



Research Article

Organochlorine Pesticide and Total Petroleum Hydrocarbon Pollution of Ilaje Coastal River Sediments, Ondo State, Nigeria

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Abstract: We investigated the presence of organochlorine pesticides (OCPs) and total petroleum hydrocarbons (TPHs) on the surface sediments sampled at the Ilaje coastal river in Ondo State, Nigeria. The samples were taken at five locations along the coast to determine their distribution in surface sediments and identify the input of industrial activities. The identified OCPs included G-BHC, d-BHC, chlorothalonil, alachlor, aldrin, dacthal, heptachlor-epoxide, g-chlordane, and trans-nonachlor, accounting for roughly 99% of the total detectable in the samples. The pesticide concentrations (dry weight) were ≤ 326.98 ng/g, with an average value of 15.49 ng/g. The pesticide levels at the various studied locations were in this order: Idiogba Police > Igbokoda > Idiogba Subu > Ayetoro > Eyunona. Furthermore, considerable negative and positive correlations exist between the various components of chlorinated pesticides. Based on the dry weight, TPH values in the samples ranged from 5.42 to 22.53 ng/g, in the order Eyunona > Idiogba Police > Idiogba Subu > Ayetoro > Igbokoda. Our data suggest that the hydrocarbons in the sediment matrices arise from anthropogenic causes other than oil spillage, such as water transportation and residential waste discharge, storm waters, rural runoff, etc. Although pollution levels are generally low, there is a need for regular monitoring and enforcement of stringent implementation of environmental laws and standards designed to curb any potential environmental pollution arising from oil spills and indiscriminate waste disposals in the coastal community.

Keywords: organic pollutants, chlorinated hydrocarbon, sediments, pollution assessment, principal component analysis

1. Introduction

Chemical pollutants from numerous anthropogenic sources are found in coastal ecosystems, posing severe hazardous consequences to marine ecosystems [1-3]. River runoffs may carry enormous quantities of these contaminants into the sea via various routes, such as sewage disposal, accidental oil spills, indiscriminate municipal and industrial discharges, automotive wastes, vehicular emissions, etc., caused by incomplete thermal oxidation of fossil fuels [4]. The release of numerous organic contaminants into the environment from these diverse sources (especially runoff or effluent discharges) is a major source of environmental depletion in many countries. Most organic pollutants incessantly enter

the sea, rivers, dams, and lakes, converting such media into environmental reservoirs for unwanted organics [5].

Various organochlorine pesticides (OCPs) and their breakdown intermediates are common organic pollutants deteriorating water bodies globally [6]. Some OCPs promote agricultural produce, which, in turn, improves human and animal health. However, these successes have been tainted by the discovery of unintended consequences in untargeted organisms [7]. Typically, OCPs are incredibly refractory to biological, photochemical, and chemical degradation. They are also prone to bioaccumulation and long-distance transfer [8]. Because of their carcinogenic, hepatotoxic, and mutagenic properties, many chemicals are classified as high-priority pollutants [9]. They often exhibit low water and high lipid solubility and are linked to significant environmental impact in various species and nearly every tropic level.

Several organochlorines have been associated with various adverse impairments in man and his environment, such as marred reproduction, endocrine disruption, and immunosuppression [10]. Organochlorine exposure has been correlated with the decline in the population of several marine mammals [8]. Most OCPs accumulate and biomagnify in the food chain, reaching larger quantities in top carnivores. As a result, organisms higher up the food chain, such as birds and mammals, may be susceptible to adverse health impacts from exposure to OCPs. Since the mid-1970s, several developed nations (including the United States of America and Sweden) have banned or restricted the use and sale of most OCPs due to their hazardous effects on aquatic organisms [11]. Despite being banned for decades, research on OCPs in various water bodies across Europe [6], Asia [12], and America [13] has found widespread occurrences of their residues. In some developing countries (e.g., Nigeria), using dichlorodiphenyltrichloroethane (DDT) for malaria control is still legal in some regions of the nation [14]. Because of their relatively high affordability and efficiency for pest management, some OCPs could still be produced and used clandestinely in agriculture under unsuspecting trade names.

Total petroleum hydrocarbons (TPHs) are common organic pollutants in organic waste [15]. Primarily, they have been employed to discover the origins of petroleum residue in marine habitats [16, 17]. Oil spills arising from lands (including oil rigs, refineries, transportation, and storage) and municipal and industrial discharges are more destructive in the cold than in warmer climates [18]. Because oil bioaccumulates in fish fillets, mollusks, mussels, and other mammals' fatty tissues, its effects on aquaculture could be severe [19]. TPHs are typically delivered into the sea as solutions, such as stormwater, runoff from agricultural and urban lands, home waste discharges, or industrial effluents. However, only a fraction of the load is retained in the solution, while the bulk gets immobilized with the sediments via flocculation, sedimentation, and coagulation [20, 21]. Therefore, sediment remains a viable sink for the biosphere's polycyclic aromatic hydrocarbons (PAHs) and other unwanted organics. At contamination levels, these organics could severely compromise the health of aquatic organisms in the ecosystem [22]. Specifically, alkanes, burnt hydrocarbons, and spent oils are the most critical components of TPHs in marine environments [20, 23].

