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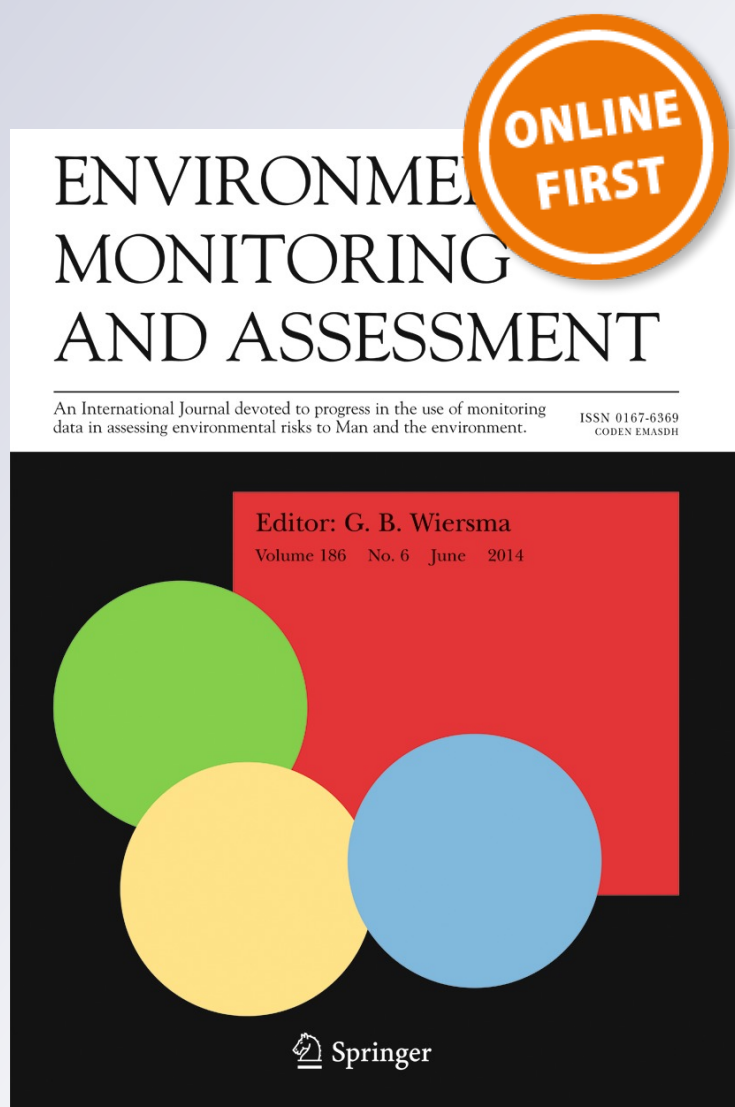
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# Occurrence and distribution of polycyclic aromatic hydrocarbons in surface microlayer and subsurface seawater of Lagos Lagoon, Nigeria

Nsikak U. Benson · Joseph P. Essien ·  
Francis E. Asuquo · Adeola L. Eritobor

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**Abstract** Polycyclic aromatic hydrocarbons (PAHs) in surface microlayer (SML) and subsurface water (SSW) of Lagos Lagoon were investigated using gas chromatography-electron capture detector (GC-ECD) technique to ascertain their occurrence and spatial distribution, origin, enrichment, and carcinogenicity. Total PAH ( $\Sigma$ PAH) concentrations ranged from 9.10 to 16.20  $\mu\text{g L}^{-1}$  in the SML and 8.90 to 13.30  $\mu\text{g L}^{-1}$  in the SSW.  $\Sigma$ PAH concentrations were relatively higher in the SML than the underlying SSW samples. The enrichment factors (EFs) of  $\Sigma$ PAHs ranged from 0.76 to 1.74 while the EFs of the individual PAHs varied from 0.50 to 2.09. In general, the EFs values calculated in this study were consistent or slightly less than the EFs reported for similar coastal seawater ecosystems. A

correlation between the EFs of fluoranthene and pyrene indicated a positive significant value ( $R=0.9828$ ,  $p<0.0001$ ,  $n=6$ ). Source analyses using the phenanthrene/anthracene and fluoranthene/pyrene ratios indicated the dominance of petrogenic-derived PAHs. Furthermore, enhanced concentrations of BaP (strong carcinogenicity) in SML and SSW samples, which resulted in higher EFs, could pose serious ecological and human health risks.

**Keywords** PAHs · Surface microlayer · Subsurface water · Enrichment · Lagos Lagoon

## Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of ubiquitous semivolatile organic compounds that are generally associated with petrogenic, pyrolytic, and diagenetic sources (Burguess et al. 2003; Dahle et al. 2003). In the past two decades, PAHs studies in coastal marine ecosystems have drawn considerable attention and are intensively investigated and monitored principally because of their bioaccumulative potential, mutagenicity, carcinogenicity, toxicity, and biopersistence (Connell et al. 1997; Sprovieri et al. 2007; Li et al. 2009; Fang et al. 2012; Qin et al. 2013). Natural (biogeochemical degradation of organic matter) and anthropogenic (crude oil spills, incomplete combustion of biomass and fossil fuels, and waste incineration) sources of PAHs in surface water, sediments, and biota of aquatic ecosystems especially in urbanized areas are

