-06
.delta.-Lindane	1.51E-04	6.03E-04	1.51E-04	1.06E-05	4.22E-05	1.06E-05
.beta.-Lindane	1.68E-04	6.70E-04	1.68E-04	1.18E-05	4.69E-05	1.18E-05
Chlordane	6.30E-05	2.51E-04	6.30E-05	4.41E-06	1.76E-05	4.41E-06

OCCs	LADD	LADD	LADD	CR	CR	CR
	Children	Teenagers	Adults	children	Teenager	Adults
.gamma.-Lindane	1.43E-04	5.69E-04	1.43E-04	1.00E-05	3.98E-05	1.00E-05
Endrin	7.14E-05	2.85E-04	7.14E-05	5.00E-06	2.00E-05	5.00E-06
Heptachlor	2.10E-04	8.37E-04	2.10E-04	1.47E-05	5.86E-05	1.47E-05
Heptachlor Epoxide (Isomer A)	1.35E-03	5.37E-03	1.35E-03	9.45E-05	3.76E-04	9.45E-05
p,p'-DDT	4.41E-04	1.76E-03	4.41E-04	3.09E-05	1.23E-04	3.09E-05
p,p'-DDE	1.85E-04	7.37E-04	1.85E-04	1.30E-05	5.16E-05	1.30E-05
Endosulfan II	1.26E-05	5.02E-05	1.26E-05	8.82E-07	3.51E-06	8.82E-07
p,p'-DDD	5.93E-03	2.36E-02	5.93E-03	4.15E-04	1.65E-03	4.15E-04
Endosulfan sulfate	7.08E-03	2.82E-02	7.08E-03	4.96E-04	1.97E-03	4.96E-04
Methoxychlor	1.89E-04	7.53E-04	1.89E-04	1.32E-05	5.27E-05	1.32E-05

4. Conclusion

The study has shown that organochlorine compounds were present in the environmental media from the two communities where samples were collected for analysis. The organochlorine compounds have been known to bioaccumulate in animals and humans, with the potential to cause health-related risks [41]. Some of the concentrations of the OCCs were above WHO [42], and USEPA allowable limits and the correlation of their OCCs concentration in the environmental media revealed similarity in their source. This also suggests the crude oil spill that occurred in the two communities and the river's flow from one community to another as a possible secondary source. Some compounds appeared in the results spectrum resulting from biodegradation of the original OCCs, such as Heptachlor epoxide (Isomer A), which have the potential of causing health problems in humans. The value of the concentrations observed for Heptachlor Epoxide and other related compounds necessitated the risk assessment of the OCCs to the entire populace within each community. The mathematical model for non-cancer risk and cancer risk was deployed to analyze the potential of health-related problems that might be seen among children, teenagers and adults. The risk assessments focus more on the water obtained from the river that flowed through the two communities. Although Heptachlor epoxide, Endosulfan II and Methoxychlor concentrations suggested the possibility of non-cancer and cancer risk within the populace, the analysis focused on water samples because the communities depend solely on the water for drinking and swimming.

The analytical assessment through the mathematical models revealed that Hazard quotient (HQ) and cancer risk showed that non-cancer and cancer risk could occur. Moreover, some of them were already at a level requiring protective measures for the community. Hence, the water seems unfit for drinking or swimming for the timing population within the two communities. The current study reveals the need to urgently address the crude oil spill's potential threat to the communities. There should be a further continuous monitoring of the environmental media seasonally to compare efficiency and cost-effectiveness of natural attenuation with remediation actions in the two communities as a guide for future remediation activities around other communities around Niger Delta region, where there is a similar experiences of oil spills.

