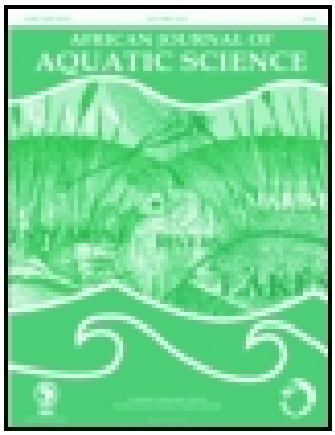

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Polycyclic aromatic hydrocarbons in water, sediment and fish from the Warri River at Ubeji, Niger Delta, Nigeria

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The Warri River at Ubeji, Nigeria, receives pollutants from an oil refinery. The levels of 16 priority polycyclic aromatic hydrocarbons (PAHs) in water, sediment and the tissue of tilapia from the Warri River were investigated in 2010 using gas chromatography with mass spectrometry. Eleven PAHs were found in the sediment and nine in fish and water, with total mean concentrations of 4 587.7 ng g^{-1}, 1 098.5 ng g^{-1} and 34 ng ml^{-1} in sediment, fish tissues and water, respectively. Lower molecular weight PAHs were predominant, with naphthalene accounting for the highest concentration in all samples. Carcinogenic PAHs detected included benzo(a)pyrene, benzo(a)anthracene and chrysene. The predominance of lower molecular weight PAHs in the study area is an indication of recent pollution of petrogenic origin from the Warri Refining and Petrochemical Company's refinery.

Keywords: bioaccumulation, crude oil industry, toxicology, water pollution

Introduction

There are abundant natural resources, including oil, natural gas and a rich biological diversity, in the Niger Delta area (Zabbey 2004). The demand for oil as a source of energy for industries, automobile and household consumption has resulted in a corresponding increase in the operational activities of oil and associated industries. More than 90% of the petrochemical plants in Nigeria are situated in the Niger Delta region (Essien and Antai 2005), but many do not have standard surveillance technologies for neutralising oil effluents before disposal, leading to high levels of pollutants in the environment (Li et al. 2005; Uzoekwe and Oghosanine 2011). Petrochemical plant activities have a considerable impact on the health of the ecosystem and on biological diversity. Rivers and other waterbodies around these refineries are used for discharging waste, posing significant threats to the aquatic biota and man (Achudume 2009).

Several industrial chemical substances are used and discharged into the waterbodies, with possible impacts on the structure and function of aquatic ecosystems. Some of these are emitters of polycyclic aromatic hydrocarbons (PAHs) (Johnson-Restrepo et al. 2008), which are pervasive contaminants in the aquatic ecosystem and a major environmental threat due to their high toxicity for organisms, carcinogenic properties and their ability to induce DNA damage (Incardona et al. 2005; Johnson-Restrepo et al. 2008). Oil refinery effluent can kill organisms directly through coating and asphyxiation, contact poisoning or through exposure to water-soluble components. Toxic effects from such effluents close to their outfall point include disruption of animal metabolism and incorporation into the organism's fatty tissue (Wake 2005; Achudume 2009). Bioaccumulation, bioconcentration and trophic transfer due to such pollutants from refineries have also been documented (Logan 2007).

Fishes constitute a large percentage of the diversity of organisms that inhabit rivers and other waterbodies, and, worldwide, a large portion of the human population depends on catches from the wild as a source of animal protein. One of the most exploited groups of fish species in rivers is tilapia, which has high tolerance to poor water quality and eats a wide range of natural food organisms (Ugwumba and Ugwumba 2007; Lasheen et al. 2012). Tilapia are of great economic importance in the fisheries of many waterbodies, including Nigeria. In addition, they are good sentinels and bioindicators of pollution due to their ability to integrate the effect of contaminants over time (Lasheen et al. 2012). But the impact of pollution has led to the reduction, migration and eradication of natural fish stocks. Zenetos et al. (2004) reported that hydrocarbon pollutants in water and sediment at an environmentally relevant concentration elicit effects such as the reduction in species richness and community diversity. Fishes can be exposed to PAH-contaminated sediment and water through various pathways such as dermal absorption, ingestion and respiration (Logan 2007), often resulting in negative effects on the marketability of the fish.

