Determination of polycyclic aromatic hydrocarbons (PAHs) on selected dumpsites in Abeokuta Metropolis, SW, Nigeria

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Abstract

Knowledge of the concentration of polycyclic aromatic hydrocarbon (PAHs) in urban soils remains insufficient in developing countries like Nigeria despite their toxic effects and suspected human carcinogens, mutagens and endocrine disruption. This study aimed to determine the concentration of PAHs in soil of three dumpsites in Abeokuta metropolis, Ogun State, Nigeria. Concentrations of individual PAHs were determined using Gas Chromatography Flame Ionization Detector (GC-FID). The total PAHs concentrations at 0-15 cm depth were 29.0 mg/kg, 41.6 mg/kg and 11.9 mg/kg for Igbore, Saje and Alogi dumpsites respectively while the corresponding total PAHs concentrations at 15-30 cm depth were 9.3 mg/kg, 28.3 mg/kg and 11.0 mg/kg respectively. These concentrations were slightly lower than the Dutch guideline limits of 40 mg/kg except for that of Saje at 0-15 cm depth. The amounts of fluoranthene at Igbore dumpsite in the two depths were 23.64 mg/kg and 8.02 mg/kg, with a total sum of 10 PAHs compounds of 19.12 mg/kg. The results showed that the highest concentration of a single PAHs compound was at Saje dumpsite with fluoranthene value of 33.75 mg/kg and 22.74 mg/kg at the depths of 0-15 and 15-30 cm respectively. Isomer ratio for fluoranthene/pyrene was 2.69 at Alogi dumpsite, which suggested that the PAHs were from pyrogenic sources. Carcinogenic PAHs constituted about 1.29-15.69% of the total PAHs detected in the dumpsite raising concerns of human exposure through the food chain.

Keywords: Solid waste; open dumpsite; polycyclic aromatic hydrocarbons; contamination; health risk; toxicity

Introduction

Soil pollution is of high priority in urban centres due to factors such as industrialization, urban population growth, increasing motor vehicle ownership and the likes that generate many wastes. Inadequate waste management has important public health implications being the main carrier and propagator of infectious diseases apart from water. Worldwide, cities are typified and faced with several pressing challenges, ranging from population explosion, unemployment, crime, waste management, and general environmental degradation [1]. Presently, so many people are now living in the cities and increasing volumes of waste are becoming a real headache for town planners, developers and local authorities concerned [1-4]. Waste is an inevitable aspect of human life because all human activities such as domestic, commercial, industrial, healthcare and agriculture generate wastes which can pose risk to the environment and to public health [5-10]. In 2007, the average waste generated per capita in Organisation for Economic Cooperation and Development (OECD) countries was 556 kg, while the amount of waste generated in cites in developing countries is also rapidly increasing [11]. For instance, Bangkok (Thailand) and São Paulo (Brazil) generate 534 and 550 kg per capita respectively. Kuala Lumpur (Malaysia) generates more than the OECD average, at 815 kg per capita per year [12-13]. Abeokuta (Nigeria) alone generates 2.288 m^3 of wood wastes per day from sawmills activities [14]. Nigeria as a developing country is faced with limited options for safe waste disposal, thus faces significant risk of epidemic and other health hazards from indiscriminately disposed waste.

Open dumpsites are characteristics of Nigerian cities and lower-income people disproportionately reside around these sites where they are exposed to chemicals that are present in amounts far above what is safe for people and for wildlife. Municipal solid wastes are mostly burnt in the open dumpsites/ incinerators and these discharges pollutants into the air, water and soil leading to occupational and environmental exposures to toxic chemicals and subsequent health risks affecting waste workers, the general public, and the environment. Burning creates thick smoke that contains carbon monoxide, soot and nitrogen oxides, all of which are hazardous to human health and degrade urban air quality. Air pollutants deposited on soil, vegetation and water can lead to indirect exposures through ingestion of locally produced foods or water, and dermal absorption due to contact with contaminated dusts, soil and water [15]. Pollutants come from different mix of pathways for persistent and/or bioaccumulative pollutants, e.g., polycyclic aromatic hydrocarbons (PAHs), dioxins, and furans that undergo chemical and physical transformations, cycling in and out of soil, vegetation, and surface water [16-18]. PAHs are a group of chemicals that are formed during the incomplete burning of coal, oil gas, wood, garbage, or other organic substances, such as tobacco and charbroiled meat, coal and gasoline [19-25]. Once these compounds are released into the air by any process, they are transported to the far areas and may be deposited on soil particles, plants and in water bodies [26-28]. PAHs may play a role in the health effects of respirable particulate matter, often measured as PM10 or PM2.5 concentrations in air [21, 29-31]. They are regarded as environmental pollutants [30, 32]. and are of great concern because they are toxic to aquatic life and because several are suspected human carcinogens, mutagens and some are suspected endocrine disrupters [17, 21, 33-36]. Carcinogenic PAHs include: Benzo (a) anthracene (B[a]A), Benzo(a)pyrene (B[a]P), Benzo(b) fluoranthene (B[b]F), Benzo (k) fluoranthene (B[k]F), Chrysene (Chry), indeno[1,2,3-cd] pyrene (IP), dibenz [a,h]anthracene (Db[a,h]A) [34].

