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DISTRIBUTION, SOURCES AND TOXICITY POTENTIALS OF POLYCYCLIC AROMATIC HYDROCARBONS IN SOIL AROUND THE VICINITY OF BALOGUN-BIRRO DUMPSITE OF OSHOGBO, NIGERIA

(Taburan, Sumber dan Potensi Ketoksikan Polisiklik Aromatik Hidrokarbon di dalam Tanah Sekitar Tapak Pelupusan Balogun-Birro, Oshogbo, Nigeria)

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Abstract

Contamination of soil within the vicinity of dumpsites by toxic and persistent organic pollutants is of environmental concern because of their carcinogenic, genotoxic and environmental persistence. Waste disposal sites have been identified as potential source of PAHs accumulating in soil. Assessment of level, distribution and sources of PAHs in environmental media is important for evaluation of ecotoxicological and health effect. This study investigated the distribution, sources and level of PAHs in soil within the vicinity of Balogun-Birro Dumpsite in Osogbo, Nigeria and their potential impacts on human health. Soil samples were collected at ten points within the vicinity of the dumpsite. The level of the 16 USEPA PAHs in the soil samples were determined by gas chromatography – flame ionization detector (GC-FID). The total concentration of the 16PAHs ranged between 0.1137mg/kg to 5.6491mg/kg. Samples from the main dumpsite and the mechanic workshops had highest PAHs concentrations of 5.6491mg/kg and 3.6529mg/kg respectively. The distribution of PAHs ring size is in the order of 3>4>5>6>2. Carcinogenic fractions represent 34.74% of the total PAHs. The total concentration of carcinogenic PAHs ranged from 0.06425mg/kg to 1.6775mg/kg. Diagnostic ratios of PAHs indicate that pyrogenic activities are major sources of PAHs. The study had revealed increasing accumulation of carcinogenic PAHs in soil within the vicinity of the dumpsite.

Keywords: Polycyclic Aromatic Hydrocarbons (PAHs), carcinogenic, dumpsite, toxicity equivalent potency, pyrogenic

Abstrak

Pencemaran tanah di sekitar tapak pembuangan oleh pencemar organik yang toksik dan tahan lama adalah isu alam sekitar yang mendapat perhatian kerana ia bersifat karsinogenik, genotoksik dan kekal di alam sekitar. Tapak pelupusan sisa telah dikenal pasti sebagai sumber berpotensi kehadiran PAHs di dalam tanah. Penilaian aras, taburan dan sumber pencemar PAHs dalam media alam sekitar adalah penting bagi menilai kesan ekotoksikologi dan kesihatan. Kajian ini menilai aras kandungan, taburan, dan sumber PAHs di dalam tanah di sekitar tapak pelupusan Balogun-Birro Osogbo, Nigeria dan kesannya kepada kesihatan manusia. Sampel tanah telah diambil dari 10 titik persampelan di sekitarnya. Aras kandungan 16 USEPA PAHs id dalam tanah ditentukan oleh kromatografi gas – pengesan nyala pengionan (GC-FID).Jumlah kepekatan bagi 16 PAHs di antara julat 0.1137 mg/kg hingga 5.6491 mg/kg. Sampel daripada tapak pelupusan utama dan bengkel mekanik masing – masing merekodkan kepekatan PAHs tertinggi iaitu masing – masing ialah 5.6491 mg/kg dan 3.6529 mg/kg. Taburan PAHs mengikut gelang aromatik adalah mengikut tertib 3>4>5>6>2. Pecahan karsinogenik mewakili 34.74% daripada jumlah keseluruhan PAHs. Jumlah kepekatan karsinogenik PAHs adalah dari julat 0.06425 mg/kg untuk 1.6775 mg/kg. Nisbah diagnostik PAHs menunjukkan bahawa aktiviti-aktiviti pirogenik adalah sumber utama bagi PAHs. Kajian telah menunjukkan peningkatan penumpukan bagi karsinogenik PAHs di dalam tanah di sekitar tapak pelupusan.

Kata kunci: Polisiklik Aromatik Hidrokarbon, karsinogenik, tapak pelupusan, potensi ketoksikan, pirogenik

Introduction

Environmental pollution by toxic and persistent organic pollutants is a widespread problem facing major cities in developing countries. Over the past three decades, there has been increasing concern over the public health issues attributed to environmental pollution in developing countries. The World Health Organization (WHO) estimated that 23% of deaths in developing countries are attributed to environmental factors and over two hundred million people globally may be affected by exposure to persistent and toxic substances [1, 2]. Polycyclic aromatic hydrocarbons (PAHs), Polychlorinated biphenyls (PCBs), Pesticides and heavy metals have been identified as toxic and persistent xenobiotic pollutants accumulating in environmental media and pose serious health risk [3].

Lack of proper waste management facilities is one of the leading causes of environmental pollution and degradation in developing countries. Increasing population and development of small scale industries have led to an increase in the generation of domestic and industrial wastes in most cities and major towns in Nigeria. However, there is no regulation on the proper management of these wastes. Most cities lack proper waste disposal facilities [4, 5], heaps and accumulation of waste are seen in open dumpsites which lack proper treatment facilities [6]. The manners in which wastes are disposed are creating serious health and environmental problems. Studies have shown that soils and groundwater aquifers have been polluted due to disposal of wastes in open waste dumpsites [7-9]. Dumpsites are the oldest form and unorganized method of waste treatment [10].

