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Assessment of Polycyclic Aromatic Hydrocarbons in Underground Water around the Viccinity of Balogun-Biiro Dump Site, Oke Bale, Osogbo, Nigeria

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Abstract

Well-water samples were collected from the vicinity of Balogun-biiro dump site located in Okebaale Osogbo, Osun state, Nigeria. The polycyclic aromatic hydrocarbons were determined qualitatively and quantitatively using GC-FID. The concentration of polycyclic aromatic hydrocarbons in the water samples ranged from 0.01235 µg/kg to 0.05365 µg/kg with mean concentration ranging from 0.00094 µg/kg to 0.00335 µg/kg respectively. The highest concentration of *∑16 PAHs* was recorded in S6 and it was observed that there is decline in polycyclic aromatic hydrocarbons concentrations from point of water pollution. There was a significant concentration of both the lower and higher rings polycyclic aromatic hydrocarbons in the samples. These distributions as well as various polycyclic aromatic hydrocarbons diagnostic indices calculated showed that the sources of polycyclic aromatic hydrocarbons in the samples were both petrogenic and pyrogenic. The mean concentrations of polycyclic aromatic hydrocarbons recorded in the water samples showed a little bit enhanced values than the recommended tolerable limits, which indicated some level of pollution in the water samples.

Keywords: PAHs, BOD, COD, Balogun-biiro, Dump-site

Introduction

The demand for fresh water is always there with the ever-increasing population in the world. Many millions suffer from frequent and debilitating water borne illnesses. About half of the inhabitants of developing countries in particular do not have access to safe drinking water and 73% have no sanitation, some of their wastes eventually contaminate their drinking water supply leading to a high level of suffering (Mason, 1992). The sources of water pollution vary and involve almost every significant human activity. These include mostly the dumping of domestic wastes, sewage, agricultural wastes and industrial effluents into water bodies (Collocott and Dabson, 1974, Maitera *et al.*, 2010). The wastes dumped on land are also eventually washed into water e.g. animal dung, litters, wind deposited pollutants. Pollutants, when deposited into the soil can also leach into the surrounding water aquifer thereby polluting the underground water. Every human use of water, whether for drinking, irrigation, and industrial processes or for recreation has some quality requirements in order to make it acceptable (Maitera *et al.*, 2010).

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Therefore, there is need for regular examination of organic matter present in underground water to ascertain their portability quality. The evaluation criteria can be in form of determination of some physicochemical parameters (e.g. Biochemical Oxygen Demand, BOD and Chemical Oxygen Demand, COD), and Polycyclic aromatic hydrocarbons (PAHs).

Several PAHs may induce a number of adverse effects, such as immunotoxicity, genotoxicity, carcinogenicity, and reproductive toxicity (Van Metre *et al.,* 1997, Sverdrup *et al.,* 2002). Members of this class of compounds have been identified as exhibiting toxic and hazardous properties and for this reason USEPA (U.S. Environmental Protection Agency) has included 16 PAHs on its list of priority pollutants to be monitored in water and wastes (National Research Council, 1997). PAHs are by-products from the incomplete combustion or pyrolysis of organic material. Residential heating, incineration, internal combustion engines and industrial activities, such as coke production, oil refining, aluminium production, non-ferrous metal smelting, etc., are all major sources of PAHs (Kipopoulou *et al.,* 1999; Nadal *et al.,* 2004, Li *et al.,* 2006, Sojinu *et al.,* 2010, Adedosu *et al.,* 2011). In general, PAHs are useful in providing information about the pollution status and also the source of pollution (i.e. petrogenic or pyrogenic). Molecular indices based on the ratios of individual PAH levels in sediment can be used to assess the origin of PAHs. For example, phenanthrene/anthracene (Phe/An) and fluoranthene/pyrene (Flu/Pyr) congener ratios are examples that are widely used to distinguish between PAHs from diverse origins (Guinan *et al.,* 2001, Qiao *et al.*, 2006, Sojinu *et al.,* 2010, Adedosu *et al.,* 2011).

In the present study, the quantity of BOD and COD will be determined, and also investigate PAH contamination in the area and identify possible PAH sources. This will assist in providing information about the level of pollution of the underground water in the study area.

Sampling and experimental methods

Well-water samples were collected at six different locations in the vicinity of a dumpsite located in Balogun-biiro area of Osogbo, Osun state, Nigeria. BOD was determined by weighing water sample into 200 mL capacity bottle was filled to the brim and minimized the contact with air. 1 mL of the manganite solution was added to the bottom of the bottle and followed by 1 mL of alkali-iodine-azide solution. The bottles were stoppered and shook well.

