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PRELIMINARY STUDY ON POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) IN WATER SAMPLES FROM OYUN AND ASA RIVERS, ILORIN, KWARA STATE

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ABSTRACT

This study was concerned with the evaluation of the levels of polycyclic aromatic hydrocarbons (PAHs) in water samples collected from Asa and Oyun River within Ilorin in Kwara State. Gas Chromatography-Mass spectrometry has been used for the analytical determination. A total of 52 hydrocarbons were found to be present in the water samples. These two rivers can be said to be contaminated with PAHs. The pollution can be attributed to both anthropogenic and natural sources. The water needs to be adequately treated and regularly monitored. Future evaluation of human health risk assessments, seasonal monitoring of PAHs in the rivers and possible remediation studies are recommended.

Keywords: PAHs, Hydrocarbons, Gas chromatography, Remediation, Asa and Oyun Rivers

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs), also known as poly-aromatic hydrocarbons or polynucleararomatic hydrocarbons, is a class of diverse organic compounds containing two or more fused aromatic rings of carbon and hydrogen atoms, they are organic compounds which are widely distributed in the environment (Chen *et al.,* 2007). They do not contain heteroatomic or carry substituent. The simplest example of PAHs is Naphthalene. PAHs are lipophilic (they mix more easily with oil than water). The larger PAH are less water-soluble and less volatile. PAHs are one of the most widespread organic pollutants (Allamandola *et al.*, 1999)

In addition to their presence in fossil fuels they are also formed by incomplete combustion of carbon-containing fuels such as wood, coal, diesel etc. Naturally existing PAHs have been suggested as the chemical building blocks that participated in the origin of life (Allamandola *et al.*, 1999). Normally low concentration levels of PAHs, formed by the incomplete combustion of organic materials during natural processes, have been supplemented by industrialization processes and the synthesis of new chemical compounds liberated mainly through an atmospheric route in vapor phase and particle form or soot (Walker, 2001). Other sources of PAHs in the environment are spills and direct discharges of petroleum and its

derivatives to the soil or aquatic systems (Mastandrea *et al.,* 2005).
PAHs are strongly hydrophobic (fear of water) and difficult to biodegrade (biodegration is the chemical dissolution of materials by bacteria or other biological means). They are adsorbed readily onto sludge particles in wastewater treatment plants (Mastandrea *et al.,* 2005) and adhere chemically to the organic matter of soil and sediments rather than staying in the solution (Zhu *et al.,* 2008). PAHs may exhibit a wide range of hazardous effects on aquatic organisms, including acute toxicity, developmental and reproductive toxicity, photo-induced toxicity, mutagenicity and carcinogenicity (Ditoro et al., 2000)

Sediment associated PAHs are known to exhibit narcotic effects in benthic organisms, (Barron *et al.,* 2004) and also have been implicated in the development of tumors in bottom feeding fish and in the induction of malformations, (as well as in loss of fertility and immune deficiency in many organisms, including oysters(Reynaud and Deschaux, 2006) which, when contaminated, can in turn be the cause of lung cancer in humans (Law *et al.,* 2002) Because of these known and potential risks, PAHs have been classified as priority pollutants by both the U.S. Environmental Protection Agency and the European Community (Zhou *et al.,* 1998). The objective of this study was to evaluate the concentration levels of PAHs in water samples collected from Asa and Oyun River, Ilorin using GC-MS Gas chromatographic techniques.

Asa River is situated outside Ilorin, Kwara Sate capital city; this river was constructed by Julius Berger PLC in order to increase the supply of water to the town and state. Asa river dam consist of three sections: a 400 m long earth fill dam, a 150 m long concrete gravity dam and a lateral earth dam with a length of 160 m. The earth fill dam is 26 m high above the lowest level of Asa River with width of 150 m at the dam foot and 5m at the crest. It supplies the bulk of water used by people in Ilorin and its environ for different activities depending on the point of contact. To some it is used for laundry and recreation, for some industries it supplies cooling water and the river to others is a convenient point of waste discharge from both the home and industries. It is however this same water that was dammed at some point, treated and distributed to serve the domestic needs of the people.

The reconstruction of historical inputs of manmade chemicals is important for improving management strategies and evaluating the success of recent pollution control measures (Santschi *et al.,* 2000). Contaminants such as hydrocarbons' heavy metals and pesticides have been known to have direct toxic effects when released into the aquatic environment the sediments constitute the sink for these pollutants (Forstner *et al.,* 1998). Populations and communities in nature may be directly or indirectly affected by exposure to pollutants.Oyun Reservoir is located at Offa, Kwara State, Nigeria on longitude 08°30' N and latitude 08°15' E. It’s a dam reservoir on Oyun River, created to supply portable water for domestic and industrial uses to an estimated population of about 300,000 people. Subsistence and commercial fishing activities are also carried out on the reservoir.