In Nigeria, wastes are dumped in open dumpsites scattered around many cities and major towns without consideration of environmental and health impacts. Most dumpsites are located within the vicinity of living communities. People living within this vicinity of dumpsites may be at greater risk of potential exposure to toxic pollutants through exposure to contaminated soil, groundwater and air [11, 12]. Heavy pollution of dumpsite may results in an elevated accumulation of contaminants in soil and groundwater aquifer. In Nigeria, studies on assessment of toxic pollutants in dumpsites have been carried out by many researcher but most studies are focused on the pollution of soil and groundwater aquifer within the vicinity of dumpsites by heavy metals [10-15] without consideration of the effect of other pollutants such as PAHs. However, waste disposal sites can be a concentrated source of PAHs on a local scale [16, 17]. Few studies have been reported on the assessment, and toxicity potential of PAHs contaminated soil within the vicinity of dumpsites.

Polycyclic aromatic hydrocarbons (PAHs) are some of the most widely spread organic pollutants in the environment [18, 19]. PAHs occur naturally in fossil fuel and are products of incomplete combustion of organic matter [20- 22] and they are found in soil, water, air and sediments [23]. It has been estimated that about 90% of total environmental burden of PAHs reside in surface soil [24]. Tang *et al.*, [25], observed that adsorption, transportation and partitioning mechanism of organic pollutants including PAHs in soil and sediments is determined by the organic carbon content. Environmental concerns have been focused on PAHs due to their immunotoxicity, genotoxicity, reproductive toxicity and carcinogenic potential [26, 27]. The United States Environment Programme (USEPA), have identified 16 PAHs as priority pollutants that require environmental monitoring. These include naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a) anthracene, chrysene, benzo(k)fluoranthene, benzo(b)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthraces, benzo(g,h,i)perylene and indeno(1,2,3cd)pyrene [28], and The International Agency on cancer Research have identified seven PAHs as potential carcinogen [28-30]. Investigation of spatial distribution, source and level of PAHs in contaminated soil would help to identify the associated risk. The aims of this study are to investigate the concentration, sources and distribution of PAHs in soil and to assess the potential impact of PAHs on the health of people living within the vicinity of Balogun-Birro, dumpsite in Oshogbo, South West Nigeria.

Materials and Methods

Description of Study Area

The Balogun-Birro dumpsite is a municipal open dumpsite located at the Oke-Bale area of Oshogbo in Osun State, South West Nigeria. It is the main dumping site receiving most of the solid waste from the area. It is located at latitude 07°46^{I} N and longitude 0° 43^{I}E. Figure 1, shows the map of Osogbo with an insert of the sampling points. The site is surrounded by residential buildings and auto repair workshops. Dumping at the site is unrestricted and contains mixtures of both organic and inorganic waste materials, including organic industrial, agricultural, domestic, medical wastes and other miscellaneous materials such as used engine oil, metals and ash. Waste are burnt indiscriminately on the dumpsite without proper regulation on the toxic effect of such waste polluting the atmosphere and toxic pollutants from the wastes may leached into soil, contaminating groundwater aquifer within the area and may also run off into nearby surface water bodies thus extending environmental and health risks to the communities living within the vicinity as well as those using the runoff receiving water bodies for domestic and agricultural purposes.

