Journal of Applied Sciences

ISSN 1812-5654

OPEN ACCESS Journal of Applied Sciences
ISSN 1812-5654
DOI: 10.3923/jas.2022.84.91

Research Article
Compositional Pattern and Tissue Concentration of Polycyclic Aromatic Hydrocarbons (PAHs) in Bivalve Shellfish from Niger Delta, Nigeria

[1]Sunday Peter Ukwo, [2]Moses Columba Ekanem and [1]Linus Sylvester Ndah

[1]Department of Food Science and Technology, University of Uyo, Uyo, Nigeria
[2]Department of Food Technology, Akwa Ibom State Polytechnic, Ikot Osurua, Ikot Ekpene, Nigeria

Abstract
Background and Objective: Bivalve shellfish such as Bloody cockle (*Anadara senilis*), Donax clam (*Donax rugosus*), Knife clam (*Tagelus adansonaii*) and Mangrove oyster (*Crassosstra gasar*) are the most abundant soft-bodied invertebrate inhabiting the brackish and intertidal mudflat of the Niger delta. They are considered as nutritious and healthful food items as well as a biological matrix for environmental monitoring. The study investigated compositional patterns and tissue concentration of polycyclic aromatic hydrocarbons (PAHs) in bivalve shellfish. **Materials and Methods:** Four samples of bivalve shellfish harvested from four locations in the Niger delta were assessed for PAHs concentrations through the use of Gas chromatography. **Results:** Results obtained from the compositional pattern of PAHs indicated the dominance of low molecular weight PAHs at Andoni location while other study locations were dominated with high molecular weight PAHs. The tissue burden of PAHs indicated bloody cockle (53.75 $\mu g\ kg^{-1}$), knife clam (50.00 $\mu g\ kg^{-1}$), mangrove oyster (40.34 $\mu g\ kg^{-1}$) and Donax clam (36.94 $\mu g\ kg^{-1}$), while diagnostic ratio showed that the PAH burden originated from the petrogenic source at Andoni while those of other locations were from pyrogenic or combustion processes. PAHs are recognized as major contributor to environmental pollution affecting aquatic ecosystems under the influence of human mediated activities. **Conclusion:** From the results obtained, the compositional pattern of PAHs in bivalve tissue found in the study locations are typical of an areas under the influence of intensive anthropogenic activities. Therefore bivalve shellfish harvested from these locations can induce potential deleterious health effects to the consumers.

Key words: PAHs, bivalve shellfish, tissue concentration, biological matrix, Niger Delta

Citation: Ukwo, S.P., M.C. Ekanem and L.S. Ndah, 2022. Compositional pattern and tissue concentration of Polycyclic Aromatic Hydrocarbons (PAHs) in bivalve shellfish from Niger Delta, Nigeria. J. Appl. Sci., 22: 84-91.

Corresponding Author: Sunday Peter Ukwo, Department of Food Science and Technology, University of Uyo, Uyo, Nigeria

Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Industrial contaminants in marine ecosystems and biota include a different group of compounds that have entered the sea through natural and anthropogenic activities[1]. Some of these contaminants are also formed during volcanic activities, bush burning, incomplete combustion of petroleum and related compounds as well as during waste incineration. These compounds are classified under the persistent organic pollutants[2]. Persistent Organic Pollutants (POPs) are organic compounds that subsist in the environment, bio-accumulate in the food chain, with the possibility of causing harmful effects to the health of living organisms and the environment. This group of priority pollutants consists of Polycyclic Aromatic Hydrocarbons (PAHs).

Polycyclic Aromatic Hydrocarbons (PAHs) include widespread environmental contaminants that may originate from anthropogenic activities such as incomplete combustion and pyrolysis processes of organic substances, gas flaring and domestic/municipal incineration and natural sources[3,4].

The fate of PAHs in the environment is reported to be non-biodegradable[5] and this implies non-reduction in accumulation and bio-magnification along the food chain[6]. PAHs are rapidly accumulated but also fairly readily metabolized in some seafood. PAHs are assimilated by seafood from exposure through food, water and sediments to a concentration far higher than those of the surrounding medium. Polycyclic aromatic hydrocarbons readily accumulate in the fatty tissues of seafood following uptake due to their lipophilic nature[7]. Unlike other organic contaminants, the retention of PAHs and their metabolites in fish tissues is higher at low temperatures when compared to shellfish at the same condition which metabolized PAHs poorly and inefficiently and therefore they tend to accumulate at higher concentrations of different PAH congeners more than the surrounding medium[8]. Bivalve shellfish such as clams, oysters and mussels, easily pile up PAHs residues from the polluted waters in higher quantities when compared to higher fishes. The most likely reason for this difference is that although fish readily break down PAHs into water-soluble compounds that are then excreted, bivalve molluscs, however, lacks any appreciable capability to break down these compounds[9]. Reports have indicated that the accumulation of PAHs in oysters generally exceeds that of higher types of seafood[8,10]. In oysters (*Crassostrea virginica*) the bioaccumulation factor (BCFs) for PAHs ranged from 189-18000 and in clean water concentrations of some PAHs decreased in a week to less than a tenth of the peak concentrations. Nordic[8], reported the accumulation levels in different species of shellfish and the transient changes in pollution as a consequence of an oil spill. Low concentrations of Low Molecular Weight (LMW) PAHs were generally found in fish and crustaceans, whereas molluscs close to the spill rapidly took up whole oil in their tissues. Most species of bivalve molluscs consumed in Nigeria are harvested from the brackish water that is exposed to varying amounts of chemical and environmental contaminants such as industrial chemicals, toxic residues from various anthropogenic activities.

