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*Research Article*

# Polycyclic Aromatic Hydrocarbon Concentrations in Water, Sediments, and Biota (*Oreochromis niloticus* and *Penaeus monodon*) from the New Calabar River, Buguma, Niger Delta, Nigeria

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## ABSTRACT

The concentrations and distribution of the 16 USEPA priority polycyclic aromatic hydrocarbons (PAHs) were determined in surface water, bottom sediment, liver tissue of Nile tilapia (*Oreochromis niloticus*), and whole tissue of black tiger prawn (*Penaeus monodon*) collected from three locations (upstream, midstream, and downstream) along the New Calabar River at Buguma, Rivers State, Nigeria, over two sampling events. PAH analysis was performed by gas chromatography–mass spectrometry. Cancer risk was estimated using the benzo[a]pyrene toxic equivalency quotient (BaPTEQ) approach and the incremental lifetime cancer risk (ILCR) model, with an ingestion rate of 0.2 kg/day representative of a Niger Delta fishing community. The PAH profile across all matrices was dominated by low molecular weight compounds (2–3 rings), particularly phenanthrene, fluorene, anthracene, fluoranthene, and pyrene, indicating petrogenic contamination consistent with illegal artisanal refining activities in the area. Benzo[a]pyrene was not detected in any sample. Among the high molecular weight PAHs, benzo[a]anthracene was the most widely distributed, detected across all matrices in both sampling events, and consistently exceeded USEPA permissible limits. Benzo[a]anthracene contributed over 97% of the total BaPTEQ in edible tissues. ILCR values in Sampling 1 were below the $10^{-6}$ threshold for both fish liver ($1.46 \times 10^{-8}$) and prawn ($6.67 \times 10^{-9}$), indicating negligible cancer risk. In Sampling 2, however, ILCR values for fish liver ($1.41 \times 10^{-6}$) and prawn ($1.88 \times 10^{-6}$) exceeded the $10^{-6}$ threshold, indicating low but potentially significant cancer risk requiring monitoring. These findings demonstrate that dietary exposure to carcinogenic PAHs through consumption of fish and shellfish from this river presents a measurable health risk.

**Keywords**: *Polycyclic aromatic hydrocarbons; Benzo[a]anthracene; Oreochromis niloticus; Penaeus monodon; Niger Delta*

## INTRODUCTION

The Niger Delta region of Nigeria is one of the most ecologically diverse wetland systems in Africa, supporting an exceptionally rich assemblage of aquatic and terrestrial species. However, more than six decades of intensive petroleum exploitation, together with widespread illegal artisanal refining (locally known as "kpo fire"), pipeline vandalism, gas flaring, and the discharge of industrial and municipal effluents, have subjected the waterways of this region to severe and sustained environmental contamination (Lindén & Pålsson, 2013; Osuagwu & Olaifa, 2018). Among the many classes of pollutants released into Niger Delta aquatic ecosystems, polycyclic aromatic hydrocarbons (PAHs) are of particular concern owing to their toxicity, environmental persistence, and potential to cause cancer and other chronic health effects in exposed

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organisms, including humans (Rengarajan et al., 2015; Udom et al., 2023).

Polycyclic aromatic hydrocarbons are a class of organic compounds consisting of two or more fused aromatic (benzene) rings arranged in linear, angular, or clustered configurations. They are formed primarily through the incomplete combustion of organic matter (pyrogenic sources) and from the release of unburned petroleum products (petrogenic sources) (Abdel-Shafy & Mansour, 2016). The United States Environmental Protection Agency (USEPA) has designated 16 PAHs as "priority pollutants" based on their frequency of occurrence, toxicity, and potential for human exposure. These 16 priority PAHs are conventionally classified into two groups according to molecular weight: low molecular weight (LMW) PAHs, containing two to three aromatic rings (e.g. naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene), and high molecular weight (HMW) PAHs, containing four to six rings (e.g. fluoranthene, pyrene, chrysene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-c,d]pyrene, dibenz[a,h]anthracene, benzo[g,h,i]perylene) (Andersson & Achten, 2015). This classification has important environmental and toxicological implications: LMW PAHs are relatively more water-soluble and volatile, tend to predominate in the dissolved water phase, and are associated with acute toxicity; in contrast, HMW PAHs are more hydrophobic, partition preferentially onto particulate matter and into sediments, persist longer in the environment, and include most of the compounds classified by the International Agency for Research on Cancer (IARC) as known, probable, or possible human carcinogens — notably benzo[a]pyrene, benzo[a]anthracene, chrysene, and dibenz[a,h]anthracene (IARC, 2010; Rengarajan et al., 2015).

In aquatic environments, the fate and distribution of PAHs are governed by their physicochemical properties. Upon entering a water body, LMW PAHs tend to remain in the dissolved phase or volatilise from the water surface, whereas HMW PAHs adsorb readily onto suspended particulate matter and are eventually deposited in bottom sediments (Koyama et al., 2016). Consequently, sediments serve as the primary long-term reservoir — and potential secondary source — of PAH contamination in aquatic ecosystems (Ogbonna et al., 2019). Aquatic organisms, particularly bottom-dwelling and detritivorous species, are exposed to PAHs through direct contact with contaminated water and sediments, ingestion of contaminated food, and absorption across gill and integument surfaces. Although fish possess cytochrome P450-mediated mixed-function oxidase systems capable of metabolising PAHs, the metabolic intermediates produced — including reactive epoxides and diol-epoxides — can bind covalently to cellular macromolecules such as DNA, exerting mutagenic and carcinogenic effects (Marinković et al., 2013). Furthermore, PAHs can bioaccumulate in the tissues of aquatic organisms and biomagnify through the food chain, thereby posing a significant risk to human consumers of fish and shellfish from contaminated waters (Ekpo et al., 2012; Moslen et al., 2019; Nwaichi & Ntorgbo, 2016).

