Levels And Distributions Of Pahs In Samples From Selected Facilities In Onitsha, Anambra Basin, Southeastern Nigeria

Okoro, J. E.

Geology Department, Michael Okpara University of Agriculture, Umudike, Umuahia, Abia State, Nigeria

Anachuna, N. G.

Nganje, T. N.

Adamu, C. I.

Department of Geology, University of Calabar, Calabar, Nigeria

Abstract: A geochemical study was undertaken at Onitsha to assess the levels and distributions of some selected polycyclic aromatic hydrocarbons (PAHs) introduced into the soil through anthropogenic activities. Core (0-60cm) samples were collected from selected dumpsites, auto-workshops and petrol stations in Onitsha and control site at Awka, Nigeria. Physiochemical parameters (Total Organic Carbon (TOC), and PAHs (Ace, Flu, Nap, Ant, BaP, Flan, Pyr and DahA) were analyzed using standard methods. Considering the individual PAHs in the surface soil samples from the dumpsites, the order is as follows: DahA (17.336%) > Phe (15.260%) > BaP (14.650%)> BbF (14.493%)> BkF (13.944%)> Flu (6.885%)> Any (4.225%)> Ace (3.897%)> Ant (3.193%)> Nap (3.152%)> Pyr (3.006%)> Flan (0.006%). Samples from the mechanic workshops show the order as follows: DahA (23.803%)> Any (12.733%)> Phe (12.515%)> BaP (8.778%)> Nap (7.662%)> Ace (1.823%)> Pyr (1.720%)> BkF (1.353%) > Ant (1.014%)> Flu (3.152%)> BbF(0.122%)> Flan (0.011%). PAHs in the samples from the petrol stations is in the order: DahA (41.265%)>Any (19.677%)>Phe (16.227%)> Nap (15.026%)>BaP (11.382%)> Ace (1.464%) >Ant (1.208%)>Pyr (0.973%)>Flu (0.857%)> BbF (0.045%)> Flan (0.03%). The ΣPAH were high and above both the control level and the EGASPIN 2002 standard. The ratios of Phe/Ant, Flu/Pyr and LMW/HMW indicated pyrolytic contamination in the dumpsites but petrogenic contamination in the auto-workshops and the petrol stations. The industrial and commercial activities within the area of study are the direct sources of these contaminants.

I. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) also known as polynuclear aromatic hydrocarbons or Poly-aromatic hydrocarbons are persistent organic pollutants commonly associated with burning of fossil fuel, oil spillage and decay of organic matter. They are usually produced by incomplete combustion and pyrolysis of organic matters (Fetzer, 2000). Chemically, they are composed of two or more benzene rings and do not contain heteroatoms or carry substituents (Igwe and Ukaogo, 2015). They are common in the environment and can result from both natural and anthropogenic sources (Nganje et al., 2014; IARC, 1983). There are three major sources of PAHs which include pyrogenic (those produced when organic substances are exposed to higher temperatures and under low/no oxygen); petrogenic PAHs are produced from crude oil maturation while biological PAHs are those produced during degradation of vegetative matters (Hussein and Mona, 2016).

PAHs are generally immobile in soils and sediments because of their low solubility in water (Rippen, 1992). Despite the low solubility in water, leaching and transformation in soils are obvious (Teebay et al., 1993). Accumulation in soil may lead to imminent contamination of food chains and water (Nganje et al., 2006).

PAHs constitute major environmental concerns in urban and industrial areas (Igwe and Ukaogo, 2015). Given the rapid urbanization and industrial activities at the study area, the level of contaminants in the surface soils have significant effect on human health and requires adequate attention.

II. DESCRIPTION OF THE STUDY AREA

LOCATION AND GEOLOGY

The study area lies between Latitudes 6^0 05' 56" and 6^0 12' 02"N, and Longitudes 6^0 46' 0" and 6^0 52' 30" E (fig. 1).

The main geologic units within the study area include Ameki Formation (Nanka Sand), Asaba-Ogwashi Formation, Benin Formation (Coastal Plain Sand) and Nsugbe Sandstone (figure 2).

The Ameki Formation was classified by Simpson (1955) into two lithological groups viz: the lower part which consists of fine to coarse grain sandstones and intercalations of calcareous shales and thin shelly limestone and upper part which comprise coarse, cross-bedded sandstone with bands of fine, grey-green sandstone and fine – grained fossiliferous sandstone with thin limestone bands. The age of the formation has been considered to be either early Eocene (Reyment, 1965). The Ameki Formation underlies the Imo shale (Paleocene) which conformably overlies the Nsukka Formation (Reyment, 1965).

The Ogwashi– Asaba Formation is also represented within the Palaeocene Anambra Basin (Oboh – Ikuenobe et al., 2005). This Formation, also called the Lignite "series", is characterized by widely differing lithologies comprising alternation of clays, sands, grits and lignites (Dessauvagie and Fayose, 1970; Whiteman, 1982; Parkinson, 1907).

Reyment (1965) recommended Oligocene–Miocene age for this formation. The Ogwashi–Asaba Formation is a surface lateral equivalent of the Agbada Formation which occurs in the subsurface of the Niger Delta (Short and Stauble, 1967; Assez, 1989; Akpoborie et al., 2011).

The Benin Formation (Coastal Plain Sand) consists of alternating sequence of gravel, sand, clay and alluvium which are derived from the adjoining Precambrian basement and cretaceous rocks (Short and Stauble, 1967). The age is upper Miocene–Recent (Short and Stauble, 1967; Kogbe, 1976).
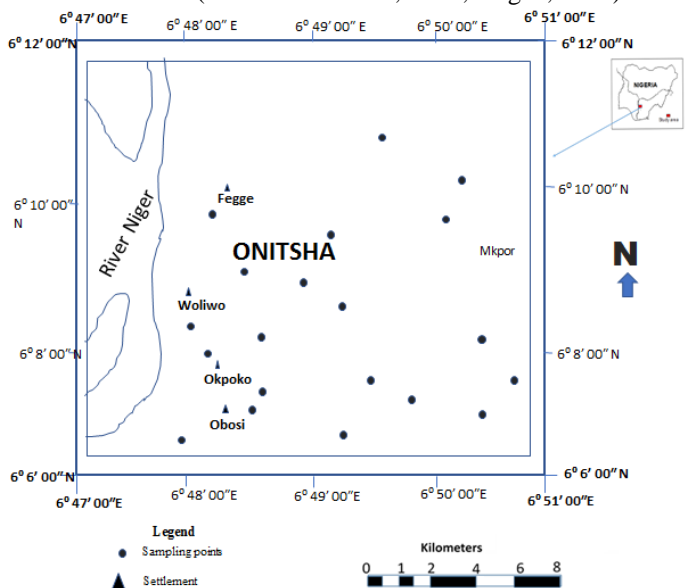

