

Article

# Risk Assessment and Source Identification of Some Persistent Organic Pollutants In Water, Sediment, and *Clarias Gariepinus* From Okrika Axis of Bonny River

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**Abstract:** Persistent organic pollutants (POPs) have been of great concern because of their toxic natures. This study investigated selected POPs in surface water, sediment and *Clarias gariepinus* (African Sharptooth Catfish) from four sampling locations along the Okrika axis of Bonny River, Rivers State, Nigeria. Water and sediment samples were collected from representative stations and fish were obtained from local fishermen. Six POP congeners (BDE-47, BDE-99, BDE-209, PCB-28, PCB-118 and PCB-153) were quantified. POPs in water ranged from  $0.32 \pm 0.02$  to  $4.73 \pm 0.23$ , in sediment from  $2.7 \pm 0.1$  to  $76.5 \pm 3.9$ , and in *Clarias gariepinus* from  $3.9 \pm 0.20$  to  $54.4 \pm 2.60$ . Accumulation data was assessed by bioaccumulation factor (BAF) and biota-sediment accumulation factor (BSAF); and human/ecological risk was estimated via estimated daily intake (EDI), hazard quotient (HQ) and hazard index (HI). Results showed widespread contamination of the Bonny River by POPs. Heavy burden of sediment-associated POPs (especially BDE-209) and biota-associated lighter congeners (BDE-47 and PCB-28) The BAF and BSAF metrics also showed that the lower-molecular weight PBDEs and light PCBs strongly partition into fish tissue while the heavier congeners are more sediment-bound. Most risk screening determined some exceedances of some of these internationally recognized guidance (WHO, US EPA and, EU environmental quality standards) for some contaminants, and the many individual HQs and cumulative HIs greater than unity in turn indicated the potential for non-carcinogenic risk from chronic exposure via water ingestion and fish consumption. Collectively, the data indicated that Bonny River is chemically stressed by mixed inputs from oil-related activities, industrial effluents and domestic discharges. The concurrence of elevated contamination indices, strong bioaccumulation and HI exceedances highlights an urgent need for monitoring, targeted source control, regulatory enforcement and remediation to protect aquatic ecosystems and public health in the Niger Delta.

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## 1. Introduction

Water pollution has become a global environmental issue, especially in the rapidly industrialization and urbanization areas. The invasion of organic pollutants in aquatic ecosystems lead to reduction of overall water quality and life threatening to aquatic life and human. Persistent organic pollutants (POPs) are exceptions with serious challenges in that its persistence, bio-accumulative property, toxicity and interference function of hormone system creates problem in organisms. Persistent organic pollutants (POPs), such as polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDT) and

derivatives, and dioxins, are listed as substances banned or severely restricted in multiple countries on account of their environmental stability and potential ecological impact in distant ecosystems [1].

Persistent Organic Pollutants (POPs) which are a group of organic compounds that are resistant to environmental degradation, extremely toxic, and can bioaccumulate and biomagnify through the aquatic food chain endangering ecosystems and human health globally. These compounds include polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs) and modern contaminants such as per- and polyfluoroalkyl substances (PFAS), among others. POPs are semi-volatile and can travel considerable distances from their point of release, making even remote ecosystems vulnerable to contamination long after their production or use has ceased [2].

Aquatic ecosystems act as ultimate sinks for POPs due to inputs from industrial discharges, agricultural runoff, effluent outfalls, and atmospheric deposition. In the aquatic environment, POPs are partitioned between dissolved phase, particulates and sediments, with sediments functioning as a relevant depot of these substances. Additionally, sediments serve as a source of exposure to POPs leading to their bioaccumulation in benthic organisms, as well as in higher trophic determinants such as commercially important fish species, including *Clarias gariepinus*—a fish that is a significant part of the diets and fisheries of Nigerians [3].

The Niger Delta is one of the most biodiverse and economically important landscapes in Nigeria — waterways such as the Bonny River face continual pollution loads from oil exploration, refining, and shipping [4].

Although global initiatives, including the Stockholm Convention on Persistent Organic Pollutants, aim to reduce or eliminate production and use of POPs, there remain important knowledge gaps about POPs (concentrations and sources) in tropical freshwater and marine systems, and ecosystem and human health risks. Specialized studies on POPs in Nigeria are still very few, especially in the Niger Delta where a combination of both anthropogenic and natural processes occur [5].

Nevertheless, few comprehensive data on the profiles of POPs in the Okirika Axis of Bonny River; land-use source, their spatial distribution over the water and sediment matrices and bioavailability (associated with health risk through consumption of *Clarias gariepinus*) exists. Such gaps limit the ability of environmental management and preparedness plans to reduce risk, and the development of evidence-based policies to protect the aquatic environment and communities that depend on it.

### Study Area

The study was conducted in the Bonny River and its adjoining creeks within Okrika Local Government Area of Rivers State, Nigeria. This area forms an integral part of the eastern Niger Delta and lies approximately 56 km upstream from the Bight of Benin, along the north bank of the Bonny River. Ecologically, it is characterized as a tidal estuarine wetland system, comprising a network of rivers, creeks, and marshlands. Shorelines are lined with dense mangrove forests, dominated by species of *Rhizophora* and *Avicennia*. Such mangroves provide vital ecological functions such as protecting shorelines from erosion, cycle nutrients, and provide breeding grounds or habitat for fishes, crabs, mollusks, and periwinkles [6].

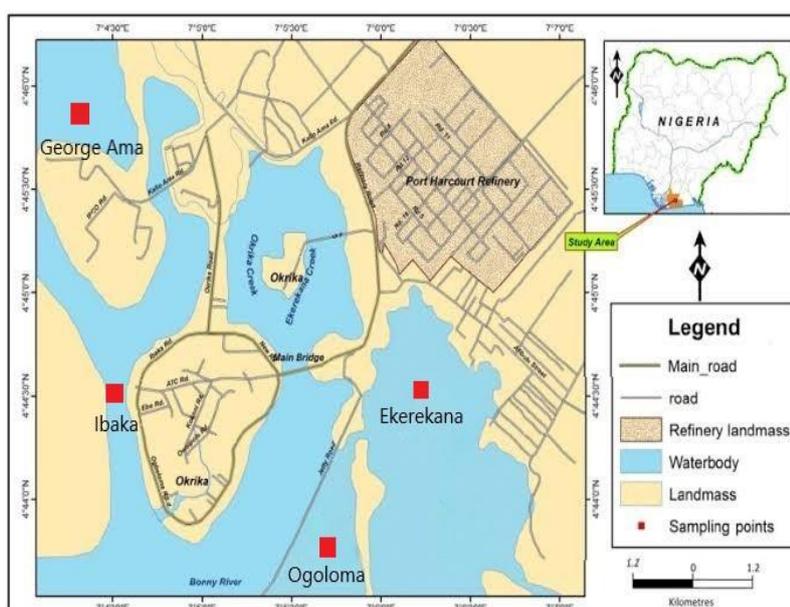
Sections of the Bonny River is a socio-economic lifeline for communities residing around it. It functions as a key thoroughfare for transporting humans and merchandise across, as well as sustaining fishing, minor enterprise, and business. Locals still earn their main living from fishing – tilapia and other aquatic species are dietary staples and also a source of commerce. Okrika Local Government Area has a population of about 222,026 people according to the 2006 Nigerian National Population Census; many this population

depend directly from the river for domestic water supply, food, transportation and income [7].

