International Journal of Sciences: Basic and Applied Research (IJSBAR)

ISSN 2307-4531
(Print & Online)

https://gssrr.org/index.php/JournalOfBasicAndApplied/index

---

# Concentrations of Organochlorine Pesticide (OCP) Residues in Environmental and Biota Samples from Azuabie and Okujagu Creeks, Upper Bonny Estuary, Nigeria

C.M. Okolocha[a]*, I.K.E. Ekweozor[b], E.R. Daka[c], M. Moslen[d]

[a]*Port Harcourt, 500102, Nigeria*

[b,c,d]*Rivers State University, 500101, Nigeria*

[a]*Email: eberrechy2011@gmail.com,*[b]*Email: ekweozor@hotmail.com*

[c]*Email: daka.erema@ust.edu.ng,*[d]*Email: moslen.miebaka@ust.edu.ng*

**Abstract**

This study evaluated the concentrations of organochlorine pesticides (OCPs) in surface water, sediment and biota (Oysters and Periwinkle) between August 2023 and June 2024. Samples were collected bimonthly from four stations located in Azuabie creek (AZ1 and AZ 2) and Okujagu Creek (OK 1 and OK2). Analysis for OCPs was accomplished using liquid-liquid extraction gas chromatographic method 1 (LL-EGC). Descriptive statistics, analysis of variance and correlation analysis were used for statistical analysis of the results. OCP values in surface water (Azuabie: 1.67±0.36 – 3,252.98±1,536.73ppb; Okujagu: 0.99±0.51 – 1,300.54±295.23ppb) did not differ significantly by location but were significant by time. OCP in sediment (Azuabie: 9.56±3.03 – 3,252.98±1,536.73ppb; Okujagu: 8.24±0.57 – 1,300.54±295.23ppb) varied significantly both by location and time. OCP values in both oysters (Azuabie: 10.36±4.34 – 882.79±232.34ppb; Okujagu: 8.69±0.54 – 971.91±94.03ppb) and periwinkles (Azuabie: 21.30±3.07 – 1.091.52±282.69ppb; Okujagu: 20.96±1.52 – 1,287.65±204.25ppb) were not significant by location but varied significantly by time.

---

*Received*: *5/19/2026*
*Accepted*: *7/19/2026*
*Published*: *7/29/2026*

---

* *Corresponding author*.

At Azuabie, there were significant correlations between the OCP concentrations in sediment and surface water; there were also significant correlations between sediment and Oyster and Periwinkle. At Okujagu, significant correlations were observed between the OCP concentrations in sediment and surface water, oyster and surface water, periwinkle and surface water, sediment and oyster, and periwinkle and oyster. The constituents recorded included Alpha-BHC, Beta-BHC, Gamma-BHC, Heptachlor, Delta-BHC, Aldrin, Heptachlor Epoxide, Alpha-Chlordane, Gamma-Chlordane, Endosulfan I, Endosulfan II, P,p'-DDE, P,p'-DDD, P,p'-DDT, Dieldrin, Endrin, Endrin Aldehyde, Endosulfan Sulfate, Methoxychlor and Endrin Ketone. The dermal hazard quotient for DDT, aldrin, alpha-chlordane and penta-chlorobenzene showed that the average values obtained were not carcinogenic (0.1ppm). Most of the individual OCP such as Alpha-BHC, Beta-BHC, Endrin, Endrin-aldehyde etc had values that exceeded the USEPA and WHO acceptable limits. This is of public health concern due to the bioaccumulation potential of the biota which are regularly consumed by the public. Preventive measures should therefore be taken to prevent continued pollution while aiding the recovery of both creeks. Measures should also be taken to ensure food safety among the population. In conclusion, the result for the toxicity limit for OCP ranged between 0.1 to 0.2 ppm which is within Occupational regulation government permissible limit of 0.1ppm and for PAH, it ranged between 1.7 to 5.1ppm which is also within OSHA limit of 0.02-6.68ppm. However, there is need for constant check and control so as to reduce it and ensure it does not exceed this limit.

***Keywords:*** Upper Bonny Estuary; Carcinogenic; DDT; Aldrin ; Food Safety.

**1. Introduction**

Organochlorine pesticides (OCPs) are effective chemicals that are frequently included in formulations for agricultural pest control. They are however environmental pollutants, persistent in the environment and several have been reported to be carcinogenic [1]. They have been extracted from environmental samples such as air, water, sediment, soils, biota especially fish, and also in food products [1,2].

In studies in rivers of south-western Nigeria, researchers [3] reported the presence of DDT, endosulfan and aldrin in water, sediment and fish samples. These authors found that all three OCPs were within the WHO maximum residual limit (MRL) in both the surface water and sediment samples, whereas in fish, aldrin exceeded the MRL. They also noted that water samples had lower values for the pollutants "(DDT = 0.010; endosulfan = 0.021 and aldrin 0.002) compared to the sediment samples (DDT = 0.016; endosulfan = 0.096 and aldrin 0.005) and fish samples (DDT = 0.010; endosulfan = 0.043 and aldrin 0.049)".

Other researchers [4] examined surface water and sediment samples from River Kaduna and River Romi in Kaduna State, Nigeria. They reported that aldrin and dieldrin were the most prevalent OCPs extracted and noted that all the OCPs extracted (p.p'-DDD, o,p'-DDD, o,p-DDE, p,p'-DDT, aldrin and dieldrin) exceeded the European Union's maximum residue limits. Similar to the findings of the authors in [3], these authors reported higher concentrations in the sediment samples.

The persistence and toxic nature of OCPs led to their being banned and restricted in several developed countries, but they are still being used in African countries [1] mostly due to weak legislation [3]. In this study, we examined

the concentrations of OCPs in surface water, sediment, periwinkle (*Tympanotonus fuscatus var. radula*) and oyster (*Crassostrea gasar*) samples from Azuabie and Okujagu Creeks of the Upper Bonny Estuary, Nigeria.

Thus, this study was limited to the assessment of OCPs in sediment and surface water samples, as well as in two aquatic organisms (periwinkles and oysters) in Azabie and Okujagu Creeks of the Upper Bonny Estuary, Nigeria. Financial constraints prevented the inclusion of other pollutants and aquatic organisms.

## 2. Materials and Methods

### *2.1 Study Area*

The Azuabie and Okujagu Creeks (Figure 1) are tributaries of the Okpoka River that flows into the Upper Bonny Estuary with many riverine settlers. Both creeks lie between latitude 7°3' N, longitude 4°48' E and latitude 7°1' 30" N and longitude 4°52" respectively (Geographic Coordinate system: GCS_WGS__1984). Both creeks are located along the Trans-Amadi Industrial Area of Port Harcourt and receive waste effluents from industrial and other activities in the area. Other activities along the creeks include dredging, artisanal fishing (periwinkles and oysters) and motorized canoe transport (boating activities). However, Okujagu has less industrial presence than Azuabie.

