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Risk Assessment of Human Exposure to 2-Methylnaphthalene, Phenanthrene and Didodecylphthalate via Consumption of Shrimps (*Macrobrachium vollenhovenii*) from Qua Iboe River Estuary, South-South Nigeria

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Abstract

Ibeno, one of the major oil producing communities in South-South Nigeria is a coastal commercial fishery hub that houses Axon-Mobil operational base and pharmaceutical/plastic industries. Shrimp species (*Macrobrachium vollenhovenii*) is a major aquatic food frequently consumed by inhabitants of the coastal area and those living hinterland, thus, being a major route of human exposure to 2-methylnaphthalene, phenanthrene and didodecyl phthalate in the area. The purpose of the study was to evaluate factors that determine bioaccumulation and assess the potential cancer and non-cancer risk posed by these contaminants through human (adult and children) exposure via shrimp's consumption using gas chromatography-mass spectroscopy. The associated sediment showed higher mean concentrations of 2-methylnaphthalene, phenanthrene and didodecylphthalate at the two sites relative to those in fresh shrimp samples and factors such as size, lipid content, physicochemical property and environmental condition influenced the uptake of these contaminants. Besides water loss, the traditional drying process enhanced the levels of phenanthrene and didodecylphthalate in dry shrimps most likely due to combustion process and relatively low volatility, respectively and lowered the level of 2-methylnapthalene linked to its relatively high volatility. The potential of cancer and non-cancer development in human were highest via dry large shrimp consumption and followed the sequence: dry small shrimp > fresh large shrimp > fresh small shrimp and were within the USEPA reference standards. Although children were more vulnerable, the exposed individuals may not exhibit notable health-associated adverse effects in the near future. Thus, adequate advocacy is needed to sen-

sitize those living in the catchments who often prefer dry shrimp in their meals on the adverse health implications of these contaminants for their survival and the need to maintain the health of the ecosystem.

Keywords

Bioaccumulation, Human Exposure, Toxicity Potential, Shrimp

1. Introduction

The occurrence of probably hazardous materials in our ecosystem has been an issue of public concern globally. Environmental contaminants from petroleum and plastic/pharmaceutical industries have been a matter of environmental concern, especially with the rapid growth in urbanization, which brings about increasing industrialization and consequential increase in commercial activities (Mario et al., 2014). Coastal regions; which are normally characterized by intensive commercial activities have often been a final destination for some industrial pollutants (Zavoda et al., 2001; Olsen et al., 2011). The impact of contaminants from petroleum source and plastic industries have been studied and documented in scientific and technical literatures in recent times. This is because effective assessment of contaminants from these sources on marine environment is necessary for decision-making related to marine habitat protection and sustenance of the ecosystem (Oyo-Ita et al., 2013; Eichler et al., 2019).

The low volatility of Polycyclic aromatic hydrocarbons (PAHs) at room temperature, relative insolubility in water, lipophilicity and their ability to biodegrade to form even more toxic molecules make PAHs highly persistent in Sediments and organic tissues (Olsen et al., 2011; Dosunmu et al., 2016). Several studies have documented the negative effects of PAHs in marine organisms and their consequential risk to humans who consume such marine organisms due to their toxicity and their potential carcinogenicity. According to MacIntosh et al. (1996), some segments of adult populace may be exposed to specific PAHs in food at levels exceeding council of the National Academy of Sciences (NAS). Environmental Working Groups have also demonstrated that unpleasant health consequence could occur in children exposed to PAHs at high concentrations. Food processing techniques such as smoking, steaming, grilling, drying, frying and roasting increase the amount of PAHs in food with smoking, grilling and roasting being the main sources (Park & Penning 2009). In the study, 2-methyl naphthalene was chosen as indicator of the Niger Delta crude oil based on its high abundance in sediments (eg. Oyo-Ita et al., 2016; Oyo-Ita et al., 2017) and sediment-dwelling biota such as crabs (Ibe et al, 2005) from the Niger Delta aquatic environment as well as the fact that among the alkylated PAHs, the reference dose (RfD) for 2-methylnaphthalene remains the only toxicity value accessible from the U.S. Environmental Protection Agency data base (USEPA) (USEPA, 2020). Whereas the choice of phenanthrene was on the premise of its

high abundance in sediment-dwelling biota such as shrimps from the Niger Delta aquatic environment contaminated by gasoline/diesel exhaust emission and other combustion process inputs (Dosunmu et al., 2016).

Phthalates are lipid-loving, they are released into the environment during production of plastics and daily use of produced goods like in the packaging of food materials. This is because phthalates do not tie indelibly as additives in product and readily migrates to water, food, soil and air (Fierens, 2012; Wen et al., 2020). In the marine environment, these contaminants persist in sediments and are driven into the waters where they bio-accumulate in organic tissues (fishes, shrimps etc.) and are transferred along the food chain. Consumption of phthalates via sea food has exposed humans to these contaminants, resulting in unpleasant effect on humans. Thus, determination of the levels of Phthalates in sea food (e.g. shrimps) becomes more pertinent. Due to the numerous health risks associated with human consumption of phthalates, the European Union (EU), United States (USA), and several countries had long commence the regulation of phthalates exposure. The United Kingdom Food Standard Agency (FSA) directs, that phthalates used for packing food should be limited to the manufacturing of resources such as adhesive material and production of dyes. Didodecyl phthalate (DDP) is a lipophilic, colourless, water-insoluble liquid and is widely used in the production of PVC as a plasticiser. Didodecyl phthalate is one among four important phthalates commonly found in the environment (Hahn et al., 2016). Didodecyl phthalate has been analysed by J-U Hahn et al., 2014 as one of the major long chained phthalates compounds commonly found in the environment because of its wide application. Considering that there is no safe exposure level to phthalates (Wittassek et al., 2009; Vandenberg et al., 2012; Tanner et al., 2020), presence of these toxic contaminants in food, even at what could be considered low doses for other chemicals, constitutes a serious health risk. The choice of didodecyl phthalates for the study was based on its high octanol-water partition co-efficient (Log K_{OW} = 9.05; Ellington, 1999).

