Bull. Chem. Soc. Ethiop. **2022**, 36(4), 779-789. ISSN 1011-3924
Printed in Ethiopia
Online ISSN 1726-801X
DOI: https://dx.doi.org/10.4314/bcse.v36i4.5

POLYCYCLIC AROMATIC HYDROCARBONS IN HARVESTED RAINWATER IN WARRI AND AGBARHO, NIGERIA

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(Received January 17, 2022; Revised July 4, 2022; Accepted July 5, 2022)

ABSTRACT. The aim of this research was to provide an overview of current knowledge, by assessing the possible contamination sources of harvested rainwater by polycyclic aromatic hydrocarbons (PAHs), its effects and possible human health risk assessment. Random sampling technique was used to collect eight rainwater samples from different roofing materials made from (asbestos, zinc, aluminium and thatch) in Warri and Agbarho (AGB). The samples were extracted using a liquid-liquid extraction (LLE) system according to the established procedures of United States Environmental Public Agency (USEPA). Under the optimized conditions, the ranges of extraction recoveries and solid-phase extraction (SPE) clean-up of the PAHs in the harvested rainwater were in the range of 71-90%. Gas chromatography-mass spectrometry (GC-MS) was used for the determination of the sixteen priority PAHs in the samples. The total concentration of PAHs for each of the roof types in Warri Refinery Petrochemical Company (WRPC) are: 0.036±0.012, 0.047±0.020, 0.045±0.018 and 0.0023±0.008 ppm for aluminium, zinc, asbestos and thatch roof, respectively. In addition, total concentration of PAHs for each of the roof types in AGB are: 0.046±0.020, 0.024±0.009, 0.023±0.008 and 0.021±0.007 ppm for aluminium, zinc, asbestos and thatch roof. The PAHs analysed exceeded the United States environmental protection agency (USEPA) standards of contamination.

KEY WORDS: AGB, GC-MS, Harvested Rainwater, LLE, PAHs, WRPC

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are aromatic hydrocarbons with two or more fused benzene rings in various structural configurations and do not contain heteroatom or carry substituents [1]. PAHs containing up to four rings are refer to as light PAHs and those that contain more than four rings are heavy PAHs. Heavy PAHs are more stable and more toxic than the light PAHs [2]. Polycyclic aromatic hydrocarbons (PAHs) are organic pollutants that are widely found in the environment [3]. They may be found in air attached to dust particles, soil, sediments, water and food. Most PAHs enter the environment during burning of most organic materials such as coal, oil, wood, gasoline, garbage and tobacco [4]. They are known to have carcinogenic, mutagenic and teratogenic properties [5-7]. The main sources of exposure to PAHs are from breathing PAHs (in wood smoke, traffic exhaust and other contaminated air), and from eating contaminated food and drinking contaminated water. PAHs may induce bladder, lungs, skin cancer etc. In addition, exposure to high levels of PAHs has been shown to produce immunosuppressive effects and causing oxidative stress during its metabolism [8-10]. The maximum allowable concentrations of PAHs in water and soil are not well known [11]. There is no standards exist for the amount of PAHs allowed in the air, but it is recommended that the levels should not be higher than 0.004 ppm due to its high risk effect [12]. PAHs are harmful persistent organic pollutants, while the lower-molecular-weight (HMW) PAHs are even more detrimental to the environment and human health. Common examples include: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a) pyrene, benzo(ghi)perylene

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*Corresponding author. E-mail: kenkennedy767@gmail.com dibenz(a,h)anthracene and indeno(1,2,3-cd)pyrene. Structure and names of the polycyclic aromatic hydrocarbons compounds are shown in Figure 1.