OCPs and TPHs are acknowledged for their environmental refractivity, bioaccumulation, and toxicity features. They have been utilized in significant quantities and will likely remain of significance for some years. Although OCPs are unquestionably relevant in large-scale agriculture, their environmental toxicity has escalated concerns that could ensure their global ban [24]. Their extensive use has made them discoverable by evaluating their residues in diverse ecological matrices, including water, air, sediments, soil, vegetation, and biota [25]. Hence, the current research will assist in filling the knowledge gap about chlorinated pesticides and TPHs on the Nigerian coast and provide management implications for future sustainable development toward achieving source control from anthropogenic activities. Our findings could help provide crucial baseline data for the environmental monitoring of OCPs and TPHs.

2. Materials and methods

2.1 The study area

The study area is located between the Greenwich meridian's longitudes of 5°45' and 6°15' and the equator's latitudes of 4°30' and 5°00'. Ilaje has a total land area of around 2,300 square kilometers. It is bordered on the west by Ogun State, on the east by Ese Odo local government and Delta State, on the north by Ika Local Government Area, and on the south by the Atlantic Ocean and the southern Bight of Benin. In general, Ondo State is divided into two geological zones. The first is the sedimentary rock region in the south, while the second is the Precambrian Basement Complex rock region in the north. The basement sedimentary rocks' limit is a few kilometers north of Aaye.

2.2 Sample collection and preparation

With the aid of a metallic core sampler, we sampled the surface sediment (0-10 cm) in July 2021 at Ayetoro, Idiogba Subu, Idiogba Police, Eyunona, and Igbokoda (Figure 1). The samples were placed in an icebox before being taken to the lab. All samples were air-dried to a consistent weight. Other extraneous items, such as plant debris, were eliminated. Then, the samples were pulverized in a glass mortar, sieved through a 0.3 mm metallic sieve, and kept at -4 °C until analysis.

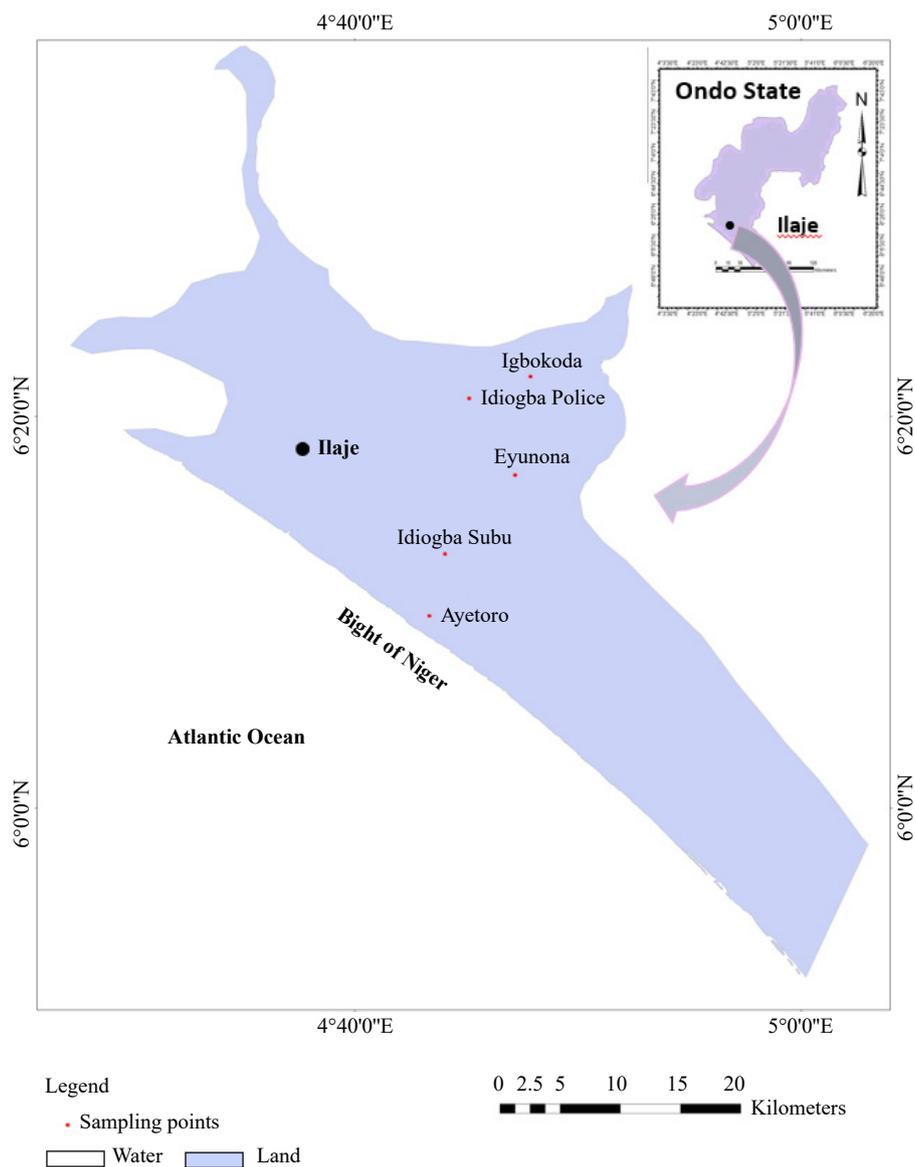


Figure 1. A map of the study indicating the sampling locations in the study area

2.3 TPH extraction from sediment samples

For further moisture removal, 10 g of the dried sample was combined with anhydrous sodium sulfate (Na_2SO_4). For spiking, 1 mL of 10 $\mu\text{g}/\text{mL}$ surrogate standard was added to the mixture before it was extracted into 200 mL of

dichloromethane using a Soxhlet extractor for 24 h. The extract was passed via a glass funnel with anhydrous Na₂SO₄ and later concentrated using a rotary evaporator [26].

