

Distribution Behaviour of Polycyclic Aromatic Hydrocarbons in Roadside Soil at Traffic Intercepts within Onitsha Metropolis, South-East Nigeria

IGWE J.C¹, UKAOGO.O.P^{1*} OBIKE.I.A¹ AND ETUSIM .P. E²

1.Department of pure and industrial Chemistry, Abia State University, P.M.B 2000 Uturu-Nigeria

2.Department Animal and Environmental Health, Abia State University, P.M.B 2000 Uturu-Nigeria

Abstract

Polycyclic aromatic hydrocarbons (PAHs) pollution in roadside soil was conducted in a developing city environment of South-Eastern Nigeria during raining season to ascertain the contamination levels and their distribution behavior in soil. The concentration of polycyclic aromatic hydrocarbons was determined at nine locations of Onitsha city, 3m distances from roadside in soil covering all the major traffic intercepts within the city. The samples were extracted in acetone and dichloromethane (1:1) using soxhlet extraction. The total concentrations of 16 PAHs ranged from 14,260 to 14,289 $\mu\text{g}/\text{kg}$, with a mean of 14,276 $\mu\text{g}/\text{kg}$ which were than the limit <10000 $\mu\text{g}/\text{kg}$ set for PAHs in the soil and the seven possible carcinogenic PAHs accounted for 17.2 % of 16PAHs detected. Chrysene was the polycyclic aromatic hydrocarbons found in highest concentration at all the intercepts ranging between 4050 to 4053 $\mu\text{g}/\text{kg}$ with the mean of 4052 $\mu\text{g}/\text{kg}$. Among different functional areas, the higher level of PAHs was found in Obosi junction (right) followed by Main market road junction (right). The composition of PAHs was characterized by the high molecular weight PAHs, among which fluoranthene, Indeno(1,2,3,-cd)Pyrene, Acenaphthene chrysene were most dominant components. A principal component analysis and PAHs isomeric ratios indicate that PAHs in Onitsha road soil mainly originated from combustion. The toxic assessment suggested that soil PAHs exposure is medium carcinogenic at present level.

Keywords: polycyclic aromatic hydrocarbons, Gas chromatography, season, traffic density, pollutants, principal component analysis, samples, concentration, carcinogenic.

1. INTRODUCTION

One of the major environmental concerns in urban and industrial areas are polycyclic aromatic hydrocarbons. They have a relatively low solubility in water, but are highly lipophilic (Sim et al., 1983). The term Polycyclic aromatic hydrocarbons (PAHs) also known as Poly-aromatic hydrocarbons or polynuclear aromatic hydrocarbons are a class of organic chemicals consisting of two or more fused aromatic rings and do not contain heteroatom or carry substituents (Fetzer, 2000). PAHs belong to the group of persistent organic pollutants (POPs). These are organic pollutant contaminants that are resistant to degradation, can remain in environment for a long period and have the potential to cause adverse environmental effects (Luch, 2005). Soil system is a major reservoir and sinks for urban pollutants because of its quantity and holding capacity for organic pollutants (Wild and Jones., 1995).

As a pollutant, PAHs are at concern because some of them have been identified as carcinogenic, mutagenic and teratogenic (ECSC, 2002).Environmental analysis often involves wide variety of matrices, ranging from air to sewage water to polluted soil samples (Khan et al., 2005; Igwe et al., 2008; Shah et al 2009).Motor vehicles are thought to be the major source of atmospheric polycyclic aromatic hydrocarbons, PAHs occur in particles (Bodzek et al., 1993).

PAHs have low water-solubility and hydrophobic property, and they can intensively diffuse in the non water phase, being adsorbed on the granules, so the soils become one of their primary environmental habitations. The residual PAHs in the soils not only influence the normal functions of the soils and decrease their environmental qualities, but also gather gradually in both animals and plants after entering the cropland ecosystem. They also enter human bodies through food chains, which cause serious harm to human health and lives (Huang and Wei, 2003).

Presently, a great deal of researches about the PAHs in soils and plants have been carried out nationally and internationally, and the main focuses are as follows: the contents and sources of the PAHs in the soils(Ding et al., 2004), distribution and migration(Ge et al., 2005), the relation between their physicochemical properties and behaviors in the soils(Ling et al., 2005), the relation between environmental factors and their behaviors(Liste and Alexander, 2000), risk assessment and management(Menzies et al., 1992); the mechanism of PAHs being adsorbed by plants(Tao et al., 2003), the influence factors, remediation of soils polluted by PAHs(Zhang et al., 2005) and so on. However, researches about PAHs in soils and plants around oily sludges are relatively less (Zhan et al., 2003).

Since these process takes place almost everywhere in ecological system ,PAHs are found in exhaust, tar, fumes, carbon and petroleum industry, cigarette smoke, forest fires, burning of energy resources, smoked

food, water, air and soil. PAHs are lasting, poorly degradable pollutants with mutagenic and carcinogenic properties (Buco et al., 2004). Automobile is an extremely important segment of modern human society. The impact of automobile emission on environment, predominantly on air and water is increasing day by day (Kumata et al., 2000). Naphthalene is the simplest example of PAHs (ECSC, 2002). PAH may also be degraded by some microorganisms in soil (Sims et al., 1983). PAHs pollutants have high molecular mass, PAHs of 4 and more condensed aromatic rings are considered to be more dangerous than 2 and 3 rings PAHs in view of their potentials (Kawamura et al., 1994). They interact with DNA resulting in mutations and cancer, Benzo(a)pyrene being one of the most toxic and carcinogenic compounds known. In animal cell PAHs are transformed by oxidases and reductases. PAHs metabolism generates reactive electrophilic metabolites, which are the actual carcinogenic compounds that cause DNA damage (Wang, 2002).