Pollution of the coastal waters in the Niger Delta has continued to attract greater attention. This is due to the high level of environmental degradation posed by petroleum production and exploitation along the coastline[11,12]. Petroleum hydrocarbon from oils spills and human-mediated activities are usually incorporated into sediments where they can persist for years gradually releasing toxic substances into the immediate and remote environments[12]. Some of the deleterious effects associated with dietary intake of these contaminants include diarrhoea and gastrointestinal disorders, immune suppression, neurological disorder, reproductive impairment, developmental retardation, cardiovascular disorder, liver disease, infertility and miscarriage[13,14]. The groups most vulnerable to dietary exposure of the contaminants are child-bearing women, children below twelve years and subsistence fish farmers[15]. For better understanding and characterization of the risk presented by chemical toxins in the environment to human and ecological receptors, most researchers used benthic organisms such as bivalves as biomonitors of the levels and long-term influences of chemical toxins within the ecosystem[16].

According to Conte *et al.*[17], seafood generally is perceived as healthy food and as an alternative source of proteins. However, consumers also have the consciousness of some safety risks, e.g., potential adverse effects of shellfish contaminants on health. Also, the ability of bivalve to bioaccumulate and bioconcentrate contaminants leaves those at the highest trophic level at the greatest concentration and risk and depending on the contaminants in contact with, a wide variety of harmful effects have been reported[18]. Fishery products are considered the major sources of human contact to pollutants such as polychlorinated biphenyls, dioxins, organ chlorines polycyclic aromatic hydrocarbons, some heavy metals and other environmental toxic substances and according to Conte *et al.*[17], some differences exist in the type and levels of contaminants among regions and as such risk assessment must be performed locally.

According to Amnesty International[19] reports, Niger Delta is most known for oil and gas production in Africa. It is also recognized to be the most polluted area on earth. The prevailing widespread pollution has severely impacted negatively on the food product especially seafood obtained from the coastal waters of this region. Research has determined that there is bioaccumulation of Benzo(a)pyrene (BaP), other hydrocarbons and heavy metals has occurred in a toxic level in major high protein contents seafood such as periwinkle (*Tympanotonus fuscatus*), mudskipper and other seafood[20]. Yakubu[21] reported a benzene concentration of 0.155-48.2 μg m^{-3} in this area and this concentration represents 1:10,000 cancer risk as benzene and its associated compounds such as Polycyclic Aromatic Hydrocarbons (PAHs) and Polychlorinated Biphenyls (PCBs) are known carcinogens. Also, Gobo *et al.*[22] argued that the prevalence of diarrhoea in coastal communities of Nigeria is on the rise because of the consumption of seafood and other animals products that have been in contact with toxic contaminants.

Bivalve including mangrove oysters, bloody cockle, clams among others in the suspension or filter feeders. They take up chemical contaminants and microbes from the polluted Niger Delta waters and accumulate them in their tissue posing serious concern to their quality and safety. Therefore, the continuous consumption of bivalve molluscs from the Niger Delta waters posits or exemplifies the conflict between food benefits and food risks. The objective of this study is to investigate the compositional pattern and tissue concentration of polycyclic aromatic hydrocarbons (PAHs) in bivalve shellfish harvested from the coastal waters of the Niger Delta, Nigeria.

MATERIALS AND METHODS

Study location: The study location lies along the Atlantic coastline in the Niger Delta Region of Nigeria. Four locations were chosen for this study (Andoni, Bonny, Ibeno and Iko town). The locations were chosen because of their popularity in artisanal fishing activities particularly on bivalve shellfish which also served as an important delicacy and food for the locales. Shellfish also served as a major source of income and employment for the people in these communities. The locations are essentially estuarine with brackish water characterized by fine sandy beaches surrounded with mangrove swamp and intertidal mudflat in which Nypa vegetation dominate. The area is also naturally endowed with an abundance of rivers, creeks and streams which received water and waste from the hinterland into the Atlantic Ocean. Also, this coastal environment has continued to suffer from environmental degradation occasioned by exploration and production of petroleum, liquefied natural gas production and spillage of petroleum products.

