

ECOTOXICOLOGICAL ASSESSMENT FOR POLYCYCLIC AROMATIC HYDROCARBON IN AQUATIC SYSTEMS OF OIL PRODUCING COMMUNITIES IN DELTA STATE, NIGERIA

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Abstract: The Niger Delta is unique in Nigeria because it is the home of Nigeria's oil industry, with its attendant environmental hazards such as water, land and air pollution. Polycyclic aromatic hydrocarbons (PAHs) are among the most toxic and persistent components of crude oil. The impact of PAHs in the environment will be determined by the types and quantity of each PAH. This study was therefore designed to screen some rivers in oil-producing Delta state for pollution with PAHs. Water and fish samples were collected from six Rivers (Egbokodo River in Warri, River Ethiope in Sapele, Urie River in Igbide Isoko, Asaba-Ase creek, Aragba River in Abraka, and Uzere Creek) in Delta State. The levels of PAHs were determined in the water and fish samples, and also in the processed dry ready-to-eat fish obtained from the same rivers. Generally, all the 16 priority PAHs were detected in five of the six Rivers, in three fresh fish samples and three dry ready-to-eat fish samples. The highest mean concentrations (3.79, 0.91, and 0.89 ppm) of PAH in water samples were in Rivers Ethiope, Asaba-Ase and Egbokodo respectively. Fresh fish samples from Aragba, Oteri, and Egbokodo Rivers had PAH values of 10.35, 0.36, 0.09 mg/kg wet weight respectively, while dry ready to eat fish from Oteri, Asaba-Ase, and Sapele had 29.33, 23.96, 0.39 mg/kg, respectively. Total bioconcentration factors (BCF) ranged from 0.0-1.73 in the rivers, except for aragba, which had a very high BCF (554.6) for anthracene. The results from this study portend a significant public health risk. An immediate attention from Nigeria's Federal Environmental Protection Agency is required in order to protect the river from further pollution and the people living in these communities.

Keywords: Polycyclic aromatic hydrocarbon, Fish, Aquatic pollution, Niger Delta, Nigeria

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Özet:**Nijerya, Delta Eyaleti, Petrol Üreticisi Topluluklarının Su Sistemlerinin Polisiklik Aromatic Hidrokarbonlar Açısından Ekolojik Değerlendirmesi**

Nijer Deltası, Nijerya'nın petrol endüstrisini barındırması ve bunun çevresel etkileri, su, kara ve hava kirliliği nedeniyle benzersizdir. Polisiklik aromatik hidrokarbonlar (PAHs) çok toksik ve kalıcı ham petrol bileşenlerindedir. PAH'ların çevreye olan etkisi tür ve miktarlarına bağlı olarak değerlendirilecektir. Bu çalışma, PAH kirliliğinin tespiti amacıyla petrol üretimi yapılan deltadaki akarsuların incelenmesi şeklinde düzenlenmiştir. Su ve balık örnekleri altı akarsudan alınmıştır (Egbokodo River in Warri, River Ethiope in Sapele, Urie River in Igbide Isoko, Asaba-Ase creek, Aragba River in Abraka, and Uzere Creek). Sularda, balıklarda ve aynı bölgeden elde edilmiş hazır işlenmiş balık örneklerinde PAH seviyeleri analiz edilmiştir. Altı derenin beşinde, üç balık örneğinde ve üç hazır gıda ürünüde genel olarak bilinen 16 öncelikli PAH tespit edildi. Tespit edilen en yüksek PAH konsantrasyonları Ethiope, Asaba-Ase ve Egbokodo (sırasıyla 3.79, 0.91 ve 0.89 ppm) göllerindeydi. Aragba, Oteri ve Egbokodo akarsularından alınan taze balık örneklerinde sırasıyla 10.35, 0.36, 0.09 mg/kg PAH, Oteri, Asaba-Ase ve Sapele akarsularından elde edilen hazır gıda örneklerinde ise sırasıyla 29.33, 23.96, 0.39 mg/kg PAH tespit edilmiştir. Faktörlerin total biyokonsantrasyonu (BCF) akarsularda 0.0 – 1.73 aralığında bulunmuştur. Bu değer Aragba akarsuyunda anthracene açısından diğerlerinden farklı olarak çok yüksek seviyelerde tespit edilmiştir (554.6). Bu çalışmanın sonuçları halk sağlığı açısından önemli riskleri ortaya koymaktadır. Nijerya Çevre Koruma Ajansı'nın acil önlemler alması bu bölge insanının sağlığının korunması ve daha ileri kirliliğin önüne geçilmesi açısından önemlidir.