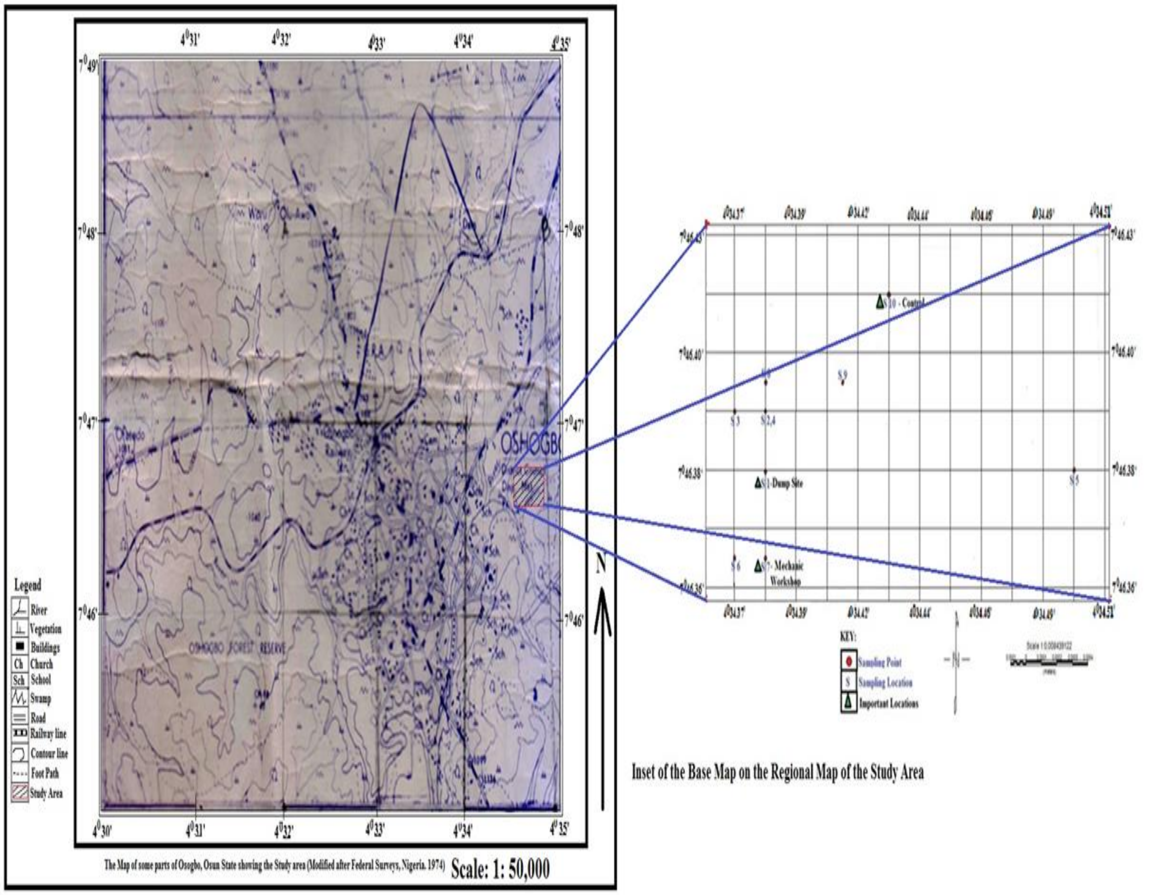

Figure 1. Extract map of Oshogbo showing the study area and insert of base map of the study site showing the sampling coordinates.

Sampling and Samples Collection

Top soil samples were collected in February 2012 at an interval of 50m, from ten different sampling points within the vicinity of the Balogun Biiro dumpsite in Oshogbo Nigeria (Figure 1). Duplicate samples were collected from each point and composited to represent samples from each point. Table 1 shows the sampling point description and coordinate. The sampling points were labeled S1, S2, S3, S4, S5, S6, S7, S8, S9 and S10. Soil samples were collected at 0-10cm deep at each of the sampling point with a soil auger and stored in a stainless steel lined with aluminum foil. Samples were air dried at room temperature, ground and sieved with a 5mm mesh size and wrapped with aluminum foil and stored at room temperature prior to analysis.

Table 1. Description of Sampling Point

Sampling Point	Coordinate	Description of Related Activities
S1	07^0 46' 18'' N, 004^0 34' 18'' E	Dumpsite
S2	07^0 46' 19'' N, 04^0 34' 18'' E	Close to dumpsite
S3	07^0 46' 19'' N, 04^0 34' 17'' E	Close to dumpsite
S4	07^0 46' 19'' N, 04^0 34' 18'' E	Close to dumpsite
S5	07^0 46' 18'' N, 004^0 34' 15'' E	Close to Mechanic Workshops and dumpsite
S6	07^0 46' 16'' N, 004^0 34' 17'' E	Close to Mechanic Workshop
S7	07^0 46' 16'' N, 04^0 34' 18'' E	Mechanic Workshop
S8	07^0 46' 20'' N, 04^0 34' 18'' E	Close to dumpsite
S9	07^0 46' 20'' N, 04^0 34' 21'' E	Close to dumpsite
S10	07^0 46' 22'' N, 04^0 34' 23'' E	Far distance from the main dumpsite and mechanic workshop but within the vicinity of the dumpsite

Reagents and Materials

All the reagents used for the analysis are of high purity analytical grade (HPLC grade) and are used as provided by the supplier. Hexane, dichloromethane, sodium sulphate (99.0%) and silica gel (100-200 mesh, 75-100µm) were purchased from Sigma Aldrich (Bistol Scientific, Nigeria). 16 EPA PAHs standard mixture (2000µg/mL in methylene chloride) was purchased from (RESTEK, USA). The sodium sulphate was purified by heating at 400^{o}C for 4 hours prior to use. All glassware used in the study were soaked in dilute nitric acid and washed with distilled water before each use.

Extraction and Cleanup of samples

Samples extraction and cleanup were carried out according to USEPA (Ultrasonic Method 3550C) and USEPA (Silica gel cleanup Method 3630C) respectively with little modifications. 10g of dried soil sample mixed with anhydrous sodium sulphate (1:1) was ultrasonically extracted with 50 mL mixture of acetone and dichloromethane (1:1) for 45 minutes and centrifuge for 10 minutes. The supernatant was collected and extraction was repeated three times with fresh 50 mL portion of dichloromethane. The supernatant were collected together and concentrated by a rotary evaporator to about 2mL the solvent was exchanged for hexane for cleanup. The cleanup column was prepared by slurring about 10g of activated silica gel (about100-200mesh, activated at 200 ^{o}C for 16 hours) with dichloromethane into a chromatography column. About 1g of anhydrous sodium sulphate was added to the top of the column. The column was pre-eluted with 50 mL of n-hexane. The concentrated extracts were transferred quantitatively to the top of the column with an additional 5mL of dichloromethane and eluted with 25 mL of n-hexane followed by 50 mL of hexane/dichloromethane (2:3 V/V). The n-hexane extract was discarded and the hexane/dichloromethane extract was concentrated with a rotary evaporator under nitrogen to about 0.5 mL and adjusted to 1 mL with n-hexane for chromatographic analysis.