The New Calabar River is one of the major riverine systems in Rivers State, Nigeria. It traverses several industrial and densely populated areas, receiving inputs from petroleum refineries, artisanal refining operations, domestic wastewater, and agricultural runoff along its course (Basoene & Bameyi, 2020; Dienye & Woke, 2015; Edori et al., 2021). Previous studies have documented elevated total hydrocarbon and heavy metal concentrations in both the water column and sediments of this river system (Edori et al., 2021; Wokoma, 2014). Buguma, a large fishing town situated along the New Calabar River within the coordinates 4°44′N and 6°52′E, is the headquarters of Asari-Toru Local Government Area and a prominent centre for artisanal fishing. The livelihoods of the Buguma community depend heavily on fish and shellfish harvested from the river. Illegal oil bunkering and artisanal refining activities in and around Buguma are known to discharge petroleum-derived pollutants directly into the river, yet comprehensive data on the concentrations and distribution of specific PAH compounds across different environmental matrices (water, sediment, and biota) in this stretch of the river remain limited.

*Oreochromis niloticus* (Nile tilapia; family Cichlidae) is one of the most economically important freshwater fish species in the Niger Delta. It is a detritivorous and omnivorous species that feeds on organic debris, algae, and bottom-associated material, making it susceptible to accumulating contaminants present in sediments and the water column (El-Sayed & Fitzsimmons, 2023; Ugwumba & Ugwumba, 2007). *Penaeus monodon* (black tiger prawn; family Penaeidae) is one of the most widely consumed and commercially valuable crustacean species in the region. Prawns are benthic organisms that burrow into and feed on sediment-associated detritus, placing them in direct and prolonged contact with sediment-bound contaminants (Moslen et al., 2019). Both species are frequently consumed by communities along the New Calabar River and are therefore important sentinel organisms for assessing PAH exposure and the potential risk of dietary PAH intake by human consumers.

This study therefore aimed to (i) determine the concentrations and distribution of the 16 USEPA priority PAHs in water, sediments, the liver of *O. niloticus*, and the tissues of *P. monodon* collected from three locations (upstream, midstream, and downstream) along the New Calabar River at Buguma across two sampling periods; (ii) identify which individual PAHs exceeded USEPA permissible limits, with particular attention to the carcinogenic HMW PAHs; and (iii) evaluate the pattern of PAH contamination across the different environmental matrices to assess the extent of PAH pollution in this riverine ecosystem and its implications for aquatic organisms and human consumers.

## MATERIALS AND METHODS

### Study area

This study was conducted along the New Calabar River at Buguma (4°44′N, 6°52′E), the headquarters of Asari-Toru Local Government Area, Rivers State, Nigeria. Buguma is an island community surrounded by water and mangrove forest in the Niger Delta region. The climate is tropical, characterised by heavy rainfall and high relative humidity. The area receives pollutant inputs from illegal artisanal oil refining ("kpo fire") operations, domestic wastewater discharges, and surface runoff from surrounding communities.

### Sampling design and sample collection

Three sampling locations were established along the New Calabar River: downstream (4.734°N, 6.857°E), midstream (4.729°N, 6.863°E), and upstream (4.723°N, 6.872°E). The selection of sampling points was based on proximity to known anthropogenic activities (particularly illegal refining operations), the direction of surface water flow, and accessibility. Sampling was conducted two times during the rainy season, designated as Batch 1, and Batch 2.

**Table 1.** GPS Coordinates of the three Individual Sampling Stations Along the New Calabar River, Buguma (Distinct from the General Town-Level Coordinates given in the Introduction and Study Area).

| Location | Latitude (°N) | Longitude (°E) |
|---|---|---|
| Downstream | 4.734 | 6.857 |
| Midstream | 4.729 | 6.863 |
| Upstream | 4.723 | 6.872 |

At each sampling event, the following samples were collected from each of the three locations:

(a) Surface water. Surface water samples were collected in clean glass bottles by submerging the bottle below the water surface to minimise contamination by surface films. Bottles were sealed underwater to prevent air entrapment. Samples were labelled with waterproof ink indicating the location, date, and time of collection, placed on ice, and transported to the laboratory in Port Harcourt for analysis.

(b) Sediment. Bottom sediment samples were collected from each location using a grab sampler. Samples were placed in clean, labelled glass containers and kept on ice during transportation to the laboratory.

(c) Fish (*Oreochromis niloticus*). Specimens of Nile tilapia were obtained from local fishermen at each sampling event. Fish were stored on ice and transported to the laboratory, where they were dissected under sterile conditions. The liver was excised from each fish, as the liver is the primary organ for xenobiotic metabolism and PAH bioaccumulation, and was stored at −20°C until analysis.

(d) Prawn (*Penaeus monodon*). Black tiger prawn specimens were obtained from the same fishermen at each sampling event. Whole prawn samples were stored on ice, transported to the laboratory, and kept at −20°C until extraction and analysis.

### PAH extraction and clean-up

PAH extraction was carried out based on the method described by Kanchanamayoon and Tatrahun (Kanchanamayoon & Tatrahun, 2008), with modifications for each matrix, as follows:

*Fish liver*. The liver tissues were homogenised and 10 g of the homogenised sample was thoroughly mixed with anhydrous sodium sulphate ($Na_2SO_4$) to remove residual moisture. Twenty millilitres of n-hexane were added as the extraction solvent. The mixture was covered with aluminium foil to prevent evaporation and sonicated to facilitate separation of extracts. The supernatant was concentrated using a rotary evaporator. The concentrated extract was then purified using a chromatographic clean-up column packed at the base with 1 cm of glass wool, overlaid with 2 g of activated silica gel and a layer of anhydrous $Na_2SO_4$. The column was pre-eluted with 20 mL of n-hexane before the extract was loaded. The purified eluate was concentrated and collected in 2 mL glass vials for instrumental analysis.

*Water*. Water samples (100 mL) were transferred from refrigerated storage to a fume cupboard. Each sample was poured into a separatory funnel and extracted by liquid–liquid partitioning with 10 mL of n-hexane. After vigorous agitation and phase separation, the organic layer was passed through filter paper containing anhydrous $Na_2SO_4$ and silica gel to remove residual water and co-extractives. The filtered extract was collected in a 2 mL glass vial for analysis. The extraction procedure was performed for water samples from all three locations.

*Sediment*. Two grams of sediment sample was weighed into a clean 50 mL beaker and extracted with 10 mL of n-hexane. The mixture was thoroughly mixed and allowed to settle. The extract was filtered through a Buchner funnel fitted with filter paper containing anhydrous $Na_2SO_4$ and silica gel into a clean, solvent-rinsed container. The filtrate was concentrated to a final volume of 2 mL for analysis.