2.4 Silica gel clean up

The organic extracts were cleaned in a chromatographic column (10 mm i.d. × 30 cm) bearing 10 g activated silica gel, capped with a 2-cm-thick layer of anhydrous Na₂SO₄. 20 mL of *n*-pentane eluted the material before being concentrated and exchanged using *n*-hexane. For quality assurance, a blank sample was handled similarly to this process [27].

2.5 GC analysis

The analytes' concentrations were determined analytically using an HP-5 fused silica capillary column (30 m; 0.32 mm i.d. × 0.25 m film) and gas chromatography (Agilent 7820A GC, Agilent, Santa Clara, CA, USA) equipped with a flame ionization detector. Helium was the carrier gas, passed at 1.75 mL/min (average face velocity of 29.47 cm/s), and the detector was set to 300 °C. For 1 minute, the column temperature was held at 40 °C before ramping it to 320 °C at 7 °C/min [19].

From the stock solutions, working standards for the alkanes and surrogate (1-chlorooctadecane) were produced and stored in amber bottles at 4 °C. With *n*-hexane, we developed 0.05-20 g/mL working range standards to calibrate the instrument. The Agilent Chemstation chromatography software calculated the average response factor for each analyte using plotted calibration curves with correlation coefficients between 0.9846 and 0.9919. All the analytes' estimated linearity was within $R^2 \geq 0.990$. Adding an unresolved complex mixture (UCM), we calculated the TPH as the sum of *n*-alkane concentrations eluted from nC9 to nC36 [28].

2.6 Quality control

Analytical and high-performance liquid chromatography (HPLC)-grade reagents and solvents were used, respectively, to ensure reliable results. Blanks and spiked samples were intermittently analyzed in duplicate. However, no interference was discovered in any of the blanks. With eight replicate injections of a middle-level calibration standard, we calculated the limit of detection (LOD) for *n*-alkanes [29-31]. We derived the LOD by multiplying the "t" value at a confidence level of 99% with the instrument response, resulting in values within 0.06-0.13 µg/L. The instrument's relative standard deviation (RSD) was often less than the maximum limit of 25%, ranging from 3.61 to 8.32% for the *n*-alkanes [32]. The recoveries of spiked samples determined the method's efficiency at 20 µg/L (within 76-137%), with an average ranging between 87% and 127% for water and sediment samples. Similarly, the recovered 1-chlorooctadecane spiked into the samples, ranging from 44% to 96%, falling within the allowed 40%-140% range for hydrocarbons [32].

2.7 Data analysis

The IBM SPSS version 20 (IBM, Armonk, NY, USA) and Microsoft Excel (2016 version) packages did the statistical analyses. A one-way ANOVA was performed for several groups, with standard errors calculated to illustrate the measure of dispersion. A correlation compared the relationships between groups, and significance was assessed as $p < 0.05$. [17]. The link between regional socioeconomic levels and pesticide concentrations in mangrove sediment was investigated using the Pearson correlation. Data visualization and calculations were done in Origin Pro v9.9 and the Microsoft Excel 2019 package. Principal component analysis (PCA) was utilized to examine the correlations between the chlorinated pesticide concentrations and sampling sites and between the TPH and sampling sites and identify the potential factors. The PCA enables more empirically robust data analysis than conventional techniques, yielding a better understanding of data variability [33].

3. Results and discussion

3.1 Levels of OCPs in the sediments

Table 1 shows the OCP concentrations in coastal river surface sediments from the Ondo State coastal zone. The examined quality of surface sediments can also inform about likely contamination during sampling [34]. However, the current study assumed all precautions to avoid introducing contaminants that might compromise the integrity of the data were taken and adhered to.

Table 1. Concentrations of OCPs (ng/g) in the sediment samples

OCP/ Location	Ayetoro	Idiogba Subu	Idiogba Police	Eyunona	Igbokoda
Etridiazole	0.0051	ND	ND	ND	0.0100
Chloroneb	ND	ND	ND	ND	ND
a-BHC	0.4068	0.3651	ND	ND	ND
Simazine	ND	ND	ND	ND	ND
Atrazine	ND	ND	ND	ND	ND
b-BHC	ND	0.2237	0.1616	0.3977	ND
g-BHC	10.67	16.40	6.748	7.966	8.352
d-BHC	50.03	89.32	327.0	7.486	189.3
Chlorothalonil	13.59	3.237	3.462	7.990	9.228
Alachlor	12.31	64.75	14.40	15.41	25.18
Aldrin	5.55	17.12	4.469	2.244	10.02
Dacthal	18.62	19.66	21.75	15.53	8.336
Heptachlor epoxide	4.570	10.37	22.79	8.044	11.26
g-chlordane	9.569	9.900	13.02	4.938	8.150
trans-nonachlor	11.90	8.868	7.372	8.789	14.13
ΣOCPs	137.2	240.2	421.2	78.80	283.8

ND = not detected. Each value is a mean of duplicate analyses with a negligible difference.

Etridiazole, chloroneb, a-BHC, simazine, atrazine, b-BHC, g-BHC, d-BHC, chlorothalonil, alachlor, aldrin, dacthal, heptachlor-epoxide, g-chlordane, and trans-nonachlor were among the OCPs found in this coastal zone. The cumulative OCPs (dry weight) ranged from ND to 326.978 ng/g, with an average of 15.49 ng/g, indicating significant spatial variance of the chlorinated pesticides (Figure 2).