Gas Chromatograph Analysis of Sample Extracts

The concentration of PAHs in the sample extracts were determined according to USEPA Method 8100 using Gas Chromatograph coupled to a Flame Ionization Detector (Agilent 5890 GC-FID) with little modifications. The separation was carried out on an HP5 (30 m x 0.25 mm id) fused silica capillary column. 1.0 µL of the extract was injected using split/splitless (25:1) injection mode. Helium was used as the carrier gas at a flow rate of 1 mL/ min and nitrogen was used as the makeup gas. The oven temperature was programmed from 60 ºC (held for 2 min) to 180 ºC at a rate of 3 ºC min^{-1}, from 180 ºC to 250 ºC at a rate of 5 ºC min^{-1} and from 250 ºC to 330 ºC at a rate of 15 ºC min^{-1} and then held for 8 min. The USEPA 16 priority PAHs standard mix was analyzed using the same instrumental conditions. The identification of PAHs was by comparison of samples retention times with that of the USEPA standard mix. The quantification was performed by the five point external calibration curve of the standard. For quality control recovery studies was carried out by spiking samples of known concentration of PAHs with PAH mix standard of known concentrations and analyzed by the test method. Two methods blanks (solvents) were also analyzed along with the samples. The concentrations of the PAHs in the method blanks are below the method detection limit.

Analysis of Total Organic Carbon, TOC

The total organic carbon was determined by the Walkey-Black method [31]. About 5g of the dried soil sample was ground to pass through 0.5 mm sieve. 0.5 g of each sample was measured in triplicate and transferred into different 250 mL Erlenmeyer flask. 10 mL of 1 N $K_2Cr_2O_7$ solution was added into each flask and swirl gently to disperse the soil. 20 mL of concentrated H_2SO_4 was rapidly added. The flask was gently swirled immediately until the soil and reagents are mixed, and then swirled more vigorously for 60 seconds. The flask was rotated again and allowed to stand on a sheet of asbestos for about 30 minutes. After standing for 30 minutes, 100 mL of distilled water was added to the mixture to provide a clear suspension for viewing the end point, three drops of ferroin indicator was then added and the resulting solution titrated with 0.5 N ferrous sulphate solution. As the end point was approached, the solution took on a greenish cast and then changed to dark green at which point ferrous sulphate was added drop by drop until the colour changes rapidly from blue to maroon red. This procedure was then repeated for the remaining samples. The blank titration was carried out. The result of the TOC was then calculated as equation 1 below

$$\%\ \text{Organic Carbon in Soil} = [(A-B) \times 0.003 \times 100 \times F] / C \qquad (1)$$

where as A is normality of $K_2Cr_2O_7$ x ml of solution, B is normality of $FeSO_4$ x ml of solution, C is mass of air-dry soil (g) and F= correction factor = 1.33

Results and Discussion

The Health Investigation Level, (HIL) for total PAHs have been based on the sum of the 16 USEPA priority PAHs for most contaminated sites [32]. The concentration of the 16 PAHs were determined in the soil sample within the vicinity of the dumpsites. These include Napthalene (Nap); Acenapthene, (Ace-nap), Acenaphtalene, (Ace-naph), Fluorene, (Flu), Phenanthrene, (Phen), Anthracene, (Anth), Flouranthene (Flan), Pyrene (pyr), benzo(a)pyrene, (B(a)P), Benzo(a)anthracene (B(a)A), Benzo(b)flouranthrene (B(b)F), Benzo(k)flouranthrene (B(k)F), Indeno(123-cd)pyrene (IP), Dibenzo(a,h)anthracene (Dib(ah)A and Benzo(ghi)pyrelene (B(ghi)P). The source, toxicity potency and distribution of these PAHs were assessed in the study.

Distribution and Level of Polycyclic Aromatic hydrocarbon

The concentrations and distributions of the 16 EPA priority PAHs in the dumpsite soil were presented in Table 2. The result (Table 2) shows that, the concentration of PAHs in the soil sample do not follow a specific order of distribution, all the 16 USEPA priority PAHs were detected in the soil at varied concentration. The total EPA PAHs concentrations found in the soil ranged from 0.11374mg/kg to 5.6491mg/kg with a mean concentration of 0.0718±0.01mg/kg and 0.35307±0.23mg/kg (Table 2). The highest PAHs concentration (5.64913mg/kg) was detected in soil samples around the mechanics workshops (point S7) within the vicinity of the dumpsite. Fluoranthrene (0.75197 mg/kg) a class 3 carcinogenic compound [31] and fluorene (0.67488 mg/kg) were found in highest concentrations at S7. This shows that wastes from the mechanic workshop are contributing to the contamination of soil within the vicinity of the dumpsites by PAHs. The concentration of total USEPA PAHs on the main dump area (sampling point S1 and S2) are 3.09671mg/kg and 3.65275mg/kg respectively with a mean concentration of 0.1935±0.23 mg/kg and 0.22829±0.14 mg/kg respectively. The concentration of pyrene (0.67420 mg/kg) and chyrsene (0.64619 mg/kg) were the highest at point S1 and phenanthrene (0.44119 mg/kg) was the highest at point S2 when compared with other detected PAHs. The total and mean concentrations of PAHs at area close to the main dump area (S3, S4 and S5) and mechanics workshop (S6) is higher than the total concentrations in soil at the main dump and mechanic workshop. This shows that the dumps and activities within the mechanics workshop are leading to the accumulation of PAHs in soil within the vicinity of the dumpsites. The concentration of the individual PAHs at point S5 is lowest when compared with other sampling point. The total PAHs concentration at S5 was 0.11374mg/kg with a mean concentration of 0.00718±0.01mg/kg.