*Prawn*. Whole prawn tissue was macerated to obtain a homogeneous paste. Ten millilitres of n-hexane were added and carefully mixed with the sample. The mixture was filtered through a glass funnel fitted with filter paper containing anhydrous $Na_2SO_4$ and silica gel. The filtered extract was concentrated to a final volume of 2 mL for instrumental analysis.

### GC-MS analysis

The determination of PAHs in all sample matrices (water, sediment, fish liver, and prawn) was carried out following standard procedures (USEPA, 1986). Sample analysis was performed using gas chromatography coupled with mass spectrometry (GC-MS). The carrier gas was helium at a constant flow rate of 1.5 mL/min.

The inlet temperature was maintained at 280°C. An HP5-MS capillary column (Agilent Technologies; 15 m × 0.25 µm film thickness) was used for chromatographic separation. The oven temperature programme was as follows: initial temperature of 50°C held for 1 min, ramped

at 20°C/min to 325°C, and held for 2 min. The MS ion source temperature was maintained at 230°C, and the mass spectrometer was operated in selected ion monitoring (SIM) mode using the characteristic m/z values for each of the 16 USEPA priority PAHs. Identification of individual PAH compounds was based on comparison of retention times and mass spectra with those of certified reference standards. Concentrations were expressed in mg/L for water samples and mg/kg for sediment, fish liver, and prawn samples.

### Health risk assessment

The potential carcinogenic risk to humans from dietary exposure to PAHs through consumption of fish (*O. niloticus*) and prawn (*P. monodon*) from the New Calabar River was estimated using the toxic equivalency factor (TEF) approach and the incremental lifetime cancer risk (ILCR) model, following established guidelines (Nisbet & LaGoy, 1992; USEPA, 1993).

Benzo[a]pyrene toxic equivalent concentration (BaPTEQ). The carcinogenic potency of the PAH mixture detected in each biota sample was expressed as a benzo[a]pyrene toxic equivalent concentration (BaPTEQ) using the equation:

$BaPTEQ = \Sigma (C_i \times TEF_i)$

where $C_i$ is the concentration (mg/kg) of the individual PAH compound i in the tissue sample, and $TEF_i$ is the toxic equivalency factor for that compound relative to benzo[a]pyrene (BaP). The TEF values used were those proposed by Nisbet and LaGoy (1992), as follows: naphthalene (0.001), acenaphthylene (0.001), acenaphthene (0.001), fluorene (0.001), phenanthrene (0.001), anthracene (0.01), fluoranthene (0.001), pyrene (0.001), benzo[a]anthracene (0.1), chrysene (0.01), benzo[b]fluoranthene (0.1), benzo[k]fluoranthene (0.1), benzo[a]pyrene (1), indeno[1,2,3-c,d]pyrene (0.1), dibenz[a,h]anthracene (1), and benzo[g,h,i]perylene (0.01).

Estimated daily intake (EDI). The estimated daily intake of BaPTEQ through fish or prawn consumption was calculated as:

$EDI = (BaPTEQ \times IR) / BW$

where IR is the ingestion rate of fish or prawn (assumed to be 200g/day (0.2 kg/day for an adult in a fishing community (Ekweozor et al., 2017), and BW is the average adult body weight (assumed to be 70 kg).

Incremental lifetime cancer risk (ILCR). The incremental lifetime cancer risk associated with dietary PAH exposure was estimated using the equation:

$ILCR = EDI \times CSF \times ED \times EF / AT$

where CSF is the oral cancer slope factor for BaP (7.3 per mg/kg/day; Ukwo et al., 2023), ED is the exposure duration (assumed to be 70 years for lifetime exposure), EF is the exposure frequency (365 days/year), and AT is the averaging time (ED × 365 days).

The ILCR values were interpreted according to USEPA guidelines: values below $10^{-6}$ indicate negligible cancer risk; values between $10^{-6}$ and $10^{-4}$ indicate a low but potentially acceptable risk requiring monitoring; and values exceeding $10^{-4}$ (Ogidi et al., 2021) indicate a serious cancer risk requiring intervention.

## RESULTS

### PAH concentrations in water

The concentrations of the 16 USEPA priority PAHs in surface water samples from three locations along the New Calabar River at Buguma are presented in Tables 1 and 2. PAH detection patterns varied between locations and sampling events.

In Sampling 1 (Table 2), the downstream location had the highest number of detected PAHs, with 11 of the 16 priority compounds present in surface water: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo[a]anthracene, and benzo[k]fluoranthene. Individual PAH concentrations in downstream water ranged from 0.00033 mg/L (chrysene) to 0.00791 mg/L (acenaphthylene). In contrast, only chrysene (0.00034 mg/L) was detected at the midstream location, and no PAHs were detected at the upstream location. Two compounds exceeded their respective USEPA permissible limits: chrysene (0.00034 mg/L at midstream; limit: 0.0002 mg/L) and benzo[a]anthracene (0.00218 mg/L at downstream; limit: 0.0001 mg/L). Both are classified as probable human carcinogens (IARC Group 2B).

In Sampling 2 (Table 3), the spatial distribution of PAHs shifted. At the downstream location, only benzo[a]anthracene was detected (0.00075 mg/L), which exceeded the USEPA permissible limit of 0.0001 mg/L. At midstream, six PAHs were detected at concentrations ranging from 0.00031 mg/L (phenanthrene) to 0.00085 mg/L (anthracene). At upstream, five PAHs were detected, ranging from 0.00048 mg/L (fluoranthene) to 0.00064 mg/L (chrysene). Chrysene exceeded the USEPA permissible limit at both midstream (0.00054 mg/L) and upstream (0.00064 mg/L). Benzo[a]anthracene also exceeded the permissible limit at midstream (0.00034 mg/L).

Across both sampling events, the PAHs most frequently detected in water were low molecular weight (LMW) compounds (2–3 rings): phenanthrene, anthracene, fluoranthene, pyrene, fluorene, and acenaphthylene. The high molecular weight (HMW) carcinogenic PAHs — benzo[b]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, indeno[1,2,3-c,d]pyrene, and benzo[g,h,i]perylene — were not detected in any water sample. Benzo[k]fluoranthene was detected only in downstream water during Sampling 1 (0.00101 mg/L). The only HMW PAHs that exceeded USEPA permissible limits in water were chrysene and benzo[a]anthracene.