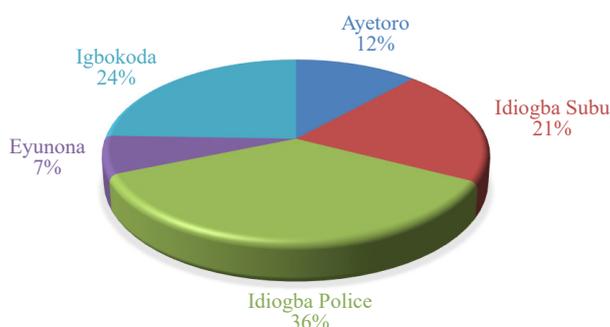


Figure 2. Distribution of cumulative pesticides in the coastal sediment samples of Ilaje, Ondo State

The Idiogba Police (421.2 ng/g) at the jetty, facing the mangrove zone, had the highest pesticide concentrations, followed by the river channel locations. Lower cumulative OCPs were generally found at Eyunona (78.80 ng/g) and other supratidal zone sampling stations. We discovered that river transport and tidal influence were this area's principal sources of chlorinated pesticides. The high levels of pesticides observed at the Idiogba Police could result from anthropogenic activity in the vicinity, such as wastewater discharge, fishing, farm runoff, farming, and effluents from boating and commercial operations. Another source of the high level of pesticides in the water body could be its proximity to the jetty, which residents in the coastal zone heavily use. The chlorinated pesticide components in the sediment samples varied greatly: chloroneb, simazine, and atrazine were absent, while etridiazole, a-BHC, and b-BHC were either very low or nonexistent (Table 1). g-BHC, d-BHC, chlorothalonil, alachlor, aldrin, dacthal, heptachlor epoxide, g-chlordane, and trans-nonachlor were found in all surface sediments of Ondo coastal rivers, accounting for 98-99% of Σ OCPs.

3.2 TPH Levels in the sediments

Similar to the OCPs, we quantified the TPHs in the sediment samples. The concentrations ranged from 5.42 to 22.53 ng/g on a dry weight basis (Table 2). All locations showed the presence of the twelve examined TPHs, except hentriacontane which was undetected at Ayetoro (along with Pentadecane, 2,6,10,14...) and Idiogba Subu.

Table 2. TPH concentrations (ng/g) in the sediment samples

TPH/ Location	Ayetoro	Idiogba Subu	Idiogba Police	Eyunona	Igbokoda
Dodecane	0.21	0.08	0.17	0.17	0.14
Tridecane	0.33	0.14	0.19	0.11	0.26
Tetradecane	0.25	0.11	0.14	0.53	0.16
Tetracosane, 3-ethyl-	1.18	0.34	0.23	0.34	0.44
Heneicosane, 11-decyl-	0.60	1.42	0.68	0.27	0.40
Pentadecane, 2,6,10,14...	ND	0.10	0.15	0.66	0.51
Pristane	5.08	2.40	2.02	1.46	0.14
Octadecane	1.65	0.32	0.31	5.39	0.76
Octacosane	0.51	4.69	0.63	1.58	0.91
Nonacosane	0.18	1.24	1.45	5.12	0.57
Triacantane	ND	ND	7.33	6.64	0.83
Hentriacontane	0.19	0.99	0.33	0.26	0.30
Σ TPH	10.18	11.83	13.63	22.53	5.42

ND = not detected. Each value is a mean of duplicate analyses with a negligible difference.

The TPH distribution in the study area differed from that of OCPs. The maximum TPH concentration was found at Eyunona (22.53 ng/g) and the lowest at Igbokoda (5.42 ng/g). This observation could be attributed to potential hydrocarbon volatilization from the sediment and TPH biodegradation as the temperature rises. Higher temperatures have also been linked to a faster photochemical degradation rate of airborne hydrocarbons, likely responsible for the lower levels of pollutants seen during the dry season elsewhere [35]. Still, the emission rates (e.g., vehicle, biomass, and coal) increased, contributing to higher hydrocarbon concentrations in the wet season when our sampling took place (i.e., in July) [36]. The following is the order of TPH concentration decrease: Eyunona > Idiogba Police > Idiogba Subu > Ayetoro > Igbokoda. Generally, the mineral oil in the sediment samples was below the Nigerian 50 mg/kg permissible limit in Nigeria [37, 38].

Massoud et al. [39] stated that sediment's TPH levels of 10-15 mg/kg are considered unpolluted, while those within 15-50 mg/kg should be considered somewhat polluted. Thus, the sediment samples in the current study were in the unpolluted and moderately polluted ranges. The higher values could emanate from substantial industrial and shipping activity in the coastal zone, such as the port's operating influence near the river mouth, which can increase rainwater flow into the bay from the rural region. Other potential sources include vehicle deposits, oil spills, and engine leaks on asphalt-tarred highways, which are harmful to benthic species when they accumulate in the surficial sediment, thus causing developmental abnormalities, reproductive capacity loss, and various diseases in marine mammals [40].

In general, TPH levels in the sediment were significantly lower than in most other coastal environments, such as Ceuta Harbour in North Africa [41], Musa Bay [42], and the Barnegat Bay-Little Egg Harbor Estuary in the United States [43]. On the other hand, water from a few other places worldwide contained petroleum hydrocarbon amounts similar to those found in this study area. Examples include the shoreline and mangroves of the northern Persian Gulf [44], Todos os Santos Bay, Brazil [45], and the southeast coast of India [44, 46].