PAHs, in particular: naphthalene, 1-methyl naphthalene, 2-methyl naphthalene, Acenaphthene, 2-ethynaphthalene, fluorine, phenanthrene, anthracene, fluorantharene and pyrene are found to be problem in the soil [15, 31, 37]. Principal isomers such as phenanthrene, fluoranthene and pyrene produced in burnt waste have very limited water solubility and are likely to be immobilised largely due to sorption onto the waste and superficial soils [38-39].

Efforts to control the emission of PAHs have led to the use of source identification methods [21] and certain PAHs concentration ratios to benzo[e]pyrene (B[e]P) have been successfully used to differentiate PAHs sources [21,40]. However, Dachs *et al.* [41] that profiles obtained from environmental monitoring may differ from actual source data due to factors such as mixing of PAHs from different sources, degradation during transport, weather condition and type of fuel used in a particular source. In other studies such as Shen *et al.* [42], BeP is sometimes used to indicate the aging process of PAHs rather than source apportionment. Inadequate information, insufficient resources and poor legislation encourage uncontrolled and improper dumping of waste in many state capitals in Nigeria [43] thus exposing the people to health risks associated with PAHs. The greater amounts of PAHs observed in most urban soils and the close proximity of these soils to humans may increase the probability of human exposure to these pollutants via inhalation, ingestion, or dermal contact [44]. However, knowledge of the long-term fate of compounds such as PAHs in most urban centres in Nigeria remains insufficient therefore, it is imperative to determine and monitor concentrations of PAHs in the soils of dumpsites. This is an essential step in reducing the possible risk to people living nearby. Accurate assessment requires information on the concentrations and compositions of the PAHs in the dumpsites; and clarification on their long-term fate in the environment. The aim of the study was to determine the concentration of polycyclic aromatic hydrocarbon in three dumpsites in Abeokuta metropolis, Ogun State, Nigeria, and to compare them with those of international standards such as the Netherlands Ministry of Housing, Spatial Planning and the Environment [45]. The specific objectives of study also included the determination of the physicochemical properties of soil samples obtained from the dumpsites.

Materials and methods
1) Study area

Abeokuta metropolis is the administrative headquarters of Ogun state, southwestern Nigeria. It is situated between latitude 3° 20′ and 3° 54′ and longitude 7° 9′ and 7° 39′ on the east bank of the Ogun River, around a group of rocky outcropings that rise above the surrounding wooded savanna. Major part of the metropolis is in the Abeokuta South Local Government Area, with other parts extending into other local government areas such as Abe kuta North and Odeda. Abeokuta is the largest city in the state regarded as the "Gateway to Nigeria". It lies about 78 km north of Lagos, and presently covers about 2320 km^2 of land which have continued to expand in all direction due to increasing urbanization and rapid population growth. Abeokuta metropolis had a population of 593,140 according to the 2006 census [46] with estimated growth rate of 3%. The entire city is characterized by the problem of very poor solid waste management with major centres polluted with heaps of refuse. Refuse are dumped on roadsides, road median, road junctions, and market places. In many cases, especially after the monthly sanitation exercise, refuse are dumped directly on the roads obstructing traffic flow and causing traffic congestion.

2) Sampling sites

Sampling sites were located in three different open dumpsites namely Saje (N07°10′, E03°23′), Igbore (N07°09′, E03°20′) and Alogi (N07°17′, E03°25′) all in Abeokuta, Southwestern Nigeria (Fig. 1). The selection of these dumpsites was based on the fact that the only major legal (controlled) solid wastes landfill recommended by the State Waste Management Board (SWMB) and other two illegal (uncontrolled) ones created by the public were considered. Major activities within the vicinity of the dumpsites were markets, residential, transportation, auto mechanic workshops, hospitals, sawmill and motor parks.

All these activities contribute different types of waste disposed on the selected dumpsites. Generally the wastes in the dumpsites include household waste (kitchen garbage), plastics, ceramics, paper, glass, fabrics, metals, commercial and non-hazardous industrial wastes and electronic wastes. Geographical coordinates of all locations were taken using a Garmin (GPSMAP) Global Positioning System (GPS).
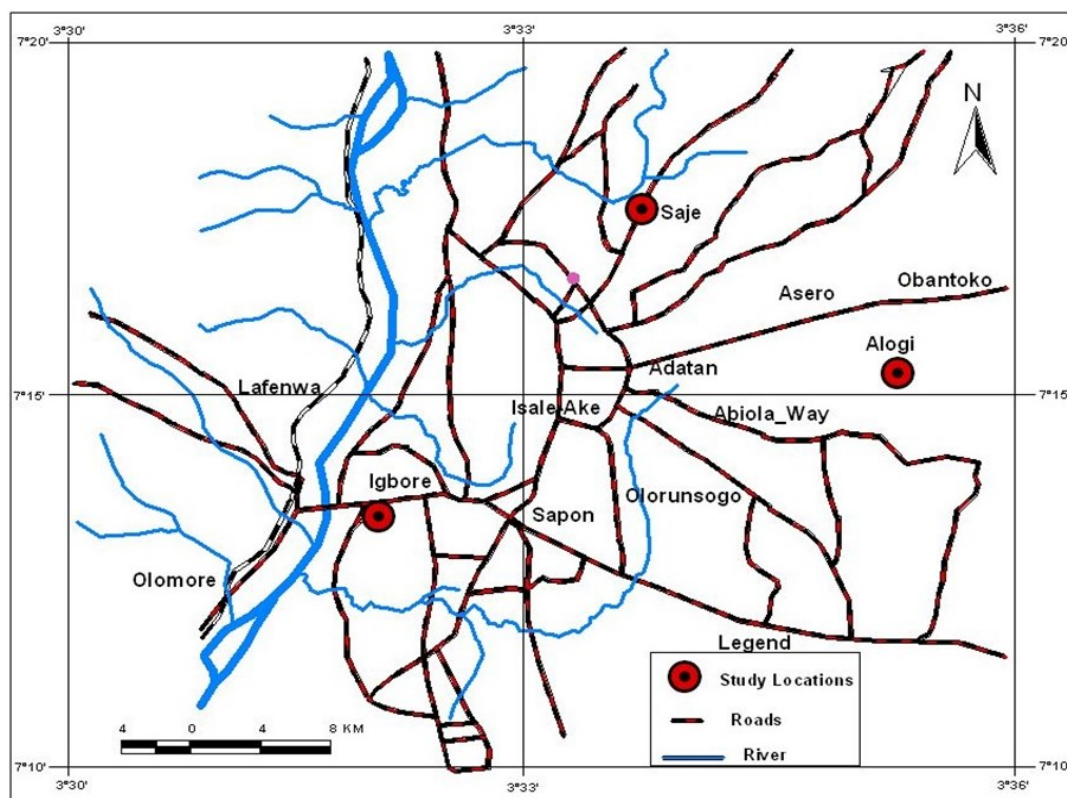

