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POLYCYCLIC AROMATIC HYDROCARBON CONCENTRATIONS IN SOIL OF THREE COMMUNITIES IN RIVERS STATE

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ABSTRACT

The study was conducted in three communities in Rivers State. These communities include Okochiri community in Okrika, Mgbuodohia in Obio-Akpor and Chokocho in Etche. Soil at two different depths were sampled on a composite basis using EGASPIN 2018 procedures, extracted and analyzed for sixteen priority PAHs using US EPA 8270 (2014) procedures. Studies show the total concentration of PAHs in soil sample taken from Okochiri community in Okrika at depths of 0 - 15 cm and 15 - 30 cm was found to be 145.32 mg/kg and 101.6 mg/kg during the dry season respectively but in the wet season the total concentration was found to be 607.08 mg/kg and 242.46 mg/kg at the two depths. In Mgbuodohia, the dry season result for the two depths, showed a total concentration of 14.68 mg/kg and 27.33 mg/kg and, 16.12 mg/kg and 14.94 mg/kg in the wet season. In Chokocho, the result showed a total concentration of 4.33 mg/kg and 252 mg/kg in the dry season and 23.87 mg/kg and 10.23 mg/kg in the wet season. Result showed a higher concentration of PAHs in the tops soil (0- 15 cm) compared to the subsoil at the depth (15 - 30 cm). The total PAHs concentration was consistently higher in the wet season than in the dry season. The concentration of PAHs was found to be majorly higher in the topsoil than the subsoil both in the dry and wet season. Diagnostic ratios reveal major source to be petrogenic. The concern for the environment and humans should prompt important stakeholders to take measures that will lead to mitigate the impact of these toxic chemical.

Keywords: polycyclic aromatic hydrocarbons, vertical depths of soil samples, seasonal variations, incomplete combustions.

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INTRODUCTION

Polycyclic aromatic hydrocarbons have been described as composed of two or more benzene ring in linear or cluster forms. Sources of PAHs are broadly classified as natural and anthropogenic. While the natural source could be cosmological, biological, volcanic eruptions, and endogenic geological, the anthropogenic sources are numerous. Anthropologically, PAHs are the result of the incomplete combustion of organic matter. These anthropogenic sources are numerous, and are connected to human activities that involve incomplete combustion and includes production of creosote, Rovinskii *et al.*, (1988), aluminium Belykh *et al.,* (1998), cement Belis *et al.,* (2011) asphalt and the petrochemical industry Kurteeva *et al.,* (2006), emissions from road transportation Nikiforova and Alekseeva (2002), soil irrigation using contaminated water (Labana *et al*., 2007; El-Motaium *et al*., 2009). PAHs have been sufficiently demonstrated to be ubiquitous, toxic, mutagenic. Though their source is mostly associated with activities like combustion, their ubiquity is so far-reaching that they are even found in arctic region where there are minimal anthropogenic activities that involve burning of organic matter. Several studies show they are found in the three matrices of soil, water, and air. There are also several studies that establish that the levels or concentration of PAHs in soil is generally higher in soil compared to water and air. Many studies about the level/concentration of PAHs in soil have been conducted by collecting soil samples from the topsoil. Comparatively, fewer studies of the level of PAHs in soil have been conducted at different soil depths, especially in the Niger Delta region.

There is a large number of polycyclic aromatic hydrocarbons, however, sixteen of them have been prioritized by the World Health Organization, WHO, as they are often used as a benchmark to determine the level of environmental pollution and human toxicity. They include Naphthalene, Acenaphthylene, Fluorene, Phenanthrene, Anthracene, Acenaphthene, Chrysene, Fluoranthene, Pyrene, Benzo(a)anthracene, Benzo (a) pyrene, Benzo(b)fluoranthene, Benzo (k) fluoranthene, Dibenzo (a,h) anthracene, Benzo(ghi)perylene and Indeno (1,2,3,cd) pyrene as priority environmental pollutants. In terms of their weight, they have been classified as low molecular, medium-molecular and high molecular-weight polycyclic aromatic hydrocarbons.