The distribution of high molecular weight PAHs, (∑HMW) and low molecular weight PAHs, (∑LMW) in the soil samples (Table 2) show that ∑HMW are the dominant in the dumpsite soil. The total concentration of ∑HMW is higher than (∑LMW) at most of the sampling points (S1, S4, S5, S7, S8, S9, S10). The lower molecular weight PAHs with lower numbers of ring are volatile and easily biodegradable than the high molecular weight PAHs which are more persistent in the environment. The percentage relative concentration of the PAHs based on the numbers of rings to the total concentrations of PAHs in the dumpsite soil (17.12841mg/kg) was shown in Figure 2. The concentration of PAHs in the soil samples based on the ring size are in the order of 3-ring > 4-ring >5-ring > 6-ring > 2-ring. The three rings sized PAHs; acenaphthlene, fluorene, phenanthrene, anthracene, acenaphthylene were the most abundant in the dumpsite soil with a relative abundance of 43.80%. The percentage abundance of the four rings PAHs, fluoranthene, chrysene, benzo(a)anthracene and pyrene was 32% and abundance of five ring PAHs; benzo(k)fluoranthene, benzo(k)fluoranthene , benzo(a)pyrene was 16% . The six rings and two rings PAHs was the lowest with an abundance of 5.50% and 2.41% respectively (Figure 2).

Table 2. Concentrations of Polycyclic Aromatic Hydrocarbon in soil samples from Balogun-Biiro Dumpsite in Oshogbo (mg/kg)

PAHs	**Sampling Points**				
	S1	**S2**	**S3**	**S4**	**S5**
Naphthalene	0.00267	0.37052	0.01425	0.00254	0.00051
Acenaphthylene	0.00421	0.14336	0.00692	0.06294	0.03292
Acenaphthene	0.00209	0.26362	0.32753	0.04287	0.00132
Fluorene	0.00002	0.49429	0.52784	0.06924	0.00023
Phenanthrene	0.03623	0.44119	0.39314	0.05118	0.00063
Anthracene	0.54004	0.15408	0.02132	0.02819	0.00006
Fluoranthene	0.18841	0.10400	0.05652	0.07712	0.00976
Pyrene	0.67420	0.27611	0.00208	0.02750	0.00367
*Benzo(a)anthracene	0.64619	0.26445	0.01856	0.02536	0.00676
*Chrysene	0.13343	0.35450	0.02421	0.03326	0.01045
*Benzo(k)fluoranthene	0.30112	0.088214	0.00626	0.00103	0.00339
*Benzo(b)fluoranthene	0.25271	0.03747	0.02615	0.03515	0.00042
*Benzo(a)pyrene	0.09223	0.28792	0.02219	0.02923	0.01540
*Indeno(1,2,3cd)pyrene	0.07087	0.20000	0.01593	0.02021	0.01276
*Dibenzo(a,h)anthracene	0.06466	0.15996	0.01521	0.01795	0.01507
Benzo(g,h,i)perylene	0.08763	0.01306	0.00213	0.00222	0.00039
∑LMW PAHs	0.58526	1.86726	1.29100	0.25696	0.03567
∑HMW PAHs	2.51145	1.78568	0.18924	0.26903	0.07807
∑16 EPA PAHs	3.09674	3.65294	1.42164	0.52599	0.11374
MEAN	0.19354	0.22829	0.09251	0.32873	0.00718
SD	0.23	0.14	0.17	0.23	0.01
∑CPAHs	1.56121	1.39251	0.12851	0.16291	0.06425
% TOC	6.30	6.66	6.34	6.38	6.70

Table 2 (Cont'd). Concentrations of Polycyclic Aromatic Hydrocarbon in soil samples from Balogun-Biiro Dumpsite in Oshogbo (mg/kg)

PAHs	**Sampling Points**				
	S6	**S7**	**S8**	**S9**	**S10**
Naphthalene	0.00084	0.02498	0.00674	0.00341	0.00067
Acenaphthylene	0.07838	0.59791	0.00083	0.06155	0.00033
Acenaphthene	0.21382	0.38857	0.00132	0.04183	0.00019
Fluorene	0.08012	0.67488	0.00217	0.07562	0.00045
Phenanthrene	0.00950	0.49665	0.00152	0.05703	0.00047
Anthracene	0.12297	0.52958	0.08271	0.03179	0.30732
Fluoranthene	0.00547	0.75197	0.02180	0.08989	0.01073
Pyrene	0.00246	0.50460	0.08497	0.03316	0.04375
*Benzo(a)anthracene	0.00912	0.50826	0.06995	0.02989	0.03968
*Chrysene	0.02218	0.32248	0.01463	0.03913	0.01569
*Benzo(k)fluoranthene	0.01693	0.34572	0.04902	0.01018	0.01948
*Benzo(b)fluoranthene	0.00042	0.00987	0.03493	0.00116	0.02500
*Benzo(a)pyrene	0.01489	0.28967	0.09973	0.03157	0.06946
*Indeno(1,2,3cd)pyrene	0.00225	0.19967	0.07969	0.02285	0.05274
*Dibenzo(a,h)anthracene	0.00187	0.00188	0.06760	0.02187	0.10229
Benzo(g,h,i)perylene	0.00099	0.00244	0.11447	0.00251	0.05387
∑LMW PAHs	0.50563	2.71257	0.09529	0.27123	0.30943
∑HMW PAHs	0.07658	2.93656	0.63679	0.28221	0.43269
∑16 EPA PAHs	0.58221	5.64913	0.73208	0.55344	0.74212
MEAN	0.03639	0.35307	0.04575	0.03459	0.04638
SD	0.06	0.25	0.23	0.03	0.08
∑CPAHs	0.06766	1.6775	0.41555	0.15665	0.32434
% TOC	7.66	7.18	6.74	7.50	6.30