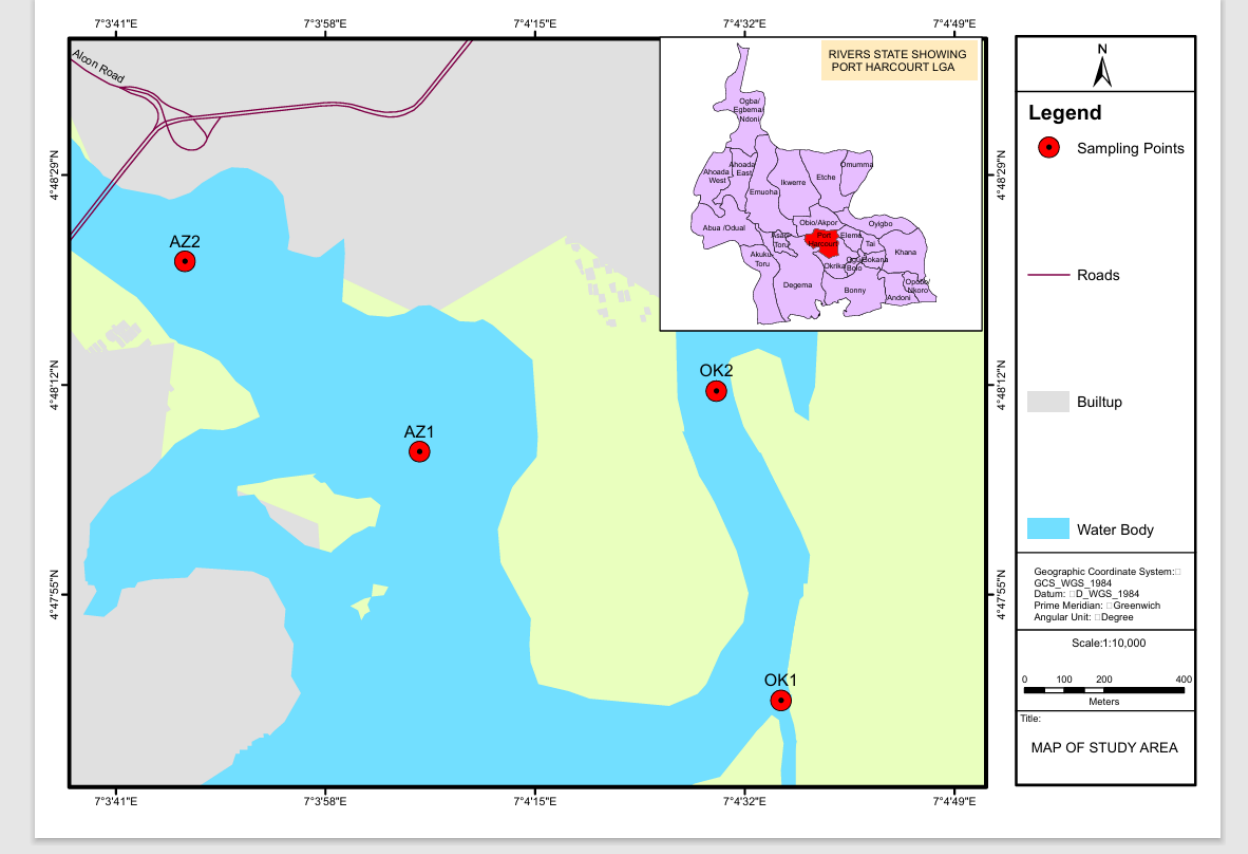


**Figure 1:** Map showing Location of Study site where Sediment, water, Biota

(oysters and periwinkles) samples were collected

### *2.2 Field Sampling*

#### *2.2.1 Sampling Stations/Design*

Two locations were established at each Creek. Samples were collected from both locations in each Creek, analyzed and mean values used as the data obtained. Sampling was done bimonthly from August 2023 to June, 2024 at low tide.

Thus, duplicate samples of surface water were collected 15-25cm below the water surface from the sampling stations. These were immediately preserved in ice-packed coolers and transported to the laboratory for detailed analysis.

Sediment samples were collected using level in two replicates at each sampling station during each sampling period and the deeper part of the sediment was collected using Ekman grab (Van -Veen type) [5,6]. Sediments were packed with aluminum foil into clean ziploc bags, labelled with a masking tape and transported to Laboratory (EISL-Ebic Integrated Services Ltd). Sediments were air dried and ground to powder using a laboratory mortar and pestle, passed through a 2mm sieve and stored at -20$^{o}$C until analysed [6].

Samples of periwinkles *(Tympanotonus fuscatus*) and oysters (*Crassostrea gigas*) used for the analysis were obtained with the help of fishers who harvested them from the creeks. The samples were thoroughly washed with sea water, placed in separate labeled cellophane bags and preserved in ice cooled box. The samples were subsequently transported to the Marine Biology Laboratory, Department of Animal and Environmental Biology, Rivers State University, Port Harcourt, and stored in the freezer at (-10°C) prior to laboratory analysis.

### *2.3 Laboratory Analysis*

#### *2.3.1 Sample Preparation*

The soft parts of the biota were obtained by cracking the shells and then placed on a foil paper and oven dried at 80°C for 24 hours to obtain a dry tissue. The dried tissues were ground to powder form with ceramic mortar and pestle, sieved to obtain a uniform particle size using 2 mm mesh size and preserved in a well labeled plastic bottle indicating each location and month.

#### *2.3.2 Analysis of OCPs*

The experimental procedure involved the use of n-hexane and dichloromethane obtained from Sigma-Aldrich in St Louis, MO, USA. Additionally, analytical grade silica gel and alumina from Merck in Darmstadt, Germany, as well as analytical grade anhydrous $Na_2SO_4$ from Honeywell Fluka in Seelze, Germany, were used as received. Furthermore, a mixed standard solution containing the 20 OCPs was acquired from AccuStandard Inc in New Haven, CT, USA.

### *2.3.3 Extraction and Clean-up*

The extraction of OCPs from the samples utilized the Soxhlet extraction method. A 10.0 g sample was mixed with an equal mass of anhydrous $Na_2SO_4$ and then subjected to Soxhlet extraction for 4 hours using a 100 mL aliquot of a 1:1 dichloromethane (DCM)/n-hexane mixture. The resulting extract was concentrated to 2 mL using a rotary evaporator and purified in a column packed with silica gel/alumina. Subsequently, the OCPs were eluted from the column using a 30 mL mixture of 1:1 DCM/n-hexane, and the elute was further reduced to 1 mL under a slow-flowing stream of nitrogen gas.