Rapid uptake of oil PAH by exposed fish poses a potential threat to human consumers of fish due to biomagnification along the food chain (Logan 2007). The accumulation of PAHs occurs in all aquatic organisms, and their concentration in tissues is influenced by environmental

concentration, level and time of exposure, and species ability to metabolise the compounds. Bioaccumulation assays have been used previously to show the presence of PAH compounds in the tissues of animals in contaminated waters (Tarja and Aimo 2004).

The aim of the present research was to examine polycyclic aromatic hydrocarbon levels in water, sediment and tilapia from the Warri River at Ubeji, Niger Delta, Nigeria. This study site was chosen because the river receives effluent directly from the petroleum industry, unlike other surrounding rivers, such as the Umah, Omagino, Ugbuwangwe, Egbokodo and Escravos, which receive effluent from industries other than the petrochemical industry.

Materials and methods

Study area

The study area stands about 13 m above sea level, with flat topography, a mean annual rainfall of 3 200 mm occurring throughout the year, and a mean temperature of about 28 °C (Mode et al. 2010). The geology of the region comprises a highly aquiferous formation, >100 m thick, containing surface alluvium – the Somebreiro deposits (a deltaic plain sand intercalated with peat or clay), overlying the Benin, Agbada and Akata stratigraphic formations (Olobaniyi and Efe 2006). The Warri River is a major navigable channel of the Niger Delta in southern Nigeria which flows into the Forcados River, which in turn drains into the Atlantic Ocean (Figure 1). The river is known to supply water for drinking, domestic use, irrigation of farm lands, recreational activities, as well as fishing and transportation. Three sampling stations were established on the Warri River at Ubeji, a village adjacent to the Warri Refining and Petrochemical Company, which was commissioned in 1978. Industrial wastes from the refinery are discharged into a small creek where it enters the Warri River at Ubeji. Uzoekwe and Oghosanine (2011) indicated that the effluents were treated before being discharged. The sampling stations were located 1.7 km (Station I), 2.3 km (Station II) and 3.7 km (Station III) downstream from the discharge point.

Sample collection

Fish, sediment and water samples were collected at each sampling station in five replicates in March 2010. Control samples were taken from the Eleyele River, which has no known source of industrial or petrogenic pollution. Water samples were collected by lowering a cleaned and dried one-litre plastic container below the water surface to a depth of 13–20 cm, and then adding 5 ml of HCl to each sample. Samples from the sediment surface, to a depth of 10 cm, were collected approximately 10 m from the shoreline with the aid of a van Veen grab. Five freshly caught fish of 10–11.5 cm total length (TL) from each station were obtained from local fishermen, frozen and transported to the laboratory, where they were identified to species level.

PAH extraction

Gill and muscle samples from *Tilapia zillii*, *Oreochromis niloticus* and *Hemiorechromis fasciatus*, and sediment samples, were analysed for PAH according to the procedures of Sloan et al. (1993), modified as follows. Fresh wet samples of 5 g each of sediment and tissues