PAHs compounds are extracted from filter with a solvent and analyzed by high performance liquid chromatography with fluorescence detector or gas chromatography with flame ionization detector or gas chromatography-mass spectrometry (Soltanali and Shama Hagani, 2008). The US Environment Protection Agency (US EPA) has identified 16 PAHs as priority environmental pollutants. Among them, US EPA considers seven, i.e. benzo[a]anthracene, chrysene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, dibenz[a,h]anthracene and inde-no[1,2,3-cd]pyrene, as probable human carcinogens (NTP, 2005).

PAHs (which are known for their strong mutagenic, carcinogenic and toxic properties) are composed of carbon and hydrogen atoms arranged in the form of fused benzene rings (Sims, et al 1983). PAHs are the most toxic among the hydrocarbon families (Catoggio, 1991). Therefore, this work focuses on determining the levels and distribution behaviour of PAHs in soil at traffic intercept in Onitsha metropolis. This will help to elucidate the level of soil contamination in Onitsha by PAHs and to create awareness to the inhabitants about exposure dangers.

2. MATERIALS

Sampling sites

Onitsha is one of the prosperous, fast developing cities and one of the major expanding cities in Nigeria. Onitsha is a commercial, educational, and religious centre close to river port on the eastern bank of the Niger river in Anambra State, southeastern Nigeria. Today, Onitsha is a modern day urban society, there is an army barrack, a school of metallurgy, and it is the home of the biggest market in the whole of Africa, called the Onitsha Main Market. Onitsha has the population of 561,106 people as at the 2006 census (NPC, 2006). Onitsha is located at 6.14543 (latitude in decimal degrees), 6.78845 (longitude in decimal degrees) at an average elevation/altitude of 72 meters.

Based on population and traffic density, nine locations were divided into places of high population and traffic density i.e. (where traffic density was high during 7am to 8pm) and places of low traffic and population density (places with low traffic speed and average population density during 7am to 8pm). The samples were collected at the following places :- Obosi junction(OJ), Main-market junction(MJ), Upper-Iweka Junction (UJ), Head-bridge junction(HJ), Nkpor junction(NJ) (areas of high traffic and population density) and Fegge junction(FJ), DMGS junction(DJ), 3-3 junction (3J), Owerri road(OJ) (areas of low traffic and population density). Total of 18 samples were collected from both sides of the road (left and right sides) in triplicate samples. The map of Onitsha showing the sampling points in figure 3.1