Alternatively, about 50ml of the water sample was weighed into an Erlenmeyer conical flask. 100ml of methanol hexanol mixture was added into the 50ml of water and stirred mechanically on a magnetic stirrer. The mixture was then transferred into 25ml separator funnel and shaken vigorously and allowed to stand for 20 minutes. The lower aqueous mixture was drained off and discarded. The solvent layer was then mixed with methanol and then shaken vigorously. The lower methanol layer was separated and the volume was concentrated to about 5ml in a rotatory evaporator. The sample extract was then used in the HPLC analysis.

### *2.3.4 Chromatographic Analysis*

The determination of OCP identities and concentrations in the sample extracts was conducted using a gas chromatography-mass spectrometry system, specifically the Agilent 6890N with 5973 mass selective detector, manufactured by Agilent Technologies based in Santa Clara, USA. A DB-5 capillary column with dimensions of 30 m length, 0.25 µm film thickness, and 0.25 mm internal diameter was utilized for compound separation. The carrier gas employed was pure helium at a consistent flow rate of 1mL/min, and sample injection into the gas chromatograph was achieved using the pulsed splitless mode with a 1µL sample volume. The GC column temperature program consisted of an initial temperature of 70 ℃, which was maintained for 5 minutes, followed by an increase to 180 ℃ at a rate of 15 ℃ per minute, further ramping to 230 ℃ at 3 ℃ per minute, and, finally, an increase to 300 ℃ at a rate of 2 ℃ per minute.

### *2.4 Quality Assurance/ Quality Control*

Method blanks were used to validate the analytical method. The OCPs were not detected in the method blanks. The OCPs quantification was carried by an external calibration method. Linear regression coefficient (r2) values of 0.9991 to 0.9999 were obtained for the calibration lines. The limits of detection (LOD) and quantification (LOQs) were determined as three and ten times the signal-to-noise ratio of the blanks respectively. The LODs and LOQs for the OCPs ranged from 0.01 to 0.05 ng g-1 and 0.03 and 0.15 ng g-1 respectively.

### *2.5 Toxicity Assessment and Risk Characterization for OCPs*

Dermal absorbed dose (DAD), cancer slope factor (CSF), dermal cancer (DCR) and dermal hazard quotient (DHQ) were computed for DDT, Aldrin and Alpha-chlordane using values from Azuabie.

### *2.5.1 Dermal Absorbed Dose (DAD) for Adults*

Dermal Absorbed Dose (DAD) for adults at the study locations was calculated as follows.

$$DAD = \frac{DA_{event} \times EF \times ED \times EV \times SA}{BW \times AT} \quad [7]$$

Where: DAD = Dermal Absorbed Dose (mg/kg-day); $DA_{event}$ = Absorbed dose per event (mg/cm$^2$-event); SA = Skin surface area available for contact (cm$^2$) = 18,000 (for adults); EV = Event frequency (events/day) = 1; EF = Exposure frequency (days/year) = 350; ED = Exposure duration (years) = 30 (for adults); BW = Body weight (kg) 70 kg (adult), 15 kg (child); AT = Averaging time (days) non carcinogenic effects AT = ED x 365 d/yr; Carcinogenic effects AT = 70 yr x 365 d/yr.

$$DA_{event} = C_{soil} \times AF \times CF \times ABS_d \quad [7]$$

Where $C_{soil}$ = Chemical concentration in soil; CF = Conversion factor; AF = Adherence factor of soil to skin (mg/cm$^2$-event; $ABS_d$ = Dermal absorption fraction.

### *2.5.2 Derivation of Cancer Slope Factor Based on Absorbed Dose*

Cancer Slope Factor based on Absorbed Dose at Azuabie was calculated as follows.

$$SF_{ABS} = \frac{SF_o}{ABS_{GI}} \quad [7]$$

Where $SF_{ABS}$ = Absorbed slope factor; $SF_o$ = Oral slope factor (mg/kg-day); $ABS_{GI}$ = Fraction of contaminant absorbed in gastrointestinal tract (dimensionless) in the critical toxicity study.

### *2.5.3 Calculation of Dermal Cancer Risk*

Dermal Cancer Risk was calculated as follows.

$$Dermal\ Cancer\ Risk = DAD \times SF_{ABS} \quad [7]$$

Where DAD = Dermal Absorbed Dose (mg/kg-day); $SF_{ABS}$ = Absorbed cancer slope factor (mg/kg-day)$^{-1}$.

### *2.5.4 Calculation of Dermal Hazard Quotient*

Dermal Hazard Quotient was calculated as follows.

$$Dermal\ Hazard\ Quotient = \frac{DAD}{RfD_{ABS}} \quad [7]$$

Where DAD = Dermal Absorbed Dose (mg/kg-day); $RfD_{ABS}$= Absorbed reference dose (mg/kg-day); $RfD_{ABS} = RfD_o \times ABS_{GI}$

**Table 1:** Health Risk for OCP (ppm)

| OCP (ppm) | SURFACE WATER | SEDIMENT | OYSTER | PERIWINKLE |
|---|---|---|---|---|
| AZUABIE CREEK | 3.25 | 3.25 | 0.88279 | 1.09 |
| | 0.06 | 1.41 | 0.19754 | 0.18 |
| | 0.00 | 0.02 | 0.01036 | 0.10 |
| | 0.04 | 0.66 | 0.10756 | 0.28 |
| | 0.00 | 0.01 | 0.03486 | 0.05 |
| | 0.00 | 0.03 | 0.01151 | 0.02 |
| OKUJAGU | 1.30 | 1.30 | 0.97191 | 1.29 |
| | 0.13 | 1.15 | 0.12816 | 0.35 |
| | 0.00 | 0.01 | 0.01378 | 0.07 |
| | 0.02 | 0.35 | 0.06622 | 0.22 |
| | 0.00 | 0.01 | 0.03324 | 0.04 |
| | 0.00 | 0.03 | 0.00869 | 0.02 |
| AVERAGE | 0.401168333 | 0.685884167 | 0.205551667 | 0.309741667 |
| TOXICITY | 0.276745975 | 0.473157192 | 0.141799817 | 0.213675289 |
| WITHIN LIMIT | *0.2 | - | *0.1 | *0.2 |

*Shows within permissible limit

PERMISSIBLE LIMIT—FOR **PAHs** SET BY OSHA (Occupational safety & health Administration) AND NIOSH-0.1ppm FOR WORKPLACE=0.2

**FOR OCCUPATIONAL REGULATIONS.GOV- Toxicity ranged from 0.02-6.68pp**

**Source: Okolocha, C.M. Concentrations of Organochlorine pesticide (OCP) and (PAH) residues in environmental and biota samples from Azuabie and Okujagu Creeks**

### *2.6 Data Analysis*

The data were analysed using descriptive analysis (means, range). Two-way Analysis of variance (ANOVA) was used to test for significant difference between stations and also between months using SPSS version 20.0 software. Pearson correlation was used to test for the relationship between concentrations of organo chlorine pesticides in all samples. These were done using MS Excel.