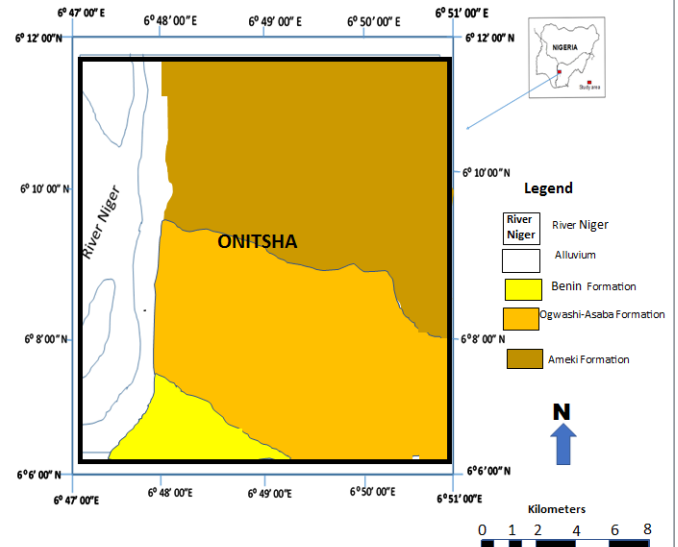*Figure 1: Location map of the study area showing some settlements and sample collection points*

Figure 2: The geologic map of the study area

III. REVIEW OF LITERATURE

Despite its economic gains, health of humans, animals, plants and microorganisms have been compromised due to activities associated with fossil fuel extraction, processing and use. Fossil fuel exploration, exploitation, transportation, consumption, spills and disposals are some of the ways in which oil pollutants get into the environments.

Previously, knowledge of PAH burden of soils in the tropical cities was scarce (Wilcke et al., 1998). However, recent trend has shown a much attention in this field. Among the many studies is the work done by Nganje et al. (2014) that focused on the fate, distribution and sources of polycyclic aromatic hydrocarbon in contaminated soils in parts of Calabar Metropolis. Surface soil samples were collected with motorized auger and analyzed using GC-MS. The result of the interpretation show that PAHs enrichment of the samples was from petrogenic and pyrogenic sources.

Igwe and Ukaogo (2015) assessed the environmental effects of polycyclic aromatic hydrocarbons and discovered that PAHs have a wide range of impacts on air, water and soil which negatively affects living organisms. According to the study, PAHs in the air often adsorb on dust particles in the atmosphere where they undergo photo oxidation in the presence of sunlight. Some of the wide range of PAH-induced ecotoxicological effects in a divers suite of biota, including microorganisms, aquatic biota, amphibians, reptiles, birds and terrestrial mammals according to the study were reported as follows: eye irritation, childhood asthma, skin irritations, mutagenic effects, birth defects, decrease in body weight, skin irritants, leukemia, childhood asthma, nausea, vomiting, diarrhea and confusion, kidney damage, liver damage, jaundice, cataracts, tumors of the gastrointestinal tract and lungs, tumors of the breast and lungs, skin irritation, breakdown of red blood cell, heart malformations and increase in mammary tumors in rats. PAH-induced phytotoxic effects on plants were found to be rare because certain plant contain

substances that can protect against effects whereas others can synthesize PAH that act as growth hormones.

Nganje *et al.* (2012) worked on polycyclic aromatic hydrocarbons in surface water and soil in the vicinity of fuel-oil spillage from a tank farm distribution facility at Esuk Utan, Calabar Municipality, Nigeria by collecting, analyzing and interpreting soil and water samples from the site. It was discovered that the surface water and soil in the study area were heavily polluted by PAHs.

The physicochemical properties of soils affected by refined petroleum products were assessed by Ezeigbo et al, (2012) in Eluama community in Abia State, southeastern Nigeria. The physicochemical properties of the soil samples were evaluated using different analytical methods. The results showed that organic carbon, organic matter, calcium and magnesium increased with increase in pollution while nitrogen, potassium, sodium and phosphorus decreased with increase in pollution. The pH became more basic as pollution decreased. Also, concentration of heavy metals increased as soil increases with pollution. This analysis also revealed that the polluted soil when compared with the control (soil from unpolluted farmland) is unsuitable for agricultural activities as full remediation has not taken place.

Nganje *et al.* (2007) worked on the distribution of PAHs in the surface soils from petroleum handling facilities in Calabar, Southeastern Nigeria by collecting surface soil samples (0-15cm) from petroleum handling facilities (generating plants, mechanic workshops, petroleum dispensing stations, airport fuel dump and leaking pipeline). The samples were taken with a stainless-steel spatula, wrapped with aluminium foils which were cleaned with toluene before being transferred to the laboratory where it was analysed using GC-MS. Interpretation of the result indicated that the highest level of concentration of total PAHs were observed in petrol stations and mechanic workshops.

Godson *et al,* (2009) worked on the comparative assessment of soil pollution by polycyclic aromatic hydrocarbons in two Niger Delta communities (Eleme and Ahoada East) by collecting surface soil samples (0-15cm) using auger and analyzing in the laboratory using standard methods. Descriptive and inferential statistics were employed in analyzing the samples which indicated that the samples have PAHs levels above EPA (1994) guideline values.

Chukwujindu *et al.* (2016) assessed the concentrations and health risk of polycyclic aromatic hydrocarbons in surface soils of an urban environment in the Niger Delta. The concentrations and compositional patterns of the US EPA (2014) 16 priority polycyclic aromatic hydrocarbons (PAHs) were determined in surface soils of an urban environment in the Niger Delta with a view to providing information on the sources, extent of contamination and human health risks of PAHs in these soils. Surface soil samples were collected using standard field methods and the analyses were performed by means of gas chromatography-mass spectrometry (GC-MS) after extraction of the soils with exane/dichloromethane and clean-up of the extracts. The results indicated that there is a high potential risk of cancer development as a result of exposure of PAHs via ingestion, dermal contact and inhalation. The diagnostic ratios indicated that the PAHs in these soils originated mainly from pyrogenic processes.