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widespread and variable (Law 1994; Readman et al. 2002; Latimer and Zheng 2003; Ahrens and Hickey 2003; Kannan et al. 2005; Orgi et al. 2006; Benson et al. 2007; Benson and Essien 2009). Many researchers have indicated that coastal lagoons, harbors, and estuaries are potential hotspots of PAHs contamination, and are mainly originated from anthropogenic sources (Tian et al. 2004; Abbas and Brack 2005; Benson and Essien 2009; Ya et al. 2014). Many PAHs congeners are carcinogenic or mutagenic. Eight PAHs typically considered as possible carcinogens are benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene (B(a)P), dibenzo(a,h)anthracene, indeno(1,2,3-cd)pyrene, and benzo(g,h,i)perylene (Menzie et al. 1992; Wang et al. 2002).

PAHs can be divided into three main classes according to their characteristic fingerprints. The most important input of PAHs into the marine environments is from pyrolytic sources, anthropogenic industrial activity, or natural fires. These sources give rise to complex mixtures of PAHs characterized by high abundance of parent PAH and a low proportion of alkylated PAHs. The second group is constituted of petroleum hydrocarbons (petrogenic sources) due to petroleum transportation, off-shore exploration, or natural oil seeps. The composition of petroleum hydrocarbons is very complex and is characterized by a high abundance of alkylated PAHs. Finally, some PAH compounds may have a diagenetic origin. Most frequently detected perylene can be derived from biogenic precursors via short-term diagenetic process. Perylene could also be derived from aquatic material or diatoms (Venkatesan 1988; Burgess et al. 2003; Dahle et al. 2003). In the case of diagenetic origin, very few compounds are generated in comparison to the complex mixtures of PAHs generated by the other sources. The relative abundance and occurrence of PAHs with two- and three-ring hydrocarbons can be used to distinguish between petrogenic and pyrogenic sources (Robertson 1998). More specifically, the phenanthrene/anthracene (PHE/ANT) and fluoranthene/pyrene (FLT/PYR) ratios are widely used to distinguish between PAHs of diverse origin (Budzinski et al. 1997).

Lagos Lagoon represents a highly stressed coastal lagoon due to increasing pressure on its coastal resources from natural processes and anthropogenic activities such as urbanization and

industrial development. The Lagoon system is also subjected to accidental and intentional domestic wastes such as industrial effluents, municipal inputs, and crude oil spillage (which arise from pipe lines leakage, accidental spills from tankers, and wastewater from industries among others). For more than four decades, various multinational companies operating onshore and offshore the coastal environment in Nigeria have undertaken the exploitation of the vast crude oil resources especially along the coastline and marine systems. Following this, Nigeria's coastal aquatic ecosystems have been prone to increasing ecological challenges owing to diverse pollutants released into them. Lagoons and estuaries by their nature are highly fragile habitats. Therefore, it is imperative to ascertain and characterize their pollution statuses. These goals can be achieved through routine systematic generation of environmental data and information over a time frame with a view to ascertaining the magnitude of their pollution status.