The levels of OCPs and PAHs found in the coastal sediment in the current study were similar to those found elsewhere but not in coastal regions. For instance, Qu et al. [47] investigated soil and air samples. Also, our results are similar to previous studies on the nature and distribution of TPHs and OCPs in coastal sediments. Specifically, PAHs have been found chronically embedded in the sediment, shaping the bacterial and crustacean communities [48]. More recently, another study carried out in Tanzania showed the presence of these organic pollutants at ppb levels, both in dry mass and lipid concentrations [49]. Here, the low-molecular-mass PAHs were found in relatively higher proportions than their high-molecular-weight counterparts. More critical is the possibility of bioaccumulating these pollutants, including OCPs, in the lipid structures of marine animals, which could be transferred along the food chains to humans. Hence, a transboundary study of these organics should be done to ensure the safety of exposed ecosystems and humans. Since previous studies [6, 12, 47-49] have identified the relationship and co-existence of OCPs, it is imperative to investigate the same in this study.

3.3 Relationship between TPHs and OCPs in the sediments

At the two confidence intervals (0.01 and 0.05), there was no association between the overall contents of TPHs and OCPs in the sediment samples (Table 3). This observation shows that the point sources of these compounds in the sediment of coastal rivers come from various places. Nonetheless, there was some correlation between their components and TPH's constituents (Table 4). Dodecane has a significant negative correlation with octacosane and hentriacontane, while tetradecane has a significant positive correlation with octadecane and hentriacontane. At varying confidence intervals, the chlorinated pesticides also showed some correlation (Table 5). Etridiazole showed a positive relationship with trans-nonachlor, g-BHC had a positive relationship with alachlor, which displayed a strong positive relationship with aldrin, and heptachlor epoxide portrayed a strong positive relationship with d-BHC. This significant association between TPHs and OCPs suggests that the chemical constituents entered the coastal river from similar sources.

Table 3. Matrix of Pearson correlation between TPHs and OCPs in sediment samples

		TPHs	OCPs
TPHs	Pearson correlation	1	-.441
	Sig. (2-tailed)		.457
OCPs	Pearson correlation	-.441	1
	Sig. (2-tailed)	.457	

No. of observations = 5.

Table 4. Matrix of Pearson correlation among TPHs in the sediment samples

		C ₁₂ H ₂₆	C ₁₃ H ₂₈	C ₁₄ H ₃₀	C ₂₆ H ₅₄	C ₃₁ H ₆₄	C ₁₉ H ₄₀	C ₁₉ H ₄₀	C ₁₈ H ₃₈	C ₂₈ H ₅₈	C ₂₉ H ₆₀	C ₃₀ H ₆₂	C ₃₁ H ₆₄
C ₁₂ H ₂₆	Correlation	1	.536	.433	.592	-.716	.526	.459	.361	-.880*	.041	.995	-.911*
	Sig. (2-tailed)		.351	.466	.293	.173	.474	.437	.550	.049	.948	.062	.031
	N	5	5	5	5	5	4	5	5	5	5	3	5
C ₁₃ H ₂₈	Correlation	.536	1	-.338	.809	-.215	-.015	.472	-.388	-.575	-.769	-.791	-.477
	Sig. (2-tailed)	.351		.578	.098	.728	.985	.423	.519	.311	.129	.419	.416
	N	5	5	5	5	5	4	5	5	5	5	3	5
C ₁₄ H ₃₀	Correlation	.433	-.338	1	.050	-.631	.800	-.023	.997**	-.222	.852	.372	-.466
	Sig. (2-tailed)	.466	.578		.937	.253	.200	.971	.000	.719	.067	.757	.429
	N	5	5	5	5	5	4	5	5	5	5	3	5
C ₂₆ H ₅₄	Correlation	.592	.809	.050	1	-.131	.541	.796	.009	-.348	-.453	-.899	-.380
	Sig. (2-tailed)	.293	.098	.937		.833	.459	.107	.989	.566	.444	.289	.528
	N	5	5	5	5	5	4	5	5	5	5	3	5
C ₃₁ H ₆₄	Correlation	-.716	-.215	-.631	-.131	1	-.847	.246	-.592	.827	-.370	.300	.924*
	Sig. (2-tailed)	.173	.728	.253	.833		.153	.690	.293	.084	.540	.806	.025
	N	5	5	5	5	5	4	5	5	5	5	3	5
C ₁₉ H ₄₀	Correlation	.526	-.015	.800	.541	-.847	1	-.690	.797	-.458	.616	-.324	-.681
	Sig. (2-tailed)	.474	.985	.200	.459	.153		.310	.203	.542	.384	.790	.319
	N	4	4	4	4	4	4	4	4	4	4	3	4
C ₁₉ H ₄₀	Correlation	.459	.472	-.023	.796	.246	-.690	1	-.062	-.073	-.324	.981	-.070
	Sig. (2-tailed)	.437	.423	.971	.107	.690	.310		.921	.908	.595	.126	.911
	N	5	5	5	5	5	4	5	5	5	5	3	5
C ₁₈ H ₃₈	Correlation	.361	-.388	.997**	.009	-.592	.797	-.062	1	-.153	.873	.340	-.404
	Sig. (2-tailed)	.550	.519	.000	.989	.293	.203	.921		.806	.053	.779	.500
	N	5	5	5	5	5	4	5	5	5	5	3	5
C ₂₈ H ₅₈	Correlation	-.880*	-.575	-.222	-.348	.827	-.458	-.073	-.153	1	.086	.136	.962**
	Sig. (2-tailed)	.049	.311	.719	.566	.084	.542	.908	.806		.890	.913	.009
	N	5	5	5	5	5	4	5	5	5	5	3	5
C ₂₉ H ₆₀	Correlation	.041	-.769	.852	-.453	-.370	.616	-.324	.873	.086	1	.573	-.117
	Sig. (2-tailed)	.948	.129	.067	.444	.540	.384	.595	.053	.890		.612	.851
	N	5	5	5	5	5	4	5	5	5	5	3	5
C ₃₀ H ₆₂	Correlation	.995	-.791	.372	-.899	.300	-.324	.981	.340	.136	.573	1	.014
	Sig. (2-tailed)	.062	.419	.757	.289	.806	.790	.126	.779	.913	.612		.991
	N	3	3	3	3	3	3	3	3	3	3	3	3
C ₃₁ H ₆₄	Correlation	-.911*	-.477	-.466	-.380	.924*	-.681	-.070	-.404	.962**	-.117	.014	1
	Sig. (2-tailed)	.031	.416	.429	.528	.025	.319	.911	.500	.009	.851	.991	
	N	5	5	5	5	5	4	5	5	5	5	3	5