Adebola and Oyeleke (2017) worked on the heavy metals and polycyclic aromatic hydrocarbons in soil from e-waste dumpsites in Lagos and Ibadan by collecting and analyzing surface and subsurface soil samples from major e-waste dumpsites in Lagos and Ibadan. The aim was to evaluate the potential contaminant contribution from e-waste activities within the area of study. Control samples were collected at the Botanical Garden, University of Ibadan. Samples were analyzed for heavy metals after acid digestion using atomic absorption spectrophotometry (AAS) while PAHs were extracted using cold solvent extraction and quantified by gas chromatography-mass spectrometry (GC-MS). Contamination and ecological risks were assessed using soil contamination indices such as contamination factor, geo-accumulation and pollution load indices. The potential ecological risk index was also use to categorize contaminant concentrations and associated impacts. Soil physico-chemical characteristics such as pH and total organic matter were also determined.

The results indicated that there are serious metals accumulations with very high ecological risks observed at every e-waste dumpsite. The total PAHs in the soil of e-waste dumpsites were significantly higher than in the control soil. This work signifies that indiscriminate dumping and open burning of e-waste are potential sources of PAH and toxic metal emissions, which can pose serious human health and ecological risks.

Bayowa and Agbozu (2016) researched on the seasonal variation of PAHs in marshy sediments from Warri City. Sediment samples were collected from four locations within the city while the control samples were also collected 20 km away. The samples were collected from January to March for dry season and June to August for rainy/wet season and levels of 16 USEPA priority PAHs were determined using GC-FID. This research indicated that the PAHs concentration was higher in dry season than rainy season at all the study sampling stations and the control.

Anegbe et al. (2016) worked on the impact of inorganic and organic pollutants in soil from the vicinity of mechanic workshops in Benin City using standard methods. The studies revealed elevated levels of these pollutants due to the activities of the artisans.

IV. MATERIALS AND METHODS

FIELD PROCEDURE: Reconnaissance survey was undertaken prior to the actual sample collection activities in order to identify possible sampling points, assess background information, site conditions and historical data. The reconnaissance survey was also used to identify variable possible routes, assess the topography, geology and traffic volume as well as economic land use (commercial and industrial activities) patterns within the study area. The sampling points were selected based on the information gathered during this reconnaissance survey.

During sampling (two weeks after the reconnaissance), twenty (20) surface soil samples were collected at the depth of 0 - 60cm within the vicinity of dumpsites (5), auto-workshops (10) and petrol stations (5) using soil auger from the locations

shown in figure 1. One soil sample was also collected from an undeveloped plot of land at Awka to serve as the control.

The instruments used for collecting the soil samples were a T- shaped manual soil auger, hand trowel and amber-colored bottles. At each sampling location, the auger was decontaminated by cleaning the blades with white handkerchief soaked with methylated spirit and drilled into the soil in an anti-clockwise direction. When it penetrated the soil up to the pre-marked 60cm depth, it was brought out in a clockwise direction. The soil samples that stacked to the auger screw were collected using a decontaminated hand trowel before putting them separately into pre-labeled amber-coloured bottles. The control soil sample was collected at a similar depth in an undeveloped plot of land with a very low volume of traffic and no industrial activities at Awka and labeled. All the samples were preserved in an ice box to minimize degradation.

The metal spades of the soil auger and the hand trowel were cleaned with methylated spirit in between sample collection points in order to eliminate cross-contamination. In total, twenty-one soil samples were collected and taken in a big ice box to the laboratory for analyses.

LABORATORY PROCEDURES

TOTAL ORGANIC CARBON DETERMINATION

Approximately 10g of the sample was weighed into a 250ml beaker and 20ml of conc. H_2SO_4 was added followed by 10ml of potassium dichromate. It was heated at 230-250°C using heating mantle for 30mins before being brought down and allowed to cool. The solution was made up to 200ml with distilled water after which 5 drops of phenanthroline indicator was added and it was titrated against 0.4mol ferrous ammonium sulphate. The blank was equally carried out. The blank means everything without the sample. The following was used to calculate for the TOC after the titration:

$$TOC = \frac{(1- T/S)}{10} \qquad (1)$$

where; T = titre value for blank
S = titre value for sample
10 = sample weight

PAHs EXTRACTION AND QUANTIFICATION

This was achieved by means of Soxhlet extraction method. About 50 g of the dried, homogenized and sieved soil sample was weighed and wrapped in a filter paper before being placed in a thimble and placed into the soxhlet apparatus. 200 ml of the extracting solvent (n-hexane) was added into the Soxhlet flask and the condenser was connected to the inflow (of water) while the outflow of water was from a running tap. The Soxhlet apparatus was mounted on a regulated heating mantle. And the heating mantle set slightly above the boiling point of n-hexane (68°C). The extraction lasted for approximately 2hrs with repeated refluxing.

CONCENTRATION, CLEAN UP AND SOLVENT EXCHANGE

After getting the oily extract through reflux, a separating funnel was set up and some quantity of cotton wool was added in the funnel. The cotton wool was moistened with some quantity of n-hexane. Furthermore, 1g of magnesium silicate and 0.5g of sodium sulphate was added on the cotton wool inside the funnel. The sodium sulphate helps to remove excess water while the magnesium silicate makes the extract purer. The oily extract was poured into the separating funnel before opening the knob on the funnel. The leachate was collected into a sample container and taken to the GC where it was injected into the machine using a syringe. Separation occurs as the vapor constituent partition between the gas and liquid phases. The sample was automatically detected as it emerges from the column by a Flame Ionization Detector FID. PAH quantification was achieved by CLARITY-GC interfaced software.

