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Spatial Assessment of Polycyclic Aromatic Hydrocarbons in Streambed Sediments

I.A. Ololade[a*], L. Lajide[b] and N.A. Oladoja[a]

[a]Department of Chemistry and Industrial Chemistry, Adekunle Ajasin University,
P.M.B 001, Akungba-Akoko, Ondo-State, Nigeria
[b]Department of Chemistry, Federal University of Technology, P.M.B 734. Akure, Nigeria

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Abstract. The occurrence and seasonal changes of polycyclic aromatic hydrocarbons (PAHs) in oil-contaminated sediment from selected oil areas of Ondo State, Nigeria were studied using gas chromatography–mass spectrometry. Six PAHs were identified and quantified with phenanthrene and carbazole, recording the highest and the least concentrations during the dry and wet seasons. Mean PAHs content ranged from 0.06 - 4.42 ìg/g and 0.09 - 6.0 ìg/g during the dry and the wet seasons, respectively. Significant correlations were observed ($\alpha = 0.05$) between the two seasons but without significant mean difference ($p = 0.05$). For anthracene and phenanthrene, the compound toxic units (TU) were >> 1 and far exceeded the available consensus-based guidelines about the expected adverse effects. Results of the study call for further investigations especially with aquatic species due to the transfer of PAHs to humans via food chain.

Keywords: sediments, hydrocarbons, polycyclic aromatic hydrocarbons, gas chromatography mass spectrometry, oil spill

Introduction

Increasing exploration and exploitation of petroleum in the Ondo coastal region of Western Nigeria has lead to greater risk of contamination from oil spill. Prominent among the hydrocarbon residue resulting from oil spill are the polycyclic aromatic hydrocarbons (PAHs) (Koh *et al.,* 2004; Law *et al.*, 2002). Sources of production of PAHs are both natural and human. Because of their low aqueous solubilities (0.003 to 0.34 mg/litre) and high octanol-water partition coefficient (log Kow = 3.4 – 7.6), PAH compounds in aquatic system tend to be associated with sediment and biota (Kannan *et al.,* 2005; Koh *et al.,* 2004; NOAA, 1998). Sediments, in general, have been employed to monitor the pollution of aquatic environments for the reason that PAHs, generally existing in low concentrations in the water column, have a propensity to associate preferentially with the sediments and attain considerable concentration (Kurunthachalam *et al.*, 2008; German Ministry of Environment, 1993; Forstner and Wittmann, 1983).

Aromatic hydrocarbons are generally more toxic than aliphatic ones, with their toxicity increasing with the increase in the number of rings and degree of alkyl substitution. However, solubility decreases with increasing number of rings and alkyl groups. Thus, the most toxic petroleum hydrocarbons may be the compounds of 4-5 ring aromatics, although the most toxic contribution may be exerted by mono or dinuclear aromatics. Research shows PAHs have negative effect on humans, mammals, invertebrates, birds and fish. As of 2001, about 17 PAHs have been registered as priority pollutants and with sufficient evidence to be considered toxic, carcinogenic and mutagenic (Zahodiakin, 2002; US EPA, 1993).

Studies have shown that each source of PAHs has a characteristics pattern and the usefulness of PAH isomer ratios, such as phenanthrene/anthracene (tricyclic aromatic, MW178) can be demonstrated for source identification (Ololade and Lajide, 2009; Ikenaka *et al.*, 2005). Lower molecular weight PAHs e.g. phenanthrene and anthracene are known to be acutely toxic to aquatic organisms and are more easily degraded unlike the higher molecular weight compounds which tend to predominate in sediments where they are subjected to burial, resuspension, and degradation reactions (Villeneuve *et al.*, 2002). The biodegradation of PAH probably occurs more slowly in aquatic system than in soil (Clement Associates, 1985).

