

Potential sources and variation of polycyclic aromatics hydrocarbons in selected aquatic media of jetties within Port Harcourt and its environs

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Abstract

The study considered the sources and variability of poly aromatic hydrocarbons (PAHs) concentrations in crabs and sediments from Iwofe and Borikiri areas of Port Harcourt City, Rivers State. Gas chromatography coupled with flame ionization detector (GCFID was used to evaluate the levels of PAHs in the samples.). The mean concentration of (PAHs) in crab of Iwofe River was $2.8E-5 \pm 2.5E-4$ mg/kg, and tPAHs for Iwofe was $1.2E-2 \pm 1.8E-3$ mg/kg and the most dominant PAHs were Fluorene ($4.0E-3 \pm 1.0E-3$ mg/kg), Benzo (a) Pyrene ($3.2E-3 \pm 2.0E-4$ mg/kg), and Benzo (a) Anthracene ($1.4E-3 \pm 2.0E-4$ mg/kg). Borikiri location had tPAHs concentration of $3.3E-2 \pm 5.3E-4$ mg/kg and Dibenz (a, h) Anthracene ($1.5E-2 \pm 1.0E-5$ mg/kg), Benzo (a) Pyrene ($8.2E-3 \pm 4.0E-5$ mg/kg), and Benzo (a) Anthracene ($4.0E-3 \pm 2.0E-5$ mg/kg) all had elevated concentrations. The mean values of PAHs in sediments was $4.9E-3 \pm 3.7E-3$ mg/kg. Iwofe location recorded total PAHs of $4.5E-3 \pm 5.6E-5$ mg/kg, Benzo (a) Pyrene, Pyrene, and Fluorene had the highest concentration with values of $3.2E-3 \pm 1.0E-5$ mg/kg, $5.0E-4 \pm 2.3E-5$ mg/kg, and $3.0E-4 \pm 1.0E-5$ mg/kg. Borikiri had total PAHs of $5.3E-3 \pm 4.4E-4$ mg/kg, Benzo (g,h,i) Perylene, Indeno (1,2,3-cd) Pyrene, and Naphthalene had the highest concentrations of $1.8E-3 \pm 1.8E-4$ mg/kg, $1.4E-3 \pm 1.0E-4$ mg/kg, and $7.0E-4 \pm 3.0E-6$ mg/kg respectively. The sources identification for crab and sediments from both jetties indicated variable sources of PAHs of the study area; combustion, petrogenic and pyrogenic sources. The result indicated that the crab and sediments of the study area have been contaminated with PAHs.

Keywords: polycyclic aromatic hydrocarbons, sources, crab, sediments, and pollution

Introduction

The environment is the sum total of man's surrounding; air, water, plants, animals as well as abiotic and biotic components. There are four inter-connecting spheres that constitute the environment. They include the atmosphere, hydrosphere, lithosphere and biosphere (Udosen, 2012) [18]. Hydrosphere makes up about 75% of the earth's surface either as oceans, lakes, ponds, streams, and the ocean occupied major part of the earth surface. For the survival of life forms in the environment, water is very necessary and also water is a universal solvent. Water play a vital role for the survival Of living organisms despite its usage as a universal solvent.

The anthropogenic activities alters the genuine conditions of the environment, Thus, pollution had its origin with the development and urbanisation of Cities, mining of minerals and natural resources which could lead to the spills and discharge of petroleum hydrocarbons into the environment. Oil spills and seepages are precursors to the release of contaminants into the environment especially PAHs.

PAHs are a group of fused benzene ring compounds formed due to inadequate burning or intense procedures that involved organic matter, which is associated with low supply of oxygen (Benner *et al.*, 1990) [6]. They are also formed due to the exposure of composite organic materials to elevated temperatures or compressions. The origin of some PAHs could be traced to pigments and steroids. The presence of PAHs in soil strata may be from a numerous sources, which are crude oil spills and other pyrolytic activities like the incomplete incineration of organic remains such wood burning and animal tissues (Benner *et al.*, 1990;