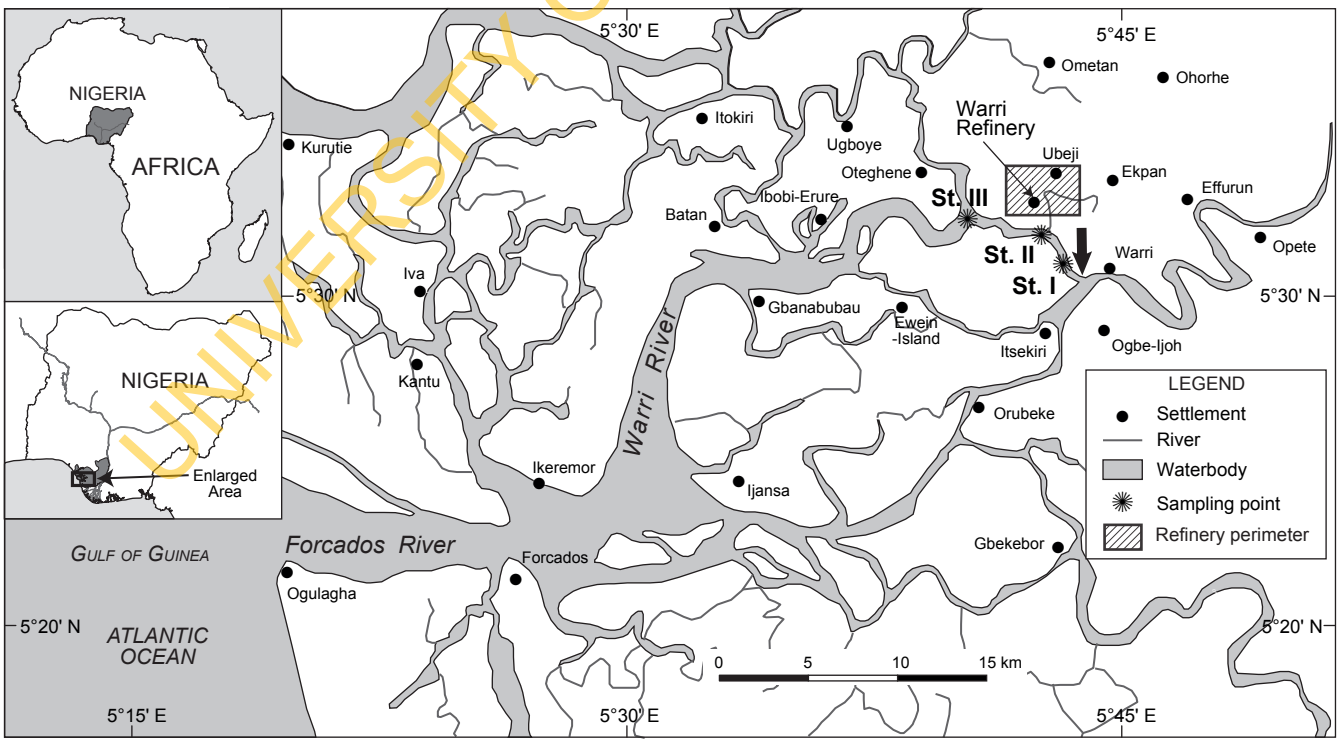

Figure 1: Map of the study area on the Warri River, Niger Delta, indicating effluent discharge point (arrowed) and sampling stations

were solvent-extracted by homogenisation with dichloromethane and 5 g of sodium sulphate to absorb water. Surrogate standards (decaflourobiphenyl in iso-octane, 50 µl) were used for measuring the recovery of the analytes after 25 ml acetone and petroleum spirit had been added in equal proportions. The extracts were then filtered through a gravity-flow column of silica/alumina to remove the highly polar solvent. The filtered extracts were concentrated to 1 ml. For water samples, 200 ml were used in a sodium sulphate column with 30 ml of dichloromethane. The column was removed and 1.5 ml of iso-octane was added. The sample extracts were evaporated to 5 or 6 ml under vacuum, using a rotary evaporator at 30–35 °C, and solvent exchanged to iso-octane. The solvent extract was separated from the solid matrix by centrifugation, then filtered and concentrated as described earlier.