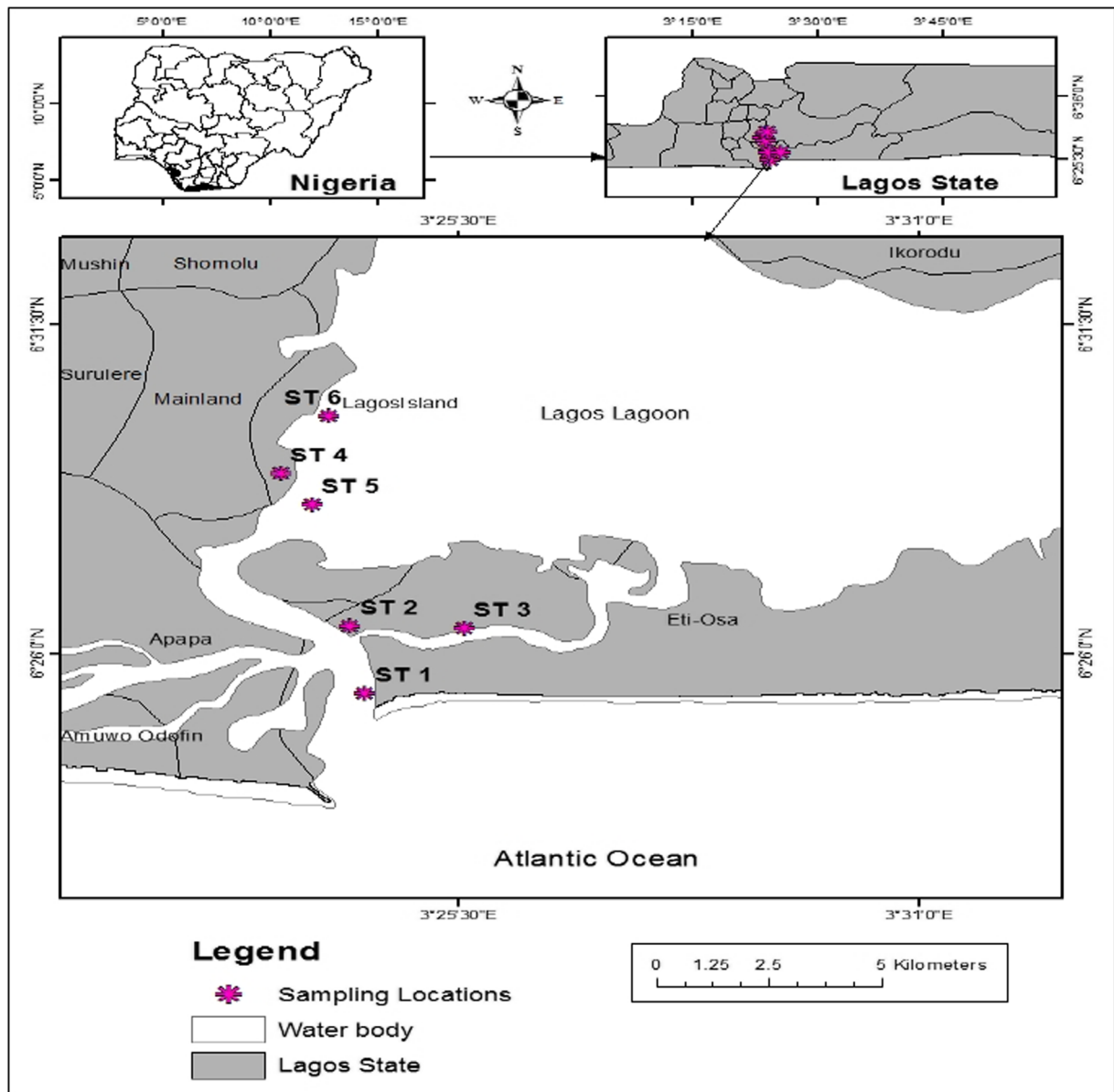
Documented studies on hydrocarbons concentrations in surface microlayer (SML) and subsurface water (SSW) of Lagos Lagoon are sparse. However, evidence of the occurrence of petroleum hydrocarbons in surface water, sediment, and local seafood species of an aquatic ecosystem in the oil-producing Niger Delta has been reported (Asuquo et al. 1999; Osuji and Ezebuoro 2006; Anyakora and Coker 2006; Benson and Essien 2009). Very limited data is available on concentrations and spatial variability of PAHs in the current study area. There are no published reports documenting the occurrence of PAHs in the SML water in the Lagos Lagoon, and there are no data concerning PAHs enrichment in the SML and SSW in this coastal lagoon system, showing that studies are required. The surface microlayer as well as the subsurface layer, being the subtle portions of aquatic systems owing to increasing pollution issues of ecological safety, are of great concern globally. The main aims of this study are (1) to provide first assessment data of PAHs concentrations in SML and SSW of Lagos Lagoon, (2) to determine the spatial distribution of PAHs in the surface microlayer and subsurface seawater, and (3) to evaluate the potential sources and fates of PAHs in Lagos Lagoon.

## Materials and method

### Description of study area

The Lagos Lagoon (Fig. 1) is an aquatic ecosystem, strategically located within the Lagos metropolis, cutting across the southern part of the metropolis, and links the Atlantic Ocean (in the west and south) and Lekki Lagoon (in the east). It is about 6,354.788 km<sup>2</sup> in area and 285 km in perimeter. The lagoon comprises three main segments: the Lagos Harbour, Metropolitan, and

the Epe Division segments. The Lagoon provides places of abode and recreation and means of livelihood and marine transportation. There is a significant proliferation of urban and industrial establishments along the coastline of the Lagoon, which has led to the unregulated introduction of a complex mixture of both urban and untreated industrial effluents into the Lagos Lagoon. In addition to wastewater from industries, there are domestic sewage discharges and garbage and wood shavings from sawmill depots along the shores of the lagoon.



**Fig. 1** Map of Lagos Lagoon and surrounding areas showing the water sampling locations. *Inset:* map of Nigeria and Lagos State

## Sample collection and pretreatment

With the aid of global positioning system (GPS), six sample stations were designated and their coordinates recorded. The designated stations were Oceanography jetty (ST1), Bonny camp (ST2), Falomo Bridge (ST3), Apapa (ST4), Ijora (ST5), and Okobaba (ST6). Water samples from six locations (Fig. 1) were collected using improvised screen sea surface microlayer sampler and Niskin water sampler. The screen sampler consists of the screen (a wire mesh of about 10 to 16 wires per inch), two handles attached to a framework, which supports this screen having a dimension of 65 by 45 cm. Surface microlayer (SML) water samples were collected by holding the rectangular screen by its handles in a horizontal position and parallel to the ocean surface for about 5 s after which the screen was withdrawn and then replaced. This was done several times before taking each sample in order to condition the screen wires to the chemical substance in the water. The screen was then withdrawn from beneath the surface of the water through the sea-air interface while still maintaining the horizontal position. As the screen is raised through the water below the surface, seawater merely flows between the wires and when passing through the surface, thin segment of the surface layer between the wires was then immediately tilted towards one rear corner of the frame, so that the collected surface water can drain into a glass collection container. On the other hand, subsurface layer water samples were collected using Niskin bottles lowered to 15 to 20 cm. Precisely 12 samples each of surface microlayer and subsurface seawater were taken from the designated locations.

