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DISTRIBUTION PATTERN, SOURCES AND ECOLOGICAL RISK ASSESSMENT OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN SEDIMENTS OF WARRI RIVER, NIGER DELTA, NIGERIA

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ABSTRACT

The distribution, pollution sources and ecological risk of the 16 priority PAHs were investigated in surface sediments of the Warri River, Niger Delta Nigeria. Sediment samples were collected from six points along the river during the wet and dry seasons. The concentrations of PAHs were determined using gas chromatography equipped with flame ionization detector after ultra-sonication with hexane and dichloromethane. The mean concentrations of the ∑16 PAHs in the sediments ranged from 1158 to 1993 µg/kg for the entire study period. The concentrations of ∑16 PAHs during the wet season were significantly higher than those of the dry season. The 3-ring PAHs were the dominant PAH compounds in the sediments. The sources and ecological risk of PAHs were assessed using diagnostic ratios and sediment quality guidelines (SQGs) respectively. The diagnostic ratios revealed that PAHs in the sediment of Warri River originated mainly from pyrogenic and petrogenic sources with greater inputs from pyrogenic sources. The ecological risk evaluation of PAHs in these sediments indicated low toxicity and that they would pose little or no ecological risk.

Keywords: Ecological Risk, Niger Delta, PAHs, Sediments, Sources, Warri River.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) formed one of the vital group of organic contaminants in the environment. PAHs are made up of two or more aromatic rings fused together in different orientations [1]. They arise from both natural and man-made sources. Natural sources of PAHs include forest fire and volcanic eruption while the man-made sources consist of pyrogenic and petrogenic sources. The man-made sources include the incomplete burning and pyrolysis of substances like fossil fuels, biomass, other organic substances,

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industrial processes as well as non-combustion derived petrogenic crude oil [2]. The high molecular weight PAHs consisting of 4-6 rings usually originate from pyrogenic sources while lower molecular weight PAHs consisting of 2-3 rings originates from petrogenic sources [3]. As a result of their persistent and toxic nature, carcinogenic and mutagenic tendencies, long range transportation and widespread distribution in the environment, PAHs have gained a lot of attention and 16 of them has been listed as priority pollutants in the United States Federal Water Pollution Control Act (1972) and the United States Clean Water Act (1997) [4]. Once produced, PAHs are introduced into aquatic ecosystems via atmospheric transport and deposition, surface runoff, oil leakages and waste water discharge [5]. Warri River is one of the main coastal and navigable rivers of the Niger Delta. The River spread across several tributaries around Warri city. It lies between latitude 5.00^{o} and 6.30^{o} N and longitude 5.21^{o} and 6.45^{o} E. Warri River started from Utagba-Uno and flows through Agbarho, Otokutu, Effurun, Ovwian, Aladja, Ogbe- Ijoh and enters the Forcados River which emptied into the Atlantic Ocean. Considering the significance of the Warri River and the kind of human activities taking place in the study area, it becomes necessary to carry out studies to determine the levels of PAHs in the River. There is limited information on the distribution of PAHs in the surface sediment of the Warri River as there are only a few studies available on the PAHs distribution in the sediments of the Warri River. [11] studied the concentrations of PAHs in the Sediment of Ekpan creek of the Warri River, [12] gave an account of PAHs in the Warri River at Ubeji. Thus, the objectives of the present study are to determine the distribution, sources and ecological risks of PAHs in surface sediments of the Warri River.

MATERIALS AND METHODS

Sample Locations

Six locations designated as SW1 to SW6 were strategically selected along the Warri River for this study. The six sampling locations were chosen based on the anthropogenic activities taking place in these locations.

Sample Collection

The sediment samples were collected using a stainless-steel grab sampler. Samples were stored in glass containers, labelled appropriately and kept in ice chest. The samples were transported to the laboratory where they were freeze dried, sieved through 2 mm mesh, and stored at 4 ^{o}C until analysis.

PAHs Extraction and Cleanup from Sediment Samples

The PAHs in the sediment samples were extracted and cleanup using the USEPA-3550C- ultrasonic extraction method [13]. A

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mass of 10.0 g of the sediment samples was mixed with the same amount of sodium sulphate (Na_2SO_4). The resulting mixture was extracted by ultrasonication with 50 ml of hexane/dichloromethane (DCM) (1:1 v/v) at 30 °C for 30 minutes and filtered. The extract was evaporated to 1 mL by using a rotary evaporator and purified by solid phase extractions with silica gel and alumina. The PAHs were subsequently eluted with 15 mL hexane and dichloromethane (9:1). The eluted fraction was evaporated to approximately 0.5 ml using a stream of nitrogen gas.

