

Occurrence and Diagenetic Evolution of Perylene in the Sediments of Oginigba Creek, Southern Nigeria

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ABSTRACT: Perylene and penta-aromatic hydrocarbons were determined in sediments as part of a study that was dedicated to the aquatic ecosystem of Oginigba Creek (southern Nigeria) in order to carry out a critical corroboration of occurrence and diagenetic evolution of perylene in the sediments of the creek. The results show that the annual mean levels of perylene ranged from 396.27–507.19 mg/g dry weight at the various Stations. The observed values for total penta-aromatic hydrocarbons were high (867.3 – 1243.14mg/g dry weight) in all the stations sampled. One origin index or concentration ratio of Ip/Ip+BghiP was also used to evaluate the suitability of the penta-aromatic hydrocarbons as a tracer to distinguish between contaminations arising from different sources. The values for the sampling stations therefore ranged from 0.41 to 0.81. A critical appraisal of the PAH index, consequently, suggested that petroleum combustion is the major penta-aromatic hydrocarbon source in the sediments of the creek. The PAH group profile shows that perylene was high in the sediments and would pose apparent effects in fauna. The high concentration of perylene in the sediments was also indicative of an in situ biogenic derivation. Furthermore, a concentration of perylene 31.88% of total penta-aromatic hydrocarbons established a credible diagenetic origin.

Key words: Oginigba Creek, Perylene, Penta-aromatic hydrocarbons, Sediments, Diagenetic origin

INTRODUCTION

Sediments of aquatic environment act as a major reservoir of metals and also as a source of contaminants (Priju and Narayana, 2007; Praveena, *et al.*, 2008). The present study is part of a study that was dedicated to the aquatic ecosystem of Oginigba Creek. Oginigba Creek, which is a shallow, tidal and brackish creek of 4km in length and about 100-200m in width, is situated around the southwest part of the Obio-Akpor Local Government Area of Rivers State of southern Nigeria. The creek passes through Oginigba community and empties into the Bonny River. It receives abattoir, urban, poultry wastes, wastes from the drainpipe of ACM/Michelin (a tire production company) etc. The study area enjoys the humid tropical climate, which was characterized by the hot and wet conditions derived

from the movement of the Inter-Tropical Convergence Zone (ITCZ) north and south of the equator and experiences consistently high temperatures (about 32°C) all year round. Since temperature varies only slightly, rainfall distribution, over space and time, becomes a single most important factor. The implication is that there is a prolonged rainy season in the area. The study area, therefore, has two major seasons, the dry season and the wet season (Okafor and Opuene, 2007). Sediments in general have been used to examine the pollution of aquatic environments for the reason that perylene and the penta-aromatics generally existing in low concentrations in the water column have a propensity to associate preferentially with the sediments to attain considerable concentration levels (Xiao-Jun, *et al.*, 2006). In addition, the transport and fate of these classes of polycyclic

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aromatic hydrocarbons (PAHs) in aquatic ecosystems have received some attention in southern Nigeria because of concerns over accumulation (Okafor and Opuene, 2007). Perylene has an absorption maximum at 434nm and as with all PAHs, water solubility of 1.2×10^{-5} mmol/L and a molar extinction coefficient of 38,500/M/cm at 435.75nm. In cell membrane cytochemistry, perylene is used as a fluorescent lipid probe. It is also used as a blue-emitting dopant material in Organic Light-Emitting Diodes, either pure or substituted. Perylene can also be used as an organic photoconductor. Its absorption data is not available; however, by analogy to other PAHs, primarily benzo [a] pyrene, it would be expected to be absorbed from the gastrointestinal tract, lungs, and skin of fauna in sediments of aquatic ecosystems with potential for impacts. It or its derivatives may be carcinogenic and is considered to be a hazardous pollutant (EPA, 1991). In addition, perylene may result from both organic matter digenesis and anthropogenic processes (Baumard, *et al.*, 1998). However, the diagenetic contribution usually outweighs the inputs from other sources, and is responsible for the general increase over the last 100 years (Hites, *et al.*, 1997).