Prior to laboratory analysis, the water samples collected were stored in clean, well-labeled glass bottles, preserved in ice-packed coolers, and transported to the laboratory. Prior to analysis, the water samples were preserved in the refrigerator at 4 °C for 1 day. A portion of each sample was taken out for determination of total suspended solids using a portable data logging spectrophotometer.

## Determination of PAHs concentration in water samples

### *Extraction and fractionation of water samples*

The water samples sediments were extracted and fractionated using liquid/liquid extraction method (USEPA

1997). The procedural extraction method was strictly followed in order to minimize interferences that may have arisen from contaminants in glassware, solvents, reagents, and other sample processing apparatus. The separating funnel was cleaned by thoroughly rinsing with dichloromethane ( $\text{CH}_2\text{Cl}_2$ ). This was followed by washing with hot water and detergent and thereafter thoroughly rinsed with tap water and reagent water. Prior to use, the funnel was drained and left in an oven maintained at 200 °C for about 1 h.

About 25 mL of dichloromethane was added to 25 mL of water sample to be extracted in a separating funnel and sealed with a stopper. This was manually shaken vigorously for 3 to 5 min, and the mixture was allowed to separate and settle. The shaking process allowed a thorough interspersion between the two immiscible solvents, thereby maximizing the contact between the solvent phases, and hence assisted mass transfer while allowing efficient partitioning to occur. It was necessary to periodically vent the excess pressure generated during the shaking process. After 10 min, the organic solvent was ran off and retained in a collection flask (beaker). Fresh organic solvent was later added to the separating funnel and the process repeated thrice with the aqueous layer. The four portions of the organic phase were combined and evaporated to 1-mL volume using a rotary evaporator.

The extracted and sieved samples (50 g) were weighed and spiked with predeuterated PAH cocktail as internal standard (naphthalene- $\text{d}_8$ , acenaphthylene- $\text{d}_8$ , anthracene- $\text{d}_{10}$ , acenaphthene- $\text{d}_{10}$ , fluoranthene- $\text{d}_{10}$ , phenanthrene- $\text{d}_{10}$ , fluorine- $\text{d}_{10}$ , pyrene- $\text{d}_{10}$ , chrysene- $\text{d}_{12}$ , benzo[a]pyrene- $\text{d}_{12}$ , benzo[b]fluoranthrene- $\text{d}_{12}$ , benzo[a]anthracene- $\text{d}_{12}$ , benzo[ghi]perylene- $\text{d}_{12}$ , dibenzo[a,h]anthracene- $\text{d}_{14}$ , and indeno[1,2,3-cd]pyrene- $\text{d}_{12}$ ) (ES2528, Promochem, Wesel, Germany), and extracted with dichloromethane (DCM) using a temperature-programmed Soxhlet extractor at 65 °C for 24 h. The extracts were reduced to dryness and redissolved in *n*-hexane. The extracts were fractionated on a glass column packed with 30 g of alumina deactivated with 4.5 % water. Aliphatic and polycyclic aromatic hydrocarbons were eluted with 50 mL of hexane: DCM (95/5 %, *v/v*) and the polar fractions were eluted with DCM. The PAH fractions were concentrated by rotary evaporation. Before GC/MS analysis, fractions were dried under nitrogen and redissolved in DCM.

*PAHs analysis and quantification using GC-ECD*

A gas chromatograph (GC, Agilent 6890 series) coupled to a mass spectrometer (MS, model 5971, Hewlett-Packard) was used to quantify extractable organic PAHs. Aliquots of each sample were injected using 30:1 split ratio onto a 30 m, 0.25 mm inner diameter, HP-SMS 5 % phenyl methyl siloxane capillary column. The operational conditions were as follows: 40–280 °C at 6 °C/min, injector temperature 300 °C, scan range 40–500 amu, scan rate 1.53 scans/s, and source temperature of 320 °C. Helium was used as the carrier gas (at 1.5 mL/min). The PAHs were determined in selective ion-monitoring mode (SIM mode) with ionization energy of 70 eV. The *m/z* peaks corresponding to the molecular masses of the individual PAH were used for identification and quantification. Concentrations of PAH were calculated relative to the predeuterated internal standard.

## Data management and analysis

Analytical data obtained from laboratory analyses were extracted from respective chromatogram and quantitative results tables. These raw data indicated sample type, identification, amount, dilution factor, injection volume, and concentrations. A number of parameters indicative of possible petroleum contamination were calculated. Total PAHs ( $\Sigma$ PAH), the sum of all the PAH analytes was estimated, and the PHE/ANT and FLT/PYR ratios were calculated to indicate sources of hydrocarbon input. The PHE/ANT >10 and FLT/PYR >1 and the dominance of pyrolytic-based PAHs PHE/ANT <10 and FLT/PYR <1 were employed in elucidating the sources of PAHs in microlayer surface and subsurface water of the Lagos Lagoon.