*. Significant correlation at 0.05 level (2-tailed)

**. Significant correlation at 0.01 level (2-tailed)

C₁₂H₂₆ = Dodecane, C₁₃H₂₈ = Tridecane, C₁₄H₃₀ = Tetradecane, C₂₆H₅₄ = Tetracosane, 3-ethyl-, C₃₁H₆₄ = Heneicosane, 11-decyl-, C₁₉H₄₀ = Pentadecane 2,6,10,14...., C₁₉H₄₀ = Pristane, C₁₈H₃₈ = Octadecane, C₂₈H₅₈ = Octacosane, C₂₉H₆₀ = Nonacosane, C₃₀H₆₂ = Triacontane, C₃₁H₆₄ = Hentriacontane

Table 5. Matrix of Pearson correlation among OCPs in the sediment samples

		A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
A	Correlation	1	. ^a	-.068	. ^a	. ^a	-.789	-.196	.064	.623	-.213	.090	-.801	-.295	-.140	.971**
	Sig.		.	.913	.	.	.113	.752	.919	.262	.730	.885	.103	.630	.823	.006
B	Correlation	. ^a														
	Sig.
C	Correlation	-.068	. ^a	1	. ^a	. ^a	-.277	.797	-.456	.251	.443	.486	.407	-.543	.189	.085
	Sig.	.913652	.107	.440	.684	.455	.407	.497	.345	.760	.892
D	Correlation	. ^a														
	Sig.
E	Correlation	. ^a														
	Sig. (2-tailed)
F	Correlation	-.789	. ^a	-.277	. ^a	. ^a	1	.029	-.328	-.489	.154	-.185	.272	.059	-.436	-.723
	Sig. (2-tailed)	.113	.	.652	.	.		.963	.590	.404	.805	.766	.658	.925	.463	.168
G	Correlation	-.196	. ^a	.797	. ^a	. ^a	.029	1	-.410	-.209	.887*	.847	.249	-.391	.060	-.042
	Sig. (2-tailed)	.752	.	.107	.	.	.963		.493	.735	.045	.070	.686	.515	.923	.946
H	Correlation	.064	. ^a	-.456	. ^a	. ^a	-.328	-.410	1	-.482	-.135	-.015	.137	.921*	.770	-.166
	Sig. (2-tailed)	.919	.	.440	.	.	.590	.493		.411	.828	.981	.826	.026	.128	.789
I	Correlation	.623	. ^a	.251	. ^a	. ^a	-.489	-.209	-.482	1	-.548	-.381	-.402	-.716	-.395	.707
	Sig. (2-tailed)	.262	.	.684	.	.	.404	.735	.411		.339	.526	.502	.174	.510	.181
J	Correlation	-.213	. ^a	.443	. ^a	. ^a	.154	.887*	-.135	-.548	1	.940*	.107	-.071	.093	-.126
	Sig. (2-tailed)	.730	.	.455	.	.	.805	.045	.828	.339		.017	.864	.910	.882	.840
K	Correlation	.090	. ^a	.486	. ^a	. ^a	-.185	.847	-.015	-.381	.940*	1	-.046	-.086	.208	.151
	Sig. (2-tailed)	.885	.	.407	.	.	.766	.070	.981	.526	.017		.942	.891	.738	.809
L	Correlation	-.801	. ^a	.407	. ^a	. ^a	.272	.249	.137	-.402	.107	-.046	1	.323	.585	-.805
	Sig. (2-tailed)	.103	.	.497	.	.	.658	.686	.826	.502	.864	.942		.595	.300	.100
M	Correlation	-.295	. ^a	-.543	. ^a	. ^a	.059	-.391	.921*	-.716	-.071	-.086	.323	1	.679	-.508
	Sig. (2-tailed)	.630	.	.345	.	.	.925	.515	.026	.174	.910	.891	.595		.208	.382
N	Correlation	-.140	. ^a	.189	. ^a	. ^a	-.436	.060	.770	-.395	.093	.208	.585	.679	1	-.286
	Sig. (2-tailed)	.823	.	.760	.	.	.463	.923	.128	.510	.882	.738	.300	.208		.641
O	Correlation	.971**	. ^a	.085	. ^a	. ^a	-.723	-.042	-.166	.707	-.126	.151	-.805	-.508	-.286	1
	Sig. (2-tailed)	.006	.	.892	.	.	.168	.946	.789	.181	.840	.809	.100	.382	.641	

** Significant correlation at 0.01 level (2-tailed)
 * Significant correlation at 0.05 level (2-tailed)
^a Incomputable because of one or more constant variables