After the precipitation, 2 mL of the concentrated phosphoric acid was added to dissolve the precipitate. The released iodine was titrated with 0.025 M thiosulphate at the recorded temperature. The same procedure was repeated for the DO of day 5, the dissolved oxygen was calculated and the difference between the DO of day 1 and day 5.

BOD was calculated from DO using the following formula:

$$\text{BOD [Mg/L]} = \frac{DO_1 - DO_5 - B}{67.67}$$

Where

DO_1= the dissolved oxygen of day 1

DO_2= the dissolved oxygen of day 2

B= distilled water run blank

COD was analyzed by using the closed reflux method with spectrophotometric determination equivalent to APHA 5220D (STD Method, 1995). The sample was heated for two hours with a strong oxidizing agent, potassium dichromate. Oxidizable organic compounds react, reducing the dichromate ion ($Cr_2O_7^{2-}$) to green chromic ion (Cr^{3+}). Mercuric sulphate was added to remove chloride interferences. Spectrophotometer measurement provided essentially equivalent quantitation of the concentration of chromic ion. The result of the COD can be calculated using this formula:

$$\text{COD (Mg/L)} = (V_1 - V_2) \times N \times 800$$

Where

V_1 = volume of ferrous ammonium sulphate run down in blank experiment.

V_2 = volume of ferrous ammonium sulphate run down in test experiment.

N = normality of ferrous ammonium solution

X = volume of sample taken.

PAH was separated by weighing 200 mL of water sample and then transferred into a 1 L

separatory funnel, and 60 mL of the redistilled dichloromethane was added. The separatory funnel was shaken vigorously for about 2 minutes with periodic venting to release water vapor pressure. The organic layer was allowed to separate for 10 minutes and was recovered into the 250 mL flask. The aqueous layer was re-extracted twice with 60 mL of the extractant. The combined extract was dried by passing through the funnel containing the anhydrous sodium sulphate. The dried extract was concentrated with a steam of nitrogen gas. The soluble organic matter was separated into the aliphatic profiles and polycyclic aromatic hydrocarbon profiles by packing the glass column with activated neutral alumina. 10 mL of the treated alumina was packed into the column and cleaned properly with redistilled hexane. The extract was poured onto the alumina and was allowed to run down with the aid of the redistilled hexane to remove the aliphatic profiles into the pre-cleaned 20 mL capacity glass container. The aromatic fraction was recovered by allowing the mixture of hexane and dichloromethane in ratio 3:1 and finally removed the most polar PAH by removing with the dichloromethane into the pre-cleaned borosilicate beaker. The mixture was concentrated to 0.1 mL by stream of the nitrogen gas and subjected to gas chromatographic analysis.

The Gas chromatographic analysis was effected with a gas chromatograph HP 5890 powered with HPCHEM software with flame ionization detector (FID). The separation was effected on 30 m x 0.25 mm i.d. HP-5 fused silica column using nitrogen as carrier gas. The oven temperature started at 68 ^0C (2 min hold) followed by 21 ^0C for 16 min at 4 ^0C/min, then 15 ^0C for 4 min and 8 ^0C/min.

Results and Discussion

The Physico-chemical Parameters

The physicochemical parameters used are biochemical oxygen demand (BOD) and chemical oxygen demand (COD). BOD values ranged from 22.63 mg/L to 41.59 mg/L while the COD values ranged from 60.23 mg/L to 94.18 mg/L (Table 1). All the water samples have BOD and COD values (50 mg/L and 100 mg/L respectively) expected for unpolluted water as given by WHO (Akan, *et al.,* 2008). However, samples taken from well very close to the dumpsites have higher BOD and COD values.

Occurrence and Spatial Distribution of PAHs in the Sample

The 16 PAHs concentration and distribution in the water samples are presented in table 2; fig. 1 and the sum of which is defined as $\sum 16\ PAHs$ ranged from 0.01235 µg/kg to 0.05365 µg/kg with mean concentration ranging from 0.00094 µg/kg to 0.00335 µg/kg. The highest concentration of $\sum 16\ PAHs$ was recorded in S6 which might be as a result of waste burning from the dump site as well as used oil waste from the nearby mechanic workshop, from diffuse pollution such as wood combustion emission, coal burning stoves which are transfer to underground water by erosion and leaching. It was observed that there is decline in PAHs concentrations from point of water pollution thereby establishing the fact that the dumpsite and waste from the mechanic workshop contribute to underground water pollution in the area under study.