PAH determination and statistical analysis

Gas chromatography with mass spectrometry (HP 5890 Series II) was used to separate, identify, and quantify the polycyclic aromatic hydrocarbon compounds in the sediment, water and fish tissues. Columns measured 1.8 m × 2 mm and used helium carrier gas at a flow rate of 1 ml min^{-1}. Column temperature was set at 60 °C for 1–2 min, then raised to 120–180 °C at 20 °C min^{-1}, and finally increased to 280 °C at 6 °C min^{-1} and held for 20 min. Internal standard PAHs included acenaphthylene-d8, pyrene-d10, phenanthrene-d10, naphthalene-d8, fluoranthene-d10, benzo[a]pyrene-d12, and benzo[ghi]perylene-d12 (Sigma-Aldrich, Missouri, USA). Quantification of the PAHs was accomplished using standard calibration curves. The percentage proportions of 2- and 3-ring PAHs relative to 4-, 5- and 6-ring PAHs were used to identify sources of PAHs input into the waterbody.

Screening of 17 PAHs was carried out. The choice of PAH was informed by their toxicity, and the classification of 16 of them by the United States Environmental Protection Agency as priority pollutants (OFR 1982). These PAHs included naphthalene (Nap), acenaphthalene (Acy), acenaphthene (Ace), 2-methylnaphthalene (2-methylNap), fluorene (Flu), anthracene (Ant), phenanthrene (Phe), pyrene (Pyr), chrysene (Chr), fluoranthene (Fla), benzo(a)anthracene (B[a]A), benzo(b)fluoranthene (B[b]F), benzo(k)fluoranthene (B[k]F), benzo(a)pyrene (B[a]P), benzo(g,h,i)perylene (B[g,h,i]P1), dibenzo(a,h) anthracene (DB[a,h]A) and indeno(1,2,3-c,d) pyrene (I[1,2,3-c,d]P).

Analytical laboratory blanks were treated in the same way as actual samples, and used for quality control. The PAHs present in the appropriate blanks were subtracted from those in the sample extracts. Lower detection limit – 3.3 × SD of blank – was determined as 0.01–0.04 ng g^{-1}. The average recovery determined by adding 100 ng of PAH standards before extraction, was near 100% for all standards. The results were summarised separately for each sampling station using descriptive statistics (means and bar charts). The Kruskal–Wallis test for non-parametric analysis of variance (Zar 1984) was used to test for significant differences among stations for each of the samples. For all comparisons, a value of $p < 0.05$ was considered significant.

Results

Total mean PAH concentrations in sediment, fish and water samples from the river were 4 587.7 ng g^{-1}, 1 098.5 ng g^{-1} and 34 ng ml^{-1} wet weight, respectively (Table 1). In

Table 1: Mean concentrations (n = 15) of PAHs in sediment, fish and water from the Warri River at Ubeji in March 2010. ND = not detected, NA = not available; for the last seven PAHs: B = benzo, A = anthracene, F = fluoranthene, P = pyrene, P1 = pyrelene, DB = dibenzo, I = indeno

PAH	Molecular weight	No. of rings	Conc. in sediment (ng g^{-1})	Conc. in fish (ng g^{-1})	Conc. in water (ng ml^{-1})	CCME 2008 standard (ng ml^{-1})
Low-weight PAHs						
Naphthalene (Nap)	128.2	2	166.7	133	2.3	0.11
Acenapthalene (Acy)	152.2	3	ND	ND	ND	NA
Acenaphthene (Ace)	154.2	3	42	64.5	3.7	0.58
2-methylnaphthalene (2-methylNap)	NA		2 298.7	491	11.7	NA
Fluorene (Flu)	166.2	3	89.3	71	3.7	0.30
Anthracene (Ant)	178.2	3	1 601.7	148	2.7	0.012
Phenanthrene (Phe)	178.2	3	104	100.5	6	4
Subtotal			4 302.3	1 008.0	30.0	
High-weight PAHs						
Pyrene (Pyr)	202.3	4	43.7	29	1	0.025
Chrysene (Chr)	228.3	4	16.3	ND	ND	NA
Fluoranthene (Fla)	202.3	4	113.3	20.5	1.7	0.40
B[a]A	228.3	4	45	41	1.3	0.018
B[b]F	252.3	5	21	ND	ND	NA
B[k]F	252.3	5	ND	ND	ND	NA
B[a]P	252.3	5	46	ND	ND	0.015
B[g,h,i]P1	276.3	6	ND	ND	ND	NA
DB[a,h]A	278.4	6	ND	ND	ND	NA
I[1,2,3-c,d]P	267.0	6	ND	ND	ND	NA
Subtotal			285.3	90.5	4	
Total			4 587.7	1 098.5	34.0	