Sample preparation and treatments: Samples of bivalve shellfish mostly consumed in these localities were harvested manually by fishermen during low tide from intertidal estuarine mudflats of the different study locations. The bivalve specimens collected were, Bloody cockle *Anadara senilis*, Donax clam (*Donax rugosus*), Knife or Razor clam (*Tagelus adansonii*) and Mangrove oyster (*Crassostrea gasar*), They were identified at the Department of Fisheries and Aquatic Environmental Management, University of Uyo. At each sampling site, twenty samples of each bivalve specimen were collected and transferred to the laboratory within 24 hrs of collection in plastic containers washed with 5% nitric acid and rinsed with distilled water before use. At the laboratory, the bivalves were promptly cleaned of incrustations, washed in distilled water to remove all dirt. Samples were shucked with the sterile scalpel to extract the flesh and intravalvular fluid into a sterile container. The extracted tissues were homogenized for the 60 s in a stomacher (Seward Laboratory Stomacher 400, England) and stored at -20°C in a scan frost deep freezer for PAHs analysis.

Determination of concentration of polycyclic aromatic hydrocarbons in bivalve samples: The target organic contaminants in this study were the 16 US EPA Polycyclic aromatic hydrocarbons (PAHs) earmarked for global monitoring. The determination of 16 priority Polycyclic aromatic hydrocarbons (PAHs) were carried out through extraction, sample clean-up, pre-concentration or sample enrichment and instrumental analysis. Before extraction, the dried bivalve samples were ground to powder using pestle and mortar to ensure homogenization. The powdered samples were then Soxhlet extracted according to the USEP a guideline as described by Cheung *et al.*[23]. Analysis of (PAHs) was done using an Agilent 6890 N Gas Chromatography with Flame Ionization Detector (GC/FID), equipped with an injector fused with a silica capillary column (DB-5 ms). Helium gas was used as the carrier with a split ratio of 50: 1 and the temperature of 300°C was maintained as set point quality control measures included the use of high purity (95-99.9%) external standard mixture. Analytical grade solvents and reagents (acetone, hexane, dichloromethane and anhydrous sodium sulphate) obtained from Merck (USA) were used for the extraction. Standard and surrogate solutions were prepared in hexane. To correct for PAH recovery efficiencies, bivalve samples were spiked with 1 mL of a solution of five internal standards (biphenyl-d, anthracene-d, phenanthrene-d, pyrene-10 10 10 d, perylene-d) each at 2 μg mL^{-1} in hexane.

Experimental design and data analysis: A two factor (4×4) factorial experiment with location and species of bivalve samples being factor A and B respectively was used to study the compositional pattern and tissue concentration of Polycyclic aromatic hydrocarbons in the Niger Delta. Data obtained from analyses were subjected to a two-way analysis of Variance (ANOVA) to evaluate the effect of location and species on bivalve molluscs. The level of significance was set at $p<0.05$. Means with significant differences were separated using Duncan-multiple range test. All experiments were conducted in triplicate and data were analyzed using XLSTAT-Pro software program, Addinsoft, Boston (USA) Version 2018.7.

RESULTS

Compositional pattern: The compositional pattern of the priority Polycyclic Aromatic Hydrocarbons (PAHs) in bivalve species from the Niger Delta are presented in Table 1 and 2 and Fig. 1, respectively. The results indicated the dominance of low molecular weight polycyclic aromatic hydrocarbons (LMW-PAHs) at Andoni location (30.03 μg kg^{-1}) while other study locations (Bonny, Ibeno and Iko town) showed the dominance of high molecular weight polycyclic aromatic hydrocarbons HMW-PAHs. Naphthalene (NaP), was absent in the bivalves harvested from three locations while Acenaphthylene (Acy) was absent in the bivalves harvested from Ibeno and Iko town locations.

Benzo(a)anthracene (BaA) and Benzo(k)fluoranthene (BkF) were equally not detected in Bonny location. The total PAH concentrations ranged from 24.68 to 62.59 μg kg^{-1} with Bonny having the highest concentration, closely followed by Andoni while Ibeno had the least concentrations.

Benzo(b)fluoranthene (BbF) had the highest concentration at Iko town (18.68 μg kg^{-1}) and Bonny (14.11 μg $μg^{-1}$) when compared to other PAH congeners. The indicator PAHs are referred to as PAH4 (benzo(a)pyrene (BaP), Chrysene (Chr) Benzo(a)anthracene (BaA) and Benzo(b)fluoranthene (BbF) were present in all the sampling locations in Table 1.

Tissue concentration: The tissue concentration of PAHs in bivalve molluscs as presented in Table 2 indicated that bloody cockle accumulated the highest concentration (53.75 μg kg^{-1}) closely followed by knife clam (50.00 μg kg^{-1} while Donax clam had the least (36.94 μg kg^{-1}). Benzo(b)fluoranthene (BbF) had the highest concentration in terms of individual PAH congeners accumulated by bivalve molluscs with the concentration of 10.39, 9.77, 7.58 and 6.67 μg kg^{-1} in bloody cockle, knife clam, donax clam and mangrove oyster, respectively. The indicators PAHs 4 were present in all bivalve samples analyzed. Also, Benzo(a)pyrene (BaP) concentration in bloody cockle, knife clam and mangrove oyster was higher than the acceptable limit of 2.0 μg kg^{-1}.