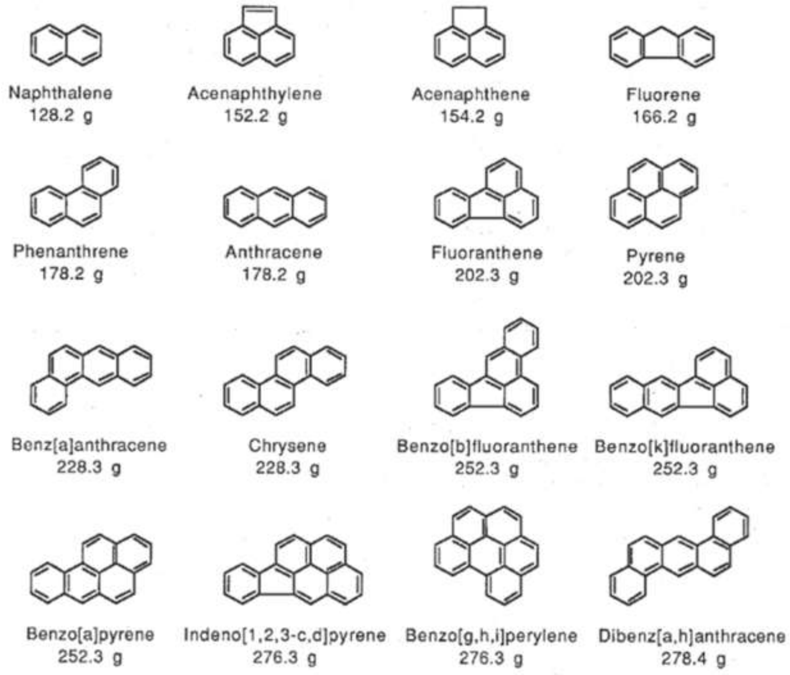

Figure 1. Structures and molecular weight of the 16 PAHs compounds [28].

PAH usually occur naturally, but they can be synthesized as individual compounds for research or other purposes. Naphthalene is the simplest example of PAHs [13]. They have a faint, pleasant odor. Few PAHs are used in medicines, dyes, pesticides and plastics [14]. The major path of exposure to PAHs in the general population is from breathing ambient indoor air, eating food-containing PAHs, smoking cigarettes, or breathing smoke from open fireplaces, from the fossil fuels that we use to drive our cars, cook our food [15-17]. Others include: cigarette smoke, exposure to industrial emissions, automobile exhausts, hazardous waste sites, jet fuel, and burn pits, and consumption of barbecued food. Human beings are also exposed to PAHs via air, water and contaminated food they ingest. Exclusive sources for benzo(a)pyrene (BaP) contamination of the environment and exposure to humans include industrial and automobile emissions, hazardous waste sites, cigarette smoke, biomass burning, waste burning, municipal incinerators, volcanic eruptions, home heating and consumption of charcoal broiled and smoked food [18-20]. PAHs exposure are known to result in symptoms such as eye irritation, nausea, vomiting depending on the level of exposure. Mixtures of PAHs are also known to cause skin irritation and inflammation. Anthracene, benzo(a)pyrene, and naphthalene are direct skin irritants while anthracene and benzo(a)pyrene are reported to be skin sensitizers, i.e. cause of an allergic skin response in humans and animals [21]. Long term exposure to PAHs is suspected to raise the risks of cell damage via gene mutation, teratogenesis and cardiopulmonary mortality [22]. Short-term exposure of PAHs on human causes eye and skin irritation, nausea, vomiting, diaorrhea, etc. Figure 2 shows the effects of long-term and short-term exposure of PAHs on humans [23]. USEPA and European Union Maximum contaminant level of PAHs is shown in Table 1.

