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Distribution and ecotoxicological significance of polycyclic aromatic hydrocarbons in sediments from Iko River estuary mangrove ecosystem

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Abstract The distribution of polycyclic aromatic hydrocarbons (PAHs) in epipelic and benthic sediments from Iko River estuary mangrove ecosystem has been investigated. Total PAHs ranged from 6.10 to 35.27 mg/kg dry weight. Quantitative difference between the total PAHs in epipelic and benthic sediments showed that the benthic sediment known for higher capability to serve as sink for chemical pollutants accumulated less PAHs. This implies that PAHs in the epipelic sediment may plausibly be from industrial sources via runoff and/or of biogenic origin. A strong pyrolytic source fingerprint has been detected with slight influence of petrogenic sources. Total organic carbon normalized PAHs (sum of 16 PAHs, 59.7 to 372.4 mg/kg OC) were under (except for ES3 and BS3) the threshold effects concentrations (TEC, 290 mg/kg OC). Total PAHs in Iko River estuary sediments were in the range between ERL and ERM.

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of ubiquitous environmental pollutants, and some of them are known to be mutagenic or carcinogenic (Ravindra et al. 2008). PAHs are released to the environment through anthropogenic activities such as the production and combustion of fossil fuels and biomass (Omar et al. 2002) and enter surface waters through different pathways including atmospheric fallout, urban runoff, and municipal/industrial effluents (Zhu et al. 2004). PAHs are hydrophobic and are taken up readily by suspended particles that are coated in a complex matrix of organic matter in aquatic environments (Shiaris and Jambard-Sweet 1989; Means et al. 1980). As a result of particle settlement, sediments tend to be the major sink for PAHs in streams, lakes, estuaries, and oceans. An understanding of the fate of PAHs in coastal environments is important, because high PAH levels in coastal ecosystems may pose a threat to human public health and the well being of biota.

The major environmental concern with crude oil is that if not handled carefully, it may pose significant hazards to human's health and earth's ecology during all stages of production, processing, transportation, and consumption. The Niger Delta of Nigeria houses refineries and other petroleum-based industries. Therefore, contamination of the environment with oil-related pollutants is inevitable. At present, pollution of streams and rivers by petroleum and its derivatives in the Niger Delta is one of the greatest ecological challenges (Olajire et al. 2005). The major causes of environmental damage have been noted to be due to accidental spillages and sometimes, intentional discharge of oil or oily wastes to water or land, through blowouts from pipes and pumps, pipeline corrosion, and spillages during transportation (Urum et al. 2006).

Very little is known about PAH's existence in the Niger Delta mangrove ecosystems not withstanding, historic cases of crude oil pollution in the region. There have been reported incidences of oils pillage and seepage in addition to gas flaring in the area (Essien and Antai 2003; Asuquo 1991). An obvious environmental unfriendly concern associated with gas flaring is the phenomenon of acid rain, resulting in high level of acidity that manifest to severe corrosion of iron roof sheets. Such was the major impact recorded in Iko town and its environs where gas flaring was achieved through horizontally positioned nozzle about two decades ago. Gas flaring was a major depositor of pollutants on water, air, and soil within this area; although municipal wastes and domestic sewage, with deposits of decayed organic matter and oil residues covering much of the bottom, grossly pollute the estuary. Residents of the riverine communities also complain of skin irritation, infertile agricultural soil, destruction of fish life and fisheries production, and deterioration of the quality of surface and ground waters (Akpan 2003). The attendant, political, and social upheavals were enormous and resulted in the withdrawal of operation by Shell, Nigeria. To date, little or no information is available on the environmental health status of the ecosystem. This study was, therefore, initiated to conduct a series of PAH analyses of sediment samples collected over time (2003, 2005, and 2007) from an abandoned oil field in Iko River estuary, located in the oil-producing community of Iko Town in Akwa Ibom State, Nigeria. Over the decades, no concerted effort has been directed towards ascertaining its recovery. In this study, however, we evaluate the PAHs trends of the mangrove estuarine sediments over times.