Gas Chromatographic Analysis

The individual PAHs in the extracts were quantified by means of gas chromatography (HP 6890 Palo Alto, C A, USA) with a flame ionization detector (FID). Separation was effected on a HP5 (cross-linked PHME siloxane) column with 0.25 µm film thickness and dimensions of
0.25 µm × 30 m. The carrier gas was helium with a linear velocity of 30 cm/s. The initial column temperature was 100 ^{O}C and it was increased at a rate of 4 ◦C/min to a final temperature of 310^{O}C. The injector temperature was maintained at 250 ^{O}C and the injection volumes were 2.0 µL in the splitless mode. The quantification was by the use of external calibrations which were obtained with PAH solutions at five concentration levels.

Quality Assurance

Extraction efficiency for the target PAHs was evaluated by spiking the samples with four deuterated PAH compounds to represent the different PAHs. The pISSN 0795 - 22066
calculated for each sample analyzed. The percent recovery ranged from 89.2 to 97.6 %. For sample cleanup, freshly prepared, packed chromatography was used for each sample.

Data Analysis

The student's t-test statistical tool was used to determine if there is significant seasonal variation in the PAHs concentrations while Analysis of Variance (ANOVA) was used to determine if there is significant variation in the PAHs concentrations among the different sampling points. The level of significance that was adopted for the analysis was P=0.05. P-value <0.05 indicated significant variation while p-value >0.05 indicated no significant variation. The diagnostic ratios of some PAH isomers was employed in identifying the potential sources of PAHs.

PAHs concentrations in sediment

The results of PAHs concentrations in sediments of the Warri River are shown in Table 1 below while the seasonal variation of the total PAHs is shown in Figure 1. The mean concentrations of the ∑16 PAHs in the sediments for the entire study period varied from 1158 to 1993 µg/kg. The concentration of ∑16 PAHs at sampling

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locations SW3 and SW2 were the lowest and highest respectively. There was significant variation ($p < 0.05$) in the concentration of ∑16 PAHs among these sites. The significant variation might be due to the different anthropogenic activities taking place at each sampling point. Also, there was significant seasonal variation ($p < 0.05$) in the concentrations of ∑16 PAHs in this study. The concentrations of the ∑16 PAHs in the dry season ranged from 348 to 557 µg/kg while that of the wet season range from 2914 to 4632 µg/kg. The concentrations of ∑16 PAHs in the wet season were significantly higher than the dry season (Figure 1). The seasonal variation might be attributable to climatic condition, effect of photo oxidation, volatilization and high degradation during the dry season [14]. Similar observation has also been reported by [14] for Euphrates River sediment in Iraq and [15] for Kor River sediment in Iran. [16] classified PAHs pollution into low (0-100 ng/g), moderate (100-1000 ng/g), high (1000-5000 ng/g) and very high (> 5000 ng/g). The sediment samples from the Warri River in this study falls into moderate to high pollution category. The range of ∑16 PAHs concentrations obtained in this study was comparable to others reported in literatures as shown in Table 2. However, the concentrations of ∑16 PAHs obtained in this study were lower than those reported for Mvudi and Nzhelele Rivers in South Africa [17].

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Table 1: Concentrations of PAHs (mean±SD) in sediments of the study area during the entire study period

