Article

Environmental Monitoring and Assessment

September 2014, Volume 186, Issue 9, pp 5519-5529

First online: 24 May 2014

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

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 (ΣPAH) concentrations ranged from 9.10 to 16.20 μg L^{-1} in the SML and 8.90 to 13.30 μg L^{-1} in the SSW. ΣPAH concentrations were relatively higher in the SML than the underlying SSW samples. The enrichment factors (EFs) of ΣPAHs 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.

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Environ Monit Assess (2014) 186:5519–5529
DOI 10.1007/s10661-014-3800-z

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N. U. Benson (✉)
Environmental Chemistry Research Group, Department of Chemistry, College of Science and Technology, Covenant University,
P.M.B., 1023 Ota, Nigeria
e-mail: nbenson@covenantuniversity.edu.ng

J. P. Essien
Department of Microbiology, University of Uyo,
Uyo, Akwa Ibom, Nigeria

F. E. Asuquo
Institute of Oceanography, Department of Physical Oceanography, University of Calabar,
Calabar, Nigeria

A. L. Eritobor
School of Environmental and Horticultural studies, Niagara College,
NL Campus, 135 Taylor Road, Welland, Ontario, Canada

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 biopersistency (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

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; Burguess 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 Ezebuiro 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.

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P.M.B., 1023 Ota, Nigeria
e-mail: nbenson@covenantuniversity.edu.ng

J. P. Essien
Department of Microbiology, University of Uyo,
Uyo, Akwa Ibom, Nigeria

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Institute of Oceanography, Department of Physical Oceanography, University of Calabar,
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Cover Date
2014-09
DOI
10.1007/s10661-014-3800-z
Print ISSN
0167-6369
Online ISSN
1573-2959
Publisher
Springer International Publishing

Keywords

- PAHs
- Surface microlayer
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Authors

- Nsikak U. Benson (1)
- Joseph P. Essien (2)
- Francis E. Asuquo (3)
- Adeola L. Eritobor (4)

Author Affiliations

- 1. Environmental Chemistry Research Group, Department of Chemistry, College of Science and Technology, Covenant University, P.M.B., 1023, Ota, Nigeria
- 2. Department of Microbiology, University of Uyo, Uyo, Akwa Ibom, Nigeria
- 3. Institute of Oceanography, Department of Physical Oceanography, University of Calabar, Calabar, Nigeria
- 4. School of Environmental and Horticultural studies, Niagara College, NL Campus, 135 Taylor Road, Welland, Ontario, Canada