V. RESULTS AND DISCUSSION

DUMPSITES

Concentrations of PAHs and TOC in the dumpsites are presented in table 1 while the pictorial illustration is shown in fig. 3. The total PAHs (ΣPAHs) ranged from 200.2 – 219.4 mg/kg with a mean±sd of 205.72±7.92. The result shows that the concentration levels of the total PAHs vary closely across the dumpsites but above the level recorded from the control (16.44 mg/kg). The ΣPAH obtained from DS 2 (219.37 mg/kg) exceeded that of the total average (205.72 mg/kg). This could be attributed to the volume of waste dumped and the age of the site which is fairly above others. The level of Σ16PAH concentration is in the order DS 3 < DS 4 < DS 5 < DS 1 < DS 2. Considering the individual 16PAH in the surface soils of the study area, the order is Fln (0.0063%) < IcdP (0.716%) < BaA (0.716%) < BghiP (0.896%) < Chr (0.955%) < Pyr (2.914%) < Nap (3.062%) < Ant (3.392%) < Ace (3.784%) < Any (4.103%) < Flu (6.461%) < BkF (13.053%) < BbF (14.072%) < BaP (14.224%) < Phe (14.816%) < DahA (16.831%). The PAHs distribution pattern indicates the predominance of three, five and six ringed components which constitute about 86.389% while others account for about 13.611% thus the order is 2 ringed < 4 ringed < 6 ringed < 3 ringed < 5 ringed.

Soil organic carbon content in addition to chemical properties and clay content are the most essential factors controlling the level of PAHs in the soil (Yang et al., 1998; Nganje *et al.,* 2007). Thus, the effect of soil organic carbon on the PAH concentrations was determined. The values obtained for TOC (%) are presented in table 2. The organic carbon (%) in the dumpsites ranges from 2.517 – 3.13% with an average value of 2.851±0.22%. In this study, high TOC (%) correspond to high Σ16PAH. This may be due to the fact that soil organic matter is an essential sorbent of PAHs (Sims and Overcash, 1983; Nganje *et al.,* 2007).

The phenanthrene to anthracene (Phe/Ant), fluoranthene to pyrene (Flu/Pyr) and HMW/LMW ratio values have been

used to ascertain the sources of PAHs (Colombo *et al.,* 1989; Soclo *et al.,* 2000; Budzinski *et al.,* 1997; Nganje *et al.,* 2007 and Adedosu *et al.,* 2015). Phe/Ant >10 represents petrogenic contamination while Phe/Ant <10 represents pyrolytic contamination (Gschwend and Hites, 1981; Colombo *et al.,* 1989; Budzinski *et al.,* 1997; Soclo *et al.,* 2000; Nganje *et al.,* 2007).

The ratio of Phe/Ant in the samples from the dumpsites varied from 3.952-5.381 (Table 2) indicating pyrolytic contamination in the dumpsites.

The fluorene to pyrene ratio (Flu/Pyr) has been recommended by Sicre *et al.,* (1987) for source determination. The flu/pyr ratio of <1 and >1 have been attributed to petrogenic and pyrolytic origin respectively. Table 2 shows that all the ratios of flu/pyr from the dumpsite soil samples are greater than 1. This also indicates pyrolytic origin.

The ratios of particular PAHs compounds and its isomers have been acknowledged as indices for source identification and to distinguish between natural and anthropogenic sources of PAHs (Adedosu *et al.,* 2015; Zhou *et al.,* 2005). The distribution of high molecular weight PAHs, (∑HMW) and low molecular weight PAHs, (∑LMW) in the soil samples from the dumpsites also shown in table 6 indicate that ∑HMW are the dominant in the dumpsites. The total concentration of ∑HMW is higher than (∑LMW) at all the sampling points within the considered dumpsites. According to Adedosu *et al.,* (2015), the lower molecular weight PAHs with lower numbers of rings (≤ 3 rings) are volatile and easily biodegradable than the high molecular weight PAHs (≥4 rings) which are more persistent in the environment.

The ratio of low molecular weight PAHS to high molecular weight PAHs lower than 1 (LMW/HMW <1) indicates a pyrogenic source while LMW/HMW>1 indicates petrogenic source (Zhang *et al.,* 2008). The LMW/HMW ratio were lower than 1 at all the dumpsites, also suggesting pyrogenic sources.

The application of the different source diagnostic ratios of PAHs have shown that dumping and combustion/burning of wastes on the dumpsites are the main source of PAHs present in the dumpsite soil.

The Institute of Soil Science and Plant Cultivation (Pulawy, Poland) classification indicated that soils with ∑PAH <0.001 mg/kg can be considered to be unpolluted (Sieciechowicz *et al.,* 2014).

The total PAH concentrations exceeded the limit of 10 mg/kg established by the EGASPIN (2002); the range established by the Dutch government for PAHs in uncontaminated soil which is 0.02-0.05mg/kg and 40 mg/kg for landscaping residential area (Ministry of Housing, Spatial Planning and Environment (MSHPE, 1994). Furthermore, concentrations of benzo(a)pyrene (BaP) at the various dumpsites were more than 1mg/kg and above the range of 1.08 – 1.32mg/Kg for UK generic assessment criteria (GAC) for residential land use (Nathanial *et al,* 2007). BaP values above these ranges are considered to be a potential risk in the environment for human health. Thus, the values obtained in the present study reveal that the environment within the study area is unsafe with regards to BaP concentrations.

Facility	Ace	Nap	Any	Ant	Flu	Phe	Pyr	Fln	BaP	BbF	BkF	DahA	BghiP	IcdP	BaA	Chr
Control	3.129	2.7	1.6	1.2	2.814	0.58	0.2	0.0105	2.037	0.03	1.12	0.4	0.21	0.120	0.150	0.140
DS 1	8.223	8.1	7.395	5.943	13.976	26.216	4.113	0.0105	32.088	27.142	26.882	38.25	3.82	0.480	1.610	1.530
DS 2	7.2	6	7.631	7	13.433	37.665	6.621	0.0103	26.027	39.6321	25.873	34.85	0.81	2.210	2.100	2.300
DS 3	6.2	5.1	8.441	8.6	12.123	27.545	6.148	0.0103	30.055	29.615	27.466	31.66	2.63	1.920	1.460	1.260
DS 4	8.2	5.7	9.252	5.9	11.429	31.558	7.271	0.0169	28.085	26.121	29.116	32.63	0.74	1.850	1.230	1.920
DS 5	9.1	6.6	9.481	7.443	15.5	29.418	5.874	0.0164	30.051	22.235	24.922	35.75	1.22	0.860	0.920	2.820
Min	6.2	5.1	7.395	5.9	11.429	26.216	4.113	0.0103	26.027	22.235	24.922	31.66	0.74	0.48	0.92	1.26
Max	9.1	8.1	9.481	8.6	15.5	37.665	7.271	0.0169	32.088	39.6321	29.116	38.25	3.82	2.21	2.1	2.82
Mean	7.785	6.3	8.44	6.9772	13.292	30.480	6.005	0.013	29.261	28.949	26.852	34.63	1.844	1.464	1.464	1.966
SD	1.112	1.142	0.934	1.127	1.597	4.492	1.183	0.003	2.296	6.537	1.596	2.611	1.342	0.749	0.441	0.619

