# Concentration Assessment And Source Evaluation of Polycyclic Aromatic Hydrocarbons (PAHs) In Soil And Crops of The Agro-Industrial Tobacco Production Area of Igboho, Nigeria

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# Abstract

The contribution of tobacco smoking and cigarette butts to global environmental pollution has been given significant attention. However, little is known about tobacco-related agricultural activities on environmental pollution by polycyclic aromatic hydrocarbons (PAHs). In this study, the spatial distributions, composition, source, and toxicity potential of polycyclic aromatic hydrocarbons (PAHs) in soil and food crops within the vicinity of the agro-industrial tobacco production area of Igboho, Nigeria was investigated. Soil and food crop (*Zea mays*, *Dioscorea alata*, and *Manihot esculenta*) samples collected from the tobacco curing site and the surrounded farmlands were analyzed for the PAHs concentrations. The identification and quantification of priority PAHs in the samples were carried out using a gas chromatograph equipped with a flame-ionization detector. The total concentration of the priority PAHs in the soil ranged between 136.70 $ng.g^{-1}$ to 889.30 $ng.g^{-1}$. The total concentration of carcinogenic PAHs ranged from 6.07 $ng.g^{-1}$ to 321.04 $ng.g^{-1}$, and the total concentration of toxic PAHs ranged from 6.27 $ng.g^{-1}$ to 254.37 $ng.g^{-1}$. The PAHs level was highest in crops from farmlands closest to the tobacco curing site. The distribution of PAHs ring size is in the order of 6-rings  4-rings 5-rings  3-rings  2, and the diagnostic indices showed that the sources of PAHs in the samples were mainly pyrogenic and associated with tobacco curing activities in the area.


# Introduction

The investigation of toxic and carcinogenic compounds present in the environmental media and food items is a critical step towards reducing the incidence and mortality rate due to cancer. Tobacco use is a well-known threat to global health and responsible for the death of about 8 million people every year (World Health Organization 2019), accounting for about 10 % of annual death worldwide. The high risk of tobacco smoking is well known, but the effect of tobacco agro-industrial activities on the environment is least reported. However, serious health risks such as green tobacco sickness, some respiratory diseases, and exposure to agrochemicals, such as pesticides and herbicide, are prominent in the tobacco-growing communities (Taylor, Arcury, and Quandt 2017). In many tobacco growing countries, evidence indicates irreparable environmental damage from tobacco agriculture, significantly when associated with the release of dangerous compounds by curing tobacco leaves and extensive use of agrochemical for best control (WHO 2017). The manufacturing of tobacco products also produces an immense amount of waste. In 1995, the global tobacco industry produced an estimated 2.3 billion kilograms of manufacturing waste and 209 million kilograms of chemical waste (Kakad and Thakare 2017; WHO 2017). Exposure to toxic chemical compounds such as nicotine, N-nitrosamines, heavy metals, acetaldehyde, heterocyclic amines, and polyaromatic hydrocarbons (PAHs) have been linked to tobacco processing (U.S. Department of Health and Human Services 2010). Among them, PAHs comprise the largest class of mutagenic and carcinogenic chemicals and are ranked ninth among chemical compounds threatening humans (Ifegwu and Anyakora 2015). PAHs are a large group of carcinogenic and mutagenic compounds formed due to the incomplete combustion of organic compounds (Rengarajan et al. 2015). Most PAHs are persistent in the environment and bio-accumulate due to their hydrophobicity and lipophilicity. PAHs enter the food chain by consuming PAHs contaminated crops (Abdel-Shafy and Mansour, 2016; Khan and Cao, 2012). Plants absorb PAHs from the soils through their roots and translocate them to the other plant parts. Due to PAHs' known toxicity, various researchers have investigated the level of PAHs in agricultural soils and crops within the vicinity of various industrial activities (Wang et al. 2018). However, studies on the level of PAHs in soil and crops associated with agro-industrial tobacco activities have not been well reported. Therefore, this study investigated the level of

PAHs in soil and crops within the vicinity of an agro-industrial tobacco plantation in Igboho, Nigeria, and assesses the probable source of the PAHs contamination toxicity potential. Priority PAHs in the samples including Naphthalene (Nap); Acenapthene, (Ace-Nap), Acenaphtalene, (Ace-Nap), Fluorene, (Flu), Phenanthrene, (Phen), Anthracene, (Anth), Flouranthene (Flo), Pyrene (pyr), benzo(a)pyrene, (B(a)P), Benzo(a)anthracene (B(a)A), Benzo(b)fluoranthene (B(b)F), Benzo(k)fluoranthene (B(k)F), Indeno(123-cd)pyrene (IP), Dibenzo(a,h)anthracene (Dib(ah)A and Benzo(ghi)pyrene (B(ghi)P) were identified and quantified. The study provides a base-line report on the level of the identified PAHs in the study area.

## Materials And Methods

# 2.1. Chemicals and sample analysis

All chemicals were of analytical grade and purchased from Sigma Aldrich, including the 16 PAHs standard, potassium heptaoxodichromate (VI) ($K_2Cr_2O_7$), concentrated tetraoxosulphate (VI) acid ($H_2SO_4$), ferrous sulphate, hexane ($C_6H_{14}$), methanol ($CH_3OH$), dichloromethane ($CH_2Cl_2$), anhydrous sodium sulphate ($Na_2SO_4$) and silica gel (100–200 mesh, 75–100 µm) and alumina. All lab wares, including sample bottles, glass dropper, pipette, conical flask, beakers, and measuring cylinder, were made of glass and washed with deionized water and chromic acid before use.

# 2.2. Description of the study area and sample collection

Igboho is one of the largest towns sprawling over a vast grassland area in the northern part of Oyo State, Nigeria. It is located within 8.83784 latitudes and 3.75628 longitudes, situated at an elevation of 405 meters above sea level. The town is bounded by Igbeti town in the south, Saki town in the west, and Kisi town is in the north. Igboho is the headquarters of the Orelope Local Government Area of Oyo State, Nigeria, and has an area of 907 $km^2$ and has a population of 104,441 according to the 2006 Nigerian population census result (National Population Census). Igboho community adopted commercial flue-cured tobacco production in 1950, and industrial tobacco agriculture becomes the main activity in the area. The soil and food crop samples were collected from the farmland and the tobacco curing site. The study area was divided into three sampling stations based on the distance of the farmland from the tobacco curing sites and was identified as TBS for the tobacco curing site and $FL_1$, $FL_2$, and $FL_3$ for farmland at a distance of 20 meters, 50 meters, and 1.0 km away from the tobacco curing site respectively. The soil samples (0–10 cm depth) were collected using a stainless-steel hand auger. Each sample was the composite of soil samples collected within 10 cm x 10 cm at each sampling station. The soil samples were packaged in aluminum foil and kept in plain paper bags for transportation to the laboratory. Similarly, food crops were harvested from ten points within each sampling station. Soil samples were dried at room temperature, crushed and sieved through 2 mm mesh size, and stored in an amber glass container at -4 $^oC$ before laboratory analysis. The soil samples were allowed to dry at room temperature after removal from the freezer and freeze-dried. The crop samples (maize, yam, and cassava) described and labeled as $FL_1M$, $FL_2M$, $FL_3M$, $FL_1C$, $FL_2C$, $FL_3C$, $FL_1Y$, $FL_2Y$, and $FL_3Y$ were collected from the farmlands at the distance of 20 m, 50 m, and 1.0 km away from the tobacco curing site respectively. The samples were wrapped with aluminum foils and kept at a temperature below − 4 $^oC$. The crop samples were unwrapped, peeled, sliced, and dried at room temperature. Each sample was blended with a grinder and sieved with a 2 mm mesh size and wrapped with aluminum foil, and stored at temperature before extraction.

