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Distribution and bioavailability of polycyclic aromatic hydrocarbons in oyster (*Saccostrea cucullate*) and periwinkle (*Littorina littorea*) from sediment in the Sombreiro River Estuary, Niger Delta, Nigeria

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ABSTRACT

In recent time, the ubiquitous, persistent and the toxicities characteristics of polycyclic aromatic hydrocarbons (PAHs) in estuarine ecosystems have generated serious concerns globally. In this study, the bioavailability and distribution of PAHs in sediments, oysters and periwinkles from the Sombreiro river estuary in the Niger Delta, Nigeria was investigated. The levels of the ∑16 PAHs in the sediment, oyster and periwinkle ranged from 495 to 12811 µg/kg, 200 to 32469 µg/kg and 2623 to 20293 µg/kg respectively. The results revealed that the sediments, oysters and periwinkles from the Sombreiro estuary were heavily contaminated with PAHs and the 3- and 4-rings being the dominant PAHs. Linear regression analysis showed that there was significant positive relationship between these matrices. Bioavailability assessment using BSAF indicated that the BSAF of ∑16 PAHs (mean BSAF = 2.38 for oyster and 3.81 for periwinkle) and that of individual PAHs except BkF, BaP, IndP and BghiP for oyster and BbF and BkF for periwinkles were > 1 and indicated that PAHs bioaccumulated in the oyster tissues. The 3- and 4- rings PAHs were more available to the oyster and periwinkle indicating greater risk of these PAHs. There was no correlation between BSAF and log K_{ow} which may be due to fresh and continuous inputs of PAHs and sampling period. The source apportionment of PAHs revealed that the PAHs were from both pyrogenic and petrogenic sources with significant contribution from pyrogenic inputs. The health risks assessed based on the actual PAHs concentrations and BSAF indicated that there was adverse non-carcinogenic risk from human exposure to the PAHs in the sediments but not from oysters and periwinkles. However, there were potential toxic, mutagenic and carcinogenic effects to humans exposed to PAHs in sediments, oysters and periwinkles from the Sombreiro estuary. In the overall, the health risk level in children were higher than the values reported for adults. The risks assessed based on actual PAHs concentrations were 34 to 389 times (for oyster) and 16 to 382 times (for periwinkle) higher than those based on BSAF. This implies that using the actual PAHs concentration in risk assessment will over overestimate the risk as most of the actual concentration is not bioavailable.

KEYWORDS: *PAHs, Sediment, Sombreiro estuary, Bioaccumulation, Niger Delta*

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) formed one of the vital group of organic contaminants in the environment. PAHs have two aromatic fused rings in diverse positioning with molecular weight ranging between 128 and 278 g/mol (Adeniji et al., **2019a**). PAHs get to the environment via biogenic, petrogenic, pyrogenic, and diagenic sources (Howard et al., 2021). Biogenic PAHs are those derived from living organisms; pyrogenic PAHs are derived from pyrolysis or incomplete incineration and burning processes; petrogenic PAHs are those from fossil fuels; and diagenic PAHs are those formed from conversion processes in sediments and soils. PAHs have been classified into low molecular weight (LMW) and high molecular weight PAHs subject to their molecular weight. The LMW-PAHs contains 2-3 rings and originates from petrogenic sources such as crude oil and can be employed as indicators to assessed oil spills and discharge into aquatic ecosystems while the HMW PAHs comprised 4-6 rings usually originates from pyrogenic sources (Emoyan et al., 2022; Tesim et al., 2021; Tesi et al., 2016). The HMW PAHs are quite immobile, have lower volatility, somewhat insoluble in water and vary lipophilic than the LMW PAHs (Adeniji et al., **2019a**). Some PAHs are endocrine disruptors, teratogenic, carcinogenic, mutagenic and genotoxic at concentrations above the maximum acceptable limit (Adeniji et al., 2019a; Iwegbue et al., 2021a; Iwegbue et al., 2021b; Adeniji et al., 2019b) while others that are not toxic very good useful synergists (Adekunle et al., 2017). As a result, PAHs have gained a lot of attention and 16 of them has been listed as priority pollutants in the United States Federal Water Pollution Control Act (1972) and the United States Clean Water Act (1997). Once formed, PAHs get to the aquatic ecosystems by atmospheric conveyance and deposition, runoff, waste water discharge etc (Hu et al., 2017).

Sediment is typically the final repository of PAHs and other pollutants in the marine ecosystem. PAHs in sediment is strongly influenced by sorption mechanisms between water and the sediment of which physicochemical characteristics play a key role (Semlali et al., 2012). In the marine ecosystem, both particle sedimentation and biota contribute to the incorporation of PAHs into the sediment. PAHs from the sediment and water column are assimilated by the biota. Water column and sediment PAH concentrations have a variety of toxicological impacts on aquatic creatures (Mirza et al., 2012). However, in relation to sediment PAHs concentrations, the bioavailable fraction is the only fraction of PAHs accumulated in biota and the most crucial in predicting harmful effects and risk assessment (Ruby et al., 2016; Ortega-Calvo et al., 2015).

When assessing PAHs bioavailability in the aquatic ecosystem bivalves including oysters and gastropod mollusk including periwinkles have been used (Gadelha et al., 2019; Thuy et al., 2018). PAHs have the potential to build up in lipid and/or fatty tissues and organs of filter feeding oysters and periwinkles because of their lipophilic character (Saunders et al., 2022; Ololade et al., 2021; Vaezzadeh et al., 2019; Loh et al., 2018; 13-17). Given their special traits, including their prevalence and dispersion, passive nature, resilience to a variety of environmental pollutants, extended life-span, slow rate of pollutants transformation etc, oysters and periwinkles are significant biomonitoring species (Ololade et al., 2021; Idowu et al., 2020; Vaezzadeh et al., 2019).

In view of risk assessment, the bioaccumulation of PAHs in oysters and periwinkles offers a more accurate indicator of pollution. The total PAHs levels in water or sediment may not give the exact risks (Thuy et al., 2018). The total PAHs levels in water could overestimate the risk because of the inherent regeneration characteristics of natural water bodies even though the PAHs' levels in the water signify the ultimate soluble, mobile and bioavailable amounts (Idowu et al., 2020; Maletic et al., 2019). Moreover, the total PAHs levels in sediment could overestimate the risk because sediment bound PAHs have the propensity to be less bioavailable (Ortega-Calvo et al., 2015). Thus, PAHs bioaccumulation in oysters and periwinkles is the best index of bioavailability. The purpose of this study is to evaluate the bioavailability of PAHs in Sombreiro River estuary in the Niger Delta, Nigeria using the oyster, *Saccostrea cucullata* and periwinkle *Littorina littorea* as biomonitor species.

MATERIALS AND METHODS

Description of study area

The Sombreiro estuary lies between longitude 06° 45' 0" E to 06° 50' 0" E and between latitude 04° 40' 0" N to 04° 45' 0" N (Figure 1). The Sombreiro estuary originates from the Niger River and is situated in the eastern part of the Orashi River. It flows towards the southernmost portion of the Niger Delta basin before emptying into the Atlantic Ocean. The total area of the estuary ranges from 117.2 to 132 km^2. The Sombreiro estuary's middle reach is brackish and looks murky when it rains. The white and red mangroves, *Ipomoea aquatica, Mimosa pigra, Nymphea lotus, Eichhornia natans*, and other plants make up the vegetation of the area. There are two seasons in the area: a wet season and a dry season. With an average annual rainfall of 2,000mm to 3,000mm, the wet or rainy season lasts from March through October. October through February are the dry months, with sporadic showers (Wokoma, and Njoku, 2017). The area is typically riverine and endowed with abundant oil and gas reserves (Figure 1). The area is largely occupied by rural populations that depend on the water for drinking, bathing, washing of clothes and fisheries (UNDP, 2006).

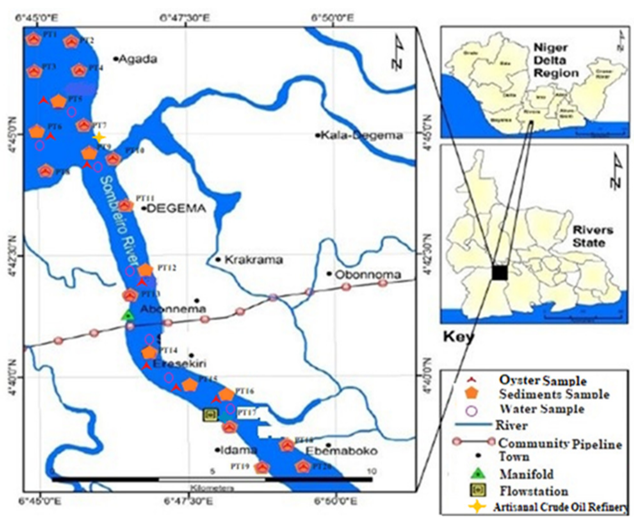


Figure 1: Map of study area.