## 3. Results

The total OCP values in surface water ranged from 1.67±0.36ppb in June 2024 to 3,252.98±1,536.73ppb in August 2023 at Azuabie, and from 0.99±0.51ppb (June 2024) to 1,300.54±295.23ppb (August 2023) at Okujagu. Higher values were obtained in August 2023 after which they remained minimal (Figure 2). Location differences were not significant ($p = 0.11$), In the sediment samples, the values ranged from 20.43±1.59ppb in December 2023 to 3,252.98±1,536.73ppb in August 2023 at Azuabie, and 8.24±0.57ppb in December 2023 to 1,300.54±295.23ppb in August 2023 at Okujagu (Figure 3). Both location ($p = 0.0539$) and monthly ($p = 0.0001$) variations were significant. Total OCP values in the oyster samples ranged from 10.36±4.34ppb in December 2023 to 882.79±232.34ppb in August 2023 at Azuabie, and 8.69±0.54ppb in June 2024 to 971.91±94.03ppb in August 2023 at Okujagu (Figure 4). Location differences were not significant ($p = 0.903$) but monthly variations were

significantly higher in August 2023 ($p = 3.76 \times 10^{-9}$).

In the periwinkle samples, the values ranged from 21.39±3.07ppb in June 2024 to 1,091.52±282.69ppb in August 2023 at Azuabie, and 20.96±1.52ppb in June 2024 to 1,287.65±204.25ppb in August 2023 at Okujagu (Figure 5). Location differences were not significant ($p = 0.328$) but monthly variations were significantly higher in August 2023 ($p = 2.46 \times 10^{-8}$).

The OCP constituents extracted included aldrin, dieldrin, endrin, P,P'-DDT, P,P'-DDE, P,P'-DDD, endrin, endosulfan I, endosulfan II, endrin aldehyde, endosulfan sulphate, methoxychlor, heptachlor, Alpha-BHC, Beta-BHC, Gamma-BHC, Delta-BHC, heptachlor epoxide, Gamma-chlordane, Alpha-chlordane, endosulfan, and endrin ketone. Their concentrations in surface water, sediment samples and biota across both study locations and months are presented in Figures 2 to 5.