**Results and discussion**

## Concentrations and spatial distributions of PAHs in SML and SSW

Table 1 shows the individual PAHs analyzed in the present study. The results of the analyses PAHs in surface microlayer and subsurface water samples from the Lagos Lagoon system are presented in Tables 2 and 3, respectively. PAHs suites including naphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthalene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene,

**Table 1** Polycyclic aromatic hydrocarbons analyzed in this study

	PAHs compounds	Abbreviation
1.	Naphthalene	NAP
2.	2-Methylnaphthalene	2-MENAP
3.	Acenaphthylene	ACY
4.	Acenaphthalene	ACE
5.	Fluorene	FLO
6.	Phenanthrene	PHE
7.	Anthracene	ANT
8.	Fluoranthene	FLA
9.	Pyrene	PYR
10.	Chrysene	CHR
11.	Benzo(a)anthracene	BaA
12.	Benzo(k)fluoroanthene	BkFA
13.	Benzo(b)fluoroanthene	BbFA
14.	Benzo(a)pyrene	BaP
15.	Benzo(g,h,i)perylene	BghiP
16.	Dibenz(a,h)anthracene	DahA
17.	Indeno(1,2,3-cd)pyrene	IP

chrysene, benzo(a)anthracene, benzo(k)fluoroanthene, benzo(b)fluoroanthene, benzo(a)pyrene, benzo(g,h,i)perylene, dibenz(a,h)anthracene, and Indeno(1,2,3-cd) pyrene were detected in the surface microlayer and subsurface layer water samples analyzed. The average concentration, range, standard deviation, and coefficient of variation in the levels of individual suites are also presented in Table 3.

The levels of acenaphthylene detected were 0.3 and 0.2 µg/L in the surface microlayer water samples from ST3 and ST5 locations, respectively (Table 2), with an average of 0.25 µg/L, standard deviation of  $7.1 \times 10^{-5}$  mg/L, and coefficient variation value of 28.2 % were found in the SML in (Table 4). ACE was not detected in the subsurface water sample. The concentration of phenanthrene in the surface microlayer water of the lagoon ranged between 5.3 and 9.8 µg/L. Its concentration was, however, less variable (25.3 %) with an average of 6.6 µg/L. The subsurface water samples recorded a mean phenanthrene concentration of 5.9 µg/L, with minimum and maximum levels of 4.7 and 7.9 µg/L, respectively (Table 3). Notably, the highest concentration of phenanthrene in subsurface water was recorded at ST5. Standard deviation and coefficient of variation calculated from data derived from the six locations investigated were  $1.2 \times 10^{-3}$  mg/L and 20.6 %, respectively.



**Table 2** Concentrations ( $\mu\text{g/L}$ ) and source analysis of PAHs in surface microlayer water samples from Lagos Lagoon, Nigeria

	ST1	ST2	ST3	ST4	ST5	ST6
Naphthalene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
2-Methylnaphthalene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Acenaphthylene	<LOD	<LOD	0.3	<LOD	0.2	<LOD
Acenaphthalene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Fluorene	0.5	<LOD	<LOD	<LOD	<LOD	<LOD
Phenanthrene	9.8	6.0	6.1	5.3	5.5	6.6
Anthracene	0.2	<LOD	<LOD	<LOD	<LOD	<LOD
Fluoranthene	2.9	2.3	2.3	1.9	2.2	2.6
Pyrene	2.3	1.8	1.8	1.5	1.7	2.1
Chrysene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Benzo(a)anthracene	0.2	0.2	0.2	0.1	0.2	0.2
Benzo(k)fluoroanthene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Benzo(b)fluoroanthene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Benzo(a)pyrene	0.3	0.4	0.4	0.3	0.3	0.3
Benzo(g,h,i)perylene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Dibenzo(a,h)anthracene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Indeno(1,2,3-cd)pyrene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
$\Sigma\text{PAH}$	16.20	10.70	11.10	9.10	10.10	11.80
PHE/ANT ratio	49	–	–	–	–	–
FLT/PYR ratio	1.3	1.3	1.3	1.3	1.3	1.2

PHE phenanthrene, ANT anthracene, FLT fluoranthene, PYR pyrene, <LOD = below limit of detection and indicates 0  $\mu\text{g/L}$

Fluoranthene is the most commonly detected PAH in water and is associated primarily with petrogenic sources, coal-tar linings of cast iron or ductile iron distribution pipes that are employed to channel wastewaters and industrial effluents. It comprises naphthalene and a benzene unit connected by five rings, and is a member of the class of PAHs known as nonalternant PAHs because it has rings other than those with six carbon atoms. This PAH suite was detected more in the SML than the SSW samples. The concentrations of fluoranthene in the SML ranged between 1.9 and 2.9  $\mu\text{g/L}$  for samples obtained from ST4 and ST1, respectively. The concentrations in the SML were less variable (14.5 %) with an average of 2.4  $\mu\text{g/L}$  (Table 3). The SSW had a mean concentration of 2.4  $\mu\text{g/L}$  with minimum and maximum levels of 2.2 and 2.7  $\mu\text{g/L}$ , respectively. The highest concentration of fluoranthene in SSW was recorded at ST5 and ST6 locations (Table 3). Pyrene concentrations in the SML water samples varied from 1.5 to 2.3  $\mu\text{g/L}$  (Table 2). The values recorded were less variable (15.3 %) with an average of 1.9  $\mu\text{g/L}$ . The SSW recorded mean

concentration of 1.9  $\mu\text{g/L}$ , with minimum and maximum pyrene levels of 1.6 and 2.1  $\mu\text{g/L}$ , respectively (Table 3). High levels of pyrene pollution in SSW samples were detected at the ST5 and ST6 locations.