## 2.3. Determination of Total Organic Carbon

The total organic carbon was determined by the Walkley-Black method (Kakad and Thakare 2017; Matus et al. 2009). About 5g of the dried soil and food crop samples were grounded to pass through a 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 swirled gently to disperse the samples. 20 mL of concentrated $H_2SO_4$ was rapidly added. The flask was gently swirled immediately until the sample and reagents were 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 suspension for viewing the endpoint, three drops of ferroin indicator were then added, and the resulting solution titrated with 0.5 N ferrous sulphate solution. As the endpoint 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 color 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 **Equ. (1)** A is the normality of $K_2Cr_2O_7$ x ml of solution, B is the normality of $Fe_2SO_4$ x volume of solution, C is the mass of air-dried soil (g), and F is the correction factor (1.33).

$$\% \text{ Organic carbon in soil} = \frac{[(A-B)\ X\ 0.003\ X\ 100\ X\ F)]}{C} \quad (1)$$

## 2.4. Determination of PAH in soil and food crops

Sample extraction and cleanup were carried out according to a previously reported method with modification (Adedosu et al., 2015). In brief, 10 g of dried soil sample was mixed with 10 g of anhydrous sodium sulfate and were extracted with 100 mL of 1:1 (v/v) acetone-dichloromethane mixture for 2 hours. The extract for each sample was collected into a pre-treated conical flask. The extraction was repeated with a new proportion of 100 mL of 1:1 (v/v) methanol-dichloromethane mixture for 2 hours. The supernatant for each sample was added to the previous ones obtained. The process was also repeated for all the food crop samples. A rotary evaporator concentrated the extracts to 2.0 mL and evaporated to dryness at room temperature after that. A prepared glass column was packed with 3.0 g of activated alumina adsorbent and 12 g of activated silica gel. The extracts were fractionated with 25 mL of n-hexane to obtain aliphatic fraction, 25 mL of n-hexane and dichloromethane (2:3) to obtain aromatic fraction (PAHs fraction), and 25 mL of methanol to obtain polar fraction. The PAHs fraction was concentrated by rotary evaporation to about 1 mL and carefully transferred into a sample vial and kept in the refrigerator until required for analysis. The concentration of PAHs in the sample extracts was determined according to USEPA Method 8100 using a Gas Chromatograph coupled with a Flame Ionization Detector (Agilent 5890 GC-FID) 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 $mL.min^{-1,}$ 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 mins. The USEPA 16 priority PAHs standard mix was analyzed using the same instrumental conditions to obtain the calibration curve. The identification of PAHs was by comparison of sample retention times with that of the USEPA standard mix. The quantification of PAHs in the samples was achieved using the external standard calibration curve method. The peaks of all the reference standards are well resolved.

## 2.5. Quality control and assurance

The laboratory and analytical procedures were monitored with strict quality assurance and control measures. Laboratory quality control procedures include analysis of method blanks (Solvents), spiked blanks, and sample duplicates. The spiked sample analysis and recovery studies of PAHs were achieved by adding known concentrations of PAHs standards to previously analyzed soil samples of known PAHs concentrations. The average recoveries of the PAHs were between 92 % -120 % for the 19 PAHs.

# Results And Discussion

## 3.1. PAHs concentrations in the soil of the tobacco agro-industrial area of Igboho

The concentrations of priority PAHs in the soil samples are shown in Table 2. The result showed that PAHs are ubiquitous in the soil samples of Igboho. The total concentration of the priority PAHs ($\sum$PAHs) in the soil samples ranges from 136.70 $ng.g^{-1}$ to 889.30 $ng.g^{-1,}$ with an average concentration of 569.78 ± 53.23 $ng.g^{-1}$. The soil samples in the vicinity of the tobacco curing site (TBS) accumulated the highest amounts of PAHs at a mean concentration of 889.30 $ng.g^{-1}$. The distribution pattern of PAHs shows that the PAHs concentration decreases with distance from the TBS. The PAHs levels were 792 $ng.g^{-1}$ at 20 m ($FL_1$), 461 at 50 m ($FL_2$), and 136.7 $ng.g^{-1}$ at 1.0 km away from TBS. The distribution pattern shows TBS's significance as the primary point source of PAHs pollution in the area. The average PAHs concentrations in the soil samples (569.78 ± 53.23 $ng.g^{-1}$) of the study area were higher than those of urban soil in Lagos, Nigeria (254 $ng.g^{-1}$, (Adetunde et al. 2014)), Agbabu, Nigeria (209.7 $ng.g^{-1}$,(Olajire et al. 2007)) and the concentration of soil samples in the agricultural soil of the Teskelewu community, Nigeria (236.40 $ng.g^{-1}$, (Enuneku 2019)), southern subtropical area of China (318.2 $ng.g^{-1}$, (HAO et al. 2007)). However, the average PAHs concentration in the soil was lower than that of the agricultural soil of Nanjing, China (3330 $ng.g^{-1}$,(Wang et al. 2015)) and 917 $ng.g^{-1}$ in agricultural soil of Changzhi, China (Liu et al. 2017). The result indicated that people should be cautious about environmental quality around the area's tobacco agricultural farms.

Table 1
Description of sampling stations in the study area.

| Sampling Point | Coordinate | Description of activities |
|---|---|---|
| TBS | $08^0 51' 910'' N, 003^0 46' 066'' E$ | Tobacco curing site |
| $FL_1$ | $08^0 51' 904'' N, 003046' 097'' E$ | Farmland 20 m from curing site |
| $FL_2$ | $08^0 52' 003'' N, 003046' 089'' E$ | Farmland 50 m from curing site |
| $FL_3$ | $08^0 52' 403'' N, 003046' 518'' E$ | Farmland 1 km from curing site. |

Table 2
Level of PAHs in the tobacco agricultural area of Igboho ($ng.g^{-1}$)

| PAHs | Sampling Point | | | |
|---|---|---|---|---|
| | TBS | $FL_1$ | $FL_2$ | $FL_3$ |
| Naphthalene | 2.78 | 2.10 | 2.20 | 1.90 |
| Acenaphthyl | 2.19 | ND | 2.55 | 1.67 |
| Acenathene | 4.65 | 1.83 | 2.27 | 2.27 |
| Fluorene | 5.79 | 2.65 | 3.19 | 2.63 |
| Phenanthren | 1.58 | 5.97 | 4.92 | 7.47 |
| Anthracene | 7.74 | 4.17 | 3.95 | ND |
| Fluoranthen | 2.26 | 10.3 | 1.01 | 3.49 |
| Pryrene | 42.72 | 5.38 | 7.42 | 8.04 |
| Benzo(a)pyr | 3.69 | 5.07 | 153.0 | 7.10 |
| Benzo(a ) anthracene | ND | 43.78 | ND | ND |
| Chrysene | 241.5 | 46.94 | 10.73 | 19.41 |
| Benzo(e )pyrene | 85.54 | 53.08 | 86.90 | 39.14 |
| Benzo(b)fluoranthene | 5.74 | 4.77 | 7.22 | 5.54 |
| Benzo(k)fluoranthene | 21.00 | ND | ND | ND |
| Benzo(j)fluoranthene | 118.60 | 22.18 | 22.03 | 18.88 |
| Benzo(a)pyrene | 11.31 | 12.63 | 17.12 | 13.15 |
| 7,12-Dimethylb | 60.54 | 242.6 | 74.34 | ND |
| 3 Methylcholanthrene | 70.78 | 29.06 | ND | ND |
| Indeno(123cd)pyrene | 133.10 | 38.00 | ND | ND |
| ∑LMW PAHs | 24.93 | 16.73 | 19.08 | 15.94 |
| ∑HMW PAHs | 796.75 | 514.13 | 379.77 | 104.76 |
| ∑19 EPA PAHs | 889.30 | 792.10 | 461.00 | 136.70 |
| MEAN | 46.81 | 41.69 | 24.26 | 7.19 |
| SD | 0.085 | 0.081 | 0.030 | 0.011 |
| ∑CPAHs | 321.04 | 267.57 | 211.40 | 62.09 |