A marked distribution pattern of the PAHs concentration in the sample was shown in fig. 2 with predominance of 2,3,4,5, and 6 rings (Fig.2; Table 3). The 2-rings PAHs is approximately 9% of $\sum 16\ PAHs$, 3-rings PAHs approximately 24%, 4-rings PAHs accounted for 48%, 5-rings PAHs approximately 18% and 6-rings accounted for 1%. These results show that the sources of PAH are both pyrogenic and petrogenic (Sojinu *et al.,* 2010; Adedosu *et al.,* 2011). The PAHs with lower rings are tends to be strongly adsorbed and associated with the organic matter fraction in water.

PAHs source diagnostics in the soils

The source diagnostic indices are calculated from interpretative PAHs concentration and presented in table 4. The values of these ratios have been used extensively to distinguish between petrogenic and pyrogenic sources of PAHs. The phenanthrene/anthracene ratio of the water samples ranged from 0.067-0.57. The value of fluorene/pyrene ratio ranged from 0.29-7.25 in

Table 1: Values of BOD and COD in the samples

S/N	Samples	COD (mg/L)	BOD (mg/L)
1	S1	63.11	29.02
2	S2	68.28	31.52
3	S3	65.41	22.63
4	S4	82.79	33.66
5	S5	60.23	24.12
6	S6	94.18	41.59

BOD-Biochemical oxygen demand, COD-chemical oxygen demand

S1- N 07^0 46′ 21, E 004^0 34′ 21;
S2- N 07^0 46′ 22, E 004^0 34′ 19;
S3- N 07^0 46′ 22, E 004^0 34′ 17;
S4- N 07^0 46′ 20, E 004^0 34′ 20;
S5-N 07^0 46′ 20, E 004^0 34′ 19;
S6- N 07^0 46′ 20, E 004^0 34′ 19

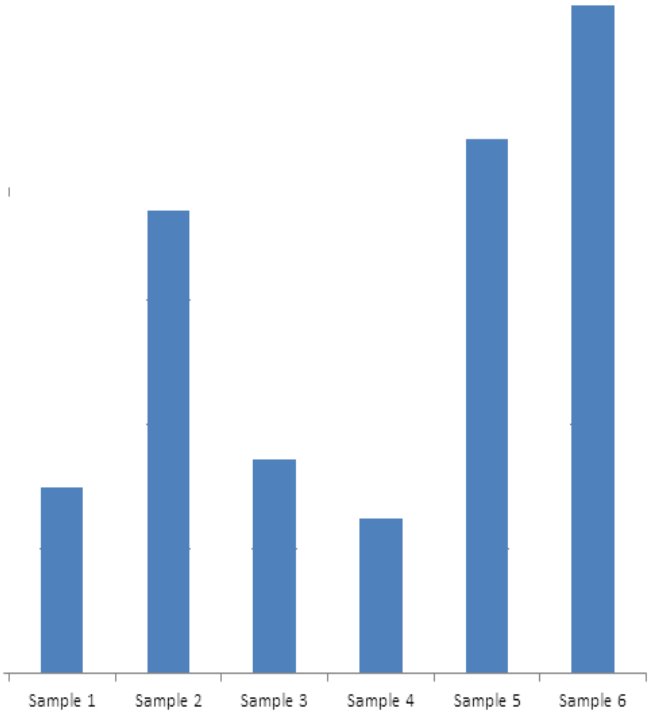

Figure 1: Total concentrations of PAHs in the samples (μg/kg)