Freeman and Catteil, 1990) [6], practice of composting for fertilizer production using plant and animal wastes (Smith *et al.*, 2001) [17] and electrical generating plants and flare boilers (Van Brummelen *et al.*, 1996) [19]. PAHs are transported over long distances because they persist in the atmosphere (Bakker *et al.*, 2001) [5]. Inengite *et al.*, (2012) [12] reported that large amount of PAHs are produced by the cracking of crude oil. PAHs are compounds which contains only carbon and hydrogen fused together in three or more benzene rings containing. Variation in the arrangement of the rings may possibly lead to changes in the physical and chemical behaviour of polycyclic compounds. Different types of polycyclic compounds exists and they are classified as polycyclic organic matter (POM), polynuclear aromatic hydrocarbons, polynuclear aromatics (PNAs) and polynuclear hydrocarbons (ATSDR, 2009). Polycyclic compounds constitute some of the toxicants discharge to the environment and most of which are carcinogenic. Prolong exposure of PAHs to human normally causes health challenges such as cancer and mutation of genes (ATSDR,2009) The various anthropogenic activities in the Niger Delta area had introduced petroleum products into the environment and these contains PAHs, heavy metals which have persistent potentials to remain and increase in environmental settings. This purpose of the study is to evaluate the sources and variability of PAHs in crabs and sediments from Borikiri and Iwofe parts of Port Harcourt. Crabs and other aquatic organisms such as periwinkle oysters and prawn are consumed regularly by the inhabitants of these areas of the city, thus it becomes very imperative to carry out this research.

Materials and Method

Study Area

Port Harcourt is a cosmopolitan city and is the headquarter of Rivers State. It has an area of about 1811.6 Km² with a population estimate of about 3 million persons. It is the main city of Rivers state and it has grown to join nearby towns to form a large city. Port Harcourt is situated within latitude 4°45'N and 4°55'N and longitude 6°55'E and 7°55'E respectively. Iwofe is located at Rumuolumeni area of Port Harcourt, while Borokiri is located in old Port Harcourt main City. It lies at latitude 4°49'N and longitude 7°35'E. Borokiri and Iwofe lies at the southern part of the city with adjoining creeks which are tributaries of New Calabar River where many human activities that discharge petroleum products occurs daily.

Sample Collection

Fresh samples of crab (*Brachyura*) were obtained directly from fisherman at the two study sites. At each site, twenty (20) similar size of crab samples were collected alive and placed in plastic containers. They were then transported to the Department of Chemistry, Ignatius Ajuru University of Education Rumuolumeni Port Harcourt for authentication, identification and analysis. On the other hand the sediment samples were collected with soil auger during low tide from 0-10 cm depth at the sites and were placed in a polymeric containers that were labelled accordingly.

Sample Preparation

The crab samples were opened and a stainless knife was used to remove the muscles from the shells of all the samples. The samples were mixed together to obtain an aggregate sample. Thereafter, the samples were oven dried at temperature of 105°C until a constant weight was obtained. The dried sample was then homogenised before extraction. The sediment samples were allowed to dry freely

in the open air. They were placed on polyether material for 14 days in the laboratory to dry and later oven dry at 105 °C and later ground to powder before extraction.

Sample extraction

Five (5) g of ground sample was wrapped with a Whatman fibre paper and was extracted using Soxhlet extractor through 100 ml Dichloromethane (DCM) and mixture was allowed for continuous extraction for a period of 24 hours. The rotatory apparatus was allowed to spin at a rate of 6 cycles/hr. A rotatory evaporator operated at 40 °C was used to concentrate the obtained extract (Paramanik and Rajalakshmi, 2013)^[16].

Sample GC Analysis

PAHs was determined by the use of gas chromatography (6890 series), which was furnished with a twin detector (FID-ECD), double support and triple as automatic sampler by means of helium transporter gas and a quadrupole mass spectrometer (Agilent 5975 MSD) centred on the method of USEPA (1994). A 2.0 µl volume of the extracts were introduced into the GC port operated at the column settings. HP-5 cross-linked PH-ME siloxane, of length 30m, internal dimension of 0.25 mm, 1 µm thick fitted with helium carrier gas fixed in the faultless, continuous current approach flow rate of 1.2 ml/min. The various PAHs determined in the various samples were established by means of the existence of shift ions, which either qualifies or quantifies the observed component as revealed by way of their retention times that corresponds to their separate criteria or standards and reports from literature;

Results and Discussion

The results of the analysis of PAHs in both crab and sediment samples are shown in Tables 1 and 2.