Table 1: Concentrations (m g/kg) of the different PAHs across the dumpsites

Facility	TOC (%)	ΣPAH	Phe/Ant	Flu/Pyr	LMW/HMW
Control	1.821	1.821	16.4405	0.0707	2.0986
DS 1	3.131	3.131	205.7815	4.411	3.398
DS 2	3.251	3.251	219.3664	5.381	2.029
DS 3	2.811	2.811	200.2313	4.919	2.357
DS 4	2.813	2.813	201.0169	5.349	1.572
DS 5	2.981	2.981	202.2054	3.952	2.639
Min	2.811	2.811	200.2313	3.9524	1.5719
Max	3.251	3.251	219.3664	5.3807	3.398
Mean	3.0015	3.0015	205.7203	4.8024	2.3989
SD	0.22423	0.22423	7.9187342	0.6168	0.6853

Table 2: Tabular presentation of the diagnostic ratios, TOC (%) and the ΣPAHs across the dumpsites
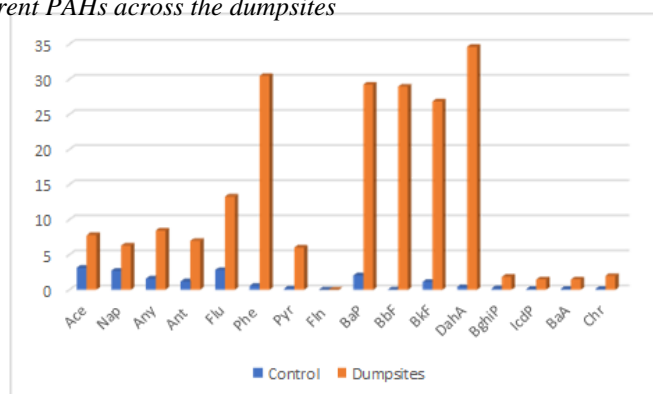

Figure 3: Bar chart showing the levels of the individual ΣPAHs across the dumpsites and the control site

AUTO-WORKSHOPS

The total PAHs (ΣPAHs) in the auto-workshops as shown in table 3 ranges from 340.529 – 478.698 mg/kg with a mean±sd value of 391.396±43.393. The result shows that the concentration levels of the total PAHs were very high above the level recorded from the control (16.44 mg/kg. The level of ΣPAH concentration is in the order MS 9 < MS 2 < MS 3 < MS 10 < MS 4 < MS 7 < MS 1 < MS 7 < MS 5 < MS 6 < MS 8. Considering the individual PAH in the surface soils of the auto-workshop samples, the order is Fln (0.0009%) < BbF (0.1404%) < Chr (0.72%) < Flu (0.8202%) < IcdP (1.2%) < BghiP (1.28%) < BkF (1.5%) < Ant (1.5%) < BaA (1.744%) < Ace (1.81%) < Pyr (2.134%) < BaP (7.199%) <Nap (14.075%) < Phe (17.835%) < Any (21.246%) < DahA (26.8%). The distribution pattern indicates the predominance of three and five ringed components which constitute about 77.068% while others account for about 22.932% thus the order is 6 ringed < 4 ringed < 2 ringed < 5 ringed < 3 ringed.

The organic carbon (%) in the auto-workshop samples (table 4) range from 0.162 – 3.216% with an average value of 2.207±0.9%. The ratio of Phe/Ant in the samples from the auto-workshops varied from 10.02 – 13.15 (Table 6) indicating petrogenic contamination (Phe/Ant >10). Table 6 also show that all the ratios of flu/pyr from the auto-workshops samples are less than 1, indicating pyrolytic origine for the PAHs in the auto-workshop samples.

The distribution of high molecular weight PAHs (∑HMW) and low molecular weight PAHs (∑LMW) in the soil samples from the auto-workshops also indicate that ∑LMW are the dominant in the auto-workshops. The ratio of LMW/HMW ranges from 0.922 - 1.900 with a mean±sd value of 1.399±0.29 indicating both petrogenic and pyrogenic sources.

The ΣPAH levels exceeded the limit established by the EGASPIN (2002) which is 10mg/kg; the range established by the Dutch government for PAHs in uncontaminated soil which is 0.02-0.05mg/kg and 40 mg/kg for landscaping residential area (Berset and Holzer, 1995; Van Brummelen *et al.,* 1996; MSHPE, 1994; Tim O'Hare Associates, 2002). Furthermore, concentrations of benzo(a)pyrene (BaP) at the various auto-workshops were more than 1mg/kg and above the range of 1.08 – 1.32mg/Kg for UK generic assessment criteria (GAC) for residential land use (Nathanial *et al,* 2007). Ranges above these values are considered to be a potential risk in the environment for human health.