Table 2: Occurrence and spatial distribution (μg/kg) of PAH in the samples

ABB	PAH	S1	S2	S3	S4	S5	S6
Na	Naphtalene	0.00048	0.00199	0.00396	0.00012	0.00674	0.00674
Acy	Acenaphthalene	0.00029	0.00042	0.00044	0.00002	0.00083	0.00083
Ace	Acenaphthene	0.00029	0.00021	0.00055	0.00007	0.00131	0.00131
Fl	Fluorene	0.00090	0.00002	0.00045	0.00023	0.00008	0.00022
Ph	Phenanthrene	0.00155	0.00036	0.00028	0.00124	0.00064	0.00152
An	Anthracene	0.00271	0.00540	0.00289	0.00290	0.00640	0.00827
Flu	Fluoranthrene	0.00152	0.00188	0.00207	0.00052	0.00101	0.00616
Pyr	Pyrene	0.00179	0.00067	0.00076	0.00180	0.00088	0.00085
BaA	Benzo(a)anthracene	0.00428	0.00065	0.00088	0.00025	0.00110	0.00070
Chr	Chrysene	0.00212	0.01334	0.00100	0.00044	0.02609	0.01858
Bkf	Benzo(k)fluoranthrene	0.001170	0.00899	0.00107	0.00103	0.00407	0.00490
Bbf	Benzo(b)fluoranthrene	0.003530	0.00301	0.00253	0.00372	0.00246	0.00035
Bap	Benzo(a)pyrene	0.00165	0.00009	0.00010	0.00001	0.00014	0.00100
Inp	Indo(1,2,3-cd)pyrene	0.00009	0.00007	0.00008	0.00002	0.00005	0.00008
DahA	Dibenzo(a,h)anthrazene	0.00074	0.00007	0.00009	0.000001	0.00007	0.000067
B[ghi]P	Benzo(g,h,i)perylene	0.000447	0.000008	0.000007	0.00001	0.0011	0.00012
	TOTAL	0.01503	0.03719	0.01717	0.01235	0.04298	0.05365
	MEAN	0.00094	0.002324	0.001073	0.000772	0.002686	0.003353

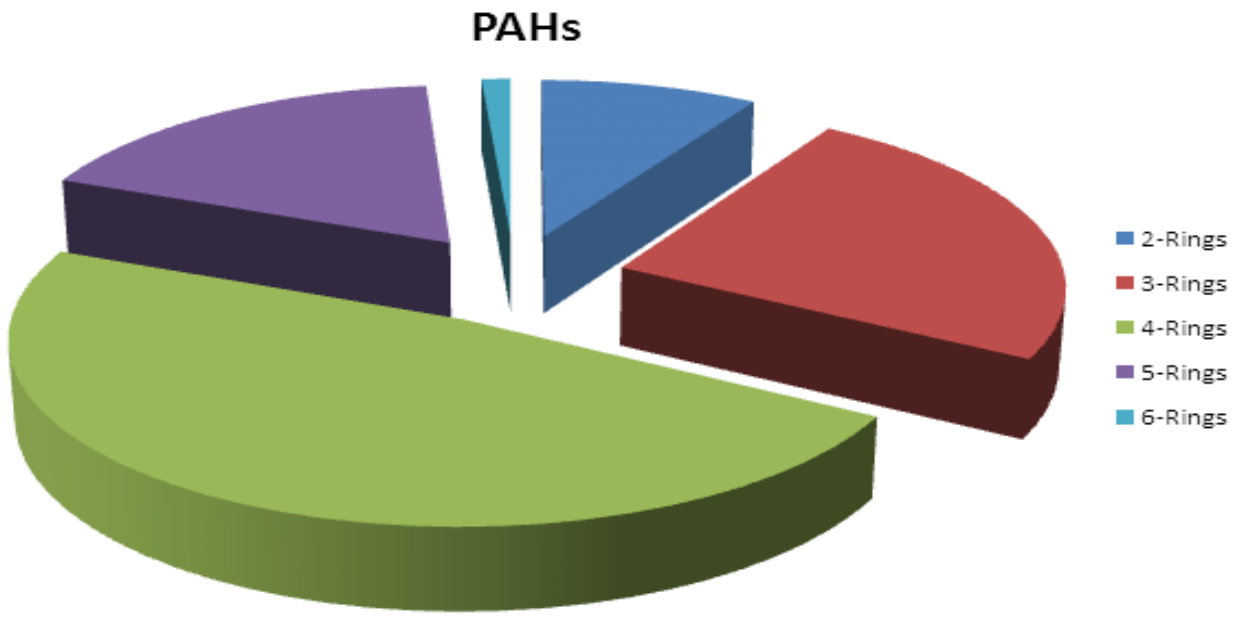

Figure 2: Spartial Distributions of PAH Based on Ring Size in the Samples

Table 3: Relative distribution pattern (μg/kg) and percentage composition of individual PAHs in the samples

Samples	1	2	3	4	5	6	∑ Total	%
2-rings	4.75091e-7	1.99319e-6	3.95692e-6	1.15820e-7	2.48119e-5	6.74046e-6	1.57627e-5	8.84
3-rings	5.74363e-6	6.41240e-6	4.61975e-6	4.44819e-6	8.16409e-6	1.41036e-5	4.34917e-5	24.38
4-rings	5.85446e-6	1.65469e-5	4.71196e-6	3.00921e-6	2.90950e-5	2.62916e-5	8.55092e-5	47.94
5-rings	1.68695e-6	1.20895e-5	3.69739e-6	4.75814e-6	3.01205e-6	6.24931e-6	3.14934e-5	17.66
6-rings	1.27375e-6	1.44284e-7	1.80185e-7	2.06973e-8	2.24281e-7	2.61758e-7	2.10495e-6	1.18
							1.78362 e-4	