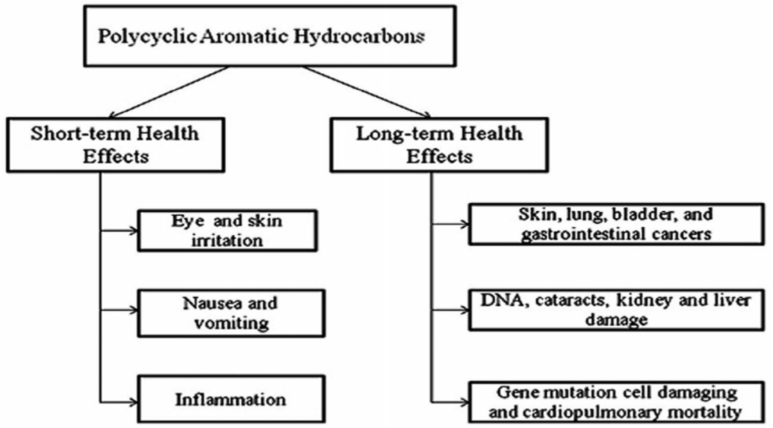

Figure 2. Effects of short and long-term exposure to PAHs.

Table 1. PAHs maximum contaminant in water.

PAHs	European Community (ppm)	USEPA (ppm)
Napthalene	-	-
Acenapthylene	-	-
Acenapthene	-	-
Fluorene	-	0.0002
Phenanthrene	-	0.0002
Anthracene	-	0.0002
Fluoranthene	0.0003	-
Pyrene	-	0.0002
Chrysene	-	0.0002
Benz(a)anthr	-	0.0002
Benzo(b)fluo	0.0003	0.0002
Benzo(k)fluo	0.0003	0.0002
Benzo(a)pyren	0.0003	0.0002
Indeno(1,2,3)pyr	0.0003	0.0002
Benzo(g,h,i)perilr	0.0003	-
Dibenz(a,h)anth	-	0.0002

The aim of this research was to investigate the distribution and seasonal variation of sixteen PAHs in harvested rain water as a priority pollutants from four different roofing materials made of (asbestos, zinc, aluminium and thatch) including the control (rainwater collected directly from the sky) in Warri and Agbarho, Delta State of Nigeria.

EXPERIMENTAL

Description of the study area

The locations selected for these analyses were Warri refining and Petrochemical Company (WRPC) and Agbarho town (nearby town to Warri). The studied areas are located in Delta State, Nigeria. The region lies within latitude 60°10' and 60°45' north of the equator and between longitudes 60°10' and 60°30' east of the Greenwich Meridian, of southern part of Nigeria [24].

This region is known by her frequent annual rainfall (usually all the months of the year) ranging from 3000 to 4500 mm. The high rainfall, humidity and river discharge during the rainy season combined with the low, flat terrain and poorly drained soils result in extensive flooding.

Pre-treatment

To obtain accurate results, proper sample pre-treatment procedures as prescribed by Ngabe *et al.* [25] were employed to eliminate potential contamination of the harvested rainwater samples. Sample containers were washed with nitric acid, HNO_3, overnight and rinsed with distilled water and dried under the sun for about 4-5 hours. Sample containers were properly and neatly labeled to enhance good record keeping. Rainwater samples that were collected from Warri Refinery were labeled,'WRPC' while Samples from Agbarho were labeled 'AGB'.

Method of sampling

A random sampling technique was employed in selecting the sampled household [26]. Eight (8) samples were collected from different roofing materials (asbestos, zinc sheets, alumnium sheets and thatch) in Warri and Agbarho, i.e. four samples from Warri and four from Agbarho. The samples were collected in the month of February, 2019. Four homes each in Warri and Agbarho with the targeted roof type were selected randomly and rainwater samples were collected. The containers were raised from the ground by placing them on top of tripod stand in order to avoid sand splash and other ground-based contaminations of the harvested rainwater samples [27]. The rainwater samples were collected from the entry points of the household into sterilized bowl then were later transferred to the containers and well labeled in the two sites.