Figure 1 (a) shows the PAHs' composition profiles in the soil of the Tobacco agricultural area of Igboho based on the PAHs ring size. The PAHs are generally classified based on the number of aromatic rings as 2-rings, 3-rings, 4-rings, 5 rings, and 6-rings PAHs. The composition pattern is in the order of 6-rings  4-rings 5-rings  3-rings  2-rings. The six-ring sized PAHs have a relative abundance of 34.50%. The percentage abundance of the four rings

PAHs, fluoranthene, Chrysene, benzo(a)anthracene, and pyrene was 32.46%, and the abundance of five-ring PAHs benzo(k)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene was 29%. The three rings sized PAHs; acenaphthene, fluorene, phenanthrene, anthracene, acenaphthylene, have a relative abundance of 3.53%, while two rings PAH has the least concentration in the soil samples of the area. To be more specific, as summarized in Table 2, the concentration of Chrysene (241.50 ng.g-$^{1}$), a four-membered ring PAHs and indeno-(123cd)pyrene (133.10 ng.g-$^{1}$), a six-membered ring PAHs were the highest at the curing site (TBS). Compared to the TBS, the concentrations of Chrysene and indeno-(123cd)pyrene were lower for the farmland samples. The five-membered ring, benzo(j)fluoranthene concentrations were also high with mean concentrations of 118.60 ng.g-$^{1}$ at the curing site (TBS). The Benzo(j)fluoranthene in the farmland samples was 22.18 ng.g-$^{1}$, 22.03 ng.g-$^{1}$, and 18.88 ng.g-$^{1}$, respectively. The concentration of all the detected PAHs was high at the curing site (TBS) and decreased across the farmlands. The PAHs ring-size distribution profile suggested that the incomplete combustion of the tobacco leaves and waste could be the main source of PAHs contamination in the soil sample. High molecular weight PAHs are found to be 89.6 %, 64.8 %, 82.4 %, and 76.7 % of the total PAHs concentrations at TBS, $FL_1$, $FL_2$, and $FL_3$, respectively.

# 3.2. Level and compositions of PAHs in food crops

The total concentration of PAHs in the food crop samples from the agricultural farmland was also evaluated. Table 3 shows the level of PAHs in *Zea mays*, *Dioscorea alata*, and *Manihot esculenta* collected from the farmland around the curing sites' vicinity Igboho. The total concentration of PAHs in the *Zea mays* crop samples ranged between 2.16 ng.g$^{-1}$ to 126.00 ng.g$^{-1}$ with a mean concentration of 0.113 ± 0.05 ng.g$^{-1}$ and 6.63 ± 0.27 ng.g$^{-1}$. The highest concentration of PAHs (126.0 ng.g$^{-1}$) was detected in the *Zea mays* samples ($FL_1M$) harvested from the farmland close to the tobacco curing site (TBS). Also, the highest level of carcinogenic PAHs like Benzo(b)fluoranthene (13.12 ng.g$^{-1}$) and Chrysene (11.64 ng.g$^{-1}$) were found in the *Zea mays samples* at $FL_1$. The concentration of PAHs in the *Zea mays* samples at $FL_1M$, $FL_2M$, and $FL_3M$ was lower than other crop samples due to the phytovolatilization process that removed PAHs from the soils and groundwater and transferred into the vapor phase via plant leaves (Brady, 1990).

Table 3

Level of PAHs ($ng.g^{-1}$) in the crops of the Agro-tobacco farming area of Igboho, Nigeria

| PAHs | Sampling point and food crop type | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $FL_1M$ | $FL_2M$ | $FL_3M$ | $FL_1C$ | $FL_2C$ | $FL_3C$ | $FL_1Y$ | $FL_2Y$ | $FL_3Y$ |
| Naphthalene | 2.16 | 2.18 | ND | 2.26 | 2.15 | 2.13 | 2.37 | 2.18 | 2.01 |
| Acenaphthyl | I.70 | ND | ND | ND | ND | ND | ND | ND | ND |
| Acenathene | 2.08 | ND | ND | ND | 1.59 | 1.62 | ND | 1.80 | 1.80 |
| Fluorene | 2.77 | ND | ND | 3.24 | 3.36 | 3.21 | 3.39 | 3.43 | 2.65 |
| Phenanthren | 3.92 | ND | ND | 5.42 | 7.32 | 3.44 | 5.08 | 6.45 | 3.93 |
| Anthracene | 4.82 | ND | ND | 4.92 | 5.43 | 4.85 | 4.22 | 5.08 | 3.77 |
| Fluoranthen | 4.53 | ND | ND | 10.10 | 2.14 | 6.83 | 10.2 | 1.92 | 6.32 |
| Pryrene | 6.28 | ND | ND | 5.12 | 13.24 | 5.13 | 4.82 | 12.90 | 5.11 |
| Benzo(a)pyrene | 5.16 | ND | ND | ND | 38.12 | 8.34 | 37.88 | 8.97 | ND |
| Benzo(a ) anthracene | ND | ND | ND | 51.12 | 12.06 | 10.10 | ND | ND | ND |
| Chrysene | 11.64 | ND | ND | 53.14 | 33.26 | 2.85 | 52.48 | 33.80 | 1.99 |
| Benzo(e )pyrene | ND | ND | ND | 88.16 | 14.38 | 6.89 | 89.01 | 14.52 | 5.72 |
| Benzo(b)fluoranthene | 13.12 | ND | ND | 7.27 | 6.02 | 1.92 | 7.24 | 5.83 | 1.89 |
| Benzo(k)fluoranthene | 58.12 | ND | ND | 10.02 | ND | ND | 10.45 | ND | ND |
| Benzo(j)fluoranthene | 5.12 | ND | ND | 28.12 | 16.12 | 11.02 | 27.60 | 16.73 | 11.45 |
| Benzo(a)pyrene | ND | ND | ND | 51.12 | 12.06 | 10.10 | 51.01 | 12.86 | 10.14 |
| 7,12-Dimethylb | 4.13 | ND | ND | 21.12 | ND | ND | 20.94 | ND | ND |
| Methylcholanthrene | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| Indeno(123cd)pyrene | 8.70 | ND | ND | ND | ND | ND | ND | ND | ND |
| ∑LMW PAHs | 17.28 | 2.16 | ND | 11.92 | 13.11 | 12.82 | 15.06 | 12.69 | 2.01 |
| ∑HMW PAHs | 15.00 | ND | ND | 210.86 | 65.71 | 58.94 | 311.72 | 107.93 | 41.62 |
| ∑19EPA PAHs | 126.0 | 2.16 | ND | 288.10 | 84.82 | 81.34 | 326.5 | 143.8 | 71.62 |
| MEAN | 7.88 | 0.13 | ND | 20.58 | 6.06 | 5.81 | 21.77 | 9.59 | 4.78 |
| SD | 0.01 | 0.003 | ND | 0.025 | 0.0091 | 0.0085 | 0.02 | 0.01 | 0.008 |
| ∑cPAHs | 95.71 | ND | ND | 193.79 | 63.70 | 25.97 | 142.12 | 52.49 | 14.02 |

Tobacco curing site (TBS), Farmland 1 ($FL_1$), Farmland 2 ($FL_2$), Farmland 3($FL_3$), Maize 1($FL_1M$), Maize 2 (FL2M), Maize 3 ($FL_3M$), Cassava 1 ($FL_1C$), Cassava 2 ($FL_2C$), Cassava 3 ($FL_3C$), Yam 1 ($FL_1Y$), Yam2 ($FL_3Y$), Below detection limit (N.D.)