	SW1				SW2				SW3				SW4				SW5				SW6			
	MEAN	**STD**	**MIN**	**MAX**	**MEAN**	**STD**	**MIN**	**MAX**	**MEAN**	**STD**	**MIN**	**MAX**	**MEAN**	**STD**	**MIN**	**MAX**	**MEAN**	**STD**	**MIN**	**MAX**	**MEAN**	**STD**	**MIN**	**MAX**
Nap	121	14	ND	132	762	813	ND	1628	909	1269	ND	1806	110	116	ND	266	225	202	ND	413	14	0	ND	14
Acy	28	4	ND	31	79	69	ND	143	52	62	ND	124	314	360	ND	835	68	54	ND	128	111	75	ND	174
Ace	219	386	ND	906	86	57	ND	159	124	55	ND	183	161	132	ND	315	120	121	12	287	143	108	ND	212
Flu	130	195	ND	422	100	108	ND	227	163	179	ND	386	105	67	ND	183	174	112	ND	294	200	186	ND	405
Phen	309	390	ND	835	164	42	ND	204	59	59	ND	138	168	108	ND	292	470	833	ND	1951	92	100	ND	216
Ant	288	405	ND	994	342	475	ND	1026	296	495	ND	1036	286	443	ND	1064	143	28	111	187	395	256	ND	680
Flt	76	75	ND	162	217	391	11	1007	20	14	ND	37	162	142	11	373	82	54	17	134	109	89	ND	227
Pyr	92	116	ND	285	84	52	13	138	110	184	ND	386	82	60	19	162	105	85	27	216	273	381	ND	940
BaA	144	192	11	512	209	327	4	856	87	91	12	245	95	87	19	220	106	106	14	292	105	70	17	180
Chry	97	81	11	233	130	224	4	573	105	102	15	283	73	52	14	122	71	59	12	130	98	89	18	201
BbF	97	71	ND	138	202	210	ND	476	23	13	ND	32	63	71	ND	113	67	59	12	130	122	87	ND	222
BaP	57	62	ND	136	176	173	ND	422	89	75	ND	181	14	0	ND	14	75	109	ND	201	90	53	ND	122
BkF	13	3	ND	15	73	68	ND	147	47	59	ND	115	72	85	ND	132	66	73	ND	117	59	67	ND	153
IndP	74	77	ND	128	96	57	ND	130	14	1.5	ND	16	75	56	ND	109	103	87	ND	185	74	77	ND	128
DahA	79	115	ND	212	84	103	ND	157	17	5.5	ND	21	89	106	ND	164	77	93	ND	143	62	67	ND	109
BghiP	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TOTAL	**1369**	**1718**	**125**	**4735**	**1993**	**2331**	**97**	**5855**	**1158**	**1452**	**192**	**4025**	**1391**	**1274**	**112**	**2811**	**1537**	**1379**	**416**	**3690**	**1261**	**1362**	**80**	**3772**

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2-ring	121	14	ND	132	762	813	ND	1628	909	1269	ND	1806	110	116	ND	266	225	202	ND	413	14	0	ND	14
3-ring	776	1217	52	3157	545	645	42	1647	557	633	ND	1653	791	850	48	1941	856	905	231	2625	501	585	17	1645
4-ring	368	389	51	1068	641	766	55	2005	275	229	55	623	412	323	64	831	364	289	80	757	522	545	48	1473
5-ring	139	93	12	250	435	462	ND	1089	133	77	ND	239	154	127	ND	296	152	170	12	449	211	228	11	527
6-ring	74	77	ND	128	96	57	ND	130	14	1.5	ND	16	75	56	ND	109	103	87	ND	185	74	77	ND	128