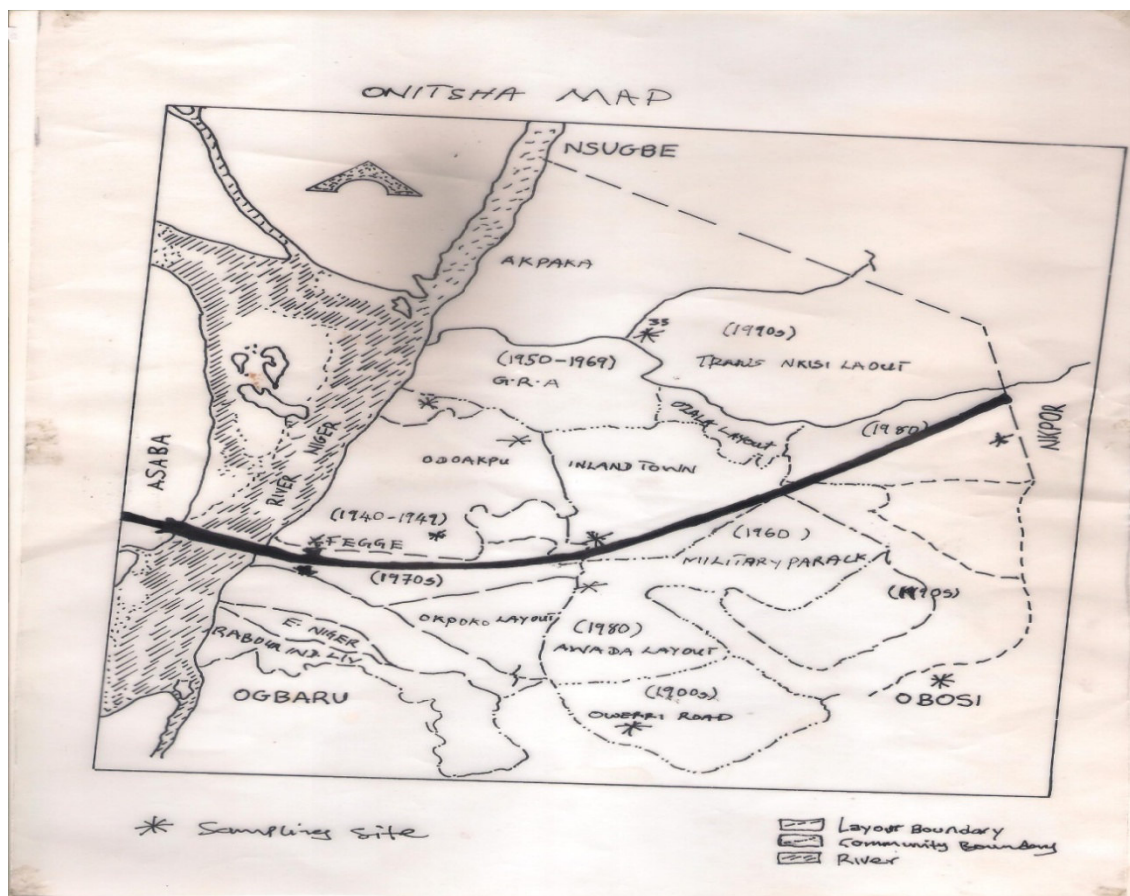


Fig 3.1 Map of Onitsha showing the sampling points.

SAMPLE COLLECTION AND TECHNIQUE

Samples were collected from each sampling location at a distance of 3m from different direction of the roadside (left and right side). Samples were collected by scooping 6cm below the surface layer top soil and stored in polyethylene bags. They were then taken to the laboratory, stones, leaves and other extraneous materials were sieved out before analysis. All samples were dried in a hot oven maintained at 40 to 60°C for the removal of free moisture. The samples were preserved in a desiccator and stored in the dark before extraction.

3. EXTRACTION OF PAHs

All reagents were of analytical grade, used as purchased without further purification. About 10g of pre-dried soil samples were heated at 40 to 60°C to remove any trace of moisture before extraction. Dried soil sample were homogenized in a mortar and then transferred in soxhlet apparatus and extracted using acetone and dichloromethane (1:1 ratio) as solvent at the rate of 3 cycles for 8 hours. The extract were allowed to cool and filtered through filter paper .The filtrate was concentrated to 1ml volume using water bath .The samples prepared was preserved in amber coloured tubes stored in a refrigerator below 4°C before analysis. Samples were analyzed for identification and concentration of PAHs by Gas-Chromatography-Flame ionization Detector(GC-FID) model 6890 made by Hewlett Packard.

4. RESULTS AND DISCUSSIONS LEVELS OF PAHs

The result of average concentration of Σ PAHs determined in 18x3 soil samples during the rainy season at a distance of 3m from different directions of the road (right and left side) have been shown in Table 4.1 and Table 4.2. In the present study 16 PAHs as listed by the united states Environmental Protection Agency (US EPA) were determined namely Naphthalene(Na); Acenaphthene (Ace); Acenaphthylene(Acy); Fluorene(FI); Fluoranthene(Flu), 1,2-Dibenzathracene(1,2-D); chrysene(Chr); Benzo (k) fluoranthene B(k)F; Benzo (b) fluoranthene B(b)F Benzo (a) pyrene (BaP); indeno (1,2,3-cd) pyrene(IP); 1,12-Benzoperylene(1,12-B); 1,2,5,6-DiBenzathracene (1,6-D); pyrene (pyr); Anthracene(An) and phenanthrene(phe). Although not all the 16 PAHs were detected from the soil samples results were perhaps due to close proximity of intercepts from road side in the form of buildings, plants, shops in areas of high population and traffic density. The total PAHs from each site

and locations are shown in Table 4.1. OJR has the highest concentration of some PAHs among the nine locations from a distance of 3m from the roadside with the mean value of 1.66 mg/kg and the lowest was UJR with the mean value of 0.17 mg/kg. Moreover IcdP, one of the most potent carcinogenic PAHs was more in the soils and had the highest concentration in MJR with mean value of $1220 \pm 70 \mu\text{g}/\text{kg}$. The higher concentration of ΣPAHs ($>1000 \mu\text{g}/\text{kg}$) were detected in soil samples at OJR, OJL, MJR, MJL, 3JR, 3JL, and FJR which were highly polluted by heavy traffic emission and industrial activities, The lower concentration ($<1000 \mu\text{g}/\text{kg}$) were observed in soil samples at NJR, HJL, HJR, HJL, OR, OL, UJR, UJL, DJR and DJL. These locations were not affected directly by industrial activities and heavy traffic except HJR and UJL which always have a heavy traffic between 4.00pm to 7.00pm, but had low PAHs concentration. This is because the rains must have washed the PAHs down below 3m. The concentration of $\Sigma 7\text{c-PAHs}$ accounted for 0.5% of ΣPAHs in roadside soil from Onitsha. B(a)P, one of the most potent carcinogenic PAHs was not detected in all the soil samples. The obtained data for PAHs concentration in soil samples compared with data from literature were found to remarkably vary. As shown above in Table 4.5, the concentration of ΣPAH in this study with the mean value of $14276 \pm 11.78 \mu\text{g}/\text{kg}$ was lower than those in soil from USA ($58680 \mu\text{g}/\text{kg}$) (Rogge *et al.*, 1993), Tilahuac and Milpa Alta, Mexico ($9130-11220 \mu\text{g}/\text{kg}$ and $11430-35770 \mu\text{g}/\text{kg}$) (Rutilio *et al.*, 2011). But PAHs concentration level in Onitsha roadside soil was higher than those in soil of Tokushima, Japan ($611 \mu\text{g}/\text{kg}$) (Yang *et al.*, 2002), Hong Kong, China, Miami, Florida ($1869 \mu\text{g}/\text{kg}$) (Banger *et al.*, 2010), Kota Bharn, Malaysia ($1450 \mu\text{g}/\text{kg}$) (Fadzil *et al.*, 2008).