Anahtar Kelimeler: Polisiklik Aromatic Hidrokarbonlar, Balık, Su Kaynaklarında Kirlilik, Nijer Deltası, Nijerya

Introduction

The Niger Delta is located in Southern Nigeria and is Africa's largest delta, covering about 70,000 square kilometers, and with about one-third of it made up of wetlands, and the third largest world mangrove forests. The Niger Delta is unique in Nigeria because it is the home of Nigeria's oil industry. Exposure to oil or its constituent chemicals can alter the ecology of aquatic habitats and the physiology of marine organisms (Chindah *et al.*, 2004). When oil pollution gets in water, some of its components are degraded and dispersed by evaporation, photochemical reactions, or bacterial degradation, while others are more resistant and may persist for many years, especially in shallow waters with muddy sediments (Mucha *et al.*, 2003).

Polycyclic aromatic hydrocarbons exist naturally in the environment, but at considerably low levels, they become potentially dangerous when detected in high quantity due to anthropogenic activities (Wills, 2000, Koller, *et al.*, 2004). They are considered to be hazardous because they have carcinogenic and mutagenic properties, and are stable in the environment (Guinan *et al.*, 2001). A major source of PAHs in the environment is fossil fuel combustion processes, crude oil, coal and oil shale (Mastal and Callen, 2000). It is therefore of paramount importance that a constant assess-

ment of susceptible water bodies be carried out to monitor the level of polycyclic aromatic hydrocarbons considering the potential impact of PAHs on aquatic ecosystem and public health. This study was therefore designed, to screen for polycyclic aromatic hydrocarbons in selected Rivers in oil producing communities in Delta state, Nigeria. The bioconcentration levels of PAHs in fishes sourced from these Rivers were also determined.

Materials and Methods**Study Area**

Six water bodies were selected in Delta state as follows: Egbokodo River in Warri, River Ethiope in Sapele, Urie River in Igbide Isoko, Asaba-Ase creek, Aragba River in Abraka, and Uzere Creek. The choice of sample locations was influenced by their distance from industrial locations. Three of the six rivers (Egbokodo River in Warri, Uzere Creek and Urie River in Igbide Isoko) are situated in locations with known oil exploratory activities. The other three locations (River Ethiope, Asaba-Ase creek and Aragba River) had other on-going human activities (Sawmill, domestic and university respectively). Some of the sample points are presented beneath as Figure 1.

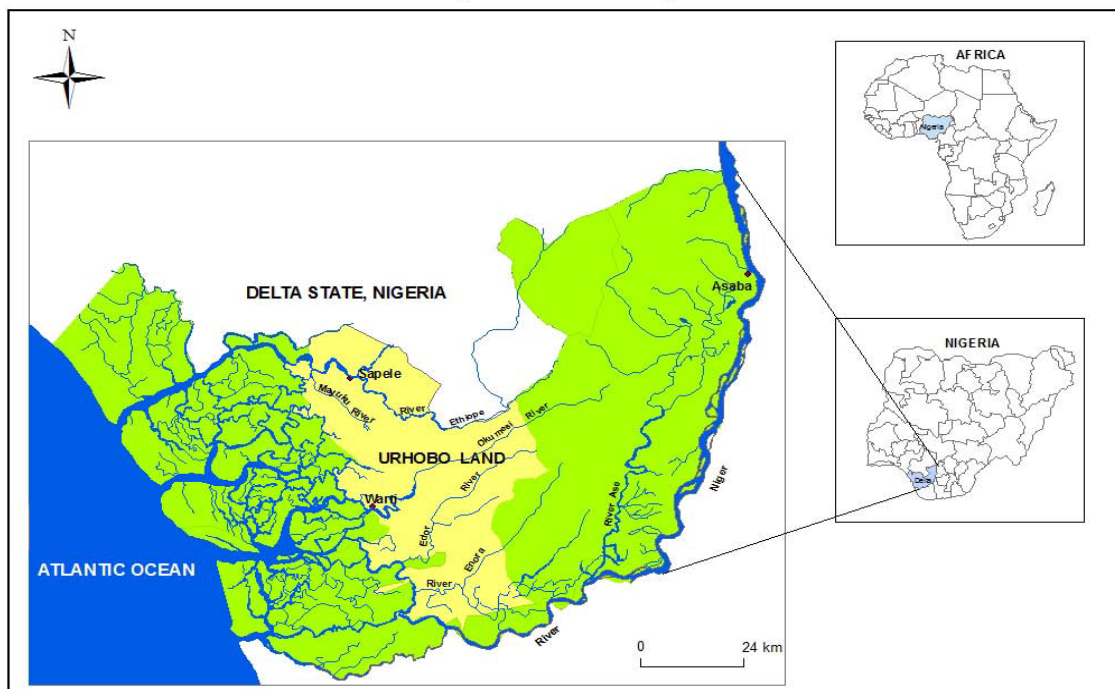


Figure 1. Map of Delta state showing some of the sampled rivers (Source: *Urhobo Historical Society, 2008*)

Sample collection

Sampling was conducted on six Rivers and creeks within Delta state in February, 2009. Upstream and downstream water samples were collected from each water body. Water samples were collected at a 30cm depth in pre-cleaned 500 ml plastic bottles and accurately labeled. Available live fish samples of different species were purchased from the local fishermen at each sampling site, the samples were immediately cleaned of particulate debris and packed in labeled clean plastic bags and immediately preserved in coolers containing ice packs. All samples were kept on ice during transportation to the laboratory for analysis. Some of the fish samples were processed into dry ready-to-eat samples by smoke-drying over coal heat before being analysed.