That Bonny River system, despite its importance to the ecosystem and the economy, has been subjected to more environmental pressures. The boat repair and maintenance along its banks are also a significant source of pollution, with the river receiving discharges of petroleum diesel and antifouling paints containing organotins and alkylphenols. In-treated metal scrap yards also exacerbate contamination, with leaching oxidation metallic components introducing class A heavy metals such as cadmium, lead and mercury into the aquatic system. Pollution load is further intensified by domestic waste disposal as all domestic wastes like untreated sewage, house refuse are dumped into the rivers. These wastes frequently consist of pharmaceuticals, synthetic detergents, and microplastics which have brought endocrine-disrupting chemicals like nonylphenol, bisphenol A (BPA), and triclosan into the river [6].

The third worst source of pollution comes from industrial activities. 2.1 Site Description The Port Harcourt Refining Company (PHRC) which is a government-owned crude oil refinery located a few kilometers from the area of study constantly release into the river effluents that are contaminated with hydrocarbons, phenolic compounds, heavy metals, polychlorinated biphenyl (PCBs) and other persistent organic pollutants (POPs). The issue of contamination is further exacerbated by the constant occurrence of crude oil and refined products to leakage due to petroleum exploration activities, oil bunkering, and illegal refining operations. Such spills are known to excrete phenols, benzene derivatives, and chlorinated hydrocarbons, each of which are an endocrine-disrupting toxic and environmentally persistent pollutant [7].

These numerous anthropogenic pressures have synergistic effects that have changed the river's physicochemical properties and have the potential to compromise the ecological integrity of the system. The fact that POPs persist in the environment, together with their bioaccumulative properties and their ability to act as endocrine and developmental disruptors in aquatic organisms and humans, highlight the need for ongoing environmental surveillance in this region. Despite the alarming prevalence of these contaminants, their distribution and associated risks remain poorly understood in the Niger Delta which is critical for biodiversity conservation [5], public health, and sustainable development since the local population has been shown to heavily depend on the river for food, water, and their livelihood [6].



**Figure 1.** Map of Bonny River showing Sampling Locations

## 2. Materials and Methods

A random composite sampling approach was adopted in this study to obtain representative concentrations of persistent organic pollutants across the Okrika axis of Bonny River. Four stations were strategically selected, namely Ibaka (Station 1), George Ama (Station 2), Ogoloma (Station 3), and Ekerekana (Station 4), each reflecting different levels of anthropogenic influence such as industrial discharges, agricultural runoff, urban settlements, and relatively undisturbed areas that served as comparative controls. At each station, multiple sub-samples were randomly collected and combined to form a composite sample within a 1 km radius. This mitigated site to site variability and better represented average contaminant levels for each site.

Composite samples were extracted in triplicate for precision, and reproducibility assessment. Analytical determination of POPs was based on gas chromatography–mass spectrometry (GC–MS). Before all instrumental analysis, routine extraction and clean-up processes were applied to eliminate interferences, and to enrich the target compounds.

Laboratory scale reagents were used for the sample preparation and analysis. Acid digestion and stabilization used hydrochloric acid (HCl), nitric acid (HNO<sub>3</sub>), perchloric acid (HClO<sub>4</sub>), and sulphuric acid (H<sub>2</sub>SO<sub>4</sub>). Compounds were extracted using organic solvents (methanol, acetone, and n-hexane) and silica gel was used for column purification to remove the co-extracted impurities. Residual water from extracts was removed using anhydrous sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) and sodium chloride (NaCl) further promoted phase separation during solvent partitioning (43, 80). All reagents and solvents were of analytical grade and this to minimize background contamination.

The study adhered to rigorous quality assurance and quality control (QA/QC) protocols. Water samples were collected in pre-cleaned amber glass bottles to avoid photodegradation, immediately preserved in ice-filled coolers at 4 °C, and transported for analysis to the laboratory within the recommended holding times. Each analytical batch was accompanied by blanks, duplicates and spiked samples and calibration was performed with certified reference standards. The triplicate analyses of every sample reduced these experimental errors even more and confirmed statistical robustness.

This multi-faceted methodology comprising composite sampling, stringent QA/QC and sensitive instrumental methods yielded high quality reproducible data appropriate for assessing contamination, evaluating risk, and comparing both regionally and globally.

### Sample Collection

Sampling was done at four (4) selected points as follows Ibaka, George Ama, Ogoloma and Ekerekana all in the Bonny River and its neighbouring creeks in Okrika, Rivers State, with the point of collection having common approach by boat among the stations (see figure 1). In order to better understand spatial distribution of persistent organic pollutants (POPs) in the environment and the associated ecological and human health risks, samples were collected specifically for POPs analysis.

Triplicate water samples were collected from each location in amber glass bottles, later composited for representativeness. Pellets, samples were collected using a grab sampler to depths greater than 60 cm, composited over three sampling points per station and placed in solvent-rinsed glass jars to prevent contamination. Twice they placed samples directly in coolers on ice. Prior to transportation, fish were wrapped in pre-baked aluminum foil to prevent contamination from plastics, put in sealed labeled containers, and stored on ice.

The samples collected (water, sediment, *Clarias gariepinus*) were referred to the sampling date, time, place and type [4]. Specimens were immediately transported to the laboratory in coolers containing ice packs, where they were subjected to extraction and instrumental analysis. These procedures complied with normal international protocols

which guarantees the quality of the samples and generates reliable data for the evaluation of POPs in Bonny River and nearby creeks.

### **Sample Preparation and Analysis**

#### **Preparation of Standards**

To prepare the standards for the analysis of persistent organic pollutants (POPs) by GC-MS, a special approach was used: high purity ( $\geq 98\%$  purity) certified reference materials (CRMs) were selected for analysis. These standards were appropriately weighed and diluted in solvents like hexane for the non-polar compounds and acetone/methanol for the polar compounds. The stock solution was usually to a 1 mg/mL (1000  $\mu\text{g/mL}$ ) solution stored in amber glass vials at  $-20^\circ\text{C}$  and working standards were prepared by serial dilution of the stock solution with concentrations from 1  $\mu\text{g/mL}$  to 500  $\mu\text{g/mL}$  depending on expected environmental sample concentrations. We then added internal standards to verify reproducibility and quality. Calibration standards were injected into the GC-MS, and a calibration curve was produced, with the correlation coefficient ( $R^2$ )  $\geq 0.99$  for precision quantification. We also tested matrix-spiked samples and blanks to evaluate the recovery and efficiency of the extraction method. The internal standard provided precision, and frequent recalibration means consistent reproducible results.

#### **Preparation of Water Samples for POPs Analysis**

The extraction of persistent organic pollutants (POPs) from water samples was conducted using a liquid-liquid extraction (LLE) technique, tailored to the non-polar and hydrophobic nature of POPs. The procedure began with filtering the water samples through glass fiber filters to remove suspended solids and particulates. Each sample was acidified to a  $\text{pH} \leq 2$  using concentrated hydrochloric acid (HCl) to stabilize the POPs and prevent microbial activity. The acidification also enhanced the partitioning of POPs into the organic solvent.