Figure 1 Location of selected dumpsites in Abeokuta

3) Collection of soil samples

This study analysed sixteen different PAHs (Naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(ah) anthracene, benzo (ghi)perylene, and indeno (1,2,3-cd) pyrene) which were obtained from dumpsite soils from different parts of Abeokuta metropolis. Collection of soil samples were conducted according to the method of [47]. There were five sampling points on each dumpsite. Undisturbed surface soil was collected from the selected dumpsites with the aid of a stainless soil auger at a depth of 0-15 cm (top soil) and 15-30 cm (subsoil). Soil samples consisted of composite of five sub-samples each collected from the four corners and the centre of a 10 m×10 m square in the dumpsites at the two different depths. Composited soil samples were transferred into polyethylene bags for transportation to the laboratory. Top soil (0-15 cm) samples were also taken from a site located about 5 km away from the dumpsite to serve as control. The control site is of minimal human activities and is not a dumpsite.

4) Soil preparation and analysis

Soils used for the determination of physico-chemical properties were dried at ambient temperature (22°C), crushed in a porcelain mortar and sieved through 2 mm mesh sieve. Physicochemical properties were determined in triplicates.

4.1) Determination of pH

Soil pH was determined according to [48]. Twenty millilitres of distilled water was added to 10 g of soil sample in a glass beaker. The solution was shaken

for 20 min using electrically operated shaker for proper mixing, left for 30 min, and shaken again for 5 min. The pH of the supernatant was then determined using Orion research digital pH meter model 407.

4.2) Moisture Content

The moisture content of the soil is an indication of the amount of water present in the soil. It was determined according to the method described by [49]. One gram of a representative sample of the soil was placed in a clean dry crucible of known mass. The mass of the container and soil were determined (W_2) using an analytical balance (OHAUS Advance AR 3130 Model). The crucible was placed in an oven maintained at $110\pm5°C$ for 4 h to obtain a constant weight (W_1). The measurement was done in duplicate. Percentage moisture was calculated as follows:

% Moisture = $(W_2 - W_1)$/Sample weight

where W_2 = weight of crucible+weight of sample before oven drying and W_1 = weight of crucible+ weight of sample after oven drying.

4.3) Particle size analysis

Particle size analysis was determined according to the method of [50]. Fifty grams of the soil sample was soaked overnight with 50 ml of cagon solution. The mixture was then transferred into a 1000 ml measuring cylinder and was made up to mark. The mixture was shaken and left for 40 s before dipping the hydrometer into it to determine the sandy content while the clay and silt were determined after 3 hrs interval (for the mixture to settle down) through the same process. The temperatures were then recorded simultaneously. Percentage sand, percentage clay and percentage silt were calculated as follows:

% sand = $100 - [H_1 + 0.2(T_1 - 68) - 2.0]2$
% clay = $[H_2 + 0.2(T_2 - 68) - 2.0]2$
% silt = $100 - (\% \text{ sand} + \% \text{ clay})$

where H_1 and H_2 were the hydrometer readings at 40 s and 3 h respectively at corresponding temperature readings T_1 and T_2

4.4) Determination of organic carbon

The organic carbon content of soils was determined by the Walkey-Black and digestion method as described by [49]. About 1 g of soil sample was placed into a block digester tube (sample weight) and 5 ml of potassium dichromate solution and 7.5 ml of concentrated H_2SO_4 were added. The tube was placed in a pre-heated block at $145-155°C$ for 30 mins; it was then removed and allowed to cool. The digest was quantitatively transferred into a 100 ml conical flask and 0.3 ml of O-phenanthrene-ferrous complex (ferroin) indicator solution was added, then stirred and mixed properly using magnetic stirrer. The digest was titrated with ferrous ammonium sulphate solution with end point indicating a change from greenish to brown colouration. The organic carbon content expressed in percentage as follows was based on 77% recovery factor:

%Organic C = $[N(T-B)/W] * 0.390$

Where N = Normality of $KMnO_4$,
        T = Volume of $KMnO_4$ used in titration of soil
        B = Volume of $KMnO_4$ used in titration of blank
        W = Weight of soil in gram.