Facility	Ace	Nap	Any	Ant	Flu	Phe	Pyr	Fln	BaP	BbF	BkF	DahA	BghiP	IcdP	BaA	Chr
Control	3.129	2.7	1.6	1.2	2.814	0.58	0.2	0.0105	2.037	0.03	1.12	0.4	0.21	0.120	0.150	0.140
MS 2	6.983	64.347	98.776	6.811	5.375	68.213	10.2	0.056	16.432	0.41	4.116	81.33	5.45	3.93	7.26	2.6
MS 4	4.9	46.334	92.332	5.442	3.6	71.542	5.4	0.054	17.229	1.22	5.438	76.43	5.13	3.24	8.54	2.81
MS 6	6.113	61.329	83.433	5.112	5.1	62.292	11.122	0.0121	24.216	0.058	5.553	78.89	4.81	5.1	6.53	1.88
MS 9	5.6	65.3	74.836	5.227	4.1	68.1	10.1	0.021	24.814	0.211	5.186	86.54	3.86	4.33	8.11	2.32
MS 12	5.3	65.3	81.337	6.102	4.124	67.952	9.312	0.0102	35.32	0.061	4.553	120.5	6.55	3.83	6.44	3.33
MS 13	7.2	74.6	82	6.733	5.676	75.221	10.3	0.972	38.689	1.06	6.892	124.9	4.43	4.52	4.53	4.21
MS 15	13.6	36.374	83.281	6.112	1.2	69.358	6.2	0.062	28.943	0.431	5.562	128.1	5.63	5.4	5.72	2.54
MS 16	7.1	54.7	95.8	5.115	1.399	65.529	10.8	0.076	37.398	1.542	6.516	173.5	3.87	6.43	6.35	2.56
MS 18	2.7	43.69	66.129	5.811	0.83	68.214	4.5	0.088	33.385	0.081	6.3	87.22	4.45	5.87	8.44	2.82
MS 19	11.7	38.9	73.638	6.261	0.7	81.546	5.6	0.058	25.375	0.42	5.037	93.22	5.92	4.33	6.33	3.11
Min	2.7	36.374	66.129	5.112	0.7	62.292	4.5	0.0102	16.432	0.058	4.116	76.4	3.86	3.24	4.53	1.88
Max	13.6	74.6	98.776	6.811	5.676	81.546	11.122	0.972	38.689	1.542	6.892	174	6.55	8.54	8.54	4.21
Mean	7.12	55.087	83.156	5.873	3.21	69.797	8.353	0.141	28.18	0.549	5.515	105	5.01	4.698	6.825	2.818
SD	3.067	12.381	9.708	0.6033	1.882	5.065	2.462	0.278	7.529	0.506	0.821	29.5	0.84	0.938	1.208	0.6

Table 3: Concentrations (in mg/kg) of the ΣPAHs across the auto-workshops

Facility	TOC (%)	ΣPAH	Phe/Ant	Flu/Pyr	LMW/HMW
Control	2.98	382.289	10.02	0.527	1.901
MS 2	2.32	349.641	13.15	0.667	1.786
MS 4	0.162	361.55	12.19	0.459	1.617
MS 6	3.112	368.655	13.03	0.406	1.534
MS 9	1.622	420.021	11.14	0.443	1.212
MS 12	2.848	451.897	11.17	0.551	1.254
MS 13	3.216	398.531	11.35	0.194	1.113
MS 15	2.361	478.698	12.81	0.13	0.922
MS 16	1.372	340.529	11.74	0.184	1.223
MS 18	2.078	362.148	13.02	0.125	1.424
MS 19	0.162	340.529	10.02	0.125	0.9220574
Min	3.216	478.698	13.15	0.667	1.9008757
Max	2.2071	391.396	11.96	0.368	1.3986032
Mean	0.9011	43.393	0.998	0.185	0.2939542
SD	2.98	382.289	10.02	0.527	1.901

Table 4: Presentation of the diagnostic ratios, TOC (%) and the ΣPAHs across the auto-workshops
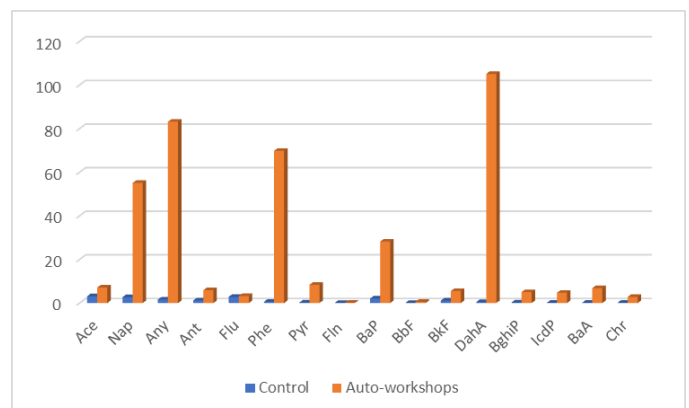

Figure 4: Bar chart showing the levels of the individual ΣPAHs across the auto-workshops and the control site

PETROL STATIONS

Levels of PAHs and TOC in the soil samples from the petrol stations are presented in table 5 while the pictorial illustration is shown in fig. 6. The total PAHs (ΣPAHs) ranged from 300.499 – 345.403 mg/kg with a mean±sd of

329.128±17.137 mg/kg. The result shows that the concentration levels of the total PAHs vary closely across the petrol stations. They are also found to be above the level recorded from the control (16.44 mg/kg). Considering the individual 16PAH in the surface soils of the study area, the order is BkF (0.029%) < Fln (0.759%) < IcdP (0.777%) < BghiP (0.81%) < BaA (0.873%) < Chr (1.034%) < Pyr (2.697%) < Flu (3.489%) < Phe (5.497%) < BaP (6.096%) < BbF (6.34%) < DahA (7.5%) < Ant (8.487%) < Ace (10.64%) < Nap (15.537%) < Any (29.426%). The distribution pattern indicates the predominance of two and three ringed components constituting about 73.087% while others account for about 26.91% thus the order is 3 ringed < 2 ringed < 5 ringed < 4 ringed < 6 ringed.

TOC (%) values are presented in table 5. It ranges from 2.213 –2.998% with an average value of 2.715±0.302%. The recorded TOC (%) values vary closely as the ΣPAH across the study facilities.

Diagnostic ratios (Phe/Ant, Flu/Pyr, LMW/HMW) also included in table 6 were equally employed to access the origin and sources of the contaminants. The Phe/Ant varied from 0.53 – 0.936 as shown in (Table 6) indicating petrogenic contamination. The Flu/Pyr also ranges from 0.799 – 0.951 (all less < 1) as also shown in table 6. The distribution pattern shows the predominance of HMW PAHs over the LMW just as the ratio of LMW/HMW which is > 1 indicate petrogenic source.