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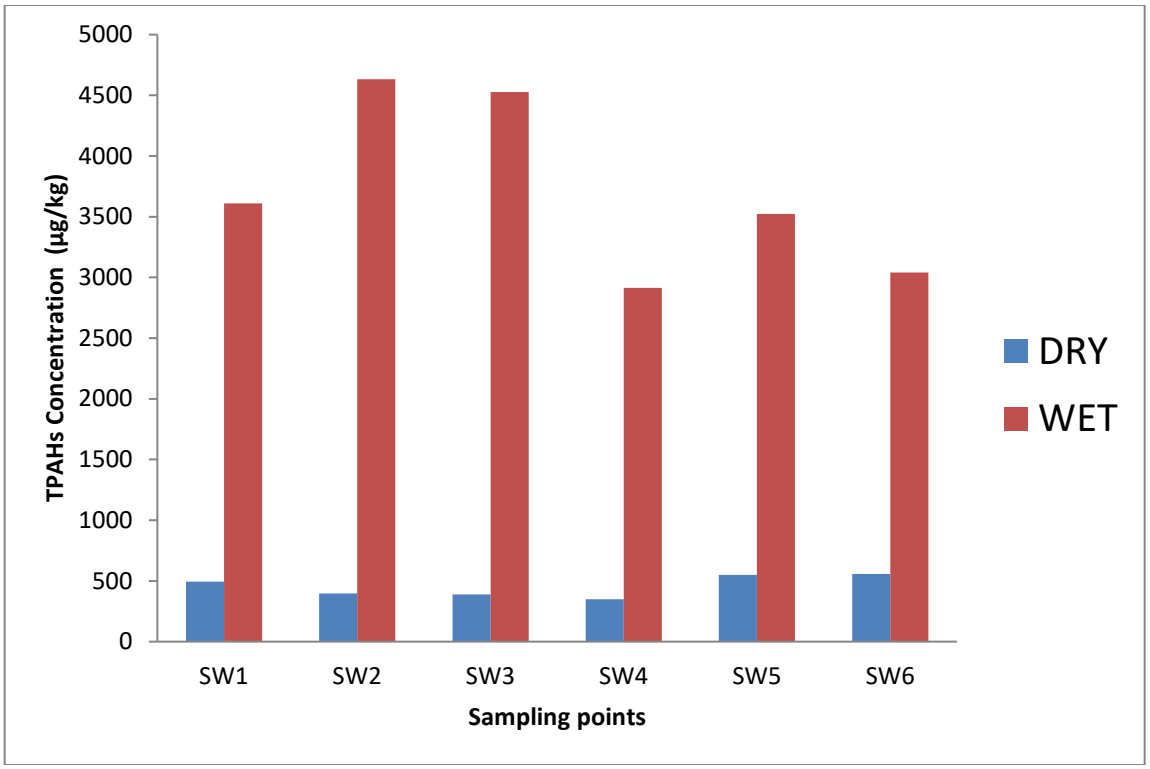

Figure 1: Seasonal variations of TPAHs in sediments

Occurrence Pattern and Profiles of PAHs in Sediments

The occurrence pattern of the PAHs in this study is as shown in Figure 3. The occurrence pattern of the PAHs followed the trend; 3-ring > 4-ring > 2-ring > 5-ring > 6-ring. The lower molecular weight PAHs were the dominant PAHs compounds in this study. A similar trend was also observed by previous researchers [18]. The predominance of low molecular weight PAHs in the sediment of this study area reflects the presence of significant combustion products from low temperature pyrolytic processes and / or petrogenic sources [19]. The mean concentrations of naphthalene, which is the only two rings PAH compound was found to range from 14.3 at sampling location SW6 to 909 µg/kg at sampling location SW3 during the entire study period. Naphthalene makes up 0.7 to 43 % of the total PAHs concentrations. The 3-ring PAHs are the dominant PAH compounds in these sediments. The mean concentrations of the sum of 3-ring PAHs (i.e. Acy + Ace + Flu + Phe + Ant) ranged from 695 to 1033 µg/kg and accounted for 32.8 to 55.3 % of the total PAHs concentrations. The maximum and minimum concentrations of the sum of 3-ring PAH were found at sampling locations SW4 and SW3 respectively. The occurrence pattern of the 3-ring PAH compounds is in the order of Ant > Phen> Flu > Ace > Acy. The concentrations of Acy ranged from 28.0 to 314 µg/kg and makes up 1.5

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to 16.8 % of the total PAHs. Acenapthene ranged from 86.0 to 219 µg/kg and constituted 3.1 to 12.0 % of the total PAHs. Flu was detected at concentrations ranged from 100 to 200 µg/kg and comprised 3.6 to 10.3 % of the total PAHs. The concentrations of Phen and Ant ranged from 59.4 to 470 µg/kg and 143 to 395 µg/kg and constituted 2.8 to 24.1 % and 7.3 to 20.3 % respectively of the total PAHs. The mean concentration of the sum of 4ring PAHs (Flt+Pyr+BaA+Chry) ranged from 322 to 641 and makes up 15.2 to 30.1 % of the total PAHs. The occurrence pattern of the 4-ring PAH compounds followed the order BaA > Pyr > Flt > Chry. Fluoranthene was detected at concentrations which ranged from 2.0 to 217 µg/kg and consisted 1.0 to 8.6 % of the total PAHs concentration. Pyrene was detected at concentrations which ranged from 84.1 to 273 µg/kg and makes up 3.0 to 14.0 % of the total PAHs concentration. Benzo(a)anthracene was detected at concentrations which ranged from 87.0 to 209 µg/kg. Benzo(a)anthracene constituted 4.1 to 7.9 % of the PAHs concentrations in these sediments. Chrysene was detected at concentrations of 70.7 to 130 µg/kg and constituted 3.6 to 5.3 % of the total PAHs concentrations. The mean concentration of the sum of the five ring PAHs (BbF+BkF+BaP+DahA) ranged from 175 to 535 µg/kg. The sum of the five ring PAHs constituted 8.3 to 19.1 % of the total PAH concentrations. The concentrations of Benzo(b)fluoranthene and benzo(a)pyrene ranged from 22.9 to 202 µg/kg and 13.8 to 176 µg/kg respectively. They make up 1.1 to 7.2 % and 0.7 to 6.3 % of the total PAHs concentrations. The concentrations of BkF ranged from 12.8 to 72.7 µg/kg, while that of dibenzo(a,h)anthracene ranged from 16.7 to 88.5 µg/kg . They both constituted 0.7 to 3.9 % and 0.8 to 4.7 % of the total PAHs respectively. Indeno(1,2,3 cd)perylene was the only six ring compound detected in these sediments. The concentration of IndP ranged from 73.6 to 103 µg/kg and makes up 0.7 to 5.3 % of the total PAHs concentrations.