Table 1: Concentration (±std) in mg/ Kg of polycyclic aromatic hydrocarbons in crab samples from the study area

PAHs(mg/Kg)	Iwofe	Borokiri	Mean	EUR 2019
Nap	1.3E-3±1.2E-4	2.5E-3±3.4E-4	1.9E-3±8.5E-4	
Ace	-	-	-	
Acen	-	-	-	
Flo	4.0E-3±1.0E-3	1.0E-3±1.0E-4	2.0E-3±2.2E-3	
Phe	-	5.0E-4±2.0E-5	2.5E-4±3.5E-5	
Ant	-	-	-	
Flu	9.0E-4±3.0E-5	-	4.5E-4±6.4E-4	
Pyr	8.0E-4±3.0E-6	-	4.0E-4±5.7E-4	
BaA	1.4E-3±2.0E-4	4.0E-3±2.0E-5	9.0E-4±7.1E-4	
Chr	-	-	-	
BbF	5.0E-4±3.0E-6	2.0E-4±2.0E-6	3.5E-4±2.1E-4	
BkF	-	-	-	
BaP	3.2E-3±2.0E-4	8.2E-3±4.0E-5	5.7E-3±3.5E-3	2.0E-3
BgP	-	1.1E-3±1.0E-6	5.5E-4±7.8E-4	
DbA	-	1.5E-2±1.0E-5	7.4E-3±1.0E-2	
IdP	-	-	-	
Total PAHs	1.2E-2±1.8E-3	3.3E-2±5.3E-4	2.0E-2±1.5E-2	1.2E-2

Note: - = Not Detected, Nap. = Naphthalene, Ace. = Acenaphthylene, Acen = Acenaphthene, Flo. = Fluorene, Phe.= Phenanthrene Ant.= Anthracene, Flu.= Fluoranthene, Pyr.= Pyrene, BaA = Benz (a) Anthracene, Chr.=Chrysene, BbF = Benzo (b) Fluoranthene, BkF = Benzo (k) Fluoranthene, BaP = Benzo (a) Pyrene, BgP = Benzo (g,h,i) Perylene, DbA = Dibenz (a,h) Anthracene and IdP = Indeno (1,2,3-cd) Pyrene

Table 1 revealed that tPAHs 1.2E-2±1.8E-3 mg/Kg were found in Iwofe River, while the most dominant PAHs were fluorene (4.0E-3±1.0E-3 mg/kg), benzo (a) pyrene (3.2E-3±2.0E-4 mg/Kg), and benzo (a) anthracene (1.4E-3±2.0E-4

mg/kg).On the other hand, the following PAHs; acenaphthylene, acenaphthene, phenanthrene, anthracene, chrysene, benzo (k) fluoranthene, benzo (g,h,i) perylene, dibenz (a, h) anthracene, and indeno (1,2,3-cd) Pyrene were

not detected at Iwofe. The result at Borikiri showed that tPAHs of $3.3E-2 \pm 5.3E-4$ mg/Kg was obtained at the site and the PAHs with elevated concentration were dibenz (a, h) anthracene ($1.5E-2 \pm 1.0E-5$ mg/kg), benzo (a) pyrene ($8.2E-3 \pm 4.0E-5$ mg/kg), and benzo (a) anthracene ($4.0E-3 \pm 2.0E-5$ mg/kg). Though, PAHs such as; acenaphthylene, acenaphthene, anthracene, fluoranthene, pyrene, chrysene, benzo (k) fluoranthene, and indeno (1,2,3-cd) Pyrene were not detected. The results indicated that the non-carcinogenic PAHs obtained were more than the carcinogenic compounds. The overall mean of PAHs was $2.0E-2 \pm 1.5E-2$, while the PAHs with the overall highest mean concentration was DbA ($7.4E-3 \pm 10E-2$ mg/Kg).

The concentrations of PAHs in crab samples from Borokiri was found to be higher when compared with those of Iwofe. This may possibly be ascribed to the higher levels of human activities in the area, and also the age of the organism because older organisms bioaccumulate more chemical substances than the younger ones (Abdolahpur *et al.*, 2014)^[1]. Generally the levels of PAHs obtained in crab samples were slightly above the allowed limit. This could be credited to the oil and gas flaring activities, water transportation, vessels refuelling, boat building, and dredging activities rampant in the area.

The observed concentration of benzo (a) pyrene was below the set limit stipulated by European Commission (EC) of 0.002mg/Kg which indicated low contamination from carcinogenic PAHs. The result showed that dibenz (a, h) anthracene contributed (37%), benzo (a) pyrene (28.5%), fluorene (10%), and naphthalene (9.5%) to the total PAHs. The results showed that ring 4 and 5 were more in the non-carcinogenic and carcinogenic PAHs.

The mean concentration ($2.0E-2 \pm 1.5E-2$ mg/kg) of PAHs of this study was below the concentration ($63.43 \mu\text{g/g}$) reported by Amos-Tautua *et al.*, (2013). However, the reported values of Ladipo *et al.*, (2012) and Abdolahpur, *et al.*, (2014)^[1] on pelagic fish were higher than the results obtained in this work.

