JCHR (2019) 9(3), 203-216

Journal of Chemical Health Risks

www.jchr.org

ORIGINAL ARTICLE

Sources and Cancer Risk Exposure of Polycyclic Aromatic Hydrocarbons in Soils from Industrial Areas in Southeastern, Nigeria

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(Received: 11 April 2019 Accepted: 28 September 2019)

KEYWORDS

Polycyclic Aromatic Hydrocarbons; Diagnostic ratios; Incremental life time cancer risk (ILCR); South East (Nigeria)

ABSTRACT: This study investigated the cancer risk exposure of Polycyclic Aromatic Hydrocarbons (PAHs) in Soils from industrial areas in South Eastern States of Nigeria. PAHs concentrations in soil samples from study sites ranged from below the limits of detection (0.01±0.00) in Ishiagu to 2.67±0.02 in Akwuuru. Total PAHs (∑PAHS) concentrations in most crop samples had values 13, 9.55, 22.12 <0.01, 5.85 Mg/kg for Abia, Imo, Anambra, Ebonyi and Enugu Soils respectively. The diagnostic ratios indicated both pyrolytic and petrogenic sources of pollution suggesting that there is no point source of pollution in the industrialized areas. The secondary evaluation on carcinogenic PAHs in soil for Akwuuru and Osisioma showed significant dominance above other soils analyzed for the different states. Estimated daily intake of PAHs in soils was within the interval of 2.54819E-06mg/kg/body to 8.57844E-05 mg/kg/body (Adults) and 2.67993E-06 mg/kg/body to 9.02193E-05 mg/kg/body for children. The summation of the Incremental Life Time Cancer Risk for Oral, Inhalation and Dermal routes for Soils fell at the upper limit of the tolerable range(10^{-6}-10^{-4}).Values were: 4.40E-04, 2.69E-05,9.07E-4, BDL and 2.37 E04 and 4.25E-04,2.60E-05,8.70E-04, BDL, 2.29E-04 for Adults and Children in Abia, Imo, Anambra, Ebonyi and Enugu Soils respectively. These values do not indicate carcinogenic risk due to PAHs although levels of PAHs in children were higher than in Adults suggesting that children are at greater risk compared to adults since they have a longer period of exposure.

INTRODUCTION

Industrialization in every developed or developing Nation has always signaled wealth and good living but not in totality due to the release of pollutants from the industries cumulating to lethal effects in the environment and ultimately endangering human beings and other living things [1].

The high hydrophobicity and stable chemical structure causes insolubility of PAHs and therefore they can be

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DOI: 10.22034/jchr.2019.668185

adsorbed rapidly onto soil, particularly on soil organic contents [2]. Urban areas are relatively more populated and are accompanied by an increased production of traffic pollution and other industrial PAHs sources, causing a significantly higher level of pollution [3].Toxic substances like PAHs, Heavy metals etc. get absorbed in Agricultural Soils which are hydrophobic and its stable chemical structure makes PAHs easily adsorbed by Soil [4, 5]. They can be dispersed into surface/ground water through urban runoff and because they are volatile, they tend to escape into the atmosphere and are also absorbed into crops. This cycle of contamination goes on and on as plants also absorb via the roots and leaves [6]. Human beings can contact PAHs via many routes such as ingestion, inhalation, and dermal adsorption of soil dust thereby affecting the human health especially the physiologically vulnerable populace in our environment (children and elders) [7].

PAHs consist of two or more benzene rings joined together. They are environmentally ubiquitous as seen in Soils, water, air, dust etc. [8]. Their prevalent source is via anthropogenic activities such as incomplete combustion of organic substances, such as coal, petroleum, natural gas, forest products and cigarette [2, 9, 10, 11, 12, 13 and14]. They are characterized by their high toxicity as well as the potential effects of carcinogenicity, teratogenicity, and mutagenicity [11, 14].

Based on the cancer -causing ability and its occurrence, the United States Environmental Protection Agency (USEPA) has selected sixteen (16) PAHs as prevalent among others. These includes: Chrysene(Chry), Benzo(a)pyrene(BaP), Benzo(a)anthracene(BaA), Benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), Dibenzo(a,h) anthracene (DahA) and Indeno(1,2,3-cd)perylene (IndP) considered as human carcinogens and others like of naphthalene (Nap), Anthracene (Ant), Acenaphthene (Ace), Benzo(ghi) perylene (BghiP), Fluoranthene (Flt), Fluorene (Flu), Phenanthrene (Phe), Acenaphthylene (Acy), and Pyrene (Pyr) noted as non-carcinogenic PAHs[15].