The POPs were then extracted by transferring 1L of water to a separatory funnel. Dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), a non-polar solvent, was added to the funnel (1:10, v/v). After securely capping the separatory funnel, the mixture was vigorously shaken for 2–3 minutes. Some periodic venting was done to relieve pressure from the volatility of the solvent during the shaking. The mixtures were separated into organic and aqueous phases by shaking and allowing to sit. The more concentrated organic phase, which contained the targeted POPs, was vacuumed off and transferred to a clean receiving flask.

The extraction procedure was performed twice using fresh portions of dichloromethane to maximize the recovery of POPs. Residual water from the combined organic extracts was removed with a column packed with 5–10 g of anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ ). The eluate was then collected in a clean round-bottom flask and evaporated to about 1–2 mL under nitrogen stream at  $40^\circ\text{C}$ , to prevent a loss of the analytes.

To remove potential co-extracted matrix interferences, the concentrated extract was passed over a Florisil column for cleanup. Concentration was continued until the cleaned extract was reduced to a final volume of 1 mL to fit the analytical instrument. The final extract was placed in an amber tube, capped and refrigerated at  $4^\circ\text{C}$  until analysis. The prepared extract was analyzed using Gas Chromatograph-Mass Spectrometer (GC-MS) to identify and quantify the POPs in the water samples.

#### **Preparation of sediment samples for POPs analysis**

The extraction of persistent organic pollutants (POPs) from sediment samples was carried out using an optimized Soxhlet extraction method. The sediment samples were first air-dried at room temperature to remove excess moisture and then ground and homogenized using a mortar and pestle. This made it homogeneous and easier to extract. One sand sample (10 g) was weighed on a analytical balance, then NaCl was mixed in a 1:1 ratio of NaCl to sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) in order to remove remaining water.

They transferred the mixture to a cellulose extraction thimble and put it into the Soxhlet extractor. Extraction solvent was the mixture of dichloromethane and hexane (v/v 1:1). About 150 mL of this solvent mixture was filled into the round-bottom flask connected to the Soxhlet apparatus. A heating mantle provided heating to the extraction system with the temperature regulated over the boiling point of the solvent to allow constant solvent reflux without evaporated solute thermal degradation.

For 6 hours, the Soxhlet was operating with the solvent refluxing, extracting the POPs from the sediment matrix. It refers to after the extraction process, whereby the solvent containing the analytes is concentrated using a rotary evaporator at decreased pressure in order to achieve a volume of approximately 2 mL. This concentrated extract was passed through a drying column containing 10 g of anhydrous sodium sulfate to eliminate measurable traces of any residual water.

The extract was also purified by applying a Florisil column cleanup thus eliminating interferences and contaminants from the matrix. The sample was loaded after preconditioning the column with 20 mL of hexane. Fractions containing the analytes were eluted with a mixture of hexane and dichloromethane (9:1 v/v). Thirdly, the fraction of the POPs of interest was eluted, collected into a clean glass vial and concentrated down to 1 mL using nitrogen gas at 40°C.

The last extract was placed in amber glass vials, closed, and kept at 4°C until analyzed in a Gas Chromatograph – Mass Spectrometer (GC-MS) system, for the identification and quantification of POPs.

#### **Preparation of *Clarias gariepinus* samples for POPs analysis**

The preparation of biota samples (*Clarias gariepinus*) for the analysis of persistent organic pollutants (POPs) was carried out using an optimized Soxhlet extraction procedure adapted for biological tissues. The samples were washed thoroughly with deionized water to remove the external debris and then filleted with a clean stainless-steel knife. The edible muscle tissues (main location of the bioaccumulation) were separated, homogenated with a laboratory fruit blender, and air-dried at room temperature until the air moisture was decreased. To maintain the integrity of the analytes and avoid microbial degradation of samples, the samples were freeze-dried.

The homogenized and air-dried fish tissue (ca. 10 g) was accurately weighed on a precision balance and thoroughly blended with anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) in the ratio of 1 : 2 (w/w) to remove residual moisture and facilitate a dry powder suitable for extraction. It was then transferred into a cellulose extraction-thimble and introduced into the Soxhlet extractor. Approximately 150 mL of solvent mixture composed of dichloromethane and hexane (1:1, v/v) was added to the round-bottom flask of the Soxhlet system to serve as the extraction solvent.

This extraction was performed under controlled heating systems for 8 hours which then ensured continuous reflux of the solvent mixture, hence proper recovery of POPs, including polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) from the tissue matrix. The solvent extract was then concentrated to nearly 2 mL by rotary evaporator under reduced pressure following the extraction. Anhydrous sodium sulfate was used to dry the concentrated extract column, removing residual water.

A multilayer silica gel column cleanup was conducted to remove lipids and co-extracted biomolecules causing interference in the GC-MS analyses. The column was preconditioned with hexane prior to the loading of extract samples with better concentration. After drying, the POPs were eluted with hexane and dichloromethane (9:1 v/v) and the eluate was collected in a clean glass vial. The eluates were concentrated to a final volume of 1 mL under a gentle stream of nitrogen gas in a water bath at 40 °C.

The purified extract was recovered and then placed in amber glass vials, closed with Teflon-lined caps and kept at 4 °C until performed the instrumental analysis. Gas

Chromatograph-Mass Spectrometer (GC-MS) technique enabled quantitative and qualitative determination of POPs at trace levels in the target analytes range.

### Hazard quotient (HQ) and Hazard Index (HI)

The Hazard Quotient (HQ) is a quantitative tool used in risk assessment to evaluate the potential non-carcinogenic health risks posed by exposure to a chemical contaminant. It compares the level of exposure to a contaminant with a reference level known to be safe. HQ is widely employed in environmental studies to assess the risks associated with contaminants in water, sediment, or biota.

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

Where:

Ex: Exposure level to the contaminant (e.g., daily intake via ingestion or dermal absorption, typically expressed in mg/kg/day).

RfD: Reference Dose, a safe exposure level for the contaminant (in mg/kg/day), provided by regulatory agencies such as the U.S. Environmental Protection Agency (USEPA).

The Estimated Daily Intake (EDI) was calculated for each chemical and used to quantify HQ for both exposure pathways. Hazard assessment was based on RfD values reported by the U.S.EPA and WHO for chemicals with established limits:

### POPs

- BDE-47:  $1.0 \times 10^{-4}$
- BDE-99:  $2.0 \times 10^{-3}$
- BDE-209:  $7.0 \times 10^{-3}$
- PCBs:  $2.0 \times 10^{-5}$

Source: USEPA

The **Estimated Daily Intake (EDI)** was first determined for both drinking water and fish consumption pathways using the following equations:

$$EDI_{\text{water}} = \frac{C_{\text{water}} \times IR_{\text{water}}}{BW} \quad (4)$$

$$EDI_{\text{fish}} = \frac{C_{\text{fish}} \times IR_{\text{fish}}}{BW} \quad (5)$$

where  $C_{\text{water}}$  is the contaminant concentration in water ( $\mu\text{g}\cdot\text{L}^{-1}$ ),  $IR_{\text{water}}$  is the daily water ingestion rate ( $\text{L}\cdot\text{day}^{-1}$ ),  $C_{\text{fish}}$  is the contaminant concentration in fish ( $\mu\text{g}\cdot\text{kg}^{-1}$  wet weight),  $IR_{\text{fish}}$  is the daily fish ingestion rate ( $\text{kg}\cdot\text{day}^{-1}$ ), and  $BW$  is the body weight (kg).

### HQ Interpretation:

$HQ < 1$ : Indicates that the exposure level is below the reference dose, suggesting no significant risk of adverse effects.

