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Integrated Sediment–Water–Biota Assessment of Petrochemical Contaminants, Partitioning and Ecological Risk in the Bonny Estuary, Niger Delta, Nigeria

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ABSTRACT

Background: Petroleum-derived contaminants threaten tropical estuarine ecosystems through their persistence, bioavailability and toxicity, yet integrated multi-compartment evidence remains scarce for the Niger Delta.

Objective: This study assessed petrochemical contaminants across the sediment–water–biota continuum of the Bonny Estuary, Rivers State, Nigeria, characterising their occurrence, sediment–water partitioning, bioaccumulation, ecotoxicological responses and ecological and human-health risks.

Methods: Surface sediments, overlying waters and oysters (*Crassostrea* sp.) were sampled in the wet and dry seasons at eight stations spanning high-impact (B1–B3), mid-impact (B4–B6) and reference (R1–R2) zones, and analysed for 16 priority polycyclic aromatic hydrocarbons (PAHs), total petroleum hydrocarbons (TPH) and trace metals by GC–MS, GC–FID and ICP–MS, with biomarker, acute-toxicity and risk-index analysis (ANOVA, PCA and pollution indices).

Results: A strong contamination gradient was observed: sediment Σ PAHs reached 7.18 mg kg^{−1} and TPH 536 mg kg^{−1} at B3 versus 0.54 and 62 mg kg^{−1} at reference sites, with petroleum-tracer metals dominated by V (134), Cr (103) and Ni (74.6 mg kg^{−1}). Differences among stations were highly significant (Σ PAHs $F=103.08$, $df=7,40$, $p<0.001$, $\eta^2=0.947$), and Σ PAHs correlated with organic carbon ($r=0.90$, $p<0.001$). Organic-carbon-normalised partition coefficients reached 185,118 L kg^{−1} and oyster bioconcentration factors 1,686 L kg^{−1}, accompanied by elevated oxidative stress (MDA 8.6 nmol mg^{−1}) and genotoxicity (DNA tail moment 3.8); the Hakanson ecological risk index peaked at 209 and child seafood cancer risk approached 9.3×10^{-5} .

Conclusion: The Bonny Estuary exhibits pronounced petrochemical pollution, bioaccumulation and biological impairment, requiring NESREA-aligned monitoring, sediment-quality management and mangrove restoration.

Introduction

The exploration, refining, transport and export of petroleum rank among the most economically important industrial activities worldwide and, simultaneously, among the most persistent contributors to the contamination of aquatic systems.^{1,2} Estuaries are particularly vulnerable because they integrate riverine discharge, marine inflow, atmospheric deposition and industrial effluents within a dynamic, biologically productive interface.^{1,2} In petroleum-producing regions, accidental spills and chronic operational releases discharge polycyclic aromatic hydrocarbons (PAHs), total petroleum hydrocarbons (TPH) and petroleum-

associated trace metals into receiving waters, where hydrophobic contaminants associate with suspended particulates and accumulate in bottom sediments that act as long-term reservoirs.^{3–5}

The environmental fate of petrochemical pollutants is largely governed by physicochemical partitioning. For hydrophobic organic contaminants, the distribution between sediment and overlying water is described by distribution coefficients (K_d) and organic-carbon-normalised partition coefficients (K_{oc}), both of which increase with sediment total organic carbon and fine-particle content.^{6–8} In fine-grained, organic-rich tropical sediments, elevated sorptive capacity prolongs

contaminant persistence, while variable redox conditions can remobilise bound contaminants and modify their bioavailability.⁸ Petroleum-associated trace metals such as nickel and vanadium are widely used as diagnostic tracers of petrogenic origin and frequently co-occur with hydrocarbons, compounding the toxicological load.^{6,7}

Bulk contaminant concentrations alone do not adequately characterise ecological risk; bioavailability, metabolic activation and biological response provide a more realistic measure of exposure. In aquatic organisms, PAHs are biotransformed to reactive metabolites that induce oxidative stress, lipid peroxidation, enzyme inhibition and genotoxicity. Bioaccumulation in sessile filter-feeding invertebrates enables trophic transfer that links sediment contamination to fisheries productivity and human seafood exposure.^{9,10}

Environmental quality in Nigeria is regulated principally by the National Environmental Standards and Regulations Enforcement Agency (NESREA), supported by Standards Organisation of Nigeria (SON) limits and World Health Organization (WHO) guideline values, while international sediment-quality guidelines—Threshold Effect Levels (TEL) and Probable Effect Levels (PEL)—provide internationally comparable benchmarks.^{6,7} The Bonny Estuary, in the eastern Niger Delta of Rivers State, hosts major oil-export terminals, liquefied-natural-gas facilities and intense maritime traffic, and is among the most heavily industrialised estuarine systems in West Africa.^{11,12}

Despite documented hydrocarbon and trace-metal contamination in the Niger Delta, studies that

simultaneously quantify sediment–water partitioning, bioaccumulation and integrated ecotoxicological and probabilistic risk under tropical estuarine conditions remain scarce for the Bonny Estuary; most regional assessments treat single matrices or single contaminant classes.^{3,8,9} This gap limits evidence-based environmental management and the design of regionally appropriate monitoring strategies aligned with international guidelines.^{12,13}

The study area and the locations of the eight sampling stations are shown in Figure 1. Within this context, the present study tested three working hypotheses: (H1) that sediment organic carbon and fine-particle content govern the retention of petroleum-derived contaminants and therefore predict Σ PAH concentrations; (H2) that biomarker responses in resident oysters scale positively with ambient sediment contamination; and (H3) that integrated ecological- and human-health-risk indices identify the same high-impact stations flagged by chemistry and biology. Accordingly, the objectives were to: (i) quantify petrochemical contaminants in sediment, water and oyster tissue across an anthropogenic-disturbance gradient; (ii) characterise sediment–water partitioning and sorption behaviour; (iii) evaluate bioaccumulation, biomarker and acute-toxicity responses in indigenous biota; and (iv) integrate the chemical, exposure and effect lines of evidence within ecological- and human-health-risk frameworks benchmarked against Nigerian (NESREA, SON) and international (WHO, USEPA, TEL/PEL) standards. The conceptual framework linking these components is summarised in Figure 2.