The concentration of benzo(a)anthracene in the SML ranged between 0.1 and 0.2  $\mu\text{g/L}$  with average concentration of 0.18  $\mu\text{g/L}$  (Table 2). However, a consistent value of 2.4  $\mu\text{g/L}$  was recorded for the SSW samples at all the locations (Table 3). On the other hand, the concentrations of benzo(a)pyrene, B(a)P, in the SML samples were relatively low and varied between 0.3 and 0.4  $\mu\text{g/L}$ . The mean concentration benzo(a)pyrene in the SSW was 3.3  $\mu\text{g/L}$ . According to the World Health Organization, benzo(a)pyrene concentration of 0.7  $\mu\text{g/L}$  in water is harmful. This corresponds to an excess lifetime cancer risk of 10–5 (Srogi 2007). Based on this assertion, it is obvious that the Lagos Lagoon is contaminated with B(a)P and could be passed on to the food chain. This may have carcinogenic implications. Aside from the possible biotransformation of B[a]P to the biota of the Lagoon system, the sediment could readily constitute a trap of this priority PAH, and can be an essential

**Table 3** Concentrations ( $\mu\text{g/L}$ ) and source analysis of PAHs in subsurface water samples from Lagos Lagoon, Nigeria

	ST1	ST2	ST3	ST4	ST5	ST6
Naphthalene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
2-Methylnaphthalene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Acenaphthylene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Acenaphthalene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Fluorene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Phenanthrene	4.7	6.3	6.4	4.7	7.9	5.6
Anthracene	<LOD	<LOD	<LOD	<LOD	0.1	<LOD
Fluoranthene	2.2	2.3	2.4	2.0	2.7	2.7
Pyrene	1.8	1.8	1.9	1.6	2.1	2.1
Chrysene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Benzo(a)anthracene	0.2	0.2	0.2	0.2	0.2	0.2
Benzo(k)fluoroanthene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Benzo(b)fluoroanthene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Benzo(a)pyrene	0.4	0.4	0.3	0.4	0.3	0.4
Benzo(g,h,i)perylene	<LOD	0.6	<LOD	<LOD	<LOD	0.6
Dibenz(a,h)anthracene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Indeno(1,2,3-cd)pyrene	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
$\Sigma\text{PAH}$	9.30	11.60	11.20	8.90	13.30	11.60
PHE/ANT ratio	–	–	–	–	–	–
FLT/PYR ratio	1.2	1.3	1.3	1.3	1.3	1.3

PHE phenanthrene, ANT anthracene, FLT fluoranthene, PYR pyrene, <LOD = below limit of detection and indicates 0  $\mu\text{g/L}$

instrument for establishing the assimilative capacity of the Lagos Lagoon.

The concentrations of naphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthalene, fluorene, anthracene, chrysene, benzo(k)fluoroanthene, benzo(b)fluoroanthene, benzo(g,h,i)perylene, dibenz(a,h)anthracene, and indeno(1,2,3-cd) pyrene were not detected in the SML and SSW samples. These PAHs are not usually found in water in notable concentrations owing to their low solubility and high affinity for particulate matter (Srogi 2007). However, the total PAH concentrations in the SML and SSW of Lagos Lagoon were, in general, an order of magnitude comparable to those previously reported in other surface water ecosystems in Nigeria, 1.95 to 10.9  $\mu\text{g/L}$  (Anyakora and Coker 2006) and 0.02 to 0.28  $\mu\text{g/L}$  (Duke 2008). Enhanced concentration levels of PAHs in surface waters in the core oil-producing water ecosystem of Niger Delta have been reported to vary from 720.46 to 857.65  $\mu\text{g/L}$ , which indicate gross pollution of the aquatic ecosystem by PAHs (Opuene et al. 2009).

In general, it could be inferred that the total PAHs ( $\Sigma\text{PAHs}$ ) concentrations found in the SML water samples of the Lagos Lagoon were generally higher than values recorded for the SSW. Reports on similar studies show that seawater from the SML tends to characteristically concentrate surface-active organic pollutants more effectively than the underlying SSW (Wurl and Obbard 2005; Gašparović et al. 2007; Wurl and Holmes 2008; Cunliffe et al. 2013; Ya et al. 2014).