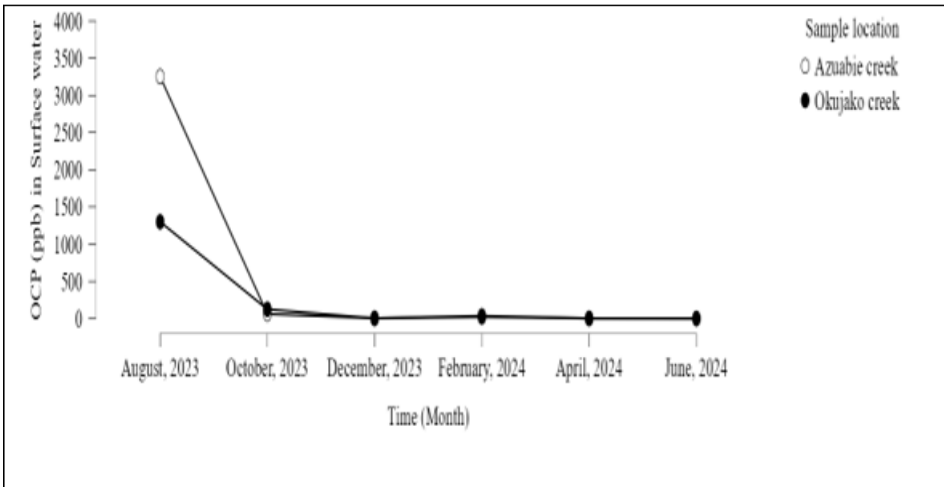


**Figure 2:** Monthly Variation in Total OCP Values in Surface Water at both Study Locations

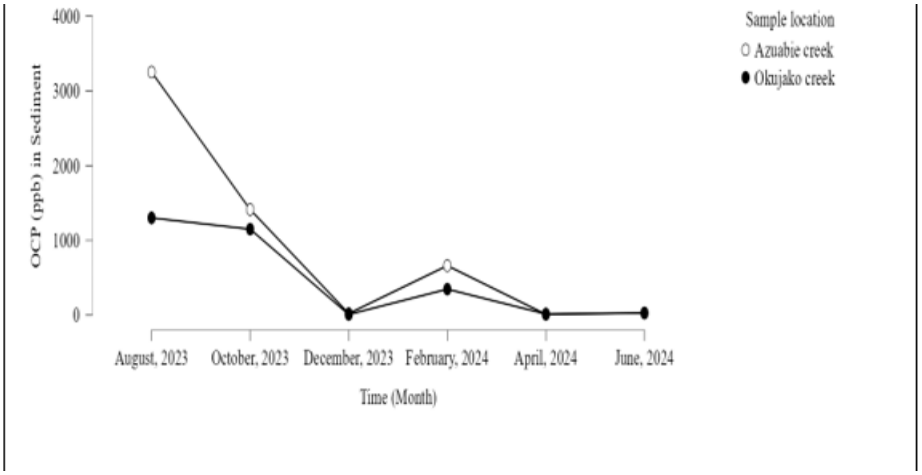


**Figure 3:** Monthly Variation of Total OCP in Sediment at both Study Locations

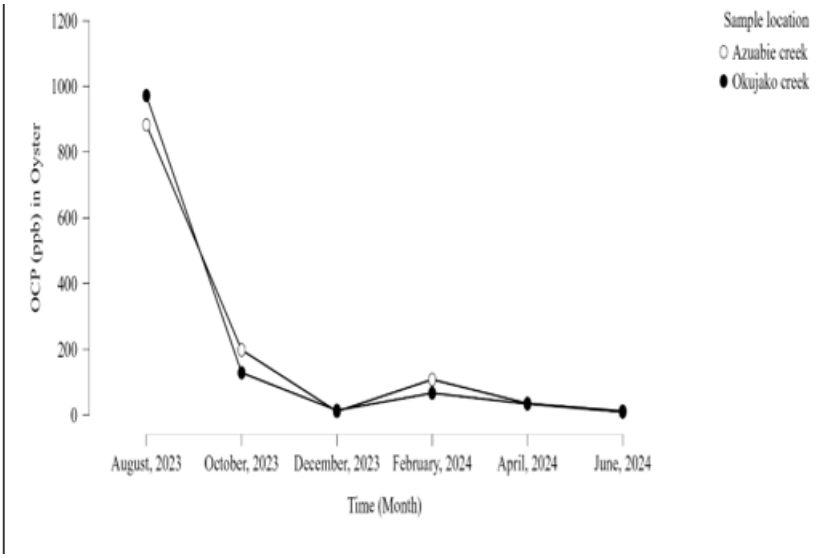


**Figure 4:** Monthly Variation of Total OCP Values in Oysters from both Study Locations

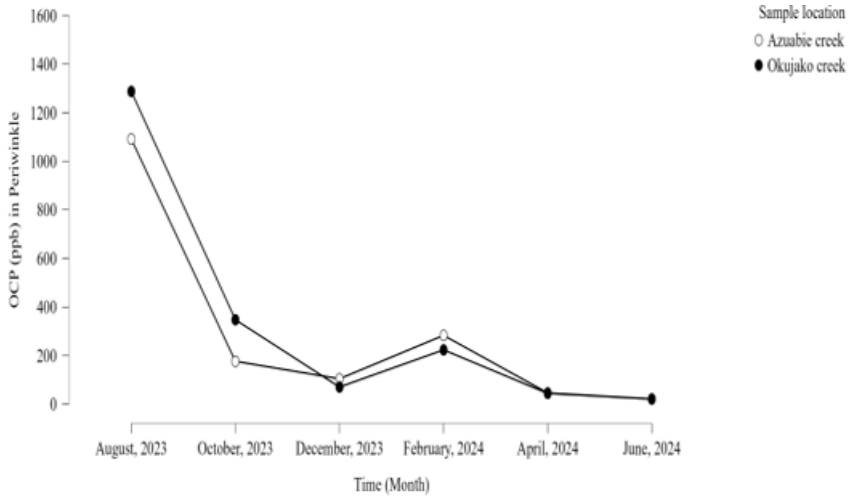


**Figure 5:** Monthly Variation of Total OCP in Periwinkles from both Study Locations

### *3.1 Toxicity Assessment and Risk Characterization on DDT, Aldrin, Alpha Chlordane, Pentachlorobenzene*

Toxicity assessment calculations were carried out on some OCPs with values obtained from Azuabie Creek. The values for Dermal Absorbed Dose, Cancer Slope Factor, Dermal Cancer Risk and Dermal Hazard Quotient were determined based on USEPA Risk Assessment Guidance for Superfund [7] and presented in Table 2.

**Correlation Analysis between Total OCP Values at Both Study Locations**

Pearson correlation results showed that all pairs of comparison in the total OCP values in all samples from both study locations were significant ($p>0.4$) (Table 2).

**Table 2:** Toxicity Assessment and Risk Characterization on DDT, Aldrin, Alpha Chlordane, Pentachlorobenzene

| OCPS | Dermal Absorb Dose | Cancer Slope Factor (SF) | Dermal Cancer Risk | Dermal Hazard Quotient | USEPA |
|---|---|---|---|---|---|
| | (DAD) mg/kg per day | mg/kg-day-1 | mg/kg-day-1 | mg/kg-day-1 | MCL/HRL(Maximum contaminant level-mg/l |
| DDT | 2.64 * 10-9 | 0.378 | 9.98 * 10-10 | 5.57 * 10-6 | 0.00005 mg/l or 50ng/l |
| Aldrin | 1.27 * 10-9 | 21.25 | 5.29 * 10-5 | 5.29 * 10-5 | 0.002 µg/l |
| Alpha-Chlordane | 1.27 * 10-9 | 0.4375 | 5.56 * 10-6 | 3.18 * 10-6 | 0.0005 mg/$m^3$ |
| Penta-chlorobenzene | 3.15 * 10-9 | Non-Carcinogenic | Non-Carcinogenic | Non-Carcinogenic | 100.0 mg/l |

*Source: Epa.gov/groundwater and drinking-water, Regulatory Determination Support Document for Dieldrin 2003*

**Table 3:** Correlation Coefficients of Total OCP Values at Azuabie

| Parameters | SW OCP | SED OCP | OYS OCP |
|---|---|---|---|
| SED OCP | *0.909654169 | 1 | |
| OYS OCP | *0.980827055 | *0.972289413 | 1 |
| PER OCP | *0.975078831 | *0.942678638 | *0.9828776 |

**Table 4:** Correlation Coefficients of Total OCP Values at Okujagu

| Parameters | SW OCP | SED OCP | OYS OCP |
|---|---|---|---|
| SED OCP | *0.742056002 | | |
| OYS OCP | *0.999142813 | *0.755901704 | |
| PER OCP | *0.983568843 | *0.834674578 | *0.988557366 |

NOTE: * shows parameters with significant values because its Values $\geq$ 0.40

## 4. Discussion

### *4.1 Concentration of OCP in Surface Water, Sediment and Biota (Oysters & Periwinkle) from Azuabie and Okujagu Creeks*

Organo chlorine pesticides (OCPs) constituted the persistent organic pollutants (POPs) recorded in this research. The OCP values in surface water, sediment, oysters and periwinkles at Azuabie ranged from 1.67 to 3,252.98ppb, 9.56 to 3,252.98ppb, 10.36 to 882.79ppb and 21.30 to 1.091.52ppb respectively. At Okujagu, the values were as follows: 0.99 to 1,300.54ppb, 8.24 to 1,300.54ppb, 8.69 to 971.91ppb and 20.96 to 1,287.65ppb in surface water, sediment, oysters and periwinkles, respectively. The highest values were recorded in sediment and surface water samples. This is because the pollutants are first released into the aquatic medium from where most, due to their hydrophobic nature, get locked up in sediment samples (sediment often acts as a sink for several pollutants) while others are taken up by aquatic organisms [8]. Also, most solid wastes that are sources of OCPs often sink to the sediment layers of creeks, due to their weight; as such, the pesticides when released have direct contact with the sediment. The concentrations recorded in surface water exceeded the regulatory maximum limit [9] of 0.1µg/l (which is equivalent to 0.1ppb). The authors in [10] set maximum residue limits of 0.3 mg/kg (= 300ppb) DDD, 0.2 mg/kg (= 200ppb) DDT, and 0.4 mg/kg (=400ppb) DDE for sediment samples, and some values of DDD and DDT obtained in this research exceeded these limits. For instance, in August, 2023 sediment samples from Azuabie reached concentrations of 405.91ppb DDD and 412.775ppb DDT respectively. Individual OCP constituents have varying maximum permissible limits. For instance, DDT 1µg/l, Endrin 0.6 µg/l, Aldrin, Heptachlor, Heptachlor Epoxide and Dieldrin 0.03µg/l, Lindane 2.0 µg/l, and Methoxychlor 20 µg/l [11]. The concentrations of the individual constituents recorded in surface water, sediment, oysters and periwinkles in the current research had values that exceeded these limits thereby proving public health risks in the use of these resources. The authors in [12] also reported that the concentrations of DDT and its metabolites in *Clarias gariepinus* and *Bagrus docm*ak from River Gongola Basin in Gombe State, Nigeria, exceeded the maximum permissible limits. Thus, direct or accidental consumption of environmental and biotic samples from such polluted waters are detrimental to public health.