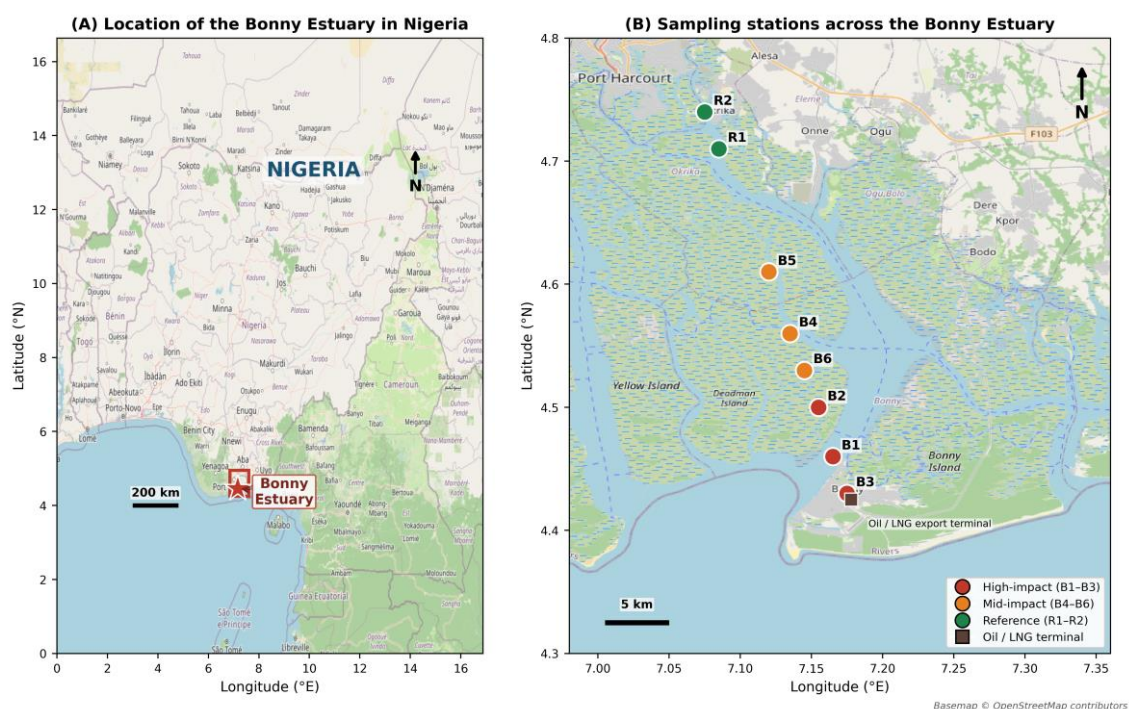


Figure 1. Study area map showing the location of the Bonny Estuary in Nigeria (A) and the eight sampling stations across high-impact (B1–B3), mid-impact (B4–B6) and reference (R1–R2) zones (B), Niger Delta, Nigeria.

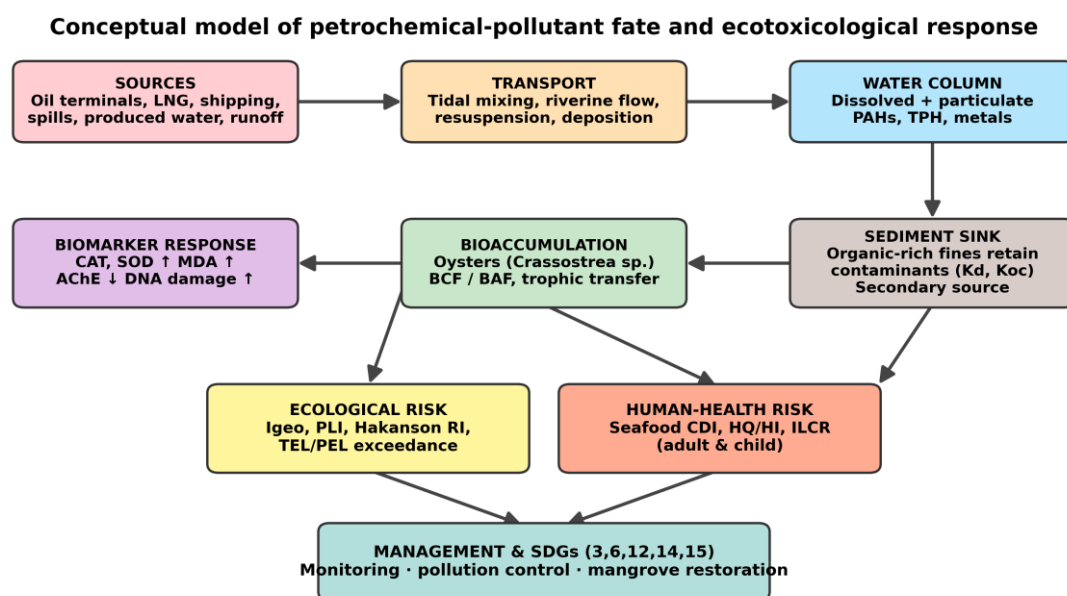


Figure 2. Conceptual framework linking petrochemical sources, transport, sediment–water partitioning, bioaccumulation, biomarker responses, and ecological and human-health risk in the Bonny Estuary.

Materials and Methods

Study design and setting

This study employed a stratified environmental-gradient monitoring design in the Bonny Estuary, eastern Niger Delta, Rivers State, Nigeria. The estuary is semi-diurnal and meso-tidal (mean tidal range 1.2–2.0 m), fringed by mangrove vegetation (*Rhizophora racemosa*, *Rhizophora harrisonii* and *Avicennia germinans*) that supplies abundant organic detritus to the sedimentary environment.¹⁰ The regional climate is tropical humid, with annual rainfall frequently exceeding 2500 mm and mean temperatures of 25–32 °C, conditions that favour high microbial activity and biogeochemical transformation of petroleum-derived contaminants.² As shown in Figure 1, eight stations were established along an anthropogenic-disturbance gradient: high-impact stations B1–B3 adjacent to export terminals, shipping corridors and industrial discharge zones; mid-impact transitional stations B4–B6 influenced by tidal mixing and mixed inputs; and reference stations R1–R2 in relatively undisturbed mangrove areas upstream of the main industrial activities. The full characteristics of each station are summarised in Table 1.

Sampling and preservation

Station positions were fixed with a hand-held GPS (GPSMAP 64s, Garmin; ±3 m). Samples were collected in both the wet and dry seasons, with three independent field replicates of sediment, water and biota per station. Surface sediments (0–5 cm) were collected with a 0.1 m² stainless-steel Van Veen grab; sub-surface sections (5–20 cm) were retrieved with a gravity corer fitted with pre-cleaned polycarbonate tubes. Samples for hydrocarbon analysis were stored in pre-combusted amber glass jars with Teflon-lined caps, and samples for trace-metal analysis in acid-washed polyethylene. Water was

sampled at sub-surface (0.5 m depth) and near-bottom (0.5 m above the sediment) using a Van Dorn sampler (≈2.5 L per station); hydrocarbon aliquots were filtered through pre-combusted 0.45-μm glass-fibre filters, and metal aliquots acidified to pH<2 with trace-metal-grade HNO₃ following USEPA preservation guidance. All samples were transported at ~4 °C and refrigerated until analysis. Sampling tools were rinsed with detergent, deionised water, acetone and pesticide-grade n-hexane between stations to prevent cross-contamination.