A = Etridiazole, B = Chloroneb, C = a-BHC, D = Simazine, E = Atrazine, F = b-BHC, G = g-BHC, H = d-BHC I = Chlorothalonil, J = Alachlor, K = Aldrin, L = Dacthal, M = Heptachlor epoxide, N = g-chlordane, O = trans-nonachlor

The correlation among the OCPs and PAHs informs the interrelationship and interdependence of each on others in the environment. The values derived agreed with a more sophisticated statistical examination of PAHs in sediments in a previous study [50]. Unlike OCPs, where some sort of correlation among the members was observed, the interrelationships of three PAHs, i.e., chloroneb (B), simazine (D), and atrazine (E), could not be established due to constant variables shared with themselves and others. Generally, correlation trend and magnitude vary widely from negative to positive and from insignificant to significant for both OCPs and PAHs. A more comprehensive statistical assessment approach was provided in our previous studies, carried out on environmental samples in the same geopolitical zone of the country [51, 52].

3.4 Principal component analysis (PCA)

This study adopted PCA to examine correlations between chlorinated pesticide concentrations and sampling sites. It also examined the relationship between TPHs and the sampling sites to discern the underlying contributing factors. The results were visualized using Origin Pro v9.9 software.

3.4.1 OCPs

As seen in the PCA plot (Figure 3a), Idiogba Subu had high principal component (PC) loadings for both PC1 and PC2 (> 0.5), while Idiogba Police had a high loading for PC1 (> 1) and a low loading for PC2 (< -1). Eyunona fell within $> 0.5 - < 1$ for both PC loadings. Together, these two PCs explained 66.09% of the variation in the sampling locations, with PC1 accounting for 36.06% and PC2 for 30.03%. In the 2D biplot (Figure 3b), smaller angles between lines and the coordinate axis indicated stronger correlations. In contrast, the shorter distances between sampling sites and the lines reflected a more significant influence of the factor on those sites. On the positive side of PC2, g-BHC appeared as a unique potential factor linked to Idiogba Subu and Ayetoro. A smaller angle was observed between the negative and positive halves of PC2, involving trans-nonachlor, chlorothalonil, and etridiazole [53]. The shorter distances between Ayetoro and Igbokoda and the lines indicated a more substantial trans-nonachlor, chlorothalonil, and etridiazole impact on these sampling sites. Lastly, the large angle between trans-nonachlor and dacthal signified a negative correlation.

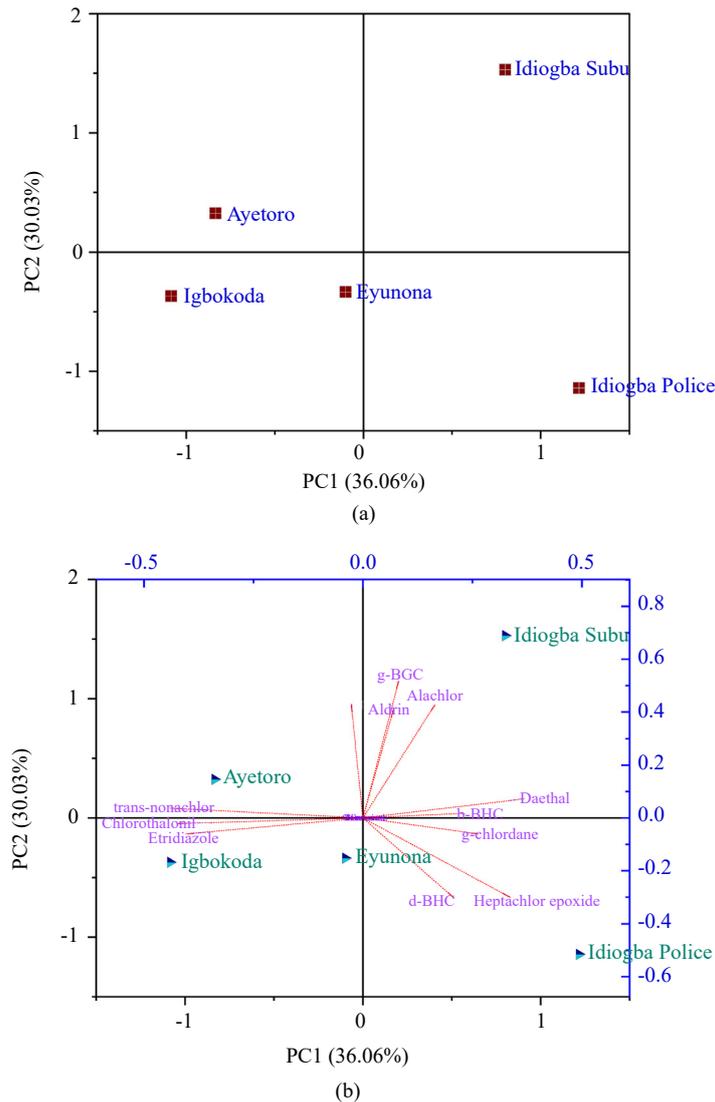


Figure 3. Scores plot (a) and 2D biplot (b) of the OCP data set

3.4.2 TPHs

As depicted in the TPH PC plot (Figure 4), Idiogba Subu exhibited notably low PC loadings for both PC1 and PC2 (< -1). Idiogba Police, Ayetoro, and Igbokoda displayed higher PC2 loadings in descending order: Ayetoro $>$ Igbokoda $>$ Idiogba Police. Eyunona, on the other hand, exhibited a notably higher loading towards the positive half of PC1 (> 1.5). These two principal components collectively elucidated a substantial 78.98% of the overall variances in the sampling locations, with PC1 contributing 35.87% and PC2 contributing 43.11%. On the negative half of PC2, octacosane emerged as a distinctive potential factor, closely associated with Idiogba Subu and Eyunona. Meanwhile, tridecane was identified as a possible factor in the positive half of PC1, as it exhibited higher concentrations in locations falling under the positive half of PC1. The significant angle between hentriacontane and dodecane indicated a negative correlation [46].