Due to trade and industry in the area, Oginigba Creek appears to be a receptor of both inorganic and organic pollutants. Furthermore, information regarding the local pollution level of the creek and its effects is limited. And in view of the physical state of the aquatic ecosystem, it seems necessary to conduct an assessment of perylene, which has no known commercial production and use in the area, in sediments so as to establish its occurrence and diagenetic evolution in the creek. And for the reason that perylene in the environment is attracting increasing attention for its widespread occurrence and potential impacts (Yunker, *et al.*, 2002; Jian, *et al.*, 2000; Xiao-Jun, *et al.*, 2006; Baumard, *et al.*, 1998; Tolosa, *et al.*, 2004; Venkatesan, 1998), the goal of this study was to

apply perylene over penta-aromatic isomers as a molecular tool to elucidate the occurrence and diagenetic derivation of perylene in the sediments of Oginigba Creek, southern Nigeria.

MATERIALS & METHODS

Five sampling stations were selected in the current study (Table 1). Surficial sediment was sampled using a stainless steel grab sampler for the period January 2006 to December 2006. The sediment samples (0-20cm depth) were scooped into pre-cleaned amber glass bottles and properly cooled in a refrigerator (4° C) until they were stored at -20° C pending further treatment.

After removing coarse materials (>2.5mm), the sediments were freeze-dried at -50°C and stored in dark bottles. The sediments were Soxhlet extracted for 8h in a cellulose thimble with dichloromethane. The extracts were further purified to avoid interferences by aliphatic hydrocarbons, porphrins, chlorins, and carotenoids, if present in the prepared matrices. The empirical purification entailed the use of neutral activity I alumina as an adsorbent. It was introduced in slurry form with hexane into 1-cm glass columns to a depth of about 10cm. Concentrated extracts were dissolved in hexane and subsequently introduced to the wet adsorbent and eluted with hexane to remove aliphatic hydrocarbons. A second eluant was benzene, which removed the aromatic components with sufficient purity for the Capillary Gas Chromatographic analysis (Okafor and Opuene, 2007).The purified aromatics were analyzed by capillary gas chromatography using an HP 6890 Series GC system equipped with a flame ionization detector (FID). The column used was a HP-5, 30 m X 0.25 mm X 0.25µm (HP Part No. 19091S-433). Hydrogen (10.2psi) was used as carrier gas at 1.5mL/min. The column was kept at 80°C for 1 minute. It was programmed to 280°C at the rate of 20°C/min. The column temperature was further programmed to a final

Table 1. Geo-referencing of sampling Stations and description of sediment samples

Stations	Longitude(E)	Latitude(N)	Sediment	
			Mean TOC (%)	Description
1	07° 02' 39.6 ^{II}	04° 49' 30.0 ^{II}	3.54	Silt
2	07° 02' 44.5 ^{II}	04° 49' 10.6 ^{II}	4.64	Silt
3	07° 02' 43.8 ^{II}	04° 49' 16.4 ^{II}	3.60	Silt
4	07° 02' 48.2 ^{II}	04° 49' 56.6 ^{II}	3.48	Silt
5	07° 02' 49.9 ^{II}	04° 49' 49.9 ^{II}	3.00	Silt

hold at 300 °C at the rate of 2.5 °C/min. Temperature of the FID and T_{ij} (1 µl, 0.01 mg each/ml, split 25/1) were kept at 325 °C.

Sub-samples of sediments were acidified to remove carbonates and the levels of total organic carbon (TOC) were determined using a CHNS Vario El III analyser. The limit of detection was 0.01 µg/g for the various PAHs studied. And in carrying out recovery analyses, a perdeuterated PAH (perylene-*d*₁₂) was added to samples prior to extraction to quantify procedural efficiency. The surrogate recovery was 90.76 ± 10.53% for perylene-*d*₁₂. Data analysis included calculating individual and total PAH concentrations, and summarizing PAH compositional indices or ratios. The PAH compositional index or ratio used in the assessment incorporated Indeno [1, 2,3-cd] Pyrene/ Indeno [1,2,3-cd] Pyrene + Benzo [g, h, i] Perylene (Ip/Ip+BghiP). A linear regression analysis was carried out for perylene and TOC. The effect of TOC on the penta-aromatic hydrocarbon concentrations was also studied using Analysis Toolpak Software (Zar, 1990).

RESULTS & DISCUSSION

Perylene concentration in sediments varied between 396.27 to 507.19 µg/g dry weights for the period January to December 2006. Perylene concentrations in sediments were higher in Station 3 than in the other sampling sites (Table 2). On the other hand, penta-aromatic hydrocarbon concentrations in the sediments ranged from 867.3 to 1243.14 µg/g dry weights with a mean concentration of 1094.63 µg/g dry weight (Table 2). Highest penta-aromatic hydrocarbon concentrations were detected in sediments from Stations 3 and 5 respectively. Higher penta-aromatic hydrocarbon concentrations in Stations 3 and 5 could be attributed to abattoir wastes, industrial wastes and traffic volume relative to Stations 1, 2 and 4 respectively. The concentration

levels of perylene and penta-aromatic hydrocarbons in the sediments are higher than the reported values for PAHs in Taylor Creek (Okafor and Opuene, 2007).