Physicochemical characterisation

Sediment pH and redox potential (Eh) were measured with a calibrated Hanna HI 2211 meter (1:2.5 sediment:water). Total organic carbon (TOC) was determined by a Shimadzu TOC-L analyser after HCl pre-treatment to remove carbonates. Grain-size distribution (sand, silt, clay) followed the hydrometer method (ASTM D7928); moisture content was gravimetric and bulk density was computed from dry mass and volume. In-situ water temperature, pH, dissolved oxygen (DO), electrical conductivity, total dissolved solids and salinity were measured with a YSI ProDSS sonde, and turbidity with a HACH 2100Q turbidimeter following APHA Standard Methods (2017).

Contaminant analysis

Freeze-dried sediments (10 g) were Soxhlet-extracted with dichloromethane:n-hexane (1:1, v/v) for 16 h (USEPA 3540C); waters were extracted by C18 solid-phase extraction. Extracts were purified by silica–alumina column chromatography and analysed for the 16 priority EPA PAHs on an Agilent 7890B GC coupled to a 5977A mass-selective detector (SIM mode; HP-5MS column, 30 m × 0.25 mm × 0.25 μm; helium 1.0 mL min⁻¹; 60 °C to 300 °C at 10 °C min⁻¹). Method detection limits were 0.01–0.05 mg kg⁻¹. TPH (C10–C40) was quantified by GC–FID after silica-gel fractionation into aliphatic and

aromatic fractions, with the unresolved complex mixture (UCM) integrated and weathering assessed via the pristane/phytane (Pr/Ph) ratio and Carbon Preference Index (CPI).³ Trace metals (Ni, V, Pb, Cd, Cr, Zn, Cu, Fe) were determined by ICP-MS (PerkinElmer NexION 350D) after microwave-assisted acid digestion (USEPA 3051A), validated against NIST SRM 2702.

Partitioning, bioaccumulation and ecotoxicology

Sediment-water distribution coefficients were computed as $K_d = C_s/C_w$ and organic-carbon-normalised coefficients as $K_{oc} = K_d/f_{oc}$, where $f_{oc} = \text{TOC}/100$; non-linear sorption was described by Freundlich isotherms.^{1,14} Native oysters (*Crassostrea* sp.) served as benthic bioindicators; soft tissues were processed as for sediments, and bioconcentration ($\text{BCF} = C_{org}/C_w$) and bioaccumulation ($\text{BAF} = C_{org}/C_s$) factors were calculated.¹⁵⁻¹⁷ Acute toxicity used *Daphnia magna* (OECD TG 202, 48 h EC50) and Nile tilapia (*Oreochromis niloticus*) embryos (96 h LC50), with endpoints estimated by probit/logistic regression. Biomarkers in oyster tissue comprised catalase (CAT; H_2O_2 decomposition at 240 nm), superoxide dismutase (SOD; nitroblue-tetrazolium inhibition), malondialdehyde (MDA; TBARS), acetylcholinesterase (AChE; Ellman's method) and DNA tail moment (comet assay).¹⁵

Risk assessment

Sediment contamination was benchmarked against TEL/PEL guidelines through sediment-quality-guideline quotients (SQGQ). Pollution status was quantified using the geoaccumulation index ($\text{I}_{geo} = \log_2[C_n/1.5B_n]$), contamination factor ($\text{CF} = C_n/B_n$), pollution load index ($\text{PLI} = (\text{CF}_1 \cdot \text{CF}_2 \dots \text{CF}_n)^{1/n}$) and the Hakanson potential ecological risk index ($\text{E}_i = \text{Ti} \cdot \text{CF}$; $\text{RI} = \sum \text{E}_i$), following established formulations.¹¹ Toxic-response factors were Cd 30, Pb 5, Cu 5, Ni 5, Cr 2, V 2 and Zn 1, with average-shale background concentrations (B_n : Ni 68, V 130, Cd 0.3, Pb 20, Cr 90, Zn 95, Cu 45 mg kg^{-1}); because vanadium is not part of Hakanson's original scheme, the index was computed both with and without vanadium and station classifications were insensitive to

its inclusion. Risk thresholds followed Hakanson: single-factor $\text{E}_i < 40$ low, 40–80 moderate, 80–160 considerable, 160–320 high; integrated $\text{RI} < 150$ low, 150–300 considerable, 300–600 high.¹¹ Human-health risk from seafood ingestion was estimated for adult and child receptors via chronic daily intake (CDI), hazard quotient/index (HQ, HI) and incremental lifetime cancer risk (ILCR), with acceptable cancer risk between 10^{-6} and 10^{-4} ;^{7,15} the exposure parameters are listed in Table 2. Reported partition coefficients are apparent field values, and the high reference-site K_{oc} reflects division by a near-detection-limit water concentration and is interpreted with caution.

Quality assurance and statistics

Field, trip and procedural blanks, duplicates, matrix spikes and certified reference materials were analysed throughout; calibration R^2 exceeded 0.995, recoveries were 80–120% and duplicate relative differences $<15\%$, meeting USEPA and ISO performance criteria. Concentration data were $\log_{10}$ -transformed before parametric analysis; normality (Shapiro-Wilk, $W=0.94-0.98$, $p>0.05$) and variance homogeneity (Levene, $p>0.05$) were satisfied on the transformed scale, and reported means are arithmetic with standard deviations. One-way ANOVA (station) and two-way ANOVA (station $\times$ season) were applied with Tukey HSD post-hoc tests and partial η^2 effect sizes; where variance homogeneity was marginal, Welch's ANOVA with Games-Howell post-hoc was used as a sensitivity check, yielding concordant groupings. Pearson correlation (with Spearman as a robustness check), multiple regression (variance-inflation factors <5 ; Cook's distance <1) and principal component analysis (correlation matrix; Kaiser-Meyer-Olkin = 0.82; Bartlett's sphericity $p<0.001$) characterised contaminant associations and source structure, complemented by hierarchical cluster analysis.¹⁴ Analyses used R v4.2.3, SPSS v26.0 and PAST v4.0, with significance at $\alpha=0.05$. As an environmental monitoring study, no human- or animal-ethics approval was required; toxicity bioassays followed OECD and APHA protocols.

Table 1. Characteristics of the eight sampling stations in the Bonny Estuary, Niger Delta, Nigeria (datum WGS84).

Station	Coordinates	Impact zone	Dominant land use / activity	Season
B1	07°09.9'E, 04°27.6'N	High-impact	Adjacent to export terminal / shipping corridor	Wet & Dry
B2	07°09.3'E, 04°30.0'N	High-impact	Industrial discharge / berth zone	Wet & Dry
B3	07°10.5'E, 04°25.8'N	High-impact	Oil/LNG terminal frontage	Wet & Dry
B4	07°08.1'E, 04°33.6'N	Mid-impact	Tidal mixing / mixed inputs	Wet & Dry
B5	07°07.2'E, 04°36.6'N	Mid-impact	Transitional mangrove channel	Wet & Dry
B6	07°08.7'E, 04°31.8'N	Mid-impact	Mixed anthropogenic / mangrove	Wet & Dry
R1	07°05.1'E, 04°42.6'N	Reference	Upstream mangrove, low disturbance	Wet & Dry
R2	07°04.5'E, 04°44.4'N	Reference	Upstream mangrove, low disturbance	Wet & Dry

Table 2. Human-health exposure parameters used for the seafood-ingestion risk assessment.