According to the criteria established by Maliszewka-Kordybach (1996), four classes of soil contamination were identified based on a total of 16 PAHs: non-contaminated ($200-600 \mu\text{g}/\text{kg}$), contaminated soil ($<200 \mu\text{g}/\text{kg}$), weakly contaminated soil ($<1000 \mu\text{g}/\text{kg}$) and strong contaminated soil ($>1000 \mu\text{g}/\text{kg}$) in general, Onitsha soil was contaminated by PAHs.

4.1 DISTRIBUTION BEHAVIOUR OF PAHS AT HIGH POPULATION AND TRAFFIC DENSITY INTERCEPTS.

The concentration of PAHs in site MJR was very high for the high population and traffic density and the presence of one of the biggest market in West Africa (Main market, Onitsha) and very busy with traffic from 8am to 4pm could be part of the reason. The ΣPAHs range from $1500 \mu\text{g}/\text{kg}$ to $1510 \mu\text{g}/\text{kg}$ with mean \pm SD of $1500 \pm 10 \mu\text{g}/\text{kg}$ as shown in Table 4.1, This is higher in concentration when compared to soil from two industrial zones in Korean Peninsula, south Korea, which ranged between 110 and $179 \mu\text{g}/\text{kg}$ (Hashmi *et al.*, 2005). The PAHs detected in these sites were 1,2-D with the mean \pm SD of $270 \pm 0.01 \mu\text{g}/\text{kg}$ and IcdP with mean $1220 \pm 0.03 \mu\text{g}/\text{kg}$ as shown in Table 4.3 Both are carcinogenic PAHs and very high compare to urban soil of Tokushima Japan ($611 \mu\text{g}/\text{kg}$) (Yang *et al.*, 2002). The concentration of PAHs in soil of site MJL was also very high because of the high traffic density in the area with ΣPAHs range of $1470-1490 \mu\text{g}/\text{kg}$ with mean \pm SD of $1480 \pm 10 \mu\text{g}/\text{kg}$ this was high compared to that of soil sample of Bus stand (J8) in Jalandhar India ($4.10 \mu\text{g}/\text{kg}$), the values of PAHs found in these sites are 1,2-DIB with the mean \pm SD of $260 \pm 0.01 \mu\text{g}/\text{kg}$ and IP with the mean \pm SD of $1220 \pm 0.03 \mu\text{g}/\text{kg}$ as shown in Table 4.4 which is also very high and shows that people in these area are at risk of developing PAHs related illness such as cancer.

The concentration of PAHs in the soil sample of site 3JR was very high due to the presence of two great institutions (Nwafor Orizu College of education and Federal Government Girls College) and industrial activities. The PAHs ranged from $1450-1470 \mu\text{g}/\text{kg}$ with mean \pm SD of $1460 \pm 10 \mu\text{g}/\text{kg}$ compare to that of urban soil of Tokushima, Japan ($611 \mu\text{g}/\text{kg}$) (Yang *et al.*, 2002), As a result of high temperature combustion and vehicle emission in these area, Flu and Chry were detected as shown in Table 4.3 with the mean \pm SD of $270 \pm 0.02 \mu\text{g}/\text{kg}$ for Flu and $1170 \pm 0.01 \mu\text{g}/\text{kg}$ for Chry which were considered as probable human carcinogens (NTP, 2005).

The concentration of PAHs in 3JL was very high due to the area heavily polluted by the heavy traffic emission and coal combustion, roasting of yam, plantain and corn (maize). The ΣPAHs ranged from $1480-1490 \mu\text{g}/\text{kg}$ with mean \pm SD of $1490 \pm 10 \mu\text{g}/\text{kg}$. Four PAHs were detected in these site as shown in Table 4.4, Flu with the mean \pm SD of $290 \pm 0.02 \mu\text{g}/\text{kg}$, chry which is probable human carcinogen (NTP, 2005) with the mean of $570 \mu\text{g}/\text{kg}$, Ace with mean \pm SD of $230 \pm 0.01 \mu\text{g}/\text{kg}$ and An with mean value of $410 \mu\text{g}/\text{kg}$.

The concentration of PAHs in soil sample of site OJR was contaminated with PAHs >1000 due to the presence of large automobile spare part market and Metallurgical institute located in this area. The ΣPAHs ranged from $1665-1670 \mu\text{g}/\text{kg}$ with mean \pm SD of $1660 \pm 0.01 \mu\text{g}/\text{kg}$. The PAHs detected were Ace with mean of $530 \mu\text{g}/\text{kg}$, 1, 2-DIB with mean value of $150 \mu\text{g}/\text{kg}$ and chr with mean value of $980 \mu\text{g}/\text{kg}$. These PAHs are probable human carcinogen (NTP, 2005). The PAHs were lower when compared with the Canadian guideline value in table 4:6.