the bottom sediment samples, 12 PAHs were detected, including Nap, 2-methylNap, Ace, Flu, Phe, Ant, Fla, Pyr, Chr, B[a]A, B[b]F and B[a]P. Chrysene was detected only in bottom sediments at Station III, as were B[b]F at Station I and B[a]P at Stations I and III (Table 2, Figure 2). Nine PAHs each, including Nap, 2-methylNap, Ace, Flu, Phe, Ant, Fla, Pyr and B[a]A, were detected in the water and fish samples (Figures 3, 4). Of the PAHs in the water samples, Ant was detected at Stations I and III, but was absent from Station II, while Fla was detected at Stations I and II.

The highest PAH concentrations were found at Station III for the fish samples, and at Station I for water and sediment. There were hardly any fish or fishing activity observed at Station I. At all stations, mean PAH concentrations in the bottom sediments were 1 104.3 ng g^{-1} [SD 2 250.4], 97.6 ng g^{-1} [SD 65.8] and 67.1 ng g^{-1} [SD 58.5], respectively. Mean PAH concentration in the fish samples varied from 101.1 ng g^{-1} [SD 114.7] at Station II to 143 ng g^{-1} [SD 179.8] at Station III. For the water samples, Stations I, II and III had mean PAH concentrations of 6.8 ng ml^{-1} [SD 5.1], 2.5 ng ml^{-1} [SD 2.8] and 2.6 ng ml^{-1} [SD 2.8], respectively. Generally, very high concentrations of Nap, 2-methylNap, Ant and Fla were recorded, and this could have influenced the high standard deviation values obtained in this study.

Mean concentrations of individual PAHs were highest in the bottom sediment samples, intermediate in the fish samples and lowest in the water samples (Table 1). Most of the detected PAHs were those of low molecular weight, comprising mainly 2, 3 and 4 rings; 5- and 6-ring PAHs were not abundant. The higher molecular weight PAHs found included Fla, Pyr, Chr, B[b]F, B[a]A and B[a]P.

The Kruskal–Wallis non-parametric test for the analysis of variance showed significant difference at $p < 0.05$ among the PAHs at the stations for the water samples, but no significant difference among the stations for PAH in the sediment and fish samples.

Discussion

The PAHs detected in the present study were dominated by lower molecular weight compounds in the water, fish and bottom sediment samples (Table 1). These compounds made up 4 302 ng g^{-1} (93.7%) of the PAHs in the sediments, 1 008 ng g^{-1} (91.7%) in the fish tissues, and 30 ng ml^{-1} (88.2%) in the water. Naphthalene was the most prevalent parent compound. Other PAH studies have also reported naphthalene as the compound that is accumulated in highest concentrations by aquatic organisms (Neff 2002). Lighter PAHs are more biodegradable and less lipholiphic, and are not expected to persist or to be absorbed as strongly as the heavier PAHs. Therefore, a high naphthalene concentration, together with the predominance of lower molecular weight