Laboratory Analysis

Preparation of water and fish samples for PAH determination

The molecules of polycyclic aromatic hydrocarbons (PAHs) are soluble in organic solvents. Prolonged boiling of the mixture of solvent and extracted product can lead to under-estimation of the contents of residues. Because of this degradation the most commonly used method of ex-

traction is cold solvent extraction by micro methods (Steinwandter, 1992). Conventional liquid-solid extraction in the form of shake flask extraction was carried out by placing about 5g weighed fish sample in a mortar and homogenizing it with equivalent weight of anhydrous sodium sulfate.

The homogenized fish sample was placed in a stoppered brown glass bottle and was dissolved with 25 mL acetone/benzene mixture (50:50 by volume). Extraction was done by shaking the bottle vigorously in a back and forth motion for 30 minutes. Samples were extracted twice. The solvent was separated from the matrix by filtration through anhydrous sodium sulfate. The extracts were combined, dried in anhydrous sodium sulfate and the volume reduced to 1 ml by rotary evaporation after which there was solvent exchange to iso-octane. The extract was thereafter carefully decanted and sieved into pre-weighed bijou bottles and allowed to evaporate for 48 hours. The weight of the dry fat sediment was taken before a process of fat separation was done by passing the fat sediment washed with peptone through layers of glass wool, 3 gms of silica gel and 1 gm of anhydrous sodium sulphate respectively. The solvent was again left to evaporate and the sediment rinsed out using iso-octane into vials, before being determined with a Gas Chromatograph (GC, HP4890, Hewlett Packard,

Avondale, PA, USA). Injector and detector temperatures were both 300°C. The column was held at 50°C for 1 min, ramped at 25°C/min to 120°C and 3°C/min to 320°C, and held for 17 min at 320°C. Helium was used as the carrier gas, with a flow rate of 0.6 ml/min at 50°C. The calculation method and quality assurance are according to Baussant *et al.* (2001). All chemicals used were of analytical grade and obtained from Sigma-Aldrich Co. (St. Louis, MO, USA).

Statistical Analysis

Data collected were computed into means with standard deviation. Means were compared statistically using students' "t-test" and ANOVA. Results were adjudged significant at 95% confidence limit.

Results and Discussion

Total PAH in water and Fish

Most of the Rivers were turbid and dirty (Figure 2); with on-going fishing activities. The results of total PAH In sampled water, fresh fish and dry ready-to-eat fish are presented as Figures 3, 4 and 5. Total PAH level in rivers was significantly higher ($p=0.0006$) in Ethiope River, while, PAH

level in fresh fish and dry ready-to-eat fish from all sampled rivers was not significantly ($p=0.47$ and 0.42 , respectively) different from one another at 95% confidence limit.