Shrimps form the main ingredient in almost all Nigerian cuisine, and this enhances their potentials as indicators for biomonitoring. The shrimp's species (*Macrobrachium vollenhovenii*) are harvested commercially in Qua Iboe River estuary and are the major microzoobenthos of the region, broadly dispersed, tolerant to a variety of salinity and temperature. Recent studies have demonstrated that all Teleost fish (fish with backbone) have the potential to effectively metabolize PAHs due to high level of cytochrome p450 enzyme in their tissues. Cytochrome p450 enzyme can bio transform PAHs in an oxidative manner to hydroxylated metabolites which can be conjugated enzymatically to form more water soluble analogues that are readily expelled. Such a biotransformation has not been reported in shrimps species (Schettler et al., 2006; Dosunmu et al., 2016). Data on recent fishery products (including shrimps) collected from the Qua Iboe River is lacking. Never the less, in 2008, the USAID/West Africa revealed a total of 579,537 metric tons of fishery products obtained for Nigeria as highest in West Africa (USAID/West Africa, 2008). Also, a more recent survey

carried out by our team revealed that data regarding levels of PAHs and phthalates in sediment-dwelling biota such as shrimps from sub-saharan African tropical mangrove areas are limited. To minimized overdependence on oversee seafood products, the government of Nigeria lately ventured into large-scale commercial fishery for local utilization and export. This in addition with the importance of shrimps to human health across the globe makes it necessary that information regarding the state of Methyl naphthalene, phenenthrene and didodecyl phthalates contamination in this biota be exigently obtained so as to document a baseline data for the region. The information is required to accentuate the impacts of these contaminants on end users, especially on the residents of the coastal communities known to consume more of this biota than those living interland.

Thus, the objective of these research were;

1) To determine the levels of methyl naphthalene, phenanthrene and didodecyl phthalates in shrimps and associated sediments.

2) Evaluate bio-sediment accumulation factor (BSAF) in order to assess the processes responsible for bioavailability of these contaminants in the study area.

3) To ascertain the impact in the concentrations of methyl naphthalene, phenanathrene and didodecyl Phthalates as a result of applying smoking as a processing technique of shrimps.

4) Assess the risk posed on human exposure through consumption of these contaminants in shrimps.

Study Area

Qua Iboe river estuary is located in Akwa Ibom State, South South Niger Delta of Nigeria (**Figure 1**). It is a part of the coastal portion of the Atlantic Ocean. The catchments has a land mass of 1200 Km^2 and situated between latitudes 4˚32'N and 5˚33'N and longitudes 7˚25'E and 8˚25'E. Ibeno beach along Qua Iboe estuary is the longest sandy beach type in West Africa; it spans up to 45 km in length and 103 m in width during low water tide. The study area is typified by semi-diurnal tide with a meso-tidal range of 2.4 m (Asuquo et al., 2022). Ibeno houses Exxon mobile operational headquarters and other plasices and pharmaceutical industries. The prime occupation of the local people is fishing, and as such the area attracts a lot of commercial activities involving seafood trading.

Ibeno is flanked to the south by the Atlantic Ocean. The area is drained mainly by Cross River and Imo River together with their tributaries (Asuquo et al., 2022). With the recent daily crude oil production at about 1.6 million barrels per day placing Nigeria as the 6^{th} highest oil producing nation in the world and Akwa Ibom state the largest oil producing state in Nigeria with 31.4% of the total oil production in the country. Ibeno stands as the largest oil producing community in Akwa Ibom state. Just recently, the Federal High Court sited in Abuja, ordered Exxon Mobile and the Nigerian National Petroleum Company (NNPC) to compensate oil communities in Ibeno local government Area of Akwa Ibom a cumulative damage of 81.9 billion over oil spillage (Adebayo, 2021).

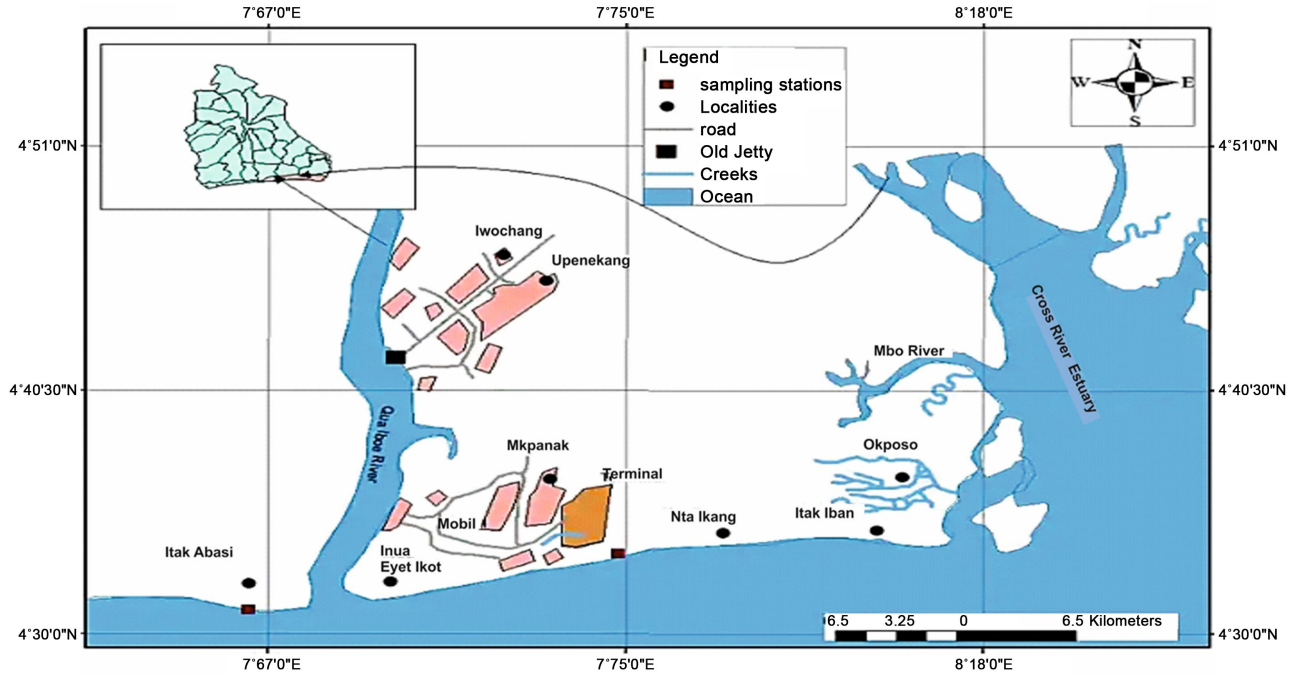


Figure 1. Map of study the area.

