

Distribution and Source of Polycyclic Aromatic Hydrocarbons in Water and Sediments from Egbe Dam in Southwestern Nigeria

Ibigbami OA*, Asaolu SS, Popoola OK, Adefemi SO, Abodunde TS, Idowu K, Olatoye RO

Department of Chemistry, Ekiti State University, PMB 5363 Ado-Ekiti, Nigeria

ABSTRACT

Egbe dam is capable of supplying potable water to the whole Ekiti State. The need for water quality is not just to protect the public health but also to support the economy and maintain a rich ecosystem. The aim of this study was to assess the level of polycyclic aromatic hydrocarbons (PAHs) in surface water and sediments of Egbe dam and also to investigate their sources using profiles and ratios. A gas chromatography (GC) coupled with flame ionization detector (FID) was used for PAHs identification and quantification after careful extraction and clean-up. The results showed the presence of the studied PAHs except naphthalene with mean concentration range of 0.009 mg/L (fluorene)-1.08 mg/L (benzo(a)pyrene) and 0.071 mg/Kg (phenanthrene)-1.37 mg/Kg (benzo(a)anthracene) in water and sediments respectively. The coefficient of variation revealed high spatial variation in the PAHs distribution level with the predominance of high molecular PAHs. The results reflected high percentage (91.6%) levels of HMW-PAHs as compared to LMW-PAHs. Some samples exceeded the compared PAHs international standard guidelines for groundwater and drinking water. Sources identification showed that the PAHs are pyrogenic. The detectable amounts of PAHs in the dam make it inevitable to conduct regular monitoring so as to ensure that the levels remain below prescribed limits by national and international standards.

Keywords: Polycyclic aromatic hydrocarbons; Surface water; Sediments; Gas chromatography; Pyrogenic; Petrogenic

INTRODUCTION

The term Polycyclic Aromatic Hydrocarbons (PAHs) refer to a ubiquitous group [1,2] of several hundred chemically-related, environmentally persistent organic compounds of various structures and varied toxicity. The major source of PAHs is the incomplete combustion of organic material such as coal, oil and wood. Pyrogenic, petrogenic, and biological are the three major types of PAH sources to the environment. The destructive distillation of coal into coke and coal tar, or the thermal cracking of petroleum residuals into lighter hydrocarbons are pyrolytic processes. Incomplete combustion of motor fuels, wood in forest fires and fireplaces, and fuel oils in heating systems are pyrogenic. PAHs formed during crude oil maturation and similar processes are called petrogens. Other sources of petrogenic PAHs include incomplete combustion of organic substances and PAHs found in petroleum products.

Sixteen (16) PAHs have been identified as priority pollutants by both the US Environment Protection Agency (USEPA) and the European Union [3]. Generally, the presence of PAHs in the environment has increased over the last 100 years; however, global concentrations may have been stabilized due to recent air and water quality regulations [4]. The PAH composition within the sediments reflects the source(s) from which the PAHs were derived. Larger concentrations of lower molecular weight PAHs (e.g. acenaphthene and fluorene) most often occur in sample matrices contaminated with naturally occurring (petrogenic) PAHs. PAHs originating from combustion (pyrolytic) sources often contain elevated concentrations of higher molecular weight and higher member-ring PAHs (e.g. phenanthrene, fluoranthene, and pyrene) and fewer low molecular weight PAHs [5].

In general, PAHs are lipophilic compounds with a high affinity for organic matter. But, the physicochemical properties of the

Correspondence to : Dr Olayinka A Ibigbami, Department of Chemistry, Ekiti State University, PMB 5363 Ado-Ekiti, Nigeria, E-mail: olayinkaibigbami@yahoo.co.uk

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PAHs vary greatly from each other. Low molecular weight PAHs are much more water-soluble and volatile than their high molecular weight counterparts, whereas the latter show higher hydrophobicity than the former [6]. Soil and sediments are good environmental compartments to record the historical environmental burden of these compounds [7]. However, very little information is available on PAHs levels, accumulation and sources in most Nigerian rivers, particularly dams which are one of the major sources of water to an average Nigerian. Therefore, the study is aimed at assessing the levels of Polycyclic Aromatic Hydrocarbons (PAHs) in surface water and sediments of Egbe dam and also to investigate their sources using profiles and ratios.