Materials and methods

Study area

Iko is located within the petroleum belt of the Niger Delta, Nigeria (latitude 7°30′ N and 7°45′ N and longitude 7°30′ E and 7°40′ E). The Iko River estuary has semi-diurnal tides and a shallow depth ranging from 1 to 7 m at flood and ebb tide. The estuary is more than 20 km long with an average width of about 15 m. Iko River takes its course from Qua Iboe River catchments and drains directly into the Atlantic Ocean at the Bight of Bonny (Ekpe et al. 1995; Benson and Etesin 2008). It has many adjoining tributaries and part drains into Imo River estuary, which opens into the Atlantic Ocean. Soft dark mudflats, usually exposed during low tide, mangrove swamps, shoals, and sandbars, characterize the shoreline of Iko River. The area is characterized by a humid tropical climate with rainfall reaching about 3,000 mm per annum.

Sampling

Three sites in Iko River estuary were chosen to represent a wide range of PAH contamination (Fig. 1). Intertidal sediment samples were obtained with a gravity corer (6.5 cm diameter and length of 100 cm) to a depth of 10 cm. The corer does not have a core catcher but uses a tight-fitting lid which closes the top of the coring tube during retrieval and thereby retains the sediment core. Subtidal sediment samples were collected using Shipek grab sampler (stainless steel, 472 × 638 × 442 mm in size) with approximate weight of 60 kg.

The sediment was sub-sampled with a sterile wooden spatula from the composite sample, and the sub-samples were placed in glass bottles, kept at lower temperature in chest coolers (0°C) to reduce microbial activities. Triplicate samples were usually obtained at each site. A time series of sediment samples was collected at various locations at the peak period of dry season in 2003, 2005, and