4.5) Organic Matter Content

The organic matter content in the soils was determined by multiplying the organic carbon content from the procedure above by 1.742 using the assumption that organic matter content is approximately 58 % carbon [49].

4.6) Determination of PAHs in Soil.

The PAHs determination was done using GC-FID and this entailed several operations including extraction, purification, and concentration. Prior to extraction, soil samples were air-dried openly on the benches in the laboratory for 48 h. The dried soil samples were then sieved using a 2 mm sieve. The soil samples extraction was done according to the method of [51]. The soil extraction process involved the use of an automatic soxhlet extraction (SELECTA, DE TGRASN). Fifty grams of the soil samples placed in a thimble were introduced into the Soxhlet ap-

paratus with 60 ml of Hexane/Ace- tone (50:50) for 30 mins. The solvent in the extract was allowed to evaporate at 105°C in an oven (Memert 100-800). The pure extract was saponified at 70°C for 2 h in a drying cabinet using 60 ml of 3.5 M methanolic KOH in a sealed flask. The flask was shaken vigorously after the first 1 h and allowed to complete the cycle. Fifty millilitres of cyclohexane was added into the flask, shaken and then transferred into a 250 ml flask with separating funnel. The flask was rinsed with 30 ml of methanol/water (4:1) and transferred into the separating funnel. The separating funnel was shaken vigorously and allowed to stand in order to separate into layers. The aqueous layer was decanted into another separating funnel and washed with 30 ml cyclohexane. The cyclohexane layer was combined with the content of the other separating funnel and rewashed with 30 ml methanol water (4:1) this was decanted and the cyclohexane phase was washed with 30 ml methanol/water (1:1), and then decanted, and cyclohexane phase was washed with 30 ml of water and allowed to separate. The cyclohexane phase was separated and concentrated to 2 ml in rotary evaporator (SEARCH Tech Instrument, RE52-2).

4.7) Cleaning of sample extract and packing the column

Silica gel (60-200 mesh) was activated at 105°C in an oven for two (2) hours. This was used to pack the column in a glass tube of about 1 cm internal diameter. Cotton wool was pre-soaked in dichloromethane (DCM) and then dried. The dried cotton wool was used to plug the tube at its base. One gram of activated silica gel was added into the tube and then tapping it to ensure that the silica was well settled to form a well packed column. Sodium sulphate was added to cover the surface of the silica gel in the tube and about 2 mm thickness was added to trap moisture (water).

4.8) Clean up

The column was preconditioned using 15 ml hexane and immediately 1 ml of reconstituted sample

was introduced on the sodium sulphate surface in the column, and gradually, 60 ml of GC-grade hexane was used to elute the sample into a DCM cleaned flask, this is the aliphatic fraction. The PAH fraction was eluted using 40 ml DCM and collected in round bottom flask. The fractions were concentrated to 1 ml in rotary evaporator, transferred into a 2 ml vial ready for injection in GC.

5) Sample analysis

The determination of PAHs was performed on a high resolution gas chromatograph system Agilent 5890 Series 11 gas chromatograph equipped with Flame ionization detector (GC-FID), with on-column capillary injection system and Hewlett-Packard model 7673 autosampler. One micro-litre of each sample was injected by the auto-sampler into the splitless mode. The separation was performed on fused silica capillary columns DB-5, 30 m x 0.25 mm internal diameter, and 0.25 μm film thickness (5% phenylsilicone, 95% methylsilicone). High purity nitrogen was used as carrier gas at flow rate of 1 mL/min and 30 mL/min respectively. The oven temperature programmed was as follows: initial temperature of 80 °C was held for 2 min, increased to 190 °C at 5 °C/min, and then increased to 280 °C at 10 °C/min. The injector and detector temperatures were set at 250 °C and 300 °C, respectively. Identification of the individual PAHs was based on comparison of retention time between samples and the standard solution. Quantification was performed by five-point calibration method (from 100 to 500 ng/mL, $r^2 > 0.992$) in all cases. The internal standard defluorobiphenyl used for recovery studies was purchased from Accustandard USA. The recoveries were satisfactory and ranged from 78.66-102.5.

5.1) GC-FID analysis conditions

An Agilent 5890 Series 11 gas chromatograph fitted with Flame ionization detector (GC-FID), with on-column capillary injection system and Hewlett-Packard model 7673 autosampler. The fused silica capillary columns DB-5, 30 m x 0.25 mm internal diameter and 0.25 μm film thickness (5 % phenyl-

silicone, 95 % methylsilicone). High purity nitrogen was used as carrier gas at flow rate of 1 mL/min and 30 mL/min respectively. The separation was performed in splitless mode with an oven temperature pro-grammed from 80 $^\circ$C was held for 2 min, increased to 190 $^\circ$C at 5 $^\circ$C/min, and then increased to 280 $^\circ$C at 10 $^\circ$C/min. The injector and detector temperatures were set at 250 $^\circ$C and 300 $^\circ$C, respectively.

6) Statistical Analysis

Data were analysed using descriptive statistics viz range, mean±standard deviation. Simple cor-relation analysis was used to examine the relation-ship between some of the analysed PAHs present in the soils. Statistical analyses were done with Pear-son bivariate correlation at 0.01 and 0.05 signi-ficance levels using SPSS Package (17.0 Version).