The concentration of PAHs in soil of site OJL were also contaminated with PAHs due to the same large automobile spare part market, where used cars are de-assembled, it is petrogenic source: The ΣPAHs range from $1320-1.360 \mu\text{g}/\text{kg}$ with the mean \pm SD of $1340 \pm 10 \mu\text{g}/\text{kg}$ which is high when compare with roadside soil of

mission chowk in jalandher, India (1090 $\mu\text{g}/\text{kg}$) (Kumar and Kothiyal, 2011). Only 1, 2-D and Flu were detected with mean values of 390 $\mu\text{g}/\text{kg}$ and 950 $\mu\text{g}/\text{kg}$ as shown on Table 4:4, other PAHs were <0.01.

For DJR and DJL are also highly populated and also have high traffic density between 7.00 am and 7.00 pm due to the presence of an institution (Denis memorial Grammar School) one of the oldest college in Onitsha and the way to Onitsha main market . And has lot of shops round the area. The ΣPAHs ranged from 660-630 $\mu\text{g}/\text{kg}$ with mean \pm SD of 610 \pm 10 $\mu\text{g}/\text{kg}$. The PAHs detected were 1,2-D with mean of 54 $\mu\text{g}/\text{kg}$,B(a)F mean of 12 $\mu\text{g}/\text{kg}$, 1P with mean of 87 $\mu\text{g}/\text{kg}$ and 1,12-B with mean of 460 $\mu\text{g}/\text{kg}$ while only two PAHs were detected at DJL, 1,2- DIB with mean of 51 $\mu\text{g}/\text{kg}$ and Chr with mean of 730 $\mu\text{g}/\text{kg}$.

For HJR and HJL are on a busy road with less traffic density and the popular river Niger with the bridge that links Onitsha and Asaba which is also a developing city in Delta state. 7 PAHs were detected on this areas, which are An with mean of 130 $\mu\text{g}/\text{kg}$, Flu with mean of 100 $\mu\text{g}/\text{kg}$ for HJR as shown on Table 4:3 While, Ace with mean value of 23 $\mu\text{g}/\text{kg}$, Acy with mean of 29 $\mu\text{g}/\text{kg}$,Fl with mean of 76 $\mu\text{g}/\text{kg}$, An with mean of 120 $\mu\text{g}/\text{kg}$ and Phe with mean value of 73 $\mu\text{g}/\text{kg}$ which is shown in Table 4:4

4.2 BEHAVIOUR OF PAHS AT PLACES OF AVERAGE POPULATION AND TRAFFIC DENSITY IN INTERCEPTS.

NJR is an area which is less populated but mostly a residential area. The sample can be used as the control sample and only 1,6-D was detected which is also considered probable human carcinogens (NTP, 2005) with the range of 210 – 270 $\mu\text{g}/\text{kg}^{-1}$ with mean \pm SD of 240 \pm 0.02 $\mu\text{g}/\text{kg}$ which is low compared to the soil of Guangzhou, in China (376 $\mu\text{g}/\text{kg}$)(Chen et al., 2005) and high when compare to the soil of Hong Kong (55 $\mu\text{g}/\text{kg}$) (Zhang et al., 2006).

NJL is also less populated and only has a high traffic at 5.00pm to 7.00pm, it is a residential area and only 1, 6-D was detected with the range of 220 -270 $\mu\text{g}/\text{kg}$ and mean \pm SD of 220 \pm 70 $\mu\text{g}/\text{kg}$ and other PAHs were not detected.

For OR and OL are less populated area. Big vehicles with diesel exhaust go through this road and the road is an inter state road, although only 1,12-B and IP were detected with mean \pm SD values of 330 \pm 10 and 360 \pm 10 $\mu\text{g}/\text{kg}$ which is low compare to the valasske, Czech republic (860-10840 $\mu\text{g}/\text{kg}$)(Placha et al., 2009) which is very high .

The concentration of PAHs in FJR were high and contaminated with PAHs. In FJR, the traffic density is low but files of plastic waste were combusted daily around the area and resulted in heavy smoke. The remaining ash gave rise to high concentration of PAHs in the soil. The PAHs ranged from 1140-1170 $\mu\text{g}/\text{kg}$ with mean \pm SD of 1160 \pm 1.01 $\mu\text{g}/\text{kg}$ which is low compare to PAHs in soil of Delhi India (4694 \pm 3028 $\mu\text{g}/\text{kg}$)(Agarwal, 2009). Only three PAHs were detected and others were <0.01 as shown in Table 4.3. These are Ace with mean of 210 $\mu\text{g}/\text{kg}$, flu with mean of 370 $\mu\text{g}/\text{kg}$ and chr with the mean \pm SD of 580 \pm 0.02 $\mu\text{g}/\text{kg}$.