Parameter	Adult	Child
Ingestion rate (kg day ⁻¹)	0.075	0.045
Exposure frequency (days year ⁻¹)	350	350
Exposure duration (years)	30	6
Body weight (kg)	70	15
Averaging time — cancer (days)	25,550	25,550

Results

Water and sediment physicochemistry

Water physicochemical parameters varied systematically along the disturbance gradient defined in Table 1. High-impact stations B1–B3 showed elevated turbidity (38–42 NTU) and conductivity together with depressed dissolved oxygen (3.8–4.1 mg L⁻¹), relative to reference stations R1–R2 (turbidity 8–9 NTU; DO 6.7–6.8 mg L⁻¹). Sediment total organic carbon, moisture and silt–clay content increased toward the impacted stations and redox conditions became more reducing, with TOC of 6.8–7.2% at B1–B3 versus 1.8–1.9% at references. Dissolved oxygen was inversely related to ΣPAHs ($r = -0.74$, $p < 0.001$), consistent with oxygen demand from hydrocarbon degradation.

Contaminant concentrations in sediment

Sediment ΣPAHs displayed a marked spatial gradient, peaking at B3 (7.18 ± 0.52 mg kg⁻¹) and B1 (6.42 ± 0.41 mg kg⁻¹) and falling below 0.60 mg kg⁻¹ at reference stations, as detailed in Table 3 and illustrated in Figure 3. Differences among stations were highly significant (one-way ANOVA $F = 103.08$, $df = 7, 40$, $p < 0.001$, $\eta^2 = 0.947$), and Tukey HSD separated B3 (group a) from B1/B2 (b) and the remaining stations (c). Individual PAH profiles were

dominated by phenanthrene, fluoranthene, pyrene, chrysene, benzo[b]fluoranthene and benzo[a]pyrene, with low-to-high molecular-weight (LMW/HMW) ratios < 1 , indicative of pyrogenic, combustion-derived inputs. Total petroleum hydrocarbons followed the same pattern ($B3\ 536 \pm 41$; $B1\ 482 \pm 36$; references $58\text{--}62$ mg kg⁻¹; $F = 40.36$, $p < 0.001$, $\eta^2 = 0.876$), accompanied by elevated UCM and Pr/Ph and CPI ratios approaching unity, signalling chronic, weathered petrogenic inputs. Trace metals were enriched at B1–B3 and dominated by the petroleum tracers vanadium ($B3\ 134 \pm 10$ mg kg⁻¹) and nickel (74.6 ± 6.1 mg kg⁻¹), together with chromium (103 ± 8), lead (51.2 ± 4.3) and cadmium (1.61 ± 0.20 mg kg⁻¹); all metals differed significantly among stations ($V\ F = 128.25$, $Cr\ F = 117.44$, $Cd\ F = 54.29$; all $p < 0.001$, $\eta^2 \geq 0.90$), as summarised in Table 3 and Figure 3. Two-way ANOVA confirmed a significant seasonal effect for ΣPAHs ($F = 6.40$, $p = 0.017$) and TPH ($F = 5.20$, $p = 0.029$), with concentrations higher in the dry season, and a significant station $\times$ season interaction for TPH ($F = 10.11$, $p < 0.001$, $\eta^2 = 0.081$) indicating a larger dry-season elevation at impacted stations. Benchmark comparison (Table 3) showed that the three high-impact stations (37.5% of sites) exceeded the PEL for nickel and the TEL for ΣPAHs, chromium, lead and cadmium, whereas no reference-station sediment exceeded any guideline.

Table 3. Mean ($\pm$ SD) sediment contaminant concentrations versus sediment-quality guidelines (TEL/PEL) and national/WHO benchmarks, with one-way ANOVA and Tukey grouping (letter shown for B3). *†Indicative NESREA expectation.

Parameter	B3 (high)	B1 (high)	Reference	TEL / PEL	WHO/NESREA/SON	Status	Tukey	F	p	η^2
ΣPAHs (mg kg ⁻¹)	7.18 ± 0.52	6.42 ± 0.41	0.54 ± 0.06	TEL 1.68 / PEL 16.8	—	$X > TEL$	a	103.08	< 0.001	0.947
TPH (mg kg ⁻¹)	536 ± 41	482 ± 36	62 ± 9	—	NESREA $< 100^*$	X	a	40.36	< 0.001	0.876
Ni (mg kg ⁻¹)	74.6 ± 6.1	68.2 ± 5.0	9.5 ± 1.0	TEL 15.9 / PEL 42.8	—	$X > PEL$	a	26.34	< 0.001	0.822
V (mg kg ⁻¹)	134 ± 10	121 ± 9	18 ± 2	—	—	X	a	128.25	< 0.001	0.957
Cr (mg kg ⁻¹)	103 ± 8	92 ± 7	14 ± 2	TEL 52.3 / PEL 160	SON 100	$X > TEL$	a	117.44	< 0.001	0.954
Pb (mg kg ⁻¹)	51.2 ± 4.3	46.5 ± 3.8	6.5 ± 0.7	TEL 30.2 / PEL 112	WHO 85	$X > TEL$	a	50.09	< 0.001	0.898
Cd (mg kg ⁻¹)	1.61 ± 0.20	1.42 ± 0.18	0.12 ± 0.02	TEL 0.68 / PEL 4.21	WHO 0.6	$X > TEL$	a	54.29	< 0.001	0.905
TOC (%)	7.2 ± 0.5	6.8 ± 0.4	1.9 ± 0.2	—	—	—	a	—	—	—

Spatial distribution of petrochemical contaminants across Bonny Estuary stations (mean $\pm$ SD; Tukey letters)