Sources evaluation using diagnostic ratios of PAHs Isomers

The diagnostic ratios of some PAH isomers have been employed in identifying the potential sources of PAHs by many researchers [20,21]. The diagnostic ratios of PAHs isomers used in this study, their interpretations and the result of source evaluation of PAHs in sediments in the present study are shown in Table 3. The Flt/(Flt+Pyr) ratio ranged from 0.16 to 0.72. Except at the sampling location SW3 that indicates that the source of PAHs is petrogenic, the values of Flt/(Flt+Pyr) for all the other sites indicates that the PAHs in these sediments from the Warri River are from petroleum combustion and combustion of fossil fuels and wood. The ratio of Ant/(Ant+Phen) ranged from 0.23 to 0.83. The Ant/(Ant+Phen) ratios were all > 0.1 indicating that the PAHs were from combustion processes. The ratio of BaA/(BaA+Chy) in this study ranged from 0.38 to 0.55. The BaA/(BaA+Chy) ratios obtained in this study

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were > 0.35. This indicates that the PAHs are from combustion of coal, wood and grasses. The ΣLMW/ΣHMW ratio obtained in this study ranged from 0.96 to 3.13. The ratios of ΣLMW/ΣHMW were > 1.0 in all the sampling location except at SW6 indicating that the PAHs are from petrogenic sources. The ratio of CPAHs/TPAHs ranged from 0.23 to 0.48. This indicates that the source of PAHs is combustion processes. The ratio of Phen/Ant in these sediments ranged from 0.20 to 3.29. This indicates that the source of PAHs is pyrolytic.. The Flt/Pyr ratio obtained in this study ranged from 0.18 to 2.58. The ratio of Flt/Pyr was < 1.0 in all sampling location except at SW2 and SW4, indicating that the PAHs in these sites are from petrogenic sources. From the result of the source evaluation, variability in the sources of PAHs in these sediment samples was observed. This variability is attributed to multiple sources.

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Table 3: PAHs in sediments

PAHs	Conc. Range	ERL	ERM	TEL	PEL	<ERL (%)	ERL-ERM (%)	> ERM	<TEL (%)	TEL-PEL (%)	>PEL (%)
Nap	14-909	160	2100	34.6	391	3 (50)	3 (50)	-	1 (17)	3 (50)	2 (33)
Acy	28-314	44	640	5.87	128	1 (17)	5 (83)	-	-	5 (83)	1 (17)
Ace	86-219	16	500	6.71	88.9	-	6 (100)	-	-	1 (17)	5 (83)
Flu	100-200	19	540	21.2	144	-	6 (100)	-	-	3 (50)	3 (50)
Phen	59-420	240	1500	86.7	544	4 (67)	2 (33)	-	1 (17)	5 (83)	-
Ant	143-395	853	1100	46.9	245	6 (100)	-	-	-	1 (17)	5 (83)
Flt	20-207	600	5100	113	1494	6 (100)	-	-	4 (67)	2 (33)	
Pyr	82-273	665	2600	153	1398	5 (83)	1 (17)	-	5 (83)	1 (17)	-
BaA	87-209	261	1600	74.8	693	6 (100)	-	-	-	6 (100)	
Chry	71-130	384	2800	108	846	6 (100)	-	-	5 (83)	1 (17)	-
BbF	23-202	320	1800	-	-	6 (100)	-	-	-	-	-
BaP	14-176	430	1600	88.8	763	6 (100)	-	-	3 (50)	3 (50)	-
BkF	13-73	280	1620	-	-	6 (100)	-	-	-	-	-
IndP	14-103	-	-	-	-	-	-	-	-	-	-
DahA	17-89	63.4	260	6.22	135	2 (33)	4 (67)	-	-	6 (100)	-
Total	1158-1993	4022	44792	1684	16770	6 (100)	-	-	5 (83)	1 (17)	-