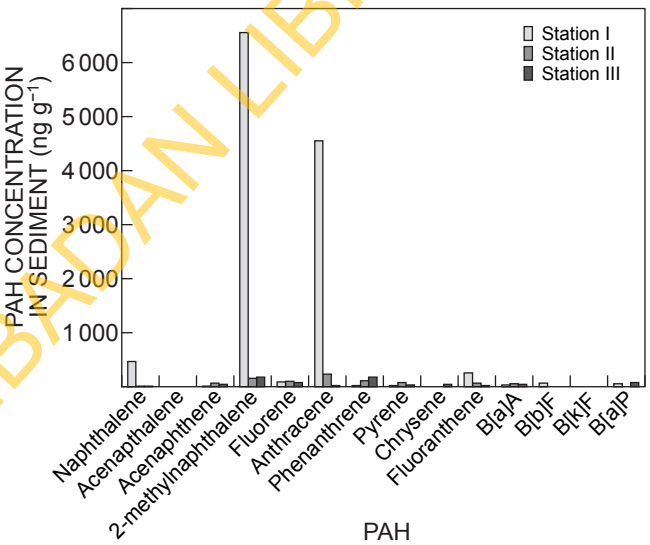

Figure 2: PAH types and concentrations in sediments of the Warri River at Ubeji in March 2010

Table 2: Mean ($n = 5$) PAH concentrations at three stations, I, II and III, on the Warri River at Ubeji in March 2010. ND = not detected; for the last seven PAHs: B = benzo, A = anthracene, F = fluoranthene, P = pyrene, P1 = pyrelene, DB = dibenzo, I = indeno

PAH	Sediment (ng g^{-1})			Water (ng ml^{-1})			Fish (ng g^{-1})	
	St. I	St. II	St. III	St. I	St. II	St. III	St. II	St. III
Naphthalene (Nap)	473	13	14	5	1	1		
Acenapthalene (Acy)	ND	ND	ND	ND	ND	ND		
Acenaphthene (Ace)	11	67	48	9	1	1	58	71
2-methylnaphthalene (2-methylNap)	6 561	155	180	17	9	9	387	595
Fluorene (Flu)	95	96	77	7	2	2	72	70
Anthracene (Ant)	4 550	237	18	4	ND	4	155	141
Phenanthrene (Phe)	21	116	175	12	4	2	96	105
Pyrene (Pyr)	24	75	32	1	1	1	31	27
Chrysene (Chr)	ND	ND	49	ND	ND	ND	ND	ND
Fluoranthene (Fla)	253	66	21	4	1	ND	21	20
B[a]A	35	53	47	2	1	1	35	47
B[b]F	63	ND	ND	ND	ND	ND	ND	ND
B[k]F	ND	ND	ND	ND	ND	ND	ND	ND
B[a]P	61	ND	77	ND	ND	ND	ND	ND
B[g,h,i]P1	ND	ND	ND	ND	ND	ND	ND	ND
DB[a,h]A	ND	ND	ND	ND	ND	ND	ND	ND
I [1,2,3-c,d]P	ND	ND	ND	ND	ND	ND	ND	ND

PAHs, is an indication of recent and extensive industrial pollution of petrogenic origin (Li et al. 2007).

Although PAH data for the present study area prior to the development of the refinery were unavailable, studies have previously been carried out in nearby waterbodies. The observations of Duke (2008) in the adjacent Ekpan Creek included 1.1982 mg kg^{-1} (1 198.2 ng g^{-1}) in sediments and 0.1169 mg l^{-1} in water, both for low molecular weight PAHs. The same study also found that a higher percentage of the PAHs in water samples, but not in sediments, were lighter ones. The present study indicated much greater concentrations of lighter PAHs in water, fish and sediments. This calls for continuous biomonitoring and greater industrial attention to pollutant control.