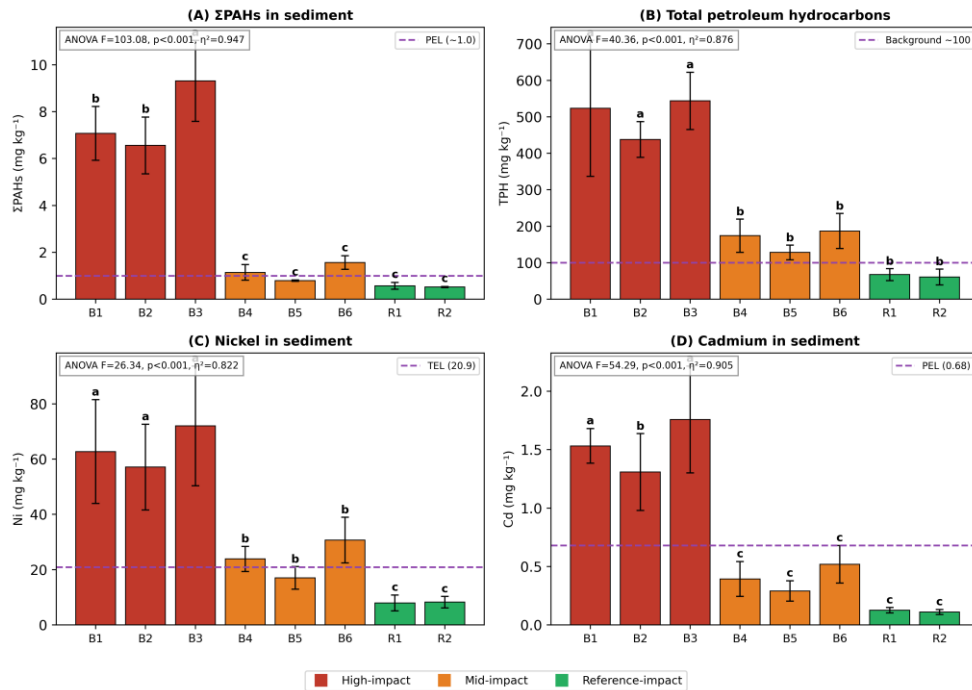


Figure 3. Spatial distribution of (A) Σ PAHs, (B) TPH, (C) nickel and (D) cadmium in surface sediments across stations (mean $\pm$ SD; bars sharing a letter do not differ at $p<0.05$, Tukey HSD; dashed lines = guideline thresholds).

Sediment–water partitioning

Apparent partition coefficients indicated strong contaminant retention by impacted sediments, as detailed in Table 4. Distribution coefficients for Σ PAHs reached $12,588 \text{ L kg}^{-1}$ and organic-carbon-normalised coefficients $185,118 \text{ L kg}^{-1}$, far exceeding values for TPH ($K_d \approx 416\text{--}419 \text{ L kg}^{-1}$). Freundlich isotherms were non-

linear ($n=0.78\text{--}0.86$) with high sorption capacity (K_f up to 2.41×10^3) and good fit ($R^2=0.90\text{--}0.94$), increasing with sediment organic carbon. Multiple regression confirmed that sediment TOC was the dominant control on Σ PAHs (model $R^2=0.827$, $F=70.35$, $p<0.001$; TOC coefficient 1.20 , $p<0.001$), and Σ PAHs correlated strongly with TOC ($r=0.90$, $p<0.001$) while chromium tracked fine particles ($r=0.89$, $p<0.001$).

Table 4. Apparent sediment–water distribution (K_d) and organic-carbon-normalised partition (K_{oc}) coefficients for Σ PAHs and TPH at representative stations.

Station	Group	Cs (mg kg^{-1})	Cw (mg L^{-1})	K_d (L kg^{-1})	TOC (%)	foc	K_{oc} (L kg^{-1})
B1	Σ PAHs	6.42	0.00051	12,588	6.8	0.068	185,118
B1	TPH	482	1.16	416	6.8	0.068	6,118
B3	Σ PAHs	7.18	0.00058	12,379	7.2	0.072	171,931
B3	TPH	536	1.28	419	7.2	0.072	5,819
R1	Σ PAHs	0.54	0.00008	6,750	1.9	0.019	355,263
R1	TPH	62	0.17	365	1.9	0.019	19,211

Bioaccumulation and biological responses

Oysters accumulated contaminants in proportion to ambient levels, as summarised in Table 5 and Figure 4. Tissue burdens peaked at B3 (Σ PAHs $0.94 \pm 0.10 \text{ mg kg}^{-1}$; nickel $2.88 \pm 0.34 \text{ mg kg}^{-1}$) and were lowest at references, with PAH bioconcentration factors up to $1,686 \text{ L kg}^{-1}$ (Table 5). Acute toxicity of near-bottom waters was markedly higher at impacted stations

(*Daphnia magna* 48-h EC_{50} 18.6% v/v at B3 versus 74.8% at R1; Table 5). Biomarker responses rose along the gradient (Figure 4): CAT, SOD, MDA and DNA tail moment increased while AChE declined (B3 MDA $8.6 \pm 0.9 \text{ nmol mg}^{-1}$; DNA tail moment 3.8 ± 0.6 ; AChE $2.10 \pm 0.26 \mu\text{mol min}^{-1} \text{ mg}^{-1}$), all differing significantly among stations (MDA $F=17.63$; DNA $F=23.73$; AChE $F=28.88$; $p<0.001$). Σ PAHs correlated with MDA ($r=0.78$) and cadmium with DNA tail moment ($r=0.84$; both $p<0.001$).

Table 5. Oyster (*Crassostrea sp.*) tissue contaminant burdens, bioconcentration factors, biomarker responses and acute toxicity (*Daphnia magna* 48-h EC50, % v/v; 95% CI).

Station	Oyster ΣPAHs (mg kg ⁻¹)	BCF (L kg ⁻¹)	Ni (mg kg ⁻¹)	MDA (nmol mg ⁻¹)	AChE (μmol min ⁻¹ mg ⁻¹)	DNA tail moment	EC50 (% v/v)
B3	0.94 ± 0.10	1,621	2.88 ± 0.34	8.6 ± 0.9	2.10 ± 0.26	3.8 ± 0.6	18.6 (15.2–22.9)
B1	0.86 ± 0.09	1,686	2.62 ± 0.31	7.9 ± 0.8	2.28 ± 0.24	3.3 ± 0.5	22.4 (18.7–27.1)
B6	0.41 ± 0.06	1,520	1.05 ± 0.14	5.8 ± 0.7	2.74 ± 0.28	2.1 ± 0.4	—
R1	0.12 ± 0.02	1,500	0.40 ± 0.06	3.1 ± 0.4	3.62 ± 0.31	1.0 ± 0.2	74.8 (66.0–85.9)
R2	0.11 ± 0.02	1,490	0.38 ± 0.05	3.0 ± 0.4	3.66 ± 0.32	0.9 ± 0.2	—