2. Materials and Methods

2.1. Materials

The following analytical-grade solvents including, dicloromethane, conc. hydrochloric acid, ethylacetate, acetone, *n*-hexane, internal standards (triphenylamine and benzyl benzoate), surrogates (methylnaphthalene-d8, phenanthrene-d10 and dibenzyl phthalate) were purchased from merck (Hohenbrunn, Germany). Silica gel 40 (0.063 - 0.200 mm), anhydrous sodium sulphate, magnesium sulphate, sodium chloride and aluminium oxide 90 active neutral (0.063 - 0.200 mm) used for column chromatography were purchased also from Merck.

2.2. Sample Collection and Preservation

2.2.1. Biota

In order to get authentic data on the contamination levels of biota in the river, shrimp samples were collected from two sites (AS1-4˚59'N, 7˚91'E and AS2-4˚57'N, 7˚95'E). About 100 shrimp samples were collected from each site using a fishing trawl and separated into large size (>2 cm) and small size (<2 cm), making a total of about 200 samples (Each sampling site was a composite of 10 sampling points giving a total of 20 sampling points for the 2 sites). The collected samples were kept in separate coolers containing ice and NaCl for the biota to spill their guts without losing any hydrophobic substances, taken to the laboratory and later identified as *Macrobrachium vollenhovenii.* Some samples (both large and small shrimps for each sampling site) were separated for smoking/drying. About 2 - 3 composites of 5 g constituted large size shrimps and about 4 - 7 composite of 5 g made up the small size shrimps and labeled as, fresh-large shrimp (FLS1 -

FLS8), fresh-small shrimp (FSS1 - FSS8), dry-large shrimp (DLS1 - DLS8) and dry small shrimp (DSS1 - DSS8). These samples were stored in a deep freeze at −20˚C.

2.2.2. Sediment

Two composite associated sediment samples were also collected from the two sites (AS1-4˚59'N, 7˚91'E and AS2-4˚57'N, 7˚95'E) along the Qua Iboe river estuary using a trowel. The two sediment samples were placed in pre-cleaned sample bottles, labeled, kept in an ice-filled cooler, transferred to the laboratory, freeze-dried and stored at -20˚C till further analysis.

2.3. Grain Size and Total Organic Carbon Determination

Analysis of sediment grain size was carried as reported by Oyo-Ita et al. (2016). De-carbonation of freeze-dried sediment samples was performed using 37% hydrochloric acid repeatedly until bubbling ceased and rinsed in de-ionised water to pH 7. Further analysis by flash combustion at 1024˚C, sequel by thermal conductivity detection in triplicate was carried in a CHNS Elemental Analyser, Carlo Erba 1108.

2.4. Extraction and Clean-Up

2.4.1. Biota

Before extraction procedure, shrimp samples were "spiked" with the surrogates (methylnaphthalene-d8, phenanthrene-d10 and dibenzyl phthalate). Triphenylamine (TPhA) and benzyl benzoate were used as the internal standards. The spiking approach involved injecting 25 µL of prepared standard solution (2 ppm in *n*-hexane) of surrogate with a microsyringe into 0.5 g of sample placed in a test tube and thoroughly mixed for 2 minutes using voltex and then shaken repeatedly. The air-dried spiked sample was kept in a dark fume cupboard overnight. About 5 mL of distilled water and 10 mL of ethylacetate were added to 5 g of homogenized freeze-dried shrimp sample and mixed thoroughly for 2 minutes. This was followed by the addition of 2 g magnesium sulphate and 1 g of sodium chloride. The mixture in the tube was shaken for another 2 minutes, centrifuged at 3500 rpm for 10 min, and 5 mL of the upper organic phase was taken as an aliquot. The aliquot was evaporated to near dryness under gentle stream of N_2. A silica mini-column cleanup was made using a Pasteur pipette plugged with glass wool, 1 g of silica and a thin layer of sodium sulphate depending on the lipid content of the analyzed shrimp. The column was conditioned with 6 mL of the elution solvent [Dichloromethane: *n*-hexane (1:3, v/v)], sequel by 4 mL of *n*-hexane. The extract was then injected onto the column and analytes eluted with 10 mL of a mixture of Dichloromethane: *n*-hexane (1:3, v/v). The eluent obtained was cautiously evaporated under the gentle stream of N_2 to dryness. Re-dissolution of the residues in 0.5 mL of iso-octane was carried out, the volume made up to 500 µL and preserved in a dark-brown vial before the gas chromatography-mass spectrometry (GC-MS) analysis.

2.4.2. Associated Sediment

Prior to extraction, sediment sample was "spiked" with surrogates (methylnaphthalene-d8, phenanthrene-d10 and dibenzyl phthalate) following procedures reported for the shrimps. The sediment sample (1 g) was extracted 3x by sonication with 15 mL of solvent mixture (*n*-hexane/acetone; 1:1 v/v) for 30 min. Succeeding centrifugation for 10 min at 3500 rpm, the clear supernatant was decanted and the merged extract was evaporated to near dryness under a stream of N_2 and re-dissolved in 0.5 mL *n*-hexane before cleanup. Fractionation was performed by adsorption chromatography in an open glass column loaded on top with 1 g anhydrous sodium sulphate, middle with 2 g neutral alumina (activated at 400˚C, 5% water deactivated) and bottom with glass wool. The eluent was evaporated to around 300 µL by a gentle stream of N_2 gas and preserved in a dark-brown vial before GC-MS analysis (Kalachova et al., 2011).