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Ecological Risk Assessment of PAHs in Sediments

Sediment quality guidelines (SQGs) give a systematic basis to assess the latent effects of contaminants in soil and sediments and as such have been utilized to evaluate ecological risk of PAHs in sediments in recent times [22]. The SQGs were designed for PAHs by combining empirical analysis of chemical and biological data [23]. The SQGs are straightforward and readily accessible and recognize the effect and/or lack of effect of PAHs in sediments. The SQGs are efficient and simple in their usage; however, they may give generic result, rather than definite [24]. There are two categories of SQGs employed for ecological risk assessment. The ecological effect range low (ERL) with the biological effect range medium (ERM) [25] and the threshold effect level (TEL) with the probable effect level (PEL) [26]. A value < ERL or TEL implies that the ecological risk associated with a given PAH compound is rare. A value between the ERL and ERM or between the TEL and PEL implies that the ecological risk associated with a given PAH compound is occasional. When the value is > the ERM or PEL, it suggests that the ecological risk associated with a given PAH compound is often or frequent. So, the two categories of SQGs were employed in this study to evaluate the ecological risk of PAHs in the surface sediments of the Warri River and the result is as shown in Table 3.

Table 3: Sources of PAHs in sediments of the Warri River

Isomeric Ratio	Range	Sources	Present study
Flt/(Flt + Pyr)	< 0.4	petroleum origin	SW3, SW6
	0.4-0.5	petroleum combustion	SW1, SW5
	> 0.5	coal and biomass	SW2, SW4
Ant/(Ant + Phen)	< 0.10	petroleum input	-
	> 0.1	combustion process	SW1, SW2, SW3, SW4, SW5, SW6
BaA/(BaA + Chry)	< 0.2	Petroleum	-
	0.2-0.35	petroleum combustion	-
	> 0.35	coal and biomass combustion	SW1, SW2, SW3, SW4, SW5, SW6
LMW/HMW	< 1.0	combustion of fossil fuels or wood	SW6
	> 1.0	petrogenic sources	SW1, SW2, SW3, SW4, SW5
CPAHs/TPAHs	< 1.0	Combustion processes	SW1, SW2, SW3, SW4, SW5, SW6
	> 1.0	petrogenic sources	-
Phen/Ant	< 10.0	Pyrolytic	SW1, SW2, SW3, SW4, SW5, SW6I
	>10.0	Petrogenic	-
Flt/Pyr	<1.0	Petrogenic	SW1, SW3, SW5, SW6
	>1.0	Pyrolytic	SW2, SW4

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The result indicated that total PAHs in the sediment of the Warri River will rarely cause adverse ecological effects as 100 % and 83 % of the sampling points have total PAH concentrations less than ERL and TEL values respectively.