The two rivers “Oyun and Asa River” are sources of water in Ilorin, Kwara state. These rivers have been used to sustain human leaving such as improvement of water supply in Ilorin and other settlements along the river system as well as irrigation, fisheries and livestock development and recreation. The runoff of nitrate and phosphate into rivers fertilizes them and causes accelerated eutrophication of the waters resulting in the growth of algae or aquatic weeds on the surface of the river. When ingested, nitrates are converted into nitrite in the intestine, which then combines with hemoglobin to form methemoglobin. Methemoglobin has a reduced oxygen-carrying capacity and is particularly problematic in children who are most readily affected by this "nitrite poisoning" or "blue baby syndrome."

MATERIALS AND METHODS

Sample collection and preparation

Samples were collected at particular period of time from three designated points of both Oyun and Asa River in Kwara State. Three samples of water were collected at each sampling point for both rivers and were taken immediately to the laboratory for analysis. Water samples (2.5 L) were collected in glass bottles at the water surface and 50 cm below water level from three different locations of the site. The bottles were covered with screw caps and were immediately transported on ice chest to the laboratory. In the laboratory, the samples was preserved and refrigerated at -4^{o}C prior to further analysis.

Experimental Procedure

The organic extraction was carried out using liquid-liquid extraction (LLE), the total amount of each surface water sample (400 ml) was filtered with Whatman filter paper (i.d. 70 mm) to remove debris and suspended materials and then poured into a 500 ml separatory funnel. For the first LLE, the mixture of 50 ml n-hexane and dichloromethane (1:1 v/v) was added and shaken vigorously for 2 min before two phase separation. The water-phase was drained from the separatory funnel into a 500 ml beaker. The organic-phase was carefully poured into a glass funnel containing 10 g of anhydrous sodium sulfate. Following the second and third LLE, the water-phase was poured back into the separatory funnel to re-extract with 25 ml of the same solvent mixture. The extract was concentrated to the volume of 2 ml under a gentle stream of nitrogen using rotary evaporator and the final extract was then analyzed with Gas Chromatograph-Mass spectrometry (Siriwong *et al.*, 2009)**.**

RESULTS AND DISCUSSION

The concentration of the 52 hydrocarbons that were detected in surface water of Oyun and Asa River are shown in Table 1. In terms of individual hydrocarbon composition in water, most compounds analyzed were detected at all location sites of Oyun and Asa (3 points from river each). Table 1 below shows that the result of the entire hydrocarbons in the samples which in one way or the other have been classified as contaminants.

The highest concentration was found for (Z)-9-octadecanoic acid in Asa river and (Z, Z)-9, 12-octadecanoic acids in Oyun river and for which %compositions were 1.95% and 1.91% respectively (Table 1). Compounds such as 3-Methylhexane, 1, 3-Dimethylcyclopentane, dodecanoic acid were found in all locations of the two rivers. 3-Methylhexane, 1, 3-Dimethylcyclopentane, heptane, dodecanoic acid were found in all the three locations of Asa River while 3-Methylhexane, 1,3-Dimethylcyclopentane, toluene, 1,2,3,4,5,6,8 alpha-hexahydro-1-isopropyl-4,7 dimethylnaphthalene, dodecanoic acid were found to be present in all locations of Oyun River. Comparison of these results with what was earlier obtained in the previous studies carried out by Obiakor et al. (2014). The concentrations recorded for Naphthalene for example were measured at ng/L and its ranges from 0.027 ±0.024 ng/L -0.085± 0.055 ng/L for seasons and ND - 0.085±-0.035 ng/L for locations (Obiakor et al. 2014), respectively. This indicates that the results obtained in this study are in agreement with what Obiakor et al. (2014) findings.

