ISSN: 2576-6732 (Print)
ISSN: 2576-6724 (Online) Acta Chemica Malaysia (ACMY) 2019, VOLUME 3, ISSUE 1

Distribution, Compositional Pattern and Potential to human exposure of PAHs in Water, Amassoma axis, Nun River, Bayelsa State, Nigeria

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DOI : 10.2478/acmy-2019-0002

ABSTRACT
This study was carried out to investigate the distribution and contents of sixteen priority polycyclic aromatic hydrocarbons (PAHs) in water from Amassoma axis of the Nun River, Bayelsa State, Nigeria. The PAH contaminations in the river water samples was performed using GC-MS method. The results were similar for all of the three sampling stations. Six LMW PAHs: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene and five HMW PAHs: fluoranthene, pyrene benzo (a)anthracene, chrysene and benzo(a)pyrene were found. The $\sum PAHs$ *concentration ranged from 0.111mg/L to 0.26mg/L. In this study, PAH fingerprint ratios for determining both petrogenic and pyrogenic (pyrolytic) PAH accumulation in the environment and Toxic equivalency factor (TEF) used to estimate relative toxicity of a PAH compared to that of BaP was employed. The Ph/An ratio for water samples were 0.00, 0.33 and 0.00 in three stations, while associated figures for Fl/Py ratio values were 0.67, 0.83 and 0.50 respectively. Pearson correlation matrice analysis reveals a positive correlation between the PAHs; this could indicate a common source for some of the PAHs, however, some were negatively correlated with each other. This behavior could indicate non-point source. A comparative analysis of PAHs concentrations in the water samples with WHO standards revealed that the results obtained in this study were within the permissible levels, however, carcinogen PAHs present in the water of the Amassoma axis, Nun River may pose a threats to human health.*

Keywords*: polycyclic aromatic hydrocarbons, Amassoma, Nun River, Bayelsa State, Nigeria*

1.0 INTRODUCTION

Anthropogenic activities are on the increase in the Niger Delta region in recent time ranging from illegal or unconventional crude refining, barge ballasting, oil bunkers, industrial production, transportation, waste incineration or disposal, unconventional handling of petroleum products amongst others.
The major sources of anthropogenic PAHs are in two categories, they include: fossil fuel combustion (pyrolytic) and petroleum spillage (petrogenic), Magi *et al*., 2002; Chen *et al*., 2006; Yunker *et al*., 2002; Kafilzadeh, 2015.
Polycyclic aromatic hydrocarbons (PAHs) are organic compounds that are mostly colorless, white, or pale yellow solids. They are a ubiquitous group of several hundred chemically related compounds, environmentally persistent with various structures and varied toxicity. They have toxic effects on organisms through various actions. Generally, PAHs enter the environment through various routes and are usually found as a mixture containing two or more of these compounds, e.g. soot.(Abdel-Shafy and Mansour, 2016).
Hydrocarbons studied were selected because of their representative toxic risk. Most of them are included in the priority pollutant list, given by the US Environmental Protection Agency (US EPA). Among these compounds, four PAH (fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno-1, 2, 3-pyrene) were considered by the World Health Organisation and the European Union as pollution tracers in natural and drinking waters(Disdier, *et al*., 1999).
When polycyclic aromatic hydrocarbons find their way into the ecosystem the low molecular weight (LMW) compounds are preferentially dissolved in water, while the high molecular weight (HMW) compounds are preferentially adsorbed onto water particles or onto the living organisms.
PAHs are not synthesized chemically for industrial purposes. Nevertheless,
there are a few commercial uses for many PAHs. They are mostly used as intermediaries in pharmaceuticals, agricultural products, photographic products, thermosetting plastics, lubricating materials, and other chemical industries (Kaminski *et al*, 2008; Abdel-Shafy and Mansour, 2016).