References

- [1] Ma, R.; Zhu, J. H.; Wu, B. C.; Xue, J. X. (2016). Distribution and hazards of organic chlorides in crude oil and its distillates. *Pet. Refin. Eng.* 46 (4), 60–64.
- [2] Gutzeit, J. (2000). Effect of Organic Chloride Contamination of Crude Oil on Refinery Corrosion; NACE International: Houston, TX; Paper 00694.
- [3] Zhang, X. J. (2004) Sources and distribution of chlorides in crude and the control measures. *Pet. Refin. Eng.* 34 (2), 14–16.
- [4] National Association of Corrosion Engineers (NACE). (2004) Effect of Non-extractable Chlorides on Refinery Corrosion and Fouling; NACE International: Houston, TX, 2004; Paper 34105.
- [5] Oxychem (2014). Methyl Chloride Handbook. Oxychem Technical Information v. 11 pp. 2-3. *Pure and Applied Chemistry* 75 (8): 1123-1155.
- [6] Ugochukwu, C. N. C., and Ertel, J. (2008). Negative impacts of oil exploration on biodiversity management in the Niger Delta area of Nigeria, *Impact Assessment and Project Appraisal*, 26: 2, 139-147, DOI: 10.3152/146155108X316397A.
- [7] Ordinioha, B. (2015). The human health effects of oil exploration and exploitation in the Niger Delta region of Nigeria. 10.13140/RG.2.1.1973.2320.
- [8] Roe D., Seddon N., and Elliott J. (2019). Biodiversity loss is a development issue: A rapid review of evidence. *International Institute for Environment and Development. Issue paper IIED*. ISBN 978-1-78431-688-4. <http://pubs.iied.org/17636IIED>
- [9] Nwilo, P. C., and Badejo, O. T. (2005). Oil Spill Problems And Management in the Niger Delta. Article in *International Oil Spill Conference Proceedings*, May 2005. DOI: 10.7901/2169-3358-2005-1-567.
- [10] Omonigho, M. (2019). Tension in Delta as oil spill ravages Okpare community. *Daily post Nigeria online*. <https://dailypost.ng/2018/03/06/tension-delta-oil-spill-ravages-okpare-community/> (Accessed April 28th, 2021).
- [11] Mishra, K. Sharma, R. C., and Kumar, S. (2012). Contamination levels and spatial distribution of organochlorine pesticides in soils from India. *Ecotoxicol Environ Saf*, Vol. 76, pp. 215-225.
- [12] Badamshin, A. G., Nosov, V. V., Presniakov, and A. Y. (2021). Genesis of Organochlorine Compounds in Crude Oil and Petroleum Products (A Review). *Pet. Chem.* 61, 1190–1199. <https://doi.org/10.1134/S0965544121110141>