Seasonal and historical changes on disposition of PAHs have been determined using sediment core in several studies (Ikenaka *et al.*, 2005; Takeda *et al.*, 2003). In fact, aquatic ecosystem remains one of the major sinks of PAH contamination, which has received most attention because of the lipophilic characteristics and bioconcentration effect of PAHs (Guzzella and Depaolis, 1994). Moreover, due to the environmental significance of PAHs, extensive studies of bottom sediments of Lorence Greek Lake and urban run off have been carried out

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* Author for correspondence. E-mail: Olisa200@yahoo.com.

(Ging *et al.*, 2001). The increasing ubiquitous presence of these compounds, especially as those derived from petroleum in ocean, lakes and rivers in the form of spills necessitates the development of practical means of determining such pollutants in the natural environment. Sediment exposure to PAHs has been characterized by comparing sediment PAH concentration with sediment quality benchmarks empirically derived from 28-day toxicity tests using *Hyalella azteca* (HA-28). The database was constructed using data from several contaminated sites (MacDonald *et al.*, 2000a, b; Ingersoll *et al.*,1996). These benchmarks represent the concentration below which toxicity is frequently observed (Effects Range Median, ERM).

Little environmental data is available for the coastal region of Ondo state located within the South-Western region of Nigeria (Ololade and Lajide, 2009; Ololade *et al.*, 2009; Asaolu, 1998). The Ondo coastal region is known for biological production and is especially important for commercial fishing. Several oil wells having been located around the study area during the recent years have resulted in increased spills. The present study was undertaken as an attempt to create a friendly environment for recreational activities within the area. It is equally hoped that hydrocarbon source could be identified, which will help to establish the distribution pattern. Consequently, the most effective, hyphenated gas chromatography – mass spectrometry (GC-MS) was employed for the study based on literature guidance.

Materials and Methods

Study area. Ondo State occupies a total land area of 14 793 189 square kilometers. It lies entirely in the tropical area between longitudes 4° 30" and 6° 14" east, and latitudes 5° 45" and 8° 15" north. It is bounded to the south by the Atlantic Ocean. The research focuses upon the southern coastal area (Fig. 1). The climate is tropical with two distinct seasons: the rainy season (April-October) and the dry season (November-March), with a temperature range of 26.2 - 27.6 °C. Salinity increases in the rivers at high tide and decreases at low tide. The sampling sites are locations, previously noted for large biological production and are especially important for commercial fishing. However, the unfortunate state of affairs set in 1996 when the first oil spill occurred due to the activities of two foreign petroleum companies (Ondo State Environmental Protection Agency, 2000). Large areas of mangroves ecosystem have been destroyed within the area as a result of toxicity from persistent oil spillage. Consequent upon the negative impacts of this unpalatable experience, the present study was carried out.

Chemicals and apparatus. All chemicals were of analytical reagent grade. Dichloromethane (DCM) and hexane were all doubly distilled in all-glass apparatus while the alumina, silica gel, sodium chloride and sodium sulphate were Soxhlet extracted with *n*-hexane for 8 hs each. All glassware used were thoroughly cleaned with hot detergent, rinsed with distilled water, then methanol and dried at 120 °C for about 6 hs.

Sampling. Basically, two sites: Ayetoro and Awoye (Site A, Ayetoro; Latitude 06°6' 12.4" langitude 04°6' 36.0"; Site B, Awoye; latitude 05°55' 1.2", longitude 04°58' 49.8") with five locations at each, were selected within the ecological zone. Some of the variables that influenced the selected sites included proximity to oil well locations and high level of socio-economic activities, particularly fishing, within the area. Samples were collected during both the dry and the wet seasons. The exact positions of the sampling points were noted using the global positioning system (GPS) and the details are presented in Table 1. Samples were collected at each site, one from midstream and one from each bank in a cross section fashion and later homogenized into a composite sample from which representative samples were taken based on APHA standard method (Aderemi *et al.*, 2003). Samples were collected and wrapped inside aluminum foil after proper labelling. They were subsequently placed inside coolers containing ice-bags and transferred to the laboratory where they were preserved in the freezer prior to analysis.