However, the general uses of some PAHs are: Acenaphthene: manufacture of pigments, dyes, plastics, pesticides and pharmaceuticals. Anthracene: diluent for wood preservatives and manufacture of dyes and pigments.
Fluoranthene: manufacture of agrochemicals, dyes and pharmaceuticals.
Fluorene: manufacture of pharmaceuticals, pigments, dyes, pesticides and thermoset plastic. Phenanthrene: manufacture of resins and pesticides.
Pyrene: manufacture of pigments. Other PAHs may be contained in asphalt used for the construction of roads, in addition to roofing tar. Furthermore, specific refined products, of precise PAHs, are used also in the field of electronics, functional plastics, and liquid crystals (Kaminski *et al*, 2008; Abdel-Shafy and Mansour, 2016).
Amassoma town axis of the Nun River, Bayelsa State, Nigeria is of great significance, but very little research on PAH pollution in water has been reported in this area. Therefore, the main objectives of this study are: (1) to investigate the distribution characteristics of sixteen priority PAHs in water, (2) to explore the correlation between individual PAHs, (3) to identify possible sources of PAHs and (4) human health risk estimation

2.0 MATERIALS AND METHODS

2.1 STUDY AREA

The Nun River is a natural river geographically located in old Rivers State, and now in the present Bayelsa state, Niger Delta region, Nigeria (Fig. 1). The Nun River is complex and long freshwater river system, however, for the purpose of this study; emphasis is restricted to the Amassoma Axis. The river water is used for several purposes fishing, washing clothes, bathing and generally a major source of water supply to the community. The river lies between the coordinates of latitude 50 150N and longitude 60 05' E - 60 15'E. Nun River is a distributary and it also flows into the Atlantic Ocean (Gulf of Guinea).

Fig 1 Map and location of sampling sites

2.2 WATER SAMPLE COLLECTION

Nine (9) samples were collected from different sampling stations. The sampling stations were about 2km apart namely: upstream, Midstream and downstream. At each sampling site, three samples were collected using broad mouth 500ml glass bottles fitted tightly with aluminium foil to prevent contamination. Glass bottles were used for the collection of samples since hydrocarbons interact with plastics containers (APHA, 2005). All the samples were labeled according to each sampling point and preserved in cool boxes before taken to the laboratory for analyses.

2.3 EXTRACTION OF PAHs IN WATER SAMPLES

The reagents and chemicals used are all of analytical grade. 250ml of each water sample into a separating funnel and pH adjusted to < pH 2 + 15ml methylene chloride were extracted at room temperature. The extract was dried with 5g anhydrous Na_2SO_4 and concentrated to 1ml in rotary evaporator. Then, + 50ml of hexane and extracted down to 1ml and the concentrate was first eluted with 10ml hexane, fractioned and collected as aliphatic fraction, + 15ml methylene chloride, and collected as aromatic fraction. The extracts were further concentrated, and then analyzed by GC-MS, according to the standard methods of the American Public Health Association (APHA, 2005; Aderinola *et al*., 2018).

3.0 RESULTS AND DISCUSSION

The sixteen PAHs recommended as priority pollutants by the U.S. Environmental Protection Agency (USEPA) were determined in water samples. From the analyses of the extracts, PAHs were found at all the sampling sites. A total of eleven of the targeted EPA priority polycyclic aromatic hydrocarbons (PAHs) were quantified in surface water from Amassoma axis of the Nun River, Bayelsa State, Nigeria as shown in Table 1. The distribution of PAHs in water from Amassoma axis, Nun River, Nigeria is represented graphically in Fig 2.

Table 1: SUMMARY OF PAH CONCENTRATIONS IN WATER SAMPLES

PAHs	Min	Max	Mean	No of rings	TEFs	Type of PAHs
Nap	0.020	0.060	0.039	2	0.001	LMW
Acy	0.030	0..040	0.037	3	0.001	LMW
Ace	ND	0.001	0.001	3	0.001	LMW
Flu	ND	0.010	0.006	3	0.001	LMW
Phe	ND	0.001	0.001	3	0.001	LMW
Ant	0.000	0.010	0.007	3	0.01	LMW
Fla	ND	ND	0.004	4	0.001	HMW
Pyr	0.010	0.010	0.008	4	0.001	HMW
BaA	0..00	0.010	0.005	4	0.1	HMW
Chy	0.010	0.080	0.047	4	0.01	HMW
BbF	-	-	-	5	0.1	HMW
BkF	-	-	-	5	0.1	HMW
BaP	0.040	0.040	0.021	5	1.0	HMW
DahA	-	-	-	5	1.0	HMW
BghiP	-	-	-	6	0.01	HMW
IcdP	-	-	-	6	0.1	HMW
$\sum PAHs$	0.11	0.26	0.175			

