

## **Distribution and Sources of Polyaromatic Hydrocarbons (PAHs) in Surface Sediments of Great Kwa River, Nigeria**

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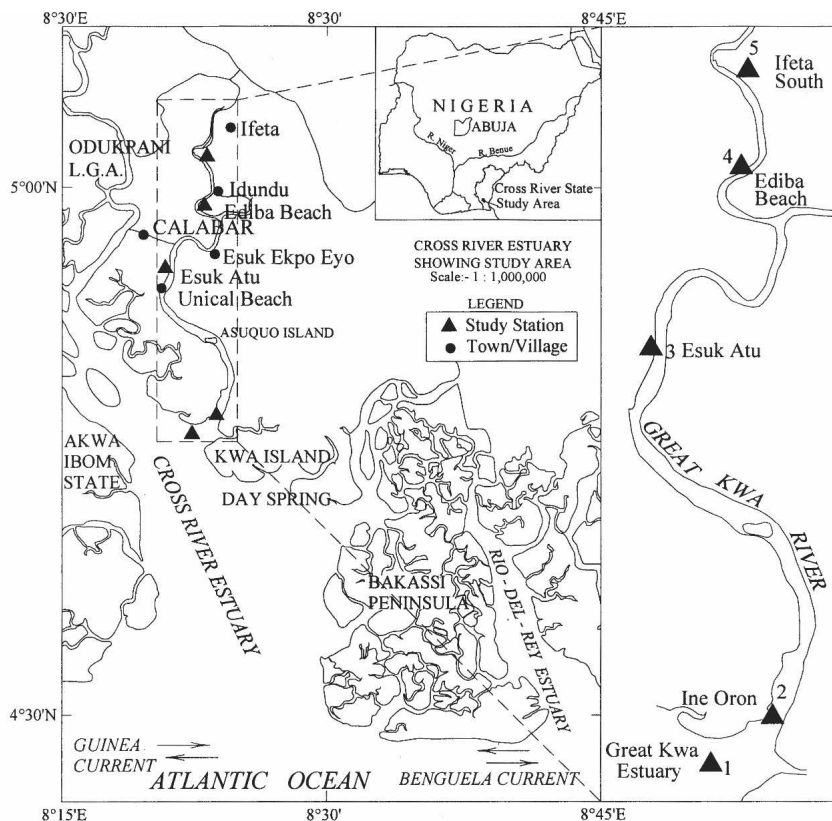
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The impacts of environmental contaminants on the nearshore marine ecosystem arising from anthropogenic activities have been reported (Clark et al. 1979). Burgess and McKinney (1999) observed that different types of non-polar trace contaminants (PAHs, polychlorinated biphenyls and pesticides) have contributed to the environmental degradation and stress of aquatic ecosystems and bioaccumulation may occur. Water quality deterioration, stunted growth, low fecundity of fishes, morbidity of organisms, smothering of fish eggs in shallow waters, toxicity and death are a few negative impacts from heavy metal and trace organic pollution of coastal habitats (Asuquo and Udoh 2002). Beyond adverse ecological perturbations of the pelagic zone, contaminated sediments have become a perennial sink for these pollutants thereby restricting the use of mineral and fishery resources. Of particular importance are the PAHs which are harmful and carcinogenic to man, fauna and flora (GESAMP 1993; Clark et al. 1997) especially the presence of benzo (a ) pyrene and derivatives (Al-Saad and Al-Tamari 1989; Asuquo et al. 1999). PAHs are relatively insoluble in water but have high affinity to adsorb to suspended particulate matter with resultant sedimentation (NRC 1985; GESAMP 1993), thereby placing emphasis on sediment analysis of aquatic PAHs (ICES 1991).

Estuaries due to their unique location as the mixing zone between inland drainage and seawater intrusion have high tendencies to accumulate toxic PAHs, which may be bioaccumulated and biomagnified within the food chain (Burgess and McKinney 1999). The Great Kwa river is part of Cross River estuarine system which is the largest estuary in West Africa and constitutes one of the busiest fishing grounds south of the Niger (Asuquo and Udoh 2002). It is located between longitudes 8° 15' and 8° 30'E and latitudes 4° 45' and 5° 15'N (Fig. 1). The lower reaches of the river are influenced by semi diurnal tides. The purpose of this study therefore was to determine the levels and distribution of PAHs in sediments of the Great Kwa river and to establish among others the degree of impacts and the pollution sources of the ecosystem. These will provide the baseline data required for formulation of regulations with respect to the discharge of wastewater into the environment and appropriate planning for the management of aquatic resources in the region.