Saponification and extraction. About 100 g partially thawed sediment sample was weighed and transferred to a pre-cleaned extraction thimble which was then placed in the inner tube of

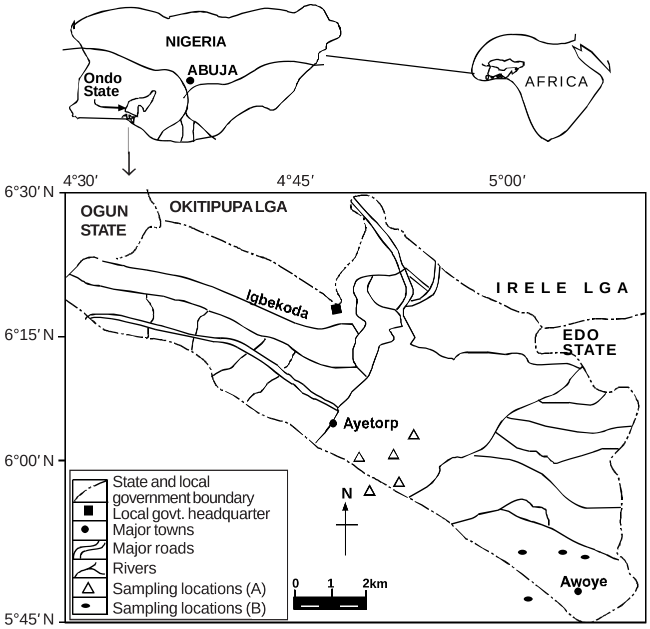

Fig. 1. Map of the study area (inset is the area map of Nigeria and Africa showing the geographical location).

the Soxhlet apparatus containing 140 ml DCM to which boiling chips had been added. Internal standards (anthracene, phenanthrene and pyrene) were used. The sediment sample was extracted for 8 hs and cooled. 20 ml of 0.7M KOH and 30 ml of pre-extracted water (with hexane) was added to the sediment solvent flask. The non-saponifiable lipids (containing the petroleum hydrocarbons) were carefully reduced to about 15 ml and then partitioned with hexane in 100 ml glass separatory funnel. 40 ml hexane was used and the mixture was thrice washed with 25 ml 0.1M Na_2CO. The separated organic layer was filtered through glass wool and anhydrous sodium sulphate to dry the extract. The volume was reduced on a water bath maintained at 30 °C. Final evaporation of the extract was carried out under nitrogen gas and later chromatographed. The extracts were eluted through a silica-alumina glass column for the removal of polar lipids and other biogenic interferences and the samples were concentrated to a volume of 5 ml. The fractions were combined and dissolved in a known amount of dichloromethane prior to GC-MS measurement (Aderemi *et al.,* 2003).

Gas chromatography – mass spectrometric (GC –MS) analyses. The capillary gas chromatography – mass spectrometry analysis were performed on a Hewlett – Packard (HP) 6890 GC series instrument coupled with a 5975 Hewlett – Packard mass spectrometer (MS). The capillary column used was of the Agilent 1909IS – 433 model with dimensions of 30 m x 0.25 mm ID x 0.25 ìm film thickness of HP- 5M5 (5% phenyl methyl siloxane). Full scan mass spectra between 35 and 500 m/z were acquired once every second. The peaks in the chromatogram were identified by comparison of the retention times and mass spectral data of reference compounds with those in the sample using MS Library Wiley and NIST (NIST, 2008). The peaks were quantified using the flame ionization detector (FID) through a five point calibration curve.