Figure 2. View of the Uzere River

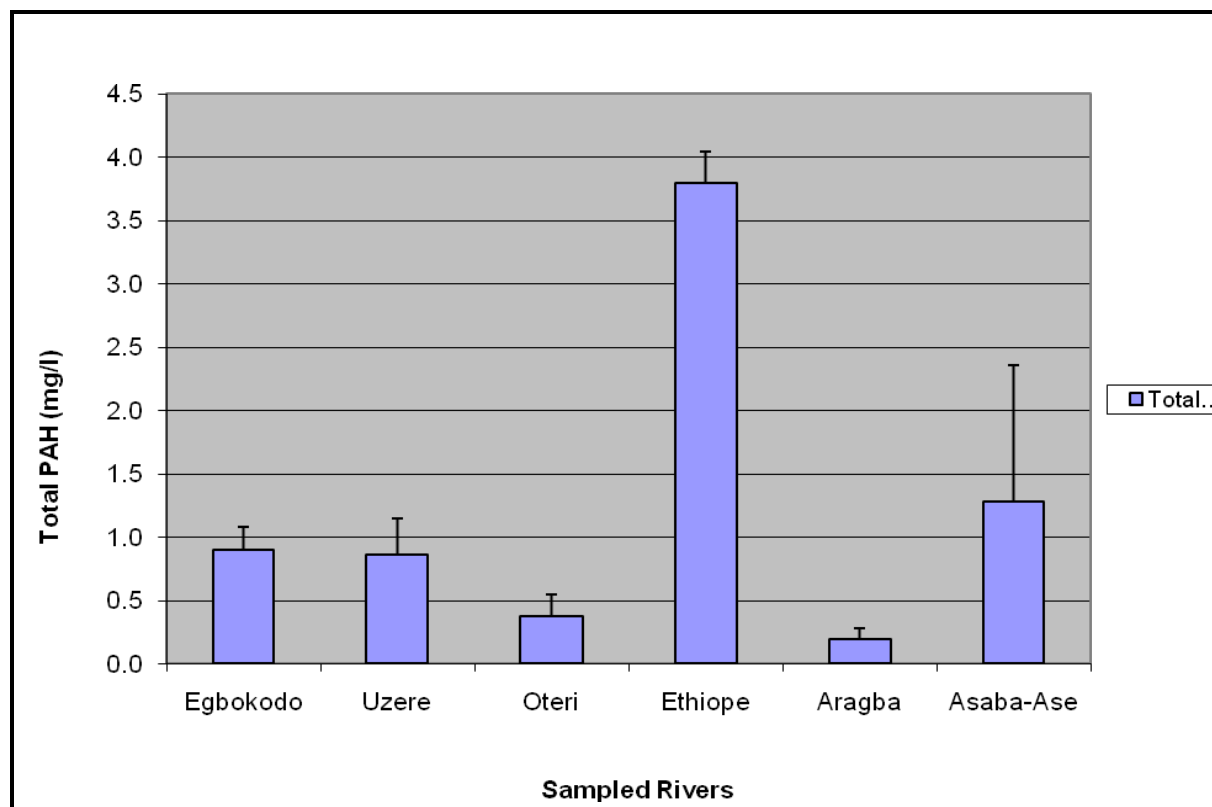


Figure 3: Total PAH in rivers sampled in Delta State

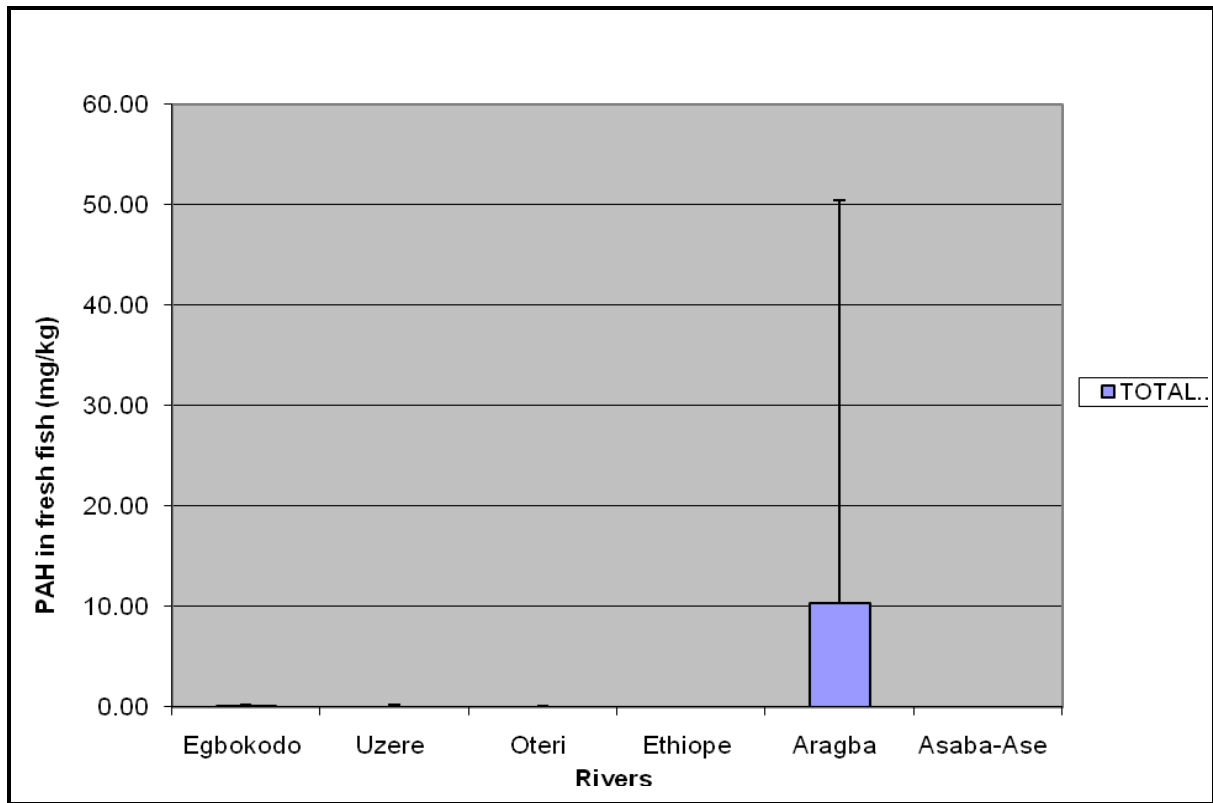


Figure 4: Total PAH in fresh fish samples from Rivers in Delta State

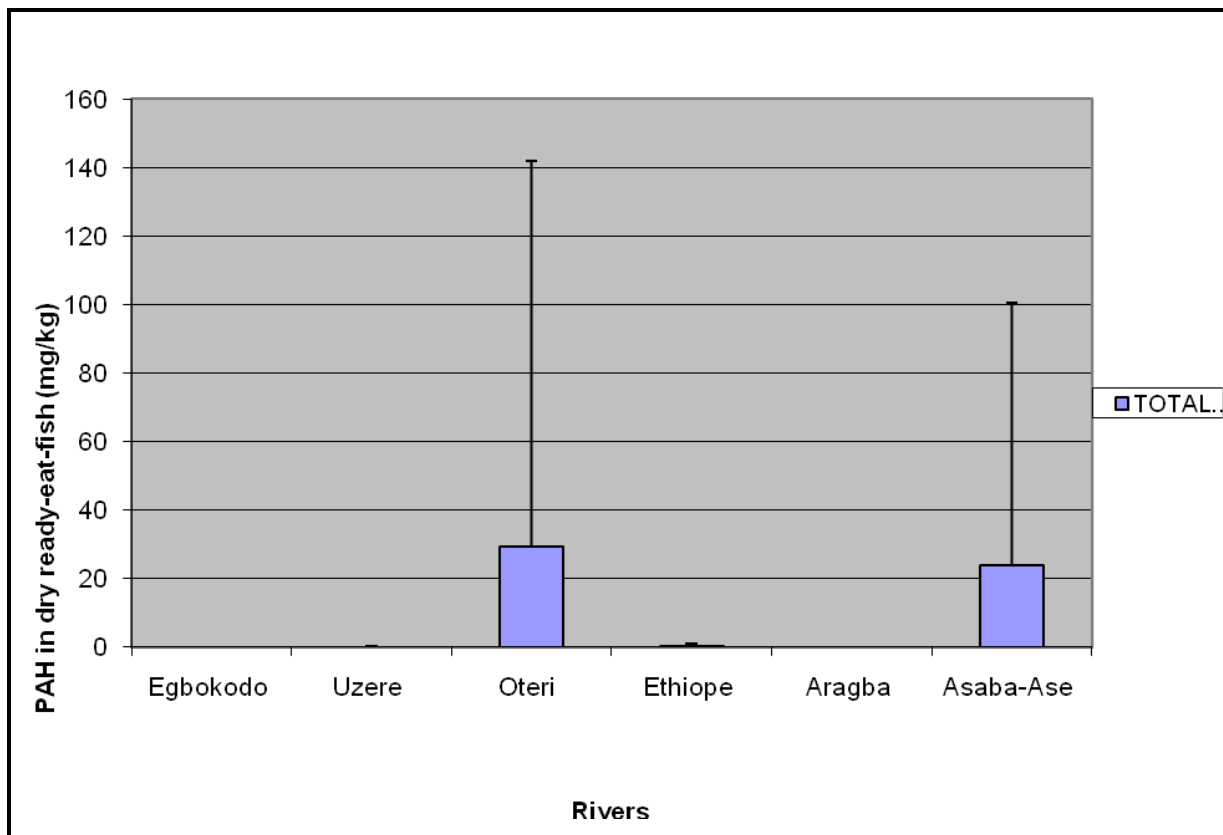


Figure 5: Total PAH in dry ready-to-eat fish from Rivers in Delta State

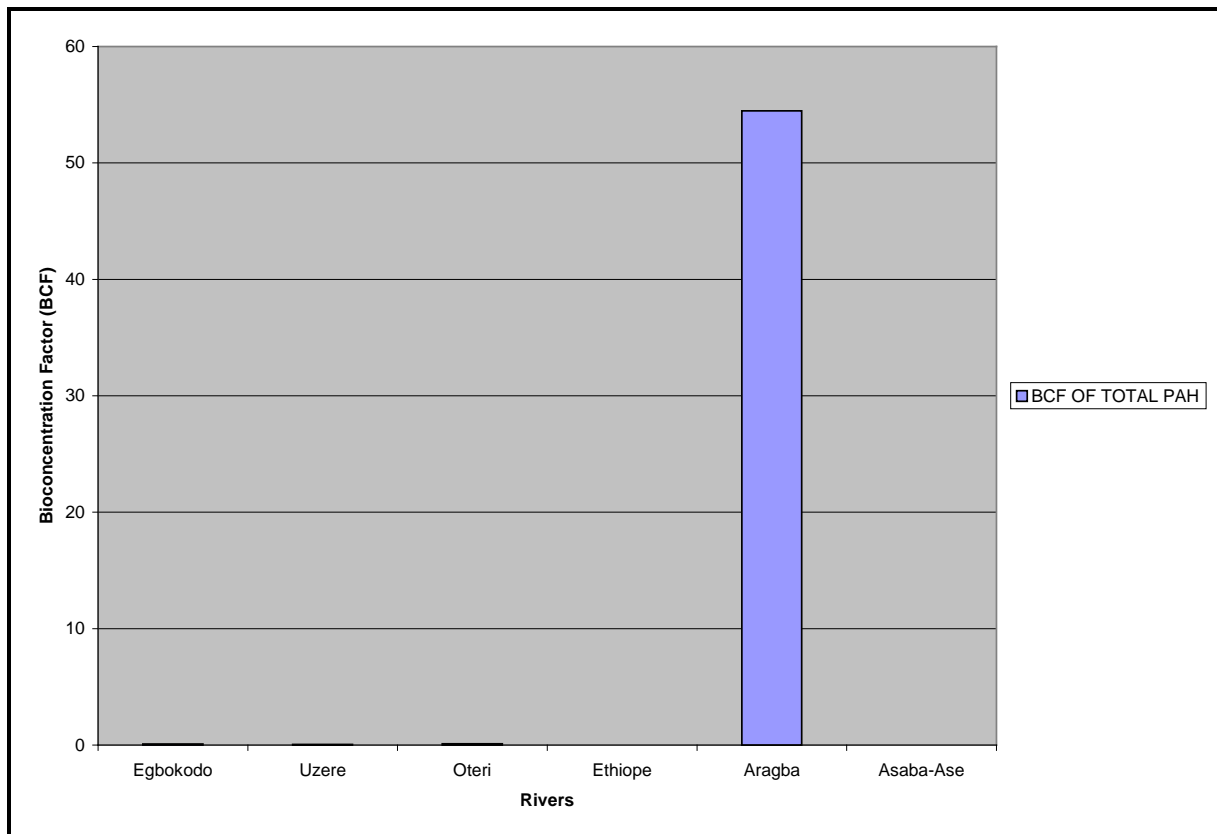


Figure 6: Bioconcentration Factor (BCF) of Total PAH from Sampled Rivers in Delta State

Speciation of poly aromatic hydrocarbons (PAH) in water and Fish

The results of the quantitative analysis of the 16 priority PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene and indeno[1,2,3,cd]pyrene) in water, fresh and ready-to-eat fish is presented in Tables 2, 3 and 4 respectively.

Bioconcentration factor (BCF) of PAH in rivers

The BCF of total PAH in the different Rivers is presented as Figure 6, while BCF of the different fractions of PAH in the sampled Rivers is given in Table 4. The ANOVA showed that the differences in the BCF of the different fractions in the Rivers was not significantly different ($p=0.42$).

The PAHs form one of the most important classes of persistent pollutants. A major source of PAHs in the environment is from fossil fuel combustion processes, crude oil, coal and oil

shale (Mastral and Callen, 2000). PAH was detected in all the rivers sampled, even those in communities where there are no oil exploratory activities. This maybe adduced to the interconnectivity of the water bodies. However, the levels in water were below 