South east, Nigeria has an area of 40,000km^2(1600sqmi) with the highest elevation of 1000m (3300ft). It is primarily located in the lowland forest region of Nigeria with a population of approximately 40million people [16]. Most people living in this area engage in peasant farming for their sole consumption or farming on a large scale as a source of livelihood. Hence, the safeness of Agricultural zones in industrialized areas in the south east of Nigeria, have become a serious environmental concern as there are few research reports available on PAHs contamination and its health risk implication to the people in the Area. Therefore, the aim of this study was:

(1) To investigate the concentrations of 16 priority PAHs in soils collected from south eastern states of Nigeria (Osisioma, Akwuuru, Ngwo, Ishiagu and Irete).

(2) To assess and evaluate the cancer risk associated with soil exposure via the dermal, ingestion and inhalation pathways.

(4) To assess the levels and sources of PAHs pollution using various diagnostic ratios.

MATERIALS AND METHODS

Description of area of study

The Southeastern zone of Nigeria presented on Figure 1 consists of five (5) major States and their individual study area. They include:

Abia: Osisioma town in Abia state with has tropical rain forest vegetation. The industry present in the area includes Tonimas Nigeria. They people living in the area engage in farming activity to earn a living.

Anambra state: Akwu-uru industrial layout is located in the Nnewi south local government area of Anambra State, Nigeria. The city spans over 2789 km^2 in Anambra State. Geographically, Akwu-uru industrial layout Nnewi falls within the tropical rain forest region of Nigeria. The area is rich in agricultural produce. Companies found in the area include Chikason Company, Ibeto group of companies, Innoson Vehicle Manufacturing Company.

Imo State: Irete is a community in Imo state that has an area of around 5100 km^2. The vegetation type is tropical rain forest vegetation. Companies found here include vegetable oil processing company (camela vegetable oil Company), Roofing sheets company (Vinal Aluminium),

Rhas construction company and other cottage companies e. g. portable water, bread bakers etc.

Ebonyi State: Ishiagu is a town in Ebonyi state, Nigeria. The climatic conditions are usually high temperature and humidity for more than half a year. Farming activities and quarrying/mining activities dominates the region. The effluents of the quarrying companies are discharged directly on the soil/ farmlands.

Finally, Enugu State: Ngwo, a town located in udi local government area of Enugu state, Nigeria. The vegetation type is tropical rain forest and guinea Savannah vegetation; hence, occupants indulge in moderate level of farming activities in the area. Most companies found at Ngwo are bottling companies which include Seven Up Company, breweries, coca-cola bottling company.

Figure 1. Map of the South Eastern States of Nigeria showing some industrial areas of study.

Collection of samples

Samples were collected at agricultural land(15-25m) around each industrial study site, the diagonal distance of each sampling area was divided into five equal points .Rhizosphere Soil (from depth of 16–30 cm) were collected by shaking it off. The soil samples after the manual removal of non soil particles were packaged in an aluminum foil and then taken to the laboratory for further preparations and analysis. At the laboratory, the soil samples were air dried for three days until a steady weight was achieved. Soils collected from each site was ground together to form a composite soil. A 2mm stainless steel mesh was used to sieve the soil to uniform sizes and particles and also ensure the removal of unwanted particles.

Extraction and sample clean up / separation

Two grams (2g) of each sample was weighed into a clean extraction container (50ml beaker) and 10ml of extraction solvent (dichloromethane) was added into the sample and stirred until it settled. The sample was now carefully filtered into a clean extraction bottle rinsed with dichloromethane with help of a filter paper and buchner funnel. The extract was concentrated to 2 ml. In the chromatographic column where cleanup will be achieved, 1cm of moderately packed glass wool was placed at the bottom of 10mm ID × 250mm Loup chromatographic column. Slurry of 2gr was prepared with activated silica in 10ml methylene chloride and placed in the column At the top of the column 0.5cm of sodium sulphate was added and rinsed with additional 10ml methylene chloride and eluted

with 20ml of dichloromethane. This was allowed to flow through the column at a rate of about 2minutes until the liquid in the column was just above the sulphate layer. The column was opened and the element was collected with a 10ml graduated cylinder. Following the recovery of the labeled fractions called 'Aliphatics' before the exposure of the sodium sulphate layer, the column was eluted with 1:1 mixture of propanone and Dichlorometane in 1-2ml increments. 8-10ml of eluent which was accurately measured was collected and concentrated to 1ml before being transferred into labeled glass vials (or ruber crimp caps) for PAHs analysis using Gas Chromatography[17, 18].Gas Chromatography Analysis was carried out according to the method of [17].