Polycyclic aromatic hydrocarbons occur naturally in crude oil. Their introduction into the environment follows leakages and such processes as incomplete combustions, hence their classification as petrogenic and pyrolytic PAHs. It follows therefore that where there is a high volume of industries and processes that are related to crude oil and other organic matter, there is the possibility of a high incidence of PAHs, though studies show that even areas where there is no high incidence of these parameters, there are evidence of significant levels of show incidences of PAHs.

There have been studies conducted by researchers that highlight the quantification and the health impact of polycyclic aromatic hydrocarbons as it affects the soils in the Niger Delta region of Nigeria, particularly in locations

where there is the sighting of refineries, illegal combustion of petroleum products for financial gains etc. Sojinu *et al.*, (2010) collected twenty soil samples from some communities very close to oil installations. The samples were transported to the laboratory in pre-cleaned polyethylene bags and stored in a freezer at -20 ◦C and subsequently shipped within 24 hours to Guangzhou Institute of Geochemistry, China, in the frozen state and stored in the freezer upon arrival. Extraction was carried out by successive elutions with 20 mL of hexane and 70 mL of hexane/dichloromethane (7/3 in v/v). Analysis was done using GC/MS. Results showed that twenty-eight PAHs were detected and found the total concentration of PAHs in the soil samples ranged from 24 to 120 ng/g with a mean value of 80 ng/g, which was found to be comparatively lower than those found in soils from two industrial zones in Korean Peninsula, South Korea, ranged from 109 to 178 ng/g Hashmi et al., (2005). Surface soils from the outskirts of Beijing, China, contained total concentrations of 16 PAHs ranging from 16 to 3884 ng/g with a mean value of 1347 ng/g Ma et a., (2005). In addition, Wild and Jones (1995) reported a mean concentration of 187 ng/g for the 16 PAHs in rural soils of the U.K.

Some studies conducted in the Niger Delta region zeroed in on the assessment of soils collected from dumpsites. Ekpete *et al.,* (2019) collected surface soil at the depth of 0 -10cm, from three dumpsites location within the Rumuigbo-Rumuokwuta axis using soil auger. These locations include Chakiricha station, Psychiatry dumpsite and Rumuokwuta dumpsites. Soxhlet extractor was used. The solvent used were methanol and dichloromethane. Analysis was carried out using gas chromatography. The result showed the present/absence of some PAHs in all three sites with the Rumuokwuta station producing the highest concentrations of PAHs followed by Chakiricha and lastly the psychiatry dumpsite. At the Chakiricha station, the concentration of phenanthrene was the highest at 4.531±1.352mg/kg while flouranthene, pyrene, chrysene and Benzo (g,h,i) Pyrene were observed to be as high as 3.888±0.896, 3.132±1.354, 3.380±1.102 and 3.630±2.011mg/kg respectively. At the psychiatric dumpsite fluorene produced the highest concentration of 5.151±1.332 mg/kg while phenanthrene and acenaphthene showed high concentrations of 3.450±1.021mg/kg and 3.248±1.261mg/kg respectively. All other PAHs were detected at the Rumuokwuta dumpsite with the exception of Benzo[k]fluoranthene. Result were as follows; naphthalene (9.575±2.013 mg/kg), acenaphthylene (8.713±1.465 mg/kg), anthracene (6.434±2.519), acenaphthene (5.748±2.134 mg/kg), chrysene (5.693±1.932 mg/kg), benzo (b) fluoranthene (5.693±2.256 mg/kg) and Indeno(1,2,3-cd) pyrene (5.014±2.561mg/kg).