10mg/L being the maximum recommended total hydrocarbon limit by the Nigerian Federal Ministry of Environment (FMENV, 1992). Although, total PAH level was highest in Ethiopie, which is the only River that takes its source solely from the Atlantic ocean; others either share source with the River Niger or just drain into the Niger.

Uptake rates and bioaccumulation levels of substances within the body tissues are of particular interest because they can be related to toxicity. Consequently, the relationships between toxicity and body burden can be used to predict impact (Chapman, 1997). Of the PAHs detected in all the water bodies, benz[a]anthracene and benzo[a]pyrene, with known record of toxicity were found to be highest in Oteri and Asaba Ase Rivers. Both indeno[1,2,3-c,d] pyrene and pyrene had the highest values of 12.4 ppm in the Ethiopie river. The value of acenaphthylene was highest

(11.75 ppm) in Uzere River. In the fresh fish samples, the fish from Aragba River had the highest value of 155.3 ppm of anthracene, while samples from Uzere River contained 0.59 ppm of acenaphtylene. This was no surprise since all the fish from Aragba River was the biggest and possibly the oldest. Fish samples from other locations were reasonably small and obviously immature. The ability of fish to metabolize PAHs may explain why benzo[a]pyrene was found only low levels in fish from Oteri and Asaba-Ase, which were the most contaminated with benzo[a]pyrene (Varanasi and Gmur, 1981). Consequently, future risk assessment studies should perhaps consider the fate and effects of the PAH metabolites to aquatic biota in which metabolization is an important excretion pathway.