Results and Discussion

Two of the chromatograms obtained during dry and the wet seasons are presented in Figs. 2 and 3, respectively. All together, about six different PAH (anthracene, azuleno[2,1-b]thiophene, benz[a]anthracene, carbazole, dibenzothiophene and phenanthrene) were identified in the sediment extracts of the two sites studied. Total PAH concentration was the sum of the concentrations of individual identified compounds. The highest total PAH concentrations (Table 1) ranging from 0.11 to 6.00 ìg/g were detected at site-B during the wet season, while the least, ranging from 0.06 to 3.02 ìg/g was detected at

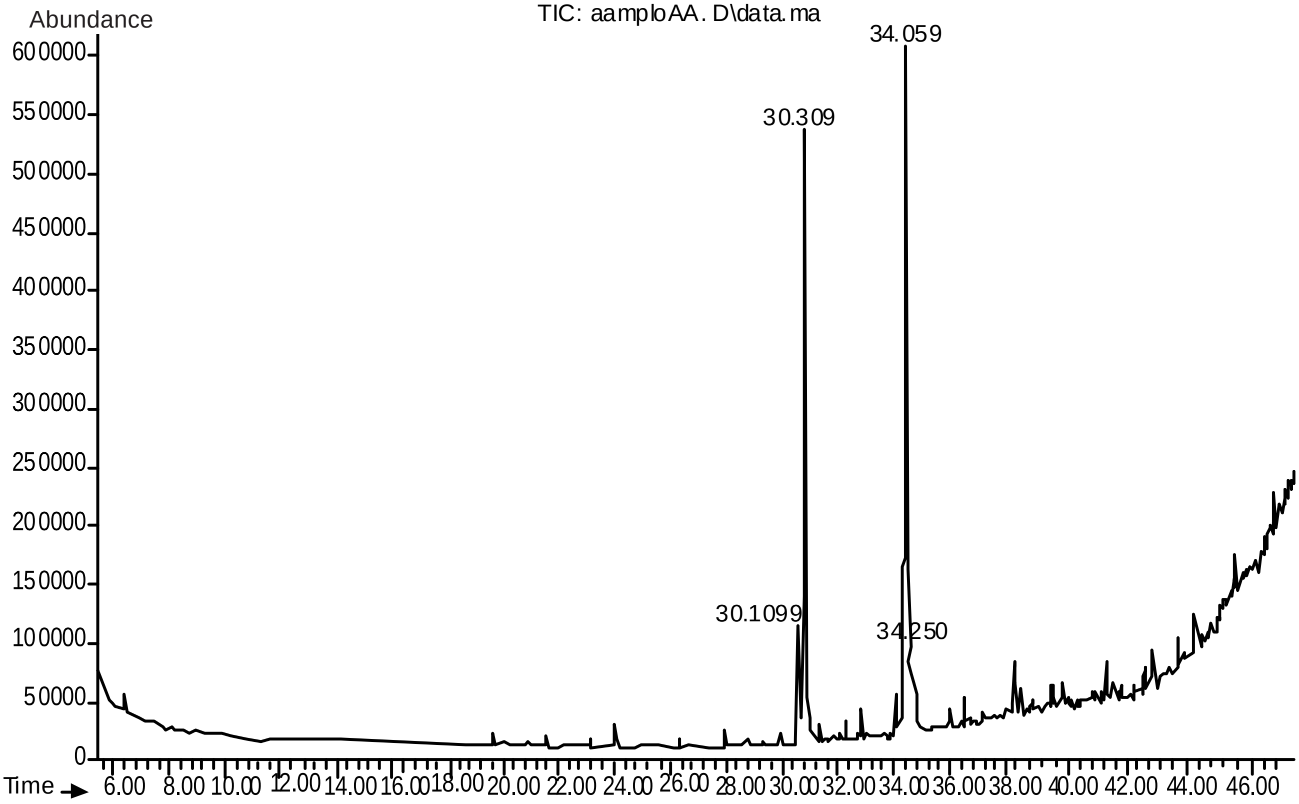

Fig. 2. A typical chromatogram of the sediment extract during the dry season.