#### Potential sources of PAHs

Petroleum-derived hydrocarbons can be recognized and are often used as tracers of petroleum contamination. In this study, the PHE/ANT and FLT/PYR ratios were employed in order to distinguish between PAHs of diverse origin. The calculations of the PHE/ANT and FLT/PYR ratios based on concentrations of respective PAH derivatives from seawater samples are shown in Tables 2 and 3 for microlayer and subsurface water samples, respectively. The concentration of anthracene

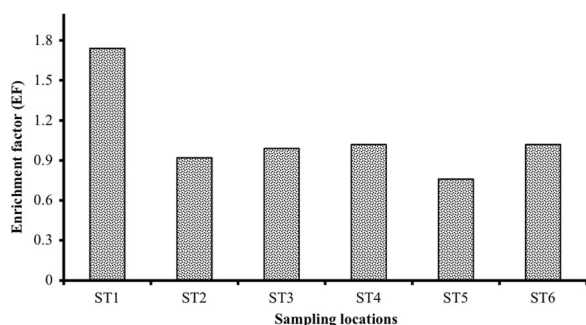
**Table 4** Summary statistics of PAH concentrations in surface microlayer and subsurface water samples from Lagos Lagoon, Nigeria

	Sample ID	Minimum (µg/L)	Maximum (µg/L)	Range (µg/L)	Average (µg/L)	Standard deviation	Coeff. of variation %
Naphthalene	SML	–	–	–	–	–	–
	SSW	–	–	–	–	–	–
2-Methylnaphthalene	SML	–	–	–	–	–	–
	SSW	–	–	–	–	–	–
Acenaphthylene	SML	0.20	0.30	0.10	0.25	$7.1 \times 10^{-5}$	28.2
	SSW	–	–	–	–	–	–
Acenaphthalene	SML	–	–	–	–	–	–
	SSW	–	–	–	–	–	–
Fluorene	SML	<LOD	0.50	–	0.50	–	–
	SSW	–	–	–	–	–	–
Phenanthrene	SML	5.30	9.80	4.50	6.60	$1.7 \times 10^{-3}$	25.3
	SSW	4.7	7.9	3.2	5.9	$1.2 \times 10^{-3}$	20.6
Anthracene	SML	<LOD	0.20	–	–	–	–
	SSW	<LOD	0.1	–	–	–	–
Fluoranthene	SML	1.90	2.90	1.00	2.40	$3.4 \times 10^{-4}$	14.5
	SSW	2.2	2.7	0.5	2.4	$2.6 \times 10^{-3}$	10.9
Pyrene	SML	1.50	2.30	0.80	1.90	$2.9 \times 10^{-4}$	15.3
	SSW	1.6	2.1	0.5	1.9	$1.8 \times 10^{-3}$	9.6
Chrysene	SML	–	–	–	–	–	–
	SSW	–	–	–	–	–	–
Benzo(a)anthracene	SML	0.10	0.20	0.10	0.18	$4.1 \times 10^{-5}$	22.7
	SSW	–	0.2	–	0.2	–	–
Benzo(k)fluoroanthene	SML	–	–	–	–	–	–
	SSW	–	–	–	–	–	–
Benzo(b)fluoroanthene	SML	–	–	–	–	–	–
	SSW	–	–	–	–	–	–
Benzo(a)pyrene	SML	0.30	0.40	0.10	0.33	$5.2 \times 10^{-5}$	15.6
	SSW	0.3	0.4	0.1	0.37	$5.5 \times 10^{-5}$	14.8
Benzo(g,h,i)perylene	SML	–	–	–	–	–	–
	SSW	–	0.6	–	0.6	–	–
Dibenz(a,h)anthracene	SML	–	–	–	–	–	–
	SSW	–	–	–	–	–	–
Indeno(1,2,3-cd)pyrene	SML	–	–	–	–	–	–
	SSW	–	–	–	–	–	–

SML surface microlayer, SSW subsurface water, <LOD = below limit of detection and indicates 0 µg/L

was predominantly below detection, except in SML samples at ST1. Consequently, the FLT/PYR ratio was used to determine the sources of PAHs. Most of the water samples analyzed satisfied the criteria of PHE/ANT <10, FLT/PYR >1. In general, SML samples indicated petrogenic-derived PAHs with FLT/PYR ratios that were greater than 1. The dominance of high

molecular weight PAHs of petrogenic origin was observed in SML samples from ST1 with PHE/ANT=49 and FLT/PYR=1.3. The PHE/ANT value shows that the station is contaminated with recalcitrant PAHs suites that are less prone to biodegradation by indigenous bacteria and fungi. Although pollution of coastal water bodies in Nigeria has over the years been speculated to

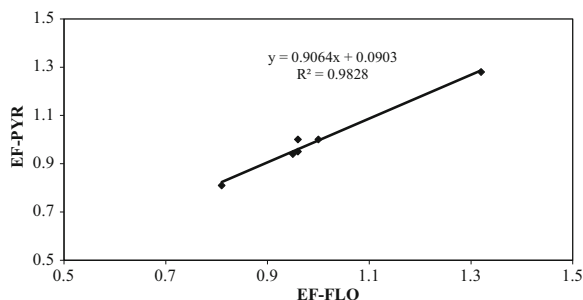


**Fig. 2** Enrichment factors of ΣPAHs in sea-surface microlayer at all locations

originate from multitudinous sources, such as crude oil spills, accidental leakages from badges, industrial discharges, agricultural activities, sewage, and domestic wastes, PAHs levels detected in water in this study suggested significant inputs from anthropogenic sources to the total pollution loading of the lagoon.