Percentage Total Organic carbon (% TOC); sum of carcinogenic PAHs (∑CPAHs); standard deviation (SD); sum of 16 EPA priority PAHs (∑16 EPA PAHs); Sum of High molecular weight PAHs (∑HMW PAHs); Sum of Low molecular weight PAHs (∑LMW PAHs).

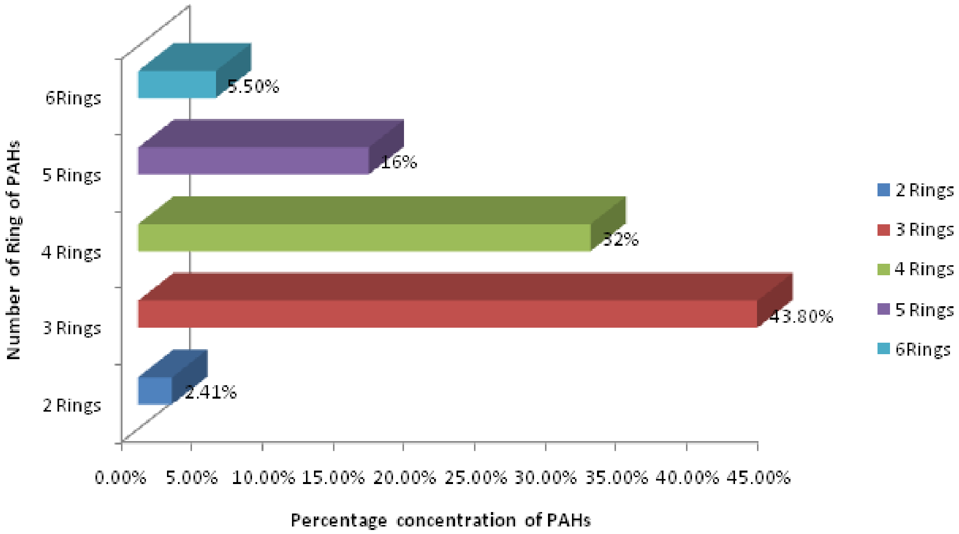

Figure 2. Percentage distribution of PAHs based on ring size in the soil sample

Carcinogenic Potency and Toxicity potential

The International Agency for Research on Cancer (IARC) and the United State Environment Programme, (USEPA) reported that chyresene, benzo(a)anthracene, dibenzo(a,h)anthrancene, benzo(a)pyrene, benzo(b)fluoroanthrene, benzo(k)flouoranthrane and indeo(1,2,3-cd)pyrene are potential human carcinogens [33]. All the listed carcinogenic PAHs are detected in the soil (Table 3). The total concentration of carcinogenic PAHs in the dumpsite soil was 5.95042 mg/kg. This represented 34.74% of the total PAHs concentrations detected in the dumpsites soil. The total concentrations of the carcinogenic PAHs at each of the sampling point were presented in Figure 3. The highest concentration of carcinogenic PAHs (1.6755mg/kg) was recorded in soil from the mechanic workshop (point S7), the concentration of carcinogenic PAHs at point the main dump area S2 and S3 are 1.39251mg/kg and 0.1285 mg/kg respectively and the lowest concentrations of the carcinogenic PAHs were recorded at point S5 (0.0642mg/kg) and S6 (0.06766mg/kg) respectively. The carcinogenic potency of benzo[a]pyrene, B(a)P has been identified, it has been listed as a group 1 carcinogen and its metabolites are said to destroy normal copying of DNA and induces mutation [34, 35]. B(a)P was detected in all the soil samples, the highest concentrations were detected at point S2 (0.28967 mg/kg) and S7(0.28967mg/kg). To assess the human health risk of carcinogenic PAHs containing mixtures, total potency equivalence (TPEs) are used to relate the carcinogenic potential of other PAHs to that of benzo[a]pyrene [36]. The soil total equivalent potency for the PAHs in the dumpsite was presented in Table 3. The TPEs values are calculated as the summation of the total concentration of each of the carcinogenic with the toxicity equivalent factor (Table 3) for each PAHs as equation 2 below:

$$\text{TPE} = \sum (\text{Ci} * \text{TEFi}) \qquad (2)$$

where as TPE is the total potency equivalent, Ci is the concentration of ith PAH. The toxic potency equivalent factor (Table 3) for benzo(a)anthracene (0.161822), dibenzo(ah)anthracene (0.46836) and benzo(a)pyrene (0.95229) are the highest of all the seven carcinogenic PAHs detected in the soil and are the most toxic and carcinogenic PAHs [36].