The total PAH concentrations exceeded the limit of 10 mg/kg established by the EGASPIN (2002); the range established by the Dutch government for PAHs in uncontaminated soil which is 0.02-0.05mg/kg and 40 mg/kg for landscaping residential area (Berset and Holzer, 1995; Van Brummelen *et al.,* 1996; MSHPE, 1994; Tim O'Hare Associates, 2002). Moreover, concentrations of benzo(a)pyrene (BaP) at the various petrol stations were above the range of 1.08 – 1.32mg/Kg for UK generic assessment criteria (GAC) for residential land use (Nathanial *et al,* 2007). Thus, the PAHs levels obtained in the present study reveal that the environment within the study area is unsafe with regards to BaP concentrations.

Facility	Ace	Nap	Any	Ant	Flu	Phe	Pyr	Fln	BaP	BbF	BkF	DahA	BghiP	IcdP	BaA	Chr
Control	3.129	2.7	1.6	1.2	2.814	0.58	0.2	0.0105	2.037	0.03	1.12	0.4	0.21	0.120	0.150	0.140
PS 1	14.25	13.6	29.23	11.8	7.3	6.94	0.65	8.15	9.4		0.0218	11.6	1.82	0.380	0.560	1.390
PS 2	12.68	18.36	34.78	9.98	6.12	4.51	5.341	0.82	9.89	9.355	0.0478	8.985	0.91	1.310	1.120	1.400
PS 3	9.31	22.56	35.66	11.342	8.23	4.53	5.335	1.2	8.22	7.71	0.04	8.194	1.63	1.420	1.830	1.280
PS 4	16.64	15.98	53.1	9.86	7.64	3.64	4.846	0.98	5.17	8.075	0.02	11.95	0.63	1.320	1.490	1.390
PS 5	16.46	30.74	38.97	12.32	6.53	3.103	3.884	1.3	8.29	6.795	0.06	8.114	0.32	0.630	0.691	1.280
Min	9.31	13.6	29.23	9.86	6.12	3.103	5.17	0.65	5.17	6.795	0.02	8.114	0.32	0.38	0.56	1.28
Max	16.64	30.74	53.1	12.32	8.23	6.94	7.297	1.3	9.89	9.4	0.06	11.95	1.82	1.42	1.83	1.4
Mean	13.868	20.248	38.348	11.060	7.164	4.545	5.341	0.99	7.944	8.267	0.038	9.769	1.062	1.012	1.138	1.348
SD	2.711	6.023	8.014	0.982	0.758	1.314	1.113	0.238	1.531	0.998	0.015	1.67	0.576	0.423	0.477	0.056

Table 5: Summary table of the ΣPAHs levels (in mg/kg) across the petrol stations

TOC (%)	ΣPAH	Phe/Ant	Flu/Pyr	LMW/HMW
Control	1.821	16.4405	0.0707	2.0986
PS 1	2.998	300.499	0.936	0.951
PS 2	2.984	318.374	0.682	0.844
PS 3	2.533	339.875	0.823	0.849
PS 4	2.847	345.403	0.775	0.751
PS 5	2.213	341.487	0.53	0.799
Min	2.213	300.499	0.53	0.799
Max	2.998	345.403	0.936	0.951
Mean	2.715	329.128	0.749	0.851
SD	0.3017	17.1371	0.137	1.181

Table 6: Tabular presentation of the diagnostic ratios, TOC (%) and the ΣPAHs across the petrol stations
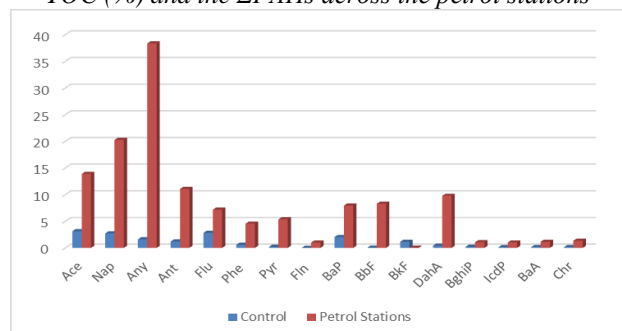
Figure 6: Bar chart showing the levels of the individual ΣPAHs across the petrol stations and the control site

VI. CONCLUSION

The distribution of PAHs in the surface soils of the selected facilities were examined. The auto-workshops show the highest levels of the considered PAHs. The concentration is in the order Petrol stations < Dumpsites < Auto-workshops. Phe and DahA were the dominant compound in the dumpsites while DahA and Any dominate in the auto-workshops. In the Petrol stations, it is Any and Nap that dominate. The distribution pattern in the dumpsites show the predominance of three, five and six ringed components constituting about 86.389% while others account for about 13.611% in the order 2 ringed < 4 ringed < 6 ringed < 3 ringed < 5 ringed. Also, the different diagnostic ratios show pyrolytic origin for the PAHs in the dumpsites. The PAHs distribution pattern in the auto-workshops indicate the predominance of three, five and six ringed components which constitute about 86.389% while others account for about 13.611% thus the order is 2 ringed < 4 ringed < 6 ringed < 3 ringed < 5 ringed. Diagnostically, the origin of the PAHs in the auto-workshops is petrogenic. The two and three ringed components is the most abundant in the samples from the petrol stations constituting about 73.087% while others account for about 26.91%. The order of abundance in the petrol stations is 3 ringed < 2 ringed < 5 ringed < 4 ringed < 6 ringed. Source evaluations indicate petrogenic contamination in the petrol stations.

The auto-workshops are showing the highest concentrations of the considered PAHs. This implies that the

emissions from the exhaust of the auto-mobiles and the disposal of spent oil on the surface soils of the facilities are the important sources of PAHs in the locations.

PAHs are well known as carcinogens, mutagens and teratogens. They pose serious threat to the health and the well-being of humans. Lung cancer is the most significant health effect to be expected from inhalation exposure to PAHs (Kim *et al.,* 2013). Therefore, the findings of this work should be a public health concern.

REFERENCES

[1] Akpoborie, N. A., Nfor, A. A., Etobro I. and Odagwe S. (2011). Aspects of the Geology and groundwater conditions of Asaba, Nigeria. Arch. Appl. Sci. Res. 3(2), 537-550.

[2] Anegbe B., Okuo, B. J. M. and Okiemen, F. E. (2016). The impact of inorganic and organic pollutants in soil from the vicinity of mechanic workshops in Benin City. International Journal of Chemical Studies, 4(3), 106-112.