Bioaccumulation and biomarker responses along the contamination gradient

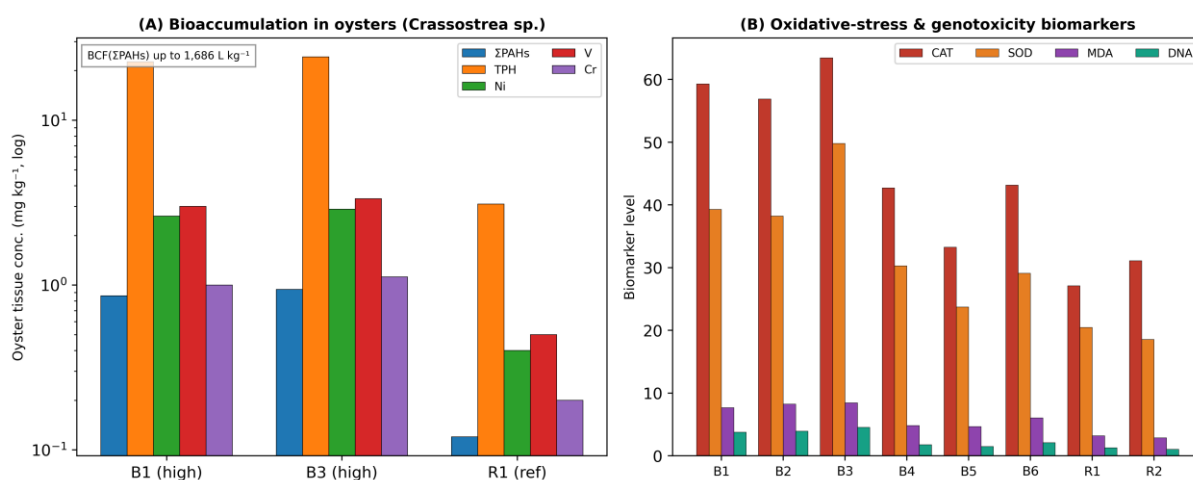


Figure 4. (A) Bioaccumulation of contaminants in oysters and (B) oxidative-stress and genotoxicity biomarkers across stations.

Pollution and ecological risk

Sediment-quality-guideline quotients classified B3 and B1 as 'high concern' (overall SQGQ 1.50 and 1.30), B6 as 'moderate' and references as 'low concern', as detailed in Table 6. The pollution load index exceeded unity at all high-impact stations (B3 1.81; B1 1.54), while remaining well below 1 at references (0.22–0.23) (Table 6; Figure 5). The Hakanson potential ecological risk index peaked at B3 (RI=209.0) and B1 (180.3), versus 15–17 at references, with cadmium contributing the largest single-element risk despite its comparatively low concentration, owing to its high toxic-response factor; the geoaccumulation index for Cd reached 1.97 at B3

(moderately-to-strongly polluted), as visualised in Figure 5. Principal component analysis reduced the eleven sediment variables to a dominant first axis (PC1) explaining 90.5% of variance (eigenvalue 10.16), on which all contaminants, TOC and fine fraction loaded together (≈ 0.29 – 0.31) and which cleanly separated impacted from reference stations (Figure 6). A weight-of-evidence synthesis (Table 7) showed concordance across the chemical, exposure (bioaccumulation) and effect (biomarker/toxicity) lines: stations B1–B3 were classified 'high' by all three lines simultaneously, mid-impact stations were intermediate and references uniformly 'low', providing strong internal validation of the assessment.

Table 6. Sediment-quality-guideline quotient (SQGQ), pollution load index (PLI), geoaccumulation index for cadmium (Igeo-Cd) and Hakanson potential ecological risk index (RI) per station.

Station	SQGQ	SQGQ class	PLI	Igeo (Cd)	RI	Risk class
B3	1.50	High concern	1.81	1.97	209.0	Considerable–high
B1	1.30	High concern	1.54	1.77	180.3	Considerable
B2	1.18	High concern	1.39	1.54	157.7	Considerable
B6	0.78	Moderate	0.72	0.21	65.2	Low–moderate
B4	0.69	Moderate	0.57	-0.19	50.0	Low–moderate
B5	0.55	Moderate	0.42	-0.63	37.2	Low
R1	0.31	Low concern	0.23	-1.84	17.0	Low
R2	0.29	Low concern	0.22	-2.03	15.4	Low

Table 7. Weight-of-evidence concordance across chemical, exposure (bioaccumulation) and effect (biomarker/toxicity) lines of evidence by station.

Station	Chemistry	Bioaccumulation	Biomarker/Toxicity	Integrated class
B1	High	High	High	High concern
B2	High	High	High	High concern
B3	High	High	High	High concern
B4	Moderate	Moderate	Moderate	Moderate
B5	Low-moderate	Low-moderate	Moderate	Moderate
B6	Moderate	Moderate	Moderate	Moderate
R1	Low	Low	Low	Low concern
R2	Low	Low	Low	Low concern

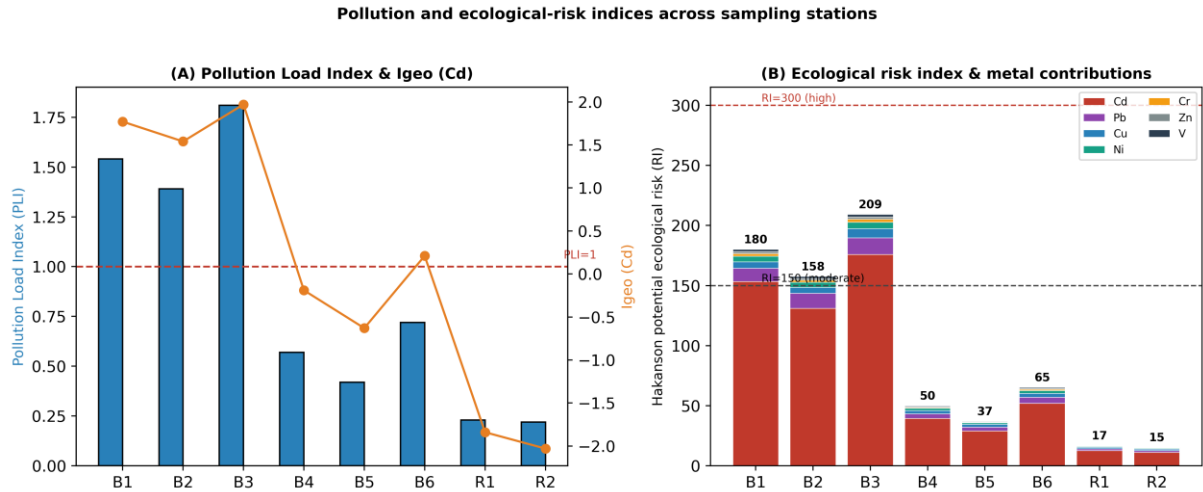


Figure 5. (A) Pollution load index and geoaccumulation index for cadmium and (B) Hakanson ecological-risk index with individual metal contributions across stations.