Surface microlayer enrichment

The SML is the thin layer in the top of the seawater column, with thickness from few micrometers to 1 mm. In the marine environment, the SML serves as a sink and source of organic contaminants and is known to play an important role in a number of biogeochemical processes such as air-sea exchanges, transport, accumulation, and degradation of organic pollutants (Del Vento and Dachs 2007; Guitart et al. 2007; Gioia et al. 2011; Cunliffe et al. 2013; Ya et al. 2014). The quantification of the SML enrichment may be well represented by the enrichment factor EF, and calculated as the ratio between SML and SSW PAHs concentrations (Hardy et al. 1987; Manodori et al. 2006). Figure 2 shows the EFs of



**Fig. 3** Correlation between the EFs of fluoranthene and pyrene

ΣPAHs at all the locations, and it ranged from 0.76 at ST5 to 1.74 at ST1. The EFs of the individual PAHs varied from 0.75 to 2.09 at ST1, 0.95 to 1.0 at ST2, 0.95 to 1.33 at ST3, 0.5 to 1.13 at ST4, 0.69 to 1.0 at ST5, and 0.75 to 1.18 at ST6. In general, the EFs values calculated in this study were consistent or slightly less than EFs reported for similar coastal seawater ecosystem. This implies, however, that the hydrodynamic conditions of the lagoon system largely influenced the distribution of PAHs between the SML and SSW. In addition, a correlation between the EFs of fluoranthene and pyrene indicated that they were significantly correlated ( $R=0.9828$ ,  $p<0.0001$ ,  $n=6$ ; Fig. 3). A similar relationship for EFs-FLO and EFs-PYR has been reported by Ya et al. (2014).

BaP-equivalent carcinogenic assessment

In estimating the potential carcinogenic risk assessment of surface water of the lagoon system, the WHO and US EPA guideline described by Nadal et al. (2004) and Zhang et al. (2012) were followed. According to this method, the toxicity of PAHs is expressed relative to a reference standard, benzo[a]pyrene, BaP. However, the overall carcinogenicity of PAHs or BaP toxic equivalence quotient (TEQ) are estimated based on the weighted sum of individual congener concentrations and the toxic equivalence factors (TEFs) relative to the cancer potency of BaP (Zhang et al. 2012). According to the WHO and US EPA, TEFs vary from 0.01 to 1 as shown in Table 5.

Therefore, carcinogenic toxic equivalence quotient was calculated as the product of the concentrations of

**Table 5** WHO and EPA toxic equivalence factors for carcinogenic PAHs

PAH congener	Abbreviation	TEF <sup>a</sup>
Chrysene	CHR	0.01
Benzo(a)anthracene	BaA	0.1
Benzo(k)fluoranthene	BkF	0.1
Benzo(b)fluoranthene	BbF	0.1
Benzo(a)pyrene	BaP	1
Benzo(g,h,i)perylene	BghiP	0.01
Dibenz(a,h)anthracene	DahA	1
Indeno(1,2,3-cd)pyrene	IP	0.1

<sup>a</sup> TEF toxic equivalence factors for cancer potency relative to BaP (Zhang et al. 2012)

each PAH congener and its TEF relative to BaP using the following equation:

$$\text{BaP-TEQ} = \sum_i C_i \times \text{TEF}_i$$

where  $C_i$  and  $\text{TEF}_i$  are the concentration and TEF, respectively, for individual PAH congeners. An expansion of this equation yields:

$$\begin{aligned} \text{BaP-TEQ} = & [\text{BaA}] \times 0.1 + [\text{Chr}] \times 0.01 + [\text{BbFA}] \times 0.1 \\ & + [\text{BkFA}] \times 0.1 + [\text{BaP}] \times 1 + [\text{IP}] \times 0.1 \\ & + [\text{DahA}] \times 1 + [\text{BghiP}] \times 0.01 \end{aligned}$$

The total TEQ of PAHs in the surface microlayer water of the Lagos Lagoon ranged between 0.3  $\mu\text{g/L}$  in sample obtained from ST4 to 0.42  $\mu\text{g/L}$  in the samples from ST2 and ST3. SSW samples from ST2 and ST6 locations recorded higher TEQs than other subsurface water samples. In general, BaP, BaA, and BghiP contributed significantly to the total carcinogenic equivalents of PAHs of both the SML and SSW of the Lagos Lagoon.

## Conclusion

This study has provided the first data on the levels of PAHs in the SML and SSW of Lagos Lagoon. The total PAH concentrations were generally low in both the surface microlayer and subsurface seawater of the Lagos Lagoon, although analysis has shown that some stations recorded elevated levels of carcinogenic PAHs. The occurrence and distribution of PAHs at ST1 and ST4 locations were relatively significant in the SML samples, which indicated comparably stronger petrogenic input of PAHs than the other sampling locations. This is expected, considering the heavy presence of industries situated and maritime activities around these locations. The concentration of phenanthrene was generally higher in both the surface microlayer and subsurface water samples of the Lagos Lagoon. Based on the PHE/ANT and FLT/PYR ratios, the PAHs in the Lagos Lagoon system were from petroleum-derived sources. However, there is serious risk of unhealthy contamination of the lagoon with PAHs, which can only be checked by reduction in inputs of petroleum wastes into the lagoon system through accidental oil spillages and seepage. Indiscriminate

discharge of untreated wastes and municipal effluents into the ecosystem should also be discouraged by relevant government agencies. Finally, short- and long-term monitoring programmes should be established to continually ascertain the pollution status of this water body.

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