$HQ \geq 1$ : Suggests potential non-carcinogenic risks to human health; the higher the HQ value, the greater the likelihood of adverse effects.

### Bioaccumulation and Biota-Sediment Accumulation of POPs

To further understand the environmental dynamics of persistent organic pollutants (POPs) in Bonny River, bioaccumulation and biota-sediment accumulation factors were calculated. These indices are useful for assessing how pollutants partition between environmental compartments and the potential for transfer through the food chain.

The **Bioaccumulation Factor (BAF)** was calculated using the formula:

$$BAF = \frac{C_{\text{biota}}}{C_{\text{water}}} \quad (6)$$

where  $C_{\text{biota}}$  is the concentration of the compound in fish ( $\mu\text{g}/\text{kg}$  wet weight) and  $C_{\text{water}}$  is the concentration in water ( $\mu\text{g}/\text{L}$ ). BAF expresses the degree to which an organism can accumulate contaminants directly from its surrounding water through respiration or passive diffusion.

The **Biota-Sediment Accumulation Factor (BSAF)** was calculated as:

$$\text{BSAF} = \frac{C_{\text{biota}}}{C_{\text{sediment}}} \quad (7)$$

where  $C_{\text{sediment}}$  is the concentration of the pollutant in sediment ( $\mu\text{g}/\text{kg}$  dry weight). BSAF describes bioaccumulation through dietary exposure pathways, reflecting the ability of organisms to assimilate contaminants from sediments either directly or via benthic food sources.

### 3. Results

**Table 1.** Mean Concentrations of POPs in Water of Bonny River

Parameter	Station 1	Station 2	Station 3	Station 4	Mean $\pm$ SD
BDE-47	0.82 $\pm$ 0.05	0.65 $\pm$ 0.04	1.21 $\pm$ 0.07	0.78 $\pm$ 0.05	0.87 $\pm$ 0.25
BDE-99	0.54 $\pm$ 0.03	0.41 $\pm$ 0.02	0.89 $\pm$ 0.05	0.47 $\pm$ 0.03	0.58 $\pm$ 0.20
BDE-209	1.92 $\pm$ 0.10	1.35 $\pm$ 0.08	2.63 $\pm$ 0.14	1.57 $\pm$ 0.09	1.87 $\pm$ 0.53
PCB-28	1.32 $\pm$ 0.07	0.95 $\pm$ 0.05	2.06 $\pm$ 0.11	1.15 $\pm$ 0.06	1.37 $\pm$ 0.48
PCB-118	0.46 $\pm$ 0.03	0.32 $\pm$ 0.02	0.71 $\pm$ 0.04	0.38 $\pm$ 0.02	0.47 $\pm$ 0.17
PCB-153	0.67 $\pm$ 0.04	0.48 $\pm$ 0.03	1.12 $\pm$ 0.06	0.59 $\pm$ 0.04	0.72 $\pm$ 0.26
$\Sigma$ PBDEs	3.28 $\pm$ 0.18	2.41 $\pm$ 0.14	4.73 $\pm$ 0.23	2.82 $\pm$ 0.17	3.31 $\pm$ 1.07
$\Sigma$ PCBs	2.45 $\pm$ 0.14	1.75 $\pm$ 0.10	3.89 $\pm$ 0.21	2.12 $\pm$ 0.12	2.55 $\pm$ 0.92

#### Legend

BDE-47 – 2,2',4,4'-Tetrabromodiphenyl ether

BDE-99 – 2,2',4,4',5-Pentabromodiphenyl ether

BDE-209 – Decabromodiphenyl ether (2,2',3,3',4,4',5,5',6,6'-Decabromodiphenyl ether)

PCB-28 – 2,4,4'-Trichlorobiphenyl

PCB-118 – 2,3',4,4',5-Pentachlorobiphenyl (a mono-ortho PCB; dioxin-like)

PCB-153 – 2,2',4,4',5,5'-Hexachlorobiphenyl

$\Sigma$ PBDEs – Sum of all measured polybrominated diphenyl ether congeners

$\Sigma$ PCBs – Sum of all measured polychlorinated biphenyl congeners

**Table 2.** Mean Concentrations of POPs in Sediment of Bonny River

Parameter	Station 1	Station 2	Station 3	Station 4	Mean $\pm$ SD
BDE-47	8.30 $\pm$ 0.50	6.90 $\pm$ 0.40	15.60 $\pm$ 0.90	9.80 $\pm$ 0.6	10.20 $\pm$ 3.90
BDE-99	5.70 $\pm$ 0.30	4.60 $\pm$ 0.30	11.20 $\pm$ 0.70	6.30 $\pm$ 0.4	6.95 $\pm$ 2.90
BDE-209	28.50 $\pm$ 1.60	22.40 $\pm$ 1.20	49.70 $\pm$ 2.50	31.30 $\pm$ 1.7	33.00 $\pm$ 11.60
PCB-28	11.80 $\pm$ 0.60	9.50 $\pm$ 0.50	22.60 $\pm$ 1.10	13.10 $\pm$ 0.7	14.30 $\pm$ 5.50
PCB-118	3.50 $\pm$ 0.20	2.70 $\pm$ 0.10	6.80 $\pm$ 0.30	4.10 $\pm$ 0.2	4.30 $\pm$ 1.70
PCB-153	5.70 $\pm$ 0.30	4.40 $\pm$ 0.20	11.30 $\pm$ 0.60	6.20 $\pm$ 0.3	6.90 $\pm$ 2.90
$\Sigma$ PBDEs	42.50 $\pm$ 2.40	33.90 $\pm$ 1.90	76.50 $\pm$ 3.90	47.40 $\pm$ 2.5	50.10 $\pm$ 18.70
$\Sigma$ PCBs	21.00 $\pm$ 1.10	16.60 $\pm$ 0.90	40.70 $\pm$ 2.00	23.40 $\pm$ 1.2	25.40 $\pm$ 9.70

#### Legend

BDE-47 – 2,2',4,4'-Tetrabromodiphenyl ether

BDE-99 – 2,2',4,4',5-Pentabromodiphenyl ether

BDE-209 – Decabromodiphenyl ether (2,2',3,3',4,4',5,5',6,6'-Decabromodiphenyl ether)

PCB-28 – 2,4,4'-Trichlorobiphenyl

PCB-118 – 2,3',4,4',5-Pentachlorobiphenyl (a mono-ortho PCB; dioxin-like)

PCB-153 – 2,2',4,4',5,5'-Hexachlorobiphenyl

$\Sigma$ PBDEs – Sum of all measured polybrominated diphenyl ether congeners

$\Sigma$ PCBs – Sum of all measured polychlorinated biphenyl congeners

**Table 3.** Mean concentrations of POPs in *Clarias gariepinus* of Bonny River

Parameter	Fish 1	Fish 2	Fish 3	Mean $\pm$ SD
BDE-47	12.4 $\pm$ 0.6	9.7 $\pm$ 0.5	16.5 $\pm$ 0.8	12.9 $\pm$ 3.5
BDE-99	8.9 $\pm$ 0.4	6.7 $\pm$ 0.3	12.8 $\pm$ 0.6	9.5 $\pm$ 3.1
BDE-209	5.1 $\pm$ 0.2	3.9 $\pm$ 0.2	7.2 $\pm$ 0.3	5.4 $\pm$ 1.7
PCB-28	17.6 $\pm$ 0.9	13.2 $\pm$ 0.6	25.1 $\pm$ 1.2	18.6 $\pm$ 6.0
PCB-118	6.3 $\pm$ 0.3	4.8 $\pm$ 0.2	9.1 $\pm$ 0.4	6.7 $\pm$ 2.2
PCB-153	13.8 $\pm$ 0.7	10.1 $\pm$ 0.5	20.2 $\pm$ 1.0	14.7 $\pm$ 5.1
$\Sigma$ PBDEs	26.4 $\pm$ 1.2	20.3 $\pm$ 1.0	36.5 $\pm$ 1.7	27.0 $\pm$ 8.1
$\Sigma$ PCBs	37.7 $\pm$ 1.9	28.1 $\pm$ 1.4	54.4 $\pm$ 2.6	40.1 $\pm$ 13.4