Instrumentation

The gas chromatography was Hewlett Packed 5890 series II, gas chromatography apparatus, coupled with flame ionization detector (FID) (Hewlett Packard, Wilmington, DE, USA), powered with HP chem station Rev. A 09:01 (10206) software to identify and quantify compounds. The GC operating conditions were as follow: fused silica column [30m×0.25μmfilmof HP-5(thickness)]; Split injection was adopted with a split ratio of 8:1, the inlet and injection temperature was set at 65°C to 3280°C. Using rubber septum and volume injected was 1ul. The column temperature was programmed as follow; hold at 65°C for 2min; 65-260°C at 12°C /min; 260°C -320°C at 15°C /min and maintained at 310°C for 8minutes and oven temperature was set at 65°C. Nitrogen was used as carrier gas (30ml/min). The hydrogen and compressed air pressure was 27.8psi at 35ml/min and 250ml/min respectively. The standards for 16 PAHs was obtained and subsequently used for the PAHs analysis. Comparison between the retention time of standards and that which was obtained from the extract of 1mL was used to identify the compounds while the quantification required individual PAHs analysis. To ensure accuracy for all the PAHs measured the determination of cross-contamination and interference according to the method of [19].

Quality control

Quality control was observed at all times during the entire course of this research. Analyses of procedural blanks were periodically carried out to ascertain quality of analytical results devoid of laboratory contamination and operational errors. The average blank concentration was subtracted from each sample to correct for methodological and equipment errors. The limit of detection and limit of quantitation were calculated as 3 and 10 times the standard deviation of the blank, respectively. The recoveries of each individual PAH varied from 93.14 to 104.92% for PHE and DahA, respectively. The calibration curves were obtained using a series of stock standard prepared through serial dilution with n-hexane to give 6 calibration standard PAH solutions containing 5, 10, 20, 30, 40, and 50 μg/L of stock solution. Calibration curves for all analyzed PAH standards (n = 6) had values of residual standard deviations that ranged between 78.05% and 101.20%, demonstrating good repeatability for the analytical method. Triplicate determinations were made Soil samples.

Health risk dietary exposure estimates

Health risk standards are not readily obtainable for all the individual PAH congeners, thus the risk of PAH congeners are ascertained with the toxicological factor approach and this is done by associating the potencies of different PAH mixtures to Benzo(a)pyrene (B(a)P). B(a)P is said to possess the highest the highest cancer causing potency (Agency for Toxic Substances and Disease Registry [20].

Toxic potency assessment

Toxicity equivalence factors (TEFs) relative to B[a]P have been provided for assessing the potential of various PAHs congeners to cause cancer as seen on Table 1 [21].These TEFs were adopted to calculate the potential toxicity of the PAH mixtures measured in this study as total benzo[a]pyrene equivalents (B[a]Peq). This method for PAHs health risk assessment [22].

Table 1. PAHs and their toxic equivalent factors (TEFs) (Nisbet and LaGoy, 1992)

PAHs	TEFs
Naphthalene (NAP)	0.001
2-Methylnaphthalene (metNAP)	0.001
Acenaphthylene (ACY)	0.001
Acenaphthene (ACE)	0.001
Fluorine (FLO)	0.001
Phenanthrene (PHE)	0.001
Anthracene (ANT)	0.01
Fluoranthene (FLA)	0.001
Pyrene (PYR)	0.001
Benz(a)anthracene (BaA)	0.1
Chrysene (CHR)	0.01
Benzo(b)fluoranthene (BbF)	0.1
Benzo(k)fluoranthene (BkF)	0.1
Benzo(a)pyrene (BaP)	1
Indeno(1,2,3-cd)pyrene (IcdP)	0.1
Dibenz(a,h)anthracene (DahA)	1

Incremental Lifetime Cancer Risk (ILCR) Of PAHS

Multi-pathway exposure for showcasing the PAHs in various media in the environment such as foods and soils can enter the human body via various gateways. These include ingestion, inhalation, or dermal contact. Assessments of the estimate of total degree of exposure, intensity, frequency, and length of time of exposure to PAHs present in the environment. USEPA [23] has provided a standard method of risk assessment of cancer widely used in most research work i.e., incremental lifetime cancer risk (ILCR)[14,24]. ILCR was used to ascertain the estimate of the quantity of human exposure to PAHs which results to in cancer in the environment. Humans can be exposed to PAHs in in soil via ingestion, inhalation, and dermal adsorption of soil dust particles. Equations (1-3) show the evaluation of ILCR for each exposure pathway.

To show quantitatively the life time probability of contracting cancer as a result of ingestion of carcinogenic PAHs, the Benzo(a)pyrene equivalents (BaPeq) concentration was also established and used to estimate the carcinogenic risk (CR).

Cancer-causing ability of B[a]P was used in the determination of oral slope factor. The oral slope factor for B[a]P is7.3(mg/kg/day) for ingestion, 3.85 (mg/kg/day) for inhalation, and 25 (mg/kg/day) for dermal adsorption, respectively. The values of assessment parameters in this study are presented on Table 2.

Table 2. Parameters used in cancer risk assessment.