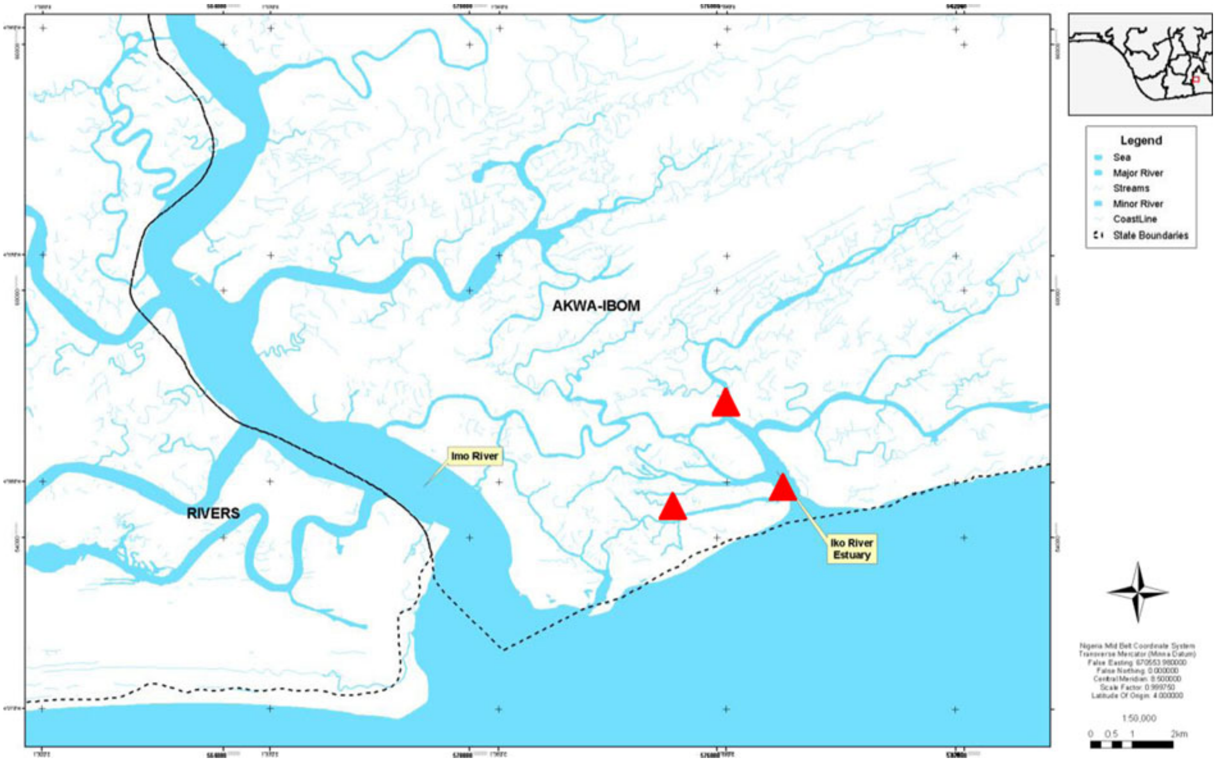

Fig. 1 Iko River Estuary showing the sampling locations (*solid triangles*)

2007 from the river for determining PAHs trends over time. Each sub-sample was placed in a pre-combusted glass jar, freeze-dried, homogenized, sieved through a mesh of 2 mm to remove stones, and stored at −20°C until further analysis.

Sediment characterization

The total carbon of the sediments was determined as described by Olajire et al. (2005). Sediment pH was measured potentiometrically in 0.01 M $CaCl_2$ with sediment/extractant ratio of 1:2 while the salinity was determined from silver thiourea (AgTU) extracts and 0.1 M silver nitrate ($AgNO_3$) titration using potassium chromate as indicator and calculated as total soluble salts (chlorides + sulfates).

Sediment extraction and fractionation

The sediments were extracted and fractionated as described Olajire et al. (2005). The dried and sieved samples (50 g) were weighed and spiked with pre-deuterated PAH Cocktail as internal standard (naphthalene-d_8, acenaphthylene-d_8, anthracene-d_{10}, acenaphthene-d_{10}, fluoranthene-d_{10}, phenanthrene-d_{10}, fluorine-d_{10}, pyrene-d_{10}, chrysene-d_{12}, benzo[a]pyrene-d_{12}, benzo[b]fluoranthrene-d_{12}, benzo[a]anthracene-d_{12}, benzo[ghi]perylene-d_{12}, dibenzo[a,h]anthracene-d_{14}, and indenol[1,2,3-cd]pyrene-d_{12}; ES2528, Promochem, Wesel, Germany) and extracted with dichloromethane (DCM) using temperature programmed Soxhlet extractor at 65°C for 24 h. The extracts were reduced to dryness and re-dissolved 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 re-dissolved in DCM.

GC/MS analysis and quantification

A gas chromatograph (GC, Hewlett–Packard HP 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 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 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 pre-deuterated internal standard.

Results and discussion

PAHs profiles in sediments from Iko River estuary mangrove ecosystem

All the sediment samples collected over the periods (2003, 2005, and 2007) of this study from Iko River estuary swamp contained detectable amount of PAHs. For compositional study, the 16 target PAHs were divided into four groups according to their number of aromatic rings. The PAHs representing 2–3-, 4-, 5-, and 6-ring PAH groups are given in Table 1. The sum concentra-

Table 1 Total PAHs concentration (mg/kg dw), concentration of 16 PAHs and total organic carbon (%) in sediments from Iko River estuary mangrove ecosystem