Chemicals and reagents

All the solvents used were of HPLC grade standard. PAHs standards (99.4-99.9%) for the 16 priority PAHs, dichloromethane (DCM), anhydrous sodium sulphate and hexane were obtained from AccuStandard Company (USA).

Sample collection

Sixty (60) samples comprising sediment, oyster and periwinkle were obtained. Twenty (20) samples each of the three matrices were obtained along the Sombreiro river estuary. Grab sampling technique was used in the collection of sediment and were kept in aluminuim foil. Oyster (*Saccostrea cucullate*) and periwinkle samples were harvested from rocks and sediments around each sampling sites. The harvested oysters and periwinkles were covered in an aluminum foil. All samples were conveyed to the laboratory in ice pack. Sediments were freeze-dried, grounded and sieved using a 2mm sieve prior to analysis.

PAHs extraction and analysis

The sediments, oysters and periwinkles were extracted and analyzed for PAHs by the USEPA method 3550C as earlier described by Tesi *et al*. [4]. In summary, a mass of 10 g of the homogenized sediment / homogenized soft tissues of oysters and periwinkle was mixed with same amount of Na_2SO_4. The mixture was soxlet extracted with 50 mL of n-hexane/DCM (1:1 v/v) for 10 h. The collected extract was concentrated to 2 mL and cleaned in a column containing neutral silica gel, alumina and Na_2SO_4 respectively. The PAHs were subsequently washed down from the column with 50 mL of DCM/hexane mixture (1:3 v/v). The solution was reduced to about 2 mL and preserved in a vial until analysis.

The PAHs in the extract were determined by gas chromatograph with a mass spectrometry (Agilent 6890 N). The temperature at injection was 250 ◦C, temperature of detector was 290 ◦C and DB-17 column (30 m × 250 μm × 0.25 μm). A very pure helium gas (99.9%) was used as the carrier gas flowing steadily at 0.8 mL/ min. A 1 μL sample was injected into the instrument in splitless mode. Initial and final oven temperatures were 150 ◦C and 310 ◦C respectively while the selective ion mode (SIM) was adopted.

Quality control and statistical analyses

The efficiency of the extraction process was appraised by utilizing blanks and matrix spiked samples. A known standard of PAHs were introduced to a number of fresh portions of samples that have previously been analyzed and following all the analytical steps. The PAHs recovered from the spiked matrices ranged from 80–92%, 85–95% and 70-89% for sediments, oyster and periwinkle respectively. None of the PAHs compounds was observed in the blanks (n=3). With the use of an external calibration procedure, the PAH levels in the samples were measured. The levels of PAHs in samples were obtained with the aid of external calibrations. The r^2 of the calibration curves gotten from the plot of peak areas versus known concentrations of PAHs varied from 0.9992 to 0.9998. The ANOVA (analysis of variance) was utilized to ascertained significance in PAHs levels of the three matrices. Inter-relationship of PAHs between matrices was established by means of regression plots. Statistical analyses were done using SPSS version 23.

Bioavailability of PAHs

PAHs bioavailability in the aquatic ecosystem is usually evaluated by relating the concentrations of PAHs in biota to those in sediment (Idowu et al., 2020). This is expressed as biota-sediment accumulation factor (BSAF) which is the ratio of PAHs levels found in biota ($PAHs_{biota}$) to that in sediment ($PAHs_{sediment}$).

$$\text{BSAF} = \frac{PAHs_{biota}}{PAHs_{sediment}} \quad (1)$$

There is bioaccumulation when BSAF ≥1 (Cortazar et al., 2008; Baumard et al., 1999). When the sampling stations are much, the relative BSAF (RBSAF) becomes suitable in relating PAHs bioavailability to biota across the stations (Idowu et al., 2020).

$$\text{RBSAF} = \frac{BSAF}{\Sigma BSAF} \times 100 \quad (2)$$

Human risk assessment from PAHs in sediment, oyster and periwinkle

The health risks of PAHs in the sediment, oyster and periwinkles in this study were evaluated using the 95% upper class limit concentrations ($C_{UCL95\%}$) of the PAHs that gives the "reasonable maximum exposure" (Shi et al., 2005; Zhang et al., 2004) and have been used extensively by several researchers (Chen et al., 2004; Shaw et al., 2004; Ko et al., 2007; Iwegbue et al., 2020; Cao et al., 2010). The $C_{UCL95\%}$ was used because the results of PAHs in these matrices leaned and skewed toward non-normal distribution (Cao et al., 2010). The $C_{UCL95\%}$ was computed using the equation (5) (Chen et al., 2004; Shaw et al., 2004);

$$C_{UCL95\%} = \mathrm{X} + \left[Z_{\propto} + \frac{\beta}{6\sqrt{n}}\left(1 + 2 * Z_{\propto}^{2}\right)\right] * \frac{SD}{\sqrt{n}} \quad (3)$$

Where,

X = arithmetic mean; $Z_{\propto}$= $(1-\propto)^{th}$ quantile of a normal data = 1.645 for 95 % confidence limit, α = possibility of having Type 1 error, β = skewness, n = samples number, SD = standard deviation.

The potential risks of humans to PAHs in the three matrices was assessed using models adopted from the USEPA. These models have been used to assess the risks of PAHs in different matrices (Tesi et al., 2016; Iwegbue et al., 2020; Ossai et al., 2021; Iwegbue et al., 2018; Emoyan et al., 2020).

BaP Carcinogenic (BaP_{TEQ}) and mutagenic (BaP_{MEQ}) equivalencies

The BaP carcinogenic equivalent (BaP_{TEQ}) and mutagenic equivalent (BaP_{MEQ}) for the seven carcinogenic PAHs in the three matrices from the Sombreiro estuary was calculated with equations
(6) and (7) respectively (USEPA, 1993);

$$BaP_{TEQ} = \Sigma C_{UCL95\%} \times \text{TEF} \quad (4)$$

$$BaP_{MEQ} = \Sigma C_{UCL95\%} \times \text{MEF} \quad (5)$$

Where, TEF and MEF correspond to PAHs carcinogenic and mutagenic powers in relation to BaP respectively. The TEF values used are shown in Table SM1.

Non-carcinogenic and carcinogenic risk assessment from PAHs exposure

The non-cancer and cancer risks of PAHs in sediment were assessed in terms of HI and TCR respectively via dermal contact and ingestion pathways. However, exposure to PAHs from oyster and periwinkles was assessed via ingestion pathway only. The non-cancer and cancer risks were evaluated using the equations below (USEPA, 1989; USEPA, 2009). Tables SM1 and SM1 provide the detailed descriptions of variables employed to assess the risk to humans.

For non-cancer risk,

$$\text{Hazard index (HI)} = \sum HQ = HQ_{ing} + HQ_{dermal} \quad (6)$$

$$HQ_{Ing} = \left[\frac{C_{UCL95\%} \times \mathrm{IngR \times EF \times ED}}{\mathrm{BW \times AT}_{nc}} \times 10^{-6}\right] / \mathrm{RfD} \quad (7)$$

$$HQ_{dermal}\text{ (Sediment only)} = \left[\frac{C_{UCL95\%} \times SA \times AF \times ABS \times EF \times ED}{BW \times AT_{nc}} \times 10^{-6}\right] / RfD \quad (8)$$

For cancer risk,

$$\text{Total cancer risk (TCR)} = \sum TCR = ILCR_{ing} + ILCR_{dermal} \quad (9)$$

$$ILCR_{Ing} = \frac{C_{UCL95\%} \times IngR \times EF \times ED \times CF \times SFO}{BW \times ATca} \quad (10)$$

$$ILCR_{dermal}\text{ (Sediment only)} = \frac{C_{UCL95\%} \times SA \times AF \times ABS \times EF \times ED \times CF \times SFO \times GIABS}{BW \times ATca} \quad (14)$$

The health risks were assessed for the actual concentrations of PAHs obtained for sediments, oyster and periwinkles and the BSAF of oyster and periwinkles. Usually, HI value above 1 shows that there is potential non-cancer risk and total cancer risk of 1×10^{-6} suggest there is potential cancer risk (Edokpayi et al., 2016).