Definition	Units	Children	Adults
Exposure frequency	(EF) Days/year	365	365 [12]
Exposure duration	(ED) Year	17	52 [12]
Average Body weight	Kg	60	32.7 [22]
Averaging time	(AT) Days	25,550	25,550 [3]
Ingestion rate of food(IRf)	kg person^{-1} day	0.345	0.345 [22]

Table 2. Continued

Inhalation rate IRi	m3/day	9.67 ± 2.39	12.44 ± 1.27[12]
Ingestion rate of soil IRs	mg/day	200	100 [3]
Exposed skin surface area(As)	cm^2	1150	2145[12]
Inhalation rate (InhR)	m^3/day	7.6	12.8[3]
Particle emission factor (PEF)	m^3/kg	1.36×10^{-9}	1.36×10^{-9} [3]
Soil-to-skin adherence factor(AF)	mg/cm^2-d	0.65 ± 1.2	0.49 ± 0.5 [12]
Dermal absorption factor(ABS)	Unitless	0.13	0.13 [12]

ILCR Dermal = Cs×As×Af×ABS×Ef×Ed / Bw×At × CSf (1)

ILCR Inhalation = Cs × Ir inhalation × Ef × Ed / Pef ×Bw × At × CSf × Cf (2)

ILCR Ingestion = Cs × Ir ingestion × Ef × Ed / Bw × At × CSf × Cf

where CS is the total of toxic equivalency quantities (TEQs) of sixteen PAHs relative to BaP using the toxic equivalency factor(TEFs) listed in Table 1.

Ratios and source identification of PAHs

The following formulas below were used for estimating the ratios and source identification of PAHs from anthropogenic sources of pyrolytic and petrogenic origin.

Diagnostic ratios (equations) used and their typically reported values in literature for source identification of polycyclic aromatic hydrocarbons

(PAHs Ratio)	Value range
ΣLMW/ΣHMW	< 1 Pyrogenic [25]
	> 1 Petrogenic
Flu/(Flu + Pyr)	< 0.4 Petrogenic [5]
	0.4–0.5 Fossil fuel combustion
	> 0.5 Grass, wood, coal combustion
	< 0.5 Petrol emissions [26]
	> 0.5 Diesel emissions
Ant/(Ant + Phe)	< 0.1 Petrogenic [26]
	> 0.1 Pyrogenic

Total Index = $Ant/(Ant + Phe) \Big/ 0.1 + Flu/(Flu + Pyr) \Big/ 0.4 + BaA / (BaA + chry) \Big/ 0.2$

a)ΣLMW = sum of the lower-molecular-weight (LMW) 2–3 ring PAHs; ΣHMW = sum of the higher-molecular-weight (HMW); Flu = fluoranthene; Pyr = pyrene; BaA = benz[a]anthracene; Ant = anthracene; Phe = phenanthrene; BaP =benzo[a]pyrene.

Secondary evaluation of carcinogenic risk on the soils

Secondary evaluation of carcinogenic PAHs for soils with multiple contaminants shows the risk posed by a contaminants eg PAHs according to the soil clean up level provided on the Clean up level look up table in mg/kg [17, 27]. When the summation of individual Ri values (ΣRi) >1, it implies further evaluation needed through site specific risk assessment.

$$Ri = Ci / CTVi \quad (7)$$

Where Ri = Risk posed by contaminant i

Ci=Maximum concentration of contaminant i

CTVi=Soil clean up level on the clean up level look up table (mg/kg)

Statistical analysis PAHs analysis

Data was analyzed statistically using IBM SPSS Statistics 20.One way analysis of variance (ANOVA) was used to determine the significant difference between PAHs concentration in Soilsamples analyzed in this study, considering a level of significance ($p \leq 0.05$). Data was reported as mean concentration of PAHs in samples ± Standard error of mean (S.E).