For FJL as shown in Table: 4.2 is an area of less population and traffic density and has a small plumber market. The area is uncontaminated. ΣPAH of the site range from 880-900 $\mu\text{g}/\text{kg}$ with mean value of 890 \pm 0.01 $\mu\text{g}/\text{kg}$, not all the 16 PAHs were detected in these site, but only five which are Chr with mean value of 22 $\mu\text{g}/\text{kg}$, Fl with mean value of 190 $\mu\text{g}/\text{kg}$, Phe with mean of 490 $\mu\text{g}/\text{kg}$, Acy with mean value of 37 $\mu\text{g}/\text{kg}$ and An with mean value of 150 $\mu\text{g}/\text{kg}$. Which are very low compare to the guideline proposed by NOAA and CCME in Table 4: 6.

TABLE 4.6 shows the recommended guideline concentration of these pollutants in soil from environmental agencies. Concentration of individual PAHs were comparable with guideline value. Low molecular weight PAHS were lower than the guideline values and assumed no adverse effect to the biota .On the other hand, on comparing the individual PAHs concentrations with recommended guideline values, the concentration of some high molecular weight PAHs were higher, especially 1,2-Dibenzathracene was higher than guidelines proposed by NOAA .

4.3 SOURCE IDENTIFICATION OF DIAGNOSTIC RATIOS OF PAHS.

It is essential to identify the origin and potential source of PAHs in the environment to assess the environmental risk. The Anthropogenic release of PAHs can be attributed to petrogenic and pyrogenic origins (Hwang et al., 2003). The PAHs of petrogenic (Petroleum derived residues) origins are characterized by the predominance of 2- 3 ring or low molecular weight, while PAHs from pyrogenic source and by the incomplete combustion of organic matter in industrial operation, garbage incinerators, power plants, vehicle engines and forest fire (combustion derived) (Baek *et al.*, 1991), are characterized with high proportion of above 4 rings or high molecular weight PAHs. LMW PAHs are generated at low temperature combustion; the HMW PAHs are generated at high temperature combustion such as vehicle emission (Mastral and Callen, 2000). The roadside soil in Onitsha contain a considerable amount of high molecular weight PAHs (0.01-0.15%) which indicated that the major input of PAHs are from vehicle emission (pyrogenic PAHs) (Zakaria *et al.*, 2002).

The diagnostic ratios of selected PAHs concentration are widely used to identify and characterize the

source (Yunker *et al.*, 2002; Zhang *et al.*, 2006; Pies *et al.*, 2008). In order to further identify sources of PAHs in Onitsha roadside soil, the isomer ratio of phe/(phe + ant), B(a)A/(B(a)A+chr), flu/(flu+pyr), and 1P/(1P +BP) were used to distinguish between petrogenic and pyrogenic sources. This is shown in Table 4:7.

The ratio of Ant/(Ant + Phe) <0.1 is taken as an indication of petroleum, while a ratio >0.1 indicates a dominance of combustion. The value of Ant/ (Ant + Phe) (< 0.1) and flu/(flu + pyr) (<0.4) ratio has been used for petrogenic source and value of >0.1 and $\geq 0.4-0.5$, respectively used for pyrogenic source (Hwang *et al.*, 2003). The high ratio (>0.5) of flu/(flu + pyr) has been used for gases, wood and coal combustion sources (Fadzil *et al.*, 2008). The ratio of BaA/(BaA+Chr) <0.2 petrogenic 0.2-0.35 implies petroleum combustion (especially liquid fossil fuel, vehicle and crude oil) and >0.35 implies combustion of coal, grass and wood (Yunker *et al.*, 2002; Hwang *et al.*, 2003). The ratio of 1P/(1P+BaP) from 0.20- 0.57 (Yu-Fen Jiang *et al.*, 2009) implies of coal combustion. In the present study, the value of An/(Ant +phe) is 0.48, all of them were higher than 0.1, the ratio of flu/(flu+pyr) were higher than 0.5 for most soil samples, the IP/(IP+BaP) ration for most samples 0.67 and ratios of BaA/(BaA+Chr) is 0.25, which is less than 0.35.

The PAH ration values in this study indicate that pyrogenic activities such as petroleum, biomass and coal combustion (Table 4:7) are the main sources of PAHs in Onitsha soils. This contamination will be an ongoing issue as PAHs are persistent and human exposure by inhalation of particles, dietary intake of contaminated food products such as vegetables, and direct contact with polluted water, soil, sediment and sludge will continue.

Also the result of this study was compared with the results of reported in literature on PAHs contamination of soil and is shown in Table 4.8.

CONCLUSION

Data from the current study showed that the concentrations of Σ PAHs in Onitsha roadside soil were in the range from 14260 to 14289 $\mu\text{g kg}^{-1}$, with a mean of 14,276 $\mu\text{g kg}^{-1}$ and the seven possible carcinogenic PAHs accounted for 17.2 % of 16PAHs. Chrysene was the polycyclic aromatic hydrocarbons found in highest concentration at all the intercepts ranging between 4050 to 4053 $\mu\text{g/kg}$ with the mean of 4052 $\mu\text{g/kg}$. Among different functional areas, the higher level of PAHs was found in Obosi junction (right) followed by Main market road (right). The composition of PAHs was characterized by the high molecular weight PAHs, among which fluoranthene, Indeno(1,2,3,-cd)Pyrene, Acenaphthene, chrysene were most dominant components. A principal component analysis and PAHs isomeric ratios indicate that PAHs in Onitsha road soil mainly originated from combustion. This study suggests that the pollution of PAHs in developing cities like Onitsha should emphasize on controlling the traffic exhaust specially diesel exhaust. The study could be of considerable significance for the planners while considering environmental remedial measures.