Accumulated PAH concentration in bivalve shellfish from study locations: The accumulated PAH concentration in bivalve tissue at different locations is shown in Fig. 1. Results indicated the highest accumulation at Andoni closely followed by Bonny while Ibeno location was the least. Bloody cockle accumulated the highest concentration of 83.14 μg kg^{-1} at the Andoni location followed by 76.47 μg kg^{-1} at the same location. Results from the interaction of species and location also showed variability in tissue concentration concerning location. Bloody cockle had the highest tissue concentration at Andoni and Bonny while mangrove oysters had the highest concentration at Ibeno and Iko town locations.

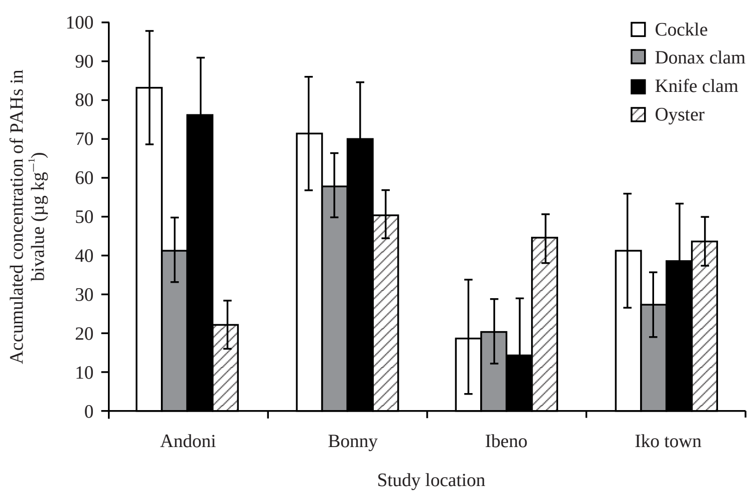

Fig. 1: Accumulated PAH concentration in bivalves species from study locations

Table 1: Compositional pattern of PAHs (μg kg^{-1}) in bivalve shellfish

PAHs	Andoni	Bonny	Ibeno	Iko Town
NaP	2.35±0.12^{a}	ND	ND	ND
Acy	7.92±1.05^{a}	3.61±0.12^{b}	ND	ND
Ace	1.28±0.25^{a}	4.06±0.01^{a}	0.84±0.14^{c}	0.18±0.01^{d}
Flu	3.87±0.40^{a}	11.35±0.05^{a}	0.89±0.10^{c}	0.76±0.14^{c}
Ant	10.45±1.01^{a}	0.88±0.20^{c}	0.95±0.24^{c}	1.91±0.12^{b}
Phe	4.16±1.12^{a}	0.30±0.02^{c}	1.69±0.01^{b}	0.16±0.14^{d}
Total LMW	30.03± 0.22^{a}	20.20±1.00^{b}	4.37±1.12^{c}	3.01±0.12^{d}
Fluo	4.04±0.51^{a}	0.88±0.11^{c}	2.25±0.03^{b}	0.71±0.14^{c}
Pyr	0.91±0.11^{c}	1.70±0.15^{b}	2.81±0.04^{a}	1.56±0.05^{b}
BaA	0.94±0.15^{b}	ND	0.91±0.20^{b}	2.29±0.01^{a}
Chr	0.15±0.02^{d}	3.13±0.01^{a}	0.51±0.01^{c}	1.02±0.12^{b}
BbF	1.32±0.01^{d}	12.26±0.01^{b}	2.15±0.11^{c}	18.68±0.02^{a}
BkF	1.18±0.10^{c}	ND	1.60±0.14^{a}	1.39±0.01^{b}
BaP	2.44±0.01^{b}	1.36±0.12^{c}	2.92±0.02^{a}	1.43±0.03^{c}
BghiP	4.30±0.01^{b}	5.11±0.01^{a}	2.19±0.10^{d}	3.79±0.01^{c}
DahP	6.99±0.11^{a}	6.99±0.11^{a}	2.45±0.11^{b}	1.51±0.01^{c}
Inp	3.58±0.15^{b}	10.98±0.02^{a}	2.52±0.12^{c}	2.50±0.02^{c}
Total HMW	25.85±0.05^{c}	42.39±1.11^{a}	20.31±0.15^{d}	34.87±0.20^{b}
∑PAHs	55.88	62.59	24.68	37.88
LMW: HMW	1.16	0.48	0.22	0.09

Means with different superscripts along the same row are significantly different (Duncan's test) $p<0.05$, Nap: Naphthalene, Acy: Acenaphthylene, Ace: Acenaphthene, Flu: Fluorene, Phen: Phenanthrene, Anth: Anthracene, Fluo: Fluoranthene, Pyr: Pyrene, perylenBaA: Benzo(a)anthracene, Chry: Chrysene, BbF: Benzo(b)fluoranthene, BkF: Benzo(k)fluoranthene, BaP: Benzo(a)pyrene, BghiP: Benzo(g,h,i), peryleneDahA: Dibenzo(a,h)anthracene, InP: Indo(1,2,3-cd)pyrene and ND: Not detected