### PAH concentrations in sediment

PAH concentrations in bottom sediment are also presented in Tables 1 and 2.

In Sampling 1, most of the 16 priority PAHs were below detectable limits (BDL) in sediment across all three locations. Only pyrene (0.00044 mg/kg, midstream) and

benzo[a]anthracene were detected. Benzo[a]anthracene was present at all three locations: upstream (0.00044 mg/kg), midstream (0.00036 mg/kg), and downstream (0.00034 mg/kg), making it the most widely distributed PAH in Sampling 1 sediments.

In Sampling 2, a greater number of PAHs were detected in sediment. Six LMW PAHs — acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, and pyrene — were detected at low concentrations (0.00032–0.00207 mg/kg) across all three locations, along with benzo[a]anthracene (0.00049–0.00098 mg/kg). The highest individual sediment concentration was recorded for fluorene at the downstream location (0.00207 mg/kg). The HMW carcinogenic PAHs (benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-c,d]pyrene, dibenz[a,h] anthracene ,and benzo[g,h,i]perylene) were all BDL in sediment in both sampling events.

Overall, the sediment PAH profile was dominated by LMW compounds and benzo[a]anthracene. Concentrations were low (0.00032–0.00207 mg/kg). The midstream location tended to have slightly higher sediment PAH levels than the downstream or upstream locations.

**PAH concentrations in fish liver (*Oreochromis niloticus***

In Sampling 1, only two PAHs were detected in the liver of Nile tilapia: naphthalene (0.00032 mg/kg) and fluorene (0.00038 mg/kg). Both are LMW PAHs and both were within the USEPA permissible limits. No HMW or carcinogenic PAHs were detected.

In Sampling 2, three PAHs were detected in fish liver: fluorene (0.00093 mg/kg), phenanthrene (0.00078 mg/kg), and benzo[a]anthracene (0.00066 mg/kg). While fluorene and phenanthrene were within the permissible limits, benzo[a]anthracene exceeded the USEPA permissible limit of 0.0001 mg/L. This is noteworthy because benzo[a]anthracene is a probable human carcinogen, and its detection above the permissible limit in an edible tissue indicates that carcinogenic PAHs are entering the food chain.

Across both sampling events, the PAH profile in fish liver was dominated by LMW compounds. The number and concentrations of detected PAHs were higher in Sampling 2 than Sampling 1.

**PAH concentration in Prawn (*Penaeus monodon*)**

In Sampling 1, only phenanthrene was detected in prawn tissue (0.00032 mg/kg), and this was within the USEPA permissible limit. All other PAHs were BDL.

In Sampling 2, seven PAHs were detected in prawn tissue: acenaphthylene (0.00055 mg/kg), fluorene (0.00207 mg/kg), phenanthrene (0.00103 mg/kg), anthracene (0.00064 mg/kg), fluoranthene (0.00049 mg/kg), pyrene (0.00055 mg/kg), and benzo[a]anthracene (0.00079 mg/kg). Most were within the USEPA permissible limits. However, benzo[a]anthracene (0.00079 mg/kg) exceeded the USEPA limit of 0.0001 mg/L.

Prawn tissue showed a wider range of detectable PAHs than fish liver, particularly in Sampling 2. This is consistent with the benthic ecology of *P. monodon*, which maintains prolonged contact with contaminated sediment through burrowing and sediment-associated feeding. The presence of benzo[a]anthracene above the permissible limit in prawn tissue poses a potential dietary health risk for the Buguma community

**Table 2:** Concentrations of 16 USEPA Priority PAHs in Water, Sediment, Fish Liver, and Prawn from the New Calabar River at Buguma — Sampling 1

| PAH Compound | Rings | DS Water (mg/L) | MS Water (mg/L) | US Water (mg/L) | US Sed. (mg/kg) | MS Sed. (mg/kg) | DS Sed. (mg/kg) | Prawn (mg/kg) | Fish Liver (mg/kg) | USEPA Limit |
|---|---|---|---|---|---|---|---|---|---|---|
| Naphthalene | 2 | 0.00230 | BDL | BDL | BDL | BDL | BDL | BDL | 0.00032 | 0.040 |
| Acenaphthylene | 3 | 0.00791 | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 0.020 |
| Acenaphthene | 3 | 0.00035 | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 0.020 |
| Fluorene | 3 | 0.00405 | BDL | BDL | BDL | BDL | BDL | BDL | 0.00038 | 0.020 |
| Phenanthrene | 3 | 0.00436 | BDL | BDL | BDL | BDL | BDL | 0.00032 | BDL | 0.020 |
| Anthracene | 3 | 0.00058 | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 0.020 |
| Fluoranthene | 4 | 0.00505 | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 0.020 |
| Pyrene | 4 | 0.00469 | BDL | BDL | BDL | 0.00044 | BDL | BDL | BDL | 0.020 |
| Chrysene | 4 | 0.00033 | 0.00034 | BDL | BDL | BDL | BDL | BDL | BDL | 0.0002 |
| Benzo[a]anthracene | 4 | 0.00218 | BDL | BDL | 0.00044 | 0.00036 | 0.00034 | BDL | BDL | 0.0001 |
| Benzo[b]fluoranthene | 5 | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 0.0002 |
| Benzo[k]fluoranthene | 5 | 0.00101 | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 0.0002 |
| Benzo[a]pyrene | 5 | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 0.0002 |

| PAH Compound | Rings | DS Water (mg/L) | MS Water (mg/L) | US Water (mg/L) | US Sed. (mg/kg) | MS Sed. (mg/kg) | DS Sed. (mg/kg) | Prawn (mg/kg) | Fish Liver (mg/kg) | USEPA Limit |
|---|---|---|---|---|---|---|---|---|---|---|
| ***Table 2:*** *Continued* | | | | | | | | | | |
| Benzo[g,h,i]perylene | 6 | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | N/A |
| Dibenz[a,h]anthracene | 5 | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 0.0003 |
| Indeno[1,2,3-c,d]pyrene | 6 | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 0.0004 |

BDL = below detectable limit. Values exceeding USEPA permissible limits are highlighted. USEPA limits shown are for water (mg/L). DS – Downstream, MS – Midstream, US – Upstream, Sed - sediments as this is a water-quality criterion, its direct application to sediment and tissue concentrations (mg/kg) is indicative only; matrix-specific benchmarks (e.g., Sediment Quality Guidelines, food safety limits for seafood) were not evaluated in this study. The specific numerical instrument detection threshold underlying BDL designations could not be retrospectively determined (see Limitations).