**Figure 1.** Locations of sampling stations on Great Kwa river, Nigeria

## MATERIALS AND METHODS

Surface sediments were collected from five stations in the Great Kwa River (Fig 1) using a Van Veen grab sampler and hand driven auger. Surface (0.2 cm) sediments were collected quarterly for one year. Each batch of sample was air dried for two days, ground and soxhlet extracted twice with a mixture of dichloromethane and methanol (60/40 w/w; Loring and Rantala 1992). Combined extracts were concentrated by controlled evaporation, saponified and then separated into groups by column chromatography packed with deactivated silica gel and alumina (1:2). The PAH fraction was eluted with dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) in hexane and concentrated at an oven temperature of 25° C for a day and then analyzed by GC-FID. GC analysis was performed using a gas chromatograph (Unicam instrument) equipped with a 30m x 0.25 mm id fused silica column coated with 100% dimethyl polysiloxane of 0.5µm film thickness. An aliquot sample (1µl) was injected in splitless mode.

The temperature was programmed from 60°C (30 min) to 100 °C at 10 °C /min. and then to 300°C at 5 °C/min. Helium was used as the carrier gas. Data were acquired and processed with an INCOS 2300 data system. Recovery studies with fortified samples indicated that the recovery efficiency exceeded 85% for compounds measured. Pearson correlation analysis was used to establish the relationships between components vis a vis the sources of the PAHs. Particle grain size and total organic carbon (TOC) from representative samples of the bulk sediments were also determined for a better appraisal of PAH residues (Loring and Rantala 1992).

## RESULTS AND DISCUSSION

PAH concentrations observed in this study are summarized in Table 1. In surface sediments  $\Sigma$ PAHs content varied from 2.38  $\mu\text{g/g}$  at station 5 (upstream) to 5.177  $\mu\text{g/g}$  at station 1 (estuary). The highest levels were at stations 1(estuary) and 3 (Esuk Atu). At the estuary, estuarine sedimentation of suspended sediments laden with PAH occurred while Station 3 was influenced by petroleum/oily waste generated from indiscriminate disposal of waste oil by artisan mechanic workshops. Layers of surface soils contaminated with such waste are washed into drainage channels which finally empty into the nearby Great Kwa river.

The distribution of PAHs measured showed that fluoranthene is the most dominant PAH having an overall mean of 2.65  $\mu\text{g/g}$  or 79.6% by mass of the PAH present in the samples, followed (not very closely) by naphthalene (0.33  $\mu\text{g/g}$ ). This confirms that anthropogenic factors are a major source of hydrocarbon input in this estuary since fluoranthene and naphthalene are among the common PAHs in fuel oil discharged from municipality effluents (Al-Saad and Al-Tamari 1989). All the other PAHs had mean values < 0.1  $\mu\text{g/g}$ .

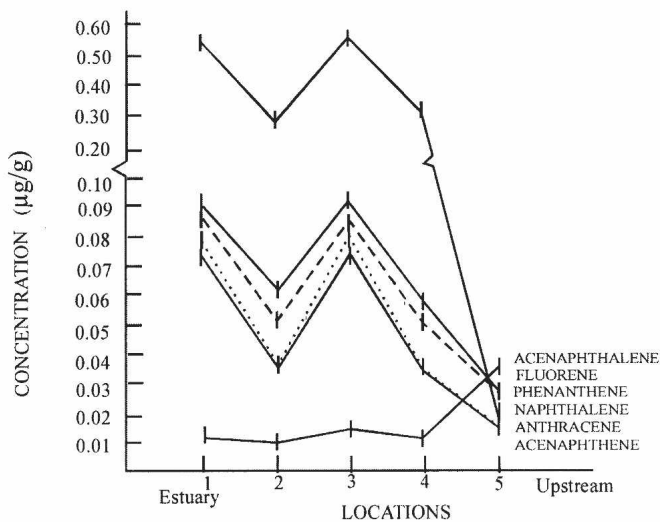
**Table 1.** Ranges  $\Sigma$ PAHs and total organic matter contents of surface sediments from Great Kwa river, Nigeria.

Parameters	Stn 1	Stn 2	Stn 3	Stn 4	Stn 5
Range ( $\mu\text{g/g}$ )	0.012-4.2	0.01-2.9	0.014-4.2	0.01-2.5	0.013-2.05
$\Sigma$ PAH ( $\mu\text{g/mg}$ )	5.18	3.38	5.18	3.03	2.38
CV%	137.7	127.7	132.7	128.6	50
TOC	9.08	1.86	9.10	1.65	1.30
Sed. Texture	Silty clay	Silt	Silt	Silt	Silty Clay

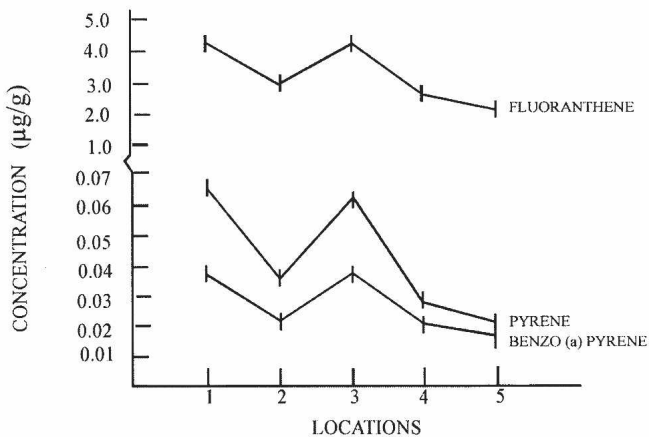
Stn. 1= Great Kwa estuary, Stn. 2 = Ine Oron, Stn. 3 = Esuk Atu , Stn.4 = Ediba beach, Stn. 5 = Ifeta south