MATERIALS AND METHODS

Study area

The study location was Egbe dam in Gbonyin Local Government Area of Ekiti, southwestern Nigeria. The dam was constructed on Ose river at Egbe-Ekiti (N:7°36', E:5°36'). The capacity of the reservoir is above 144 millions in cubic meters. The dam is located at undulating plane surrounded by highlands from which runoff also feed the reservoir during rainy season. The dam supplies water to several towns and communities within the area. Fishing and irrigation systems are practiced on the river.

Sample collection and preparation

Water samples were taken at three different locations along the course of the dam by grab method. The samples were stored in pre-cleaned glass bottles and were immediately transported to the laboratory for analysis. Sediment samples were taken from the same locations using pre-cleaned Ekman grab Sampler at a depth of 5 cm and then taken into glass bottles and labeled. The sediment samples were air-dried, ground, sieved through size 2 mm mesh and stored in glass sample bottles prior to subsequent analyses.

Sample extraction and clean-up

Extraction of PAHs in the water samples: Method 3510 as described by USEPA [8] was used to extract the PAHs from the water samples. Fifty milliliter (50 mL) of dichloromethane (DCM) was measured into a separating funnel containing 100 mL of the water sample and shaken vigorously for about 2 minutes. The mixture was allowed to settle for 30 minutes to ensure separation of the phases. After separation on standing, the aqueous layer was removed, while the organic layer was filtered into a 250 cm³ conical flask through anhydrous sodium sulphate (Na₂SO₄) salt that has been prewashed with DCM. The extraction was repeated twice using a 50 mL portion of dichloromethane and all extracts were combined. The combined organic extract was concentrated to 5 mL using a rotary evaporator at 45°C. Normal hexane (5 mL) was added to the extract in DCM to exchange the solvent and later concentrated to 2 mL in a rotary evaporator at 40°C. The extracts were transferred into 2 mL GC vials for GC analysis.

Extraction of PAHs from the sediment samples: PAHs from the sediments were extracted using Soxhlet extraction. A 20 g homogenized sample was weighed into Whatman soxhlet cellulose thimble. About 1:w/w anhydrous sodium sulphate was mixed with the sediment in order to improve Soxhlet extraction by water removal. Samples were extracted with n-hexane:dichloromethane (4:1) for 16 hours and concentrated to 2 mL using vacuum rotary evaporator [9].

Clean-up: The clean-up involved the use of a column packed with activated silica gel and anhydrous Na₂SO₄. Saturated aliphatic hydrocarbons were eluted with 20 mL of n-hexane and the aromatic hydrocarbons were eluted with 30 mL of a mixture of dichloromethane and n-hexane (2:1). The volume of the eluted fraction was reduced to 2 mL. Fraction was transferred into GC vials for subsequent injections into the GC equipped with a flame ionization detector (GC-FID).

Gas chromatographic conditions

The gas chromatographic conditions for the analysis were as follows: GC model: Agilent 7890A, Auto sampler; the carrier gas: helium; make-up: nitrogen; inlet temperature: 270°C; column type: HP5; column dimension: (30 m × 320 μm × 0.25 μm); oven program: initial temperature at 60°C for 1 minute, first ramping at 12°C for 15 minutes (210°C); maintained for 2 minutes; second ramping at 8°C for 8 minutes (320°C); maintained for 5 minutes; detector: Flame Ionization Detector (FID); detector temperature: 325°C; ignition gases: hydrogen and compressed air; The total run time was 32.25 minutes.

Determination of Limit of Detection (LOD) and Limit of Quantification (LOQ)

The internal standard calibration was obtained by using the three standard solutions with concentrations ranging between 0.2 and 10 mg/L and blank. The linear calibration curves were obtained in the tested concentration of polycyclic aromatic hydrocarbons. The limit of detection (LOD) was based on a signal to noise ratio of 3 and Limit of Quantification (LOQ) was based on the signal to noise ratio of 10 as shown in Table 1.

Determination of correlation coefficients

Correlation coefficients were determined for all the parameters. Correlation coefficients whose values were less than 0.95 were rejected but correlation coefficient values greater than 0.95 were accepted. PAHs correlation coefficient values ranged from 0.99925 and 0.99987. These made the results acceptable because it met the quality assurance standard.

Table 1: Limits of detection (LOD) and quantification (LOQ) (mg/L) for the determination of polycyclic aromatic hydrocarbons (PAHs).