**Table 3:** Concentrations of 16 USEPA Priority PAHs in Water, Sediment, Fish Liver, and Prawn from the New Calabar River at Buguma — Sampling 2

| PAH Compound | Rings | DS Water (mg/L) | MS Water (mg/L) | US Water (mg/L) | US Sed. (mg/kg) | MS Sed. (mg/kg) | DS Sed. (mg/kg) | Prawn (mg/kg) | Fish Liver (mg/kg) | USEPA Limit |
|---|---|---|---|---|---|---|---|---|---|---|
| Naphthalene | 2 | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 0.040 |
| Acenaphthylene | 3 | BDL | BDL | BDL | 0.00065 | 0.00032 | 0.00055 | 0.00055 | BDL | 0.020 |
| Acenaphthene | 3 | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 0.020 |
| Fluorene | 3 | BDL | BDL | BDL | 0.00170 | 0.00115 | 0.00207 | 0.00207 | 0.00093 | 0.020 |
| Phenanthrene | 3 | BDL | 0.00031 | 0.00056 | 0.00128 | 0.00095 | 0.00160 | 0.00103 | 0.00078 | 0.020 |
| Anthracene | 3 | BDL | 0.00085 | 0.00062 | 0.00036 | 0.00053 | 0.00071 | 0.00064 | BDL | 0.020 |
| Fluoranthene | 4 | BDL | 0.00069 | 0.00048 | 0.00045 | 0.00045 | 0.00048 | 0.00049 | BDL | 0.020 |
| Pyrene | 4 | BDL | 0.00067 | 0.00050 | BDL | 0.00053 | 0.00057 | 0.00055 | BDL | 0.020 |
| Chrysene | 4 | BDL | 0.00054 | 0.00064 | BDL | BDL | BDL | BDL | BDL | 0.0002 |
| Benzo[a]anthracene | 4 | 0.00075 | 0.00034 | BDL | 0.00049 | 0.00070 | 0.00098 | 0.00079 | 0.00066 | 0.0001 |
| Benzo[b]fluoranthene | 5 | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 0.0002 |
| Benzo[k]fluoranthene | 5 | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 0.0002 |
| Benzo[a]pyrene | 5 | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 0.0002 |
| Benzo[g,h,i]perylene | 6 | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | N/A |
| Dibenz[a,h]anthracene | 5 | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 0.0003 |
| Indeno[1,2,3-c,d]pyrene | 6 | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL | 0.0004 |

BDL = below detectable limit. Values exceeding USEPA permissible limits are highlighted. USEPA limits shown are for water (mg/L). DS – Downstream, MS – Midstream, US – Upstream, Sed - sediments As this is a water-quality criterion, its direct application to sediment and tissue concentrations (mg/kg) is indicative only; matrix-specific benchmarks (e.g., Sediment Quality Guidelines, food safety limits for seafood) were not evaluated in this study. The specific numerical instrument detection threshold underlying BDL designations could not be retrospectively determined (see Limitations).

**Health risk assessment**

The benzo[a]pyrene toxic equivalent concentration (BaPTEQ), estimated daily intake (EDI), and incremental lifetime cancer risk (ILCR) for dietary exposure to PAHs through consumption of *O. niloticus* liver and *P. monodon* tissue from the New Calabar River were calculated following the methodology described earlier and are presented in Table 4.

The TEF values applied (Nisbet & LaGoy, 1992) were: naphthalene (0.001), acenaphthylene (0.001), fluorene (0.001), phenanthrene (0.001), anthracene (0.01), fluoranthene (0.001), pyrene (0.001), and benzo[a]anthracene (0.1). BaPTEQ was calculated as $BaPTEQ = \Sigma(C_i \times TEF_i)$ using only detected compounds. The ingestion rate (IR) used was 0.2 kg/day (200 g/day), representing the estimated daily fish/shellfish consumption for an adult in a Niger Delta fishing community (Ekweozor et al., 2017). Body weight (BW) was 70 kg and the oral cancer slope factor (CSF) for benzo[a]pyrene was 7.3 $(mg/kg/day)^{-1}$ (Ukwo et al., 2023)

**Table 4:** Health Risk Assessment of PAH Exposure through Consumption of Fish and Prawn from the New Calabar River, Buguma

| Parameter | Fish Liver (Sampling 1) | Fish Liver (Sampling 2) | Prawn (Sampling 1) | Prawn (Sampling 2) |
|---|---|---|---|---|
| No. of PAHs detected | 2 | 3 | 1 | 7 |
| BaPTEQ (mg/kg) | $7.00 \times 10^{-7}$ | $6.77 \times 10^{-5}$ | $3.20 \times 10^{-7}$ | $9.01 \times 10^{-5}$ |
| EDI (mg/kg/day) | $2.00 \times 10^{-9}$ | $1.93 \times 10^{-7}$ | $9.14 \times 10^{-10}$ | $2.57 \times 10^{-7}$ |
| ILCR | $1.46 \times 10^{-8}$ | $1.41 \times 10^{-6}$ | $6.67 \times 10^{-9}$ | $1.88 \times 10^{-6}$ |
| Risk category | Negligible | Low risk* | Negligible | Low risk* |

IR = 0.2 kg/day (Ekweozor et al., 2017); BW = 70 kg; CSF = 7.3 (mg/kg/day) $^{-1}$ (Ukwo et al., 2023). TEF values from Nisbet and LaGoy (1992). *Low risk = ILCR between $10^{-6}$ and $10^{-4}$; requires monitoring (USEPA). Highlighted values exceed the $10^{-6}$ threshold.