The following compounds were found to have low concentrations: ethylcyclopentane, 4methyl-3-pentanal, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, methoxybenzenemethanamine, 1,7,7-trimethylbicyclo[2.2.1]heptan-2-one,cyclododecane,(Z)-2-dodecene,5-methyloctadecane,1-tetradecene, 8-isopropyl-1,3-dimethyltricyclo[4,4,0, 0(2,7)]dec-3-ene, 1,3-dimethylnaphthalene, 1,6-dimethylnaphthalene, 2,6-di-t-butyl-4-methylphenol, 1,2,4-alpha,5,6,8-alpha-hexanhydro-1-isopropyl-4,7-dimethylnaphthalene, tetradecene, 1, 3, 5-cycloheptatatriene, nonan-1-ol, hexacosan-1-ol which were found to have %composition of < 0.1% in Asa River. 4-methyl-3-pentenal, cyclododecane, 1-octadecene, 1-nonadecene, 3-methyl-1-hexane, 2,6,6-trimethylbicyclo[3.1.1]heptan-3-one, trans-1,3-dimetylcyclopentane, (E)-3-heptene, 4-methyldodecane, 1-tridecene, cyclononanone, 1, 1-dimethylcyclopentane, cis-1,2-dimethylcyclopentane, tran1,2-dimethylcyclopentane, 3,3,4-trimethylhexane, 2-butyloctan-1-ol, dicyclohexylmethane, pentylether, 1-docosene, (IR)-6,6-dimethylbicyclo[3.1.1]heptan-2-one were also well found to have %composition of < 0.1% which signifies a low concentration in water. Amongst all these, the compound of utmost concern is the polycyclic aromatic hydrocarbons or polynuclear aromatic hydrocarbon (PAHs) that are present in the river. In a similar research carried out by Kabzinski *et al.* (2002), the concentrations of benzo [a] pyrene and other PAHs in water at Brzustowka river and Sulejow artificial lake was high compared to the PAH concentrations recorded in this study. The results obtained in this study when compared with some international guidelines for PAHs in fresh water (Environmental Canada, 1993; WHO, 1984 and WHO, 1998). Therefore, the results obtained were not too high when compared with the acceptable limits in the guidelines (Table 2).

From Table 2 above, 1,3-dimethylnaphthalene was found only to be present in first bank location ($S.F_2$) of Asa river and it has 0.01% composition, 1,6-dimethylnaphthalene has %composition of 0.01% and it was also present only in first bank location ($S.F_2$) of Asa river, 1,2,4α, 5,6,8 α-Hexahydro-1-Isopropyl-4,7-dimethylnaphthalene is found in first bank location of Asa river and has %composition of 0.01%, this has the same %composition with 1,3-dimethylnaphthalene and they are both found only in the location ($S.F_2$), 1,2,3,5,6,8 α-Hexahydro-1-Isopropyl-4,7-dimethylnaphthalene is found to be present in two locations of Asa river and also in all the three locations of Oyun river: it has 0.31%composition (0.28 % in $S.F_2$ and 0.03 % in S.P) in Asa river. For the composition of the sample present in Oyun River, as a result, it is said to have 0.07 % (0.02, 0.03 and 0.02 respectively) composition of the compound present in the river.

CONCLUSION

The present study has shown that both the Asa River and Oyun River water are contaminated. The major sources of contamination can be traced to, industrial discharges, domestic waste disposal and application of agrochemicals on farmlands. From the study, we see that the Asa River has higher level of contamination compared to the Oyun River. This study has also shown the usefulness of gas chromatography-mass spectrometry in the monitoring of hydrocarbon contaminants in water as evidenced from the detection of polycyclic aromatic hydrocarbons such as naphthalene. It is therefore recommended that, the two rivers should be put under surveillance, being the only source of fresh water in this area.

TABLE 1: %Composition of Hydrocarbon Detected in Surface Water of Oyun and Asa River

COMPOUND	RI (KOVATS)	Mm/w	PERCENTAGE COMPOSITION (% composition)						MASS SPECTRA
			ASA RIVER			**OYUN RIVER**			
			S.F_2	**S.C**	**S.P**	**S.A**	**S.S**	**S.U**	
3-Methyhexane	671	100.2	0.20	0.18	0.18	0.16	0.16	0.20	43,56,57,70
3-Methyl-1-hexane	649	98.19			0.03			0.03	41,55,56,69
2,3,3-Trimethyl-1-butene	634	98.19	0.05						41,55,83
3,3,4-Trimethylhexane	851	128.26					0.01		41,43,57,71
1,3-Dimethylcyclopentane	682	98.19	0.03	0.03	0.01	0.03	0.02	0.03	41,55,56,70
1,1-Dimethylcyclopentane	683	98.19					0.04		41,55,56,69
Cis-1,2-Dimethylcyclopentane	723	98.19					0.01		39,41,56,70
Cis-1,3-Dimethylcyclopentane	688	98.19	0.04		0.03				41,55,56,70
trans-1,2-Dimethylcyclopentane	691	98.19					0.01	0.01	41,55,56,70
trans-1,3-Dimethylcyclopentane	685	98.19				0.01		0.01	41,55,56,70
Ethyl Cyclopentane	733	98.19	0.01						41,68,69,70
Heptane	700	100.2	0.01	0.01	0.01				41,43,57,71
4-Methyl-3-pentanal	942	98.14	0.02			0.01			41,69,83,98
Toluene	770	92.14	0.36		0.09	0.2	0.10	0.11	39,65,91,92
1,2,3-Trimethylbenzene	996	120.19	0.01						71,91,105,120
1,2,4-Trimethylbenzene	1023	120.19	0.01						28,77,105,120
4-methoxybenzenemethanam	1233	137.18	0.01						77,106,121,136