As summarized in Table 3.0, PAHs' concentration in the *Manihot esculenta* decreased from the closest farmland $FL_1C$ to the distant farmland $FL_3C$. The total EPA PAHs concentrations found in the *Manihot esculenta* ranged from 81.34 $ng.g^{-1}$ to 288.10 $ng.g^{-1}$ with a mean concentration of 15.17 ± 1.23 $ng.g^{-1}$. The highest PAHs concentration (288.10 $ng.g^{-1}$) was detected in $FL_1C$ samples around the tobacco curing site (TBS), and the lowest PAHs were recorded at the most distant farmland $FL_3$. Benzo(e)pyrene (88.16 $ng.g^{-1}$), Benzo(c)pyrene (38.12 $ng.g^{-1}$) and Benzo(j)fluoranthene were found in highest concentration in $FL_1C$, $FL_2C$, and $FL_3C$ respectively.

The result shows that PAHs' concentration in the *Dioscorea alata* decreased from the closest farmland $FL_1Y$ to the distant farmland $FL_3Y$. The total PAHs concentrations found in the *Dioscorea alata* samples ranged from 71.62 $ng.g^{-1}$ to 326.50 $ng.g^{-1,}$ with a mean concentration of 23.32 ± 2.23 $ng.g^{-1}$. The highest total PAHs concentration (326.50 $ng.g^{-1}$) was detected in $FL_1Y$ samples around the tobacco curing site (TBS). Benzo(e)pyrene (89.01 $ng.g^{-1}$), Chrysene (52.48 $ng.g^{-1}$), Benzo(a)pyrene (51.01 $ng.g^{-1}$) have the highest concentration in the *Dioscorea alata* sample at $FL_{1,}$ and Chrysene (33.80 $ng.g^{-1}$) was the highest at $FL_2$, while benzo(a) pyrene was the highest at $FL_3$. The distribution of high molecular weight PAHs (ΣHMW) and low molecular weight PAHs (ΣLMW) in the soil samples showed that ΣHMW was dominant at the tobacco curing site (TBS). The total concentration of ΣHMW is higher than (ΣLMW) at most of the sampling points. The lower molecular weight PAHs with lower numbers of rings are volatile and readily biodegradable than the high molecular weight PAHs which are more persistent in the environment (Adedosu et al. 2013). The PAHs' relative concentration based on the numbers of rings to the total concentrations of PAHs in the curing site was 17.13 $ng.g^{-1}$. The concentration of PAHs in the *Zea mays* samples based on the ring size are in the order of 5-rings  4-rings 3-rings  6-rings,  2-rings. The five-rings sized PAHs, benzo(k) fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene have a relative abundance of 51.8 %. The percentage abundance of the four rings PAHs, fluoranthene, Chrysene, benzo(a)anthracene, and pyrene was 26.4 %, and the three rings sized PAHs; acenaphthylene, fluorene, phenanthrene, anthracene, acenaphthylene have the relative abundance of 11.60 %. The six-ring size and the two-ring size recorded the least relative abundance of 6.75 % and 3.45 %. The concentration of PAHs in the *Manihot esculenta* samples based on the ring size is in the order of 5-rings  4-rings 3-rings  6-ring  2-ring. The five-rings sized PAHs; benzo(k)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene have a relative abundance of 48.07 %. The percentage abundance of the four rings PAHs, fluoranthene, Chrysene, benzo(a)anthracene, and pyrene was 40.02 %, and the three rings sized PAHs; acenaphthylene, fluorene, phenanthrene, anthracene, acenaphthylene have the relative abundance of 8.60 %. The six-ring size and the two-ring size recorded the least relative abundance of 1.70 % and 1.60 %. The concentration of PAHs in the *Dioscorea alata* samples based on the ring size is in the order of 5-rings  4-rings 3-rings  6-rings,  2-rings. The five-rings sized PAHs benzo(k)fluoranthene, benzo(a)pyrene have a relative abundance of 51.90 %. The percentage abundance of the four rings PAHs, fluoranthene, Chrysene, benzo(a)anthracene, and pyrene was 34.80 %, and the three rings sized PAHs; acenaphthylene, fluorene, phenanthrene, anthracene, acenaphthylene have the relative abundance of 7.87 %. The six-ring size and the two-ring size recorded the least relative abundance of 4.13 % and 1.30 %, respectively.

# 3.3. Total Organic Carbon content

Figure 2 shows the distribution of total organic carbon (TOC) content in the samples. It is generally observed that the values of TOC decrease with increasing distance from the tobacco curing site. This implies that tobacco

curing is the major contributor to the increasing organic matter level in the study area. The percentage of total organic carbon of the soil and crop samples shows a wide variation in their values. The percentage of total organic carbon in the soil and crop samples show a wide variation in their values that ranged from 8.3 wt. % to 13.6 wt. %. The maximum percentage TOC (13.6 wt. %) was recorded at the tobacco curing site, while the distant farmland $FL_3$ recorded the lowest value of 8.3 wt. %. These results are in line with 1.0 wt. % detention limit of Soil Guidelines Values (SGVs) in CLEA Model published by DEFRA and the Environment Agency (E.A.) in March 2002 which sets a framework for the appropriate assessment of risks to human health from contaminated land, as required by Part II (A) of the Environmental Protection Act 1990. This is also justified with a 0.5 wt% (US EPA) detection limit. The soil from the tobacco curing site showed a relatively higher TOC percentage (13.6 wt. %) than the farmlands' soil samples. The farmland $FL_1$ closest to the curing site recorded the second-highest value with (10.5 wt. %) while all the food crop samples (yam, cassava, maize) obtained from $FL_1$ recorded the highest values with 10.4 wt. %, 10.1 wt. %, 8.9 wt. % respectively. The farmland $FL_3$, the distant farmland from the curing site, recorded the smallest value with 8.3. wt. % while all the food crop samples (yam, cassava, maize) obtained from $FL_3$ recorded the lowest values with 3.1 wt. %, 5.4 wt. % and 1.9 wt. %, respectively. This is because of the contribution of various proportions of combustible residues, non-aqueous phase liquids, and natural organic matter (NOM) that have a strong affinity for contaminants. As the contaminants are released in the soil matrix, they bind to the surface and become sequestrated into the soil matrix. The hydrophobicity of these compounds constitutes the main factor determining their persistence in the environment, and they tend to be strongly absorbed by soil particles with low bioavailability and possibly accumulate in the food chain. The scatter plot in Fig. 3 (b) was used to assess the relationship between the percentage total organic carbon and the total concentration of PAHs in the soil sample were shown by the linear regression curve in Fig. 3 (b). The $R^2$ value was 0.937, showing that there is a positive correlation between the TOC and PAHs. This confirmed that the soil sample's organic carbon content increases the PAHs' adsorption at the study site.

