

*Full Length Research Paper*

# Source determination of polynuclear aromatic hydrocarbons in water and sediment of a creek in the Niger Delta region

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**Polynuclear aromatic hydrocarbons in surface water and sediment of Ekpan Creek of the Warri River were determined with GC Perkin-Elmer/Clarius 500. Compositional patterns of the PAHs were used to distinguish their sources in the aquatic system. The three diagnostic selected concentration ratios of polynuclear aromatic hydrocarbon isomer pairs confirmed that the PAHs concentrations in sediment of Ekpan Creek were from pyrogenic origin and include phenanthrene, anthracene, fluoranthene, pyrene, chrysene and benzo(a)anthracene.**

**Key words:** Polynuclear aromatic hydrocarbons, surface water, sediment, aquatic system.

## INTRODUCTION

Polynuclear aromatic hydrocarbons (PAHs) are ubiquitous in nature as evidenced by their detection in sediments, soils, air, surface waters, and plant and animal tissues primarily as a result of natural processes such as forest fires, microbial synthesis, and volcanic activities. Anthropogenic activities associated with significant production of PAHs leading, in some cases, to localized areas of high contamination include high temperature (>700°C), pyrolysis of organic materials typical of some processes used in the iron and steel industry, heating and power generation and petroleum refining. Aquatic environments may receive PAHs from accidental releases of petroleum and its products, from sewage effluents and from other sources. Sediments heavily contaminated with industrial PAHs wastes have directly caused elevated PAH body burdens and increased frequency of liver neoplasia in fishes (Eisler, 1987). The evidence implicating PAHs as an inducer of cancerous and precancerous lesions is becoming overwhelming, and this class of substance is probably a major contributor to the increase in cancer rates reported for industrialized nations (Bjorseth and Dennis, 1980).

The point sources of emissions of reportable size of polynuclear aromatic hydrocarbons are petroleum refineries, fossil fuel power plants (coal, oil), coal tar production plants, coking plants, bitumen and asphalt production

plants, paper mills, wood products manufacture, aluminum production plants and industrial machinery manufacture (NPI, 2001). The Nonpoint sources may include aerial fallout, inadvertent oil spills, and marine oil spillage (Eddy and Cherrie, 1994). Once formed, PAHs can be transported into an aquatic environment by a number of pathways including fossil fuel distribution, storm water runoff and sewage effluent. Fossil fuels including peat, coal, and petroleum are considerably rich in complex assemblages of PAHs. These compounds reach the aquatic environments through surface runoff, in wastewater, and as a result of petroleum spillage (Brooks, 1997). It was estimated that spilled petroleum contribute 374,782,200 pounds of PAHs to aquatic environments each year (Eisler, 1987). This source overwhelms all others in terms of global inputs. PAHs present in the atmosphere enter rain as a result of in-cloud and below-cloud scavenging (Van Noort and Wondergem, 1985). Because they are sometimes formed in areas that are relatively not polluted suggest that rain play a very paramount role in transport and distribution of PAHs (Quaghebeur et al., 1983). They may reach aquatic systems in household and industrial sewage effluents, in surface runoff from land, from deposition of airborne particulates, and especially from spillage of petroleum and petroleum products into aquatic environments (Lake

et al., 1979; Martens, 1982).

The study area, Ekpan Creek of the Warri River, is a receptor of various contaminants including atmospheric and chemicals carried along with urban run off. Effurun, Ekpan and Warri cities are major towns with host of anthropogenic activities which releases both industrial and domestic effluents into the Warri River. The sampling area, made up of points from a location in the creek with Latitude N 50°32.71 and Longitude E50° 43.64'. The toxic nature of the 16 USEPA priority PAHs determined and discussed in this report makes it imperative to classify and distinguish the sources of entry into the aquatic system. It is quite interesting to mention that recent studies have focused on classification of the sources of PAHs into two major types; petrogenic and pyrogenic sources. Petrogenic origin arises from PAHs formed during emissions of non-combustion derived matter including inadvertent oil spills, while pyrogenic origin arises from these formed during the incomplete combustion of coal, oil, gas wood and garbage (Neff, 1979; Cerniglia and Heitkamp, 1991). Owing to the fact that there has been limited published reports on levels of PAHs in Nigeria Rivers, it became necessary to choose a control River essentially Abraka location of the Ethiope River. Abraka location of the Ethiope River where samples were collected are on Latitude N 5° 49.456' and on Longitude E 6° 06.494'. It is an area where there is no single industrial activity, but there are considerable levels of agricultural activities. It can be described as a relatively non-polluted location of the Ethiope River. The distance between the Abraka location of the Ethiope River (Control) and the Ekpan creek of the Warri River is about 49.9 km.