ine									
1,7,7-Trimethylbicyclo [2.2.1]-heptan-2-one(camphor)	1143	152.23	0.01						41,55,81,95
Cyclododecane	1242	168.32	0.01				0.01		41,55,69,83
DodecanoicAcid	1568	200.32	0.11	0.06	0.06	0.08	0.07	0.06	43,57,60,73
(Z)-2-Dodecene	1213	168.32	0.01						41,43,55,69
5-Methyloctadecane	1845	268.52	0.01						43,57,71,85
1-Tetradecene	1392	196.37	0.03						41,43,55,70
Tetradecene	1399	196.39	0.01						43,57,71,85
Tetradecanoic Acid	1720	228.37	0.08		0.04	0.05	0.03	0.04	43,57,60,73
8-Isopropyl-1,3-dimethyl-tricyclo[4,4,0,0(2,7)] dec-3-ene	1376	204.35	0.03	0.01					93,105,119,161
1,3-dimethylnaphthalene	1940	156.22	0.01						115,128,141,156
1,6-dimethylnaphthalene	1419	156.22	0.01						77,115,141,156
1-Isopropyl-6-methyl-3-(propan-2-ylidene)-6-vinylcyclohex-1-ene		204.35	0.07						41,105,119,161
2,6-di-t-Butyl-4-methylphenol	1512	220.35	0.01						57,145,205,220
1,2,4alpha,5,6,8alpha-Hexahydro-1-Isopropyl-4,7-dimethylnaphthalene	1499	204.35	0.01						93,105,161,204
1,2,3,5,6,8alpha-Hexahydro-1-Isopropyl-	1524	204.35	0.28		0.03	0.02	0.03	0.02	105,119,134,161

4,7-dimethylnaphthalene									
1-hexadecene	1593	224.43	0.07						43,55,69,83
Hexadecanoic Acid	1984	256.42	0.54			0.14	0.11		43,57,60,73
1-octadecene	1793	252.48	0.08				0.05		43,55,69,83
1-Nonadecene	1895	266.5	0.10				0.03		43,57,83,97
(Z)-9-octadecenoic acid	2161	282.47	2.39				1.83		41,55,69.83
1,3,5-cycloheptatriene	800	92.14		0.05					39,65,91,92
Nonan-1-ol	1171	144.26		0.01					41,43,56,70
1-Eicosene	1994	280.53		0.70	0.67		0.66	0.01	57,69,83,97
(Z,Z)-9,12-octadecadienoic acid	2173	280.45			1.95	1.91			55,67,81,95
Hexacosan-1-ol	2950	382.71			0.03				43,57,83,97
2,6,6-Trimethybicyclo[3.1.1] heptan-3-one	1173	152.23				0.04			41,55,69,80
(E)-3-Heptene	714	98.19				0.01			41,55,56,69
4-methyldodecane	1259	184.36				0.01			43,57,71,85
1-Tridecene	1292	182.35				0.02			41,43,55,57
Cyclononanone	1230	140.22				0.03			41,55,83,98
Octadecanoic acid	3181	284.48				0.68		0.71	29,43,60,73
2-Butyloctan-1-ol	1848	186.33					0.01		43,55,57,83
Dicyclohexyl methane	1385	180.33					0.01		41,55,67,83
Pentyl ether	1070	158.28						0.01	29,43,55,71
(IR)-6,6-Dimethylbicyclo[3.1.1] heptan-2-one	1137	138.21						0.01	55,81,83,95
1-Docosene	2195	308.59						0.01	43,57,83,97

Table 2: %Composition of Polycyclic Aromatic Hydrocarbon Present in Water Sample

COMPOUND	RI (KOVATS)	MM/ W	PERCENTAGE COMPOSITION						MASS SPECTRA
			ASA RIVER			**OYUN RIVER**			
			S.F$_2$	**S.C**	**S.P**	**S.A**	**S.S**	**S.U**	
1,3-dimethylnaphthalene	1940	156.22	0.01						115,128,141,156
1,6-dimethylnaphthalene	1419	156.22	0.01						77,115,141,156
1,2,4alpha,5,6,8alpha-Hexahydro-1-Isopropyl-4,7-dimethylnaphthalene	1499	204.35	0.01						93,105,161,204
1,2,3,5,6,8alpha-Hexahydro-1-Isopropyl-4,7-dimethylnaphthalene	1524	204.35	0.28		0.03	0.02	0.03	0.02	105,119,134,161

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