The values of PAHs obtained in crab tissues revealed the extent of PAHs pollution in the water obtained from the study area. The most probable bases from which the PAHs were introduced into the water around the area includes oil leakages, unintended releases of oil from transport and spinning boats, releases of waste and effluents from industries, water runoff from burned garbage site, domestic wastes dumped in the river, and smoke emissions from industries, automobile exhaust, and recently the activities of illegal refineries popularly called 'Kpo fire'.

Table 2: The concentration (\pm std) in mg/Kg of polycyclic aromatic hydrocarbons in sediment samples from the two locations

PAHs(mg/kg)	Iwofe	Borikiri	Mean	USEPA 2009
Nap	$2.0E-4 \pm 1.0E-5$	$7.0E-4 \pm 3.0E-6$	$4.5E-4 \pm 3.5E-4$	0.14
Ace	-	-	-	3.40
Acen	-	-	-	
Flo	$3.0E-4 \pm 1.0E-5$	$5.0E-4 \pm 3.0E-5$	$4.0E-4 \pm 1.4E-4$	2.30
Phe	-	$4.0E-4 \pm 2.0E-5$	$2.0E-4 \pm 2.8E-4$	
Ant	-	-	-	17.00
Flu	$2.0E-4 \pm 2.0E-6$	-	$1.0E-4 \pm 1.4E-4$	2.30
Pyr	$5.0E-4 \pm 2.3E-5$	-	$2.5E-4 \pm 3.5E-4$	170
BaA	$1.0E-4 \pm 1.0E-6$	$4.0E-4 \pm 2.0E-4$	$2.5E-4 \pm 2.1E-4$	$1.5E-4$
Chr	-	-	-	0.015
BbF	-	$1.0E-4 \pm 1.0E-5$	$5.0E-5 \pm 7.0E-5$	$1.5E-4$
BkF	-	-	-	$1.5E-3$
BaP	$3.2E-3 \pm 1.0E-5$	-	$1.6E-3 \pm 2.2E-3$	$1.5E-5$
BgP	-	$1.8E-3 \pm 1.8E-4$	$9.0E-4 \pm 1.3E-3$	
DbA	ND	$1.4E-3 \pm 1.0E-4$	$7.0E-4 \pm 9.9E-4$	$1.5E-5$
IdP	-	-	-	
Total PAHs	$4.5E-3 \pm 5.6E-5$	$5.3E-3 \pm 5.4E-4$	$4.9E-3 \pm 3.7E-3$	

Note: ND = Not Detected, Nap. = Naphthalene, Ace. = Acenaphthylene, Acen = Acenaphthene, Flo. = Fluorene, Phe.= Phenanthrene Ant.= Anthracene, Flu.= Fluoranthene, Pyr.= Pyrene, BaA = Benz (a) Anthracene, Chr.=Chrysene, BbF = Benzo (b) Fluoranthene, BkF = Benzo (k) Fluoranthene, BaP = Benzo (a) Pyrene, BgP = Benzo (g,h,i) Perylene, DbA = Dibenz (a,h) Anthracene and IdP = Indeno (1,2,3-cd)Pyrene, E=Exponential

The result revealed that PAHs concentrations in the sediment samples at Iwofe had a total PAHs concentration of $4.5E-3 \pm 5.6E-5$ mg/kg and ranged 0.00 to $3.2E-3 \pm 1.0E-5$ mg/Kg. Benzo (a) Pyrene, Pyrene, and Fluorene had the highest concentration of $3.2E-3 \pm 1.0E-5$ mg/kg, $5.0E-4 \pm 2.3E-5$ mg/kg, and $3.0E-4 \pm 1.0E-5$ mg/kg respectively. However, acenaphthylene, acenaphthene, phenanthrene, anthracene, chrysene, benzo (b) fluoranthene, benzo (k) fluoranthene, benzo (g,h,i) perylene, dibenz (a,h) anthracene and indeno (1,2,3-cd) pyrene were not detected in the sediment samples. Table 2 revealed that Borikiri location had a total PAHs concentration of $5.3E-3 \pm 4.4E-4$ mg/kg that ranges 0.00 to $1.8E-3 \pm 1.8E-4$ mg/kg. The result further showed that elevated concentration of Benzo (g,h,i) Perylene, Indeno (1,2,3-cd) Pyrene, and Naphthalene were obtained which were $1.8E-3 \pm 1.8E-4$ mg/kg, $1.4E-3 \pm 1.0E-4$

mg/Kg, and $7.0E-4 \pm 3.0E-6$ mg/Kg respectively. The result showed that the values of acenaphthylene, acenaphthene, anthracene, fluorathene, pyrene, chrysene, benzo (k) fluoranthene, benzo (a) pyrene and indeno (1, 2, 3-cd) pyrene were not identified. The overall mean concentration of the total PAHs was $4.9E-3 \pm 3.7E-3$ mg/Kg and benzo (a) pyrene recorded the highest concentration.