Dry fish samples obtained from Oteri had the highest level of indeno[1,2,3-c,d]pyrene (435.8ppm) followed by Asaba-Ase river (294.07 ppm). Generally, indeno[1,2,3-c,d]pyrene was the highest PAHs in the dry fish samples. It was present in almost all the dry samples, except for Eg-bokodo and Uzere River, where it was detected

only at the level of ppb. The value recorded in this study is much higher than the recommended tolerance levels of 0.01mg/g for total hydrocarbon in fish (Jack *et al.*, 2005). Total bioconcentration factors (BCF) ranged from 0.0-1.73 in the rivers, except for Aragba, which had a very high BCF (554.6) for anthracene. Several studies have reported BCFs in fish for benzo[a]pyrene (Freitag *et al.*, 1985, Cohen *et al.*, 1994). The recommended BCF value of benzo[a]pyrene for whole fish is 583. In this study, BCF for benzo[a]pyrene was between 0-0.11. More insight into the dissolution rates of PAHs from dispersed oil droplets is required in order to more accurately predict bioaccumulation in aquatic biota. The low bioconcentration factor is in disagreement with what was expected from the partition coefficients of the larger PAHs (Baussant *et al.*, 2001). Yet the potential environmental impact recognized for these larger PAHs should not be disregarded in environmental risk assessment because they can be metabolized apparently quickly to substances with mutagenic and carcinogenic potential for the exposed organisms.