RESULT

Table 1 presents the summary statistics of PAHs concentrations in sediments, oysters, and periwinkles from the Sombreiro estuary. The total PAHs concentration was highest in periwinkles (Mean = 9092 µg/kg, Max = 20,293 µg/kg), followed by oysters (Mean = 8096 µg/kg, Max = 32,469 µg/kg) and sediments (Mean = 3732 µg/kg, Max = 12,811 µg/kg). As shown in (Table 1), naphthalene (Nap) exhibited the highest mean concentration in periwinkles (1323 µg/kg), compared to oysters (650 µg/kg) and sediments (507 µg/kg). Chrysene (Chry) recorded the highest concentration in periwinkles (Max = 13,688 µg/kg), with a mean of 2304 µg/kg, followed by oysters (Mean = 974 µg/kg) and sediments (Mean = 391 µg/kg). Table 1 also indicates that low molecular weight PAHs (LMW-PAHs) were most concentrated in periwinkles (Mean = 3894 µg/kg), followed by oysters (Mean = 3265 µg/kg) and sediments (Mean = 1648 µg/kg). High molecular weight PAHs (HMW-PAHs) followed a similar trend, with periwinkles showing the highest concentration (Mean = 5197 µg/kg), followed by oysters (Mean = 4830 µg/kg) and sediments (Mean = 2084 µg/kg).

Table 2 presents the PAHs concentrations in sediments, oysters, and periwinkles from the Sombreiro estuary alongside values reported in the literature for other aquatic environments worldwide. In sediments, PAHs concentrations in the Sombreiro Estuary ranged from 495 to 12,811 µg/kg, which is within the range reported for other Nigerian rivers, such as the Escravos River Basin (759–213,000 µg/kg) and the River Niger (2400–19,000 µg/kg). Internationally, PAHs levels in the Sombreiro Estuary sediments are comparable to those in the Weihe River, China (362–15,667 µg/kg) and the Pearl River, China (1434–10,811 µg/kg) but lower than those in the Haihe River, China (775–255,372 µg/kg) and Sydney Harbor, Australia (ND–460,336 µg/kg). For oysters, PAHs concentrations in the Sombreiro Estuary varied from ND to 32,469 µg/kg, which is higher than those reported in other locations, such as Gwangyang Bay, Korea (210–81,000 µg/kg) and the Pearl River Estuary, Guangdong (74–1164 µg/kg). The recorded PAHs levels in oysters from the Sombreiro Estuary exceed values reported in several global locations, including the Persian Gulf, Iran (126–226 µg/kg), and Can Gio Coastal Wetland, Vietnam (3.26–64.45 µg/kg). Periwinkles from the Sombreiro Estuary had PAHs concentrations ranging from 2623 to 20,293 µg/kg. This is lower than the levels reported for Ibeno River, Nigeria (27,490 µg/kg) but higher than those from other Nigerian water bodies, such as those studied by Udofia et al. (2021) (4910–6140 µg/kg). Compared to global studies, PAHs levels in periwinkles from the Sombreiro Estuary fall within the range of values reported in Nigeria but are significantly lower than those recorded in coastal areas of Nigeria by Ololade et al. (2011) (114,000–230,000 µg/kg).

Table 3 presents a comparison of Biota-Sediment Accumulation Factors (BSAF) obtained in this study with values reported in the literature. BSAF values for oysters in the Sombreiro Estuary ranged from 0.10 to 10.7, while periwinkles exhibited a higher range of 1.10 to 13.3. These values are comparable to those reported for periwinkles in the Ogbese River, Nigeria (0.23–27.2) by Ololade et al. (2021) but higher than those recorded in the mangrove ecosystem of Bodo, Nigeria (0.42–1.73) by Saunders et al. (2022). Compared to international studies, the BSAF values for oysters in the Sombreiro Estuary were within the range reported for the Mediterranean Sea, France (0.001–7.37) by Baumard et al. (1999) and higher than values from the Bay of Biscay, Spain (0.01–0.40) by Cortazar et al. (2008). However, the mean BSAF for oysters in an estuary in Australia was significantly higher (42.5) as reported by Idowu et al. (2020). For periwinkles, the BSAF values in the Sombreiro Estuary were higher than those observed in Malaysia's coastal waters for Perna viridis (0.40) by Shahbazi et al. (2009) and the intertidal mudflats for Anadara granosa (0.17–0.84) by Mirsadeghi et al. (2010). In comparison, the BSAF values for oysters and clams in USA Rivers (0.81–8.15) by Bender et al. (1988) were similar to those found in the present study.

Table 4 presents the source apportionment of PAHs in sediment, oyster, and periwinkle samples from the Sombreiro Estuary using diagnostic ratios. The LMW/HMW ratio indicates that most sediment, oyster, and periwinkle samples were primarily influenced by combustion sources, except for specific sampling points (PT4, PT5, PT6, PT7, PT8, PT14 for sediment; PT2, PT3, PT7, PT11, PT15 for oysters; and PT4, PT6, PT8, PT9, PT10, PT16, PT18 for periwinkles) which showed petrogenic input. The CPAHs/TPAHs ratio consistently suggested combustion as the dominant source across all sample types. The BaA/(BaA + Chry) ratio revealed petroleum sources at some locations (e.g., PT1, PT16 for sediments; PT10, PT11 for oysters; PT3, PT11, PT13, PT17, PT18, PT19, PT20 for periwinkles), while others exhibited petroleum combustion and coal/biomass combustion signatures. The IndP/(IndP + BghiP) ratio confirmed petroleum inputs at PT16 in sediments, whereas combustion processes (coal, wood, grass) were predominant in most other sites. Similarly, the Ant/(Ant + Phen) ratio indicated combustion processes as the primary PAH source across all samples. The Flt/(Flt + Pyr) ratio

Table 1: Summary statistics of PAHs concentrations in sediments, oysters and periwinkles from the Sombreiro estuary.

	SEDIMENTS					OYSTERS					PERIWINKLES				
	MEAN	**STDEV**	**MEDIAN**	**MIN**	**MAX**	**MEAN**	**STDEV**	**MEDIAN**	**MIN**	**MAX**	**MEAN**	**STDEV**	**MEDIAN**	**MIN**	**MAX**
Nap	507	796	35	ND	2569	650	1350	27	ND	5579	1323	2961	58	ND	9404
Acy	105	222	16	ND	896	358	617	37	ND	2435	786	1323	283	ND	4424
Ace	299	636	84	ND	2855	666	1058	193	ND	4146	497	761	72	ND	2368
Flu	378	471	107	ND	1461	375	762	10	ND	3234	279	567	0	ND	1734
Phen	277	351	118	9.0	1089	336	581	61	ND	2006	810	1205	235	ND	4777
Ant	82	87	42	ND	263	881	2060	47	ND	8739	239	327	25	ND	1194
Flt	225	358	96	ND	1588	824	1632	106	ND	6057	206	315	70	ND	1179
Pyr	303	262	254	24	987	876	1237	182	ND	4702	736	717	449	ND	2585
BaA	262	526	123	ND	2326	381	863	96	ND	3877	360	466	85	ND	1442
Chry	391	412	194	ND	1453	974	1717	128	ND	5727	2304	3084	1410	ND	13688
BbF	281	740	48	ND	3262	136	260	24	ND	897	32	47	0	ND	114
BkF	94	194	43	ND	873	97	201	11	ND	839	82	128	16	ND	507
BaP	139	237	23	ND	831	288	867	10	ND	3845	214	259	61	ND	875
DahA	121	165	41	ND	553	408	1727	0	ND	7537	333	587	0	ND	1985
IndP	117	186	13	ND	643	605	1703	0	ND	6105	356	802	0	ND	3191
BghiP	151	230	47	ND	897	276	1151	0	ND	5027	593	1178	0	ND	4466
Total	3732	3135	3157	495	12811	8096	8107	7848	200	32469	9092	5094	7852	2623	20293
2R	507	796	35	ND	2569	650	1350	27	ND	5579	1323	2961	58	ND	9404
3R	1141	1196	688	70	4145	2615	3593	1122	64	13567	2571	2649	2316	145	8074
4R	1181	1251	762	203	4941	3054	4660	1043	ND	17198	3588	3170	2744	131	14424
5R	635	850	349	ND	3397	909	2107	95	ND	8667	660	865	248	ND	2712
6R	268	333	161	ND	1047	868	1956	7	ND	6105	949	1706	ND	ND	5883
LMW	1648	1740	973	98	4802	3265	4475	1265	69	15271	3894	4412	2576	177	14221
HMW	2084	1825	1659	398	8338	4830	5319	2568	ND	17198	5197	3746	4598	2087	19132

Table 2: PAHs levels in matrices from the Sombreiro estuary with others in literatures.