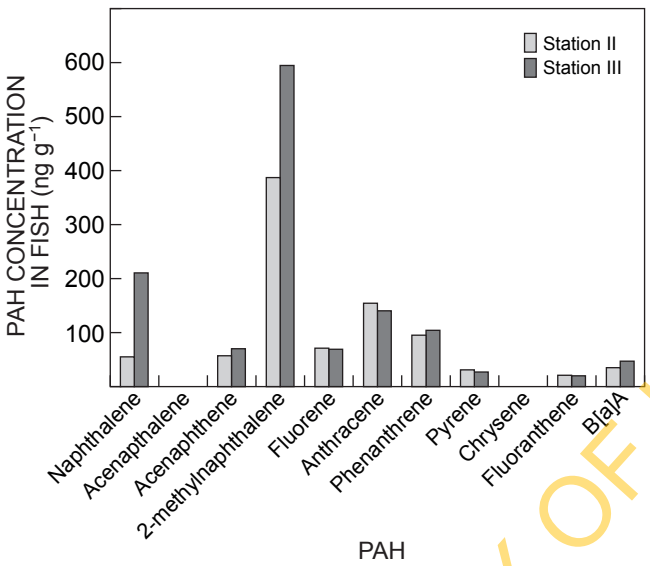

Figure 3: PAH types and concentrations in fish from the Warri River at Ubeji in March 2010; very few fish were found at Station I

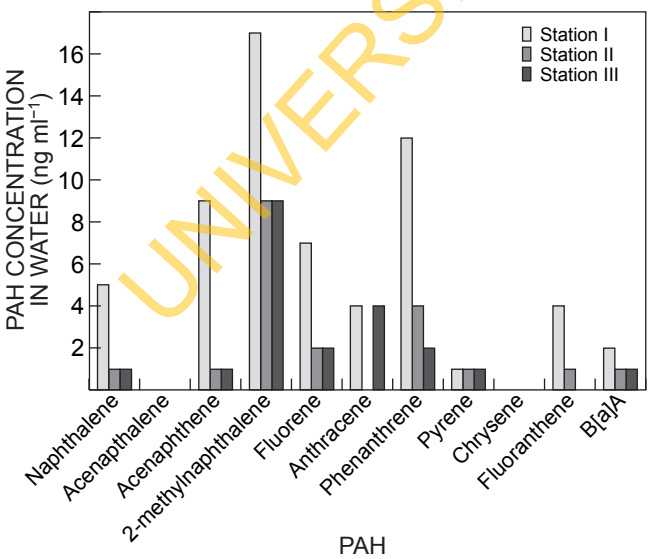

Figure 4: PAH types and concentrations in water samples from the Warri River at Ubeji in March 2010

Some of the higher molecular weight PAHs, such as chrysene, benzo(b)fluoranthene and benzo(a)pyrene, found in the bottom sediments were not detected in any fish or water sample in this study. However, benzo(a)anthracene was found in the water and fish samples in relatively low concentrations compared to that in the bottom sediments. The higher mean concentrations for heavier PAHs in the bottom sediments may not be unexpected. Since PAH solubility decreases with increasing molecular weight, this will promote the association of inorganic and organic suspended particles with PAHs. Higher molecular weight PAHs are relatively immobile because of their large molecular volume, low solubility and low volatility (Djomo et al. 1996; Nasr et al. 2010). Hence, they may become adsorbed to the sediments in a waterbody. The concentrations recorded in the Warri River bottom sediments may not have been affected by the bottom sediment type, as our observations showed that all sampling sites were clayey, with a high amount of organic matter.

Overall, mean PAH concentrations in the water and sediment samples decreased gradually from Stations I to III. This observation is consistent with increasing distance from the known discharge point of the Warri refinery, with the closest station, Station I, having high concentrations (Table 2). This trend was not observed in the fish tissues, in which PAH concentration increased markedly at Station III, which is further downstream from the discharge point than Station II, and PAHs were not detected at Station I due to the paucity of fish there. Although the Kruskal–Wallis test showed no statistical differences among stations for fish and bottom sediment samples, further investigation into the possible role of unknown man-made sources and of the process of bioaccumulation may explain this observation. The fish samples studied were tilapias, which are mainly bottom feeders and depend largely on detritus (Ugwumba and Ugwumba 2007), and can therefore take up contaminants (Adeyemi et al. 2009; Lasheen et al. 2012).