# 3.4. The diagnostic ratio of PAHs

Different researchers have employed some PAHs isomers ratios to distinguish between petrogenic, biogenic, and pyrogenic sources of PAHs in the environment (Adedosu, Adeniyi, and Adedosu 2015; Liu et al. 2010; Zakaria et al. 2002). Petrogenic sources are characterized by the predominance of low molecular weight (LMW, 2-3 ring) PAHs over the high molecular weight (HMW, 4-6 ring) PAHs. The ratio of low molecular weight PAHS to high molecular weight PAHs greater than 1.0 (LMW/HMW ≥1.0) indicates a petrogenic source of PAHs, while pyrogenic sources are characterized with the predominance of high molecular weight PAHs over the low molecular weight PAHs and LMW/HMW < 1.0 (Adedosu et al. 2015). The diagnostic ratio of PAHs in the study area is presented in **Table 4**. The values of LMW/HMW PAHs for the TBS (0.46), $FL_1$ (0.30), $FL_2$ (0.12), and $FL_3$ (0.19) were less than 1.0, suggesting a pyrolytic source of PAHs contamination. The Phe/Ant ratio allowed the separation of the pyrolytic (combustion origin) and petrogenic (unburned petroleum products) PAH sources. A Phe/Ant ratio lower than 15.0 is assumed to be of a pyrolytic origin from the combustion of plants, wood, grass, and others, whereas a value higher than 15.0 is assumed to be of combustion of petroleum hydrocarbons such as coal, crude oil, and others. The values of Phe/Ant at TBS, $FL_1$, $FL_2$, and $FL_3$ were lower than 15.0 and confirmed that the PAHs were from the combustion of plants, wood, and leaves, possibly from the tobacco-curing activities in the area.

Table 4
Diagnostic Ratio of PAHs in the soil of the Tobacco-agro industrial area of Igboho

| PAHs ratio | Diagnostic reference values | | Sampling point | | | |
|---|---|---|---|---|---|---|
| | Petrogenic | Pyrogenic | TBS | $FL_1$ | $FL_2$ | $FL_3$ |
| Phe /Ant | > 15 | < 15 | 2.04 | 1.04 | 1.30 | 0.01 |
| Flu /Pyr | < 0.4 | > 0.4 | 0.53 | 0.94 | 0.43 | 0.44 |
| BaA/Chr | < 0.25 | > 0.25 | ND | 0.93 | ND | ND |
| BeP/BaP | < 1 | > 2 | 7.56 | 3.60 | 5.10 | 2.98 |
| BbF/BkF | > 1 | < 1 | 0.27 | 0.11 | ND | ND |
| Ant/ Ant + Phe | < 0.1 | > 0.1 | 0.33 | 4.90 | 0.48 | ND |
| LMW/HMW | > 1 | < 1 | 0.46 | 0.30 | 0.12 | 0.29 |

Similarly, an Flt/Pyr ratio PAHs greater than 0.4 indicate the influence of pyrolytic PAHs, and the ratio of PAHs lower than 0.4 indicates petrogenic sources. The BaA/Chr ratio PAHs that more significant than 0.25 are assumed to be pyrolytic sources, and the BaA/Chr ratio PAHs lower than 0.25 are assumed to be petrogenic sources. The TBS, $FL_1$, $FL_3$ but $FL_2$ was 0.93, which was greater than 0.25. The BeP/BaP ratio PAHs greater than 2.0 is assumed to be of pyrolytic origin. Similarly, other PAHs ratio in Table 4 confirmed that the source of PAHs contamination in the study area is from the combustion of biomass, woods, and other organic matter due to the tobacco curing process.

# 3.5. Carcinogenic potency and toxicity potential of PAHs in the Soil and food crop samples

The International Agency for Research on Cancer (IARC) and the United State Environment Programme, (USEPA) reported that chrysene, benzo(a)anthracene, dibenzo(a,h)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene and indeno(1,2,3-cd)pyrene are potential human carcinogens. All the listed carcinogenic PAHs are detected in the soil samples of the study area. The total concentration of carcinogenic PAHs in the tobacco curing site soil (TBS) was 473.19 $ng.g^{-1}$. This represented 53.2 % of the total PAHs concentrations detected in the tobacco curing site. The total concentrations of the carcinogenic PAHs at each of the sampling points were presented in Table 5. The highest concentration of carcinogenic PAHs (473.19 $ng.g^{-1}$) was recorded in soil from the tobacco curing site (TBS). The concentration of carcinogenic PAHs decreased as the farmlands were farther away from the curing site with $FL_1$ (388.72 $ng.g^{-1}$), $FL_2$ (109.41 $ng.g^{-1}$), and $FL_3$ (38.10 $ng.g^{-1}$). The lowest concentrations of the carcinogenic PAHs were recorded at the distant farmland $FL_3$. The total concentrations of the carcinogenic PAHs at each of the sampling points decreased from the curing site across the farmlands, which indicated that the tobacco curing site was the contaminant source within the study area's vicinity. Although benzo[a]pyrene (B(a)P) can have toxic effects, a major concern is the ability of the reactive metabolites, such as epoxides and dihydrodiols, of some PAHs to bind to cellular proteins and DNA. The level of B(a)P in the soil samples was 11.31 $ng.g^{-1}$ for TBS, 12.63 $ng.g^{-1}$ for $FL_1$, 17.12 $ng.g^{-1}$ for $FL_2$, and 13.15 $ng.g^{-1}$ for $FL_3$ (**Table 5**). The B(a)P concentrations were lower than the European Union's maximum contaminant level (MCL) of 25 $ng.g^{-1}$. The B(a)P equivalent (B(a)Peqv) was calculated using the toxicity equivalent (T.E.) for each

PAH, as presented in **Table 5**. The calculated total B(a)Peqv at the TBS and surrounded farmlands $FL_1$, $FL_2$, and $FL_3$ ranged from 13.84 $ng.g^{-1}$ to 268.85 $ng.g^{-1}$. The highest B(a)Peqv was found at the TBS with 268.85 $ng.g^{-1}$, and the distant farmland $FL_3$ recorded the least value of 13.84 $ng.g^{-1}$. It is observed that the tobacco curing site TBS (268.85 $ng.g^{-1}$) has been polluted while the farmland $FL_1$ (112.21 $ng.g^{-1}$), $FL_2$ (92.29 $ng.g^{-1}$), and $FL_3$ (13.84 $ng.g^{-1}$) were slightly polluted. **Table 6** shows the total concentration of carcinogenic PAHs in the *Manihot esculenta* samples as the farmland closer to the tobacco curing site $FL_1C$ recorded the highest value of 193.79 $ng.g^{-1}$. The concentration of carcinogenic PAHs adsorbed decreased as the farmlands were farther away from the curing site with $FL_1C$ (193.79 $ng.g^{-1}$), $FL_2C$ (63.70 $ng.g^{-1}$), and $FL_3C$ (12.03 $ng.g^{-1}$), respectively. The lowest concentrations of the carcinogenic PAHs were recorded for the *Manihot esculenta* collected from the distant farmland $FL_3$. The total concentrations of the carcinogenic PAHs at each sampling point decreased from the curing site across the farmlands indicated that the tobacco curing site was the source of contaminants within the study area's vicinity.

Table 5
Carcinogenic potency and toxicity potential of PAHs in the soil of the tobacco processing industry Igboho ($ng.g^{-1}$)

| PAHs | TEF | Sampling sites | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | TBS ($ng.g^{-1}$) | | $FL_1$ ($ng.g^{-1}$) | | $FL_2$ ($ng.g^{-1}$) | | $FL_3$ ($ng.g^{-1}$) | |
| | | $\Sigma_C$PAHs | B(a)$P_{equ}$ | $\Sigma_C$PAHs | B(a)$P_{equ}$ | $\Sigma_C$PAHs | B(a)$P_{equ}$ | $\Sigma_C$PAHs | B(a)$P_{equ}$ |
| B(a)p | 0.1 | ND | 0.00 | 242.35 | 24.23 | ND | 0.00 | ND | 0.00 |
| Chr | 0.01 | 60.54 | 0.06 | 0.47 | 0.469 | 10.73 | 0.11 | 19.41 | 0.194 |
| B(k)f | 0.1 | 21.00 | 2.10 | ND | 0.00 | ND | 0.00 | ND | 0.00 |
| B(b)f | 0.1 | 5.74 | 0.57 | 4.77 | 0.477 | 7.22 | 0.72 | 5.54 | 0.554 |
| B(a)f | 1 | 11.31 | 11.31 | 12.63 | 1.63 | 17.12 | 17.12 | 13.15 | 13.15 |
| Ind | 0.1 | 133.10 | 13.31 | 38.00 | 3.80 | ND | 0.00 | ND | 0.00 |
| D(ah)A | 1 | 241.50 | 241.50 | 43.78 | 43.78 | 73.34 | 74.34 | ND | 0.00 |
| Total | | 473.19 | 268.85 | 388.72 | 112.21 | 109.41 | 92.92 | 38.10 | 13.84 |