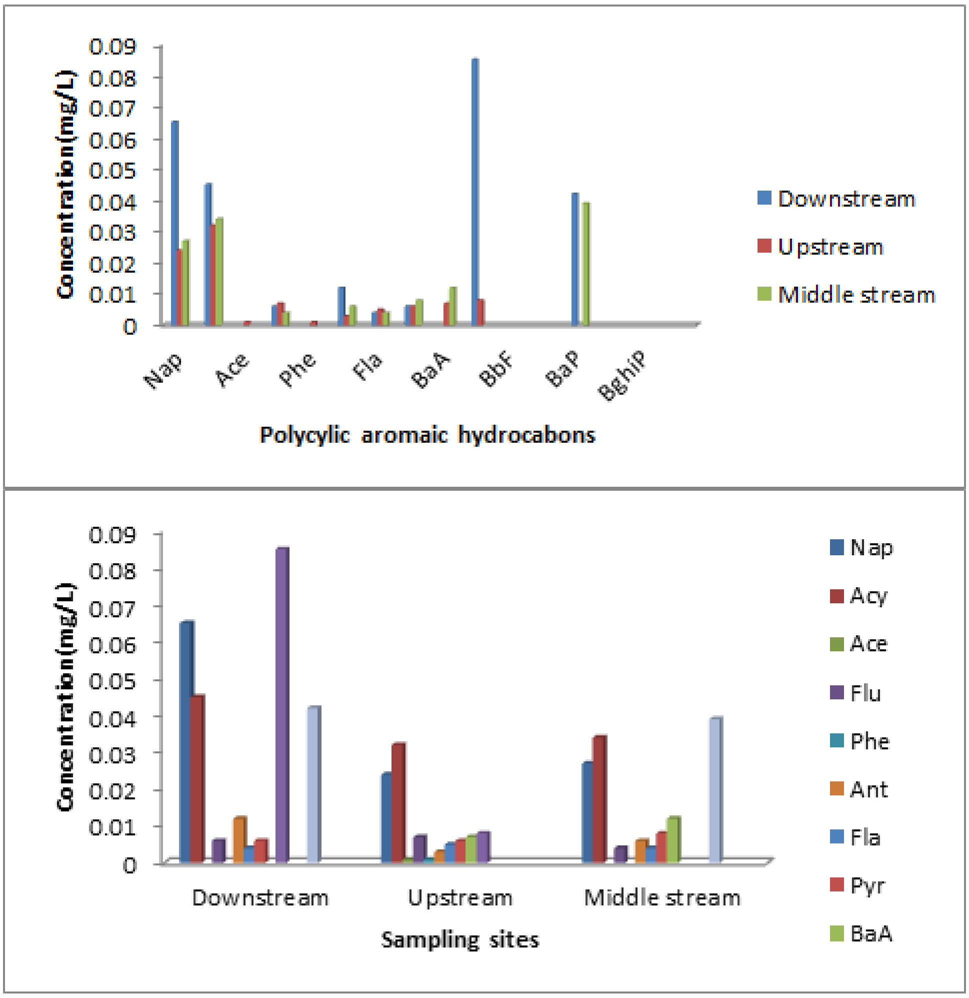

Fig 2 Distribution of total PAHs in water from Amassoma axis, Nun River, Nigeria

Total PAH concentrations in water samples ranged from 0.11mg/L to 0.26mgL with a mean concentration of 0.175mg/L. Nap, Acy, Ace, Flu, Phe, Ant, Fla, Pyr, Chy, BaA and BaP were detected in water samples in low concentration. The low concentrations could be attributed to distance from the point source occasioned with gradual dilution of the pollutant. The LMW PAHs were dominant, accounting for 58.68% of total PAHs and the HMW PAHs accounting for 43.72% of total PAHs. The low concentrations of 5-ring PAHs and absence of benzo[ghi]perylene (6 rings) were expected as 5–6 ring PAHs are non-volatile, non-biodegradable and less water-soluble, and they are usually adsorbed onto sediment (Jiries *et al.*, 2000; *Li et al.,* 2010). The concentration of Naphthalene ranged between 0.024±0.014 to (0.065±0.055 mg/L) with an average of 0.116±081 mg/L. Downstream had the highest water Naphthalene content; next was middle stream (0.027±0.012 mg/L) which is closely followed by upstream (0.024±0.014 mg/L). Nap is one of petrogenic PAHs with low molecular weight, which originates from oil spill and coal incineration (Sun *et al.*, 2016). The highest mean water acenaphthylene content (Table 1) was in dwnstream (0.045±0.020 mg/L) next was middle stream (0.034±0.04 mg/L) while was upstream (0.032±0.03 mg/L). The data shows that, concentration (mg/L) of acenaphthene in water ranged from ND to 0.001±0.00. For acenaphthene, the highest mean value was observed in upstream (0.001±0.00 mg/L), followed by downstream and middle stream had the least value (not detected). The highest water fluorene content (Table 1) was in upstream (0.007±0.001 mg/L) followed by downstream (0.006±0.001 mg/L) and middle stream (0.004±0.003 mg/L). The highest water phenanthrene content (Table 1) was in upstrem (0.001±0.00 mg/L) followed by downstream (nd) and middle stream (nd). Phe is regarded as the tracer of vehicular emissions (Sun *et al*., 2016). The values (mg/L) for anthracene (range, mean ± std) in water samples were (0.003±0.001 to 0.012±0.002, 0.007±0.003). For anthracene the highest value was observed in downstream (0.012±0.002), followed by middle stream and upstream had the