Standards and reagents

A standard mixture of the USEPA 16 priority PAHs (2000 µg/mL, dichloromethane: benzene): naphthalene (Naph.), acenaphthene (Ace.), fluorene (Fl.), phenanthrene (Phen.), anthracene (Ant.), anthracene-d10 (Ant.d10), pyrene (Pyr.), benzo[a]anthracene (B[a]A), chrysene (Chy.), benzo [b] fluoranthene (B[b]F), benzo [k] fluoranthene (B[k]F), benzo[a]pyrene (B[a]P), dibenz [a, h] anthracene (D[ah]A) and benzo [ghi] perylene (B[ghi]P) with purity higher than 98% were obtained from Supelco, Bellefonte, USA, outlet office in Nigeria. Serial dilutions of the standard solution using HPLC grade acetonitrile were made and were obtained from Chem-lab Belgium, outlet office in Nigeria [28]. All solvents used were of HPLC grade and the water was purified with a Millipore Milli-Q system (Millipore, Molsheim, France).

Calibration standards

Individual stock standard solutions (1 $mgmL^{-1}$) of the PAHs were prepared in toluene [29]. All the solutions were transferred to amber glass bottles and stored at 4°C. They were kept for 30 min. at ambient temperature prior to their use. A mixed intermediate standard solution at a concentration of 100 $ngmL^{-1}$ was prepared via appropriate dilution of the stock solutions in methanol. This solution was used as a spiking solution for validation experiments [30]. Spiked calibration standards at concentration levels of 0.35, 0.7, 1.4, 2.8, and 5.6 $ngmL^{-1}$ were prepared by addition of 35, 70, 140, 280 and 560 µL of mixed standard stock solution to 10 mL of blank water samples in each case. A stock solution of anthracene-d10 in toluene at concentration of 1 $mgmL^{-1}$ was used as internal standard [31-32]. An aliquot of 70 µL of anthracene-d10 in methanol (100 $ngmL^{-1}$) was added to the spiked water sample as internal standard. The samples so obtained were treated as described in sample preparation section.

Extraction techniques

Different extraction techniques have been developed and applied for extracting PAHs from water samples. Some of the extracting techniques include: solid-phase extraction (SPE), liquid-liquid extraction (LLE), automated SPE, dispersive micro-solid phase extraction (D-µ-SPE), solid-phase micro extraction (SPME), stir bar sorptive extraction (SBSE). The selected extraction technique, not only influences the accuracy of the results, but also determines the total analysis time and costs. In this study, water samples were extracted using a liquid-liquid extraction (LLE) system according to the established procedures of [33]. The applied extraction method was suitable for the extraction of a wide range of analytes as elaborated in the USEPA methods. In the LLE procedure, the water sample was poured into a separatory funnel and the mixture of 100 mL n-hexane and dichloromethane (1:1 v/v) was added and shaken for 2 min. The water phase was drained and then the organic phase was poured into a glass funnel containing 20 g of anhydrous sodium sulfate (to remove water) and re-extracted with 50 mL of the same solvent mixture. The extract was concentrated prior to PAHs analysis.

Clean up of extracts

SPE clean-up of the sediment extracts was carried out using a 12-port vacuum manifold from Supelco with 6 mL Supelco C18 SPE cartridges. The sorbents of SPE cartridges were conditioned with 5 mL of extracting solvents and 40% of the extracting solvent in water respectively to prepare the column for the clean-up process [34, 35]. The extraction solutions were each loaded and aspirated through the cartridge under gentle vacuum at a flow rate of less than 2 mL/min.

GC-MS instrumental analysis

According to the [36] and [37] both the HPLC and GC/MS methods are considered equally valid approaches to analyse PAHs though GC/MS is a widely used method. In this study, a GC/MS method was employed. The PAHs extracts were analyzed by using a 3800 Varian gas chromatography coupled to a Varian Saturn 2200 mass spectrometer, equipped with a 30 m× 0.25 mm i.d. WCOT CP-Sil 8 CB column [38]. The GC/MS operated under the following conditions: the initial column temperature was 70 °C. After an initial holding time of 1 min, the temperature was programmed to rise to 300 °C at a rate of 10 °C/min for 30 min. The injector and detector temperatures were 250 °C and 300 °C, respectively. Helium was used as the carrier gas at a flow rate of 2 mL/min. Method was according to the established procedure by [39]. PAHs concentrations were identified based on their retention times and confirmed by comparing their mass spectra with the reference library. Calibration curves were plotted at seven concentration levels from 2 to 2000 ng/L with standard solutions containing all studied PAHs [40]. Detection limit (DL) for individual PAHs, with a signal to noise ratio of 3, ranged from 0.8 to 2 ng/L.