2.5. Quality Assurance/Control and Instrumental Analysis

All Glass ware were pre-cleaned using ethyl acetate and acetone sequentially and heated overnight at 300˚C. For every 2 - 5 batch of samples, one analytical blank was run to identify background contamination throughout the laboratory exercise. To eliminate background contamination, the mean of the analytical blanks were subtracted from the analytes concentrations for correction of target compounds concentrations. Analysis of the fractions was archived with a gas chromatography-mass spectrometer TRACE GC-MS Thermo Finnigan (Manchester, UK) in the electron impact (EI) mode at 70 eV. A 30-m, 0.25-mm-inner diameter capillary column coated with 0.25 lm of ZB-5MS stationary phase (Phenomenex Zebron; USA) was used. Helium was the carrier gas with a constant flow rate of 1.2 mL/min. The injector temperature, in "splitless" mode, was kept at 280˚C, and after the injection, the purge valve was activated 50 s. Column temperature was kept at 60˚C for 1 min, and then the temperature was raised to 200˚C at 10˚C/min and finally to 320˚C at 4.8˚C/min, maintaining that temperature for 10 min. Ion source and transfer temperatures were held at 200˚C and 250˚C, respectively. Data acquisition was archieved in the selected ion monitoring (SIM) modes with 6 min of solvent delay and processed by the X-calibur Thermo Finnigan software (San Jose, CA, USA). Standards were used for both quantification and recovery corrections. The analysis of the samples was repeated in 3x, and relative standard deviations were obtained. Blanks were treated together with samples, and limits of detection (LOD) and limits of quantification (LOQ) were estimated as the average signal of the blanks plus three times the standard deviation of the signal of the blanks and average signal of the blanks plus ten times the standard deviation of the signal of the blanks, respectively. The targeted compounds were identified on the basis of retention time and ion fragment profile compared against authentic standards, whilst quantification was carried out using multi-point internal calibration method. A calibration curve was plotted for each compound to be quantified. The linear range of the detector was evaluated from the curve produced by plotting amount injected

versus detector signal. All evaluations were carried out in the linear ranges for each target compound.

2.6. Statistical Procedure

Descriptive statistics were applied for the generated data set. Pearson correlation analysis was used to understand the relationships among paired variables. To estimate significant differences amongst variable, one-way analysis of variance was performed. STATISTICA 8.0 software package was utilized for statistical analyses.

3. Results and Discussion

PAHs compositions and concentrations in shrimps and associated sediment

The quality assurance/quality control procedures used for the analysis of shrimp and associated sediment samples followed the established USEPA procedures and the NOAA criteria for the target compounds analysis in seafood samples (USEPA, 2006; NOAA, 2006). The certified values of these compounds in the National Institute of Standards and Technology (NIST) mussel standard reference material (SRM) were compared with the values detected in our shrimp samples. The triplicate sample relative percent difference for all the shrimp samples was less than 20% for the target compounds. The average recoveries for the analytes fell within the NOAA acceptable range of 60% - 130% (NOAA, 2006).

3.1. Bulk Properties

Environmental features and sediment bulk parameters such as total organic carbon (TOC) and grain size distribution are presented in **Table 1**. The sediment of the studied sites consisted predominantly sandy fractions probably due to the distinctive sheltered basin morphology of the study area and apparent high energy current condition of the river (Oyo-Ita et al., 2013). Site AS1 exhibited 57.20% sand, 24.6% silt and 18.2% clay. Site AS2 had 69.8% sand, 19.8% silt with a percentage clay fraction of 10.40%. The higher sand fraction found for AS1 may be attributed to the prevalence of a relatively stronger tidal current toward the mouth of the estuary. The higher clay fraction of AS2 was linked to its proximity to mud mangrove swamp (Oyo-Ita et al., 2013).

Site AS1 and AS2 exhibited low total organic carbon (TOC) values of 3.1% and 1.3%. The low TOC content may be linked to poor absorbability of the organic carbon on the dominant sand fractions and the mixing of the water-sediment confluence where the rates of organic matter degradation and delivery by microbial mediated activities are high (Dominguez et al., 2010). Fine grain sediments are known to adsorb organic matter more than coarse sandy counterpart with larger grain size (Hyun et al., 2002).

3.2. Associated Sediment Contaminants Concentrations

The concentrations of 2-methylnaphthalene (50.74 μg/g dry weight-dw) in the

Table 1. Description of sampling areas, bulk properties, concentrations (μg/g) of analyzed contaminants in associated sediment and biota sediment accumulation factors.

Site	Coordinate	Description	TOC	Associated sediment			BSAF				Grain size distribution (%)		
				2-MNaph.	Phen	DDPh	Sample code	2-MNaph.	Phen	DDPh	Sand	Silt	Clay
AS1	4˚59'N, 7˚91'E	Sparse mangrove vegetation, with athuvial covers. Weak tidal current	3.1	50.74	15.74	12.65	FSS	0.08	0.05	0.39	57.20	24.6	18.2
							FLS	0.10	0.06	0.42			
AS2	4˚57'N, 7˚95'E	Mouth of Estuary sparse Mangroves stands, strong tidal current	1.3	42.50	10.82	7.40	FSS	0.03	0.05	0.64	69.8	9.8	15.4
							FLS	0.07	0.05	0.69			

associated sediment (AS1) was higher than those found for the fresh large size shrimp samples (FLS; mean = 34.44 ± 12.30 wet weight-ww) and fresh small shrimp sample (FSS; mean = 19.20 ± 8.07). Also, concentrations of phenanthrene (15.74 μg/g dw) in associated sediments AS1 was higher than those for the FLS (mean = 5.66 ± 2.93 ww) and FSS (mean = 3.66 ± 1.55) except for the dry large shrimp samples (DLS; mean = 44.28 ± 6.89) and dry small shrimp samples (DSS; mean = 19.46 ± 4.66), whereas concentrations of didodecylpthalates (12.65 μg/g dw) in associated sediments AS1 was lower than those found for FLS (mean = 29.41 ± 0.09) and FSS (mean = 22.15 ± .41; **Table 1**).

Similar scenario was also observed in the case of associated sediment AS2, where the concentrations of 2-methylnaphthalene (44.50 μg/g dw) was higher than those found for the FLS (mean = 26.33 ± 8.77) and FSS (mean = 6.91 ± 1.37). Concentrations of phenanthrene (10.52 μg/g dw) in associated sediments AS2 was higher than those for the FLS (mean = 4.35 ± 0.93) and FSS (mean = 3.4 ± 1.19) except the DLS (mean = 33.35 ± 9.68) and dried small shrimp sample (mean = 19.80 ± 4.10) while concentrations of didodecylpthalates (7.40 μg/g dw) in associated sediments (AS2) was lower than those found for FLS (mean = 42.5 ± 0.26) and, FSS (mean = 28.12 ± 0.33) (**Table 1** and **Table 2**).