Ring number	Analyte	Sample					
		Epipelic sediment			Benthic sediment		
		ES_3	ES_5	ES_7	BS_3	BS_5	BS_7
2–3-ring PAHs	Naphthalene	4.8	1.0	1.0	3.28	1.0	1.0
	Acenaphthylene	1.33	1.0	1.0	1.08	1.0	1.0
	Acenaphthene	0.79	0.70	0.70	0.72	0.70	0.70
	Fluorene	0.53	0.70	0.70	0.49	0.70	0.70
	Phenanthrene	4.66	0.20	0.20	4.14	0.20	0.20
	Anthracene	2.04	0.40	0.37	1.98	0.40	0.40
4-ring PAHs	Fluoranthene	6.11	0.38	0.24	3.21	0.20	0.20
	Pyrene	2.28	0.23	0.20	2.94	0.35	0.20
	Benzo(*a*)anthracene	1.53	0.32	0.20	2.03	0.93	0.20
	Chrysene	1.98	0.36	0.30	2.14	0.59	0.30
5-ring PAHs	Benzo(*k*)fluoranthene	1.67	0.30	0.20	2.02	0.37	0.20
	Benzo(*b*)fluoranthene	1.48	0.20	0.20	1.18	0.20	0.20
	Benzo(*a*)pyrene	1.75	0.20	0.20	1.13	0.20	0.20
	Dibenzo(*a*, *h*)anthracene	0.76	1.70	1.70	0.55	1.67	0.20
	Benzo(*g*, *h*, *i*)perylene	1.52	0.20	0.20	1.46	0.20	0.20
6-ring PAH	Indeno(*1,2,3-cd*)pyrene	2.04	1.12	0.20	1.96	1.02	0.20
Total PAHs		35.27	9.01	7.61	30.31	9.73	6.10
Total CPAHs[a]		9.24	3.64	2.70	8.87	4.39	1.20
% Organic carbon[b]		9.47	9.93	10.1	8.35	7.64	10.21
pH[b]		6.43	6.16	6.58	6.86	7.20	6.99
Salinity (%)[b]		2.94	3.11	3.05	2.85	3.22	3.40
$\sum$ PAHs/OC (mg/kg dw)		372.4	90.7	75.3	363.0	127.4	59.7

[a] Sum of benzo(*a*)anthracene, benzo(*a*)pyrene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, dibenzo(*a*,*h*)anthracene and indeno(*1,2,3-cd*)pyrene

[b] Means of triplicate determinations (±5% of the mean); $\sum$ PAHs/OC is the total PAHs concentration normalized to organic carbon content; ES_3 (BS_3), ES_5(BS_5), and ES_7(BS_7) are epipelic(benthic) sediments collected in 2003, 2005, and 2007 respectively

tion of all the PAHs in each sediment sample was characterized by calculating the total concentration of PAHs for each group of PAH separately. It is called PAH-group profile in this study. The PAH-group profiles are then normalized by the total PAHs in the sediment (Fig. 2).

High molecular weight PAHs ($m/z \geq 202$) which were known to be persistent and had chronic toxicity to surrounding environment were more than 60% of total PAHs in all the sediments analyzed (Fig. 2). Among them, phenanthrene, fluoranthene, and pyrene were the most dominant compounds, which account for about 36.7% and 33.6% of the total PAHs in ES_3 and BS_3, respectively, while benzo(b)fluoranthene, benzo(k)fluoranthene, indeno (*1,2,3-cd*) pyrene, and benzo (g, h, i) perylene also showed high contribution in these sediments. Naphthalene was predominant among the low molecular weight PAHs.

The total PAHs in epipelic sediments were higher than that of benthic sediments. The high total PAHs concentration in the epipelic sediment may be from industrial sources via runoff and/or of biogenic origin. This is despite the higher microbial and worms activities commonly found in the "oxic" epipelic sediment which normally enhances sediment-mixing activities that simulates PAHs degradation in sediments (Gardner et al. 1979).