The ILCR values for Sampling 1 were below the $10^{-6}$ threshold for both fish liver ($1.46 \times 10^{-8}$) and prawn ($6.67 \times 10^{-9}$), indicating negligible cancer risk. However, the ILCR values for Sampling 2 exceeded the $10^{-6}$ threshold for both fish liver ($1.41 \times 10^{-6}$) and prawn ($1.88 \times 10^{-6}$), placing them in the low but potentially significant risk category ($10^{-6}$ to $10^{-4}$) that warrants monitoring according to USEPA guidelines.

The elevated ILCR values in Sampling 2 were driven almost entirely by benzo[a]anthracene, which has a TEF of 0.1 — ten to one hundred times higher than the LMW PAHs. Benzo[a]anthracene contributed over 97% of the total BaPTEQ in both fish and prawn tissues during Sampling 2. The prawn ILCR was higher than the fish ILCR in Sampling 2, reflecting both the greater number of PAHs detected in prawn tissue and the slightly higher benzo[a]anthracene concentration.

It should be noted that these ILCR values may still underestimate true cancer risk for several reasons: (i) benzo[a]pyrene, the most potent carcinogenic PAH (TEF = 1.0), was not detected but may be present below the analytical detection limit — even trace amounts would substantially increase the BaPTEQ; (ii) the calculations are based on individual PAH concentrations in single tissues and do not account for cumulative exposure from consuming both fish and prawn, drinking contaminated water, and dermal contact; (iii) the ingestion rate of 0.2 kg/day, while appropriate for an adult in a fishing community, may underestimate consumption during certain seasons or for individuals who depend heavily on aquatic resources; and (iv) children and pregnant women, who are more vulnerable to carcinogenic effects, may have different exposure profiles.

## DISCUSSION

Across all matrices and both sampling events, the PAH profile at the New Calabar River, Buguma was dominated by low molecular weight (LMW) compounds with two to three aromatic rings, particularly phenanthrene, fluorene, anthracene, fluoranthene, and pyrene. The LMW/HMW ratio exceeded 1 in water, sediment, and biota, which is widely recognised as indicative of petrogenic contamination — that is, PAHs derived from unburned petroleum products rather than from high-temperature combustion (pyrogenic) processes (Jiao et al., 2015; Zhang et al., 2008). This finding is consistent with the known pollution sources in the study area: illegal artisanal refining ("kpo fire") and oil bunkering activities discharge crude oil and incompletely refined petroleum products directly into the waterway, releasing predominantly LMW PAHs into the aquatic environment. A similar LMW-dominated PAH profile was reported by Duke (2008) in sediments (1.1982 mg/kg) (Duke, 2008) and water (0.1169 mg/L) from Ekpan Creek, another petroleum-impacted waterway in the Niger Delta, and by Anyanwu et al. (2020) in surface sediments of the Bonny Estuary, where petrogenic PAHs dominated in surface layers (Anyanwu et al., 2020) .

Among the HMW PAHs, only chrysene, benzo[a]anthracene (B[a]A), and benzo[k]fluoranthene were detected, and only in specific matrices and sampling events. Notably, benzo[a]pyrene (BaP) — the most potent carcinogenic PAH and the reference compound for toxic equivalency calculations — was not detected in any sample across any matrix. The absence of BaP, together with the absence of other highly carcinogenic HMW PAHs (dibenz[a,h]anthracene, indeno[1,2,3-c,d]pyrene, benzo[g,h,i]perylene), further supports a petrogenic rather than pyrogenic source signature, since these compounds are characteristically generated during high-temperature incomplete combustion processes (Adeniji et al., 2019; Yunker et al., 2002). However, caution is warranted: BaP and other HMW PAHs may be present at concentrations below the analytical detection limits of the GC-MS method employed, particularly since the overall PAH concentrations in this study were in the low µg/L and µg/kg range. Furthermore, the "kpo fire" process does involve heating of crude oil, which could generate some pyrogenic PAHs; however, the temperatures involved are typically lower than those in industrial combustion, which may explain the limited detection of HMW compounds. Beyond detection-limit constraints, the complete non-detection of BaP may also reflect rapid environmental attenuation: BaP is highly susceptible to photodegradation under intense ultraviolet irradiation, and the shallow, turbid, well-mixed waters of tropical estuarine systems such as the New Calabar River provide conditions conducive to rapid photolytic and microbial breakdown of BaP relative to more photostable LMW and mid-weight PAHs (Adeniji et al., 2019; Yunker et al., 2002). Microbial biotransformation by estuarine sediment and water-column bacteria adapted to chronic hydrocarbon exposure may

further contribute to its depletion. These processes, rather than an absence of BaP input, may account for its non-detection despite the clear petrogenic signature of the site.

Benzo[a]anthracene was the most widely distributed HMW PAH in this study, detected in water, sediment, fish liver, and prawn tissue across both sampling events. Its concentrations consistently exceeded the USEPA permissible limits in all matrices where it was detected. This finding is significant because B[a]A is classified as a probable human carcinogen (IARC, 2010) and has a toxic equivalency factor (TEF) of 0.1 relative to BaP (Nisbet & LaGoy, 1992), making it ten to one hundred times more toxicologically potent than the LMW PAHs detected in this study (TEF = 0.001 to 0.01). B[a]A was also the dominant contributor to the cancer risk estimates presented in this study: it accounted for more than 97% of the total BaPTEQ in both fish liver and prawn tissue during Sampling 2. The widespread occurrence of B[a]A across all matrices suggests that this compound is being continuously released from the pollution sources and is partitioning into both aquatic and biological compartments. Its detection in the edible tissues of both *O. niloticus* and *P. monodon* above USEPA permissible limits confirms that carcinogenic PAHs are entering the food chain at this location. Asagbra et al. (2015) similarly identified B[a]A as a carcinogenic PAH of concern in biota from other Niger Delta water bodies (Asagbra et al., 2015). The present results indicate that B[a]A should be considered the priority compound for monitoring and management at this site.

The downstream location had the highest PAH concentrations and the greatest number of detected compounds in Sampling 1, consistent with its proximity to known illegal refining discharge points along the New Calabar River. This pattern is expected, as artisanal refining generates liquid effluents rich in petroleum-derived PAHs that enter the river directly at or near the downstream station (Lindén & Pålsson, 2013; Okafor & Opuene, 2007). In Sampling 2, however, the spatial pattern shifted: the midstream and upstream locations showed higher PAH levels in water, while the downstream location showed higher levels in sediment and prawn. This spatial variability may reflect temporal changes in the location or intensity of bunkering activities, tidal influence on contaminant transport, or differences in hydrodynamic conditions between sampling events. The New Calabar River at Buguma is tidally influenced, and reversal of flow direction can redistribute dissolved and particulate-bound PAHs upstream from their discharge points.