Table 1. Speciation of polycyclic aromatic hydrocarbons in rivers and creeks in delta state

Polycyclic aromatic Hydrocarbon Fractions (mg/L)	Egbokodo	Uzere	Oteri	Ethiope	Aragba	Asaba-Ase
Naphthalene	1.29 ± 1.69	0.09 ± 0.13	0.16 ± 0.05	0.12 ± 1.68	0	1.31 ± 1.03
Acenaphtylene	0.89 ± 0.38	11.75 ± 16.5	0.066 ± 0.09	7.78 ± 0.38	0	0.79 ± 0.66
Acenaphtene	1.87 ± 2.65	0.07 ± 0.08	0.21 ± 0.2	2.27 ± 2.64	0.04 ± 0.05	0.47 ± 0.54
Fluorene	2.11 ± 1.33	0.04 ± 0.05	0.08 ± 0.11	3.83 ± 1.33	0.04 ± 0.05	0.98 ± 0.59
Phenanthrene	3.23 ± 3.92	0.19 ± 0.28	0.29 ± 0.25	0.54 ± 3.9	0.47 ± 0.66	1.21 ± 1.35
Anthracene	0.62 ± 0.17	0.18 ± 0.22	0.07 ± 0.006	8.05 ± 0.17	0.28 ± 0.39	0.70 ± 0.56
Fluoranthene	0.64 ± 0.18	0.13 ± 0.15	0.15 ± 0.07	0.14 ± 0.18	0.44 ± 0.62	0.72 ± 0.24
Pyrene	0.82 ± 0.91	0.06 ± 0.08	0.28 ± 0.53	12.4 ± 0.91	0.24 ± 0.34	1.43 ± 0.15
Benzo[a]anthracene	0.55 ± 0.38	0.005 ± 0.01	1.29 ± 0.75	0.20 ± 0.38	0.28 ± 0.39	1.32 ± 1.87
Chrysene	0.22 ± 0.03	0.09 ± 0.1	0.39 ± 0.39	0.19 ± 0.03	0.08 ± 0.1	0.25 ± 0.02
Benzo[b]Fluoranthene	0.13 ± 0.07	0.04 ± 0.22	0.38 ± 0.006	0.03 ± 0.07	0.16 ± 0.22	0.32 ± 0.08
Benzo[k]fluoranthene	0.26 ± 0.37	0.24 ± 0.35	0.27 ± 0.22	0.77 ± 0.37	0.17 ± 0.22	0.99 ± 1.06
Benzo[a]pyrene	0.55 ± 0.78	0.003 ± 0.76	1.08 ± 0.9	0.008 ± 0.78	0.51 ± 0.72	2.36 ± 0.45
Dibenzo[a,h]anthracene	0.08 ± 0.11	0.004 ± 0.006	0.16 ± 0.04	8.16 ± 0.11	0.04 ± 0.05	2.77 ± 3.68
Indeno[1,2,3-c,d]pyrene	0.15 ± 0.21	0.01 ± 0.014	0.64 ± 0.65	12.4 ± 0.21	0.06 ± 0.06	3.48 ± 4.53

Results are presented as mean ± standard deviation (SD)

Table 2. Speciation of polycyclic aromatic hydrocarbons in fresh fish from rivers and creeks in delta state

POLYCYCLIC AROMATIC HYDROCARBON FRACTIONS (mg/kg)	Egbokodo	Uzere	Oteri	Ethiope	Aragba	Asaba-Ase
Naphthalene	0.13	0.00	0.02	< 0.01	< 0.01	< 0.01
Acenaphthylene	0.09	0.59	0.01	< 0.01	< 0.01	< 0.01
Acenaphthene	0.19	< 0.01	0.02	< 0.01	< 0.01	0.006
Fluorene	0.21	< 0.01	0.01	< 0.01	< 0.01	0.019
Phenanthrene	0.32	0.01	0.03	< 0.01	< 0.01	0.014
Anthracene	0.06	0.02	0.01	< 0.01	155.3	< 0.01
Fluoranthene	0.06	0.01	0.02	< 0.01	< 0.01	0.016
Pyrene	0.08	0.01	0.03	< 0.01	< 0.01	0.038
Benzo[a]anthracene	0.06	< 0.01	0.13	< 0.01	< 0.01	0.002
Chrysene	0.02	0.01	0.04	< 0.01	< 0.01	0.005
Benzo[b]Fluoranthene	0.01	< 0.01	0.04	< 0.01	< 0.01	0.018
Benzo[k]fluoranthene	0.03	0.07	0.03	< 0.01	< 0.01	0.009
Benzo[a]pyrene	0.06	< 0.01	0.11	< 0.01	< 0.01	0.025
Dibenzo[a,h]anthracene	0.01	< 0.01	0.02	< 0.01	< 0.01	< 0.01
Indeno[1,2,3-c,d]pyrene	0.02	< 0.01	0.06	< 0.01	< 0.01	0.003