Legend:

BDE-47 – 2,2',4,4'-Tetrabromodiphenyl ether

BDE-99 – 2,2',4,4',5-Pentabromodiphenyl ether

BDE-209 – Decabromodiphenyl ether (2,2',3,3',4,4',5,5',6,6'-Decabromodiphenyl ether)

PCB-28 – 2,4,4'-Trichlorobiphenyl

PCB-118 – 2,3',4,4',5-Pentachlorobiphenyl (a mono-ortho PCB; dioxin-like)

PCB-153 – 2,2',4,4',5,5'-Hexachlorobiphenyl

$\Sigma$ PBDEs – Sum of all measured polybrominated diphenyl ether congeners

$\Sigma$ PCBs – Sum of all measured polychlorinated biphenyl congeners

**Table 4.** Hazard Quotient (HQ) and Hazard Index (HI) of POPs in water and *Clarias gariepinus* (fish) of Bonny River

Parameter	Mean (water) $\mu\text{g}\cdot\text{L}^{-1}$	EDI (water) (mg/kg·d)	HQ_water	Mean (fish) $\mu\text{g}\cdot\text{kg}^{-1}$	EDI_fish (mg/kg·d)	HQ_fish
BDE-47	0.87	2.49 $\times$ 10 <sup>-5</sup>	0.25	12.90	3.69 $\times$ 10 <sup>-6</sup>	0.04
BDE-99	0.58	1.66 $\times$ 10 <sup>-5</sup>	0.01	9.50	2.71 $\times$ 10 <sup>-6</sup>	0.00
BDE-209	1.87	5.34 $\times$ 10 <sup>-5</sup>	0.01	5.40	1.54 $\times$ 10 <sup>-6</sup>	0.00
PCB-28	1.37	3.91 $\times$ 10 <sup>-5</sup>	1.96	18.60	5.31 $\times$ 10 <sup>-6</sup>	0.27
PCB-118	0.47	1.34 $\times$ 10 <sup>-5</sup>	0.67	6.70	1.91 $\times$ 10 <sup>-6</sup>	0.10
PCB-153	0.72	2.06 $\times$ 10 <sup>-5</sup>	1.03	14.70	4.20 $\times$ 10 <sup>-6</sup>	0.21
<b>HI</b>			<b>3.92</b>			<b>0.61</b>

Legend:

BDE-47 – 2,2',4,4'-Tetrabromodiphenyl ether

BDE-99 – 2,2',4,4',5-Pentabromodiphenyl ether

BDE-209 – Decabromodiphenyl ether (2,2',3,3',4,4',5,5',6,6'-Decabromodiphenyl ether)

PCB-28 – 2,4,4'-Trichlorobiphenyl

PCB-118 – 2,3',4,4',5-Pentachlorobiphenyl (a mono-ortho PCB; dioxin-like)

PCB-153 – 2,2',4,4',5,5'-Hexachlorobiphenyl

**Table 5.** BSAF and BAF values for POPs in water, sediment, and *Clarias gariepinus* (fish) in Bonny River

Parameter	Mean water ( $\mu\text{g}/\text{L}$ )	Mean Sediment ( $\mu\text{g}/\text{kg}$ )	Mean Fish ( $\mu\text{g}/\text{kg}$ )	BSAF	BAF
BDE-47	0.87	10.2	12.9	1.26	14.83
BDE-99	0.58	6.95	9.5	1.37	16.4
BDE-209	1.87	33	5.4	0.16	2.89
PCB-28	1.37	14.3	18.6	1.3	13.58
PCB-118	0.47	4.3	6.7	1.56	14.26
PCB-153	0.72	6.90	14.70	2.13	20.42

Legend:

BDE-47 – 2,2',4,4'-Tetrabromodiphenyl ether

BDE-99 – 2,2',4,4',5-Pentabromodiphenyl ether

BDE-209 – Decabromodiphenyl ether (2,2',3,3',4,4',5,5',6,6'-Decabromodiphenyl ether)

PCB-28 – 2,4,4'-Trichlorobiphenyl

PCB-118 – 2,3',4,4',5-Pentachlorobiphenyl (a mono-ortho PCB; dioxin-like)

PCB-153 – 2,2',4,4',5,5'-Hexachlorobiphenyl

#### 4. Discussion

##### Concentrations of persistent organic pollutants (POPs) in water of Bonny River

The concentrations of persistent organic pollutants (POPs) in Bonny River water revealed the presence of both polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs), indicating ongoing contamination from both industrial and domestic sources. Overall, PBDEs were slightly more concentrated than PCBs, a finding that reflects their greater solubility and continued use in flame-retardant formulations.

BDE-47 was the most abundant congener among the PBDEs, constituting ranging from  $0.65 \pm 0.04$   $\mu\text{g/L}$  at Station 2 to  $1.21 \pm 0.07$   $\mu\text{g/L}$  at Station 3 and averaging  $0.87 \pm 0.25$   $\mu\text{g/L}$ , a result supported by observations worldwide where BDE-47 is frequently the predominant congener due to its widespread use in penta-BDE formulations and greater mobility in environmental compartments [32]. BDE-99 was found at a moderate level of  $0.41\text{--}0.89$   $\mu\text{g/L}$  (mean  $0.58 \pm 0.20$   $\mu\text{g/L}$ ) while BDE-209 showed the highest concentrations (individual PBDE concentrations) of all PBDEs ranging from  $1.35 \pm 0.08$   $\mu\text{g/L}$  to  $2.63 \pm 0.14$   $\mu\text{g/L}$  (mean  $1.87 \pm 0.53$   $\mu\text{g/L}$ ), and as a heavier congener it is less likely to profile in the water column due to partitioning into sediments; however, resuspension processes and the re-entry of treated effluent may account for the detection of BDE-209 concentrations within the water column.

Among PCBs, PCB-28 was the most abundant congener, ranging from  $0.95 \pm 0.05$   $\mu\text{g/L}$  at Station 2 to  $2.06 \pm 0.11$   $\mu\text{g/L}$  at Station 3, with a mean concentration of  $1.37 \pm 0.48$   $\mu\text{g/L}$  (Table 1). PCB-118 was at lower levels ( $0.32\text{--}0.71$   $\mu\text{g/L}$ , mean  $0.47 \pm 0.17$   $\mu\text{g/L}$ ), and PCB-153 varied between  $0.48 \pm 0.03$   $\mu\text{g/L}$  and  $1.12 \pm 0.06$   $\mu\text{g/L}$ , with an overall mean of  $0.72 \pm 0.26$   $\mu\text{g/L}$  (Table 1). Such a distribution pattern of PCB congeners agrees with the well-known phenomenon that in aquatic environments, lighter congeners (e.g PCB-28) tend to be more freely dispersed, while heavier congeners usually get preferentially partitioned into sediments and biota [8].