RESULTS AND DISCUSSION

Mean concentration of PAHs in soil

Rhizoshere soils around the industrial areas with various geographic coordinate locations at Ishiagu, Akwu-uru, Osisioma, Irete and Ngwo in the South Eastern, Nigeria respectively. Different parameters were used in assessing the health risk associated with the study locations (Table 2). The field co-ordinates for the various sampling sites are presented on Table 3. The mean concentration (mg/kg dry weight) of 16 USEPA priority PAHs analyzed for the Soils are presented on Table 4. Mean Concentration of PAHs in Soil samples ranged from below the limits of detection (0.01±0.00) in Ishiagu to 2.67±0.02 in Akwu-uru. All study sites had values significantly different and higher than ($P <$ 0.05) concentrations observed in Ishiagu and this is attributable to the industrial activities in the areas and particle bound deposition leading to uptake of PAHs by plant through gaseous (aerial) and uptake from soil [28,29]. PAHs concentrations in this study could be compared to the soils collected from one of the largest automobile repair and assemblage sites in uyo urban center and environs [30]. This indicates that PAHs distribution in the study sites could be attributed to industrial effluents and anthropogenic activities at the localized industries in each area. Apart from the automobile repairs other activities common among industries like spray-painting, welding, automobile techniques are also common in the location [30]. Ishiagu soil had PAHs concentrations generally BDL which may be attributed to the quarrying activities going on in that area thus exposing soil to higher degradation and secondary weathering[31]. Also, PAHs with low molecular weight are slightly aqua soluble, volatile, and mobile. Thus, they are easily removed from soils by their volatility and leaching resulting from erosion [15, 31 and 32]. This is because PAHs are thought to be removed by volatilization erosion, leaching, and plants absorption etc [30]. Although, this was not the case with site 2 and site 3 at the automobile repair shops at uyo which had PAHs concentrations BDL [30], owing to their farther distance from the source of contamination as PAHs distribution are variable based on proximity to pollution sources and sampling depth[15]. The accumulation of PAHs in all soil samples followed the order Akwuuru > Ngwo > Osisioma > Irete > Ishiagu. ∑PAH levels in soil samples were 13.00, 22.12, 9.55, 5.85mg/kg Osisioma, Akwuuru, Irete and Ngwo exceeding the DPR limit of 1mg/kg (1,000 μgkg−1) for soils except for Ishiagu (Ebonyi) which had concentrations below the WHO set limit 0.0001 mg/kg dw[17, 33 and 34]. ∑PAH concentration in soil for all the Study Soils except Akwu-uru in Anambra State were lower than the maximum range of 15 mg·kg−1 permissible by Dutch and Polish Environment Ministries in polluted soils[17]. This could be due to the unique activities; effluents generated by the industries in the location and may depict serious

environmental concerns which may be lethal to the entire populace [3]. Secondary evaluation of carcinogenic PAHs for soil (Table 5) with multiple contaminants showed that the sum of the individual Ri values (ΣRi) >1) using the soil clean up level look up table results implied further evaluation via site-specific risk assessment. The secondary evaluation on carcinogenic PAHs in soil for Anambra and Abia showed significant dominance above other study areas. However, ΣRi for all of the soils from study was > 1 i.e (59.86, 7.22, 99.31 and 26.01) for Osisioma, Irete, Akwuuru and Ngwo respectively. Therefore, requires site clean up to remediate the area [17].Also, most of the PAHs evaluated like Benzo[b]fluoranthene, Benzo[a]anthracene, Chrysene, Benzo(a)pyrene and benzo[k]fluoranthene are implicated in carcinogenesis according to the California Environmental Protection Agency[22].These high molecular weight PAHs are associated with prolonged effects due to less susceptibility to microbial degradation[33]. PAHs concentrations in soils are may vary due to proximity to pollution sources and sampling depths [3]. Consequently, the population of people living in and around the study sites may be predisposed to high risk of cancer due to long exposure to PAH compound through contaminated soil.

Source determination using PAHs diagnostic ratios (Table 6) change remarkably based on the source of the emissions to various environmental media. As a result, a site-specific correction factor, defined as the diagnostic ratio of two paired PAHs is taken specifically in a given medium. Using the correction factor from Wang *et al.* [26].The LMW-PAHS/HMW-PAHS were <1 for all study areas except Akwuuru >1 with values 0.28, 1.71, 0.25 <0.01 and 0.26 for Osisioma, Irete, Akwuuru, Ishiagu and Ngwo respectively. They persistence of high molecular weight PAHs suggests a non-petrogenic source of pollution indicating that PAHs concentrations in the areas may have accumulated as a result of various combustion activities in the industries whereas the value for Akwuuru indicated a petrogenic source of pollution. This may be attributable to the petrochemical industry located in the area. The Fla/(Fla + Pyr) ratio values were < 0.4 for most of the soil samples for various states except Akwuuru which was >0.4, suggesting pyrolytic PAH sources due to diesel emissions and wood combustion[8].This was expected as most of the industries make use of diesel engines while those of the other States signaled petrogenic source. Ant/(Ant + Phe) ratio < 0.1 is often taken as an indication of petroleum source of PAHs while a ratio > 0.1 indicates a dominance of combustion. In this study, Ant/(Ant + Phe) were >0.1 in all study locations indicating pyrolytic sources except Ishiagu which showed petrogenic source. The BaA/(BaA + Chr) ratio < 0.2 implies petroleum, from 0.2 to 0.35 either petroleum or combustion, and > 0.35 combustion[34]. In this study, BaA/(BaA + Chr) ratio values(0.65,0.9,0.67,0.64)Abia, Imo, Anambra, Enugu respectively were >0.35 indicating pyrolysis where as that of Ishiagu was vice versa . The total index was also estimated as the sum of single ratios normalized for the limit value (low temperature sources/ high temperature sources). PAHs related to high temperature processes (combustion) have a total index >4, while PAHs originating from low temperature processes (petroleum products) have a total index <4. In our study, the total index of 1.62, and 1.63 was gotten for Osisioma and Akwuuru which denotes combustion origin of PAHs **[**2**]**. These results indicate that fossil fuel burning and vehicular pollution are the prominent sources of the PAHs in roadside soil even at a heavy coal mining area. Both areas had similar companies and thus may exhibit similar characteristics both chemically and physically thus indicating like source and morphology of PAHs. In addition, the large market/business area and human activities in both areas is considerably high resulting in burning of enormous refuse thus contributing to accumulation of PAHs in both plants and soil [2]. Irete had the highest value (2.17) indicating pyrolysis in the area. The lowest was Ngwo(1.18) representing strongly pyrolytic source probably from the Coca-cola wastewater treatment plant, manufacturing machines etc. The results indicate that fossil fuel burning and vehicular pollution are the prominent sources of the PAHs in soil even at a coal mining area[26].Total index could not be gotten for Ishiagu quarrying area as results were <0.01(BDL).