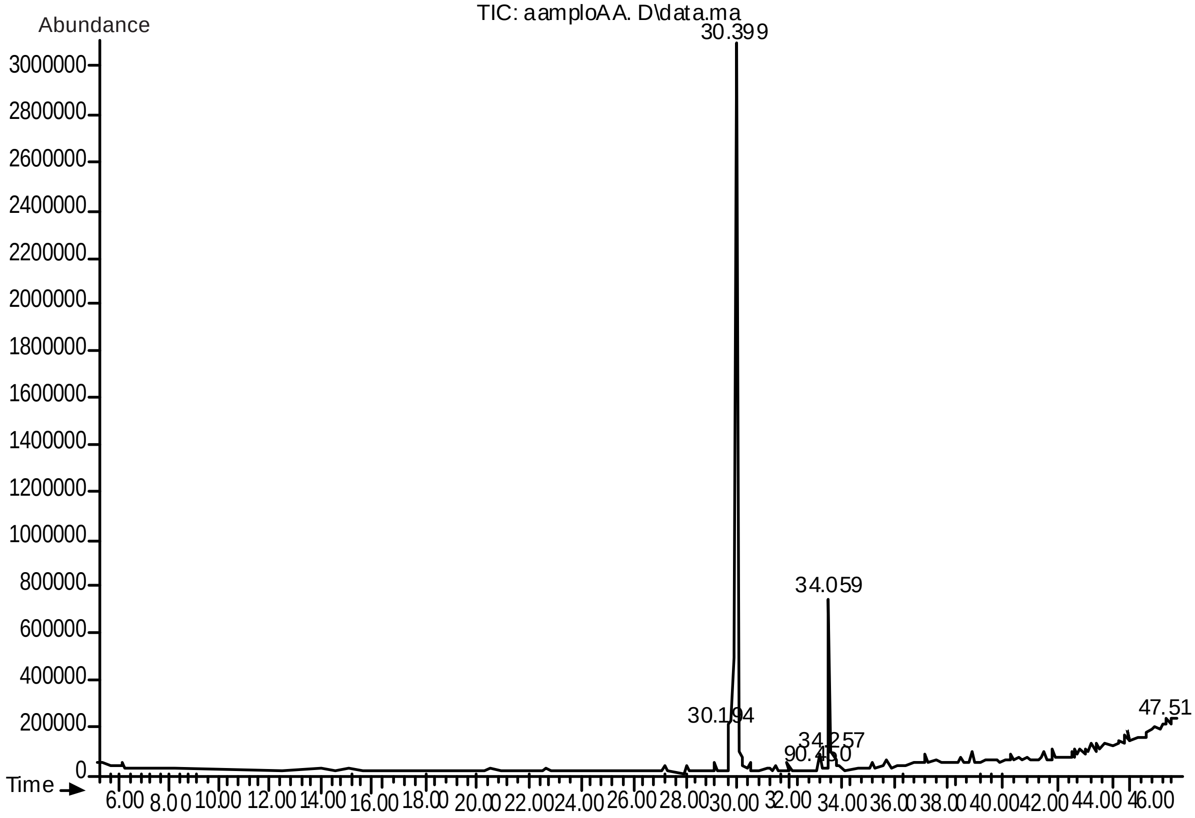

Fig. 3. A typical chromatogram of the sediment extract during the wet season.

site-A during the dry season. Phenanthrene and anthracene were the compounds, most frequently detected at the highest concentrations. The data in Table 1 also shows that concentrations are equally higher for almost all the PAHs at site-B. This may be due to the closeness of the site to the Atlantic Ocean, through which anthropogenic oil spill enters the hinterland.

The trend of the concentrations during both the seasons was almost similar with the PAH concentrating more during the wet season. Significant positive correlation ($\alpha = 0.01$) was observed between PAHs concentrations during both the seasons ($r = 0.998$ and 0.923) at site-A and B, respectively, but without any significant mean difference ($p = 0.077$ and 0.118, respectively). Though, dry season samples were first collected, it was thought that concentrations during the wet season would be less due to the prevailing ecological conditions at that time. However, the increased levels during this period further implicate continuous release of hydrocarbon residues into the area. It also re-affirms that sediments are capable of adsorbing organic pollutants such as PAHs (Ololade *et al.*, 2009; Aderemi *et al.*, 2003).