Levels detected in Bonny River water far exceed regulatory thresholds. European Union EQS for PBDEs in surface waters is  $0.0005$   $\mu\text{g/L}$ , multiple orders of magnitude lower than concentration values acquired in this study (Camino et al., 2018). Likewise, WHO guideline value for PCBs in drinking water is  $0.0005$   $\mu\text{g/L}$  and EPA guideline value is also  $0.0005$   $\mu\text{g/L}$  for PCBs in drinking water but Bonny River levels ranged from  $0.32$  to  $2.06$   $\mu\text{g/L}$  which exceeds the guideline value by a very large margin and these exceedances represent serious ecological and public health risks from the contamination of the river.

The comparatively high concentrations noted at Station 3 relative to other sites could indicate localized sources of pollution due to discharges from industries, especially petroleum refineries, or domestic waste in communities neighboring the coastal water body. The dominance of lighter PBDE (BDE-47, BDE-99) and PCB (PCB-28) profiles also suggests more recent inputs since these congeners are more hydrophilic and compared to heavier congeners, less sedentary in the environment.

While measured concentrations (in micrograms) should not be expected to be of significant toxicological importance (Table 2), PBDEs and PCBs are established endocrine-disrupting, carcinogenic, and bioaccumulative toxins that negatively affect reproduction,

immunity, and neurodevelopment at extremely low doses [9]. Consequently, the findings underscore the need for efficient treatment of wastewater, enforcement of environmental regulatory policies, and continual monitoring of Bonny River as a basin providing habitat for aquatic biodiversity and serving as a source of domestic, agricultural, and economic activities to human populations.

### **Concentrations of Persistent Organic Pollutants (POPs) in Sediment of Bonny River**

The analysis of persistent organic pollutants (POPs) in sediments of Bonny River revealed significant concentrations of both polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs), reflecting the strong affinity of these hydrophobic contaminants for particulate matter and benthic environments. Sediments, acting as both sinks and potential secondary sources, provide an important record of both historical and recent contamination events.

Among the PBDE congeners, BDE-209 was dominant, consistent with global trends where deca-BDE formulations have been widely used as flame retardants [10]. Concentrations ranged from  $22.4 \pm 1.2$   $\mu\text{g}/\text{kg}$  at Station 2 to  $49.7 \pm 2.5$   $\mu\text{g}/\text{kg}$  at Station 3, with an overall mean of  $33.0 \pm 11.6$   $\mu\text{g}/\text{kg}$ . The elevated values at Station 3 suggest localized contamination, likely linked to petroleum refining, shipyard operations, or untreated effluent discharge. BDE-47 and BDE-99 were also detected at considerable levels, ranging from  $6.9 \pm 0.4$  to  $15.6 \pm 0.9$   $\mu\text{g}/\text{kg}$  and  $4.6 \pm 0.3$  to  $11.2 \pm 0.7$   $\mu\text{g}/\text{kg}$  respectively, with overall means of  $10.2 \pm 3.9$   $\mu\text{g}/\text{kg}$  and  $6.95 \pm 2.9$   $\mu\text{g}/\text{kg}$ . The predominance of BDE-47 over BDE-99 reflects the higher persistence and bioavailability of lighter PBDE congeners, which have been widely documented in sediments of semi-industrialized regions such as the Niger Delta [8].

For PCBs, PCB-28 recorded the highest concentrations among congeners, ranging from  $9.5 \pm 0.5$  to  $22.6 \pm 1.1$   $\mu\text{g}/\text{kg}$ , with a mean of  $14.3 \pm 5.5$   $\mu\text{g}/\text{kg}$ . This was followed by PCB-153 ( $4.4$ – $11.3$   $\mu\text{g}/\text{kg}$ ; mean  $6.9 \pm 2.9$   $\mu\text{g}/\text{kg}$ ) and PCB-118 ( $2.7$ – $6.8$   $\mu\text{g}/\text{kg}$ ; mean  $4.3 \pm 1.7$   $\mu\text{g}/\text{kg}$ ). The dominance of lighter congeners (PCB-28) is typical in aquatic sediments exposed to ongoing inputs, as these compounds are relatively more volatile and soluble, allowing them to remain in circulation longer before settling. Heavier congeners like PCB-153, although less abundant in water, remain important due to their strong partitioning into sediments and eventual bioaccumulation in aquatic organisms [11].

$\Sigma\text{PBDEs}$  and  $\Sigma\text{PCBs}$  are sum concentrations which also further indicate sediment contamination.  $\Sigma\text{PBDEs}$  were determined at  $33.9 \pm 1.9$   $\mu\text{g}/\text{kg}$  (Station 2) to  $76.5 \pm 3.9$   $\mu\text{g}/\text{kg}$  (Station 3) with an average concentration of  $50.1 \pm 18.7$   $\mu\text{g}/\text{kg}$ , whereas  $\Sigma\text{PCBs}$  were  $16.6 \pm 0.9$   $\mu\text{g}/\text{kg}$  (Station 2) to  $40.7 \pm 2.0$   $\mu\text{g}/\text{kg}$  (Station 3) with a mean of  $25.4 \pm 9.7$   $\mu\text{g}/\text{kg}$ . The much higher values detected at Station 3 further confirm localized inputs of industrial or shipping origin.

Compared with the global reports, these concentrations in Bonny River sediments are within the ranges reported for particular sediments in other industrialized and semi-industrialized aquatic environments. Similar studies have reported  $\Sigma\text{PBDE}$  levels of 30–150  $\mu\text{g}/\text{kg}$  in sediment from the Pearl River Delta, China, and  $\Sigma\text{PCBs}$  of 10–60  $\mu\text{g}/\text{kg}$  in sediment from Nigeria [12][14]. The averages obtained from Bonny River place it in the same contamination group, albeit high ends for some congeners, pointing at both legacy pollution and ongoing recent inputs.

The elevated levels of POPs in sediments pose ecological risks, as benthic organisms are directly exposed through ingestion and contact, leading to biomagnification up the food chain [15]. Given that both PBDEs and PCBs are persistent, lipophilic, and endocrine-disrupting compounds, their presence in Bonny River sediments highlights a significant pathway for exposure of aquatic organisms and, ultimately, humans relying on biota from the river.

Overall, the results underscore the dual role of sediments as sinks and potential secondary sources of POPs. Any disturbance of sediments, whether through dredging, trawling, or strong hydrodynamic events, may remobilize these pollutants into the water column, sustaining chronic exposure [16]. Continuous monitoring and mitigation strategies are therefore necessary to reduce pollutant loading and protect ecological and human health in the Niger Delta region.

### **Concentrations of Persistent Organic Pollutants (POPs) in *Clarias gariepinus* of Bonny River**

The concentrations of persistent organic pollutants (POPs) in *Clarias gariepinus* (fish) samples from Bonny River provide strong evidence of bioaccumulation of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) within the aquatic food web. Fish, being higher trophic organisms, serve as important bioindicators of long-term POP exposure and are also a direct route of human exposure due to their role as a dietary staple in local communities [17].