The variations in the various ratios determined in this Study depicts that there may be no point source of pollution as various activities are carried out at the various industries and environs for example the burning of fuels by high duty industrial machines that release PAHs into the air, soil, water bodies and plants etc as well as other anthropogenic activities [17].

Table 3. The field coordinates of sample locations

locations	Latitude	Longitude
Ishiagu	5^0 56^1 55.72968^{0}N	7^0 34 16. 29804" E
Ngwo	6^0 25' 19.56072"N	7^0 24' 24.50088" E.
Akwu-uru	5^0 59' 48.50088" N	6^0 55^1 18.43788" E
Irete	5^0 30^1 0.606"N ^{0} N	6^0 59^0 31.062" E.
Osisioma	5^0 10'46.734"N	7^0 19^1 39.402" ^{0} E .

Table 4. PAHs Concentration (mg/kg dry weight) in Soils, South East, Nigeria.

PAHs	ABIA	IMO	ANAMBRA	EBONYI	ENUGU
NAP	0.10±0.01a	2.24±0.01b	0.15±0.01c	BDLd	0.04±0.00e
METNAP	0.10±0.01a	1.99±0.01b	0.15±0.01c	BDLd	0.05±0.01e
ACY	0.14±0.01a	0.94±0.02b	0.21±0.01c	BDLd	0.06±0.01e
ACE	0.20±0.01a	0.31±0.01b	0.32±0.01b	BDLc	0.09±0.01d
FLO	0.28±0.02a	0.15±0.01b	0.42±0.01c	BDLd	0.12±0.01b
PHE	1.29±0.01a	0.14±0.01b	2.04±0.01c	BDLd	0.54±0.01e
ANT	0.72±0.01a	0.26±0.01b	1.14±0.01c	BDLd	0.30±0.01b
FLA	1.79±0.02a	1.72±0.01a	2.82±0.01b	BDLc	0.74±0.01d
PYR	1.08±0.02a	1.10±0.01a	1.70±0.01b	BDLc	0.45±0.01d
BaA	0.15±0.01a	0.18±0.01a	0.24±0.01b	BDLc	0.07±0.01d
CHR	0.08±0.01a	0.02±0.00b	0.12±0.01c	BDLd	0.04±0.01e
BbF	1.69±0.02a	0.15±0.01b	2.67±0.02c	BDLd	0.70±0.01e
BkF	0.31±0.01a	0.09±0.02b	0.49±0.02c	BDLd	0.14±0.02e
BaP	0.59±0.02a	0.07±0.01b	0.92±0.01c	BDLd	0.24±0.01e
IcdP	2.16±0.01a	0.12±0.01b	3.44±0.02c	BDLd	0.89±0.01e
DahA	2.32±0.01a	0.07±0.01b	5.29±0.02c	BDLd	1.38±0.02e
	TOTAL (PAHS) 13±0.21	9.55±0.18	22.12±0.20	BDL	5.85±0.17

Values in different letters in the same column are significantly different at 0.05 level ($P \leq 0.05$) while same letters in the same column are not significantly different ($P \leq 0.05$). Naphthalene(NAP), Methyl-Naphthalene(METNAP), Acenaphthylene(ACY)Acenaphthene(ACE), Fluorene(FLO), Phenanthrene(PHE), Anthracene(ANT), Fluoranthene(FLA), Pyrene(PYR), Benzo(a)anthracene(BaA), Chrysene(CHR), Benzo(k)fluoranthene(BkF), (BaP)Benzo(a)pyrene,(BbF) Benzo(b)fluoranthene, (Icdp)Indeno(1,2,3) perylene,.(DahA)Dibenzo(a,h)anthracene)

Table 5. Secondary carcinogenic characteristics of solis using concentrations in mg/kg.