Table 3. Carcinogenic Potency of PAHs in soil within the vicinity of Balogun- Biiro Dumpsite, Oshogbo

PAHs	Level of carcinogenic PAHs (mg/kg)	TEF	B[a]P-TPE
*Benzo(a)anthracene	1.61822	0.1	0.161822
*Chrysene	0.96996	0.01	0.00970
*Benzo(k)fluoranthene	0.841344	0.1	0.08413
*Benzo(b)fluoranthene	0.42328	0.1	0.04233
*Benzo(a)pyrene	0.95229	1	0.95229
*Indeno(1,2,3cd)pyrene	0.67697	0.1	0.06770
*Dibenzo(ah)anthracene	0.46836	1	0.46836
Total	5.950424	-	1.78633

Toxicity Equivalent Factor (TEF) [44]; Benzo[a]pyrene-Toxic potency Equivalent (B[a]P-TPE); *Carcinogenic PAHs

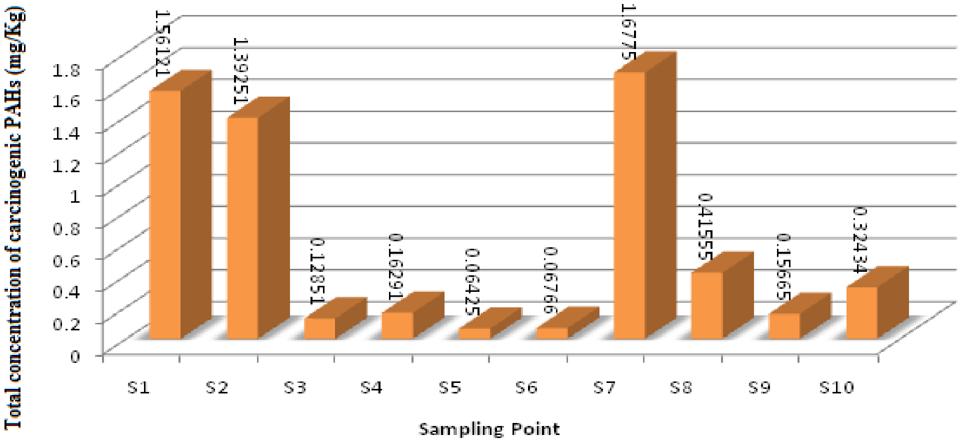

Figure 3. Concentrations of carcinogenic PAHs at each of the sampling points

Relationship between TOC and Total PAHs Concentration in Soil

The percentage total organic carbon of the soil does not show a wide variation in its value. The %TOC concentration is presented in Table 2. The %TOC ranged from 6.30 to 7.66. The maximum percentage TOC concentration (7.66%) was recorded at sampling point S6 and the lowest was at S1 and S10 (6.30%). Scatter plot was used to assess the relationship between the percentage total organic carbon and total concentration of PAHs in the soil sample (Figure 4). The fit line for the scattered plot using linear regression with R value of 0.01, showed that there is a positive correlation between the TOC and PAHs (r = 0.007), indicating that the organic carbon content of the soil sample increases the adsorption of the PAHs to the dumpsite soil.

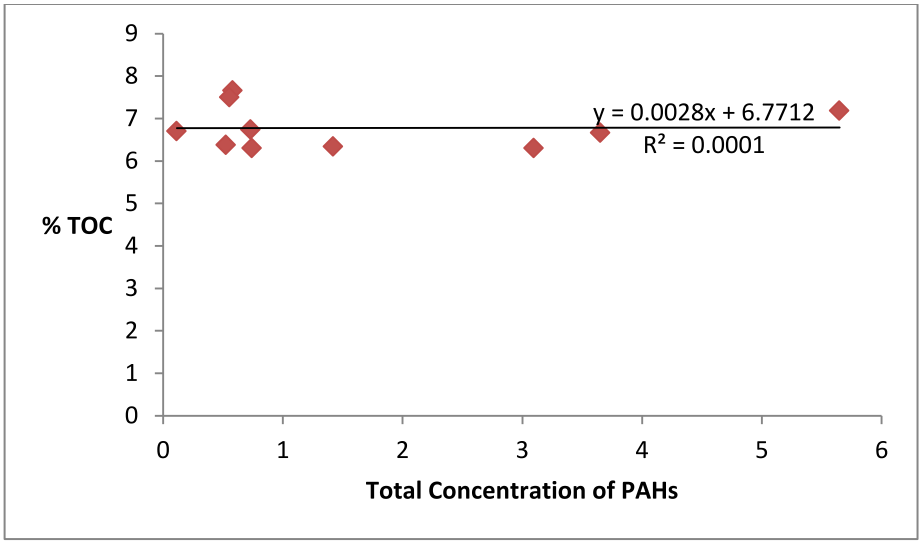

Figure 4. Scatter plot of percentage Total Organic Carbon against total concentration of PAHs in Balogun-Biiro dumpsite