River	**Concentrations (µg/kg)**	**References**
Sediment		
Sombreiro Estuary, Nigeria	495-12,811	This Study
Escravos River Basin, Nigeria	759-213,000	Iwegbue et al. (2021a)
River Niger, Nigeria	2400-19,000	Iwegbue et al. (2021b)
Ase River, Nigeria	2930-16,100	Iwegbue et al. (2021b)
Forcados River, Nigeria	1620-19,800	Iwegbue et al. (2021b)
Oturuba River, Nigeria	23461-89886	Howard et al. (2021)
Warri River at Ubeji, Nigeria	738-12147	Asagbra et al. (2015)
Ekpan creek of Warri River, Nigeria	5583-9327	Okoro et al. (2008)
Calabar River, Nigeria	1,670–20,100	Oyo-Ita et. (2013)
Buffalo River Estuary	1107–22,310	Adeniji et al. (2019b)
Mvudi and Nzhelele, South Africa	27100-55,930	Edokpayi et al. (2016)
Kaohsiung Harbor, Taiwan	4425-51,261	Dong et al. (2012)
Akaki River, Ethiopia	ND-3070	Mekonnen et al. (2015)
Haihe River, Tianjin, China	775–255,372	Jiang et al. (2007)
Sydney Harbor, Australia	ND–460,336	Birch et al. (2017)
Yamuna River, India	4500-23,600	Agarwal et al. (2006)
Weihe River, China	362-15667	Chen et al. (2015)

Athabasca River , Canada	10-34,700	Headley et al. (2001)
Malacca River, Malaysia	716-1,210	Keshavarzifard et al. (2014)
Prai River, Malaysia	1102-7,938	Keshavarzifard et al. (2014)
Pearl River, China	1434-10,811	Mai et al. (2002)
Bohai and Yellow River, China	52.3-1,871	Jiao et al. (2011)
Qinhuai River, Nanjing, China	796–10,470	Zhao et al. (2017)
Arc River, France	151–1,257	Kanzari et al. (2012)
Tuhai-Majia River, China	312–3,736	Liu et al. (2012)
Nilufer Creek, Bursa, Turkey	15.0–9,600	Karaca et al. (2014)
Yangtze River, Wuhan, China	72.4–3,995	Feng et al. (2007)
Rivers in Shanghai, China	107–1,707	Liu et al. (2008)
Malacca Strait, Malaysia	347–6,208	Keshavarzifard et al.(2017)
Djibouti-city coastal area, Djibouti	2.65–3,760	Ahmed et al. (2017)
Lagoons and estuaries, USA	7.6–6,766	Potapova et al. (2016

Table 2: Contd.

Oyster		
Sombreiro Estuary, Nigeria	ND-32469	This Study
Gwangyang Bay, Korea	210-4040	Loh et al. (2017)
Gwangyang Bay, Korea	627-81000	(Loh et al., 2017)
Pearl River Estuary, Guangdong	74–1164	Li et al. (2021)
Inter-tidal areas, Dar es Salaam, Tanzania	174-647	Gaspare et al. (2009)
Pearl River Estuary, Guangdong	20–1849	Hong et al. (2000)
Pearl River Estuary, Guangdong	306–1041	Wei et al. (2006)
Persian Gulf, Iran	126-226	Mirza et al. (2012)
Mangrove of Guadeloupe	66.0-961	Ramdine et al. (2012)
Inter-tidal area of the west coast, Korea	21.0-141	Choi et al. (2017)
Can Gio Coastal Wetland, Vietnam	3.26 – 64.45	Pham et al. (2020)
Estuaries from the coast of South Carolina	15.0-1968	Sanders et al.(1995)
Todos os Santos Bay, Brazil	1.55-37.8	Martins et al. (2019)
Yatsushiro Sea, Japan	6.5 - 350	Nakata et al. (2014)
Eastern Guangdong coast	231–1178	Yu et al.(2016)
Hong Kong coast area	39–2072	Liu et al. (2005)
Beibu Gulf, Guangxi	117–403	Ma et al. (2017)
Qingdao coastal area, Shandong	30–177	Jin et al. (2014)
Periwinkle		
Sombreiro Estuary, Nigeria	2623-20293	This study
Rivers in Niger Delta, Nigeria	4910-6140	Udofia et al. (2021)
Coastal waters, Nigeria	ND-22.4	Nwaichi and Ntorgbo (2016)
Rivers in Nigeria	7730	Ezomoh et al. (2022)
Ibeno River, Nigeria	27490	Onojake et al. (2020)
Coastal areas, Nigeria	1.564±0.017	Dokubo and Igwe (2019)
Coastal areas, Nigeria	114,000-230,000	Ololade et al. (2011)

Table 3: Comparison of BSAF obtained in this study with others in literature.

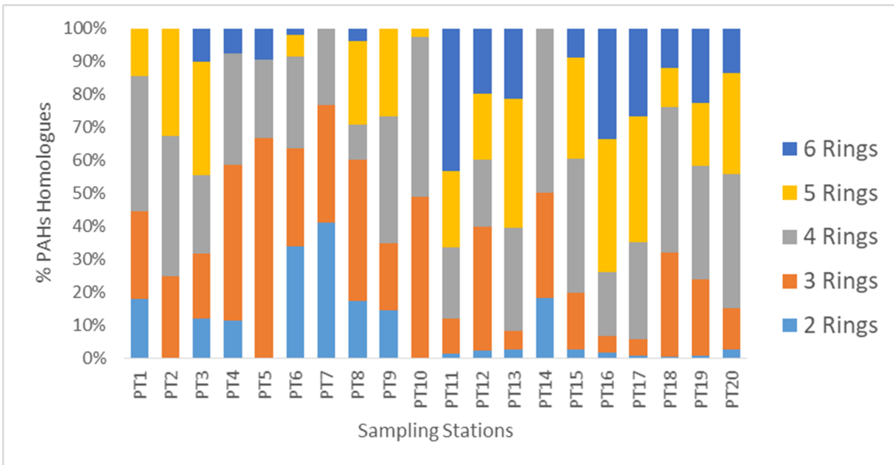
Location	Marine organism	No. of PAHs	BSAF	References
Sombreiro Estuary, Niger Delta, Nigeria	Oyster	16	0.10-10.7	This study
Sombreiro Estuary, Niger Delta, Nigeria	Periwinkle	16	1.10-13.3	This study
Mangrove ecosystem, Bodo, Nigeria	Periwinkle	12	0.42-1.73	Saunders et al. (2022)
Ogbese, River, Nigeria	Periwinkle	16	0.23-27.2	Ololade et al. (2021)
Estuary, Australia	Oyster (*Saccostrea glomerata*)	13	42.5*	Idowu et al. (2020)
Mangrove west coast of peninsular Malaysia	Oyster (*Crassostrea belcheri*)	16	0.45-2.48	Vaezzadeh et al. (2017)
Coastal water, Malaysia	Clam (*Paphia undulata*)	16	0.27-0.84	Keshavarzifard et al. (2017)
Intertidal mudflats, Malaysia	*Anadara granosa*	19	0.17-0.84	Mirsadeghi et al. (2010)
Coastal water, Malaysia	*Perna viridis*	18	0.40	Shahbazi et al. (2009)
Bay of Biscay, Spain	Oyster	16	0.01-0.40	Cortazar et al. (2008)
River, Italy	Benthic amphipod	17	0.01-1.00	Viganoa et al. (2007)
Bay, Texas, USA	Oyster	20	0.05-0.24	Qian et al. (2001)
Mediterranean Sea, France	*Mytilus sp.*	16	0.001-7.37	Baumard et al. (1999)
Baltic Sea, France	*Mytilus sp.*	16	0.01-0.34	Baumard et al. (1999)
Times Beach, USA	*Dreissena polymorpha*	16	5.60-10.4	Roper et al. (1997)
Rivers, USA	Oysters, Clams	14	0.81-8.15	Bender et al. (1988)