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Table 4.1 PAHs concentration in roadside soil at 3m distance from roadside at place of high traffic and population density.

SAMPLING ID	RANGE	MEAN±SD	MEDIAN
3.3 junction right (3JR)	1.45 – 1.47	1.46±0.01	1.46
3.3 junction Left (3JL)	1.48 – 1.49	1.49±0.01	1.49
D.M.G.S. Junction right (DJR)	0.61 – 0.63	0.61±0.01	0.62
D.M.G.S. Junction left (DJL)	0.77 – 0.79	0.78±0.01	0.77
Head-bridge junction right (HJR)	0.23 – 0.26	0.24±0.01	0.23
Head-bridge junction left (HJL)	0.31 – 0.33	0.32±0.01	0.33
Main-market junction right (MJR)	1.50 – 1.51	1.50±0.01	1.50
Main-market junction left (MJL)	1.47 – 1.49	1.48±0.01	1.48
Obosi junction right (OJR)	1.65 – 1.67	1.66±0.01	1.65
Obosi junction left (OJL)	1.32 – 1.36	1.34±0.01	1.34

Table 4.2: PAHs concentration in roadside soil at 3m distance from roadside at place of average traffic and population density showing the range, mean, SD and median (mg/kg, n=3).

SAMPLING ID	RANGE	MEAN±SD	MEDIAN
Fegge junction right(FJR)	1.14 – 1.17	1.16±1.01	1.16
Fegge junction left(FJL)	0.88 – 0.90	0.89±0.01	0.88
Nkpor junction Right (NJR)	0.21 – 9.27	0.24±0.02	0.23
Nkpor junction left(NJL)	0.22 – 0.25	0.23±0.01	0.23
Owerri road right (OR)	0.32 – 0.33	0.33±0.01	0.33
Owerri road left (OL)	0.34 – 0.37	0.36±0.01	0.36
Upper-iweka Junction right (UJR)	0.16 – 0.18	0.17±0.01	0.16
Upper-iweka Junction Left (UJL)	0.36 – 0.38	0.37±0.01	0.36

Table 4.3: Concentration of individual PAHs in selected site in Onitsha right-hand side of roadside soil (µg/kg, n=3) showing the mean±SD.

PAHs	NJR	OJR	MJR	FJR	HJR	OR	3JR	UJR	DJR
Nap	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ace	ND	530±0.02	ND	210±0.01	ND	ND	ND	ND	ND
Acy	ND	ND	ND	ND	ND	ND	ND	ND	ND
Fl	ND	ND	ND	ND	ND	ND	ND	ND	ND
An	ND	ND	ND	ND	130±0.01	ND	ND	ND	ND
Phe	ND	ND	ND	ND	ND	ND	ND	ND	ND
Flu	ND	ND	ND	370±0.01	100±0.01	ND	270±0.02	ND	ND
1,2-D	ND	150±0.01	270±0.01	ND	ND	ND	ND	170±0.01	54.0±0.01
Chr	ND	980±0.01	ND	580±0.02	ND	ND	1170±0.01	ND	ND
Pyr	ND	ND	ND	ND	ND	ND	ND	ND	ND
B(k)F	ND	ND	ND	ND	ND	ND	ND	ND	ND
B(b)F	ND	ND	ND	ND	ND	ND	ND	ND	12.0±1.22
IP	ND	ND	1220±0.03	ND	ND	ND	ND	ND	87.0±0.01
B(a)P	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,6-D	240±0.01	ND	ND	ND	ND	ND	ND	ND	ND
1,12B	ND	ND	ND	ND	ND	330±0.01	ND	ND	460±0.03

SD = Standard Deviation, ND = Not Detected

Table 4.4: Concentration of individual PAHs in the selected site in Onitsha left-hand side of roadside soil (µg/kg, n=3) showing the mean±SD.

PAHs	NJL	OJL	MJL	FJL	HJL	OL	3JL	UJL	DJL
Nap	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ace	ND	ND	ND	ND	23.0±0.02	ND	230±0.01	ND	ND
Acy	ND	ND	ND	37.0±0.01	29.0±0.01	ND	ND	ND	ND
Fl	ND	ND	ND	190±0.03	76.0±0.01	ND	ND	ND	ND
An	ND	ND	ND	150±0.01	120±0.01	ND	410±0.02	ND	ND
Phe	ND	ND	ND	490±0.01	73.0±0.01	ND	ND	ND	ND
Flu	ND	950±0.02	ND	ND	ND	ND	290±0.02	ND	ND
1,2-D	ND	390±0.01	260±0.01	ND	ND	ND	ND	ND	51.0±0.01
Chr	ND	ND	ND	22.0±0.01	ND	ND	570±0.03	ND	730±0.01
Pyr	ND	ND	ND	ND	ND	ND	ND	ND	ND
B(k)F	ND	ND	ND	ND	ND	ND	ND	ND	ND
B(b)F	ND	ND	ND	ND	ND	ND	ND	ND	ND
IP	ND	ND	1220±0.03	ND	ND	360±0.01	ND	ND	ND
B(a)P	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,6-D	220±0.03	ND	ND	ND	ND	ND	ND	360±0.01	ND
1,12B	ND	ND	ND	ND	ND	ND	ND	ND	ND

SD = Standard Deviation, ND = Not Detected

Table 4.6: Guideline for individual PAHs in soil ($\mu\text{gkg}^{-1}\text{dw}$) :comparison with this study.