PAH	LOD	LOQ
Naphthalene	0.0000015	0.0000023
Acenaphthylene	0.0000025	0.0000034
Acenaphthalene	0.0000021	0.0000030

Fluorene	0.0000017	0.0000026
Phenanthrene	0.0000032	0.0000041
Anthracene	0.0000052	0.0000084
Fluoranthene	0.0000063	0.0000091
Pyrene	0.0000049	0.0000075
Benzo(a)anthracene	0.0000044	0.0000069
Chrysene	0.0000036	0.0000042
Benzo(b)fluoranthene	0.0000039	0.0000066
Benzo(k)fluoranthene	0.0000022	0.0000033
Benzo(a)pyrene	0.0000039	0.0000052
Indeno (1, 2, 3, cd)pyrene	0.0000028	0.0000036
Dibenzo(a)anthracene	0.0000011	0.0000014
Benzo(g, h, i)perylene	0.0000012	0.0000014

RESULTS AND DISCUSSION

The concentrations of PAHs in the water samples are presented in Table 2. Also depicted are total PAHs, sum of carcinogenic and non-carcinogenic PAHs, low and high molecular weight PAHs. The PAHs concentration in the water samples ranged from ND-3.12 mg/L, with average concentration of $0.017 \pm$

0.015 (phenanthrene) to 1.08 ± 1.77 mg/L (benzo(a)pyrene). The total PAHs in the water samples ranged from 0.299-10.0 mg/L with average concentration of 3.63 ± 5.52 mg/L. The sum of the non-carcinogenic PAHs ranged from 0.111-16.3 mg/L, while the carcinogenic PAHs ranged from 0.188-8.37 mg/L. The low molecular weight PAHs ranged from 0.018-0.297 mg/L, while the high molecular PAHs were between 0.281-9.70 mg/L.

The PAHs distribution showed high spatial variation as revealed by coefficient of variation (87.1%-173%). In terms of individual PAHs composition, the entire compound except naphthalene and acenaphthylene were detected in the water samples. It was observed that the high molecular weight PAHs composition were more predominant than the low molecular weight ones. The study reflected high percentage (91.6) levels of HMW-PAHs as compared to LMW-PAHs. The mean concentration of the water exceeded the 16 EPA-PAHs and 4 EU-PAHs guidelines [10] for groundwater and drinking water. The TPAHs (0.299-10 mg/L) were higher than PAHs concentrations in water samples from rivers and estuaries, such as 21.7-138 ng/L in the Xijiang river, a major tributary of the Pearl river, South China [11], 12-130 ng/L in the Susquehanna river, the main tributary of the Chesapeake Bay, USA [12] and 12-430 ng/L in the lower Mississippi River, USA [13].

The PAHs concentrations in the sediment samples are shown in Table 3. The distributions showed predominance of high molecular weight compounds. The PAHs concentration in the sediment samples ranged from ND-2.84 mg/Kg, with mean concentration of 0.071 ± 0.124 (phenanthrene) to 1.37 ± 1.30 mg/Kg (benzo(a)anthracene).

Table 2: Concentration (mg/L) of PAHs in the water samples from Egbe dam.

PAH	W1	W2	W3	Mean	SD	CV%
Naphthalene+	ND	ND	ND	-	-	-
2 methyl naphthalene+	0.018	0.017	ND	0.545	0.063	140
Acenaphthylene+	ND	ND	ND	-	-	-
Fluorene+	ND	0.026	ND	0.009	0.015	173
Anthracene+	ND	0.127	0.033	0.053	0.066	124
Phenanthrene+	ND	0.027	0.024	0.017	0.015	87.1
Fluoranthene*	0.028	0.309	0.039	0.125	0.16	127
Pyrene*	ND	0.084	ND	0.028	0.049	173
Benzo(a) anthracene**	0.059	0.839	0.059	0.319	0.45	141
Chrysene**	ND	0.51	0.093	0.201	0.272	135
Benzo(b)fluoranthene**	0.064	0.489	0.047	0.2	0.25	125
Benzo(k)fluoranthene**	ND	0.485	ND	0.162	0.28	173

Benzo(a)pyrene**	0.065	3.12	0.044	1.08	1.77	164
Indeno(1,2,3-cd)pyrene**	ND	1.06	ND	0.353	0.612	173
Dibenzo(a,h)anthracene**	ND	1.87	ND	0.623	1.08	173
Benzo(g,h,i)perylene*	0.065	0.936	0.238	0.413	0.461	112
TPAHs	0.299	10	0.577	3.63	5.52	15.2
∑7C-PAHS	0.188	8.37	0.243	2.93	4.71	160
∑NC-PAHS	0.111	1.63	0.334	0.692	0.82	119
∑LMW-PAHS	0.018	0.297	0.057	0.124	0.151	122
∑HMW-PAHS	0.281	9.7	0.52	3.5	5.37	153
LMW-PAHS/HMW-PAHS	0.064	0.031	0.11	0.068	0.04	58.1
BaA/(BaA+Chry)	1	0.622	0.388	0.67	0.309	46.1
Phe/Ant	-	0.213	0.727	0.313	0.374	119
Flt/Pyr	-	3.68	-	1.23	2.12	172