BDE-47 was the most prevalent congener of the PBDEs, with concentrations that ranged from  $9.7 \pm 0.5$   $\mu\text{g}/\text{kg}$  in Fish 2 to  $16.5 \pm 0.8$   $\mu\text{g}/\text{kg}$  in Fish 3 (Table 1), and an overall mean concentration of  $12.9 \pm 3.5$   $\mu\text{g}/\text{kg}$ . The predominance of BDE-47 in these studies is consistent with global patterns of BDE congener distribution, because BDE-47 is one of the major components of penta-BDE technical mixtures and is more bioavailable than heavier congeners. BDE-99 had also high concentrations in fish ( $6.7$ – $12.8$   $\mu\text{g}/\text{kg}$ ; mean  $9.5 \pm 3.1$   $\mu\text{g}/\text{kg}$ ), while BDE-209 was the most abundant congener associated with sediments, but had relatively low concentrations in fish ( $3.9$ – $7.2$   $\mu\text{g}/\text{kg}$ ; mean  $5.4 \pm 1.7$   $\mu\text{g}/\text{kg}$ ). These patterns mirrors the relative inability of highly brominated congeners to bioaccumulate based upon their tendency to strongly bind to sediments and be poorly taken up in the tissues of fish.

In PCBs, the dominant congener was the lighter PCB-28, which had a concentration of  $13.2 \pm 0.6$   $\mu\text{g}/\text{kg}$  in Fish 2,  $25.1 \pm 1.2$   $\mu\text{g}/\text{kg}$  in Fish 3, and an overall mean of  $18.6 \pm 6.0$   $\mu\text{g}/\text{kg}$ . Next were PCB-153 ( $10.1$ – $20.2$   $\mu\text{g}/\text{kg}$ ; mean  $14.7 \pm 5.1$   $\mu\text{g}/\text{kg}$ ), PCB-118 was detected at much lower but still relevant levels ( $4.8$ – $9.1$   $\mu\text{g}/\text{kg}$ ; mean  $6.7 \pm 2.2$   $\mu\text{g}/\text{kg}$ ). Several of these congeners, such as PCB-153 and PCB-118, are too lipophilic coupled with high resistance to metabolic degradation, leading to extensive literature on their biota occurrence globally [8].

This subset sums together many of the concentration pressures and provides a better view of contaminant scale.  $\Sigma\text{PBDEs}$  concentrations in Fish 2 ( $20.3 \pm 1.0$   $\mu\text{g}/\text{kg}$ ) and Fish 3 ( $36.5 \pm 1.7$   $\mu\text{g}/\text{kg}$ ) has a wider fluctuations than that in Fish 1 ( $16.2 \pm 2.8$   $\mu\text{g}/\text{kg}$ ), and presenting a average concentration of  $27.0 \pm 8.1$   $\mu\text{g}/\text{kg}$ . While  $\Sigma\text{PCBs}$  were always greater, averaging  $40.1 \pm 13.4$   $\mu\text{g}/\text{kg}$  (ranging from  $28.1 \pm 1.4$   $\mu\text{g}/\text{kg}$ , Fish 2 to  $54.4 \pm 2.6$   $\mu\text{g}/\text{kg}$ , Fish 3). These values confirm that PCBs remain the dominant group of POPs in terms of bioaccumulation, reflecting both their historical usage and extreme environmental persistence.

When compared with reported values in other regions of the Niger Delta, the concentrations fall within ranges previously documented in Woji Creek, Forcados, and Lagos Lagoon, where  $\Sigma\text{PBDEs}$  and  $\Sigma\text{PCBs}$  in fish tissues ranged between  $15$ – $60$   $\mu\text{g}/\text{kg}$  [14]. Globally, similar magnitudes have been reported in semi-industrialized rivers in Asia and Europe, though values remain far higher than international quality standards. As an example, the European Food Safety Authority (EFSA) has emphasized that PBDEs and PCBs in human food fish ought to be decreased to below  $\mu\text{g}/\text{kg}$  degree because of their bioaccumulative and toxic effects [18].

The contamination patterns that were observed also have ecological and health implications. Fish 3 was the highest at most of the congeners, indicating that bioaccumulation of POP was more species-specific or age-related than body burden, possibly due to differences in diet, lipid or bathymetric habitat preference. The results for

BDE-47 and PCB-28 in particular are alarming because of the endocrine disruption, immunotoxicity, and potential carcinogenicity of these compounds. And human populations around the Bonny River, where fish provides valuable protein, face risks from chronic exposure through fish consumption on top of all this.

In conclusion, the results provide additional evidence supporting the interpretation that the Bonny River ecosystem is a site of active biomagnification of bioavailable POPs. The persistence of both PBDEs and PCBs in fish highlights the urgent need for tighter environmental controls, regular biomonitoring programs, and public awareness campaigns on potential risks of long-term exposure through seafood consumption.

### **Comparative Analysis of POPs in Water, Sediment, and *Clarias gariepinus* of Bonny River**

The distribution of persistent organic pollutants (POPs) across the three environmental media (water, sediment, and *Clarias gariepinus*) in Bonny River reveals consistent patterns of contamination, partitioning, and bioaccumulation. The mean concentrations recorded in this study demonstrated that while sediments serve as the principal sink for POPs, fish tissues exhibit the clearest evidence of biomagnification and ecological risk.

POPs concentrations in the water column were relatively low ( $\Sigma$ PBDE:  $3.31 \pm 1.07$   $\mu\text{g/L}$ ,  $\Sigma$ PCB:  $2.55 \pm 0.92$   $\mu\text{g/L}$ ). BDE-47 and PCB-28 were mostly present among their congeners, probably due to their greater solubility and mobility in the environment. On the contrary, despite its relatively low solubility, BDE-209 was detected at measurable levels (mean  $1.87 \pm 0.53$   $\mu\text{g/L}$ ) indicating continuous contamination sources possibly associated with industrial discharge and oil exploitation activities.

As expected, sediments showed the highest absolute POP concentrations with  $\Sigma$ PBDEs ( $50.1 \pm 18.7$   $\mu\text{g/kg}$ ) and  $\Sigma$ PCBs ( $25.4 \pm 9.7$   $\mu\text{g/kg}$ ) vastly exceeding those in water. Relative abundance of BDE-209 (mean  $33.0 \pm 11.6$   $\mu\text{g/kg}$ ) illustrates preferential partitioning of heavier PBDE congeners to particulate matter, and PCB-28 (mean  $14.3 \pm 5.5$   $\mu\text{g/kg}$ ) being the most abundant PCB congener emphasizes its environmental persistence despite global restrictions. Consistent with results seen for sediments within the Niger Delta, sediments are long-term and contemporary POP pollution reservoirs [14].

The highest concentrations were detected in *Clarias gariepinus* (fish), where  $\Sigma$ PBDEs and  $\Sigma$ PCBs reached mean values of  $27.0 \pm 8.1$   $\mu\text{g/kg}$  and  $40.1 \pm 13.4$   $\mu\text{g/kg}$ , respectively. This confirms bioaccumulation and trophic transfer of POPs from lower to higher levels in the aquatic food chain. BDE-47 and PCB-28 again emerged as dominant congeners in fish tissues, a pattern reflecting their bioavailability and relatively higher metabolic stability. Notably, while BDE-209 was highest in sediments, it showed comparatively lower levels in fish (mean  $5.4 \pm 1.7$   $\mu\text{g/kg}$ ), supporting evidence that highly brominated congeners have reduced bioaccumulation potential due to steric hindrance and slower uptake rates. Conversely, lighter congeners such as BDE-47 and PCB-28 biomagnify more efficiently, making them key indicators of ecological risk.