*Mean value

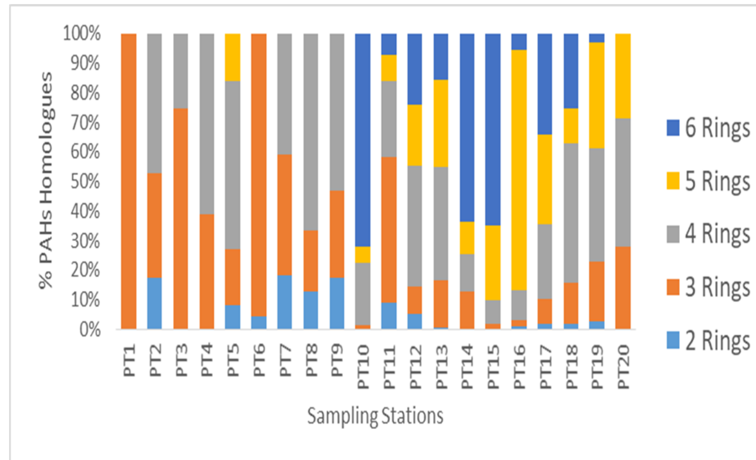
Table 4: Source apportionment of PAHs in sediment, oyster and periwinkle from the Sombreiro estuary

Diagnostic Ratio	Range	Sources	Sediments	Oysters	Periwinkles
LMW/HMW	< 1.0	Combustion of fossil fuels or wood	All samples except PT4, 5, 6, 7, 8, 14	All samples except PT2, 3, 7, 11, 15	All samples except PT4, 6, 8, 9, 10, 16, 18
	> 1.0	Petrogenic sources	PT4, 5, 6, 7, 8, 14	PT2, 3, 7, 11, 15	PT4, 6, 8, 9, 10, 16, 18
CPAHs/TPAHs	< 1.0	Combustion processes	All samples	All samples	All samples
	> 1.0	Petrogenic sources	-	-	-
BaA/(BaA + Chry)	< 0.2	Petroleum	PT1, 16	PT10, 11	PT3, 11, 13, 17, 18, 19, 20
	0.2-0.35	Petroleum combustion	PT11, 12, 14, 17, 19	PT5, 7,	PT2, 5, 7, 9, 12
	> 0.35	Coal and biomass combustion	PT3, 4, 5, 9, 10, 13, 15, 18, 20	PT9, 12, 13, 14, 15, 16, 17, 18, 19	PT4, 8
IndP/ (IndP + BghiP)	<0.2	Petroleum origin/input	PT16	-	-
	0.2-0.5	Petroleum Combustion	PT20	PT18	PT11, 12, 14, 17
	>0.5	Coal, wood, grass combustion	PT4, 11, 12, 13, 15, 17, 18, 19	PT10, 11, 12, 13, 14, 15, 16, 19	PT15, 20
Ant/(Ant + Phen)	< 0.10	Petroleum input	-	-	-
	> 0.10	Combustion process	All samples	All samples	All samples
Flt/(Flt + Pyr)	< 0.4	Petroleum origin	PT2, 7, 12, 13, 15, 16, 17, 19	PT7, 10, 11, 12, 13, 14, 16, 17	PT3, 9, 12, 13, 16, 17, 19, 20
	0.4-0.5	Petroleum combustion	PT3, 8, 11,	PT15	PT11
	> 0.5	Coal and biomass	PT1, 4, 6, 9, 14, 18, 20	PT18, 19, 20	PT14, 15, 18
Total Index (TI)	< 4.0	Low temperature combustion processes	PT1, 5, 7, 8, 12,16	PT4, 5, 11	PT1, 2, 5, 7, 11, 12, 14, 15, 17, 19
	> 4.0	High temperature combustion processes	All samples except PT1, 5, 7, 8, 12,16	All samples except PT4, 5, 11	PT3, 4, 8, 9, 13, 16, 18, 20

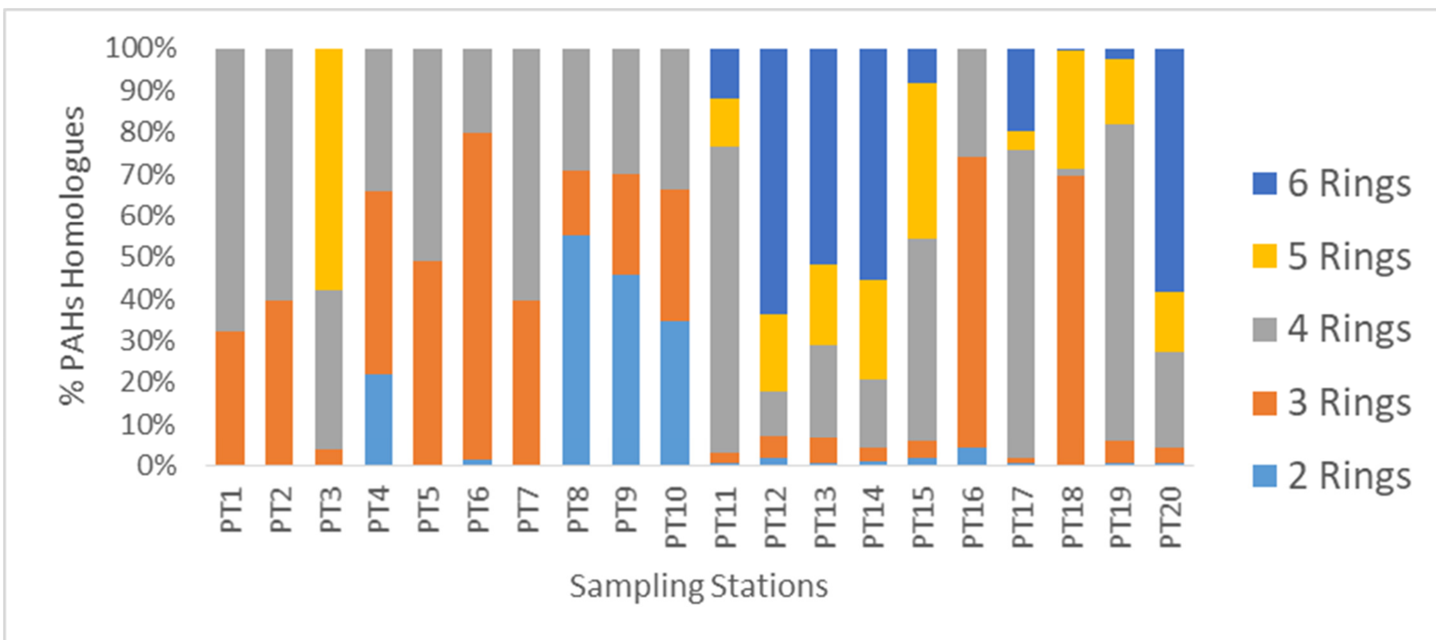
and coal/biomass combustion across different sites. The Total Index (TI) differentiated low-temperature combustion processes at PT1, PT5, PT7, PT8, PT12, and PT16 in sediments, PT4, PT5, and PT11 in oysters, and PT1, PT2, PT5, PT7, PT11, PT12, PT14, PT15, PT17, and PT19 in periwinkles, while the remaining sites exhibited high-temperature combustion processes. Figure 2 illustrates the homologous distribution pattern of PAHs in sediments (A), oysters (B), and periwinkles (C) from the Sombreiro Estuary. The distribution patterns highlight variations in PAH composition across the different matrices, indicating potential differences in sources, bioaccumulation, and environmental fate. The PAHs distribution pattern in sediments were in the order of: 4- > 3- > 5- > 2- > 6-rings (Figure 2a). The HMW PAHs were the dominant PAHs in the sediments on the average. The levels of the HMW PAHs varied from 398 to 8338 µg/kg whereas the LMW PAHs varied from 98 to 4802 µg/kg. The PAHs distribution pattern for oyster was in the order of: 4- > 3- > 5- > 6- > 2-rings (Figure 2b, 2c). Like the sediment, the HMW PAHs were the dominant PAHs in the oyster. The levels of the LWM PAHs varied



(a)



(b)



(c)

Figure 2: Homologues distribution pattern of PAHs in sediments (A), oysters (B) and periwinkles (C) from the Sombreiro Estuary