SD=Standard Deviation; CV=Coefficient of Variation; +=PAHs classified as low molecular weight PAHs; *=high molecular weight and non-carcinogenic PAHs; **=high molecular weight and carcinogenic PAHs; ∑7c-PAHs=sum of seven carcinogenic PAHs; ∑NC-PAHs=sum of non-carcinogenic PAHs; ∑LMW-PAHs=sum of low molecular weight PAHs; ∑HMW-PAHs=sum of high molecular weight PAHs; BaA=benzo(a)anthracene; Chry=chrysene; Phe=phenanthrene; Ant=anthracene; Flt=Fluoranthene; Pyr=pyrene

The carcinogenic PAHs ranged 2.65-7.27 mg/Kg, with total average concentration of 4.94 ± 2.31 mg/Kg, while the non-carcinogenic PAHs ranged from 2.31-6.98 mg/Kg with average concentration of 4.04 ± 2.5 mg/Kg. The sum of low molecular weight PAHs ranged from 0.018-0.297 mg/Kg, while the high molecular PAHs ranged from 0.251-9.70 mg/Kg. The PAHs distributions were dominated by parent PAHs, with a predominance of high molecular weight compounds. The

distributions were remarkably similar despite the variability of PAHs level. The PAHs distribution were dominated by fluoranthene, benzo(a)anthracene, pyrene, chrysene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene. The concentration of potentially carcinogenic PAHs were high (55.04%) in proportion. This confirms previous findings that high ring PAHs are usually absorbed into sediment [14,15].

Table 3: Concentration (mg/Kg) of PAHs in the sediment samples from Egbe dam.

PAH	W1	W2	W3	Mean	SD	CV%
Naphthalene+	ND	ND	ND	-	-	-
2 methylnaphthalene+	0.121	0.218	ND	0.113	0.109	96.7
Acenaphthylene+	0.179	0.216	ND	0.152	0.14	92.3
Fluorene+	ND	0.338	ND	0.113	0.195	173
Anthracene+	ND	0.567	0.39	0.319	0.29	90.9
Phenanthrene+	ND	0.214	ND	0.071	0.124	173
Fluoranthene*	0.259	2.48	0.911	1.217	1.14	93.8
Pyrene*	0.274	2.26	ND	0.845	1.23	146

Benzo(a)anthracene**	0.809	1.52	0.189	0.839	0.666	79.4
Chrysene**	0.359	2.84	1.42	1.37	1.3	95.1
Benzo(b)fluoranthene**	0.196	0.189	1.46	0.615	0.732	119
Benzo(k)fluoranthene**	0.164	0.18	0.248	1.197	0.045	22.6
Benzo(a)pyrene**	ND	0.466	0.934	0.467	0.967	100
Indeno(1,2,3-cd)pyrene**	ND	1.18	0.776	0.652	0.599	92
Dibenzo(a,h)anthracene**	1.12	0.891	0.393	0.801	0.372	46.4
Benzo(g,h,i)perylene*	1.48	0.622	1.53	1.211	0.51	92.2
TPAHs	4.96	14.2	7.74	8.98	4.76	53
\sum 7C-PAHS	2.65	7.27	4.91	4.94	2.31	46.7
\sum NC-PAHS	2.31	6.98	2.83	4.04	2.56	63.4
\sum LMW-PAHs	0.309	1.61	0.39	0.767	0.732	95.4
\sum HMW-PAHs	4.66	12.6	7.35	8.2	4.04	49.2
LMW-PAHs/HMW-PAHs	0.064	0.128	0.053	0.817	0.047	49.6
BaA/(BaA+Chry)	0.307	0.651	0.882	0.613	0.289	47.2
Phe/Ant	-	0.377	-	0.125	0.218	174
Flt/Pyr	0.945	1.1	-	0.682	0.595	87.2