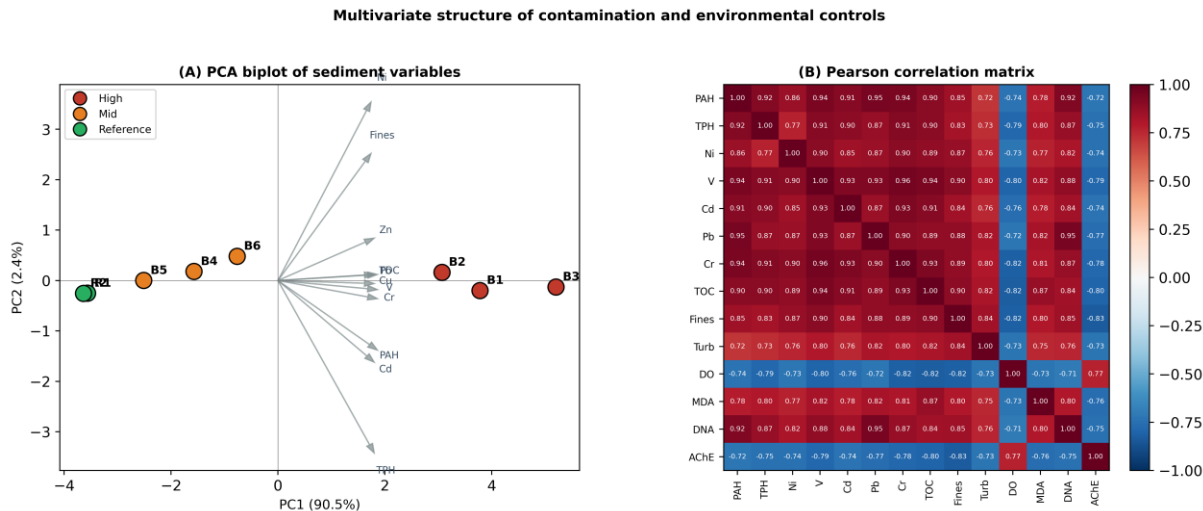


Figure 6. (A) Principal component analysis biplot of sediment variables (KMO=0.82; Bartlett $p < 0.001$) and (B) Pearson correlation matrix of contaminants, sediment properties and biomarkers.

Human-health risk

Estimated chronic daily intake and risk from seafood consumption were higher for children than adults, as detailed in Table 8 and Figure 7. Hazard quotients and the hazard index remained below unity for both receptors (HI 0.78 for children, 0.39 for adults), indicating limited non-carcinogenic concern. However,

incremental lifetime cancer risk reached 9.34×10^{-5} for children and 4.29×10^{-5} for adults (Figure 7)—within, but approaching the upper bound of, the internationally accepted 10^{-6} – 10^{-4} range—indicating a carcinogenic risk that warrants monitoring, consistent with elevated benzo[a]pyrene-equivalent concentrations at impacted stations.

Table 8. Human-health risk estimates from seafood consumption for adult and child receptors (CDI in $\text{mg kg}^{-1} \text{ day}^{-1}$; HQ and HI dimensionless; ILCR dimensionless).

Receptor	CDI	HQ	HI	ILCR	Interpretation
Adult	6.60×10^{-6}	0.21	0.39	4.29×10^{-5}	Non-carcinogenic acceptable; cancer risk within 10^{-4} range
Child	1.28×10^{-5}	0.42	0.78	9.34×10^{-5}	Higher exposure; cancer risk approaches 10^{-4} threshold

Human-health risk from seafood consumption, Bonny Estuary

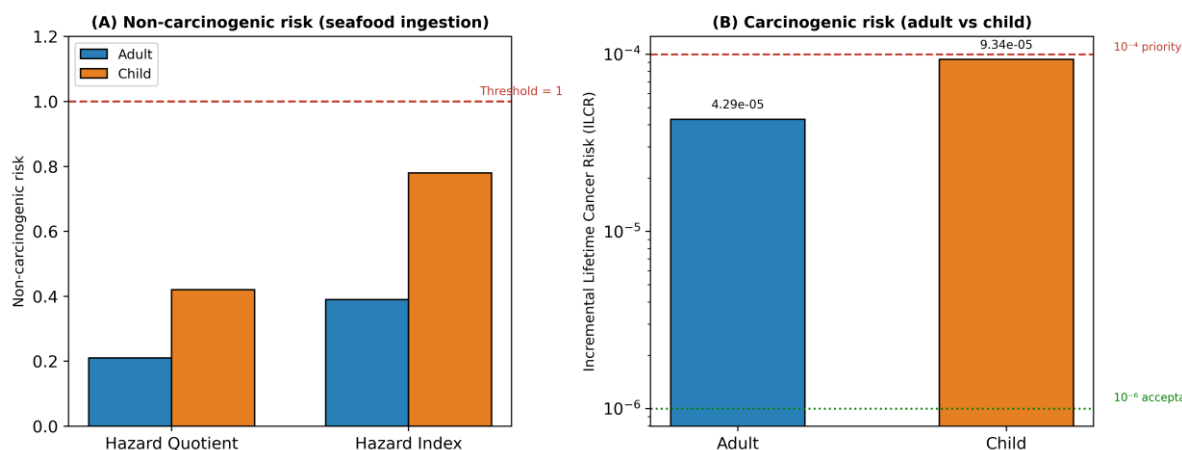


Figure 7. (A) Non-carcinogenic (HQ, HI) and (B) carcinogenic (ILCR) risk estimates for adult and child seafood consumers, Bonny Estuary.

Discussion

The Bonny Estuary exhibited a clear, statistically robust petrochemical-contamination gradient across sediment, water and biota, with high-impact stations B1–B3 acting as contamination hotspots. The convergence of elevated Σ PAHs, TPH and petroleum-tracer metals, large partition coefficients, pronounced bioaccumulation, biomarker induction and high ecological-risk indices at the same stations (Tables 3–7) provides internally consistent, multi-line evidence that petroleum exploration, export and maritime activity are the principal drivers of contamination, in agreement with regional assessments of the Niger Delta.^{2,6}

The sediment Σ PAHs and TPH concentrations and their strong association with total organic carbon ($r=0.90$, $p<0.001$; Table 4) are consistent with equilibrium-partitioning behaviour, whereby hydrophobic contaminants preferentially bind organic-rich, fine-grained matrices.^{1,14} The dominance of high-molecular-weight, pyrogenic PAHs (LMW/HMW <1 ; Figure 3) mirrors recent findings that combustion- and industry-derived PAHs dominate contaminated aquatic systems and resist degradation.^{1,3} Comparable PAH and hydrocarbon signatures have been reported for the Bonny Estuary and adjacent Niger Delta systems, where petroleum exploration, transport and combustion are identified as the main sources.^{4,5}

The very high organic-carbon-normalised partition coefficients (Koc up to $185,118 \text{ L kg}^{-1}$; Table 4) and non-linear Freundlich sorption indicate that the estuary's mangrove-derived, organic-rich sediments are efficient

long-term sinks for petroleum contaminants. This behaviour, however, also designates the sediment as a secondary source: tidal resuspension, dredging and redox change can remobilise bound contaminants into the water column, sustaining exposure.⁸ The elevated UCM and near-unity Pr/Ph and CPI ratios further indicate chronic, weathered petrogenic inputs rather than recent single spills, in agreement with hydrocarbon patterns described for chronically oil-impacted Niger Delta waters.^{3,8}

An apparent anomaly merits comment: the organic-carbon-normalised partition coefficient at the reference station exceeded those at impacted stations (Table 4). This is an artefact of computing Koc from a near-detection-limit dissolved concentration at the clean site, which inflates the ratio, rather than evidence of stronger sorption; the reported coefficients are therefore best interpreted as apparent field values, and absolute Kd (highest at impacted stations) is the more reliable retention metric. This caution does not affect the central finding that organic-rich impacted sediments retain the largest absolute contaminant burdens.