The detection of PAHs including lower molecular weight PAHs in the fish tissues is of interest, since lighter PAHs are usually more soluble and are acutely toxic. Their absorption by fish occurs during exposure to contaminated food, water and sediment (Tuyikene1995; CCME 1992, 2008). The mean total PAH concentration in fish, 1 098.5 ng g^{-1}, was slightly higher than those detected by Adeyemo and Ubiogoro (2012): 0.09 mg kg^{-1} (900 ng g^{-1}) in fish from the Egbokodo River adjacent to this study area; and by Nwabueze et al. (2011): 0.098 mg kg^{-1} (980 ng g^{-1}) in periwinkles, also in the Ubeji area where the current study was carried out. Whether this is indicative of increasing pollution requires further investigation. In addition, the detection of several of the PAHs in fish gills and muscles, including three heavy PAHs (Pyr, Flu, B[a]A), is an indication of bioaccumulation in fish. Also, the lighter PAH concentrations in the fish samples were close to those in the bottom sediments. Generally, fishes would be expected to have lower concentrations of PAHs, compared to sediments, possibly due to an effective oxidation system which allows them to metabolise and excrete these compounds rapidly (Johnson-Restrepo et al. 2008). The bottom sediments at all our sampling sites were clayey with a high amount of organic matter content, which may

reduce the availability of contaminants in the water column. However, rapid metabolism of PAHs by fish could lead to derivative metabolites which are capable of interacting with hydrophobic sites in the cell and can cause molecular deformation and perturbations. Marinkovic et al. (2013) showed that PAHs exert their toxicity following biotransformation, can be bound covalently to cellular macromolecules such as DNA, and can cause cell damage, mutagenesis and cancer.

Some of the high molecular weight PAHs detected in the present study, such as B[a]P, B[a]A and Chr, are known carcinogens with severe complications in organisms. Although B[a]P and Chr were only detected in sediments, and not in fish or water, B[a]A was detected in all three groups, and in greater amounts than the CCME standards (Table 1). High concentration and bioaccumulation of B[a]P and B[a]B in bottom-dwelling *Parophrys vetulus* was reported to cause high prevalence of idiopathic lesions and neoplasm (Bolognesi et al. 2006). Therefore, the detection of B[a]A at 41 ng g^{-1} in fish is of concern, as it may pose a threat not only to aquatic organisms but also to human consumers of fish. These findings differ slightly from those of Duke (2008), who found significant concentrations of benzo(a)pyrene and chrysene in water and sediments at an adjacent study site.

In the present study, Nap, 2-methylNap, Ace, Ant, Phe, Flu, B[a]A and Fla were detected in all samples. In particular, 2-methylNap, Ant and, to a lesser extent, Nap, were highly elevated. This is in agreement with Emoyan (2009) who found that Acy, Ace, Flu, Phe and Ant had their highest levels in water. Scoggins et al. (2007) also reported the dominance of higher molecular weight PAHs, including Fla, Chr, Pyr and B[b]F, in benthic macroinvertebrates, while Li et al. (2007) reported the prevalence of Acy, B[b]F, B[a]P, B[k]F and Fla in soil.

In general, the PAH values recorded in the present study were higher than the levels recommended for the protection of aquatic life or for drinking water, when compared with the CCME standards (Table 1). This was despite a report (Uzoekwe and Oghosanine 2011) that effluents from the refinery were being treated before discharge into the river.

This study shows that the Warri River at Ubeji is contaminated with both toxic and carcinogenic PAHs, which are at higher concentrations than the levels recommended in the guidelines for the protection of aquatic ecosystems. The pollution is suspected to be of recent and petrogenic origin, coming from the Warri Refining and Petrochemical Company. Bioaccumulation of the PAHs was also high in fish tissues, which can pose a risk to human consumers of fish. There is a need for stricter enforcement of environmental pollution policies in the Niger Delta.

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