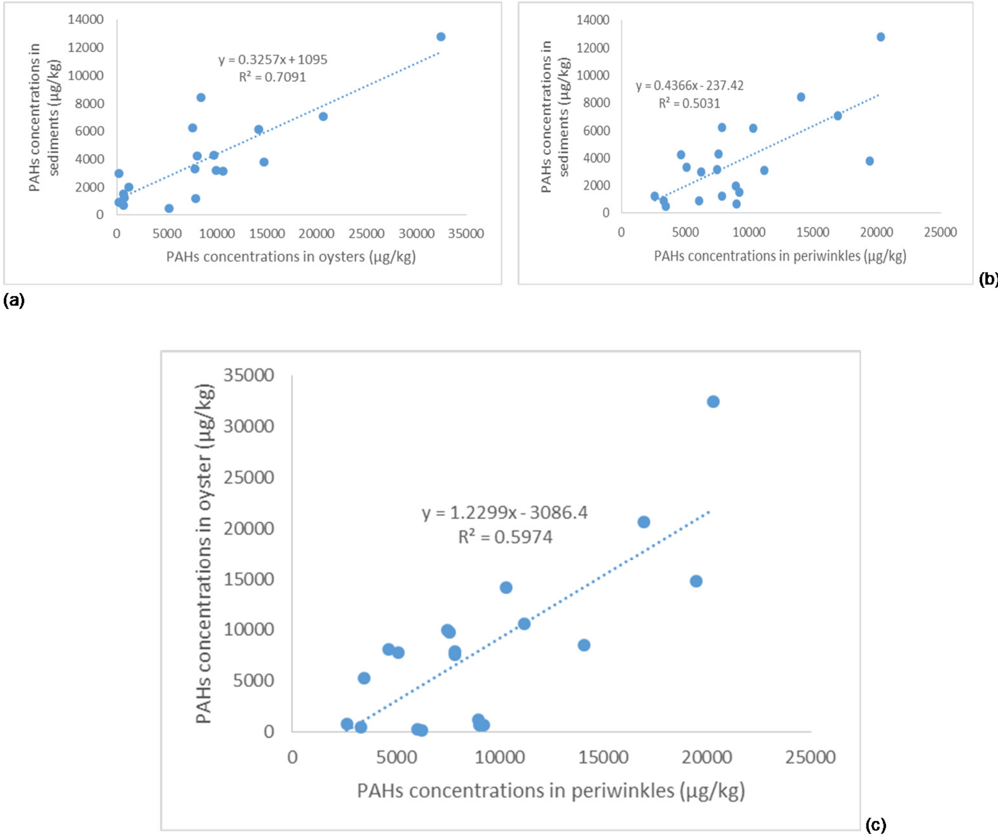


Figure 3: Regression plot of PAHs in (a) water vs sediment (b) water vs oyster (c) sediment vs oyster from the Sombreiro Estuary.

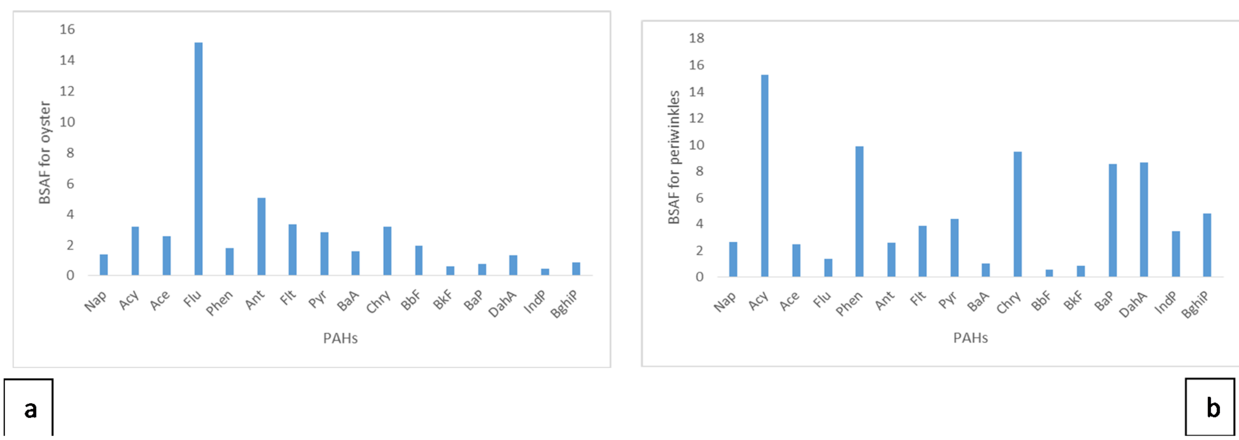
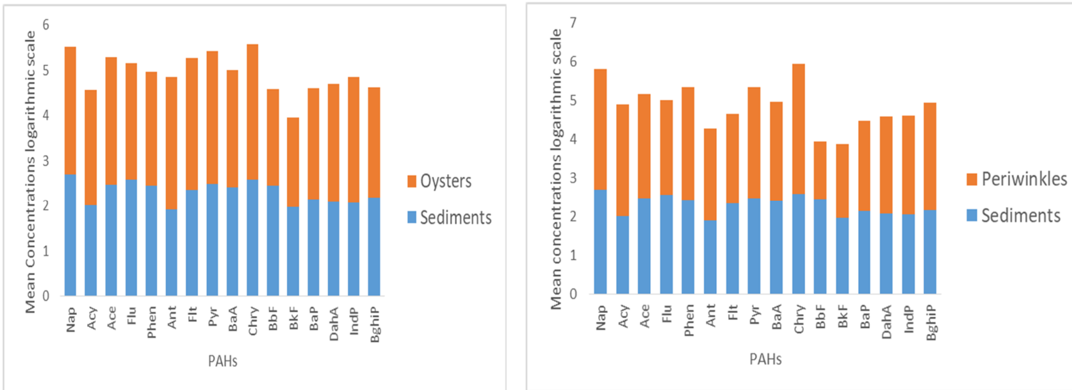


Figure 4: BSAF of individual PAHs for (a) oysters and (b) periwinkles.

from 69 to 15271 □g/kg while the HMW PAHs varied from ND to 17198 □g/kg. The PAHs distribution pattern for periwinkles was in the order of: 4- > 3- > 2- > 6- > 5-rings (Figure 2c). The HMW PAHs were also the dominant PAHs in the periwinkles. The levels of the LWM PAHs varied from 177 to 14221 µg/kg while the HMW PAHs varied from 2087 to 19132 µg/kg. Linear regression analysis was used to show the interrelationship of PAHs concentrations in these matrices as displayed in Figure 3(a-c). PAHs in sediment shows significant positive relationship with PAHs in oyster (r^2 = 0.7091) and periwinkles (r^2 = 0.5031). Also, PAHs in oysters shows significant positive relationship with PAHs in periwinkles (r^2 = 0.5974) showed a mix of petroleum origin, petroleum combustion. The BSAF of the individual PAHs except for BkF, BaP, IndP and BghiP for oyster and BbF and BkF for periwinkles were generally > 1 (Figure 4). This indicate that these PAHs compounds bioaccumulated in the oyster and periwinkle tissues. The bioavailability of the PAHs in the oyster was in the order of Flu > Ant > Flt > Acy > Chry > Pyr > Ace > BbF > Phen >



(a) (b)

Figure 5: Sediment-oyster (A) and sediment-periwinkle (B) PAHs concentrations dynamics.