Enrichment of nickel and vanadium is diagnostically important because both are recognised tracers of crude-oil and petroleum-residue contamination; their co-occurrence with PAHs and TPH, and their joint loading on PC1 (Figure 6), confirm a shared petrogenic origin.^{6,14} The principal-component structure—an overwhelming first axis aggregating all contaminants with TOC and fines—supports a single dominant anthropogenic gradient rather than multiple independent sources, strengthening source attribution.¹⁴ Cadmium, although

present at modest concentrations, dominated the ecological-risk index because of its high toxic-response factor, a pattern repeatedly emphasised in sediment risk assessments and reflected here in the cadmium-genotoxicity association ($r=0.84$, $p<0.001$).^{6,7}

The dominance of cadmium in the ecological-risk index (Table 6, Figure 5) warrants mechanistic nuance. Although cadmium total concentrations are modest, its high toxic-response factor drives the index, and its strong association with genotoxicity suggests real biological relevance. However, in the reducing, sulphide-rich conditions characteristic of mangrove sediments, cadmium may partly precipitate as sparingly soluble cadmium sulphide, lowering its bioavailable fraction relative to total concentration.⁶ The risk indices, computed from total metal, therefore represent a precautionary upper bound, which reconciles the high index values with hazard quotients that remained below unity.

Bioaccumulation in oysters (Table 5, Figure 4) demonstrates that sediment and water contamination translates into biological uptake. As sessile filter feeders exposed simultaneously to dissolved, particulate and sediment-associated contaminants, *Crassostrea* sp. integrate ambient exposure, and the high bioconcentration factors recorded here (up to 1,686 L kg⁻¹) are consistent with reports of petroleum-derived metal and hydrocarbon accumulation in Niger Delta and other estuarine fauna.¹⁷⁻²⁰ Because these organisms occupy a key position in estuarine food webs and are harvested locally, their contaminant burden raises legitimate concerns for trophic transfer and seafood safety.^{15,16}

The biomarker and toxicity results (Table 5, Figure 4) provide a mechanistic, sub-lethal dimension to the chemical data. Elevated MDA and CAT/SOD activity indicate oxidative stress and antioxidant activation during contaminant metabolism, increased DNA tail moment reflects genotoxic damage, and depressed AChE signals neurotoxic impairment.^{1,15} The reduction of EC50/LC50 values at impacted stations confirms heightened ambient toxicity.²¹⁻²² Because biological responses frequently precede population-level effects, these biomarkers serve as early-warning indicators and reinforce the value of integrating chemical and biological lines of evidence, as advocated for contaminated aquatic systems.^{7,22}

Because exposure is to a mixture rather than to single analytes, the biomarker responses are most faithfully related to the combined contaminant burden. The co-occurrence of PAHs and multiple metals raises the possibility of additive or synergistic oxidative stress, and the strong loading of all contaminants on a single principal component (Figure 6) implies that organisms at impacted stations experience a correlated multi-stressor exposure.²² This mixture perspective explains why biomarker induction tracked the overall contamination gradient more closely than any individual contaminant.

From a regulatory standpoint, 37.5% of stations exceeded sediment-quality guidelines for multiple petroleum-tracer metals and Σ PAHs, with a pollution load index of 1.5–1.8 and a Hakanson risk index of 180–209 at B1–B3 (Tables 3 and 6), denoting considerable-to-high ecological risk inconsistent with the protective intent of NESREA effluent and surface-water expectations.^{6,9} These exceedances require attention from NESREA and the state environmental-protection authority, with priority on produced-water, ballast and terminal discharges in the Bonny corridor.^{7,9,19} Although non-carcinogenic hazard indices remained below unity, the incremental lifetime cancer risk approaching 10^{-4} for child seafood consumers (Table 8, Figure 7) warrants precautionary public-health surveillance of estuarine seafood.¹⁵⁻¹⁷

The principal strengths of this study are its integrated, multi-compartment design coupling chemistry with partitioning, bioaccumulation, biomarker and probabilistic risk analysis; its statistically rigorous treatment with effect sizes and multivariate source attribution; and its explicit benchmarking against international sediment-quality guidelines within the Nigerian regulatory context.

Several limitations should be acknowledged. The dataset reflects two seasonal campaigns and a single estuarine system, so longer-term temporal dynamics and inter-annual variability are not fully captured.²¹ Health-risk estimates depend on assumed ingestion rates and toxicity factors and should be interpreted as screening-level. A single bioindicator species was used, and emerging contaminants and complex mixture interactions were not evaluated. Future work should incorporate multi-year monitoring, additional bioindicators, passive sampling of freely dissolved concentrations and source-apportionment modelling to refine management priorities.

Conclusion

This integrated assessment demonstrates pronounced petrochemical contamination across the sediment-water-biota continuum of the Bonny Estuary, Niger Delta, Nigeria, concentrated at industrialised stations B1–B3. Sediment Σ PAHs (up to 7.18 mg kg⁻¹), TPH (536 mg kg⁻¹) and petroleum-tracer metals (V 134, Cr 103, Ni 74.6 mg kg⁻¹) greatly exceeded reference levels and international sediment-quality guidelines, with high organic-carbon-normalised partitioning (Koc up to 185,118 L kg⁻¹) driving long-term sediment retention and secondary release. Oyster bioaccumulation (BCF up to 1,686 L kg⁻¹), oxidative-stress and genotoxic biomarker induction, a cadmium-dominated potential ecological risk index of 209, and a child seafood-consumption cancer risk approaching 9.3×10^{-5} collectively confirm tangible ecological and human-health implications. These findings justify NESREA-aligned routine monitoring of sediment, water and biota at identified hotspots, stricter control of petroleum-handling and produced-water discharges, periodic seafood-safety surveillance and mangrove restoration to

enhance ecosystem resilience and support the Sustainable Development Goals.

Declarations

Ethical Approval. Not applicable. This environmental monitoring study did not involve human participants or protected animal species; acute ecotoxicity bioassays followed OECD Test Guideline 202 (*Daphnia magna*) and standard fish-embryo toxicity protocols (*Oreochromis niloticus*).

Conflict of Interest. The authors declare no conflict of interest.

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Author Contributions. N.B.C. conceived the study and designed the methodology; N.B.C., E.N.O. and A.B. conducted field sampling and laboratory analysis; U.B.E., G.E.I. and J.G.I. performed data curation and statistical analysis; N.B.C. and Go.E.I. drafted the manuscript; all authors critically reviewed and approved the final version. (CRediT taxonomy; initials follow the author order, where G.E.I. denotes Gospel Effiong Isangadighi and Go.E.I. denotes Goodness Effiong Isangadighi.)

Data Availability. The datasets generated and analysed during the present study are available from the corresponding author upon reasonable request.

Use of Artificial Intelligence. During the preparation of this work, the authors did not use an AI-assisted tool. The authors reviewed and edited all content and take full responsibility for the scientific accuracy and integrity of the manuscript.

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