RESULTS AND DISCUSSION

The results obtained for the concentration of 16 polycyclic aromatic hydrocarbons in samples of harvested rainwater are presented on Tables 2-3. The results obtained showed the presence of 16 polycyclic aromatic hydrocarbons in the samples of the harvested rainwater [41, 42]. The results are presented in parts per million (ppm) and it also can be expressed as milligrams per liter (mg/L). For Warri Refinery and Petrochemical Company, WRPC, their total concentrations and standard deviations are; 0.036±0.012, 0.047±0.020, 0.045±0.018 and 0.023±0.008 ppm for aluminium roofing sheets, zinc roofing sheets, Asbestos roofing material and thatch roof, respectively.

For Agbarho (AGB), their respective total concentrations and standard deviations are; 0.046±0.020, 0.024±0.009, 0.023±0.008 and 0.021±0.007 ppm for aluminium roofing sheets, zinc roofing sheets, Asbestos roofing material and thatch roof, respectively, as shown on Table 2.

Table 2. Mean concentrations (ppm) of PAHs in water samples harvested from four Rooftops in WRPC, Warri.

PAHs	WRPC samples				
	Al-s	Zn-s	Asb	Tha	Mean
Napthalene	0.0033±0.0010	0.0030±0.0008	0.0029±0.0008	0.0015 ±0.0001	0.0027±0.0008
Acenapthylene	0.0065±0.0018	0.0047±0.0017	0.0047±0.0017	0.0023±0.0008	0.0046±0.0017
Acenapthene	0.0026±0.0008	0.0050±0.0018	0.0050±0.0018	0.0025 ±0.0008	0.0038±0.0017
Fluorene	0.0077±0.0026	0.0033±0.0008	0.0031±0.0008	0.0016±0.0002	0.0039±0.0010
Phenanthrene	0.0019±0.0002	0.0037±0.0017	0.0037±0.0008	0.0019±0.0002	0.0028±0.0008
Anthracene	0.0013±0.0002	0.0029±0.0008	0.0026±0.0008	0.0013±0.0001	0.0021±0.0007
Fluoranthene	0.0023±0.0007	0.0045±0.0017	0.0045±0.0017	0.0023±0.0008	0.0034±0.0010
Pyrene	0.0027±0.0008	0.0054±0.0018	0.0053±0.0018	0.0027±0.0008	0.0041±0.0017
Chrysene	0.0012±0.0002	0.0023±0.0008	0.0023±0.0008	0.0012±0.0002	0.0018±0.0002
Benz(a)anthr	0.0014±0.0002	0.0027±0.0008	0.0027±0.0008	0.0014±0.0002	0.0021±0.0007
Benzo(b)fluo	0.0004±0.0001	0.0006±0.0001	0.0006±0.0001	0.0003±0.0001	0.00048±0.0017
Benzo(k)fluo	0.0006±0.0001	0.0010±0.0002	0.0010±0.0002	0.0004±0.0001	0.00075±0.0026
Benzo(a)pyren	0.0017±0.0002	0.0035±0.0008	0.0034±0.0008	0.0017±0.0002	0.0026±0.0008
Indeno(1,2,3)pyr	0.0005±0.0001	0.0010±0.0002	0.0010±0.0002	0.0005±0.0002	0.00075±0.0026
Benzo(g,h,i)perilr	0.0013±0.0002	0.0027±0.0008	0.0025±0.0008	0.0013±0.0002	0.0020±0.0005
Dibenz(a,h)anth	0.00004±0.0000	0.0007±0.0001	0.0007±0.0001	0.0004±0.0001	0.00046±0.0002
Total	**0.036±0.012**	**0.047±0.020**	**0.045±0.018**	**0.023±0.008**	**0.0326±0.012**

Table 3. Mean concentrations (ppm) of PAHs in water samples harvested from four rooftops in Agbarho.