Table 6
Carcinogenic potency and toxicity potential of PAHs in *Dioscorea alata* from the farmlands (ng.g$^{-1}$)

| PAHs | TEF | Sampling sites | | | | | |
|---|---|---|---|---|---|---|---|
| | | $FL_1$ (ng.g$^{-1}$) | | $FL_2$ (ng.g$^{-1}$) | | $FL_3$ (ng.g$^{-1}$) | |
| | | $\Sigma_C$PAHs | B(a)$P_{equ}$ | $\Sigma_C$PAHs | B(a)$P_{equ}$ | $\Sigma_C$PAHs | B(a)$P_{equ}$ |
| Chry | 0.01 | 52.48 | 0.542 | 33.80 | 0.338 | 1.99 | 0.02 |
| B(k)f | 0.10 | 10.45 | 1.045 | ND | 0.00 | ND | 0.00 |
| B(b)f | 0.10 | 7.24 | 0.724 | 5.83 | 0.583 | 1.89 | 0.19 |
| B(a)p | 1.00 | 51.01 | 51.01 | 12.86 | 12.86 | 10.14 | 10.14 |
| D(a,h)A | 1.00 | 20.94 | 20.94 | ND | 0.00 | ND | 0.00 |
| Total | | 142.12 | 74.24 | 52.49 | 13.78 | 14.02 | 10.35 |

The calculated total B(a)Peqv obtained from *Manihot esculenta* samples at the farmlands was within the range 11.10–51.12 ng.g$^{-1}$. This range was above the legally permissible limit of 1.0 ng.g$^{-1}$ criteria of the European Union for processed cereal-based foods (Dennis et al.; 1984).

In Table 7, the concentration of carcinogenic compounds in the *Dioscorea alata* ranged from14.02-142.12 ng.g$^{-1}$. As previously observed for other crops, the farmlands closer to the curing site $FL_1$ recorded the highest concentration, and the distant farmland $FL_3$Y recorded the lowest concentrations of PAHs in the *Dioscorea alata*. The concentrations of PAHs in the soils determined the amount adsorbed by plants and stored in the roots. This process is called phytoaccumulation. The calculated total B(a)Peqv obtained from samples at the sampling farmlands was within the range 10.14 – 51.01 ng.g$^{-1}$. The European Union above the legally permissible limit (1.00 ng.g-1) processed this range for processed cereal-based foods (Dennis et al.; 1984). **Table 8** shows that the concentration of carcinogenic PAHs in the *Zea mays* samples ranges from 0.00 ng.g$^{-1}$ to 95.17 ng.g$^{-1}$. The highest concentration was recorded at the farmland closer to the curing site, and the concentration at other farmlands was below the detection limit. It was observed that maize could undergo phytovolatilization by mineralizing carcinogenic PAHs into harmless products such as carbon (iv) oxide, methane, and water, making the maize from $FL_2$ and $FL_3$ free from contamination (Brady, 1990).

Table 7
Carcinogenic potency and toxicity potential of PAHs in *Manihot esculenta* (cassava) from the farmlands (ng.g$^{-1}$)

| PAHs | TEF | Sampling sites | | | | | |
|---|---|---|---|---|---|---|---|
| | | $FL_1C$(ng.g$^{-1}$) | | $FL_2C$ (ng.g$^{-1}$) | | $FL_3C$ (ng.g$^{-1}$) | |
| | | $\Sigma_C$PAHs | B(a)$P_{equ}$ | $\Sigma_C$PAHs | B(a)$P_{equ}$ | $\Sigma_C$PAHs | B(a)$P_{equ}$ |
| Chry | 0.01 | 53.14 | 0.5314 | 33.26 | 0.3326 | 2.85 | 0.0285 |
| B(k)f | 0.10 | 10.02 | 1.002 | ND | 0.00 | ND | 0.00 |
| B(b)f | 0.10 | 7.27 | 0.272 | 6.02 | 0.602 | 1.92 | 0.192 |
| B(a)p | 1.00 | 51.12 | 51.12 | 12.36 | 12.36 | 11.10 | 11.10 |
| D(a,h)A | 1.00 | 21.12 | 21.12 | ND | 0.00 | ND | 0.00 |
| Total | | 193.79 | 79.61 | 63.70 | 14.50 | 25.97 | 12.03 |

Table 8
Carcinogenic potency and toxicity potential of PAHs in *Zea mays* (maize) from the farmlands (ng.g$^{-1}$)

| PAHs | TEF | Sampling sites | |
|---|---|---|---|
| | | $FL_1M$(ng.g$^{-1}$) | |
| | | $\Sigma_C$PAHs | B(a)$P_{equ}$ |
| Chry | 0.01 | 11.64 | 0.11 |
| B(k)f | 0.10 | 58.12 | 5.812 |
| B(b)f | 0.10 | 13.12 | 1.312 |
| D(a,h)A | 1.00 | 4.13 | 4.13 |
| In(123)P | 0.1 | 8.70 | 0.87 |
| Total | | 95.17 | 12.24 |

# Conclusion

The study has determined the distributions, sources, and toxicity potential of polycyclic aromatic hydrocarbon (PAHs) in the soils and food crops from the farmlands within the tobacco local processing vicinity industry. The result of total organic carbon in the soil and food samples established the accumulation of polycyclic aromatic hydrocarbon in the vicinity of the tobacco curing site and the surrounded farmlands because it was above 0.5% US EPA detection limit. The total number of PAHs identified in the study area was nineteen (19) priority polycyclic aromatic hydrocarbon compounds in which fourteen (14) were generally recorded in all samples. The total concentration of PAHs recorded in all the soil samples were above 100.0 ng.g$^{-1}$, USEPA warning limit. The concentration and spatial distribution of PAHs in all the food crop samples collected from farmland $FL_1$ were above 100.00 ng.g$^{-1}$ limits of the USEPA. The concentration PAHs found in food crop samples from farmlands

$FL_2$ and $FL_3$ was relatively close to the USEPA detection limit. However, there is a point that the vicinity of the curing site was more concentrated than the distant farmland.

Molecular matrix was used to distinguish between petrogenic and pyrogenic sources by comparing the ratio of the concentration species of PAHs obtained according to the statistical principles. The calculated values obtained depicted that almost all the PAHs were from pyrogenic sources. The concentration of higher molecular weight (HMW) was of a higher percentage than lower molecular weight (LMW), and this is an indication that the significant source of PAHs in the study area was pyrolytic. Based on the available evidence, both the International Agency for Research on Cancer (IARC, 1987) and US EPA (1994), the PAHs' carcinogenic potency in the study area was moderately high and posed a threat to human existence. The correlations coefficient matrix of concentration of individual PAHs and the total concentration of polycyclic aromatic hydrocarbon revealed that all samples from the farmlands originated from the same source.