The levels of PAHs observed in the samples collected from the sediments strata from Borikiri were found to be higher than the values detected at Iwofe. This may be attributed to intense anthropogenic activities and tidal variation within the area. Borikiri area is closer to Port Harcourt Wharf where there is loading and offloading of petroleum products and importation of other goods, Secondly, Borikiri is the main route to Bonny island where NLG Companying is located.

The total mean concentration ($4.9E-3 \pm 3.7E-3$ mg/kg) of PAHs gotten from this investigation was lower than the results observed elsewhere on PAHs (Yu *et al.*, 2006; Orecchio, 2010; Obini *et al.*, 2013) [22, 15, 14]. However, Chen *et al.* (2015) observed very high values of sediment PAHs where values were up to 200 mg/Kg in the sediment of Weigh River in Northwest China, which was higher than the result of this study.

According to Wang and Fingas (1999) [21], the source of PAHs is detected and differentiated using its distribution pattern. The ratio of the LMW to the HMW is applied in the identification of the source of the PAHs present in the environment. If LMW/HMW is less than 1 it means the sources is pyrogenic while if greater than 1, the sources is petrogenic. The ratios of Ant/(Ant+Phe) and Flt/(Flt+Pyr)

was also employed to differentiate combustion of petroleum and pyrogenic incineration. Ant/(Ant+Phe) < 0.1 points to a petrogenic root, whereas Ant/(Ant+Phe) > 0.1 specifies a pyrogenic root. Furthermore, a Flt/(Flt+Pyr) < 0.40 single out a petrogenic source. Flt/(Flt+Pyr) > 0.50 is typical of biomass/firewood incineration origin and ratios which falls within 0.4 and 0.5 is indicative of the burning of petroleum products (Yunker *et al.*, 2002) [23]. However, when Ant and Phe were undetected, the diagnostic and ring analysis is done with other PAHs (Lu and Zhu, 2012). Also, BaA/(BaA+Chr) values lower than 0.2 infers a petrogenic source, while values > 0.25 is of pyrogenic sources. The results of the ring and diagnostic analysis are shown in Table 3 and 4.

Table 3: Possible sources of PAHs in this study using the ring ratio

PAHs	Iwofe (crab)	Iwofe (Sediments)	Borikiri (crab)	Borikiri (Sediments)
LMW	0.0053	0.0005	0.004	0.0014
HMW	0.0067	0.004	0.029	0.0033
Ratio	0.791	0.125	0.138	0.454
Sources	<1 (Pyrogenic)	<1 (Pyrogenic)	<1 (Pyrogenic)	<1 (Pyrogenic)

Table 4: Possible sources of PAHs in this study using diagnostic ratio

PAHs Ratios	Iwofe (crab)	Iwofe (sediment)	Borikiri (crab)	Borikiri (Sediments)
Ant/(Ant+Phe)	-	-	-	-
BaA/(BaA+Chr)	1	1	1	1
Flu/(Flu+Pyr)	0.529	0.444	-	-

The levels of PAHs in the crab and sediment were of mixed rings because high molecular weight did not dominate the low molecular weight. The results from the two locations revealed that HMW is slightly higher than the LMW which implies slight carcinogenic. The pyrogenic PAHs are related to combusted sources that may not be link to petroleum sources. This is because the HMW were mostly pyrogenic, however the results obtained showed that the PAHs were of multi sources because the values were close to 1 (Ilechukwu *et al.*, 2016) [11]. The outcome of this investigation revealed that the major source of PAHs was pyrogenic which agreed with work reported by Al-Saad *et al.*, (2006) [3] on PAHs sources in the Euphrates River.

Conclusion

The findings of this study showed that variable levels of cancer and non-cancer causing PAHs obtained in the crab and sediments were of mixed sources and this depends on the type of activities that occurred in the study area. Generally, the levels of PAHs observed in this study were low, which revealed that pyrogenic, combustion and petrogenic were the key sources of PAHs to the environment. The study revealed that the biota (crab), and sediments around jetties of the studied areas of Port Harcourt is contaminated with PAHs. Therefore, there is need to educate / enlighten the inhabitants of the area against the danger of PAHs pollution. Because prolong exposure of PAHs to human may lead to serious health challenges such as cancer and mutation of genes if the discharge of petroleum products to the environment is not checked.

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