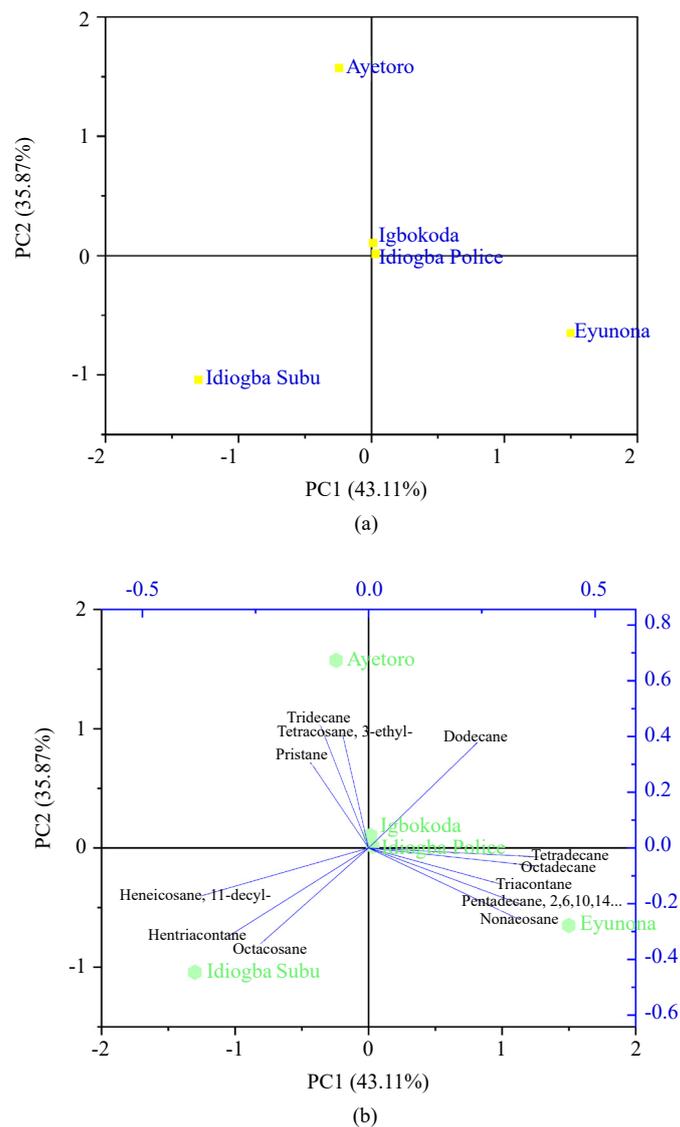


Figure 4. Scores plot (a) and 2D biplot (b) of the TPH data set

4. Conclusion

This work included extensive surveys and experimental investigations into TPHs and OCPs in the sediments of the Ondo coastal river, a typical developing coastal zone in Nigeria's southern region of the Atlantic Ocean. TPH and OCP were found in large quantities in sediment from a coastal river. Most contaminants might have originated from agricultural and industrial activities, household wastewater, and stormwater runoff, as also observed in other related studies in Nigeria.

In this investigation, 15 organochlorine pesticides were identified in surface sediment from the Ondo coastal river, with g-BHC, d-BHC, chlorothalonil, alachlor, aldrin, dacthal, heptachlor epoxide, g-chlordane, and trans-nonachlor accounting for 98-99% of the studied chlorinated pesticides. The total chlorinated pesticide (dry weight) concentrations ranged from ND to 326.98 ng/g, averaging 15.49 ng/g. The jetty had the highest detected value of pesticides, indicating that river transport, domestic waste discharge, and anthropogenic activities were their principal distribution sources. The pesticide concentrations at the various measured locations decreased in the following order: Idiogba Police > Igbokoda > Idiogba Subu > Ayetoro > Eyunona. There are considerable negative and positive connections between the various components of OCPs investigated. The TPH values ranged from 5.42 to 22.53 ng/g on a dry weight basis. The

following is the order in which TPH concentrations in the sediment decrease: Eyunona > Idiogba Police > Idiogba Subu > Ayetoro > Igbokoda. The measured result for mineral oil in sediment was below the Nigerian guideline's permissible limit of 50 mg/kg. The information suggests that the level of hydrocarbons detected in the sediment matrices is due to anthropogenic causes other than oil spillage, such as water transportation and residential waste discharge, storm waters, rural runoff, and other anthropogenic sources. Further PCA studies on the OCP data showed a more substantial trans-nonachlor, chlorothalonil, and etridiazole impact between Aiyetoro and Igbokoda. Overall, the two principal components (PC1 and PC2) explained 66.09% (OCPs) and 78.98% (TPH) of the overall variances in the sampling sites.

Despite the quantitation of the OCPs and TPHs, this study failed to establish the bioaccumulation potential of the organics, relating the concentrations to potential ecological hazards. Therefore, future studies should first establish the bioavailability and toxicity of the organics and include a hybrid statistical model for determining the ecological risk posed by PAHs and OCPs in sediments, aquatic species, water, and air.

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Data availability statement

The data associated with this research will be made available to the audience upon request from the corresponding author.

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Conflict of interest

There is no conflict of interest for this study.

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