	SOIL CTV1	C (Abia)	C (Imo)	C (Anam)	C (Ebon)	C (Enug)	C1/CTV1 (Abia)	C/CTV (Imo)	C/CTV (Anam)	C/CTV (Ebon)	C/CTV (Enug)
Benz(A)athracene	0.15	0.15	0.18	0.24	0.00	0.07	1.00	1.20	1.6	0.00	0.47
Benzo(B)Fluoranthene	0.33	0.08	0.02	0.12	0.00	0.04	5.12	0.45	8.09	0.00	2.12
Benzo(k)Fluoranthene	0.33	1.69	0.15	2.67	0.00	0.7	0.93	0.27	1.48	0.00	0.42
Dibenz(a,h)anthracene	0.33	0.31	0.09	0.49	0.00	0.14	7.03	0.21	16.03	0.00	4.18
Indeno(1, 2, 3cd)pyrene	0.33	0.59	0.07	0.92	0.00	0.24	6.54	0.36	10.42	0.00	2.7
Chrysene	0.33	2.16	0.12	3.44	0.00	0.89	0.24	0.06	0.36	0.00	0.12

Table 5. Continued.

Benzo(a)pyrene	0.015	2.32	0.07	5.29	0.00	1.38	39.00	4.67	61.33	0.00	16
ΣRi							59.86	7.22	99.31	0.00	26.01

IS RI >1?

OSISIOMA	IRETE	AKWUURU	ISHIAGU	NGWO
YES	YES	YES	NO	NO
YES	NO	YES	NO	YES
NO	NO	YES	NO	NO
YES	NO	YES	NO	YES
YES	NO	YES	NO	YES
NO	NO	NO	NO	NO
YES	YES	YES	NO	YES
YES	YES	YES	NO	YES

Table 6. Source determination using diagnostic ratios.

	ABIA	IMO	ANAMBRA	EBONYI	ENUGU
ANT/PHEN+ANT	0.36	0.65	0.36	<0.01	0.36
FLA/(FLA+PYR)	0.62	0.61	0.62	<0.01	0.18
BAA/(BAA+CHRY	0.65	0.90	0.67	<0.01	0.64
TOTAL INDEX	1.62	2.17	1.63	<0.01	1.18
LMW/HMW	0.278269	1.713068	0.250424	0.00	0.258065

ABIA	IMO	ANAMBRA		EBONYI	ENUGU
LMW/HMW	<1	>1	<1	<1	<1
ANT/PHEN+ANT	>0.1	>0.1	>0.1	<0.1	>0.1
FLA/(FLA+PYR)	<0.4	>0.4	<0.4	<0.4	<0.4
TOTAL INDEX	<4	<4	<4	<4	<4

*LMW/HMW<1--PYROLYTIC WHILE >1 PETROGENIC SOURCE
ANT/(PHEN +ANT)< 0.1 PETROGENIC WHILE>0.1 PYROLYTIC
FLA/(FLA+PYR)<0.4--PETROGENIC WHILE >0.4 PYROLYTIC
TOTAL INDEX >4 COMBUSTION <4PETROGENIC

Estimated daily intake

Multi route assessment of PAHs exposure was conducted to determine the relative cumulative exposure to PAHs via the different pathways. Estimated daily intake of PAHs in soils (Table 7). Results was within the interval of 2.54819E-06mg/kg/body to 8.57844E-05 mg/kg/body(Adults) and 2.67993E-06 mg/kg/body to 9.02193E-05 mg/kg/body for children for samples from Osisioma, Irete, Nnewi, Ishiagu and Ngwo respectively. Although, health risk to PAHs depends also on the extent of exposure, dosage, age, other existing health condition, different modes of toxicity and exposure routes. Furthermore, exposure to pollutants e.g. PAHs should not be sole determinant to the potential risk to human health exposure, duration and levels of exposure should also be considered [22].

Table 7. Average daily intake of soil for adults and children using concentration for each soil.

		Abia	Owerri	Anambra	Ebonyi	Enugu
Dermal	Adults	1.36 E-04	8.33E-06	2.80E-04	BDL	7.32E-05
	Children	6.05E-05	3.71E-06	1.25E-04	BDL	3.26E-05
Ingestion	Adults	3.04 E-04	1.86E-05	6.26 E-04	BDL	1.64E-04
	Children	3.64 E-04	2.23E-05	7.51 E-04	BDL	1.96E-04
Inhalation	Adults	1.48E-09	9.07E-11	3.05E-09	BDL	7.97E-10
	Children	6.91E-10	4.23E-11	1.42E-09	BDL	3.72E-10
Total	Adults	4.40 E-04	2.69E-05	9.07 E-04	BDL	2.37 E-04
	Children	4.25 E-04	2.60E-05	8.76 E-04	BDL	2.29 E-04