least value (0.003±0.001). The concentration of fluoranthene ranged between 0.004±0.002 to (0.005±0.001 mg/L) with an average of 0.004±0.002 mg/L. Water fluoranthene content was highest in upstream (0.005±0.001 mg/L), followed by downstream (0.004±0.003 mg/L) and middle stream recording the least similar value (0.004±0.002 mg/L). Opuene (2004) reported the following mean concentrations for some PAHs viz acenaphthylene 20.5μg/l, phenanthrene 43μg/l, anthracene 109.2μg/l of the Taylor creek aquatic ecosystem, Bayelsa State.

The highest water pyrene content was in middle stream (0.008±0.002 mg/L) (Table 1) followed closely by upstream (0.006±0.004 mg/L) and downstream (0.006±0.00 mg/L). The highest mean water benzo (a) anthracene content (Table 1) was in middle stream (0.012±0.002 mg/L) next was upstream (0.007±0.004 mg/L) while downstream was (nd). The highest mean water chrysene content (Table 1) was in downstream (0.085±0.005 mg/L) next was upstream (0.008±0.002 mg/L) while upstream was (nd). The highest mean water Benz[a]pyrene content (Table 1) was in downstream (0.042±0.030 mg/L) next was middle stream (0.039±0.020 mg/L) while upstream was (nd). These results are in agreement with those reported by (Opuene 2004; Nwineewii and Marcus, 2015).

These seven PAHs compounds has being classified as probable human carcinogens viz benzo(a)anthracene, benzo (a)pyrene, benzo (b) fluoranthene, benzo (k) fluoranthene, chrysene, dibenzo (a,h) anthracene, and ideno (1,2,3 cd) Pyrene. PAHs known for their carcinogenic, mutagenic and teratogenic properties are benzo(a)anthracene, chrysene, benzo (b) fluoranthene, benzo (j) fluoranthene, benzo (k) fluoranthene, benzo (a) pyrene, benzo (g,h,i) perlyene, dibenzo (a,h) anthracene and ideno (1,2,3 – d) pyrene (Luch, 2005).

3.1 COMPOSITIONAL PROFILE

According to the number of rings, sixteen PAHs are classified into light (2–3 rings), 4-ring, and heavy (5–6 rings) PAHs.The 2 & 3-ring PAHs were dominant in water from Ammassoma axis of the Nun River(Fig 3). The predominance of low and medium molecular weight PAHs of the study area reflects the presence of significant combustion products from low temperature pyrolytic processes and/or petrogenic sources (Chen *et al*., 2012; Garcia-Falcon *et al*., 2006; Sun *et al*., 2016).