In earlier research, the author in [13] recorded total OCP values of 0.0 to 0.03mg/l in surface water, 0.0 to 0.033mg/kg in sediment samples, 0.0 to 0.006mg/kg in crab tissues, 0.0001 to 0.0334mg/kg in Tilapia gills, and 0.0001 to 0.007mg/kg in Tilapia liver across Azuabie and Okujagu locations. Considering that both mg/kg and mg/l are equivalent to ppm and comparing with the values obtained in the current research, it can be seen that the higher concentrations obtained in the current research far exceed those obtained in the earlier study. This is accounted for both by increased dumping of both industrial and domestic wastes into the Creeks and by the persistent nature of the pollutants in the environment [14].

The OCP constituents detected were Alpha-BHC, Beta-BHC, Gamma-BHC, Heptachlor, Delta-BHC, Aldrin, Heptachlor Epoxide, Alpha-Chlordane, Gamma-Chlordane, Endosulfan I, Endosulfan II, P,p'-DDE, P,p'-DDD, P,p'-DDT, Dieldrin, Endrin, Endrin Aldehyde, Endosulfan Sulfate, Methoxychlor and Endrin Ketone. Another author [13] had also identified these OCPs in addition to Pentachlorobenzene and Decachlorobiphenyl. The authors in [15] studied the concentrations of OCPs in Ogun River, Nigeria, and reported the presence of α-HCH,

β-HCH, γ-HCH, δ-HCH, P,p'-DDE, P,p'-DDD, P,p'-DDT, Endosulfan I, Endosulfan II, Heptachlor Epoxide, Heptachlor, Endrin, Endrin Aldehyde, Endosulfan Sulfate, Methoxychlor, Aldrin and Dieldrin. In research at Indonesia, some authors [8] recorded lindane, aldrin, dieldrin, heptachlor, dichlorodiphenyltrichloroethane (DDT), and endosulfan in surface water, mollusks and fish. Thus, these OCPs are of global occurrence, and abattoir wastes, electronic wastes and other domestic, agricultural and industrial wastes as well as other anthropogenic activities contribute to their presence in natural ecosystems [14]. Environmental cost of waste is increasingly affecting the ecosystem and have become drivers of environmental deterioration and biodiversity loss [16]. Most POPs are potentially life threatening and cause damage to the heart and liver. The high numbers of waste e.g computers and debris at dumpsites located close to the current study locations accounts for high level of these POPs in the samples. It is a further confirmation that majority of PAHs and POPs found in aquatic ecosystems are from pyrogenic sources [6]. The incomplete combustion of fossil fuels (through illegal refinery of crude) and the practice of burning old vehicle tires which are common activities in both study locations also contribute to increased levels of environmental contamination by POPs. Previous studies have documented contamination of aquatic environments and biota with POPs from both domestic and electronic wastes [17]. The high level of bioavailability of POPs accounts for their higher concentrations in the environments [18, 19]. These pollutants are being absorbed by periwinkles and oysters directly from the water through their gills, hard exoskeleton, head, telson and tissues and also mostly from food [20]. Periwinkles are benthic aquatic organisms while oysters are pelagic and in frequent contact with water. Both organisms are delicacies especially in south eastern Nigeria [21]. The pollutants get absorbed into lipid-rich organs of these aquatic organisms. However, pollutants that are not rapidly metabolized are retained in the fat which then allows for their bioaccumulation in the organism; when these are consumed by other organisms at higher levels of the food chain, bioaccumulation of the pollutants continue all the way up the food chain to organisms in the higher or topmost trophic levels that eventually gets to man. The dissolved portion of these hydrophobic compounds such as (PAHs) are available to filter feeding organisms [19] e.g Periwinkle. This is a threat to benthic organisms and other organisms (like marine birds) through the marine food web because ecosystems are interconnected and contamination of one affects the other [22]. Occupational exposure to organochlorine pesticides has been linked to pulmonary cancer, prostate cancer, liver, urinary bladder, pancreatic and stomach cancers [23]. In animals, aldrin and endrin are known to be very toxic [24].

### *4.2 Health Risk Assessment in Relation to OCPs observed in the Study Area*

Risk assessment was computed for DDT, Aldrin, Alpha-Chlordane and Pentachlorobenzene based on the consumption of periwinkles from the Azuabie Creek. The Dermal Absorbed Dose (DAD) for adults for these POPs were as follows: DDT $2.64x10^{-9}$mg/kg-day, Aldrin $1.27x10^{-9}$ mg/kg-day, Alpha-Chlordane $1.27x10^{-9}$ mg/kg-day and Pentachlorobenzene $3.15x10^{-9}$ mg/kg-day.

The results for the Cancer Slope Factor based on Absorbed Dose were as follows: DDT 0.378 mg/kg-day$^{-1}$, Aldrin 21.25 mg/kg-day$^{-1}$, and Alpha-Chlordane 0.4375 mg/kg-day$^{-1}$. Pentachlorobenzene is non-carcinogenic and has no cancer slope factor; hence, there was also no need to compute dermal cancer risk and dermal hazard quotient for it.

The computed Dermal Cancer Risk results were DDT $9.98x10^{-10}$, Aldrin $2.69x10^{-8}$ and Alpha-Chlordane $5.56x10^{-10}$. According to the authors in [7], cancer risk values above 1.0 X $10^{-6}$ are above the recommended threshold. Thus, the values computed in this research were lower than the threshold, implying reduced risk of carcinogenic health effects from the consumption of periwinkles from this location. Another study [25] also reported that cancer risk assessment of PAHs in periwinkles (*Pachymelania fusca mutans*) and crab (*Scylla serrata***)** from some crude-oil contaminated regions of southern Nigeria were below the recommended threshold.

On the other hand, authors in [24] reported from their study that the computed cumulative cancer risk for Aldrin, heptachlor, and heptachlor epoxide due to consumption of fish (*Clarias gariepinus*) ranged between $4.65 \times 10^{-3}$ - $1.69 \times 10^{-2}$ and $9.31 \times 10^{-3}$ - $3.38 \times 10^{-2}$ for an adult. As such, they concluded that the risk of developing cancers from Aldrin, heptachlor, and heptachlor epoxide as a result of consuming fish from their sampling locations in Northern Nigeria was very high. From South Africa, other authors [26] reported that Hazard Quotients for Chlordane in wild mussels (*Mytilus galloprovincialis, Choromytilus meridionalis,* and *Perna perna*) showed that non-carcinogenic risk were >>1 for both adults and children consuming 250–1000 g of wild mussel meat per month (g $m^{-1}$) from the Western Cape Province coastline. They also found that the cancer risk values calculated for mean and maximum chlordane concentrations in wild mussels were above the unacceptable level of risk ($10^{-4}$) for all levels of consumption by adults and children. Even the lowest level of wild mussel consumption (250 g $m^{-1}$) resulted in unacceptable levels of non-carcinogenic and carcinogenic human health risks.