More PAHs were detected in Sampling 2 than in Sampling 1 across sediment, fish, and prawn matrices, suggesting either increased contamination inputs between the two sampling events or differing environmental conditions (e.g. rainfall, river flow, tidal state) that affected PAH solubility, partitioning, and bioavailability. Seasonal variation in PAH concentrations is well documented in tropical estuarine systems, where the onset of rainfall increases surface runoff from contaminated land, resuspends sediment-bound PAHs, and introduces fresh petroleum-derived inputs into the water column (Shilla & Routh, 2018).

The distribution of PAHs across environmental matrices in this study followed a pattern consistent with their physicochemical properties. In water, LMW PAHs predominated, reflecting their relatively higher aqueous solubility and lower tendency to adsorb to particulate matter (Koyama et al., 2016). In sediment, PAH concentrations were generally low (0.00032–0.00207 mg/kg), with both LMW compounds and B[a]A detected. The low sediment concentrations relative to water are somewhat unusual, as sediments typically serve as the primary reservoir for PAHs in aquatic systems (Ogbonna et al., 2019). This may reflect the sandy nature of the riverbed substrate at Buguma, which has lower organic carbon content and therefore lower sorptive capacity for hydrophobic organic compounds compared to fine-grained, organic-rich sediments.

The detection of PAHs in the liver of *O. niloticus* is consistent with the ecology and feeding behaviour of this species. As a detritivorous and omnivorous bottom-feeder, Nile tilapia is exposed to sediment-associated contaminants through ingestion of organic detritus (El-Sayed & Fitzsimmons, 2023; Ugwumba & Ugwumba, 2007). Fish possess cytochrome P450-mediated mixed-function oxidase (MFO) systems capable of metabolising PAHs, which typically results in lower tissue concentrations compared to invertebrates (Johnson-Restrepo et al., 2008). However, the metabolic intermediates produced during biotransformation including reactive epoxides and diol-epoxides — can bind covalently to cellular macromolecules such as DNA, exerting mutagenic and carcinogenic effects (Marinković et al., 2013).

The detection of B[a]A above the permissible limit in fish liver during Sampling 2 is therefore of concern, as it indicates that the metabolic capacity of the fish is not sufficient to eliminate this carcinogenic PAH to below-threshold concentrations.

Prawn tissue (*P. monodon*) showed a wider range of detectable PAHs than fish liver, particularly in Sampling 2 (seven PAHs versus three). This is consistent with the limited capacity of crustaceans to metabolise PAHs compared to fish. Crustaceans lack the well-developed MFO enzyme systems found in fish and consequently tend to bioaccumulate PAHs more readily (Neff, 2002). Furthermore, the benthic ecology of *P. monodon*, which involves burrowing into and feeding on sediment-associated material, places prawns in direct and prolonged contact with sediment-bound contaminants (Moslen et al., 2019). The higher B[a]A concentration in prawn (0.00079 mg/kg) compared to fish liver (0.00066 mg/kg) during Sampling 2 is consistent with this difference in metabolic capability and exposure route.

The incremental lifetime cancer risk (ILCR) assessment revealed a clear distinction between the two sampling events. In Sampling 1, the ILCR values for both fish liver ($1.46 \times 10^{-8}$) and prawn ($6.67 \times 10^{-9}$) were well below the $10^{-6}$ threshold, indicating negligible cancer risk. In Sampling 2, however, the ILCR values for fish liver ($1.41 \times 10^{-6}$) and prawn ($1.88 \times 10^{-6}$) exceeded the $10^{-6}$ threshold, placing them in the low but potentially significant risk category ($10^{-6}$ to $10^{-4}$) that

warrants monitoring and risk management according to USEPA guidelines (USEPA, 1993).

The approximately 100-fold increase in ILCR between Sampling 1 and Sampling 2 was driven almost entirely by the detection of B[a]A in edible tissues during the second sampling event. With a TEF of 0.1, even modest tissue concentrations of B[a]A produce BaPTEQ values that are orders of magnitude higher than those contributed by the LMW PAHs (TEF = 0.001–0.01). This underscores the disproportionate contribution of carcinogenic HMW PAHs to the overall cancer risk, even when they are present at low absolute concentrations.

The ILCR values obtained in this study are comparable to those reported in other Niger Delta seafood risk assessments. Saunders et al. (2022), using the same BaPTEQ approach and an identical ingestion rate of 0.2 kg/day, reported excess lifetime cancer risks of $1.3 \times 10^{-6}$ for tiger prawn and tilapia from Bodo, an oil-impacted mangrove ecosystem in the Niger Delta (Saunders et al., 2022). That study also found that the cancer risk fell within the $10^{-6}$ to $10^{-4}$ range, consistent with the present findings. The concordance between these independent studies, conducted at different locations within the Niger Delta, suggests that low-level but measurable cancer risk from dietary PAH exposure is a widespread phenomenon in fishing communities of the region.

Several factors suggest that the present ILCR estimates may underestimate the true cancer risk to the Buguma community. First, BaP, the most potent carcinogenic PAH (TEF = 1.0), was not detected in any tissue sample, but may be present below the analytical detection limit. Even trace concentrations of BaP would substantially increase the BaPTEQ and hence the ILCR. Second, the calculations are based on PAH concentrations in single tissues (fish liver or prawn) consumed individually, and do not account for the cumulative exposure arising from consuming both fish and prawn in a single meal, or from other exposure pathways such as ingestion of contaminated water, dermal contact during fishing and swimming, and inhalation of volatile PAHs. Third, the ingestion rate of 0.2 kg/day (Ekweozor et al., 2017), while appropriate for an average adult in a Niger Delta fishing community, may underestimate consumption during peak fishing seasons or for individuals who are highly dependent on aquatic protein. Fourth, children and pregnant women, who may be more vulnerable to the carcinogenic effects of PAHs, were not separately assessed in this study, and the USEPA ILCR model parameters used here are based on adult body weight and exposure duration.