This investigation has revealed that tropical mangrove ecosystems have strong capability to recover from hydrocarbons pollution impacts, evidence in support of the process of bioattenuation in the studied area (Farias et al. 2008; Sharma et al. 2002). The recovery trend recorded for the Iko River estuary mangrove ecosystem shows 74.0% and 67.6% reduction in total PAHs levels between 2003 and 2005 for epipelic and benthic sediments respectively. The recovery of Iko river estuary mangrove sediments within this period could be partly be attributed to transformation, sequestration in sediment, and volatilization of low molecular weight PAHs and could be stimulated by high nutrient availability (bioattenuation) or sediment transport, which may wash out the sediment to the sea. The low degradation rate from 2005 to 2007 can be ascribed to the phenomenon of diauxic, which may play a role in suppressing PAH transformation in the presence of alternative carbon sources other than PAHs. The concentration of dibenzo (a, h) anthracene increases from 0.76 to 1.70 and from 0.55 to 1.67 in epipelic and benthic sediments, respectively, rather than decreasing from 2003 to 2005 and was maintained at this concentration level in 2007 in epipelic sediment. Formation of the dibenzo (a,h) anthracene from other PAHs by indigenous microorganism might occur in the environment (Zuberer 1994).

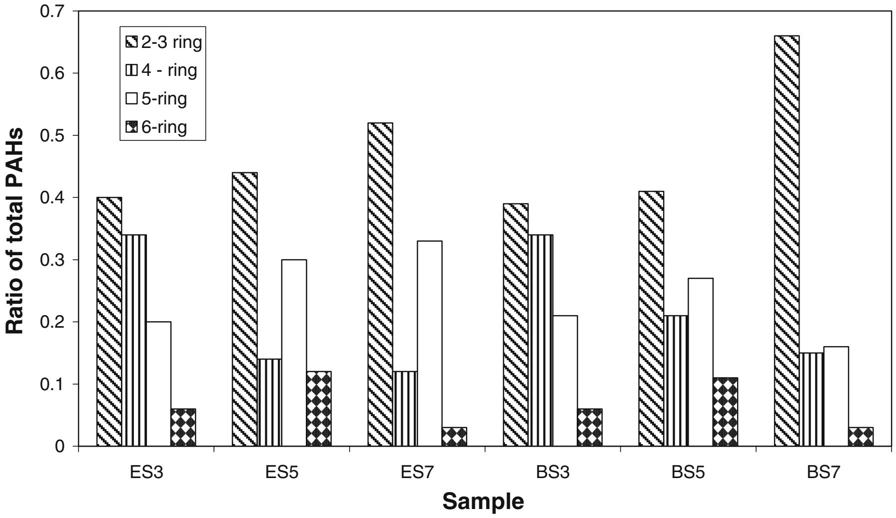

Fig. 2 Group profile of sedimentary PAHs normalized by total PAHs in the sediments of Iko River Estuary

Source identification

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, that is combustion of organic matter, 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 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). In case of diagenetic origin, very few compounds are generated in comparison to the complex mixtures of PAHs generated by the other sources.

Table 2 shows the parent PAH ratios of sediments examined in this study. In order to characterize PAHs with respect to sources, we have considered some diagnostic ratios conventionally reported in the literature for this objective (Soclo et al. 1986; Budzinski et al. 1997; Baumard et al. 1998; Steinhauer and Boehm 1992). A ratio of low to high molecular weight PAHs was examined (Soclo et al. 2000), and we obtained a range 0.28–1.41 for the Iko River sediments (Table 2). The values are greater than unity (>1) for ES_3 and BS_3, which suggest a pollution of petrogenic origin; while others are less than unity (<1), which suggest pyrolytic sources. The low values of the ratio (i.e, <1.0) for these sediments (ES_5, ES_7, BS_5, and BS_7) also show that the low molecular weight PAHs are more prone to biodegradation by indigenous sediment bacteria and fungi.

Most samples analyzed satisfied the criteria of Phen/Anth <10, Flu/Pyr >1. The ratios Flu/Pyr and Phen/Anth are used to distinguish petrogenic and pyrogenic sources of PAHs (Shi et al. 2007; Readman et al. 2002; Olajire et al. 2005). This indicates that combustion was the dominant source of the PAHs.