PAHs	NOAA	CCME	PRESENT STUDY
Naphthalene	5000	600 - 22x10 ³	<0.01
Acenaphthene	-	-	998
Acenaphthylene	-	-	66
Fluorene	-	-	266
Phenanthrene	5000	5x10 ³ -5x10 ³	563
Anthracene	-	-	810
Fluoranthene	-	-	1983
Pyrene	10x10 ³	10x10 ³ -100x10 ³	<0.01
1,2-DiBenzathracene	10000	-	1034
Chrysene	-	1000-10x10 ³	4052
Benzo (k)Fluoranthene	1000	1000-10x10 ³	<0.01
Benzo (b) Fluoranthene	1000	1000-10x10 ³	12
Benzo(a)Pyrene	1000	7000	<0.01
Indeno(1,2,3,-cd)Pyrene	1000	1000-10x10 ³	2887
1,2,5,6-DiBenzathracene	1000	1000-10x10 ³	600
1,12-Benzoperylene	-	-	1010

Guideline for resident, park, community and industrial soil, National oceanic and atmospheric administration (NOAA), Canadian council of ministers of the environment

Table 4.5: concentrations of individual and total PAHs in Onitsha roadside soil ($\mu\text{g}/\text{kg}$, n=3).

PAHs	Range	Mean	Median \pm SD	% of Σ PAHs
Nap	ND	ND	ND	ND
Ace	992 - 993	993	993 \pm 0.5	0.05
Acy	65 - 68	66	65 \pm 1.22	1.85
Fl	265 - 267	266	267 \pm 0.87	0.33
An	810 - 812	810	810 \pm 1.00	0.12
Phe	561 - 564	563	563 \pm 0.75	0.13
Flu	1982 - 1984	1983	1982 \pm 0.87	0.04
1,2-D	1032 - 1036	1034	1033 \pm 1.50	0.15
Chr	4050 - 4053	4052	4052 \pm 1.12	0.03
Pyr	ND	ND	ND	ND
B(k)F	ND	ND	ND	ND
B(b)F	10 - 13	12	13 \pm 1.22	10.16
IP	2886 - 2887	2887	2887 \pm 0.50	0.02
B(a)P	ND	ND	ND	ND
1,6D	598 - 601	600	601 \pm 1.22	0.20
1,12B	1009 - 1011	1010	1011 \pm 1.01	0.10
Σ PAHs	14260 - 14289	14276	14277 \pm 11.78	13.18
Σ 7c- PAHs	8987 - 9000	8995	8996 \pm 5.35	0.5
LMW-PAHs	4675 - 4681	4681	4681 \pm 5.21	2.52
HMW-PAHs	8553 - 8564	8561	8564 \pm 6.57	10.66

SD= standard deviations, Σ PAHs = Sum of EPA's 16PAHs, Σ 7c-PAHs= sum of possible carcinogenic PAHs, LMW-PAHs = Low molecular weight Σ of 2-3 ring PAHs, HMW-PAHs = High molecular weight Σ of > 4 rings PAHs, ND = Not Detected.

Table 4.7: Diagnostic ratio of individual PAHs concentration for sources diagnosis

PAHs ratio	values of ratio	Indicative	reference	Present Study
An/(An + Phe)	<0.1 >0.1	Petrogenic Pyrogenic	Hwang et al., 2003	0.48
Flu/ (Flu+pyr)	<0.4 ≥0.4-0.5 >0.5	Petrogenic Pyrogenic Biomass, Coal combustion	Hwang et al., 2003 Fadzil et al., 2008	0.8
B(a)A/(B(a)A +Chr)	<0.2 0.2-0.35 >0.35	Petrogenic petroleum Biomass, Coal combustion	Yunker et al., 2002 Hwang et al., 2003	0.25
IP/(IP+BaP)	0.20-0.57	Coal combustion	Yu-Feng Jiang et al., 2009	0.67

Table 4.8: Soil PAHs concentration (roadside urban) compiled from literature data.

Sr.NO	Study area	PAHs concentration (mg/kg)	Reference
1	Australia(Nathan, Brisbane)	3.30	Yang et al., (1991)
2	USA (Washington)	58.68	Rogge et al., (1993)
3	Kota Bharu Malaysia	1.45	Fadzil et al., (2008)
4	Agra, India	12.9	Amit Masih et al., (2006)
5	Jalandhar, India	4.04 and 16.38	Kumar and Kothiyal (2011)
6	Igbanko mangrove forest lagos , Nigeria	65.5-188.0	Olatunbosun et al.,(2010)
7	Delhi airport soil data,	4.43	Sharmila et al., (2007)
8	Onitsha, Nigeria	14.28	Presence Study

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