Incremental lifetime cancer risk

As shown in Table 8, the cancer risk levels of human exposure to PAHs in the Soils of the study sites apart from Ishiagu ranged from(8.30 E-06 to 2.8E-04)dermal, (1.90E-05 to 6.30E-04) ingestion and (9.10E-11 to 3.1E-09) for inhalation adsorption and (3.70 E-06 to 1.2E-04)dermal, (2.2E-05 to 7.5E-04) ingestion and (4.2- E-11 to 1.4E-09) for Adults and Children respectively Incremental Lifetime Cancer Risk (ILCR), through ingestion of Soil for children and adults was significantly higher (69.06%) than the total cancer risk from other routes(30.94 and 0.00034%) for dermal and inhalation respectively. This is also because aliments like foods apart from the soil/dust could contribute to the elevated levels [29]. Thus, inhalation of soil when compared with the other routes of exposure was negligible therefore may not be an issue of concern. Similar results were observed in human exposure to PAHs from urban soil/dust of Isfahan (Iran), Xi'an and Shanghai (China) [3, 35, 36 and 37].The cancer risk levels of ingestion in children were more than those of the adults which is attributable to their obvious playful lifestyle on soil/dust surfaces like in their playgrounds, football field and inherent hand-to-mouth activities. Hence, PAHs contaminated soil in the industrial locations may be hotspots for PAHs ingestion as well as other industrial contaminant [3, 35 and 36]. In addition, the PAH intake by a child is pertinent because of their lower body weights relative to that of adults. Therefore, the risk assessment of PAHs exposure to children from industrial soil/dust maybe considerably greater than those of adults [3, 24]. The cumulative CR(Cancer Risk) gotten via the three routes was given as (4.40E-04, 2.69E-05, 9.07E-04, BDL and 2.37E-04)for adults and (3.73E-04,2.28E-05,7.68E-04,BDL and 2.01E-04) for children in Osisioma, Irete, Akwuuru, Ishiagu and Enugu respectively. These values do not show carcinogenic risk due to PAHs intake because the potential cancer risk is within the acceptable range (10^{-6} to 10^{-4}) and a high cancer risk is a result above 10^{-4} [35, 36 and 37]. However, persistent accumulation may go beyond safe limits overtime. Also, Wang *et al*. [26] reported that the ILCR values of human exposure to PAHs from urban surface dust of Xi'an are 8.2 x 10^{-5} for children and 7.3 x 10^{-5} for adults, respectively, which are similar to those in most of the soils in present study. These values indicate that the cancer risk of human exposure to PAHs from urban soil is comparable to that from urban surface dust owing to the similarities in the characteristics of both sampling areas. The populace in the study areas may be exposed a wide range of contaminants like PAHs, other toxic substances. The synergistic effects of these contaminant groups may check during health risk determination [38, 39].As this may further increase cancer risk to Human lives.

Table 8. Life Time Cancer Risk (LCR) for Adults and Children using the total observed TEBaP concentration for each soil.

		Abia	Owerri	Anambra	Ebonyi	Enugu
Dermal	Adults	5.44E-06	3.33E-07	1.12E-05	BDL	2.93E-06
	Children	2.42E-06	1.48E-07	4.99E-06	BDL	1.30E-06
Ingestion	Adults	4.16E-05	2.55E-06	8.58E-05	BDL	2.24E-05
	Children	4.99E-05	3.06E-06	1.03E-05	BDL	2.69E-05
Inhalation	Adults	3.80E-10	2.33E-11	7.83E-10	BDL	2.04E-10
	Children	1.77E-10	1.08E-11	3.65E-10	BDL	9.53E-11
Total	Adults	4.71E-05	2.88E-06	9.70E-05	BDL	2.53E-05
	Children	5.23E-05	3.21E-06	1.08 E-04	BDL	2.82E-05

CONCLUSIONS

The risk assessment of PAHs Soil exposure through the Oral, Inhalation and Dermal pathway indicated that Estimated Daily Intake (EDI) of PAHs in samples were within the stipulated reference dose. The Incremental Life Time Cancer Risk (ILCR) via the various routes of exposure in Soils of 10^{-6} to 10^{-4} across the study locations for adults and children indicated within the safe limits (10^{-6} to 10^{-4}) and thus may not show an issue of concern. However, bioaccumulation overtime may raise the carcinogenic risk of PAHs. The diagnostic ratios for source determination of PAHs suggest that there is no point source of pollution in the industrialized study areas. Hence, prompt action is needed following the results obtained from the evaluations of the study soils. As the health of exposed population especially children may be seriously endangered overtime due to bioaccumulation of PAHs. Policy makers and other concerned stakeholders should also help in making recommendations and regulations in policy decisions and mitigating measures for environment and human health protections.

CONFLICT OF INTERESTS

They Authors declare that they have no conflict of interest

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