## MATERIALS AND METHODS

### Sampling

Sampling campaigns were carried out in December, 2003; February, 2004; May, 2004 and July, 2004. December and February were period of dry season while May and July were period of wet season. Composite samples of both water and sediment in Ekpan Creek of Warri River and Abraka location of Ethiope River were collected in the described four months. The water samples for PAHs analysis were collected in a litre amber glass bottle with Teflon-lined screw-cap, 5 mL of 1:1 HCl acid was added and cooled to about 4°C before it was taken to the laboratory prior to analysis (APHA, 1998), while sediment samples, having being collected with a sediment grab (Van Veen sediment grab sampler) into a litre chemically-cleaned glass jars with Teflon-lined screw-cap, were cooled to about 4°C, extracted within seven (7) days and extracts analyzed within 40 days.

### Analysis

The water samples for PAHs analysis were extracted with methylene chloride, dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and solvent-exchanged into hexane. Clean-up and fractionation was done using silica gel permeation chromatography. Final extracts after reconcentration using a rotary evaporator was packed in a 2 ml GC vials and analysed with a Gas Chromatograph (GC), Perkin-Elmer/Clarius 500. GC

column conditions: Column made up of 5% PMS (100/120 mesh) coated with 3% OV-17 packed in a 1.8 x 2 mm ID glass column with helium carrier gas at 40 mL/min flow rate. Column temperature held at 100°C for 4 min, then programmed at 8°C/min to a final hold at 280°C. H<sub>2</sub> and air gas were used to light up the FID. Quantification of the PAHs was accomplished using a seven-point, external standard curve (APHA, 1998). The standard curves were linear, with correlation coefficients for the investigated PAHs ranging between 0.997 and 0.999. No internal standards were however, employed in the quantification using the GC. Sediment samples, having being dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> were extracted with a mixture of dichloromethane (DCM) and acetone, thereafter solvent-exchanged with hexane. Clean-up and fractionation was done using silica gel permeation chromatography. Final extracts were similarly analysed using the same described GC. The % proportion of 2 - 3 rings PAHs relative to 4, 5 - 6 rings and diagnostic concentration ratios of PAHs isomer pairs were used to apportion sources of PAHs input into the Ekpan creek of the Warri River.

## RESULTS AND DISCUSSION

The concentrations of the detected polynuclear aromatic hydrocarbons in surface water and sediment of Ekpan Creek of the Warri River including that of the Abraka location of Ethiope River are shown on Tables 1 and 2. Acenaphthylene, a low molecular weight PAH, like naphthalene, has a concentration value of 0.0935 mg/L in surface water of Ekpan Creek, which was quite higher compare to 0.0001 mg/L observed in water of Abraka location of the Ethiope River. Benzo(a)pyrene, a known carcinogen to animals, has a mean value of 0.0026 mg/L in Ekpan Creek. The values observed were within the range reported for benzo(a)pyrene in surface water of Forcados River, in Niger Delta Area (Eloke, 2001). Benzo (a) pyrene was however not detected in the Abraka location of the Ethiope River. Total PAHs concentration of 0.1761 mg/L in water of Ekpan Creek was high compare to 0.002 mg/L and 0.003 mg/L recommended as fresh water guidelines by US EPA, 1996 and ANZECC, 1992, respectively. This calls for serious pollution concern. Contrary to reports in other creeks of the Warri River, the percentage composition of the 2, 3 - ring, low molecular weight PAHs in water of Ekpan creek was calculated to be about 63.4%, essentially higher than the percentage composition of the high molecular weight PAHs (HPAHs; Table 1). This relative abundance of low molecular weight PAHs (LPAHs) indicated that the PAHs were from petrogenic origin such as oil leakages or inadvertent oil spills. Chrysene in sediment with mean value of 0.7215 mg/kg was observed to be lower in concentration than 4.3 mg/kg reported for sediment of Buffalo River in New York (Black et al., 1985). Benzo(a)pyrene, a known carcinogen, which has produce tumors in series of laboratory animals (Pucknat, 1981), was observed to have elevated level in sediment compare to mentioned quality criteria (Table 2). The total PAHs recorded in sediment, with range 5.5830 – 9.3265 mg/kg, were within the range reported for sediment of motorway drainage surface dry detention pond at Oxted, Surrey, UK (Kamalakkannan et al., 2004), but were slightly lower than the ones reported