Using the sediment quality benchmarks empirically derived from 28 days toxicity tests using *Hyalella azteca* (HA–28) (MacDonald *et al.*, 2000a, b; USEPA,1996) all the sediment samples taken during both seasons had their PAH concentrations exceeding the ERM for anthracene, benz [a] anthracene and phenanthrene. Thus, exposure of sediment-dwelling organisms to PAHs is likely at these sampling locations. In fact, anthracene and phenanthrene exceeds the consensus-based probable effect concentration (PEC) as indicated in Table 1. However, concentration of benz [a] anthracene was found to be < PEC, but > TEC. All these observations are indicative of serious health hazards for the ecosystem.

For each PAH identified in Ondo coastal sediment, a toxic unit (TU) was calculated by dividing the sediment PAH concentration by the HA–28 ERM based on the reported model (MacDonald *et al.*, 2000a, b; Long and Morgan, 1991). The TUs for each identified PAH are included in Table 1 in parenthesis. However, guidelines for some of the identified compounds are unavailable; thus, their TUs could not be calculated. The summation of these TUs is indicative of the overall estimated PAH toxicity of the sample. As indicated in Table 1, the $\Sigma TU >> 1$, thus, adverse effects are expected based on the literature guidance (MacDonald *et al.*, 2000a, b). Phenanthrene (Phe) is generally more stable thermodynamically than

Table 1. Mean PAH concentration (ì g/g) in sediments from Ondo Coast, Nigeria

	SITE A (Ayetoro) Seasons		**SITE B (Awoye)** Seasons		Consensus-based TEC	Consensus-based PEC
PAH	Dry	Wet	Dry	Wet		
Anthracene	$2.08^{a}\pm0.47$ (12.24)*	$2.30^{a}\pm1.20$ (13.53)	$4.01^{b}\pm1.92$ (23.59)	$5.70^{b}\pm2.07$ (33.53)	0.057	0.845
Azuleno[2,1-b] thiophene	$2.40^{a}\pm1.12$	$2.49^{a}\pm1.10$	$2.32^{a}\pm0.92$	$2.64^{a}\pm1.02$	NG	NG
Benz[a]anthracene	$0.14^{ab}\pm0.12$ (0.50)	$0.16^{ab}\pm0.09$ (0.57)	$0.11^{ac}\pm0.05$ (0.39)	$0.13^{b}\pm0.07$ (0.46)	0.108	1.050
Carbazole	$0.06^{b}\pm0.02$	$0.09^{ab}\pm0.04$	$0.07^{b}\pm0.03$	$0.11^{ac}\pm0.05$	NG	NG
Dibenzothiophene	$0.18^{b}\pm0.04$	$0.25^{c}\pm0.13$	$0.16^{b}\pm0.09$	$0.20^{bc}\pm0.04$	NG	NG
Phenanthrene	$3.02^{c}\pm0.12$ (3.39)	$3.44^{c}\pm1.04$ (8.39)	$4.42^{cd}\pm2.04$ (10.78)	$6.00^{bcd}\pm2.04$ (14.63)	0.204	1.170
Σ PAH (Σ TU)	7.88(20.13)	8.73(22.52)	11.09(34.69)	14.78(48.62)		

*Values in parenthesis are Toxic Units (TU); means in the same row followed by the same superscript are not significantly different ($\alpha = 0.05$) according to Duncan's New Multiple Range Test. ERM: For anthracene (0.17 ìg/g); phenanthrene (0.41ìg/g); benz[a]anthracene (0.28 ìg/g). TEC=threshold effect concentration (MacDonald *et al.*, 2000); PEC: probable effect concentration (MacDonald *et al.*, 2000); PEL–HA 28: probable effect level for *Hyalella azteca*: 28-day test, dry weight(USEPA,1996); NG: no guidelines for TEC and PEC.