The results for Dermal Hazard Quotient were DDT $5.87x10^{-6}$, Aldrin $5.29x10^{-5}$, and Alpha-Chlordane $3.18x10^{-6}$. These values of the Hazard Quotient are less than 1 indicating lower possibilities of non-carcinogenic health hazards occurring due to consumption of periwinkles from the study area. Similarly, authors in [12] also found that the Hazard Quotient of DDT and its metabolites in *Clarias gariepinus* and *Bagrus docmak* from River Gongola Basin, Gombe State, were lower than 1, declaring no potential health risk from their consumption. In their research on the risk assessment of some POPs at Hawul River located between Adamawa and Borno States in Nigeria, however, authors in [24] reported that the hazard quotients of Aldrin and Endrin resulting from the consumption of fish (*Clarias gariepinus*) from the waterbody was greater than 1 with HQ values ranging from 1.39 – 9.85, and 1.85 –6.44 respectively; while heptachlor and heptachlor epoxide were less than 1 in the range of 0.03 – 0.56 and 0.006 – 0.07. They posited that this implied that there are very low probabilities of adverse effects due to heptachlor and heptachlor epoxide present in the fish while there are high probabilities of non-carcinogenic health effects due to aldrin and endrin. These results prove the importance of regular assessment of pollutant concentrations in food organisms.

### *4.3 Correlation of POPs in test organisms and environmental samples*

The Pearson correlation analysis showed that the total concentration of OCPs in all samples were significantly positively correlated with each other: surface water to sediment, and to oysters and periwinkles. Contrary to the findings of this research, authors in [27] reported significant negative correlation coefficients between water and sediment samples arguing that it reflected the level of sediment-water exchange. Other authors [28] correlated the concentrations of individual POPs in surface water, sediment and fish from River Niger, Nigeria. They observed variations in the correlation of the POPs: some were positively correlated between each pair of samples while

others were negatively correlated. For instance, Phenanthrene in sediment showed a moderate negative correlation with Naphthalene in water. Anthracene found in sediment had a negative correlation with Naphthalene in water. Meanwhile, Benzo[k]fluoranthene in sediment was positively correlated with Phenanthrene in fish.

Strong positive correlation between POP levels in different samples from the same environment often indicate they could have same source [28]. Thus, the correlation results indicate that the POPs in surface water, sediment, oysters and periwinkles from the study locations in this study are generally from the same source. The major sources are petrogenic [29] and pyrogenic (from the waste dumps located close to the locations). These dumps contain waste electronics, slaughterhouse wastes, and other domestic and industrial wastes which are known to significantly pollute the environment with OCPs [30, 31].

## 5. Conclusion and Recommendations

Total OCP residue concentrations were evaluated in surface water, sediment and biota (periwinkle and oyster) samples in Azuabie and Okujagu Creeks. Lower values were obtained in the biota (Oyster-0 to 206ppm and Periwinkle 0 to 508ppm). Though location differences were significant only for the sediment samples.

Some concentrations of these constituents recorded in surface water (Delta-BHC, Heptachlor & Aldrin etc), sediment, oysters and periwinkles exceeded the USEPA and WHO maximum residue limits thereby proving public health risks in the use of these resources. Results of the cancer risk assessment were all less than 1 for OCP showing reduced risk of carcinogenic health effects. There was strong positive correlation between the total OCP concentrations in all samples examined, thus indicating they were from the same source, likely petrogenic and runoff from refuse dumps. From the findings of this research, it is recommended that municipal waste disposal systems should be upscaled with the introduction of waste separation practices.

## References

[1]. C. Olisah, O. O. Okoh and A.I. Okoh. “Occurrence of organochlorine pesticide residues in biological and environmental matrices in Africa: A two-decade review”. *Heliyon*, vol. 6, e03518, Mar. 2020.

[2]. B. Gevao, P.B. Kurt-Karakus, A. Birgul, K. Martinez-Guijarro, C. Sukhn, D. Krishnan, S, Rajagopalan, M. Hajeyah, M. Bahloul, H. Alshemmari and M.I. Orif. “Ambient air concentrations and risk assessment of selected organochlorine pesticides (OCPs) across five Middle Eastern countries”. *Journal of Environmental Exposure Assessment*, vol. 1, http://dx.doi.org/10.20517/jeea.2022.05, May 2022.

[3]. J.N. Nuntah, O.J. Abolagba, J.O. Igene, S.F. Usifoh, C.E. Omoti and C.O. Usifoh. “Organochlorine pesticide concentrations in selected rivers in South-West Nigeria”. *South Asian Research Journal of Agriculture and Fisheries*, vol. 2, pp. 74-78, Jun. 2020.

[4]. A. Abba, Y. Ibrahim, J. Yakubu, A.J. Maina and J.C. Akan. “Assessment of organochlorine pesticide residues in water and sediment in selected areas of River Kaduna, Kaduna State, Nigeria”. *Journal of Chemical Technology*, vol. 1, pp. 126-133, Sep. 2025.

[5]. American Public Health Association (APHA). *Standard Methods for the Examination of Water and Wastewater* (19th ed.). Washington, D.C.: American Public Health Association Inc., 1995, pp. 117-118.

[6]. A.A Okunola, A. Adekunle, K. Xijun, L. Bin, Z. Yuling and H. Xia. "Comparative evaluation of environmental contamination by electronic wastes in Nigeria and China". *Science of the Total Environment***,** vol. 423, pp. 62-72, Mar. 2012.

[7]. United States Environmental Protection Agency (USEPA). *Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual (Part E, Supplemental Guidance for Dermal Risk Assessment).* Washington, DC: U.S. Environmental Protection Agency, 2004, pp. A1-E2.

[8]. K. Oginawati, S.H. Susetyo, S.I. Rahmawati, S.B. Kurniawan and S.R.S. Abdullah. "Distribution of organochlorine pesticide pollution in water, sediment, mollusk, and fish at Saguling Dam, West Java, Indonesia". *Toxicological Research*, vol. 38, pp. 149-157, Mar. 2021.

[9]. United States Environmental Protection Agency (USEPA). *National Primary Drinking Water Regulations.* 2015, pp. 550–560. Available online: https://www.epa.gov/sites/production/files/2015-11/documents.

[10]. European Commission. *Commission Regulation (EU) 2020/585 of 29 April 2020 amending Regulation (EC) No 396/2005 of the European Parliament and of the Council as regards maximum residue levels for chlorpyrifos and chlorpyrifos-methyl in or on certain products*. Official Journal of the European Union 2020 L 135/3.