PAHs	AGB samples				
	Al-s	Zn-s	Asb	Tha	Mean
Napthalene	0.0029±0.0008	0.0015±0.0002	0.0014±0.0002	0.0015±0.0002	0.0018±0.0002
Acenapthylene	0.0046±0.0017	0.0024±0.0008	0.0023±0.0008	0.0024±0.0008	0.0029±0.0008
Acenapthene	0.0050±0.0018	0.0025±0.0008	0.0025±0.0008	0.0024±0.0008	0.0031±0.0010
Fluorene	0.0031±0.0008	0.0016±0.0002	0.0016±0.0002	0.0015 ±0.0002	0.0020±0.0005
Phenanthrene	0.0037±0.0017	0.0018±0.0002	0.0019±0.0002	0.0018 ±0.0002	0.0023±0.0008
Anthracene	0.0027±0.0008	0.0013±0.0002	0.0014±0.0002	0.0013 ±0.0002	0.0017±0.0002
Fluoranthene	0.0045±0.0017	0.0023±0.0008	0.0023±0.0008	0.0024 ±0.0008	0.0029±0.0008
Pyrene	0.0054±0.0018	0.0027±0.0008	0.0027±0.0008	0.0028±0.0008	0.0034±0.0010
Chrysene	0.0023±0.0008	0.0012±0.0002	0.0011±0.0002	0.0013 ±0.0002	0.0015±0.0002
Benz(a)anthr	0.0028±0.0008	0.0014±0.0002	0.0014±0.0002	0.0013 ±0.0002	0.0017±0.0002
Benzo(b)fluo	0.0005±0.0001	0.0003±0.0001	0.0003±0.0001	0.0004 ±0.0001	0.0004±0.0002
Benzo(k)fluo	0.0010±0.0002	0.0004±0.0001	0.0005±0.0001	0.0006 ±0.0001	0.0006±0.0002
Benzo(a)pyren	0.0035±0.0010	0.0017±0.0002	0.0017±0.0002	0.0016 ±0.0002	0.0085±0.030
Indeno(1,2,3)pyr	0.0010±0.0002	0.0005±0.0001	0.0005±0.0001	0.0004 ±0.0001	0.0006±0.0001
Benzo(g,h,i)perilr	0.0024±0.0008	0.0012±0.0002	0.0013±0.0002	0.0014±0.0002	0.0016±0.0002
Dibenz(a,h)anth	0.0008±0.0002	0.0003±0.0001	0.0005±0.0001	0.0003 ±0.0002	0.00048±0.0017
Total	**0.046±0.020**	**0.024±0.009**	**0.023±0.008**	**0.021 ±0.007**	**0.0285±0.008**

It is assumed that benzo(a)pyrene is an indicator of water contamination with polycyclic aromatic hydrocarbons. The total concentration and standard deviations of PAHs for each of the roof types in WRPC are 0.036±0.012, 0.047±0.020, 0.045±0.018 and 0.0023±0.008 ppm for aluminium, zinc, asbestos and thatch roof respectively as shown in table2. The contamination with benzo(a)pyrene is in the range of 0.0017±0.0002-0.0035±0.0008 ppm for the four roofing sheets in WRPC and 0.0016±0.0002-0.0035±0.0008 ppm for Agbarho. The concentrations of some hydrocarbons was much higher, for example, fluorene (0.0077±0.0026 ppm for Al-s roof) in WRPC (Table 2), acenapthylene (0.0065±0.0018 ppm for Al-s roof) in WRPC, acenapthene with high concentration of (0.0050±0.0018 for Al-s roof ppm) in AGB settlement in Table 3 and (0.0050±0.0018 for Zn-s and asb) in table2. Also, napthalene has high values of (0.0054±0.0018 ppm for Al-s roof) in AGB in table3, also similar values of 0.0054±0.0018 and 0.0053±0.0018 ppm for Zn-s and asb roofing material respectively in WRPC (Table 2). The PAHs analysed exceeded the United States Environmental Protection Agency (USEPA) standards.