The PAH contents of the sediment increase with increased organic matter content in the silty-clay soils than the silt soils alone (Table 1). The presence of silty-clay appear to modify the adsorptive and retentive capacity of the sediments thereby increasing the amount of PAH found in such sediments. Spatial variability of TOC also indicated an increasing trend towards the estuary and a high value of TOC (9.1%) at the urban drainage discharge points was recorded (station 3).

Except at station 5 (Ifeta), all other locations showed marked variability in the concentration of the components (CV > 125%). The rate of sedimentation, the sedimentation pattern and the silty-clay texture of the sediments contributed to the observed variability in the levels of PAH components.



**Figure 2.** Spatial variation of low molecular weight PAH components in sediments from Great Kwa river estuary, Nigeria.



**Figure 3.** Spatial variation of high molecular weight PAH components in sediments from Great Kwa river estuary, Nigeria .

Figs. 2 and 3 illustrate the spatial variations of the PAH components at the different sampling stations. Generally, the PAH concentrations increased



downstream with the lowest values at station 5 (Ifeta south) about 35 km from the estuary. The extent of contamination are indicated by the error bars signifying irregularity in amounts of PAH inputs into the river from point sources.

A pair-wise correlation analyses (Table 2) showed that there was a significant ( $P < 0.01$ ) variation in the PAH concentrations measured at each location implying that human-influenced factors such as quality of storm water runoff, discharges from industrial or residential area and estuarine sedimentation/siltation markedly control their levels. According to Al-Saad and Al-Tamari (1989) the distribution of PAHs in sediment could also occur through atmospheric fallout especially in oil producing areas. Adjacent to the Great Kwa estuary (station 1) is the Gulf of Guinea with several oil wells/platforms offshore where vertical gas flarings occur daily. These sources are channels through which PAHs may be added to the system (NRC 1985; Clark et al. 1997).

**Table 2** Correlations between the chemical components of PAH extracted from Great Kwa River surface sediments.

	Naphthalene	Acenaphthalene	Acenaphthene	Fluorene	Phenanthrene	Anthralene	Fluoranthene	Pyrene	Benzo (a) anthracene
Naphthalene		-0.70	0.98	0.59	0.993	0.96	0.70	0.93	0.07
Acenaphthene			-0.55	-0.58	-0.69	-0.49	-0.051	-0.47	-0.27
Acenaphthalene				0.998	0.98	0.992	0.98	0.99	0.09
Fluorene					0.99	0.995	0.988	0.98	0.99
Phenanthrene						0.97	0.97	0.86	0.56
Antralene							0.99	0.99	0.996
Fluoranthene								0.998	0.994
Pyrene									0.996
Benzo (a) anthracene									

The Great Kwa River estuary is surrounded by mangrove swamps and covered by mangrove vegetation and other aquatic plants which may contribute some PAHs to the sediments. Favourable diagenetic processes can produce a mixture of PAHs from polycyclic biogenic precursors due to bacterial decomposition of lipids, terrestrial higher plants or terpenoids (Tisot and Welte 1984; Al Saad and Al Tamari 1989). During the study, evidence from Pearson correlation analysis showed that some PAH components like acenaphthalene could be of biogenic origin as indicated by negative and low correlation ( $r < -0.27$ ,  $p < 0.01$ ,  $n=45$ ) with other components (Table 2). These observations are corroborated by the fact that the concentrations of acenaphthalene were the lowest observed ( $<0.033\mu\text{g/g}$ ) indicating background levels.

In Nigeria, several regulatory measures have been instituted for the control and management of oil pollution and waste generation. These include Petroleum Decree No.51 of 1959, Oil Pipeline Ordinance Decree (CAP 145) of 1965, Oil in Navigable Water Regulation of 1968, Petroleum Drilling and Production Regulation of 1969, Department of Petroleum Resources (DPR) Guidelines and Standards for the petroleum industry of 1987 and Federal Ministry of Environment (FMENV formerly FEPA) Decree of 1989, amended 1992 among others. Presently, the petroleum industry is statutorily managed by the Nigerian National Petroleum Corporation (NNPC) and the FMENV monitors the activities of new and existing companies and ensure compliance of waste or effluent discharge within permissible limits.

In this study, both biogenic (acenaphthalene and benzo-a-pyrene) and anthropogenic (fluoranthene, naphthalene) sources of input are pertinent though in small amounts. Most PAHs are adsorbed on detrital organic matter which are transported and deposited at the estuary especially during slow current (slag tide). The comparatively minimal level of the low molecular weight components indicate rapid volatility of these components activated by high solar radiation.

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