Table 4: Molecular indisces of PAHs in the samples

Sample	Ph/An	Fl/pyr	Bap/Chr	Na/Ace	An/Phen+An	Fl/Fl+pyr	BaA/BaA+Chr	Inp/Inp+Bghip
S1	0.57	0.85	0.08	1.65	0.64	0.34	0.17	0.16
S2	0.067	2.79	0.0069	9.53	0.94	0.03	0.95	0.89
S3	0.09	2.71	0.09	7.16	0.91	0.37	0.47	0.92
S4	0.43	0.29	0.02	1.72	0.70	0.12	0.36	0.76
S5	0.10	1.15	0.0055	6.46	0.91	0.09	0.04	0.34
S6	0.18	7.25	0.05	5.12	0.84	0.72	0.04	0.41

S1- N 07^0 46′ 21, E 004^0 34′ 21;
S2- N 07^0 46′ 22, E 004^0 34′ 19;
S3- N 07^0 46′ 22, E 004^0 34′ 17;
S4- N 07^0 46′ 20, E 004^0 34′ 20;
S5-N 07^0 46′ 20, E 004^0 34′ 19;
S6- N 07^0 46′ 20, E 004^0 34′ 19

the samples. Benzo(a)pyrene/chrysene ratio ranged from 0.01-0.09 The value of naphathalene/acenaphthene ratio ranged from 1.65- 9.53 in the samples. The ratios of anthracene/(phenanthrene + anthracene) ratio, Fluoanthrene/(Fluoanthrene + pyrene) i.e. (Flu/202), Benzo(a)anthracene/(benzo(a)anthracene + chrysene) i.e. (BaA/202) and Indeno(1,2,3-cd) perylene/(Indeno(1,2,3cd) perlene+benzo (g,h,i) perylene) i.e. (icdp / 228) value ranged from 0.64-0.94, 0.03-0.72, 0.04-0.95 and 0.16-0.92 respectively. These ratios indicate both petrogenic and pyrogenic sources (Yunker et al., 2002, Olajire and Brack 2005, Li *et al.,* 2006, Fagbote and Olanipekun 2010, Sojinu *et al.,* 2010, Adedosu *et al.,* 2011).

The mean concentrations of PAHs recorded in the water samples (Table 5) were generally higher than the recommended tolerable limit (Canadian 2008, Netherland 2008). The relatively higher concentrations of PAHs in the samples indicated pollution of the water resulted from the anthropogenic activities due to the presence of dumpsites in the study area. The indiscriminate discharge of used engine oil at the nearby mechanic workshop might also contribute to the source of PAHs. The highest concentration of PAHs was recorded in water sample (i.e. S6) collected from well close to the dump site and mechanic workshop.

Conclusion

This work determined the concentration, distribution and potential sources of PAHs in the water samples collected from wells in the vicinity of a dumpsite and a mechanic workshop located at Balogun biiro, Oke-baale, Osogbo in Osun state. The concentration of PAHs in the water samples ranged from 0.01235 µg/kg to 0.05365 µg/kg. A very high concentration of PAHs was recorded in S5 and S6 water samples with values of 0.04298 µg/kg and 0.05365 µg/kg respectively. These samples are collected very close to the dumpsite and mechanic workshop. The distributions of lower and higher rings PAH and various diagnostic indices obtained indicated both pyrogenic and petrogenic sources. Presently the water samples taken from wells in the study area showed significant level of pollution when compared with the recommended tolerable limits.

Table 5: Comparison of the Concentration of some Selected PAHs in the Study Area with the Canadian

PAHs	Mean Concentration of PAH in the Sample (µg/kg)	[a]Mean concentration of PAH(µg/kg)	[b]Mean concentration of PAH(µg/kg)
Nap	0.00338	0.00011	NA
Ace	0.00062	0.00058	0.0012
Fl	0.00032	0.0003	0.00007
Ant	0.00476	0.000012	0.00007
Phe	0.00093	0.0004	0.0003
Flu	0.00219	0.00004	0.0003
Pyr	0.00113	0.000025	NA
Chr	0.01026	NA	0.00034
B[a]A	0.00131	0.000018	0.00001
B[a]P	0.00050	0.000015	0.00005
Bkf	0.00354	NA	0.00004
B[ghi]P	0.00028	0.000033	0.00006

[a]Canadian (2008), [b]Netherlands(2008), NA: Not Available

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