Results and Discussion

The pH of the soil and other selected physico-chemical properties are shown in Table 1. The soils generally had pH ranging from 6.65 to 7.85. The mean soil pH for Igbore, Saje and Alogi dumpsites was 7.14±0.17, 7.70± 0.09 and 7.33±0.10 at both depths respectively, indicating a slightly alkaline pH of soil. The mean pH was above the critical value of 6-6.5, which has implications on soil nutrients. Most soil nutrients are readily available when soil pH is at 6.5, but when pH rises above this level, nutrient elements such as manganese, phosphorous, iron, and copper and zinc will become less available. When soil pH drops below 6.5, man-ganese can reach toxic level for some sensitive plants. In addition, the mean soil organic carbon content of Igbore, Saje and Alogi dumpsites were 7.15±0.32, 5.57±0.60 and 1.10±0.09 at both depths respectively. Organic carbon content of Alogi dump-site soil was below critical value (3-5). Low organic carbon content in Alogi soil showed that there was increase in weathering activities (photochemical oxi-dation) and leaching of water-soluble organic matter, while Saje and Igbore were above the critical value. Igbore dumpsite soil had the highest mean organic matter (12.39±1.12) followed by Saje (9.70±0.60) and lowest value was found in Alogi (2.50±0.10) for both depths. From the result, it was shown that three different dumpsites soil contain different proportion of organic matter in them and this might be due to variation in soil properties and environmental factors.

The soil texture was predominately sandy loam at the Alogi and Saje dump sites, while that of Igbore was a loamy sand (Table 1), which might be due to the large volume of human waste disposed at this site. Human excreta were observed to litter the dumpsites since most people living close to the sites lack sanitary facilities.

Table 1 Mean with standard deviation and range of physico-chemical properties of soils in Alogi, Saje and Igbore dumpsites (n=3)

Location	Mean/Range (depth)	pH	Texture	Sand (%)	Silt (%)	Clay (%)	Organic matter (%)	Moisture content (%)	Temperature (°C)
Igbore	Mean±SD	7.14 ± 0.17	Loamy sand	82.02 ± 0.9	8.64 ± 1.06	9.34±0.92	12.39±1.12	4.39±0.02	27.45±2.17
	Range (0-15 cm)	6.65 - 7.30		79.52 – 81.50	8.0 – 12.0	8.48 – 10.48	11.73 – 13.80	4.49 – 5.58	27.3 – 27.80
	Range (15-30 cm)	7.26 – 7.38		83.52	5.28 –9.20	7.2 – 11.20	11.21 – 12.42	4.09 – 4.39	27.3 – 27.70
Saje	Mean±SD	7.70 ± 0.09	Sandy loam	71.52 ± 0.8	13.24±1.06	15.24±1.0	9.70±0.6	8.28±0.01	27.83±2.13
	Range (0-15 cm)	7.45 - 7.85		69.52-70.00	17.28 – 18.00	12.48 – 13.22	9.49 – 12.42	8.28 – 8.58	27.3 – 27.80
	Range (15-30 cm)	7.74 - 7.77		72.09-73.52	8.48 – 11.20	15.28 – 18.00	6.93 – 9.66	7.88 – 8.38	27.4 – 28.80
Alogi	Mean±SD	7.33 ± 0.10	Sandy loam	77.52 ± 0.8	12.76 ± 0.15	9.72±0.5	2.51±0.1	4.79±0.01	27.55±2.06
	Range (0-15 cm)	7.43 - 7.44		75.52–77.52	13.28-14.00	9.2 – 11.20	2.59 – 2.69	4.59 – 5.09	27.5 – 27.80
	Range (15-30 cm)	7.43-7.46		77.52 – 79.56	9.20 – 13.28	9.2 – 11.28	2.28 – 2.42	4.49 – 4.99	27.4 – 27.50
Control	Mean ±SD	6.20±0.02	Loamy sand	80.04 ± 0.05	9.46±0.05	10.50±0.06	13.07±0.03	10.06±0.02	27.5±0.05
	Range (0-15 cm)	6.10-6.30		78.96-81.12	9.50-10.2	10.46-10.53	13.04-13.10	10.04-10.08	27.3 – 27.80

1) Concentration levels of PAHs

Table 2 shows the concentrations of PAHs at both depths of soil from three dumpsites. Acenaphthene, fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, di benzo (a,h) anthracene were found in detectable and measurable amount at both soil depths at Igbore dumpsite, while naphthalene, acenaphthylene, fluorene, acenaphthene, anthracene, fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno (1,2,3-cd) pyrene were found in both soil depths at Saje dumpsite. More so, at the Alogi dumpsite some different PAHs were detected along with the ones detected from two other dumpsites such as phenanthrene, pyrene and chrysene at the depth of 0-15 cm, naphthalene, acenaphthene fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, di benzo(a,h), anthracene at both soil depths. The PAH analysis showed that five out of sixteen PAHs prioritized by EPA/WHO were present in soil at Igbore dumpsite, while ten and nine PAHs were present at Saje and Alogi dumpsite soil respectively. Only two PAHs (acenaphthene and fluoranthene) were detected in the soil samples taken from the control site at very low concentrations (0.20 and 1.26 mg/kg respectively). The structures of the fourteen detected PAHs are shown in Figure 2.