Table 3. Speciation of polycyclic aromatic hydrocarbons in ready-to-eat dry fish from rivers and creeks in delta state

Poly-aromatic Hydrocarbon Fractions (mg/kg)	Egbokodo	Uzere	Oteri	Ethiope	Aragba	Asaba-Ase
Naphthalene	< 0.01	0.009	< 0.01	0.11	< 0.01	< 0.01
Acenaphthylene	< 0.01	1.175	< 0.01	0.78	< 0.01	< 0.01
Acenaphthene	< 0.01	0.007	< 0.01	0.23	0.04	< 0.01
Fluorene	< 0.01	0.004	4.11	0.38	0.04	< 0.01
Phenanthrene	< 0.01	0.020	< 0.01	0.05	0.47	< 0.01
Anthracene	< 0.01	0.018	< 0.01	0.81	0.28	< 0.01
Fluoranthene	< 0.01	0.013	< 0.01	0.01	0.44	< 0.01
Pyrene	< 0.01	0.006	< 0.01	1.24	0.24	< 0.01
Benzo[a]anthracene	< 0.01	0.000	< 0.01	0.02	0.29	< 0.01
Chrysene	< 0.01	0.009	< 0.01	0.02	0.08	< 0.01
Benzo[b]Fluoranthene	< 0.01	0.005	< 0.01	0.00	0.16	< 0.01
Benzo[k]fluoranthene	< 0.01	0.024	< 0.01	0.08	0.17	< 0.01
Benzo[a]pyrene	< 0.01	0.000	< 0.01	0.00	0.51	0.13
Dibenzo[a,h]anthracene	< 0.01	0.000	< 0.01	0.82	0.04	65.32
Indeno[1,2,3-c,d]pyrene	< 0.01	0.001	435.8	1.24	0.06	294.07

Table 4. Bioconcentration factor (bcf) of the different fractions of pah in rivers

POLY-AROMATIC HYDROCARBON FRACTIONS (mg/L)	Egbokodo	Uzere	Oteri	Ethiope	Aragba	Asaba-Ase
Naphthalene	0.100	0.000	0.125	0.000	0.000	0.000
Acenaphthylene	0.100	0.050	0.167	0.000	0.000	0.000
Acenaphthene	0.100	0.000	0.095	0.000	0.000	0.013
Fluorene	0.090	0.000	0.125	0.000	0.000	0.019
Phenanthrene	0.090	0.050	0.103	0.000	0.000	0.012
Anthracene	0.093	0.110	0.142	0.000	554.640	0.000
Fluoranthene	0.093	0.077	0.133	0.000	0.000	0.022
Pyrene	0.097	0.167	0.107	0.000	0.000	0.027
Benzo[a]anthracene	0.110	0.000	0.101	0.000	0.000	0.002
Chrysene	0.091	0.222	0.103	0.000	0.000	0.020
Benzo[b]Fluoranthene	0.077	0.000	0.105	0.000	0.000	0.056
Benzo[k]fluoranthene	0.110	0.291	0.107	0.000	0.000	0.009
Benzo[a]pyrene	0.110	0.000	0.102	0.000	0.000	0.011
Dibenzo[a,h]anthracene	0.120	0.000	0.118	0.000	0.000	0.000
Indeno[1,2,3-c,d]pyrene	0.138	0.000	0.094	0.000	0.000	0.001

The International Agency for Research on Cancer (IARC) has determined that benz[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[j]-fluoranthene, benzo[k]fluoranthene, and indeno[1,2,3-c,d]pyrene are possibly carcinogenic to humans (IARC, 2011). The US Department of Health and Human Services (DHHS) has determined that benz[a]anthracene, benzo[b]-fluoranthene, benzo[j]fluoranthene, benzo[k]-fluoranthene, benzo[a]pyrene, dibenz[a,h]-anthracene, and indeno[1,2,3-c,d]pyrene are known animal carcinogens (US DHHS, 2011). Smoking of fish samples did not significantly increase the level of PAH in comparison to the fresh samples, probably because all fish samples were skinned before digestion.

Conclusion

This report on the concentration of polycyclic aromatic hydrocarbon in the surface water and fish from aquatic system in Niger Delta should contribute to the baseline for monitoring of the water for pollution from oil exploratory activities.

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