- [13] Sohail E, Waseem A, Chae WL, Jong JL, Imitiaz H. (2004). Endocrine Disrupting Pesticides: A Leading Cause of Cancer among Rural People in Pakistan. *Experimental Oncology* 26 (2): 98–105.
- [14] Eqani, S. A., Malik, R. N., Katsoyiannis, A., Zhang, G., Chakraborty, P., Mohammad, A., and Jones, K. C. (2012). Distribution and risk assessment of organochlorine contaminants in surface water from River Chenab, Pakistan. *Journal of Environmental Monitoring*, 14 (6), 1645. doi: 10.1039/c2em11012a.
- [15] Tongo, I., Ezemonye, L. N., Nupe, P. and Ogbomida, E. (2014). Levels, distribution and human health risk assessment of organochlorine pesticide residues in surface water from Ikpoba River, Nigeria. *Nigerian Journal of Scientific Research*, 13 (1): 26-34.
- [16] Ogbeide, O., Tongo, I. and Ezemonye, L. N. (2015). Risk assessment of agricultural pesticides in water, sediment, and fish from Owan River, Edo State, Nigeria. *Environ Monit Assess* 187, 654. <https://doi.org/10.1007/s10661-015-4840-8>.
- [17] Jayaraj, R., Megha, P., and Sreedev, P. (2016). Organochlorine pesticides, their toxic effects on living organisms and their fate in the environment. *Interdisciplinary toxicology*, 9 (3-4), 90–100. <https://doi.org/10.1515/intox-2016-0012>
- [18] Škrbić, B. D., Marinković, V., Antić, I., and Gegić, A. P. (2017). Seasonal variation and health risk assessment of organochlorine compounds in urban soils of Novi Sad, Serbia. *Chemosphere*, 181, 101–110. doi: 10.1016/j.chemosphere.2017.04.
- [19] Jin, X., Liu, Y., Qiao, X., Guo, R., Liu, C., Wang, X., & Zhao, X. (2019). Risk assessment of organochlorine pesticides in drinking water source of the Yangtze River. *Ecotoxicology and Environmental Safety*, 182, 109390. doi: 10.1016/j.ecoenv.2019.109390.
- [20] Adeyinka, G. C., Moodley, B., Birungi, G. (2019). Evaluation of organochlorinated pesticide (OCP) residues in soil, sediment and water from the Msunduzi River in South Africa. *Environ Earth Sci* 78, 223 (2019). <https://doi.org/10.1007/s12665-019-8227-y>.
- [21] USEPA (2001). Methods for Collection, Storage and Manipulation of Sediments for Chemical and Toxicological Analyses. Technical Manual. EPA-823-B-01-002. US Environmental Protection Agency, Office of Water, Washington, DC, USA.
- [22] Schuster K. J, Gioia R, Moeckel C, Agarwal T, Bucheli TD, Breivik K. (2011). Has the burden and distribution of PCBs and PBDEs changed in European background soils between 1998 and 2008? Implications for sources and processes. *Environ Sci Technol*; 45: 7291–7.
- [23] Method 8081B Rev. 2, Update IV, Feb 2007, and Method 8000C Test Methods for Evaluating Solid Waste, SW-846, Third Edition, Final Update III, December 1996 (USEPA, Office of Solid Waste and Emergency Response, Washington, DC).
- [24] Hu, L., Zhang, G., Zheng, B., Qin, Y., Lin, T., and Guo, Z. (2009). Occurrence and distribution of organochlorine pesticides (OCPs) in surface sediments of the Bohai Sea, China. *Chemosphere*, 77 (5), 663–672. doi: 10.1016/j.chemosphere.2009.07.
- [25] Da, C., Liu, G. and Yuan, Z. (2015). Levels and distribution of organochlorine pesticides in surface sediment after flood season from the old Yellow River Estuary, China. *Water Science & Technology: Water Supply*. v15, p6.
- [26] Ge, J.; Woodward, L. A.; Li, Q. X.; Wang, J. (2014). Occurrence, distribution, and seasonal variations of polychlorinated biphenyls and polybrominated diphenyl ethers in surface waters of East Lake, China. *Chemosphere* 2014, 103, 256–262.
- [27] Yahaya, A., Okoh, O. O., Okoh A. I., and Adeniji, A. O. (2017). Occurrences of Organochlorine Pesticides along the Course of the Buffalo River in the Eastern Cape of South Africa and Its Health Implications. *International Journal of Environmental Research and Public Health*. 14, 1372; doi: 10.3390/ijerph14111372.
- [28] ECETOC (2016) Guidance for Effective Use of Human Exposure Data in Risk Assessment of Chemicals.
- [29] Hamilton, D. J.; Ambrus, Á.; Dieterle, R. M.; Felsot, A. S.; Harris, C. A.; Holland, P. T.; Katayama, A.; Kurihara, N.; Linders, J.; Unsworth, J. (2003). Regulatory limits for pesticide residues in water (IUPAC Technical Report). *Pure Appl. Chem*. 75, 1123–1155.
- [30] Witczak, A. and Abdelgawad, H. (2014). Assessment of health risk from organochlorine pesticides residues in high-fat spreadable foods produced in Poland. *J. Environ. Sci. Health., Part B* 49: 917–928.
- [31] U.S. EPA. (2002). A Review of the Reference Dose and Reference Concentration Processes. U.S. Environmental Protection Agency, Risk Assessment Forum, Washington, DC, EPA/630/P-02/002F.
- [32] Nelson, J., Poirier, L. E., and Lopez Linares, F. A. (2019). Determination of Chloride in Crude Oils by Direct Dilution using Inductively Coupled Plasma Tandem Mass Spectrometry (ICP-MS/MS). *Journal of Analytical Atomic Spectrometry*. doi: 10.1039/c9ja00096h.
- [33] D'Annibale, A., Ricci, M., Leonardi, V., Quarantino, D., Mincione, E., and Petruccioli, M. (2005). Degradation of aromatic hydrocarbons by white-rot fungi in a historically contaminated soil. *Biotechnol. Bioeng*. 90 (6), 723-731.
- [34] Liu, G., and Li, X.. (2012). Preparation of an organochlorine transfer agent for crude oil and performance evaluation. 42. 51-54.
- [35] Matsutani, Hiroshi (1996). JPH09234338A-Photolysis of organochlorine compound <https://patents.google.com/patent/JPH09234338A/en#citedBy>
- [36] Fuentes S., Claudia B. Sergio C. Juliana S. and Amoroso, M M. (2010). Microorganisms capable to degrade organochlorine pesticides.
- [37] Olutona, G. O., Olatunji, S. O. and Obisanya, J. F. (2016). Downstream assessment of chlorinated organic compounds in the bed-sediment of Aiba Stream, Iwo, South-Western, Nigeria. *SpringerPlus* 5, 67. <https://doi.org/10.1186/s40064-016-1664-0>
- [38] Unyimadu, J. P., Osibanjo, O., and Babayemi, J. O. (2019). Concentration and Distribution of Organochlorine Pesticides in Sediments of the Niger River, Nigeria. *Journal of health and pollution*, 9 (22), 190606. <https://doi.org/10.5696/2156-9614-9.22.190606>.

- [39] Pokethitiyook, P., and Poolpak, T. (2012). Heptachlor and Its Metabolite: Accumulation and Degradation in Sediment. *Pesticides - Recent Trends in Pesticide Residue Assay*. doi: 10.5772/48741.
- [40] Huang, Y., Xiao, L., Li, F., Xiao, M., Lin, D., Long, X., and Wu, Z. (2018). Microbial Degradation of Pesticide Residues and an Emphasis on the Degradation of Cypermethrin and 3-phenoxy Benzoic Acid: A Review. *Molecules*, 23 (9), 2313. DOI: 10.3390/molecules23092313.
- [41] Abbasi, Y. (2021). Evaluating and Monitoring the Environmental Exposure to Pesticide Residues in the Lake of Naivasha Basin (Kenya). M. Sc. Thesis. The University of Twente Library.
- [42] World Health Organization (WHO) (2003). Endosulfan though Australian Environment Laws classifies threshold level at 0.03µg/L (IUPAC, 2003).