## Declarations

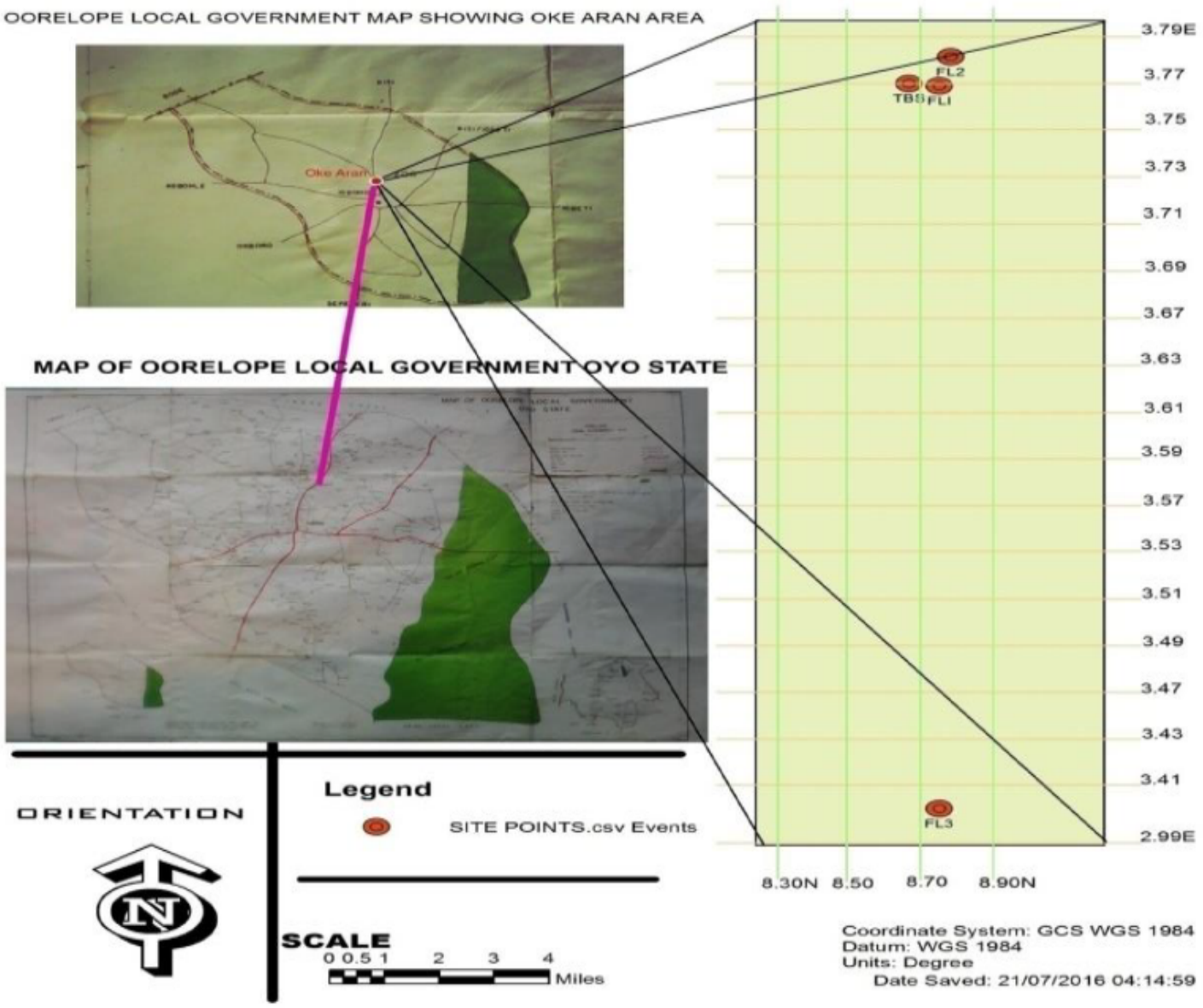
Authors declare no conflict of interest

## References


1. Abdel-Shafy, Hussein I. and Mona S. M. Mansour. 2016. “A Review on Polycyclic Aromatic Hydrocarbons: Source, Environmental Impact, Effect on Human Health, and Remediation.” *Egyptian Journal of Petroleum* 25(1):107–23.
2. Adedosu, T. A., H. O. Adedosu, O. S. Sojinu, and A. A. Olajire. 2013. “N-Alkanes and Polycyclic Aromatic Hydrocarbons (PAHs) Profile of Soil from Some Polluted Sites in Niger Delta, Nigeria.” *Environmental Earth Sciences* 68(8):2139–44.
3. Adedosu, Taofik Adewale, Omotayo Kayode Adeniyi, and Haleema Omolola Adedosu. 2015. “Distribution, Sources and Toxicity Potentials of Polycyclic Aromatic Hydrocarbons in Soil around the Vicinity of Balogun-Birro Dumpsite of Oshogbo, Nigeria.” *Malaysian Journal of Analytical Sciences* 19(3):636–48.
4. Adetunde, Oluwatoyin T., Graham A. Mills, Kehinde O. Olayinka, and Babajide I. Alo. 2014. “Assessment of Occupational Exposure to Polycyclic Aromatic Hydrocarbons via Involuntary Ingestion of Soil from Contaminated Soils in Lagos, Nigeria.” *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering* 49(14):1661–71.
5. Enuneku, A. A., 2019. “Assessment of Polycyclic Aromatic Hydrocarbons in Agricultural Soils of Teskelewu Community and Environs Impacted By Gas Flaring in Delta State, Nigeria.” *Journal of Applied Sciences and Environmental Management* 23(10):1861–66.
6. HAO, Rong, Hong Fu WAN, Yan Tun SONG, Hong JIANG, and Shao Lin PENG. 2007. “Polycyclic Aromatic Hydrocarbons in Agricultural Soils of the Southern Subtropics, China.” *Pedosphere* 17(5):673–80.
7. Ifegwu, Okechukwu Clinton, and Chimezie Anyakora. 2015. “Polycyclic Aromatic Hydrocarbons: Part I. Exposure.” Pp. 277–304 in *Advances in Clinical Chemistry*. Vol. 72.
8. Kakad, Rutuja R., and Sunil B. Thakare. 2017. “Experimental Study of Waste Management System for Malpani Group of Tobacco Industry.” *International Journal of Engineering Research* 6(8):379.