Phenanthrene concentrations in the associated sediment were lower relative to methylnaphthalenes. This can be attributed to differences in source points and higher biodegradation of phenanthrene compared to other PAHs (Mackay et al., 1997). The lower concentration levels of the analyzed PAHs found at site AS2 agrees with previous studies, which showed that Mangrove sediments harbor more zenobiotic bacteria consortium capable of enhancing degradation of the analyzed PAHs (Hunter et al., 1986; Tam et al., 2002). Similarly, AS1 exhibited higher DDPh (12.6 μg/g dw) than AS2 (7.40 μg/g dw) and may be attributed to differences in environmental conditions such as seasonal water flow and river quality factors like temperature, pH and oxygen supply (Huang et al., 2008).

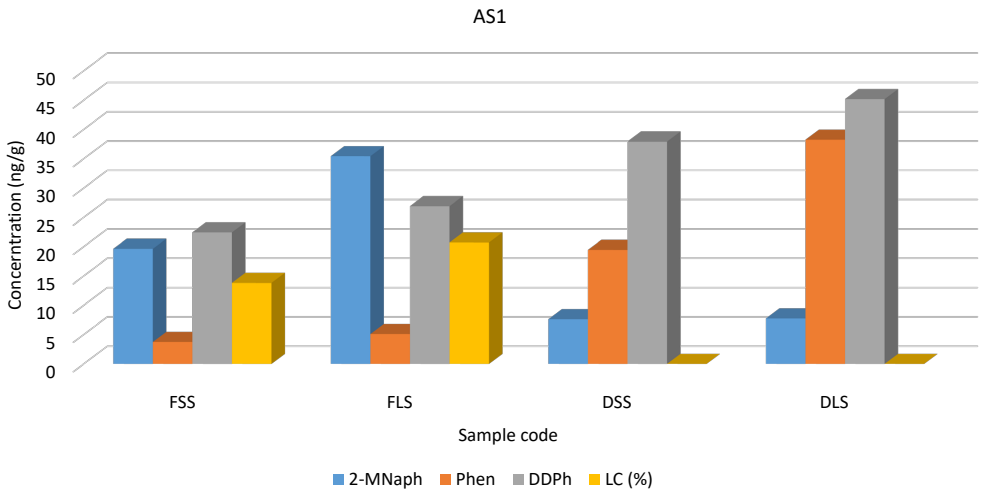
Table 2. Lipid content and concentrations (μg/g ww) of analyzed compounds in shrimps from site AS1 and AS2.

Sample code	AS1				AS2			
	2-MNaph	Phen	DDPh	LC (%)	2-MNaph	Phen	DDPh	LC (%)
FSS_1	16.10	3.08	20.02	12.7	6.82	4.02	21.08	15.05
FSS_2	20.14	2.01	23.21	15.84	7.80	5.11	23.27	13.17
FSS_3	18.17	4.75	19.41	12.1	7.81	3.08	25.08	15.18
FSS_4	18.02	6.56	21.09	13.44	7.92	2.05	30.95	14.76
FSS_5	26.14	4.14	25.74	14.79	7.88	4.14	31.08	12.05
FSS_6	9.40	4.15	24.02	13.63	6.0	4.72	31.41	13.64
FSS_7	20.61	2.10	20.02	12.90	3.95	2.40	29.01	13.94
FSS_8	25.05	2.50	23.72	14.13	6.90	2.20	33.14	11.50
FLS_1	27.41	9.51	25.368	18.57	24.74	5.00	35.81	17.38
FLS_2	15.05	4.71	26.52	22.81	10.05	2.17	31.21	19.42
FLS_3	37.79	2.02	30.5	21.05	18.70	3.59	36.11	19.15
FLS_4	37.17	8.81	22.55	21.38	25.58	4.27	41.71	18.70
FLS_5	22.05	8.17	20.39	19.92	34.79	4.12	46.21	18.90
FLS_6	41.14	2.57	28.46	20.33	30.91	3.11	51.01	19.76
FLS_7	53.70	6.10	30.64	18.90	37.02	4.81	48.17	20.47
FLS_8	41.22	3.40	29.41	20.74	28.82	3.47	50.05	19.10
DSS_1	5.94	18.16	33.58		2.14	15.16	51.02	-
DSS_2	6.10	20.79	45.53		2.72	18.79	50.85	-
DSS_3	8.25	22.24	38.49		5.11	22.01	48.20	-
DSS_4	10.81	23.41	39.55		3.14	25.11	56.58	-
DSS_5	7.51	15.71	41.10		4.07	25.01	51.60	-
DSS_6	8.65	18.24	40.28		3.71	14.17	41.41	-
DSS_7	8.79	11.21	34.45		2.03	18.00	63.31	-
DSS_8	5.01	25.91	30.52		2.75	20.17	61.41	-
DLS_1	9.18	32.42	40.51		8.25	16.98	60.14	-
DLS_2	11.52	47.4	45.86		11.40	42.24	59.07	-
DLS_3	7.41	48.50	38.95		10.41	30.79	65.29	-
DLS_4	11.52	29.57	47.78		13.79	35.79	58.61	-
DLS_5	10.21	36.09	40.94		9.82	40.92	51.11	-
DLS_6	11.42	41.56	45.74		7.17	20.90	66.28	-
DLS_7	7.57	35.22	52.91		9.40	41.36	58.65	-
DLS_8	11.81	35.22	48.72		7.34	37.79t	60.617	-