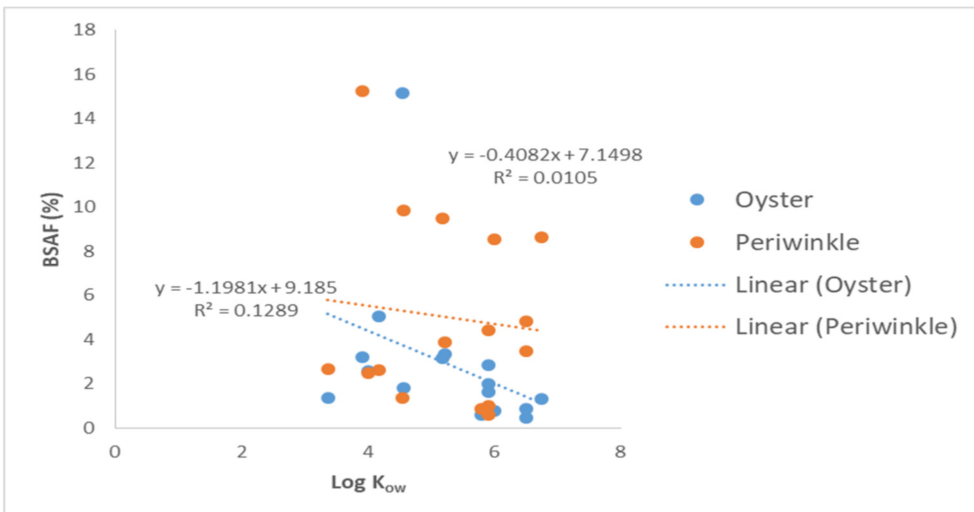


Figure 6: Plot of BSAF versus log K_{ow} of PAHs

BaA > Nap > DahA > BghiP > BaP > BkF > IndP while for periwinkle it followed the order: Acy > Phen > Chry > DahA > BaP > BghiP > Pyr > Flt > IndP > Nap > Ant > Ace > Flu > BaA > BkF > BbF. The 3- and 4- rings PAHs were more available in this study. The PAH bioavailability in *S. cucullate* and periwinkle tissues in our study, typically revealed the dominant PAHs (3-4 rings) in the Sombreiro river estuary. This suggest that the PAHs' levels in oyster and periwinkles could have been in thermodynamic equilibrium as the PAHs levels in the sediment (Cortazar et al., 2008; Baumard et al., 1999) (Figure 5).

The relationship between BSAF values and log K_{ow} of PAHs in this study is shown in Figure 6. There was no significant correlation between BSAFs of PAHs and log Kow for oysters (R^2 = 0.1289) and periwinkle (R^2 = 0.0105).

DISCUSSION

Polycyclic aromatic hydrocarbons (PAHs) are persistent organic pollutants that pose significant environmental and health risks due to their toxic, mutagenic, and carcinogenic properties (Anyanwu et al., 2020; Kim et al., 2018). In aquatic environments, PAHs are introduced through both natural and anthropogenic sources, with petroleum exploration, industrial activities, and urban runoff being the primary contributors (Neff, 2002; Yunker et al., 2002). The bioavailability and distribution of PAHs in sediments and aquatic organisms depend on several factors, including hydrodynamic conditions, sediment composition, and organic matter content (Baumard et al., 1998; Ololade et al., 2011).

The fate of PAHs in estuarine systems is influenced by their physicochemical properties, particularly their molecular weight. Low-molecular-weight (LMW) PAHs, which have two or three aromatic rings, are more soluble in water and tend to degrade more rapidly due to microbial activity and photolysis (Johnsen & Karlson, 2007). In contrast, high-molecular-weight (HMW) PAHs, which contain four or more rings, exhibit lower solubility and higher affinity for particulate matter, leading to accumulation in sediments and aquatic organisms (Zhang et al., 2019; Amdany et al., 2014). The predominance of

HMW PAHs in environmental matrices is often associated with pyrogenic sources, such as combustion of fossil fuels, whereas LMW PAHs are typically derived from petrogenic sources, including crude oil spills and refinery discharges (Lima et al., 2005; Guo et al., 2011).

The spatial distribution of PAHs in estuarine ecosystems is largely controlled by hydrodynamic processes, which influence the transport, deposition, and resuspension of contaminants (Stout & Wang, 2008). Areas with high industrial activities and petroleum infrastructure tend to have elevated PAH concentrations due to frequent discharges from refineries, pipelines, and artisanal refining activities (Nwaichi & Ntorgbo, 2016; Iwegbue et al., 2020). Furthermore, estuaries receiving runoff from urban and agricultural sources often exhibit significant PAH contamination, as land-based pollutants are transported via surface water flow (Berrojalbiz et al., 2014; Adeniji et al., 2017).

Bivalves and gastropods are widely used as bioindicators of PAH pollution due to their ability to accumulate these compounds from water and sediments (Baumard et al., 1999; Kim et al., 2018). The bioaccumulation of PAHs in aquatic organisms is influenced by their feeding behavior, lipid content, and metabolic capacity to biotransform these compounds (Frenzel et al., 2010; Barhoumi et al., 2016). Filter-feeding organisms such as oysters can accumulate high levels of PAHs through ingestion of contaminated particulate matter, while periwinkles, which feed on biofilms and detritus, may also exhibit significant PAH uptake (Ololade et al., 2011; Onojake et al., 2020). The presence of PAHs in biota raises concerns regarding potential human exposure, particularly in communities that rely on contaminated seafood as a dietary staple (Anyakora et al., 2005; Iwegbue et al., 2019).

The relationship between PAH concentrations in sediments and aquatic organisms provides insights into contamination pathways and potential risks to the ecosystem (Guo et al., 2011; Zhang et al., 2019). Strong correlations between PAH levels in sediments and biota suggest that sediment-bound contaminants are bioavailable and can be transferred through the food web (Kim et al., 2018; Yunker et al., 2002). However, variations in bioaccumulation patterns may arise due to differences in species-specific metabolic responses, environmental conditions, and contaminant sources (Neff, 2002; Frenzel et al., 2010).

The persistence of PAHs in estuarine environments necessitates effective monitoring and management strategies to mitigate their impact on aquatic ecosystems and human health (Barhoumi et al., 2016; Anyanwu et al., 2020). Regulatory frameworks such as sediment quality guidelines and seafood safety thresholds play a crucial role in assessing contamination levels and guiding remediation efforts (DPR, 2002; Maliszewska-Kordybach, 1999). Given the potential risks associated with PAH contamination, targeted interventions, including improved waste management, pollution control measures, and sustainable oil extraction practices, are essential for reducing environmental contamination and ensuring ecosystem integrity (Adeniji et al., 2017; Berrojalbiz et al., 2014).

PAH contamination in estuarine environments remains a critical environmental concern, particularly in regions with extensive petroleum-related activities. The distribution and bioaccumulation of PAHs in sediments and aquatic organisms provide important indicators of pollution sources and ecological risks. Effective mitigation strategies, including regulatory enforcement and pollution control measures, are necessary to reduce PAH contamination and safeguard both environmental and human health.

Oyster-sediment accumulation factor

The bioaccumulation of polycyclic aromatic hydrocarbons (PAHs) in aquatic organisms is a critical factor in understanding the fate and transport of these contaminants in marine ecosystems (Baumard et al., 1999; Ma et al., 2010). Bioaccumulation occurs when the uptake of PAHs by an organism exceeds their elimination rate, leading to an increased concentration in tissues over time (Ololade et al., 2021; Idowu et al., 2020). The bio-sediment accumulation factor (BSAF) is a widely used parameter to assess the extent to which sediment-bound PAHs are absorbed by biota and provides insights into bioavailability and contamination risks (Vaezzadeh et al., 2019; Keshavardzifard et al., 2017).

The accumulation of PAHs in marine organisms is influenced by their molecular weight, hydrophobicity, and partitioning behavior between sediment, water, and biota (Mirsadeghi et al., 2013; Qian et al., 2001). High-molecular-weight (HMW) PAHs, due to their strong hydrophobic nature, tend to bind more readily to organic matter in sediments and have lower bioavailability in the water column (Yawei et al., 2018; Ramdine et al., 2012). Conversely, low-molecular-weight (LMW) PAHs, which are more water-soluble, can be taken up more efficiently by aquatic organisms through passive diffusion and ingestion of contaminated particles (Cortazar et al., 2008; Baumard et al., 1999). However, despite their higher solubility, LMW PAHs can also be eliminated more rapidly, leading to variations in their accumulation across different species (Voogt et al., 1991; Ortega-Calvo et al., 2015).

Bioaccumulation in filter-feeding organisms such as oysters is primarily driven by their feeding behavior and the partitioning dynamics of PAHs between sediments and water (Zhou & Wong, 2000; Ololade et al., 2021). The exposure pathway of PAHs in oysters includes both direct uptake from water and ingestion of sediment-associated particles, which may explain variations in bioaccumulation patterns (Idowu et al., 2020; Vaezzadeh et al., 2017). The relative bio-sediment accumulation factor (RBSAF) provides additional insight into bioavailability by normalizing the accumulation of PAHs against sediment concentrations, revealing the efficiency of bioaccumulation in different environmental conditions (Lobo et al., 2010; Mirsadeghi et al., 2013).