Finally, we considered the ratio Naph/Phen that was used to assume the presence of fresh and unweathered petroleum if it is greater than unity (Dahle et al. 2003). In this study, all except $BS_3$are greater than unity, further evidence in support of petrogenic input for PAHs in these sediments. This implies that there are plausibly, other sources of hydrocarbon pollutants despite the withdrawal of Shell Nigeria activities in Iko Town. However, ambiguity and difficulty in the interpretation of results always occurred if more than two criteria are used to determine possible sources (Prerira et al. 1999; Belanchen et al. 1997); therefore, the reliability of results of these ratios should be checked by the amount of particular PAH compounds. The predominance of alkylated and 2–3-ring PAHs indicates a petrogenic source of pollution while the predominance of 4–6-ring PAHs is related to pyrolytic origin (Dahle et al. 2003; Norta et al. 2001). In view of prevalent anthropogenic activities within and around the Iko River estuary and its environs, and the relatively high abundance of 2–3- and 4-ring PAHs, it can be inferred that Iko River estuary sediments have a mixed pattern of pyrolytic and petrogenic inputs of PAHs.

Table 2 PAH ratio in the sediment samples from Iko River Estuary Mangrove Ecosystem

Sample	PAH ratio			
	LMW/HMW	Phen/Anth	Flt/Pyr	Naph/Phen
ES3	1.41	2.28	2.68	1.03
ES5	0.37	0.50	1.65	5.0
ES7	0.34	0.54	1.20	5.0
BS3	1.17	2.09	1.09	0.79
BS5	0.28	0.50	0.57	5.0
BS7	0.67	0.50	1.00	5.0

Naph naphthalene; *Anth* anthracene; *Phen* phenanthrene; *Flt* fluoranthene; *Pyr* pyrene

[a] Ratio of sum of phenanthrene to pyrene relative to sum of benzo(a)anthracene to benzo(g,h,i)perylene

Ecotoxicological significance

The effects range low (ERL) and the effects range medium (ERM) values were used for assessment of the aquatic sediment with a ranking of low to high impact values (Long et al. 1995). ERL and ERM represent the concentrations below and above which toxic effects are probable respectively. The range between ERL and ERM represents concentrations where toxic effects are probable. Several PAH components in Iko River estuary sediments were in the range between ERL and ERM; while almost all the sediments collected in 2003 were above ERM (Table 3), indicating their potential toxic impact.

A "Consensus Approach" that combines sediment guidelines from correlative and equilibrium partitioning approaches were also used to create a consensus threshold effects concentration (TEC), median effects concentrations (MEC), and probable effects concentrations (PEC) (Swartz 1999). He observed a clear distinction between threshold values below which effects were unlikely (TEC, 290 mg/kg OC), an intermediate clustering where effects may be observed (MEC, 1800 mg/kg OC), and a grouping where effects were probable (PEC, 10,000 mg/kg OC).

The greatest certainty in predicting the absence or presence of sediment toxicity occurs at sediment contaminant concentrations that are lower than TEC or greater than the PEC values, respectively. Toxicity does occur at contaminant concentrations between the TEC and PEC values, with the amount of toxicity dependent on the particular contaminant and with the incidence of toxicity greater than that which occurs at the TEC concentration but less than that which occurs at the PEC concentration (MacDonald et al. 2000a). The TEC, MEC, and PEC concentrations in the consensus-based sediment quality guidelines (CBSQGs) define four possible ranges of concentration for contaminants (i.e, $\leq$ TEC; $>$ TEC $\leq$ MEC; $>$ MEC $\leq$ PEC; and $>$ PEC). For most reliable consensus-based SQG contaminants, there is a consistent and incremental increase in the incidence of toxicity to sediment-dwelling organisms with increasing chemical concentrations (MacDonald et al. 2000a, b).