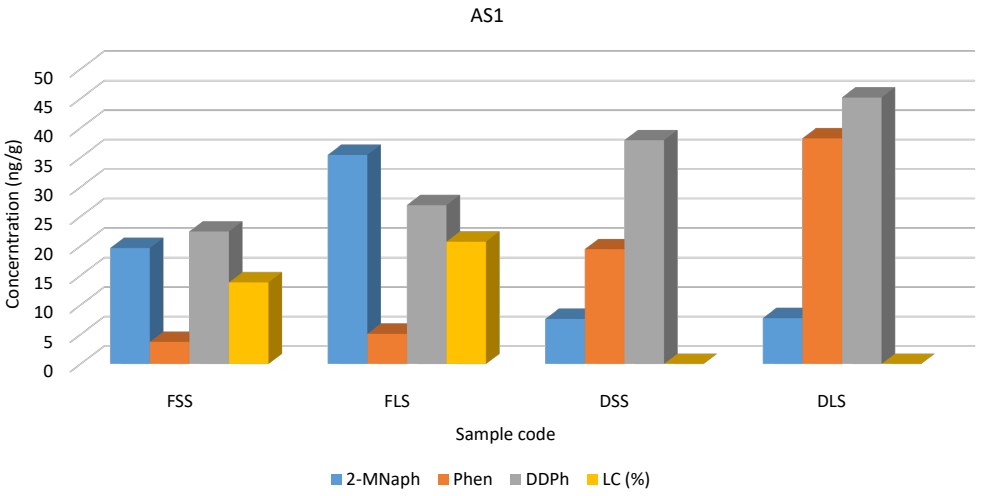
Note: FSS = Fresh Small Shrimp, FLS = Fresh Large Shrimps, DSS = Fresh Small Shimps, DSS = Dry Small Shrimps.

3.3. Lipid Contents and Concentrations of Analyzed Compounds in Shrimp Samples

The lipid content for FLS ranged from 18.57% - 22.81% with a mean of 20.46% ± 1.37% and a range of 12.81% - 15.84% with a mean of 13.69 ± 1.21 was the lipid content found for the FSS at site AS1 (**Table 2**; **Figure 2**). At AS2, the lipid content for FLS was in the range 17.38% - 20.47% with a mean of 19.11 ± 0.89 and a range of 11.50% - 15.18% with a mean of 13.66 ± 1.36 was the lipid content found for the FSS (**Table 2**; **Figure 2**). Lipid content (LC) is a principal storage site for these contaminants (Muncaster et al., 1990). Lipid contents in biota tissues has been reported to influence transport of hydrophobic compounds in the tissues, indicating that the larger the lipid content, the faster the uptake and slower the excretion of these contaminants (Hanson et al., 1998).



(a)



(b)

Figure 2. Mean Lipid content and concentrations of analyzed compounds in shrimps from site AS1 and AS2 (*Note*: *FSS* = *Fresh Small Shrimp*, *FLS* = *Fresh Large Shrimps*, *DSS* = *Fresh Small Shrimps*, *DSS* = *Dry Small Shrimps*).

2-Methylnaphthalene concentrations for FLS ranged from 15.05 μg/g ww to 53.70 μg/g ww (mean = 34.44 ± 12.30) and a range 9.40 - 26.14 μg/g ww was found for FSS with a mean of 19.20 ± 8.07. DLS was in the range 7.41 - 11.81 μg/g ww (mean = 10.08 ± 1.82) while a range 5.01 - 10.81 μg/g ww was recorded for the DSS with a mean of 7.63 ± 1.89 at site AS1 (Table 2; Figure 2). In the case of AS2, the 2-methylnaphthalene concentrations for the FLS ranged from 10.05 - 37.02 μg/g ww (mean = 26.33 ± 8.77) and a range 3.95 - 7.92 μg/g ww was found for FSS with a mean of 6.89 ± 1.37. DLS and DSS on the other hand ranged from 7.17 μg/g ww to 13.79 μg/g ww (mean = 9.69 ± 2.21) and 2.03 - 5.11 μg/g ww (mean = 3.21 ± 1.5) respectively (Table 2; Figure 2).

Phenanthrene concentrations ranged from 2.02 - 9.51 μg/g ww (mean = 5.66 ± 2.93) for FLS, 2.01 - 6.56 μg/g ww (mean = 3.66 ± 1.55) for FSS, 29.57 to 48.50 μg/g ww (mean = 38.25 ± 6.89) for DLS and 11.21 - 25.91 μg/g ww (mean = 19.46 ± 4.66) for the DSS at site AS1 (Table 2; Figure 2). In the case of AS2, the phenanthrene concentrations for the FLS were in the range 2.17 - 5.00 μg/g ww (mean = 3.82 ± 0.93) while a range 2.05 - 5.11 μg/g ww was found for FSS with a mean of 3.47 ± 1.19. DLS ranged from 16.98 μg/g to 42.24 μg/g (mean = 32.71 ± 9.68) and a range 14.17 - 25.11 μg/g was found for the DSS with a mean of 19.80 ± 4.10 (Table 2; Figure 2).

Concentrations of Didodecyl phthalate ranged from 20.39 μg/g ww to 30.64 μg/g ww (mean = 26.72 ± 3.76) for FLS, 19.41 - 25.74 μg/g ww (mean = 22.15 ± 2.32) for FSS, 38.95 to 52.91 μg/g ww (mean = 45.17 ± 4.76) for DLS and 30.52 - 45.53 μg/g ww with a mean of 37.93 ± 4.81 for the DSS at site AS1 (Table 2; Figure 2). For site AS2, the didodecyl phthalates concentrations for the FLS were in the range 31.21 - 50.05 μg/g (mean = 42.53 ± 7.45) while a range 21.08 - 33.14 μg/g ww (mean = 28.12 ± 4.41) was found for FSS. DLS ranged from 51.11 μg/g to 66.28 μg/g (mean = 59.97 ± 4.65) and a range 41.41 - 63.31 μg/g was found for the DSS with a mean of 53.04 ± 7.15 (Table 2; Figure 2).

The tissue burden of the targeted compounds did not vary widely in shrimps samples which indicated that the organisms did not have different selectivity for the analyzed compound. It appears therefore that the organisms exhibited similar degree of bioavailability, capacity of large and small size shrimps to metabolise the analyzed compounds as well as similarity in the analysed compounds biotransformation extent of the large and small size shrimps. It is likely that the different stages in their life cycle might be responsible for the varying levels of the analysed compounds in large and small size shrimps.

This results to a higher uptake of contaminants in tissues with high LC than those with low LCs. To ascertain the veracity of this general assertion, we subjected the generated data to one-way analysis of variance (ANOVA) at a confidence level of 95% so as to evaluate the significance of the relationship between contaminant body load and biota LCs. The F value for the LC; 0.43 was less than the critical F value of 2.72 (df = 12; $p = 0.99$), indicating that no significant relationship existed between the paired variables.