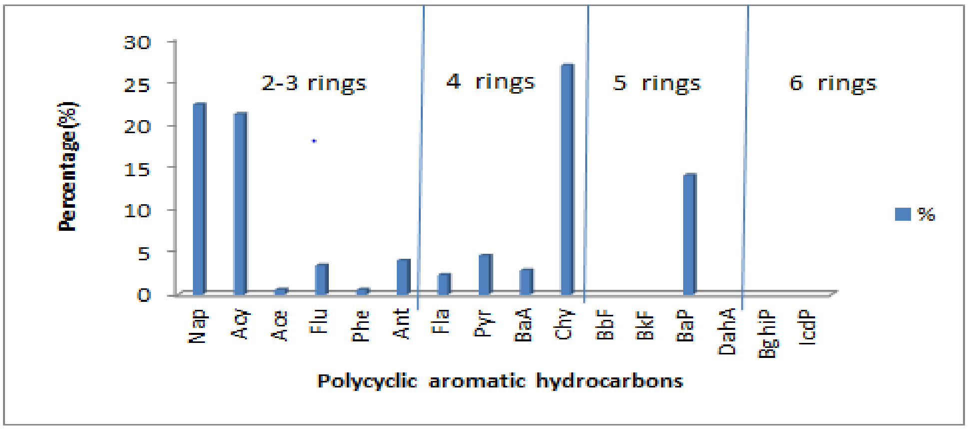

Fig 3 Compositional profile of PAHs in water from Amassoma axis, Nun River

3.2 CORRELATION BETWEEN PAHS

Statistical multivariate methods were used to study the data by considering the objects and the determined parameters as variables, by building a Pearson's correlation matrix (PCM) and the data presented in Table 2. The PCM analysis provided a means of statistically ascertaining the association/correlation of one parameter with another. PCM analysis reveals a positive correlation between the PAHs; this could indicate a common source for some of the PAHs, however, very few of the PAHs are negatively correlated with each other. This behavior could indicate non-point source.

Table 2: Correlation coefficient matrix of mean PAH concentrations in surface water

	Nap	Acy	Flu	Ant	Fla	Pyr	BaA	Chy	BaP	$\sum PAHs$
Nap	1									
Acy	0.804	1								
Flu	0.631	0.047	1							
Ant	0.677	0.982	-0.143	1						
Fla	-0.030	-0.619	0.756	-0.756	1					
Pyr	-0.881	-0.990	-0.189	-0.945	0.500	1				
BaA	-1.000	1.000	-1.000	-1.000	1.000	0.00	1			
Chy	1.000	1.000	-1.000	1.000	-1.000	-1.000	0.00	1		
BaP	1.000	1.000	1.000	1.000	0.00	1.000	0.00	0.00	1	
$\sum PAHs$	-0.019	0.579	-0.787	0.723	-0.999	-0.457	1.000	1.000	-1.000	1

*correlation is significant at the 0.05 level (2-tailed)
*correlation is significant at the 0.01 level (2-tailed)

3.3 ORIGINS OF PAHS

PAH fingerprint ratios for determining both petrogenic and pyrogenic (pyrolytic PAH accumulation in the environment has been used by various workers in their studies ((Magi *et al*., 2002; Chen *et al*., 2006; Yunker *et al*., 2002; Kafilzadeh, 2015). In this study, ratios of Ph/An and Fl/Py was employed. The ratio of Ph/An greater than 10 is generally regarded as Petrogenic PAHs source, and ratio less than 10 can be taken as combustion derived source. Similarly, Fl/Py ratio greater than 1 come from pyrolytic origins while ratios of less than 1 seem to show petrogenic source (Qiu *et al*., 2009). In the present research, Ph/An ratio for water samples were 0.00, 0.33 and 0.00 in three stations, while associated figures for Fl/Py ratio values were 0.67, 0.83 and 0.50 respectively

3.4 HUMAN HEALTH RISK ESTIMATIONS

The TEFs, first introduced by Nisbet and LaGoy (1992) for determining the carcinogenic potencies of individual PAHs B(A)Pteq by multiplying the PAH concentration in the sample by the individual toxicity equivalency factor (TEF) and has been used by various workers in their studies(Tongo *et al.,* 2017; Karyab *et al*., 2013). The TEF is an estimate of the relative toxicity of individual PAH fractions compared to benzo(a)pyrene. Toxic equivalency factors have been applied as a useful tool for the regulation of compounds with a common mechanism of actions (e.g PAHs). The results revealed that the mean PAHs concentration as BaP equivalent was in the range of 1.0E-6 – 0.021mg/L in the water samples.

4.0 CONCLUSION

The town of Amassoma is well known as it played host to the famous Niger Delta University which has spurred the population size. This study was carried out to check sixteen priority polycyclic aromatic hydrocarbons (PAHs) in water samples collected from Amassoma axis, Nun River, Nigeria. The total PAHs ranged from 0.11mg/L to 0.26 mg/L with mean concentration of 0.175mg/L in water samples. The PAHs with 2–3 rings were dominant in the water samples. The ratios of Ph/An and Fl/Py suggest that the main source of PAHs in the study area could be ascribed to oil-related activities (petroleum) combined with weaker combustion contribution. Therefore, the authors recommend stringent pollution control measures to safeguard the water system.

COMPETING INTERESTS
Authors have declared that no competing interest exist.

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