**Table 1.** Concentrations of PAHs (mg/L) in surface water of Ekpan Creek and Abraka (control).

Components	MW	Ekpan		Abraka	
		Mean	Range	Mean	Range
Naphthalene	128.2	0.0201	0.0015 - 0.0523	0.000247	0.000025 - 0.00068
Acenaphthylene	152.2	0.0935	0.006734 - 0.2105	0.000584	0.000343 - 0.000867
Acenaphthene	154.2	0.0033	0.00325 - 0.0033	0.000064	ND
Fluorene	166.2	ND	ND	0.000068	ND
Phenanthrene	178.2	ND	ND	0.000075	0.000046 - 0.000105
Anthracene	178.2	ND	ND	0.000058	ND
<b>Total LPAH</b>		<b>0.1169</b>	<b>0.0015 - 0.2105</b>	<b>0.001096</b>	<b>0.000025 - 0.000105</b>
Fluoranthene	202.3	ND	ND	ND	ND
Pyrene	202.3	ND	ND	ND	ND
Benzo(a)anthracene	228.3	ND	ND	ND	ND
Chrysene	228.3	ND	ND	ND	ND
Benzo(b)fluoranthene	252.3	0.0034	0.00324 - 0.0035	0.000067	ND
Benzo(k)fluoranthene	252.3	0.0035	0.0032 - 0.0037	0.000827	ND
Benzo(a)pyrene	252.3	0.0026	0.001246 - 0.0033	ND	ND
Dibenzo(a,h)anthracene	278.4	0.0087	0.000546 - 0.0248	0.000101	0.000098 - 0.000105
Benzo(g,h,i)perylene	276.3	0.0046	0.00314 - 0.0085	0.000019	ND
Indeno(1,2,3-cd)pyrene	267	0.0052	0.002186 - 0.0088	0.000205	ND
<b>Total HPAH</b>		<b>0.0280</b>	<b>0.000546 - 0.0248</b>	<b>0.001219</b>	<b>0.000098 - 0.000105</b>
<b>Total</b>		<b>0.1761</b>	<b>0.02439 - 0.2836</b>	<b>0.001038</b>	<b>0.00017 - 0.00186</b>

LPAH = Low molecular weight PAHs; HPAH = high molecular weight PAHs; and MW = molecular weight.

**Table 2.** Concentrations of PAHs (mg/kg) in sediment of Ekpan Creek and Abraka (control).

Components	MW	Ekpan		Abraka	
		Mean	Range	Mean	Range
Naphthalene	128.2	0.1192	0.0016 - 0.2525	0.000432	0.000235 - 0.00063
Acenaphthylene	152.2	0.1935	0.024 - 0.5215	0.000423	0.000015 - 0.000742
Acenaphthene	154.2	0.0447	0.0124 - 0.0954	0.000124	ND
Fluorene	166.2	0.2958	0.0052 - 0.9652	ND	ND
Phenanthrene	178.2	0.3322	0.0624 - 0.9658	ND	ND
Anthracene	178.2	0.2128	0.0132 - 0.6855	ND	ND
<b>Total LPAH</b>		<b>1.1982</b>	<b>0.0016 - 0.9658</b>	<b>0.000979</b>	<b>0.000015 - 0.000235</b>
Fluoranthene	202.3	0.7334	0.0325 - 1.4528	ND	
Pyrene	202.3	0.8582	0.0245 - 1.5247	ND	0.000025 - 0.00052
Benzo(a)anthracene	228.3	1.2945	0.965 - 1.624	ND	0.00015 - 0.00036
Chrysene	228.3	0.7215	0.6325 - 0.8105	ND	ND
Benzo(b)fluoranthene	252.3	0.6622	0.0033 - 0.9857	0.000067	ND
Benzo(k)fluoranthene	252.3	0.3852	0.035 - 0.7964	0.000827	ND
Benzo(a)pyrene	252.3	1.0134	0.8695 - 1.2015	ND	ND
Dibenzo(a,h)anthracene	278.4	0.6596	0.0354 - 0.985	0.000101	ND
Benzo(g,h,i)perylene	276.3	0.5354	0.0413 - 0.7476	0.000019	ND
Indeno(1,2,3-cd)pyrene	267	0.8646	0.7425 - 0.956	0.000205	ND
<b>Total HPAH</b>		<b>7.7279</b>	<b>0.0033 - 1.624</b>	<b>0.001219</b>	<b>0.000025 - 0.00052</b>
<b>Total</b>		<b>7.6441</b>	<b>5.5830 - 9.3265</b>	<b>0.001038</b>	<b>0.000488 - 0.00235</b>

**Table 3.** Selected ratios of PAH isomer pairs for Sediment and Water of Ekpan Creek of the Warri River.

Sample	Phenanthrene/Anthracene	Fluoranthene/Pyrene	Chrysene/Benzo(a)anthracene
Sediment in Ekpan	1.561	1.170	0.557
Water in Ekpan	0.000	0.000	0.000

for sediment of Rivers in Monaco, France. High molecular weight PAHs were relatively more abundant in the sediment from Table 2. Contrary to observed compositions of PAHs in surface water, the dominance of HPAHs in the sediment could be associated with long term accumulation resulting from surface runoff, municipal and industrial waste discharges and aerial deposition. Leakages and inadvertent spills could remain afloat for some short time before biodegradation and photo-degradation of the PAHs present would take place. However, the three diagnostic selected concentration ratios of PAHs isomer pairs shown on Table 3 confirmed that the PAHs concentrations in sediment of Ekpan Creek were from pyrogenic origin.

## Conclusion

Composition of PAHs in surface water was found to be largely different from that of the sediment of Ekpan Creek of the Warri River. While the origin of PAHs in the surface water was determined to be petrogenic because phenanthrene, anthracene, fluoranthene, pyrene, chrysene and Banzo [a] anthracene were not detected, that of the sediment were from pyrogenic sources. There could have been unprecedented phenomena during the periods of sampling campaigns such as inadvertent oil or fuel leakages from barges or transportation media along the water course which could possibly have played a major role in this sharp variation in source distinction between surface water and sediment of the aquatic system.

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