The maximum PAHs concentration found in Igbore dumpsite soil was fluoranthene (23.64 mg/kg) and the minimum was dibenzo (a,h) anthracene (0.16 mg/kg) at the depth of 0-15 cm, while at the depth of 15-30 cm, the maximum PAHs concentration was fluoranthene (8.12 mg/kg) and the minimum was benzo(k) fluoranthene (0.12 mg/kg). Furthermore, the maximum PAHs concentration found in Saje dumpsite soil was fluoranthene (33.75 mg/kg) and the minimum was acenaphthylene (0.80 mg/kg) at depths of 0-15 cm and at the depth of 15-30 cm the maximum PAHs concentration was fluoranthene (22.74 mg/kg) and the mini- mum was acenaphthylene (0.05 mg/kg). However, the Alogi dumpsite soil does not follow the same trend as other dump-sites because the maxi- mum concentration in Alogi was fluoranthene (7.75 mg/kg) at the depth of 15-30 cm and the minimum was naphthalene (0.08 mg/kg) at the depth of 0-15 cm. The highest concentration of PAHs was found at the depth of 0-15 cm in Igbore and Saje except in Alogi.

Concentration of PAHs decreases with depth in both Igbore and Saje dumpsite soils. Saje had the highest PAHs concentration out of the three dumpsites, and this value could result in serious health hazards. The high value of PAHs obtained may be due to burning of plastic materials, printer roller, electronic waste and other domestic garbage being disposed on the site. PAHs in soil contaminate underground water when leached into it, which might lead to pollution of nearby water sources and aquatic ecosystem. It might cause great loss in aquatic lives such as fishes and other marine species which when consumed by human might lead to serious health effects.

The mean value for the sum of ten PAHs compound in the soil at Saje dumpsite was 34.95 mg/kg at both soil depths, which was very close when compared with the intervention level (level for soil remediation) for the sum of ten PAHs. Though this value was slightly lower than the Dutch guide-line limits, it could still lead to serious health hazard to the community when these compounds leach into the nearby water bodies. The mean value for the sum of ten PAHs compound in soil at Igbore and Alogi dumpsites was (19.17 mg/kg) and (11.49 mg/kg) at both soil depths respectively and their values were lower than the "intervention level" for the sum of PAHs, defined for a standard soil at the "new Dutch list" which specifies the value of 40 mg/kg for a total sum of ten PAHs in soil as reported in [52]. PAHs are subject of studies due to the harmful effects they have on the environment and the health of human being due to their high degree of mutagenicity and carcinogenicity [53]. Consequently, elevated levels are typically found in urban environments, with strong correlations

between the levels of PAHs in the environment and population density being frequently observed [54-57]. Although they are relatively insoluble in water, their highly hazardous nature merits their positioning in potable waters and wastewaters [58-59]. PAHs accumulate in bottom sediments in urban streams and are taken up by aquatic organisms. In non-polluted areas, studies have shown that the PAHs concentrations were usually in the range of 5 - 50 mg/kg originating from industries and other diffuse sources.

Table 2 Concentrations of PAHs (mg/kg) in soils of Alogi, Saje and Igbore dumpsites

USEPA PAHs	Igbore		Saje		Alogi		Control
	0-15cm	15-30cm	0-15cm	15-30cm	0-15cm	15-30cm	0-15cm
Two-ring							
Naphthalene	ND	ND	1.56	ND	0.08	ND	ND
Three-ring							
Acenaphthylene	ND	ND	0.80	0.05	ND	ND	ND
Fluorene	ND	ND	3.22	0.10	ND	ND	ND
Acenaphthene	1.00	1.06	0.88	3.62	3.30	2.88 0.20	
Phenanthrene	ND	ND	ND	ND	0.40	ND	ND
Anthracene	ND	ND	ND	0.64	ND	ND	ND
Four-ring							
Fluoranthene	23.64	8.12	33.75	22.74	4.81	7.75 1.26	
Pyrene	ND	ND	ND	ND	ND	ND	ND
Benzo(a)anthracene	ND	ND	ND	ND	ND	ND	ND
Chrysene	ND	ND	ND	ND	0.45	ND	ND
Five-ring							
Benzo (b) fluoranthene	4.00	ND	ND	0.23	0.08	ND	ND
Benzo (k) fluoranthene	0.23	0.12	1.29	0.19	0.85	0.40	ND
Benzo (a) pyrene	ND	ND	ND	0.56	ND	ND	ND
Dibenz(a,h)anthracene	0.164	ND	ND	ND	0.18	ND	ND
Six-ring							
Indeno(1,2,3-c,d)pyrene	ND	ND	ND	ND	ND	ND	ND
Benzo(g,h,i)perylene	ND	ND	ND	0.218	ND	ND	ND
Min	0.16	0.10	0.80	0.05	0.08	0.40 0.20	
Max	23.64	8.12	33.75	22.74	4.86	7.75 1.26	
Σ 16 PAHs	29.0	9.30	41.6	28.3	11.9	11.0 1.46	
Mean PAHs @both depths	19.2		34.9		11.5 0.73		
Σ Carcinogenic PAHs*	4.55	0.12	1.29	0.98	1.38	0.40	-
% Carcinogenic PAHs	15.69	1.29	3.10	3.46	11.6	3.64	-