The impact of smoking as a processing technique of shrimps was observed in the dry shrimp samples. Phenanthrene concentrations were higher in the dry shrimp's samples relative to their fresh counterparts. At site AS1, DLS had the highest mean concentration of 38.25 ± 6.89 μg/g, remarkably higher than that found for the FLS (5.66 ± 2.93 μg/g). Similar pattern was observed in the dry shrimps from site AS2. The results are in agreement with those reported by Anayat et al. (2014) and Hasam et al. (2011) which recorded highest phenanthrene concentration levels amongst other PAHs in smoked foods.

The mean concentration of didodecylphthalate was comparable to 2-methylnaphthalene in fresh shrimp samples, but became enhanced in the smoked dry samples at both sites (**Figure 2**). These enhanced levels may be linked to reduced water content, lower volatility and higher $\log_{Kow}$ value of didodecylphthalate compared with the other analyzed compounds (Das et al., 2021; Ogunwole et al., 2021). The living habitat of shrimps, the natural and catalytic degradation, and the physico-chemical properties of phthalates (eg. log k_{ow}) have been shown to influence the bioavailability of phthalates in fresh shrimps (Barron et al., 1995; Huang et al., 2008; Adeniyi, 2008; Baloyi et al., 2021).

3.4. Biota Sediment Accumulation Factor

The transfer of analyzed contaminants from sediment to shrimps creates a pathway from their exposure to humans. The biota-sediment accumulation factor (BSAF) serves as the appropriate index to evaluate the accumulation profile of analyzed contaminants (Huang et al., 2008). BSAF, also known as "accumulation factor" is defined by Wang et al. (2004) as;

$$\mathrm{BSAF} = \frac{C_b / F_1}{C_s f_{oc}}$$

where C_b is the biota contaminant concentration (μg/g ww), f_l is biota lipid content fraction by weight, C_s is sediment contaminant concentration (μg/g dw) and f_{oc} is the organic carbon fraction of the sediment (fraction by weight).

The calculated BSAF values for 2-methylnaphthalene, phenanthrene and didodecylphthalate in FLS were 0.10. 0.06 and 0.42., respectively, while those in the FSS were 0.08, 0.05 and 0.39, respectively at site AS1. At site AS2, FLS exhibited BSAF values of 0.07, 0.05 and 0.69, respectively for 2-methylnaphthalene, phenanthrene and didodecylphthalate, while those for the FSS were 0.03, 0.05 and 0.64 with respect to the analysed compounds (**Table 1**). The relatively lower bioavailability of 2-methylnaphthalene and phenanthrene at the two sites may be associated with protective capacity of soot particles from petroleum combustion processes (e.g. gas flaring and gasoline exhaust emission arising from boating/fishing activity) which may prevent PAHs uptake (Yunker et al., 2003). In addition, Dosunmu et al. (2016) reported that soot particles from atmospheric deposition are too tiny to be preserved by filter feeders such as shrimps. The present scenario fosters maintenance of the ecosystem health as well as increases

the prospective utilization of the study area as site for commercial fishery activity. Despite the aforementioned merit, the observed relatively higher bioavaiabiity levels recorded for didodeceylphthalate may be linked to its high logK_{ow} value of 9.05. As earlier stated, the living habitat of shrimps and the physiochemical properties of phthalates have been shown to influence the bioavailability of phthalates in marine biota (Sabijic, 1987; Burkhard, Brigit, & Randolph, 2003; Lin et al., 2003). The higher BSAF values found for didodecylphthalate at site AS2 relative to AS1 may be associated with its high turbid environment occasioned by sediment resuspension and mixing processes that occur at the estuary throughout the year due to double impact of backwash and wave swash from the open sea and tidal current of macro-tidal amplitude. Because of its relatively higher affinity toward sediment compared to the studied PAHs, the resident shrimps being directly in contact with the sediment may have absorbed parts of didodecylphthalate associated re-suspended particles.

3.5. Human Exposure and Toxicity Assessment

Assessment of health risk was performed to gauge the likelihood of adverse health effects in humans as a consequence of exposure to 2-methylnaphthalene, phenanthrene and didodecylphthalate through consumption of shrimps in the studied river estuary. Cancer risk (CR) and Hazard Quotient (HQ) developed by USEPA were used as models for assessment of carcinogenic and non-carcinogenic health risk in children and adults population (USEPA, 2020).

The Chronic Daily Intake (CDI) models for adults and children is given thus

$$\text{CDI-ingestion} = \left(\frac{\text{CS} \times \text{IR}_F \times \text{EF} \times \text{ED} \times \text{TF}}{\text{BW} \times \text{AT}} \right)$$

where CS is concentration of compounds in μg/g, IRF is food ingestion rate 0.0548 μg/capital/day, EF is exposure frequency (350-day year^{-1}), ED is exposure duration (26 years for adults and 6 years for children), TR is target risk (1×10^{-6} mg/mg) for carcinogen, BW is body weight (80 kg for adults and 15 kg for children), AT is average time (non-carcinogens = ED × 365 days), (carcinogen = 70 × 365).

Although 2-methylnaphthalene has been included as PAH of concern under Section 304(a) of the U.S. Clean Water Act and despite the fact that 2-methylnaphthalene causes health risk as a result of its prospective carcinogenetic, many toxicologists ignored 2-methylnaphthalene in their cancer risk assessments. CDI of 2-methylnaphthalene consumption via shrimps (fresh and dry) for adult and children exposure scenarios were found to be highest in FLS (FLS8.4E-09 and 1.0E-08) and followed the sequence FLS > FSS > DLS > DSS, and those of phenanthrene was highest in DLS (1.1E-08 and 1.3E-08) and was in the order DLS > DSS > FLS > FSS at site AS1. In the case of didodecylphthalate, the CDI was highest in DLS (3.0E-08 and 1.6E-07) and follow the sequence DLS > DSS > FLS > FSS at site AS1 (**Table 3**). Similarly trend was also observed at site AS2, where CDI of 2-methylnaphthalene consumption via shrimps (fresh

and dry) for adult and children exposure scenarios was highest in FLS (6.4E-09 and 7.9E-09) and follow similar trend FLS > FSS > DLS > DSS, and those of phenanthrene highest in DLS (8.1E-09 and 1.0E-08) and follow the trend DLS > DSS > FLS > FSS. In the case of didodecylphthalate, the CDI was highest in DLS (3.9E-08 and 2.1E-07) and follow the sequence DLS > DSS > FLS > FSS (Table 4).