However, the results indicate that individual PAHs can cause different degree of adverse ecological effects on the aquatic organisms in the Warri River. For instance, the concentrations of Nap in 50 % of the sampling points were <ERL, ERL-ERM and TEL-PEL. The concentrations of Phen in 67 % and 83 % of the sampling points fall into <ERL and TEL-PEL respectively. The concentrations of BaA in 100% of the sampling points were <ERL and TEL-PEL while the concentrations of BaP in 100 % and 50 % of the sampling points were <TEL and in TEL-PEL respectively. This indicates that there is the likelihood of rare to occasional adverse ecological effect on aquatic organisms in the sediment of the Warri River by Nap, Phen, BaA and BaP. The concentrations of Acy in 83 % of the sampling points were within the ERL-ERM and TEL-PEL values while the concentrations of DahA in 67 % to 100 % of the sampling points are within the ERL-ERM and TEL-PEL values respectively. This implies that Acy and DahA can cause occasional ecological effects on the living organism in the sediments of the Warri River. The concentrations of Ace in 100 % and 83% of the sampling points were within the ERL-ERM and > PEL value respectively. The concentrations of Flu in 100 % of the sampling points were between ERL-ERM while 50 % each of the sampling points have concentrations between TEL-PEL and > PEL. This suggests that Ace and Flu can cause occasional to often adverse ecological effects to organisms in the sediments of the Warri River. The concentrations of Ant in 100 % of the sampling points were < ERL values. Also, the concentrations of Ant in 83 % of the sampling points were > PEL value. This means that Ant in the sediments of Warri River can cause rare to often adverse ecological effects on organisms in the sediments. The concentration of Flt in 100 % and 67 % of the sampling points were <ERL and TEL respectively while that of Pyr in 83 % each of the sampling points were < ERL and < TEL. Also, the concentrations of Chry in 100 % and 83 % of the sampling points were < ERL and < TEL values respectively while the concentrations of BbF and BkF in 100 % of the sampling points were less than their respective ERL values. This indicates that Flt, Pyr, Chry, BbF and BkF will rarely cause adverse ecological effects on the aquatic organisms of the Warri River.

CONCLUSION

This study aimed at determining the distribution, pollution sources and ecological risk of PAHs in sediment of the Warri River, Niger Delta Nigeria. The result of PAHs concentrations in the sediment indicated that the sediments are

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highly polluted with PAHs. The distribution of PAHs followed the order 3-ring > 4-ring > 2-ring > 5-ring > 6-ring. The diagnostic ratios showed that the PAHs originated from both pyrogenic and petrogenic sources with greater input from pyrogenic sources. The ecological risk indicated that total PAHs in the sediment of the Warri River will rarely pose ecological risk though some individual PAHs will pose occasional ecological risk.

REFERENCES

[1] Mekonnen K. N., Chandravanshi B. S., Redi-Abshiro M., Ambushe A, A., McCrindle R, I., & Moyo S., (2015). Distribution of polycyclic aromatic hydrocarbons in sediments of Akaki River, Lake Awassa and Lake Ziway, Ethiopia. *Environmental Monitoring and Assessment.* 187: 474-480. DOI: 10.1007/s10661-015-4669-1

[2] Riccardi C, Fillippo P. D, Pomata D., Basilio M.D., Spicaglia S., & Buiarelli F., (2013). Identification of hydrocarbon sources in contaminated soils in three industrial areas. *Science of the Total Environment*. 430: 13-21

[3] Tavakoly Sany SB., Hashim R., Salleh A., & Rezayi M., Mehdinia A., & Safari O., (2014) Polycyclic aromatic hydrocarbons in coastal sediments of Klang Strait, Malaysia: *Distribution pattern, risk assessment and sources.* PLoS One. 9(4): e94907

[4] Bixian M, Jiamo F., Gan Z., Zheng L., Yushun M., Guoying S., & Xingmin W., (2001**).** Polycyclic Aromatic Hydrocarbons in sediments from the Pearl River and estuary, China: spatial and temporal distribution and sources. *Applied Geochemistry*.; 16: 1429-1445

[5] Hu J, Liu C, Guo Q, Yang J., Okoli C. P., Lang Y., Zhao Z., Li S., Liu B., & Song G., (2017) Characteristics, source and potential ecological risk assessment of polycyclic aromatic hydrocarbons (PAHs) in the Songhua River Basin, North East China. *Environmental Science and Pollution Research*. 24: 17090-17102

[6] Yohannes YB, Ikenaka Y, Saengtienchai A, Watanabe KP, Nakayama SM., & Ishizuka M., (2013**)** Occurrence, distribution and ecological risk assessment of DDTs and heavy metals in surface sediments from Lake Awassa- Ethiopian Rift Valley Lake. *Environmental Science and Pollution Research*.; 20(12): 8663-8671

[7] Semlali A, Chafik A, Talbi M, et al. Origin and distribution of polycyclic aromatic hydrocarbons in Lagoon ecosystems of Morocco. The Open Environmental Pollution and Toxicology Journal. **2012**; 3(Suppl 1-M5): 37-46

[8] Guo W, He M, Yang Z, et al. Aliphatic and polycyclic aromatic hydrocarbons in the Xihe River, an urban river in China's Shenyang city: Distribution and risk assessment. Journal of Hazardous Materials. **2011**; 186: 1193-1199

[9] Olobaniyi SB, Efe SI. Comparative assessment of rainwater and groundwater quality in an oil producing area of Nigeria. Journal of Environmental Health Research. **2006**; 6: 111–117.