9. Khan, Sardar, and Qing Cao. 2012. “Human Health Risk Due to Consumption of Vegetables Contaminated with Carcinogenic Polycyclic Aromatic Hydrocarbons.” *Journal of Soils and Sediments* 12(2):178–84.
10. Liu, Geng, Wenjiong Guo, Junjie Niu, Xiangsheng An, and Long Zhao. 2017. “Polycyclic Aromatic Hydrocarbons in Agricultural Soils around the Industrial City of Changzhi, China: Characteristics, Spatial Distribution, Hotspots, Sources, and Potential Risks.” *Journal of Soils and Sediments* 17(1):229–39.
11. Liu, Shaoda, Xinghui Xia, Lingyan Yang, Mohai Shen, and Ruimin Liu. 2010. “Polycyclic Aromatic Hydrocarbons in Urban Soils of Different Land Uses in Beijing, China: Distribution, Sources and Their Correlation with the City’s Urbanization History.” *Journal of Hazardous Materials* 177(1–3):1085–92.
12. Matus, Francisco J., Mauricio Escudey, Juan E. Förster, Marlen Gutiérrez, and Andrew C. Chang. 2009. “Is the Walkley-Black Method Suitable for Organic Carbon Determination in Chilean Volcanic Soils?” *Communications in Soil Science and Plant Analysis* 40(11–12):1862–72.
13. Olajire, Abass A., Abass O. Alade, Adejare A. Adeniyi, and Ojeyemi M. Olabemiwo. 2007. “Distribution of Polycyclic Aromatic Hydrocarbons in Surface Soils and Water from the Vicinity of Agbabu Bitumen Field of Southwestern Nigeria.” *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering* 42(8):1043–49.
14. Rengarajan, Thamaraiselvan, Peramaiyan Rajendran, Natarajan Nandakumar, Boopathy Lokeshkumar, Palaniswami Rajendran, and Ikuo Nishigaki. 2015. “Exposure to Polycyclic Aromatic Hydrocarbons with Special Focus on Cancer.” *Asian Pacific Journal of Tropical Biomedicine* 5(3):182–89.
15. Taylor, Publisher, Thomas A. Arcury, and Sara A. Quandt. 2017. “Health and Social Impacts of Tobacco Production Health and Social Impacts of Tobacco Production.” *Environmental Health,* 0813(March 2017):37–41.
16. U.S. Department of Health and Human Services. 2010. *How Tobacco Smoke Causes Disease: The Biology and Behavioral Basis for Smoking-Attributable Disease*.
17. Wang, Chun hui, Shao Hua Wu, Sheng lu Zhou, Hui Wang, Bao Jie Li, Hao Chen, Yan na Yu, and Ya xing Shi. 2015. “Polycyclic Aromatic Hydrocarbons in Soils from Urban to Rural Areas in Nanjing: Concentration, Source, Spatial Distribution, and Potential Human Health Risk.” *Science of the Total Environment* 527–528:375–83.
18. Wang, Di, Jing Ma, Hao Li, and Xingchang Zhang. 2018. “Concentration and Potential Ecological Risk of PAHs in Different Layers of Soil in the Petroleum-Contaminated Areas of the Loess Plateau, China.” *International Journal of Environmental Research and Public Health* 15(8).
19. WHO. 2017. *Tobacco and Its Environmental Impact: An Overview*.
20. World Health Organization. 2019. *WHO Global Report on Trends in the Prevalence of Tobacco Use Third Edition*.
21. Zakaria, Mohamad Pauzi, Hideshige Takada, Shinobu Tsutsumi, Kei Ohno, Junya Yamada, Eriko Kouno, and Hidetoshi Kumata. 2002. “Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in Rivers and Estuaries in Malaysia: A Widespread Input of Petrogenic PAHs.” *Environmental Science and Technology* 36(9):1907–18.

# Figures




## Figure 1

Map of Oorelope local government of Oyo state showing the study area's location and the sampling points. Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

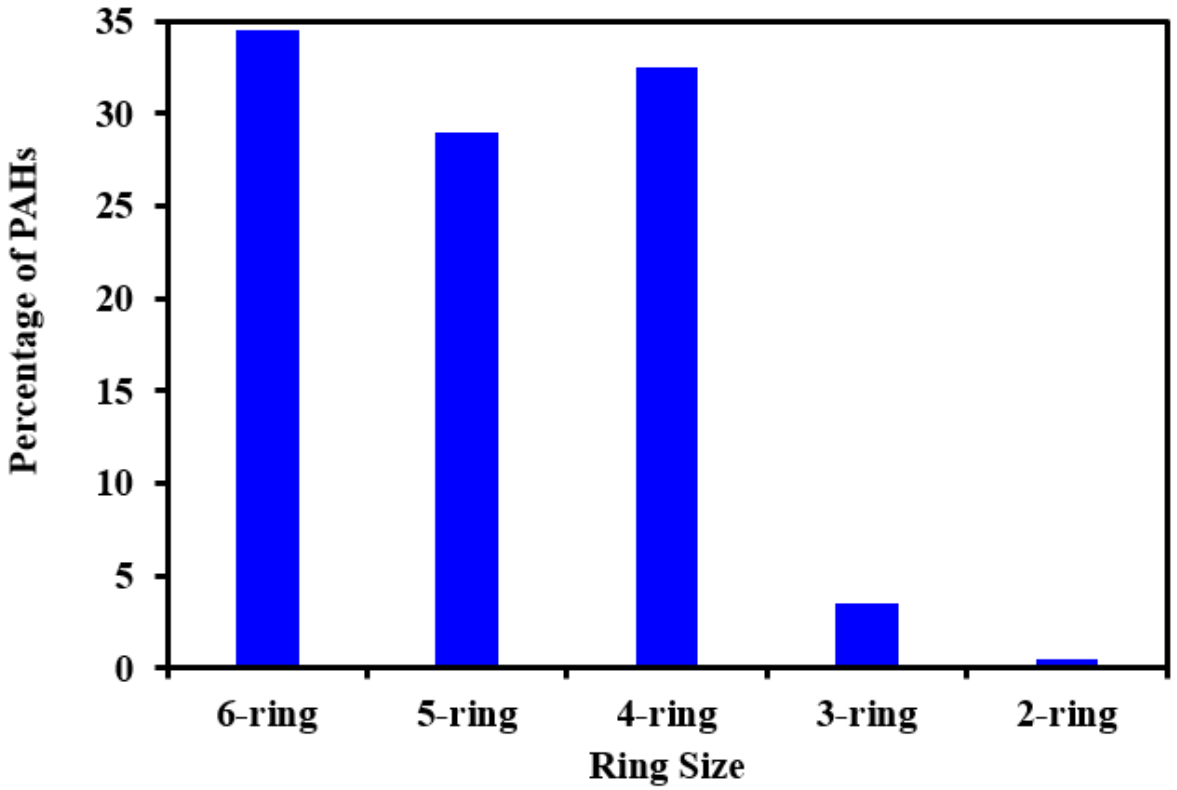



Figure 2

Percentage distribution of PAHs in soils samples

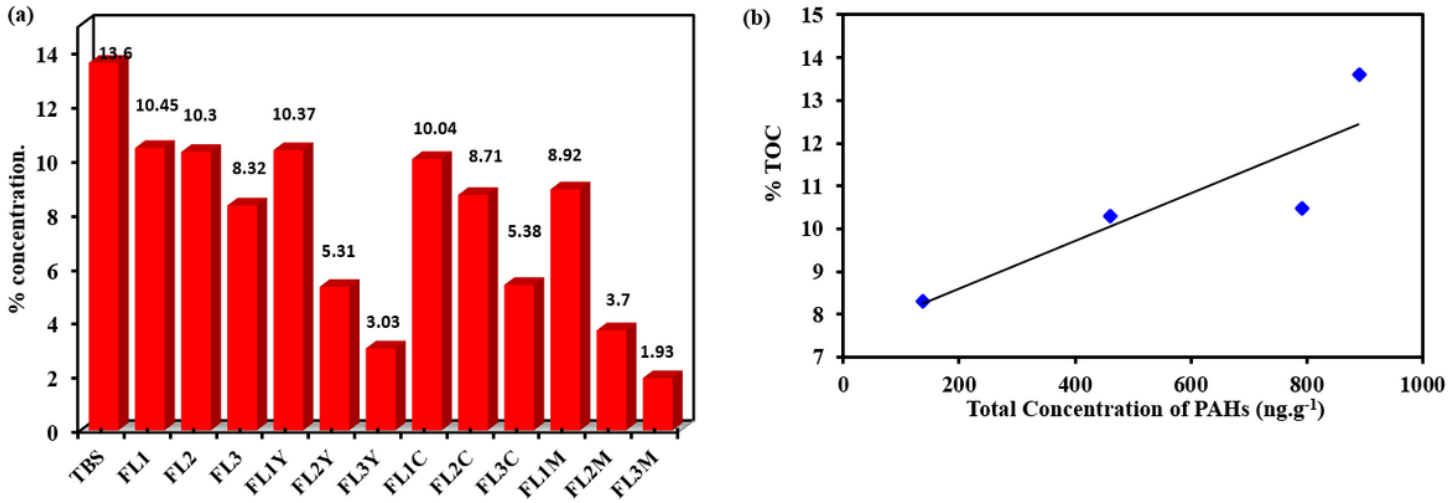



Figure 3

(a) Distribution of % TOC in soil and food crop samples and (b) scatter plot showing the relationship between the percentage total organic carbon and the total concentration of PAHs in the soil sample.