In WRPC, the mean concentration values graph for each PAHs compound is shown in Figure 3, the highest mean concentration values were determined for acenapthylene and pyrene with mean values of 0.0046±0.0017 and 0.0041±0.0017 ppm respectively (table2). On the other hand, the lowest mean concentraion of 0.00046±0.0002 ppm was determined for dibenz(a,h)anthracene (Table 2). As it appears from the results presented in Tables 2, Warri Refinery Petrochemical Company and households emit large amounts of pollutants (mainly PAHs) into the atmosphere. This could be explained by the heavy industrial pollution as expected from the activities of the petrochemical company. The results were compared to the works of Stackelberg *et al*. [43] and Vilhunen *et al.* [44, 45] and find out to be higher, this may be due to the Warri Refinery Petrochemical Company emission of large amounts of pollutants (mainly PAHs) into the atmosphere. They found that total PAHs concentration ranged from 38 to 4953 ng/L.

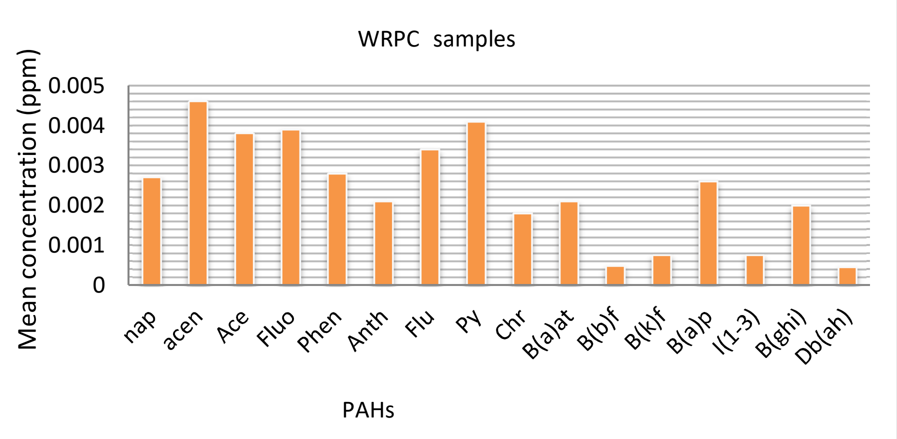

Figure 3. PAHs mean concentraton in WRPC water samples in the four rooftops.

However, The concentrations of some hydrocarbons were much smaller, for example, dibenz(a,h)anthracene (0.0003±0.0001 ppm) in AGB in table3, Benzo(b)fluo (0.0003±0.0001 ppm) in both settlement in Table 2 and 3, indeno(1,2,3)pyr (0.0005±0.0001 ppm) in WRPC in Table 2, also (0.0004±0.0001 ppm) in AGB, Table 3. Similarly, benzo(k)fluo has a low PAHs values of (0.0004±0.0001 ppm) in both WRPC and AGBA as shown in table 2&3. Their total concentration ranged from 0.021±0.007 – 0.046±0.020 ppm for AGB and 0.023±0.008 – 0.047±0.020 ppm for WRPC, respectively, in Table 2 and 3. In AGB, the mean concentration values graph for each PAHs compound is shown in Figure 4, with the smallest average concentration of 0.0004±0.0002 ppm (in Table 3) was determined for benzo[b]fluoranthene. On the other hand, the highest mean average concentration of 0.0085±0.030 ppm was determined for benzo(a)pyrene (in Table 3) as well. All the values from the four roofing materials were above the recommended maximum standard value of United States Environmental Protection Agency (USEPA) standards.