Table 2: Tissue concentrations of PAHs (μg kg^{-1}) in bivalve shellfish

PAHs	Cockle	Donax clam	Knife clam	Oyster
NaP	ND	1.77±0.01^{a}	ND	0.58±0.01^{b}
Acy	3.38±0.01^{d}	0.73±0.12^{d}	3.17±0.25^{c}	4.25±0.11^{a}
Ace	0.41±0.01^{c}	0.47±0.11^{c}	3.68±0.11^{a}	1.81±0.11^{b}
Flu	5.59±0.02^{a}	3.20±0.14^{c}	4.12±0.10^{b}	3.96±0.10^{b}
Ant	4.35±0.11^{a}	3.56±0.11^{b}	4.29±0.12^{a}	1.98±0.11^{c}
Phe	0.38±0.4^{b}	1.34±0.11^{c}	3.12±0.11^{a}	1.47±0.14^{b}
Total LMW	14.11±0.05^{b}	11.07±0.01^{c}	18.38±1.00^{a}	14.05±0.01^{b}
Fluo	4.18±0.12^{a}	1.73±0.11^{b}	0.98±0.10^{c}	0.98±0.14^{c}
Pyr	1.44±0.22^{c}	2.29±0.12^{a}	1.53±0.01^{c}	1.71±0.15^{b}
BaA	1.07±0.01^{b}	0.48±0.11^{c}	ND	2.60±0.20^{a}
Chr	3.23±0.14^{a}	0.15±0.10^{d}	0.40±0.01^{c}	1.02±0.01^{b}
BbF	10.39±0.01^{a}	7.58±0.14^{c}	9.77±0.11^{b}	6.67±0.12^{d}
BKF	1.32±0.11^{b}	1.55±0.12^{a}	1.29±0.01^{b}	ND
BaP	2.22±0.05^{a}	1.20±0.14^{b}	2.39±0.02^{a}	2.34±0.14^{a}
BghiP	4.69±0.02^{a}	1.89±0.01^{d}	4.33±0.14^{c}	4.48±0.01^{b}
DahP	4.34±0.02^{b}	4.31±0.11^{d}	6.47±0.11^{a}	2.81±0.11^{c}
Inp	6.77±0.12^{a}	4.68±0.01^{b}	4.45±0.10^{c}	3.68±0.01^{d}
Total HMW	39.64±0.02^{a}	25.87±0.16^{c}	31.62±0.05^{b}	26.29±0.10^{c}
∑PAHs	53.75	36.94	50.00	40.34
LMN: HMW	0.36	0.43	0.58	0.53

Means with different superscripts along the same row are significantly different (Duncan's test) $p<0.05$, Nap: Naphthalene, Acy: Acenaphthylene, Ace: Acenaphthene, Flu: Fluorene, Phen: Phenanthrene, Anth: Anthracene, Fluo: Fluoranthene, Pyr: Pyrene, perylenBaA: Benzo(a)anthracene, Chry: Chrysene, BbF: Benzo(b)fluoranthene, BkF: Benzo(k)fluoranthene, BaP: Benzo(a)pyrene, BghiP: Benzo(g,h,i), peryleneDahA: Dibenzo(a,h)anthracene, InP: Indo(1,2,3-cd)pyrene and ND: Not detected

DISCUSSION

Polycyclic Aromatic Hydrocarbons (PAHs) have been considered as trace contaminants of the marine ecosystem. They are recognized as a major contributor to environmental pollution affecting the aquatic ecosystem under the influence of human activities[24,25]. Compared with levels from another part of the world, the compositional patterns of PAHs found in the study locations are typical for the area under influence of intensive anthropogenic activities. Similarly, the elevated tissue concentration of PAHs in bivalve samples in this study locations are pointers to the levels of environmental pollution in these locations vis-à-vis the human health risk associated with people of the Niger Delta consuming or depending on these bivalves as their daily source of protein. The mean values obtained from the analysis of the concentration of PAH congeners in different samples as affected by locations, species and their interactions were significantly different at ($p<0.05$). The elevated concentrations of LMW-PAHs in Andoni were a result of the high concentration of two PAH congeners anthracene (10.45 μg kg^{-1}) and acenapthylene (7.92 μg kg^{-1}). This result agrees with the findings of Anyakora *et al.*[25], which revealed that fish samples in the Niger Delta have higher LMW-PAHs, especially anthracene and phenanthrene which indicated high PAHs concentration from petrogenic sources. It is important to note that Andoni is contiguous with Ogoni land which has been described by Amnesty International[19] in their separate- reports as the most polluted marine ecosystem in the world due to leakages of petroleum products from pipelines, wellheads, spillages and other anthropogenic activities. Andoni is located at the bank of the Atlantic ocean received water and other wastes from the Ogoni land and this may account for the concentration and pattern of PAHs accumulated by bivalves samples from the area. Also, Anyakora *et al.*[25] had earlier suggested that the Niger Delta is a coastal environment being highly polluted with PAHs given the level of petroleum production, the expectation would have been a petrogenic source of PAHs. But this present study showed the dominance of HMW-PAHs and a pyrogenic source of PAHs in other study locations (Bonny, Ibeno and Iko town) which is consistent with the report of Nwaich and Ntorgbo[26] who noted that other sources of PAHs contamination could contribute at different degrees. In a related study on the PAH burden in some fish species from Bonny and Cross River estuaries, in the Niger Delta, Effiong *et al.*[27] noted that the compositional pattern of PAHs in the Niger Delta showed the dominance of three and four-ringed PAH congeners and they were the greater source of PAH burden. The diagnostic ratios showed that the PAH burden emanated from pyrogenic or combustion activities. Similarly, Yakubu[21] concluded that the continuous and efficient gas flaring and artisanal refining of petroleum products by locals have led to incomplete combustion giving rise to the formation of hazardous products especially PAHs, therefore, the nature of anthropogenic activities in a particular location can determine the compositional patterns as well as the origin of PAH burden in the study location of which the findings of this study agreed and supported that position.