[10] Agbozu IE, Bayowa AV, Oghama OE. Critical analysis of Polycyclic aromatic hydrocarbons ring size distribution in marshy soils and

ISSN 0795 - 22066

sediments in Warri city and its environs, southern Nigeria. British Journal of Applied Science & Technology. **2017**; 20(6): 1-16

[11] Okoro D. Source determination of polycyclic aromatic hydrocarbons in water and sediment of a creek in the Niger Delta region. African J. Biotechnol. **2008**; 7(3): 282- 285

[12] Asagbra MC, Adebayo AS, Anumudu CI, et al. Polycyclic aromatic hydrocarbons in water, sediment and fish from the Warri River at Ubeji, Niger Delta,
Nigeria. African Journal of Aquatic Science. **2015**; 1-7

[13] USEPA. Testing Methods for Evaluating Solid Waste, Physical and Chemical Methods, Method 3550C; Ultra-Sonication Extraction. 2007; Retrieved on March 25, 2016 from http://www.epa.gov/solidwaste/hazard/testmethods/sw846/pdfs/3550c.pdf

[14] Mohammed AB, Al-Taee MMS, Hassan FM. The study of some PAH compounds in Euphrates River sediment from Al-Hindiya Barrageto Al-Kifil city, Iraq. Scientific Conference, College of 4th Science, Babylon University. CSASC English Ver. **2009**; 4: 216-230.

[15] Kafilzadeh F, Shiva AH, Malekpour R. Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Water and Sediments of the Kor River, Iran. Middle-East Journal of Scientific Research. **2011**; 10(1): 1-11

[16] Baumard P, Budzinski H, Garrigues P. Polycyclic aromatic hydrocarbons in sediments and mussels of the western Mediterranean sea. Environ. Toxicol.Chem. **1998**; 17: 765-776

[17] Edokpayi JN, Odiyo JO, Popoola OE, et al. Determination and distribution of polycyclic aromatic hydrocarbons in rivers, sediments and wastewater effluents in Vhembe District, South Africa. Int. J. Environ. Res. Public Health. **2016**; 13: 387-397

[18] Dong CD, Chen CF, Chen CW. Determination of polycyclic aromatic hydrocarbons in industrial harbor sediments by GC-MS. Int Journal. Environ Res Public Health. **2012**; 9: 2175-2188.

[19] Mai BX, Fu HM, Sheng GY, et al. Chlorinated and polycyclic aromatic hydrocarbons in riverine and estuarine sediments from Pearl River Delta, China. Environ. Pollut. **2002**; 117: 457–474.

[20] Chen CW, Chen CF, Dong CD, et al. Composition and source apportionment of PAHs in sediments at river mouths and channel in Kaohsiung Harbor, Taiwan. J. Environ. Monit. **2012**; 14: 105–115

[21] Tesi GO, Iwegbue CMA, Emuh FN, et al. Lagdo Dam Flood Disaster of 2012: An Assessment of the concentrations, sources, and risks of PAHs in floodplain soils of the lower reaches of River Niger, Nigeria. J. Environ. Qual. **2016***;* 45: 305–314

[22] Liu W, Ma L, Abuduwaili J, et al. Distribution, source analysis and ecological risk assessment of polycyclic aromatic hydrocarbons in the topical soil of the Issyk-Kul Lake Basin. Environ. Monit. Assess. **2017**; 189: 398-408

[23] Long ER, Field, LJ, Macdonald DD. Predicting toxicity in marine

ISSN 0795 - 22066

sediments with numerical sediment quality guidelines. Environmental Toxicology and Chemistry. **1998**; 17(4): 717-727

[24] Long ER, Macdonald DD, Smith SL, et al. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environ. Manage. **1995**; *19*, 81–97.

[25] Macdonald DD, Carr RS, Calder FD, et al. Development and evaluation of sediment quality guidelines for Florida coastal waters. Ecotoxicology. **1996**; 5: 253–278

ISSN 0795 - 22066