Appraisal of non-carcinogenic health risks was accomplished by estimating the hazard quotient [HQ] for non-carcinogenic risks from exposure to 2-methylnaphthalene, phenanthrene and didodecylphthalate, the HQ was calculated as the quotient between the CDI against the reference dose [RfD]. Hazard quotient HQ = CDI/RfD

Table 3. Chronic daily intake and hazard risk quotient of 2-methylnaphthalene, phenanthrene and didodecyl phthalates consumption via shrimps for site AS1.

Adult Exposure Scenario									
Sample ID	CDI (ug/g/day)			RfD (ug/g/day)			HQ		
	2-MNaph	Phen	DDPh	2-MNaph	Phen	DDPh	2-MNaph	Phen	DDPh
FSS	4.7E-09	8.9E-10	5.4E-09	0.004	0.04	20	1.2E-06	2.2E-08	2.7E-10
FLS	8.4E-09	1.4E-09	1.8E-08				2.1E-06	3.5E-08	9.0E-10
DSS	1.9E-09	4.7E-09	2.5E-08				4.8E-07	1.2E-07	1.3E-09
DLS	2.5E-09	1.1E-08	3.0E-08				6.3E-07	2.8E-07	1.5E-09
Children Exposure scenario									
FSS	5.8E-09	1.1E-09	6.7E-09	0.004	0.04	20	1.5E-06	2.8E-08	3.4E-10
FLS	1.0E-08	1.7E-09	9.4E-08				2.5E-06	4.3E-08	4.7E-09
DSS	2.3E-09	5.8E-09	1.3E-07				5.8E-07	1.5E-07	6.5E-09
DLS	3.0E-09	1.3E-08	1.6E-07				7.5E-07	3.3E-07	8.0E-09

Table 4. Chronic daily intake and hazard risk quotient of 2-methylnaphthalene, phenanthrene and didodecyl phthalates consumption via shrimps for site AS2.

Adult Exposure Population									
Sample ID	CDI (ug/g/day)			RfD (ug/g/day)			HQ		
	2-MNaph	Phen	DDPh	2-MNaph	Phen	DDPh	2-MNaph	Phen	DDPh
FSS	1.7 E-09	8.5 E-10	1.8 E-08	0.004	0.04	20	4.3E-07	2.1E-08	9.0E-10
FLS	6.4 E-09	1.1 E-09	2.8 E-08				1.6E-06	2.8E-08	1.4E-09
DSS	7.8 E-10	4.8 E-09	3.5 E-08				2.0E-07	1.2E-07	1.8E-09
DLS	2.4 E-09	8.1 E-09	3.9 E-08				6.0E-07	2.0E-07	2.0E-09
Children Exposure Population									
FSS	2.1 E-09	1.0 E-09	9.9 E-08	0.004	0.04	20	5.3E-07	2.5E-08	5.0E-09
FLS	7.9 E-09	1.3 E-09	1.5 E-07				2.0E-06	3.3E-08	7.5E-09
DSS	9.6 E-10	5.9 E-09	1.9 E-07				2.4E-07	1.5E-07	9.5E-09
DLS	2.9 E-09	1.0 E-08	2.1 E-07				7.3E-07	2.5E-07	1.1E-08

HQ of 2-methylnaphthalene consumption via shrimps (fresh and dry) for adult and children exposure scenarios was found to be highest in FLS (2.1E-06 and 2.5E-06) and in the order FLS > FSS > DLS > DSS, and those of phenanthrene highest in DLS (2.8E-07 and 3.3E-07) in the trend DLS > DSS > FLS > FSS at site AS1. In the case of didodecylphthalate, the HQ was highest in DLS (1.5E-09 and 8.0E-09) and follow the sequence DLS > DSS > FLS > FSS at site AS1 (Table 3). At site AS2, HQ of 2-methylnaphthalene consumption via shrimps (fresh and dry) for adult and children exposure scenarios was highest in FLS (1.6E-06 and 2.0E-06) and was in order FLS > DLS > FSS > DSS while Phenanthrene was highest in DLS (2.0E-07 and 2.5E-07) and follow the sequence DLS > DSS > FLS > FSS. In the case of didodecylphthalate, the HQ was highest in DLS (2.0E-09 and 1.1E-08) and follow the sequence DLS > DSS > FLS > FSS (Table 4).

Generally, assessment of cancer and non-cancer risk for adult and children exposure to 2-methylnapthalene, phenanthrene and didocylphthalate via shrimps consumption revealed values, which fall within the USEPA reference standards, respectively. The hazard quotients for children and adult were less than one revealing that exposed population may not exhibit significant health related adverse effects over a period of time.

4. Conclusion

In this study, assessment of the factors responsible for bioaccumulation of 2-methylnaphthalene, phenanthrene and didocylphthalate in shrimps at two sites (AS1 and AS2) from Qua Iboe river estuary and their associated human (adult and children) health risk were undertaken. Results showed that size, lipid content, physicochemical property and environmental condition were the important determinant factors involved in the bioaccumulation of these contaminants in fresh shrimps.

Besides water loss, the traditional drying process enhanced the levels of phenanthrene and didodecylphthalate in shrimps most likely due to combustion process and relatively low volatility, respectively and lowered the level of 2-methylnapthalene due to its relatively high volatility.

Human health risk assessment indicated that both cancer and non-cancer risk indices fell within the USEPA tolerable limits. Thus, adequate advocacy is still needed to sensitize the residents of the coastal communities who often prefer to consume dry shrimp in their meals on the adverse health implications of these contaminants for their survival and the need to maintain the health of the ecosystem cannot be overemphasized.

With the emerging data on host of eco-toxicological implications of didodecylphthalate, 2-methylnaphthalene and phenanthrene, the need for swift remediation measure/strategies cannot be overemphasized and requires technological intervention for rapid removal of these compounds from the environment via various available processes such as adsorption, coagulation-flocculation, biochar

mediated microbial degradation, etc. Due to differences in physicochemical properties of these contaminants, a more robust approach should be developed for effective remediation of these components.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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