The individual tissue burden of the total PAHs in the bivalve samples in the Niger Delta differ widely from one location to the other which revealed that the organisms have different selectivity for a range of PAH congeners. The variation might be ascribed to factors such as different degrees of bioavailability of the compounds and variable capacities of the organisms[28]. Similarly, the non-detection of some of these PAHs in the study was in line with other published observations[29,30]. For example, Lindén and Pålsson[24], did not detect dibenzo(a)anthracene, benzo(a)pyrene, benzo(b) fluoranthene and benzo(k)fluoranthene in muscles of both marine and freshwater species of shellfish from the Hongkong markets. The non-detection of certain PAH congeners in this study could be an indication of the absence of the compound in the sample, concentration below the detected limit or other factors earlier mentioned. The variation and preference for either LMW-PAHs and HMW-PAHs have been noted in this study and according to Zhao *et al.*[30], HMW-PAHs are usually taken up by bivalve predominantly through diet while LMW-PAHs are mostly accumulated through the water. Furthermore, while HMW-PAHs can be metabolized by some large fishes and not accumulated, bivalve molluscs lack the necessary ability to metabolize them hence they are usually accumulated[31]. Bloody cockle and knife clam being benthic are usually buried in the muddy bottom while Donax clam is found at the open coast at the intertidal section of the Niger Delta coast. These differences in their habitat may account for the higher accumulation of PAHs by bloody cockle, Knife clam than Donax clam comparatively. The abundance of HMW-PAHs in bivalve samples especially carcinogenic Benzo(a)pyrene (BaP), Benzo(b)fluoranthene (BbF) and Ind (123-cd)pyrene (InP) in concentrations above their acceptable EU limit of 2, 5 and 3 μg kg^{-1}, respectively are considered a serious health concern[26] and a s the study is the baseline, further investigation would be needed to generate enough evidence for advisory purposes. Similar reports of exceeding regulatory agencies acceptable limit in benzo(a)pyrene (2 μg kg^{-1}) and other carcinogenic PAHs were observed in marine shellfish species sampled from Ghana[4], Nigeria[26,32] and Egypt[33]. The metabolites of carcinogenic PAHs especially the acceptable marker benzo(a)pyrene can form complexes by binding with cellular DNA and can alter the genetic sequence and consequently can promote cancer[34]. The result of this study revealed the varied concentration of the total PAHs below and above 50 μg kg^{-1} which is considered as the limit for background pollution[35]. However, the presence of carcinogenic PAHs and owing to their associated carcinogenic risks, there is a need to protect bivalve consumers from dietary exposure of bivalve with increased PAH burden.

CONCLUSION

The compositional pattern of the 16 priority Polycyclic Aromatic Hydrocarbons (PAHs) in bivalve species indicated the dominance of low molecular weight PAHs in the Andoni location while Bonny, Ibeno and Iko town locations were dominated with high molecular weight PAHs. The diagnostic ratio also showed a petrogenic source at the Andoni location while other locations were from the pyrogenic or combustion processes. The concentration and tissue burden of PAHs showed that bloody cockle has the highest followed by knife clam while donax clam had the least. Also, the pattern and composition of PAHs is the reflection of the type of anthropogenic activities prevalent at the location while the concentration and tissue burden could be attributed to the benthic nature of bloody cockle and knife clam. Also, benzo(b)fluoranthene (BbF) had the highest concentration in terms of individual PAH congeners accumulated by bivalve samples while the indicator PAH benzo(a)pyrene concentration was above the acceptable limit of 2.0 μg kg^{-1}. Although some shellfish consumers may not consider the possibility of instant negative health consequences resulting from the accumulation of these contaminants in their tissues cannot be ignored, their long term effects especially in coastal areas where the consumption and exposure of aquatic life to oil spills need to be monitored closely. Polycyclic aromatic hydrocarbon is rapidly deposited by shellfish fatty tissues through their feeding pattern. The key result to be considered when studying the related health risk of PAHs is the carcinogenic effect. Human exposure to higher molecular weight PAH congeners has been characterized with a higher risk of cancer in several tissues depending on the route of exposure and the form of PAH. Therefore, maintaining clean environmental quality is vital for several socio-economic reasons. For instance, loss of confidence in seafood safety can negatively affect the seafood market.