*Carcinogenic PAHs: Benzo (a) anthracene (B[a]A), Benzo(a)pyrene (B[a]P), Benzo(b)fluoranthene B[b]F), Benzo(k)fluoranthene (B[k]F), Chrysene (Chry), indeno[1,2,3-cd] pyrene (IP), dibenz [a,h]anthracene (Db[a,h]A)
Source: Boström *et al*. (2002)
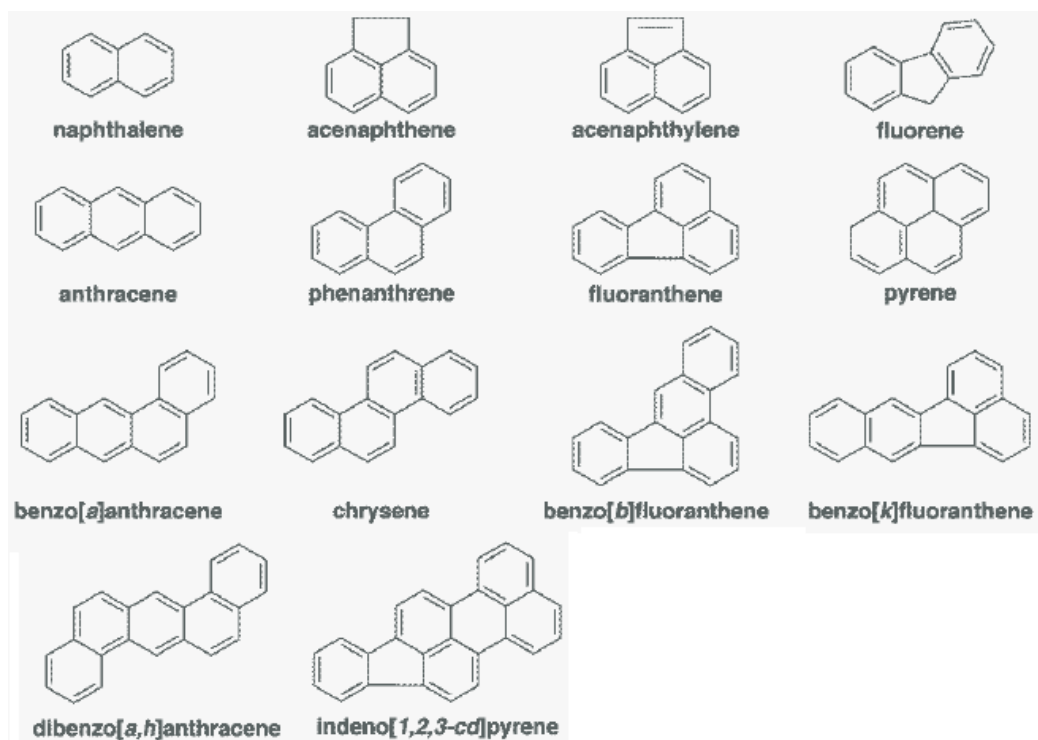ND - Not Detected; detection limits for all the PAHs were 0.02 mg/kg

Figure 2 Structures of 14 identified PAHs in soil

2) Correlation analysis

Table 3 shows that Naphthalene had a significantly high correlation with other PAHs such as Acenaphthylene (0.999), Fluorene (0.999) at 0.05 level of significance, while Acenaphthene was also significantly correlated with Phenanthrene, Pyrene and Chrysene. This positive correlation among the PAHs possibly indicates that all landfills are of similar geological nature. Positive correlations ($r^2 = 0.032$; $p = 0.05$) were observed between organic matter content and PAHs in dumpsite soils in the study area (Figure 3). It implies that high amount of PAHs mainly occur in soils with high organic matter content. This corroborated with studies that have shown that organic matter played an important role in controlling PAHs in polluted soils [57, 60-61].

Table 3 Correlations of 10 Dutch listed PAHs found in the study areas

	Nap	Acena	Flu	Ace	Anth	Flh	B[b]F	B[k]F	B[a]P	IP
Nap	1									
Acena	0.998*	1								
Flu	0.999*	1.000*	1							
Ace	-0.542	-0.531	-0.538	1						
Anth	-0.993	-0.996	-0.998	0.537*	1					
Flh	0.771	0.763	0.768	-0.953	-0.768	1				
B[b]F	-0.498	-0.508	-0.501	-0.459	0.502	0.169	1			
B[k]F	0.810	0.818	0.813	0.054	-0.813	0.251	-0.912	1		
B[a]P	1.000*	1.000*	1.000*	-0.538	-1.000	0.768	-0.502	0.813	1	
IP	0.504	0.493	0.500	-0.999	-0.500	0.938**	0.498	-0.098	0.500	1

* Correlation is significant at the 0.05 level (2-tailed)