Total organic contents (TOC) in the sediments analyzed were in the range of 9.475 to 10.21%. Total PAHs (sum of 16 target PAHs) normalized by TOC varied from 59.7 to 372.4 mg/kg OC. These values (except for ES_3 and BS_3) are far less than the suggested TEC value, implying that the PAHs levels in Iko River estuary sediments are unlikely to cause adverse effects on sediment flora and fauna and also reflect the extent to which the indigeneous bacteria and fungi of the sediments have been able to biodegrade the toxic PAHs in these sediments over the periods under investigation. The ES_3 and BS_3 have values of 372.4 and 363.0 mg PAH_{tot}/kg OC, respectively, which are greater than TEC level but less than MEC value (i.e, $>$TEC $<$ MEC), thus indicating that these sediments are likely to cause adverse effects on benthic-dwelling species in 2003. The possible presence of co-occurring toxic compounds from

Table 3 Pollution criteria of PAH compounds for sediment matrix (mg/kg)

Compund	ERL	ERM	ES3	ES5	ES7	BS3	BS5	BS7
Naph.	0.16	2.10	4.8^{b}	1.0^{a}	1.0^{a}	3.28^{b}	1.0^{a}	1.0^{a}
Acy.	0.044	0.64	1.33^{b}	1.0^{a}	1.0^{a}	1.08^{b}	1.0^{a}	1.0^{a}
Ace.	0.016	0.50	0.79^{b}	0.70^{b}	0.70^{b}	0.72^{b}	0.70^{b}	0.70^{b}
Flu.	0.019	0.54	0.53^{a}	0.70^{b}	0.70^{b}	0.49^{a}	0.70^{b}	0.70^{b}
Phen.	0.240	1.50	4.66^{b}	0.20^{a}	0.20^{a}	4.14^{b}	0.20^{a}	0.20^{a}
Anth.	0.853	1.10	2.04^{b}	0.40^{a}	0.37^{a}	1.98^{b}	0.40^{a}	0.40^{a}
Flt.	0.60	5.10	6.11^{b}	0.38^{a}	0.24^{a}	3.21^{a}	0.20^{a}	0.20^{a}
Pyr.	0.665	2.60	2.28^{a}	0.23^{a}	0.20^{a}	2.94^{b}	0.35^{a}	0.20^{a}
BaA	0.261	1.60	1.53^{a}	0.32^{a}	0.20^{a}	2.03^{b}	0.93^{a}	0.20^{a}
Chry.	0.384	2.80	1.98^{a}	0.36^{a}	0.30^{a}	2.14^{a}	0.59^{a}	0.30^{a}
BbF	NA	NA						
BkF	NA	NA						
BaP	0.43	0.001	1.75^{b}	0.20^{a}	0.20^{a}	1.13^{b}	0.20^{a}	0.20^{a}
DBA	0.063	0.260	0.76^{b}	1.70^{b}	1.70^{b}	0.55^{b}	1.67^{b}	0.20^{a}
BgP	NA	NA						
InP	NA	NA						
$\sum$ PAH	4.0	44.79	35.27^{a}	9.01^{a}	7.61^{a}	30.31^{a}	9.73^{a}	6.10^{a}

ERL effects range low; *ERM* effects range medium

[a] PAH are in the range between ERL and ERM

[b] PAH are the range above ERM; NA, not available

petroleum oils and photoactivation of PAHs in these sediments (ES3 and BS3) may also enhance their toxicity to aquatic organisms, and this may have implications in certain types of habitats (Ankley et al. 2002).

Conclusion

The study showed high total PAH levels at the onset, with the disappearance of PAHs in both sediment types within two years. This investigation has revealed that tropical mangrove ecosystems have strong capability to recover from hydrocarbons pollution impacts, evidence in support of the process of bioattenuation in the studied area. The recovery trend recorded for the Iko River estuary mangrove ecosystem shows 74.0% and 67.6% reduction in total PAH levels in 2003 and 2005 for epipelic and benthic sediments respectively. The recovery of Iko River estuary mangrove sediments within this period could partly be attributed to transformation, sequestration in sediment, and volatilization of low molecular weight PAHs and could be stimulated by high nutrient availability (bioattenuation) or sediment transport, which may wash out the sediment to the sea. The indications of PAHs distribution in mangrove sediment point out the complexity of investigating the fate of PAHs in these environments and difficulty of defining general PAHs level

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