Diagnostic Ratio for Source Identification

The ratios of specific PAHs compounds and its isomers have been identified as indices for source identification and to distinguish natural and anthropogenic sources of PAHs. Different researchers have employed ratios of specific PAHs isomers to distinguish petrogenic, biogenic and pyrogenic PAHs sources [36, 37, 38, 39 & 40]. Petrogenic sources are characterized with the predominance of low molecular weight (2-3 ring) PAHs over the high molecular weight (4-6ring) PAHs. The ratio of low molecular weight PAHS to high molecular weight PAHs greater than 1 (LMW/HMW >1) indicates a petrogenic source [41]. The diagnostic ratio of PAHs in the dumpsite soil presented in Table 4, showed that the values of LMW/HMW PAHs were greater than 1 at point S2, S3 & S6, suggesting a petrogenic source and the values at the rest sampling points are less than one suggesting a pyrogenic source at this points.

The ratio of anthracene to anthracene plus phenanthrene greater than 0.10 (Anth/Anth+Phen > 0.10) is an indication of pyrogenic origin [42] and fluoroanthrene to fluoroanthrene plus pyrene greater than 0.50 (Flan/Flan+Pyr > 0.50) is an indication of grass, wood and coal combustion [3, 43]. All the values of Anth/(Anth+Phen) was greater than 0.1 except at point S3 & S5. This is an indication that the PAHs are from pyrogenic sources. The value of Flan/(Flan+Pyr) at sampling point S3,S4, S5, S6, S7 and S9 were higher than 0.50 suggesting pryrogenic sources of PAHs from combustion of grass, wood or biomass deposited on the dumpsites. Yunker et al.,[37] reported that a ratio of bezo[a]anthracene to bezo[a]anthracene plus chyresene (B[a]A/B[a]+Chyr) less than 0.2, 0.2-0.35 and greater than 0.35 are indication of petrogenic, mixed and pyrogenic sources respectively. The value of B[a]A/B[a]A+Chyr for all the point is greater than 0.35 indicating that the PAHs source is mainly of combustion sources but the value at S6 (0.29) is greater than 0.2 but less than 0.35 suggesting a mixed source of both pyrogenic and petrogenic combustion at S6. The value of Indeno(1,2,3cd)pyrene ratio Indeno(1,2,3cd)pyrene plus Benzo(ghi)perylene greater than 0.5 suggests a combustion source[37]. The ratio of IP/(IP +B(ghi)P) for the dumpsite soil samples were greater than 0.5 at S2,S3,S4,S5,S6,S7 and S9 signifying a combustion source of PAHs from grass and wood, the values at S1 (0.45), S8 (0.44) and S10 (0.49) are lesser than 0.50 but greater than 0.2. The application of the different source diagnostic ratios of PAHs have shown that combustion of waste (wood, plants, domestic wastes) on the dumpsite are the main source of PAHs present in the dumpsite soil. However, some ratios have suggested combustion products of petrogenic sources.

Table 4. Diagnostic Ratio of PAHs in Balogun-Biiro Dumpsite, Oshogbo

Sampling Points	**Phen/ Anth**	**An/Phen + An**	**Flan/ Pry**	**Flan/(Pry + Flan)**	**B(a)P/ Chry**	**B(a)A/(B(a)A + Chy)**	**IP/IP+ B(ghi)P**	**LMW/ HMW**
S1	0.067	0.94	0.28	0.22	069	0.83	0.45	0.23
S2	2.86	0.26	0.38	0.27	0.81	0.43	0.94	1.05
S3	18.4	0.05	27.17	0.96	0.97	0.43	0.88	6.82
S4	1.82	0.36	2.80	0.74	0.88	0.43	0.90	0.96
S5	10.5	0.086	2.66	0.73	1.47	0.39	0.97	0.46
S6	0.08	0.93	2.22	0.69	0.67	0.29	0.69	6.60
S7	0.94	0.52	1.49	0.60	0.89	0.61	0.98	0.92
S8	0.02	0.98	0.26	0.20	0.68	0.83	0.44	0.15
S9	1.74	0.36	2.71	0.73	0.08	0.43	0.90	0.96
S10	0.002	0.10	0.25	0.20	4.43	0.72	0.49	0.72

Fluroanthrene (Flan), Pyrene (Pyr); Anthracene (An); Phenanthrene (Phen); Low molecular weight (LMW); High molecular weight (HMW); Benzo[a]pyrene, B(a)P; Benzo[a]anthracene, (B(a)A); Benzo[ghi]pyrene, B(ghi)P; Indeno[123Cd]pyrene, (IP)

Conclusion

The study has assessed the level, source and impact of waste dumpsite on the soil quality and human health within the vicinity of the Balogun-Biiro Dumpsite in Osogbo, Nigeria. It is evident that there is contamination of the soil within the vicinity of the dumpsite by PAHs. The PAHs resulted mostly from pyrogenic sources which includes indiscriminate burning of refuse and biomass. The mechanic workshops within the area have also contributed to the contamination of the soil by petrogenic PAHs. The dumpsite constitutes a health risk for the people living within the vicinity of the dumpsite due to the accumulation of carcinogenic PAHs in the dumpsite soil which could leach to groundwater and runoff into nearby surface water bodies around the area. Therefore, it is recommended that an improved waste management system should be established and the area should be remediated.

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