Comparing across media, the clear trend of water < sediment < fish illustrates the classic POP partitioning and biomagnification model. The transition from dissolved forms in water to particle-bound forms in sediments, and finally to concentrated residues in fish tissues, underscores the long-term persistence of these pollutants and their ability to infiltrate aquatic food webs. This trend is consistent with global studies and demonstrates that Bonny River is undergoing similar contaminant dynamics as other semi-industrialized and oil-impacted aquatic systems worldwide.

The elevated POP burdens in *Clarias gariepinus* are of particular concern, as they represent a direct pathway of human exposure through dietary intake. In regions such as the Niger Delta, where fish are a staple protein source, the accumulation of PCBs and PBDEs poses serious health risks, including endocrine disruption, immunotoxicity,

reproductive impairment, and potential carcinogenic effects. The dominance of lighter congeners, which are more bioavailable and toxicologically potent, further exacerbates the concern [19].

This integrated assessment demonstrates that while sediments act as a reservoir of POPs, fish provide the most sensitive measure of ecological and human health risk. The findings emphasize the urgent need for continuous monitoring of POPs across environmental compartments, stricter enforcement of effluent control, and comprehensive public health advisories in communities reliant on Bonny River for sustenance.

#### **Human Health Risk Assessment - Hazard Quotient (HQ) and Hazard Index (HI)**

The potential health risks associated with exposure persistent organic pollutants (POPs) through water consumption and fish ingestion were assessed using the Hazard Quotient (HQ) and Hazard Index (HI) approach. The risk assessment of persistent organic pollutants (POPs) in Bonny River revealed distinct exposure concerns, reflecting both their chemical behaviors and sources within the aquatic system.

More worrying patterns were seen in the results for POPs. Brominated diphenyl ethers (BDE-47, BDE-99, BDE-209) were at lowest elevations in HQs in both water and fish (<0.25) but PCBs were prevalent in the overall risk (maximum). In water, HQ values for PCB-28 and PCB-153 exceeded the risk threshold of 1.0, with values of 1.96 and 1.03, respectively, and PCB-118 was close to the threshold, with an HQ of 0.67. The total HI for water-borne POPs was 3.92, highly higher than 1, thus validating that direct use of water from Bonny River entails high non-carcinogenic risk to local population.

Compared with the calculated risk of POPs in fish, their HQ values were relatively low (0.04 (BDE-47) to 0.27 (PCB-28), and total HI 0.61). Although this suggests no urgent human health risk at the assumed daily fish consumption level, the lipophilicity and bioaccumulation capacities of PCBs and BDEs point to potential long-term ecological consequences. Persistent organic pollutants (POPs) are also subject to biomagnification in aquatic food webs, resulting in increased tissue concentrations in fish, birds and mammals [20]. PCBs have been associated with immunotoxicity, endocrine disruption and reproductive impairment in aquatic organisms, leading to implications for fish recruitment and biodiversity of contaminated systems [21].

In summary, our findings, and indeed results from similar studies elsewhere in the world, provide a clear indication that POPs, particularly the PCB category of POPs, are the most immediate threat to human beings through exposure by water and moderate threats by fish consumption. Although indicative of the industrial activity, oil-related pollution and poor waste management practices affecting the river system, the presence of this contaminant highlights these concurrent threats.

#### **Bioaccumulation and Biota–Sediment Accumulation behavior of POPs in Bonny River**

The bioaccumulation results for PBDEs and PCBs in Bonny River show clear patterns of how these pollutants move through the aquatic environment and enter fish tissues. Among the PBDEs, BDE-47 and BDE-99 showed the highest levels of accumulation, with BAF values of 14.83 and 16.40. These high values indicate that both congeners are easily taken up by fish directly from the water. Their BSAF values (1.26 and 1.37) also show that they can accumulate from sediments, suggesting that both water and sediment act as active sources of exposure. This behaviour is typical of the lighter PBDEs, which are more mobile, more bioavailable, and more likely to accumulate in living organisms. In contrast, BDE-209 showed very low BAF (2.89) and extremely low BSAF (0.16), which means it does not easily transfer from sediment or water into fish. This is expected, as BDE-209 is a heavier, highly brominated compound that binds strongly to particles and sediments, making it less available for biological uptake.

For the PCBs, the accumulation was even stronger. PCB-153 recorded the highest values among all congeners, with a BAF of 20.42 and a BSAF of 2.13. This confirms its

strong tendency to build up in fish tissues over time, largely due to its stability, fat-solubility, and resistance to breakdown. PCB-118 and PCB-28 also showed high BAF values (14.26 and 13.58) and BSAF values above 1, which indicates that sediments are an important route of exposure for these compounds as well. These observations agree with studies in other parts of the Niger Delta, such as the Forcados River and Lagos Lagoon, where lighter PCBs consistently showed high bioaccumulation and strong sediment influence.

Overall, the POP results show a clear difference between lighter and heavier congeners. The lighter PBDEs and PCBs—such as BDE-47, BDE-99, PCB-28, PCB-118, and PCB-153—were found to accumulate strongly in fish, while heavier congeners like BDE-209 remained mostly in sediment. This pattern is important because the compounds that accumulate more easily are also those known to cause more serious toxic effects, including hormonal disruption, immune problems, and developmental issues.

## 5. Conclusion

Persistent organic pollutants (POPs) pose serious threats to human health and the environment; nevertheless, information on their environmental status and potential ecological risks is highly limited in Nigeria. These results confirmed that the Bonny River contains chemically stressed by persistent, bioaccumulative and human health hazard POPs. It could therefore cause harm to populations that rely on water and water products from the river over the long term. These findings highlight an urgent need for monitoring, regulation, and remediation to protect ecological health and human health.

### Recommendations

- a. Public awareness and community engagement: local populations should be made aware of the health risks of drinking polluted water and eating fish. Promote the use of alternative safer tools, like boiling or filtering the water and limiting the consumption of fish from the contaminated hotspots.
- b. Environmental and Human Health Protection: Aquatic biomonitoring should be included in national water-quality assessment programs. Health studies in human populations in Bonny River dependent communities should be mounted to assess exposure and potential adverse health effects via bioaccumulation of POPs.
- c. Remedial Action:- Cost-effective green cleaning technologies, especially plant-based green technologies like phytoremediation, contribution of biochar, and constructed wetlands, should be tested in order to promote the cleaning of the river system. Focusing on hot spot clean-up (e.g. by oil terminals, industrial outfalls) should be targeted.

### Contribution to knowledge

- a. Application of Pollution Indices to Organic Pollutants: The study applied contamination factor (CF) and pollution load index (PLI) — indices often used for heavy metals — to POPs in water, sediment, and *Clarias gariepinus*. This innovative approach provides a clearer interpretation of contamination levels and environmental health risks linked to organic pollutants.
- b. Bioaccumulation and Bioavailability Insights: By calculating Bioaccumulation Factors (BAF) and Biota-Sediment Accumulation Factors (BSAF), the study quantified how pollutants partition between environmental compartments. This highlights the bioaccumulative nature of the pollutants in fish, contributing to knowledge on trophic transfer and ecological risk.

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