anthracene (Ant) and the ratio Phe/Ant is a reflection of the origin of PAHs; petrogenic or pyrogenic in the environment (Ikenaka *et al.,* 2005). A high ratio of Phe/Ant (≈ > 15) is characteristic of petrogenic source, while pyrogenic is characterized by lower ratio. In the present report, the ratio Phe/Ant was 1.28 ± 0.16 (average ± SD, n = 8) in the sediment. Thus, the PAHs are more from the pyrogenic than petrogenic source. The data further imply that the oil residues consist mainly of the heavier portion which tend to sink and become sedimented. This may be due to the fact that PAHs, because of their hydrophobic character, show strong adsorption affinity to solid particles in aqueous matrices (Lombas-Garcia *et al.,* 1998). Thus, the extent of hydrocarbon adsorption was found to be positively correlated (r = 0.8335) with the organic carbon (OC) present in the sediment during both the dry and the wet seasons (Fig. 4).

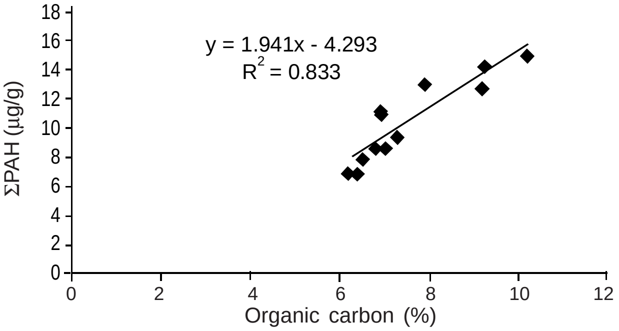

Fig. 4. Σ PAH concentrations with sediment organic carbon content ($p < 0.05$).

The impact of the PAHs in Ondo costal environment on populations of benthic organisms may be very devastating based on the fact that the concentration of PAHs measured in the sediments are comparable to other contaminated sites in which severe impacts have been observed (Ikenaka *et al.,* 2005; Aderemi *et al.,* 2003; Pavlova and Ivanova, 2003). Thus, sediment-dwelling or burrowing organisms such as crabs, periwinkles etc. are at the greatest risk especially during the wet season because PAHs tend to remain bound to organic sediment (Kannan *et al.,* 2003, 2005; Koh *et al.,* 2004). Aquatic organisms that reside on the sediment surface, restricted to the water column only, are likely to receive less concentration from the sediment-bound PAH, and are, therefore, at less risk. The occurrence of PAHs, even at the levels obtained in this report within the environment is of concern due to their carcinogenic properties, and their ability to exert toxic effects through the aryl hydrocarbon receptor (AhR) mediated mechanism, similar to those of dioxins (Villeneuve *et al.*, 2002). Several workers have shown that most PAHs such as carbazole, phenanthrene etc. have shown to be mutagenic and carcinogenic in laboratory studies (Aderemi *et al.*, 2003; Ghauch *et al.*, 2000; Ericson *et al.*, 1999; Qanh *et al.*, 1999; MacCoy and Black, 1998; Robertson,1998; Myers *et al.*, 1987). It is hoped that some site-specific resident organisms and important marine species will be investigated to further establish the present findings.

Conclusion

Oil spills have occurred several times along the Ondo coast in Nigeria–which is at the Gulf of Guinea–as a result of upsurge in oil exploration and exploitation activities. The present study demonstrates the adsorbing capacity of sediments for the toxic pollutants such as PAHs. It was also observed that these chemical pollutants are capable of building up (bioaccumulate) within the system, which poses serious threat to sediment dwelling organisms, other aquatic biota and eventually the man-through the food chain system. The study showed that the PAHs are more of a pyrogenic than a petrogenic origin. The temporal increase during the rainy season is indicative of slow degradation and efficient adsorption into the sediment matrices. It is recommended that investigations on site-specific resident organisms should be carried out for their PAHs status. This will assist appropriate food regulatory agencies in policy formulation on sea-food products.

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