Naphthalene (Nap), Acenaphthylene (Acena), Acenaphthene (Ace), Fluorine (Flu), Anthracene (Anth), Fluoranthene (Flh), Benzo (a) anthracene Benzo (b) fluoranthene [B(b)F], Benzo (k) fluoranthene [B(k)F], Benzo (a) pyrene [B(a)P], In-deno(1,2,3-cd)pyrene {[IP]
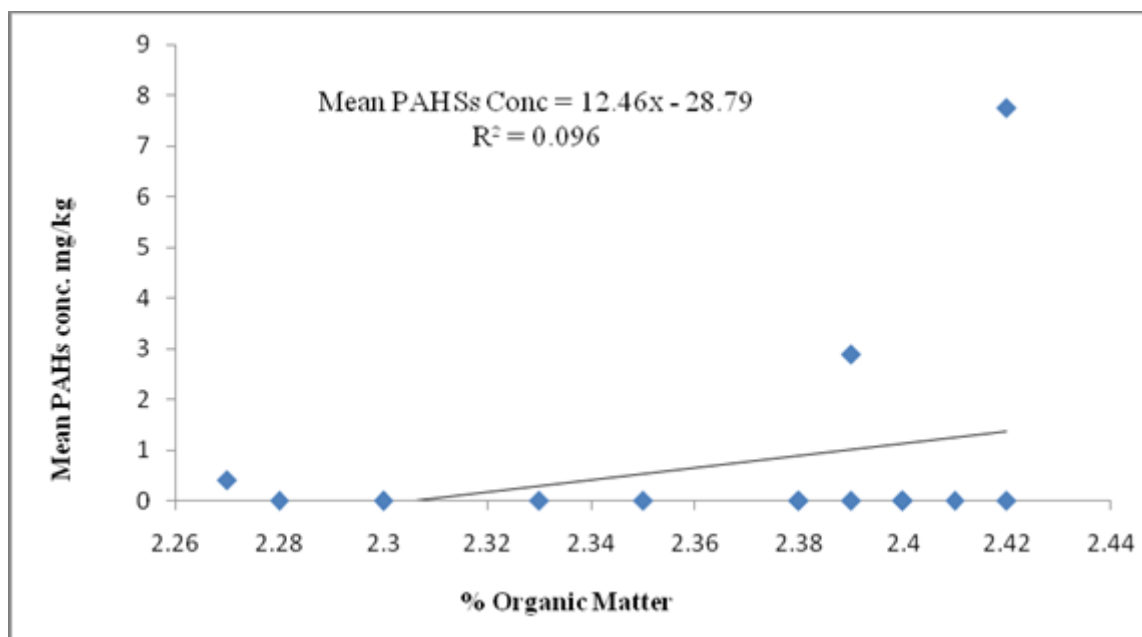
Figure 3 Relationship between organic matter content and
the concentration of sum of PAHs in the dumpsites.

3) Sources of PAHs in dumpsite soils

To discern the sources of PAHs in soils, various researchers [62-63] have used the diagnostic or isomer ratios of different PAHs. Isomer ratios phenanthrene/anthracene {Phe/Anth}, Benzo (a) anthracene/chrysene {B[a] A/Chry}, and fluoranthene/pyrene {FLH/PYR} have being used to suggest the sources of the PAHs. Fluoranthene /pyrene ratio (FLTH/PYR) is often used to distinguish between pyrolytic and petrogenic sources [64-65]. Fluoranthene is less thermodynamically stable than pyrene and a predominance of FLH over PYR is characteristic of pyro- genic source. Ratios of FLH/PYR was only determined for topsoil (0-15 cm) at Alogi because most of the PAHs were below detection limits at other sites. The FLH/PYR for the topsoil at Alogi dumpsite was 2.69. It is well known that the fluoranthene /pyrene less than one indicates petrogenic source of contamination while a ratio of more than one indicates pyrogenic sources [64,66]. Furthermore, the ratio of fluoranthene to fluoranthene + pyrene {Flh/ Flh +Pyr} was used to confirm whether the dominant source of PAHs in the dumpsite soils originated from the pyrogenic

processes. The Flh/ Flh +Pyr ratio for the topsoil at Alogi dumpsite was 0.728 which was corroborated by other studies [28, 64, 67-68]. Yunker and Macdonald had earlier suggested that the ratio of fluoranthene to fluoranthene + pyrene greater than 0.5 indicates pyrogenic sources, particularly the burning of fossil fuel [62].

Pyrogenic sources according to [69] include high-temperature combustion products such as incomplete combustion of organic materials (combustion of fossil fuel, vehicular engine combustion, smelting, and waste incinerators). Pyrogenically produced PAHs are primarily compounds with unsubstituted aromatic rings and these PAHs are often called parent PAH structures [70]. Although the pyrogenic source seems to dominate, petrogenic sources could have made minor contributions due to the location of the dumpsites along major transport routes [71-72].

Conclusions

The research work showed that there were detectable, variable and non-detectable amounts of the 16 PAHs profile investigated in the soils from three different dumpsites at Saje, Alogi,

and Igbore within Abeokuta metropolis. The Saje dumpsite had the highest concentration of PAHs followed by Igbore. The soil samples from Saje and Igbore dumpsites were highly polluted with fluoranthene with an individual mean value (topsoil and subsoil) of 28.25 mg/kg and 15.88 mg/kg respectively and Alogi dumpsite having mean value of 6.28 mg/kg. The total sum for 10 PAHs compounds for Saje dumpsite was 35.49 mg/kg being the highest and only legal dumpsite in Abeokuta metropolis unlike the Alogi and Igbore dumpsites, which are illegal dumpsites. The study revealed that the dumpsites are principal sources of PAHs in the study area because of the combustion of wastes. Another reason may be due to the increasing vehicular traffic and other human activities around the areas. Uncoordinated and inadequate management of waste material on the dumpsites studied can undoubtedly present a pollution risk and a potential health hazard, therefore improvement in waste management system, restriction on the kind of waste that can be handled, and environmental legislations designed to minimize pollution should all ensure there is no significant risk to the health of the local population. It is recommended that the government should consider a basement treatment for dumpsites before use. This will provide sorption surfaces for pollutant and prevent groundwater contamination. In addition, it is important to ensure longterm safety from hazardous substances generated in the dumpsites.

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