SIGNIFICANCE STATEMENT

This study exposes the consequences of blatant and consistent abuse of the environment by International oil and gas companies operating in the Niger Delta region of Nigeria and the negligence of government and regulatory bodies in addressing the menace. This study discovered that bivalve shellfish harvested from the coastal waters of the Niger Delta contains a significant amount of Polycyclic Aromatic Hydrocarbons (PAHs) which is adjudged to be at toxic levels from a regulatory standpoint. The Niger Delta is known to be the most polluted area on earth and from the results obtained in this study the prevailing pollution has severally impacted negatively on the shellfish quality and safety. Therefore bivalve shellfish harvested from these locations can induce potential deleterious health effects to the consumers except something urgent is done by government and international oil and gas companies operating in this area.

REFERENCES

1. Ryder, J., I. Karunasagar and L. Ababouch, 2014. Assessment and Management of Seafood Safety and Quality. FAO, Italy, ISBN: 978-92-5-107511-1, Pages: 455.
2. Markmanuel, D.P. and J.M. Horsfall, 2015. Assessment of non-carcinogenic human health risk of some heavy metals in land snails commonly consumed in Bayelsa State, Nigeria. Res. J. Chem. Sci., 5: 61-66.
3. Arias, A.H., C.V. Spetter, R.H. Freije and J.E. Marcovecchio, 2009. Polycyclic aromatic hydrocarbons in water, mussels (*Brachidontes* sp., *Tagelus* sp.) and fish (*Odontesthes* sp.) from bahía blanca estuary, Argentina. Estuarine Coastal Shelf Sci., 85: 67-81.
4. Bandowe, B.A.M., M. Bigalke, L. Boamah, E. Nyarko, F.K. Saalia and W. Wilcke, 2014. Polycyclic aromatic compounds (PAHs and oxygenated PAHs) and trace metals in fish species from Ghana (West Africa): Bioaccumulation and health risk assessment. Environ. Int., 65: 135-146.
5. Doyle, E., L. Muckian, A.M. Hickey and N. Clipson,2008. Microbial PAH degradation. Advances in Applied Microbiology, Laskin, A.I., G.M. Gadd and S. Sariaslani (Eds.), Elsevier Inc., Netherlands, ISBN: 9780080922270, pp: 27-66.
6. Halek, F., G. Nabi and A. Kavousi, 2008. Polycyclic aromatic hydrocarbons study and toxic equivalency factor (TEFs) in Tehran, IRAN. Environ. Monit. Assess., 143: 303-311.
7. Shen, H., Y. Huang, R. Wang, D. Zhu and W. Li *et al*., 2013. Global atmospheric emissions of polycyclic aromatic hydrocarbons from 1960 to 2008 and future predictions. Environ. Sci. Technol., 47: 6415-6424.
8. Binderup, M.L., N. Ministerråd and N. Råd, 2004. The effect of oil spills on seafood safety: An example of the application of the Nordic risk analysis model. Nordic Council of Ministers, Copenhagen, ISBN: 9789289310567, Pages: 214.
9. Gratz, S.R., L.A. Ciolino, A.S. Mohrhaus, B.M. Gamble and J.M. Gracie *et al*., 2011. Screening and determination of polycyclic aromatic hydrocarbons in seafoods using QuEChERS-based extraction and high-performance liquid chromatography with fluorescence detection. J. AOAC Int., 94: 1601-1616.
10. Gilroy, D.J., 2000. Derivation of shellfish harvest reopening criteria following the new carissa oil spill in coos bay, Oregon. J. Toxicol. Environ. Health, 60: 317-329.
11. Wala, C., A.I. Hart, B.B. Babatunde and N. Zabbey, 2016. Assessment of human health risk from heavy metal loads in freshwater clam, Ergeria radiata, from the Nun River, Niger Delta, Nigeria. J. Environ. Earth Sci., 6: 10-20.