The individual PAH concentrations detected in water, sediment, and biota in the present study were generally lower than those reported in heavily impacted Niger Delta sites. Anyanwu et al. (2020) recorded total PAH concentrations of 8,699–22,528 µg/kg in sediment cores from the Bonny Estuary (Anyanwu et al., 2020), while Ihunwo et al. (2021) reported ΣPAHs of 5,619–12,795 ng/g in sediment from Woji Creek, Port Harcourt (Ihunwo et al., 2021). In contrast, the sediment concentrations at Buguma ranged from BDL to only 0.00207 mg/kg (2.07 µg/kg), which is substantially lower. Similarly, the water concentrations in the present study (BDL–0.00791 mg/L) were lower than those reported from heavily industrialised waterways. This suggests that the Buguma stretch of the New Calabar River, while clearly receiving PAH inputs from illegal refining activities, is not as heavily contaminated as some other Niger Delta sites that are closer to major industrial oil operations or refineries. Nevertheless, the exceedance of USEPA permissible limits by B[a]A and chrysene, and the low but measurable cancer risk, indicate that the contamination is sufficient to warrant concern and continued monitoring.

In fish, the PAH concentrations detected in this study were lower than those reported by Adeyemo and Ubiogoro (2012), who found 0.09 mg/kg total PAHs in fish from the Egbokodo River (Adeyemo & Ubiogoro, 2012), and by Nwabueze et al. (2011), who recorded 0.098 mg/kg in periwinkles from the Ubeji area (Nwabueze et al., 2011). The relatively low tissue concentrations may reflect the generally lower environmental PAH levels at this site, as well as the metabolic capacity of *O. niloticus* to biotransform PAHs. However, it is worth noting that a single compound (B[a]A) at a low absolute concentration was sufficient to produce an ILCR above the $10^{-6}$ threshold due to its relatively high TEF.

## CONCLUSION

This study assessed the concentrations and distribution of the 16 USEPA priority PAHs in water, sediment, fish liver (*Oreochromis niloticus*), and prawn tissue (*Penaeus monodon*) from three locations along the New Calabar River at Buguma, Rivers State, Nigeria. The PAH profile across all matrices and both sampling events was dominated by low molecular weight compounds, consistent with petrogenic contamination from the illegal artisanal refining and oil bunkering activities that characterise the study area. Among the high molecular weight PAHs, benzo[a]anthracene was identified as the principal carcinogenic compound of concern: it was the most widely distributed HMW PAH across all matrices, consistently exceeded USEPA permissible limits, and contributed more than 97% of the total benzo[a]pyrene toxic equivalent concentration in edible tissues. Benzo[a]pyrene, the most potent carcinogenic PAH, was not detected in any sample.

The health risk assessment, based on the BaPTEQ-ILCR approach using a fish ingestion rate of 0.2 kg/day representative of Niger Delta fishing communities, indicated negligible cancer risk during Sampling 1 (ILCR < $10^{-6}$) but low and potentially significant cancer risk during Sampling 2 for both fish liver (ILCR = $1.41 \times 10^{-6}$) and prawn (ILCR = $1.88 \times 10^{-6}$). These values exceed the $10^{-6}$ threshold established by USEPA as the lower boundary of acceptable risk and are comparable to ILCR values reported for similar species at other oil-impacted sites in the Niger Delta.

Based on these findings, the following recommendations are made: (i) regular monitoring of PAH levels in water, sediment, and commercially harvested species from the New Calabar River at Buguma should be instituted, with particular attention to benzo[a]anthracene and other carcinogenic HMW PAHs; (ii) enforcement of existing regulations against

illegal artisanal refining and oil bunkering in the Buguma waterway should be strengthened, as these activities are the most likely source of the petrogenic PAH contamination documented in this study; and (iii) public health awareness programmes should be developed to inform the Buguma fishing community of the potential risks associated with long-term consumption of fish and shellfish from contaminated waters, particularly for vulnerable groups such as children and pregnant women.

## LIMITATION OF THE STUDY

This study has several limitations that should be considered when interpreting the findings. First, PAH concentrations in sediment and biological tissues (mg/kg) were compared against a USEPA water-quality criterion (mg/L) rather than matrix-specific benchmarks such as Sediment Quality Guidelines or food safety limits for seafood (e.g., EU Regulation 2023/915); these matrix-appropriate benchmarks were not incorporated into the original study design, and the exceedances reported for sediment and tissue matrices should therefore be interpreted as indicative rather than definitive regulatory exceedances.

Second, method detection limits, limits of quantification, surrogate recovery percentages, matrix spike recoveries, and certified reference material analyses were not retained from the original analytical work and cannot be retrospectively reconstructed; BDL values in this study should accordingly be interpreted with appropriate caution, as they may reflect either true absence or concentrations below the detection capability of the method used.

Third, fish liver was analysed because it is the principal organ of xenobiotic metabolism and detoxification in fish, and the first tissue in which absorbed PAHs are concentrated and biotransformed following uptake, making it a sensitive indicator of overall PAH exposure and bioaccumulation in the study organism. However, the human health risk assessment applied a muscle-based fish ingestion rate to these liver-derived PAH concentrations rather than to muscle tissue directly; as muscle samples were not collected in the original sampling design, the reported ILCR values for fish should be regarded as indicative, liver-based estimates of bioaccumulation-related exposure rather than a precise measure of dietary risk from muscle consumption.

Fourth, the risk assessment considered only adult exposure parameters (70 kg body weight); child-specific exposure data were not collected, and children in fishing communities may experience disproportionately higher weight-adjusted intake and greater developmental vulnerability than reflected in the adult-based estimates presented here.

As this study was conducted more than four years ago, the original raw data and laboratory records needed to address these gaps are no longer available. Future studies of this river system should incorporate matrix-specific regulatory benchmarks, full QA/QC reporting, muscle tissue analysis, and child exposure parameters to provide a more complete risk characterisation.

## CONFLICT OF INTEREST

The authors declare there is no conflict of interest regarding this manuscript.

## AUTHORS' CONTRIBUTIONS

Conceptualization, study design and methodology, MJ; sampling, practical work, and drafting initial manuscript, TI and PN; supervision, reviewing and editing of manuscript, MJ. All authors have read and agreed to the published version of the manuscript.

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