SD=Standard Deviation; CV=Coefficient of Variation; +=PAHs classified as low molecular weight PAHs; *=high molecular weight and non-carcinogenic PAHs; **=high molecular weight and carcinogenic PAHs; \sum 7c-PAHs=sum of seven carcinogenic PAHs; \sum NC-PAHs=sum of non-carcinogenic PAHs; \sum LMW-PAHs=sum of low molecular weight PAHs; \sum HMW-PAHs=sum of high molecular weight PAHs; BaA=benzo(a)anthracene; Chry=chrysene; Phe=phenanthrene; Ant=anthracene; Flt=Fluoranthene; Pyr=pyrene

Comparatively, the total PAHs (4960-14,200 ng/g) reported in this study were within the range reported by Mai et al. [16] in Pearl river Guangdong; while the values (102.9-3419.2) reported by Guo et al. [17] for Daliao river; Yu et al. [18], 464-2621 ng/g in Lanzhou Reach Yellow river; Zhu et al. [19] 91.3-1835 ng/g in Qiantang river, Zhejiang were lower as compared with the present study.

The relative distribution of individual PAH can be used to study the sources of the PAH [18, 19]. For PAHs source in the river water and sediments, useful ratios were adopted. The BaA/(BaA+Chry) ratios for water and sediment samples were below 1.0 (i.e 0.388-1.00 and 0.307-0.882, respectively) [20]. This suggest more pyrogenic source of PAHs such that a BaA/(BaA+Chry) ratio>0.350 indicate pyrogenic combustion of fossil fuel sources, while those<0.200 has been attributed to petrogenic sources [21]. Ratios of fluoranthene to pyrene [19,22] or the low molecular weight (LMW-PAHs) to high molecular weight (HMW-PAHs) [23] are the two indexes most frequently used to assess the origin of PAHs. This is because concentrations of pyrene are much higher in the fossil fuels and their byproducts than fluoranthene concentration [24] and the petrogenic

contamination are dominated with LMW-PAHs [25-27]; while pyrolytic contamination are characterized with HMW-PAHs [28]. The ratio of LMW-PAHs/HMW-PAHs ranged from 0.031-0.110 and 0.053-0.128 for water and sediment samples respectively. The LMW-PAHs/HMW-PAHs ratios indicate that HMW-PAHs were generally predominant compared to the LMW-PAHs. The ratios of LMW-PAHs/HMW-PAHs showed <1, indicating that the sources of these PAHs are pyrogenic.

Ratios of phenanthrene to anthracene (Phe/Ant) and fluoranthene to pyrene (Flu/Pyr) have also been used [29-31]. PAHs of petrogenic origin are generally characterized by Phe/Ant value>10, while combustion processes showed Phe/Ant (<10). For fluoranthene to pyrene ratio (Flu/Pyr) values>1, and (Flu/Pyr) values<1, the sources have been attributed to pyrolytic and petrogenic sources [32]. The Phe/Ant ratio in water ranged from 0.213-0.727, while the sediment showed 0.377. The Flu/Pyr ratio in water showed 3.68, while the sediment ranged from 0.945-1.10. The results indicated by the Phe/Ant and Flu/Pyr ratios also showed that PAHs in Egbe River originate from pyrolytic sources.

CONCLUSION

The study depicts the presence of PAHs in water and sediment samples of Egbe dam. The results revealed that the high molecular weight PAHs composition were more predominant than the low molecular weight PAHs in both surface waters and sediments. The PAHs composition in the samples shared similar pattern and was dominated by 4-6 rings PAHs. Analysis of BaA/(Ba+Chry), Flu/Pyr, LMW-PAHs/HMW-PAHs and Phe/Ant suggested pyrolytic in the sample matrices. Some of the water samples exceeded the compared international standard guidelines for groundwater and drinking water which necessitate regular and continuous monitoring of the river so as to ensure safety of the water before consumption.

DECLARATION

All the principles of a good ethical research were respected.

CONSENT FOR PUBLICATION

Not applicable.

AVAILABILITY OF DATA AND MATERIAL

Not applicable.

COMPETING INTERESTS

The authors declared that they have no competing interests.

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AUTHORS' CONTRIBUTIONS

Ibigbami OA and Asaolu SS developed the study conception and design. Ibigbami OA, Abodunde TS and Popoola OK wrote the manuscripts, contributed in the analysis and interpretation of the data. Abodunde TS, Idowu K and Olatoye RO were involved in the sampling and bench work. Ibigbami OA, Asaolu SS and Adefemi SO contributed in the critical revision of the intellectual content of the manuscripts. All the authors read and approved the final manuscript.

ETHICAL CONSIDERATIONS

Not applicable.

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