[3] Assez, L. O (1989). In: Kogbe (ed). Geology of Nigeria. Rockview Publ., Jos, 311-334

[4] Budzinski, H., Jones, I., Bellocg, J., Pierard, C., and Garrigues, P. (1997). Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde estuary. Marine Chemistry, 58, 85-97.

[5] Colombo, J. C., Pelletier, E., Brochu, C., Khalil, M. and Catoggio, J. a. (1989). Determination of hydrocarbon sources using n-alkanes and polycyclic aromatic indexes. Environmental Science and Technology, 23, 888-894.

[6] Dessauvagie, T. F. and Fayose, E. A. (1970). Excursion A: Cretaceous and Tertiary rocks of Southern Nigeria. In: Dessauvagie, T. F. and Whiteman, A. J. (eds). African Geol., 659 – 665.

[7] EGASPIN (2002). Environmental Guidelines and Standards for the Petroleum Industry in Nigeria, 279.

[8] Fetzer, J. C. (2000). The Chemistry and Analysis of the large polycyclic aromatic hydrocarbon. Polycyclic aromatic compound (New York: Wiley) I27, 143.

[9] Godson, R. E. E. A., Mynepalli, K. C. S. and Godwin, O. E. (2009). A comparative assessment of soil pollution by polycyclic aromatic hydrocarbons in two Niger Delta communities, Nigeria. African Journal of Pure and Applied Chemistry, 3 (3), 031-041.

[10] Gschwend, P. M. and Hites, R. A. (1981). Fluxes of the polycyclic aromatic to marine and Lacustrine sediments in the Northeastern United States. Geochemica et Cosmochemica Acta, 45, 235 – 2367.

[11] Hussain, K., Balachandran, S. and Rafiqul, H.R. (2015). Sources of Polycyclic Aromatic Hydrocarbons in sediments of the Bharalu River, a tributary of the River Brahmaputra in Guwahati, India. Ecotoxicol. Environ. Saf. 122, 61–67.

[12] Hussein, I. A. and Mona S. M. M. (2013). A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation. Egyptian Journal of Petroleum, 25, 107–123.

[13] IARC (1983). Polynuclear aromatic compounds. Part 1, Chemical, environmental and experimental data in IARC monographs on the evaluation of the carcinogenic risk of chemicals to human. Vol. 32, World Health Organization International.

[14] Igwe, J. C. and Ukaogo, P. O. (2015). Environmental Effects of Polycyclic Aromatic Hydrocarbons. Journal of natural Sciences Research, 5 (7), 2224-3186.

[15] Kogbe, C. A. (1976). The Cretaceous and Paleogene Sediments of Southern Nigeria. In: Kogbe, C. A., Ed., Geology of Nigeria, Elizabethan Publishers, Lagos. 273-282.

[16] Nganje, T. N., Edet, A. E., Ibok, U. J., Ukpabio, E. J., Ibe, K. A. and Neji, P. (2012). Polycyclic aromatic hydrocarbon in surface water and soil in the vicinity of fuel-oil spillage from a tank farm distribution facility, Esuk Utan, Calabar Municipality, Nigeria. Environ. Earth Sci., 67, 81-90.

[17] Nganje, T. N., Edet, E. A. and Ekwere, S. J. (2007). Distribution of PAHs in surface soils from Petroleum Handling Facilities in Calabar. Env. Mont. Assessment, 130, 27-34.

[18] Nganje, T. N., Neji, P. A., Ibe, K. A., Adamu, C. I. and Edet, A. (2014). Fate, Distribution and sources of polycyclic aromatic hydrocarbon (PAHs) in contaminated soils in parts of Calabar Metropolis, South Eastern Nigeria. J. Appl. Sci. Eviron. Management, 18(2), 317-325.

[19] Oboh-Ikuenobe, Obi, C. G. and Jaramilo, C. A. (2005). Lithofacies, palynofacies and sequence stratigraphy of Palaeogene strata in southeastern Nigeria. Journal of African Earth Sciences, 41 (1-2), 79-101.

[20] Parkinson, J. (1907). The post – Cretaceous Stratigraphy of Southeastern Nigeria. Quart. Jour. Geol. Soc. London. 63,331 – 320.

[21] Reyment, R. A. (1965). Aspects of the Geology of Nigeria. Ibadan University Press, Ibadan, Nigeria, 145.

[22] Short, K. C. and Stauble, A. J., (1967.) Outline of the geology of the Niger Delta. Bulletin American Association of Petroleum Geologist 54, 761-779.

[23] Sims, R. C. and Overcash, M. R. (1983). Fate of polynuclear aromatic compounds (PNAS) in soil plant systems. Research Review, 88, 2-68.

[24] Soclo, H. H., Garrigues, P. H. and Ewald, M. (2000). Origin of polycyclic aromatic hydrocarbons (PAHs) in coastal marine sediments; case studies in Cotonou (Benin Republic) and Aquitane (France) areas. Marine Pollution Bulletin, 40, 387-396.

[25] Tebay, R. H., Welp G. and Brummer, G. W. (1983). Gehalte an polyzyclischen aromatischen Kohlenwasserstoffen (PAK) and deren Verteilungsmuster. In Unterschledlich belasteten Boden. Z. Pfiazernernachr, Bodenk, 156, 1-10.

[26] Whiteman, A. (1982). Nigeria: Its petroleum geology, resources and potential. Graham and Trotman, 1, 382.

[27] Wilcke, W., Muller, S., Kanchanakool, C. N. and Zech W. (1998). Urban Soil Contamination in Bangkok: heavy metal and aluminium partitioning in top soils. Geoderma, 86, 211- 228.

[28] Yang, G. P., Liu, X. L. and Zhang, J. W. (1998). Polycyclic aromatic hydrocarbons in the environment; Hoomogous series in soil and recent marine sediments.

[29] Yang, W., Lang, Y., Li, G. (2014). Cancer risk of polycyclic aromatic hydrocarbons (PAHs) in the soils from Jiaozhou Bay wetland. Chemosphere, 112, 289–295.

[30] Zhou, J., Wang, T., Huang, Y., Mao, T and Zhong, N. (2005). Size distribution of polycyclic aromatic hydrocarbons in urban and suburban sites of Beijing, China. Chemosphere, 61, 792-799.