A significant factor that controls the concentration of these PAHs in sediment is supposed to be TOC. A positive correlation in particle-associated PAH concentration with TOC was found in many aquatic ecosystems, such as the Pearl River Estuary (Xiao-Jun, *et al.*, 2006). In this study, the effect of TOC on the penta-aromatic hydrocarbon concentrations was also studied. A linear regression analysis showed that the penta-aromatic concentrations of the PAHs in the sediments was not correlated to the organic carbon content with $r^2 = 0.275$, which indicated that TOC does not influence the distribution pattern of the penta-aromatic hydrocarbons in the sediments; that could be attributed to labile organic carbon from microbes such as phytoplankton and zooplankton in sediments that may have masked the relationship between the penta-aromatic hydrocarbons and TOC (Xiao-Jun, *et al.*, 2006). Furthermore, the concentration levels of perylene in the sediments were not correlated to organic carbon content with $r^2 = 0.0175$, which may also be due to the reason adduced for the non-correlation of the penta-aromatic hydrocarbons and TOC respectively. Conversely, the net implication is that the concentration levels of the PAHs are in excess of the Overall Apparent Effects Threshold of Long and Morgan (1990) and may be mutagenic and carcinogenic to fauna.

PAH isomer pair ratio such as Ip/Ip+BghiP has been used as distinct chemical tracer to infer possible sources of PAHs in environmental samples (Yunker, *et al.*, 2002). Based on the PAH isomer pair ratio measurements compiled by Prahl and Carpenter (1983), a ratio of Ip/Ip+BghiP < 0.2 indicates petroleum, 0.2 to 0.5 indicate petroleum combustion, and > 0.5 indicates combustion of coal, grass and wood. The ratio of

Table 2. Mean concentrations of PAHs in sediments (µg/g dry weight)

Parameter	Acronym	Sampling Station				
		1	2	3	4	5
Benzo [b] Fluoranthene	BbK	727	815.21	1049.12	1002.8	1074.43
Benzo [k] Fluoranthene	BkF	314.3	352.02	423.81	377.74	404.46
Benzo [a] Pyrene	BaP	442.51	495.61	727.21	669.31	717.11
Dibenzo [a, h] Anthracene	DA	140.3	157.48	180.64	157.48	168.71
Benzo [g, h, i] Perylene	BghiP	432.17	484.03	507.19	463.18	396.272

Ip/Ip+BghiP shows that the penta-aromatics are from petroleum combustion (Table 3).

Table 3. Origin index of PAHs in sediments

Parameter	Sampling Station				
	1	2	3	4	5
IP/IP + BghiP	0.41	0.41	0.43	0.42	0.39
Perylene, %	49.83	49.76	41.24	39.92	31.88
10 % of 5-Ring PAHs	86.73	97.27	122.98	116.28	124.31

In addition, perylene has been found widely in a variety of marine, riverine sediments and peat (Jiang, *et al.*, 2000). It is, in general, a diagenetic product derived from its natural precursors during early diagenesis (Venkatesan, 1998). Only trace amounts of perylene are produced during combustion. A concentration of perylene > 10% of total penta-aromatic hydrocarbons has been suggested to indicate a probable diagenetic input; or else a probable pyrolytic origin is indicated (Baumard, *et al.*, 1998). Nonetheless, Tolosa, *et al.* (2004) found that a less than 20% of perylene over penta-aromatic isomers indicated a typical pyrolytic source of this compound. Elevated concentrations (from 209.00 to 245.28 $\mu\text{g}/\text{kg}$ dry weight) of perylene relative to the other PAH compounds in sediment samples were obtained in this study. Percentages of perylene over the penta-aromatic isomers varied from 39.92% to 49.76% in sediment samples (Table 2), which was indicative of an *in situ* biogenic origin.

CONCLUSION

Perylene and penta-aromatic hydrocarbons were determined in sediments of Oginigba creek in order to apply perylene over the penta-aromatic hydrocarbons as a molecular tool to elucidate the occurrence and diagenetic evolution of perylene in the sediments of the creek. The high concentration of perylene over the penta-aromatic hydrocarbons established a convincing diagenetic derivation of perylene in the sediments.

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