12. Zabbey, N. and B.B. Babatunde, 2015. Trace metals in intertidal sediment of mangrove-sheltered creeks in Niger Delta, Nigeria: Variability before and after crude oil spillage. Afr. J. Environ. Sci. Technol., 9: 371-378.
13. Mochungong, P. and J. Zhu, 2015. DDTs, PCBs and PBDEs contamination in Africa, Latin America and South-Southeast Asia-A review. AIMS Environ. Sci., 2: 374-399.
14. de Jager, C., N.H. Aneck-Hahn, M.S. Bornman, P. Farias and M. Spanò, 2012. DDT exposure levels and semen quality of young men from a malaria area in South Africa. Malaria J., Vol. 11. 10.1186/1475-2875-11-s1-p21.
15. FAO and WHO., 2011. Food and agriculture organisation of the United Nations. Report of the joint FAO/WHO expert consultation on the risk and benefit of fish consumption. FAO Fisheries and Aquaculture Report No. 978 Rome. 1-63 https://apps.who.int/iris/handle/10665/44666
16. Sarkar, S.K., H. Cabral, M. Chatterjee, I. Cardoso, A.K. Bhattacharya, K.K. Satpathy and M.A. Alam, 2008. Biomonitoring of heavy metals using the bivalve molluscs in Sunderban mangrove wetland, Northeast Coast of Bay of Bengal (India): Possible risks to human health. Clean: Soil Air Water, 36: 187-194.
17. Conte, F., A. Passantino, S. Longo and E. Voslářová, 2014. Consumers' attitude towards fish meat. Ital. J. Food Saf., 3: 178-181.
18. Figueira, E., A. Lima, D. Branco, V. Quintino, A.M. Rodrigues and R. Freitas, 2011. Health concerns of consuming cockles (*Cerastoderma edule* L.) from a low contaminated coastal system. Environ. Int., 37: 965-972.
19. Amnesty International, 2018. Negligence in the Niger Delta; Decoding shell and Eni's poor record on oil spills. Amnesty International Publication London UK. https://www.amnesty.ch/ de/themen/wirtschaft-und menschenrechte/fallbeispiele/nigeria/dok/2018/nigeria-fahrlaessigkeit-von-shell-eni/negligence-in-the-niger-delta.pdf
20. Ordinioha, B. and S. Brisibe, 2013. The human health implications of crude oil spills in the Niger Delta, Nigeria: An interpretation of published studies. Niger. Med. J., 54: 10-16.
21. Okhumode Y., 2017. Addressing environmental health problems in ogoniland through implementation of united nations environment program recommendations: Environmental management strategies. Environments., Vol. 4.
22. Gobo, A., G. Richard and I. Ubong, 2010. Health impact of gas flares on igwuruta / umuechem communities in rivers state. J. Appl. Sci. Environ. Manage., 13: 27-33.
23. Cheung, K.C., H.M. Leung, K.Y. Kong and M.H. Wong, 2007. Residual levels of DDTs and PAHs in freshwater and marine fish from Hong Kong markets and their health risk assessment. Chemosphere, 66: 460-468.
24. Lindén, O. and J. Pålsson, 2013. Oil contamination in ogoniland, Niger Delta. AMBIO, 42: 685-701.
25. Anyakora, C., H. Coker and M. Arbabi, 2011. Application of polynuclear aromatic hydrocarbons in chemical fingerprinting: The Niger Delta case study. Iran. J. Environ. Health Sci. Eng., 8: 75-84.
26. Nwaichi, E.O. and S.A. Ntorgbo, 2016. Assessment of PAHs levels in some fish and seafood from different coastal waters in the Niger Delta. Toxicol. Rep., 3: 167-172.
27. Effiong, I.A., F.I. Bassey, C.M.A. Iwegbue, O.D. Ekpa and S.A. Williams *et al*., 2016. Polycyclic aromatic hydrocarbons in three commercially available fish species from the bonny and cross river estuaries in the Niger Delta, Nigeria. Environ. Monit. Assess., Vol. 188. 10.1007/s10661-016-5479-9.
28. Zuloaga, O., A. Prieto, A. Usobiaga, S.K. Sarkar and M. Chatterjee *et al*., 2009. Polycyclic aromatic hydrocarbons in intertidal marine bivalves of sunderban mangrove wetland, India: An approach to bioindicator species. Water, Air, Soil Pollut., 201: 305-318.
29. Nasr, I.N., Neveen, H.A. EL-Enaen and T.A. Yosef, 2012. Study of some polycyclic aromatic hydrocarbons residues in fish at sharkia governorate markets in relation to public health. Global Veterianaria, 8: 670-675.
30. Zhao, Z., L. Zhang, Y. Cai and Y. Chen, 2014. Distribution of polycyclic aromatic hydrocarbon (PAH) residues in several tissues of edible fishes from the largest freshwater lake in China, Poyang Lake, and associated human health risk assessment. Ecotoxicol. Environ. Safety, 104: 323-331.
31. Ramesh, A., S.A. Walker, D.B. Hood, M.D. Guillén, K. Schneider and E.H. Weyand, 2004. Bioavailability and risk assessment of orally ingested polycyclic aromatic hydrocarbons. Int. J. Toxicol., 23: 301-333.
32. Anyakora, C., A. Ogbeche, P. Palmer and H. Coker, 2005. Determination of polynuclear aromatic hydrocarbons in marine samples of siokolo fishing settlement. J. Chromatogr. A, 1073: 323-330.
33. Said, T.O., 2007. Determination of persistent organic pollutants in sediment and fish of the western coast of Alexandria, Egypt. Chem. Ecol., 23: 289-302.
34. Mohammed, Z., J.C. Akan, L.I. Bukar and A.M. Idi, 2017. Cancer and non-cancer risk associated with PAHs exposure from consumption of fish from Komadugu River Basin, Yobe State, Nigeria. J. Aquat. Pollut. Toxicol., Vol. 1.
35. Ruiz, Y., P. Suarez, A. Alonso, E. Longo, A. Villaverde and F.S. Juan, 2011. Environmental quality of mussel farms in the vigo estuary: Pollution by PAHs, origin and effects on reproduction. Environ. Pollut., 159: 250-265.