The relationship between BSAF and log Kow (octanol-water partition coefficient) is critical in predicting PAH bioaccumulation potential. Generally, PAHs with log Kow values between 5 and 5.6 are most readily accumulated by marine organisms (Voogt et al., 1991; Ololade et al., 2021). Compounds with log Kow values greater than 6 are strongly adsorbed to sediment particles, reducing their bioavailability, while those with lower log Kow values (<5) tend to be more readily metabolized and excreted (Semple et al., 2004; Ortega-Calvo et al., 2015). The bioaccumulation of HMW PAHs in marine organisms may also be enhanced by water turbulence, which resuspends sediment-bound contaminants and facilitates their uptake (Baumard et al., 1999; Vaezzadeh et al., 2017).

The predominance of 3- and 4-ring PAHs in bioaccumulated tissues suggests that these compounds are more bioavailable and persistent within the estuarine ecosystem (Keshavardzifard et al., 2017; Ramdine et al., 2012). The accumulation of these PAHs in oysters and periwinkles is likely driven by their passive diffusion, ingestion of suspended particulates, and metabolic interactions within the digestive tract (Idowu et al., 2020; Yawei et al., 2018). Moreover, the high bioaccumulation of PAHs in oysters suggests that sediment-derived PAHs play a dominant role in the contamination of aquatic organisms, reaffirming previous findings that sediment serves as a long-term reservoir for hydrophobic organic pollutants (Cortazar et al., 2008; Ma et al., 2010).

Given that bioavailable PAHs are the fractions most likely to induce toxic effects, their accumulation in marine biota represents a significant ecological and human health risk (Ortega-Calvo et al., 2015; Semple et al., 2004). The persistence of these contaminants in filter-feeding organisms implies potential biomagnification within the food web, leading to prolonged exposure for higher trophic levels, including humans who consume contaminated seafood (Ololade et al., 2021; Idowu et al., 2020). Therefore, continuous monitoring of PAH bioaccumulation in estuarine ecosystems is essential for assessing pollution levels, understanding contamination pathways, and implementing effective risk management strategies (Mirsadeghi et al., 2013; Zhou & Wong, 2000).

Polycyclic aromatic hydrocarbons (PAHs) are persistent organic pollutants that originate from both natural and anthropogenic sources, including fossil fuel combustion, petroleum spills, and biomass burning (Baumard et al., 1999; Yunker et al., 2002). Their accumulation in aquatic ecosystems poses significant ecological and human health risks due to their carcinogenic and mutagenic potential (Barreca et al., 2014; Iwegbue et al., 2020). This study assessed PAH contamination in sediments, oysters, and periwinkles from the Sombreiro estuary, providing insight into their bioaccumulation, source apportionment, and associated health risks.

BaPTEQ and BaPMEQ in sediments and biota

The toxic equivalency concentrations of benzo[a]pyrene (BaPTEQ) and benzo[a]pyrene mutagenicity equivalency (BaPMEQ) in sediment, oyster, and periwinkle were significantly high, indicating potential health risks. The observed values in sediments (400 µg/kg) exceeded both the Dutch target value (33 µg/kg) and the Method B clean-up level (137 µg/kg), highlighting contamination levels that surpass environmental safety thresholds (Juhasz & Naidu, 2000; CCME, 2010). Furthermore, the BaPTEQ concentrations in oysters (1452 µg/kg) and periwinkles (725 µg/kg) were well above the screening level of 0.67 µg/kg for PAHs in seafood meant for human consumption (U.S. EPA, 2013). These findings suggest that chronic exposure to PAHs via seafood consumption could pose carcinogenic and mutagenic risks, necessitating pollution control and remediation efforts in the estuary.

The hazard index (HI) values indicated that PAH exposure from sediments posed non-cancer risks for children (HI > 1), which aligns with previous studies showing children's higher susceptibility to environmental pollutants due to their lower body weight and increased intake rate relative to body mass (ATSDR, 2019). However, HI values for oyster and periwinkle ingestion were below the threshold of 1, indicating no significant non-carcinogenic risks.

Total cancer risk (TCR) values were above the acceptable threshold of 1×10^{-6} for both children and adults, signifying potential carcinogenic risks from sediment and seafood exposure (U.S. EPA, 2013). The PAHs contributing most to TCR followed the order: BaP > IndP > BbF > BaA > DahA > Nap > BkF > Chry, with BaP—a known Group 1 human carcinogen—being the most significant (IARC, 2010). The findings highlight the vulnerability of children, whose TCR values were approximately 26 times higher than those of adults for sediment exposure and 15 times higher for biota, further reinforcing concerns about childhood exposure to environmental contaminants.

Notably, the health risk estimates based on actual PAH concentrations were significantly higher ($p < 0.05$) than those derived from bioavailable PAH concentrations (CUCL95% of BSAF). This overestimation has been recognized in other studies, as the total PAH concentration does not always reflect bioavailability and toxicity (Ortega-Calvo et al., 2015). Thus, risk assessments should consider bioavailability to avoid exaggerated exposure estimates.

Source apportionment of PAHs

The combined use of diagnostic ratios and principal component analysis (PCA) enabled effective source identification of PAHs in the Sombreiro estuary. The LMW/HMW ratio indicated that most PAHs originated from combustion processes, except for specific stations where petrogenic sources were dominant. The Ant/(Ant + Phen) and CPAHs/TPAHs ratios confirmed combustion as the primary source, which is consistent with studies in other industrialized and oil-producing regions (Tesi et al., 2016; Iwegbue et al., 2020).

PCA results further supported the conclusion that PAHs in sediment, oysters, and periwinkles primarily originated from high-temperature combustion (speedboat emissions, gas flaring, and artisanal refining) and to a lesser extent from petrogenic activities. These findings align with studies on PAH pollution in the Niger Delta, where oil exploration and illegal refining activities contribute significantly to hydrocarbon contamination (Iwegbue et al., 2020; Tesi et al., 2021).

Bivalves and gastropods, such as oysters and periwinkles, have long been recognized as effective bioindicators of marine pollution due to their filter-feeding behavior and ability to bioaccumulate contaminants over time (Baumard et al., 1999; Keshavarzifard et al., 2017). This study demonstrated that PAH compositional patterns in oyster and periwinkle were similar to those in sediment, and the highest PAH concentrations in biota were detected at stations with the highest sediment PAH levels. The lack of significant differences ($p > 0.05$) between PAH concentrations in sediment and biota further supports their utility in environmental monitoring.

Moreover, the ability of these organisms to accumulate PAHs from both pyrogenic and petrogenic sources highlights their effectiveness in tracking pollution sources. The high PAH concentrations in their tissues suggest potential risks to higher trophic levels through biomagnification, reinforcing the need for continuous monitoring and management interventions.

Conclusion

The distribution and bioavailability of PAHs in sediment, oyster and periwinkle from the Sombreiro river estuary in the Niger Delta, Nigeria were investigated. The results revealed that the sediments, oysters and periwinkles from the Sombreiro estuary were heavily contaminated with PAHs and the 3- and 4-rings being the dominant PAHs. Linear regression analysis showed that there was significant positive relationship between these matrices. Bioavailability assessment using BSAF indicated that the BSAF of ∑16 PAHs and that of individual PAHs except BkF, BaP, IndP and BghiP for oyster and BbF and BkF for periwinkles were > 1 and indicated that PAHs bioaccumulated in the oyster tissues. The 3- and 4- rings PAHs were more available to the oyster and periwinkle indicating greater risk of these PAHs. There was no correlation between BSAF and log K_{ow} which may be due to fresh and continuous inputs of PAHs and sampling period. The source apportionment of PAHs revealed that the PAHs were from both pyrogenic and petrogenic sources with significant contribution from pyrogenic inputs. The health risks assessed based on the actual PAHs concentrations and BSAF indicated that there was adverse non-carcinogenic risk from human exposure to the PAHs in the sediments but not from oysters and periwinkles. However, there were potential toxic, mutagenic and carcinogenic effects to humans exposed to PAHs in sediments, oysters and periwinkles from the Sombreiro estuary. In the overall, the health risk level in children were higher than the values reported for adults. The risks assessed based on actual PAHs concentrations were 34 to 389 times (for oyster) and 16 to 382 times (for periwinkle) higher than those based on BSAF. This imply that using the actual PAHs concentration in risk assessment will over overestimate the risk as most of the actual concentration is not bioavailable.

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