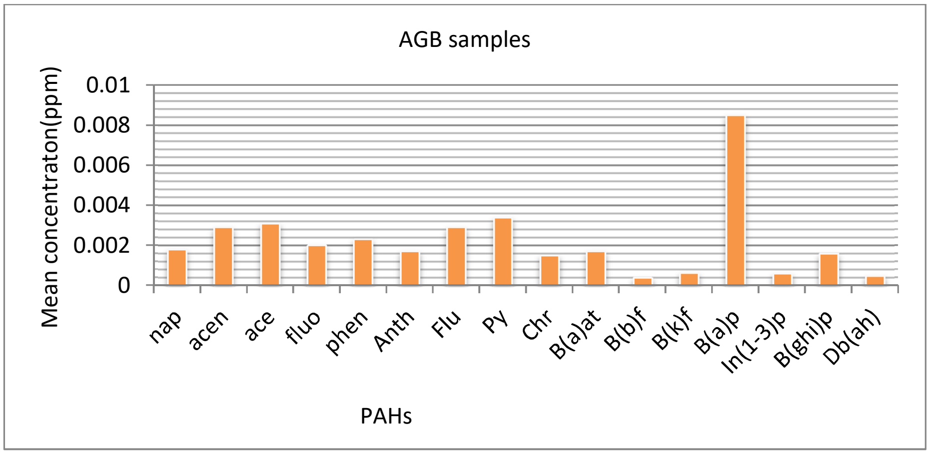

Figure 4. PAHs mean concentration in AGB water samples in the four rooftops.

In WRPC (Table 2), aluminum sheets has a total low concentration of 0.036±0.012 ppm, this may be due to the effect of type of roofing material because aluminium have a smooth surfaces and high heat capacity, which ensures that depositions on the sheets dry off quickly and swept off from the surfaces by wind before rainfall. Asbestos roof material in WRPC (Table 2) have a high total concentration of 0.045±0.018 ppm, this may be due to the effect of roofing materials because asbestos have a rough surfaces, however, have the tendency to retain most contaminants. This in turn may alter the quality of harvested water from these surfaces.

As it appears from the results presented in Table 2 and 3, both Warri Refinery Petrochemical Company and households emit large amounts of pollutants (mainly PAHs) into the atmosphere, which makes all the values from the four roofing materials to exceed the recommended maximum standard value of United States Environmental Protection Agency (USEPA) standards. The implication of this is that it might cause toxicity, carcinogenic, mutagenic and teratogenic to both to human and aquatic organisms, which might eventually leads to death.

Further assessment and monitoring of PAHs is encouraged, since this research work only captured the first annual rainfall in February, there might be seasonal variation of PAHs because of their ubiquity in the environment, their persistence and bio accumulative properties and their potential for toxicity, carcinogenic, mutagenic and teratogenic, both to human and aquatic organisms. All the analyzed results were reported in parts per million (ppm).

CONCLUSION

The results obtained show the presence of 16 polycyclic aromatic hydrocarbons in the harvested rainwater samples from WRPC and AGB. Types of roofing tops and settlements affect the quality of harvested rainwater parameters. Rainwater harvested from aluminium rooing sheets gave least amount of pollutants, hence, safer for consumption after subjecting it to water treatment. Rainwater harvested from asbestos and thatch roofing materials gave high amount of pollutants, hence, not safe for consumption, except for domestic uses such as washing, mobbing, cleaning, laundry, bathing and toilet flushing.

ACKNOWLEDGEMENTS

The Authors are thankful to Chemistry Department, Federal University of Agriculture, Makurdi, Benue State, Nigeria. To my irreplaceable mum, Mrs. Erienu Florence Atajomavwo.

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