[11]. World Health Organization (WHO). *Protecting groundwater for health: managing the quality of drinking-water sources.* Geneva: World Health Organization, 2006.

[12]. A.H. Santuraki, Z. Abdu, A.U. Babayo and A.G. Abdulkadira. "Concentration and Human Health Risk Assessment of Dichlorodiphenyltrichloroethane in Two Species of Fish Muscle from River Gongola Basin and its Dam, Dadinkowa, Gombe State, Nigeria". *Journal of Applied Science and Environmental Management*, vol. 26, pp. 1909-1914, Dec. 2022.

[13]. C.M. Okolocha. "Evaluation of persistent organic pollutants in sediment and biota obtained from Azuabie and Okujagu Creeks in the Upper Bonny Estuary, Nigeria". MSc, Rivers State University, Port Harcourt, 2018.

[14]. T. Krithiga, S. Sathish, A.A. Renita, D. Prabu, S. Lokesh, R. Geetha, S.K.R. Namasivayam and M. Sillanpaa. "Persistent organic pollutants in water resources: Fate, occurrence, characterization and risk analysis". *Science of The Total Environment*, vol. 831, 154808, Mar. 2022.

[15]. R. Alani, A. Lawal, S. Awonuga and B. Alo. "Distribution of Organochlorine Pesticide Residues in Surface Water and Sediments of Ogun River at Kara Abattoir, Ogun State, Nigeria". *Nigerian Journal of Environmental Sciences and Technology*, vol. 6, pp. 270-282, Mar. 2022.

[16]. G.D. Gasperina. "Environmental decay and the illegal market in e-waste from a European perspective: current problems and future directions". *Revista Catalana De Dret Ambiental*, vol. I, pp. 1 – 54, Nov. 2010.

[17]. J.B. Puckett., S. Westervelt, R. Guitierrez and Y. Takamiya. *The Digital Dump Exporting Re-use and Abuse to Africa*. The Basel Action Network, pp. 1- 43, 2005.

[18]. P. Baumard, H. Budzinski and P. Garriques. "Polycyclic Aromatic Hydrocarbons in Sediment and Mussels of the Western Mediterranean Sea". *Environmental Toxicology and Chemistry*, vol. 17, pp.765-776, Nov. 1998.

[19]. P. Baumard, H. Budzinski, P. Garrigues, H. Dizer and P.D. Hansen. "Polycyclic aromatic hydrocarbons

in recent sediments and mussels (*Mytilus edulis*) from the Western Baltic Sea: occurrence,

[20]. bioavailability and seasonal variations". *Marine Environmental Research*, vol. 47, pp. 17-47, Feb. 1999.

[21]. B.G. Onwumere and A.A. Oladimeji. "Accumulation of metals and histopathology in *Oreochromis niloticus* exposed to treated NNPC Kaduna (Nigeria) petroleum refinery effluent". *Ecotoxicology and Environmental Safety*, vol. 19, pp. 123-134, Apr. 1990.

[22]. O.O. Ezomoh, F.M. Bigbo, E. Loveday and E. Wodu. "Vitamin and mineral contents in shrimps, oysters and periwinkles harvested from Brass Local Government Area in Bayelsa State, Nigeria". *EAS Journal of Nutrition and Food Sciences*, vol. 4, pp. 123-127, Nov. 2022.

[23]. N.R. Ekere, N.M. Yakubu, T. Oparanozie and J.N. Ihedioha. "Levels and risk assessment of polycyclic aromatic hydrocarbons in water and fish of Rivers Niger and Benue confluence Lokoja, Nigeria". *Journal of Environmental Health Science and Engineering*, vol. 17, pp. 383-392, Feb. 2019.

[24]. O.E. Akinrinade, F.O. Agunbiade, R. Alani and O.O. Ayejuyo. "Implementation of the Stockholm Convention on persistent organic pollutants (POPs) in Africa–progress, challenges, and recommendations after 20 years". *Environmental Science: Advances*, vol. 3, pp. 623-634, Feb. 2024.

[25]. A.U. Dewa, J. Nelson and S.A. Olawale. "Distribution and Risk Assessment of Aldrin, Endrin, Heptachlor, and Heptachlor Epoxide in Some Villages in Hawul River Basin". *International Journal of Ground Sediment and Water*, vol. 22, pp. 1795-1813, Apr. 2025.

[26]. G.E. Odesa and D.U. Olannye. Health risk assessment of PAHs and heavy metal levels in periwinkles (*Pachymelania fusca mutans*) and crabs (Scylla serrata) consumed in crude oil-contaminated coastal regions of Southern Nigeria. *Toxicology Reports*, vol. 14, 101852, Jan. 2025.

[27]. D.C. Firth, P.E. Strydom, L. Auerswald and L.C. Hoffman. "A Human Health Risk Assessment of Persistent Organic Pollutants in Wild Marine Mussels from the Western Cape Province of South Africa". *Foods*, vol. 14, 2226, Jun. 2025.

[28]. S. Cui, Q. Fu, T. Li, W. Ma, D. Liu and M. Wang. "Sediment-Water Exchange, Spatial Variations, and Ecological Risk Assessment of Polycyclic Aromatic Hydrocarbons (PAHs) in the Songhua River, China". *Water*, vol. 8, pp. 1-13, Aug. 2016.

[29]. E.Q. Umudi, E.K. Obruche, M.I. Sani, G.C. Onwugbuta, I.S. Aghemwenhio, S.C. Ikechukwu, P.D. Clark, A.G. Essiet, O.I. Eresanya, M.C. Ibe and A. Hashimu. "Evaluation of Polycyclic Aromatic Hydrocarbons (PAHs) Contents of Fishes, Waters and Sediments of River Niger: Human Health Risk Assessment". *Journal of Basic and Applied Science Research*, vol. 3, pp. 187-199, Oct. 2025.

[30]. M. Moslen and A. Aigberua. |Heavy Metals and Hydrocarbon Contamination of Surface water in Azuabie Creek within Bonny Estuary, Nigeria". *Journal of Applied Science and Environmental Management*, vol. 22, pp. 1083-1088, Aug. 2018.

[31]. K. Ajekwene, E. Aigbokhan, O. Akindele, M.E. Yibowei, F.P. Momoh and U.K Ugonna. "Electronic waste (e-waste): sources, proliferation, effects & management in developing nations". *IOSR Journal of Engineering*, *12*, 12-27, Jan. 2022.

[32]. P.J. Berríos-Rolón, M.C. Cotto and F. Márquez. "Polycyclic Aromatic Hydrocarbons (PAHs) in Freshwater Systems: A Comprehensive Review of Sources, Distribution, and Ecotoxicological Impacts". *Toxics*, *13*(4), 321, Apr. 2025.