Loremikan *et al.,* (2020) collected soil samples from locations where there is active market, semi-industrial area and residential area over the dry and wet season using soil auger. Loremikan *et al.,* (2020) found the total PAHs at Market dumpsites and semi-industrial area to be less than 1 but still sufficient to pose a moderate level of contamination during the wet season. The level of PAHs during the dry season was also found to pose moderate risk, as there was a significant amount of high molecular weight PAHs. Fagbote & Olanipekun (2013) studied the concentration of PAHs in Agbabu, Nigeria. Samples were collected in the dry and wet season and Soxhlet extraction was used to recover the PAHs. Analysis was conducted using the Agilent 6890N Gas chromatography coupled with mass spectrometer. At a particular site, the concentration of PAHs detected during the dry season was higher than in the wet season: (0.07 ± 0.036ppm for dry) and (0.69 ± 0.19ppm for rainy). However, they found that the overall concentration of PAHs was high in the wet season than in the dry season. A similar conclusion was reached by Teaf (2008). Liu et al., (2017) conducted a similar study, but this time they sought the level of PAHs at different depths; 0-20cm, 20-50cm and 50-100cm. There was no clear pattern in the concentration of PAHs with depth. While some PAHs increased in concentration with depth, others decreased in concentration.

The staple source of revenue in Nigeria is crude oil. The exploration and processing of crude oil is usually accompanied by pollution which impacts human beings and the environment. Currently, there is serious attempt to diversify the economy to other sectors, notably the agricultural sector. In Port Harcourt, there is significant agricultural activities. As the city lies in the tropics, irrigation is important for healthy agricultural practices. Researchers found that they arrive in soils during their irrigation with contaminated water and the occurrence of PAHs in soils results in a high level of pollution, and eventually the fate of this toxic chemical is the plants which are ingested by plants and animals (Shurubor, 2000; Labana et al., 2007; El-Motaium, 2009). Both the health implication and economic implication and ramification should propel stakeholders like the government, individuals involved in the illegal refining of crude oil, farmers etc., to take steps towards amelioration of the environment and introduction of policies that will lead to sustainable development and growth.

MATERIALS AND METHODS

Study Area

The study area, Port Harcourt is located in the Niger Delta region of Nigeria and is the capital of Rivers State. It has the second largest seaports in Nigeria. It is located on the Bonny River about 64km, (40 miles) from the sea). The area lies between longitude 60 4 1 S- 70 1 1 E and latitude 40 401 - 50 001N. It covers an estimated area of 1811.6 square kilometers. The city is slightly elevated but no significant structural control on the evolution of the drainage network and surface forms are dissembled. Port Harcourt is the hub of industrial, commercial, administrative and other activities in the state. The city is often referred to as the treasure base of the nation.

Table-1. Sampling points and sampling coordinates of the three communities in Rivers State.

Location Description	Sampling Code	Latitude	Longitude
Okrika 1	OK1	$04^{o}\ 45^{I}\ 0.7^{II}$	$007^{o}\ 06^{I}\ 7.6^{II}$
Okrika 2	OK2	$04^{o}\ 44^{I}\ 57.1^{II}$	$007^{o}\ 06^{I}\ 05.9^{II}$
Okrika 3	OK3	$04^{o}\ 44^{I}\ 59.9^{II}$	$007^{o}\ 06^{I}\ 16.1^{II}$
Mgbuodohia 1	MGB1	$04^{o}\ 47^{I}\ 03.4^{II}$	$006^{o}\ 57^{I}\ 56.0^{II}$
Mgbuodohia 2	MGB2	$04^{o}\ 47^{I}\ 02.8^{II}$	$006^{o}\ 57^{I}\ 54.3^{II}$
Mgbuodohia 3	MGB3	$04^{o}\ 47^{I}\ 01.9^{II}$	$006^{o}\ 57^{I}\ 52.5^{II}$
Chokocho 1	CH1	$04^{o}\ 59^{I}\ 37.4^{II}$	$007^{o}\ 03^{I}\ 23.1^{II}$
Chokocho 2	CH2	$04^{o}\ 59^{I}\ 35.44^{II}$	$007^{o}\ 03^{I}\ 21.0^{II}$
Chokocho 3	CH3	$04^{o}\ 59^{I}\ 38.6^{II}$	$007^{o}\ 03^{I}\ 20.6^{II}$

The study was conducted in different area in Rivers State. Some of the sampling locations are in Port Harcourt. Port Harcourt is situated in Rivers State in the Niger Delta region of Nigeria. The three areas include Okochiri community in Okrika (Okrika local Government Area), Mgbuodohia in Obio-Akpor Local Government Area and Chokocho in Etche Local Government Area. The sites were samples were collected are clearly shown by their coordinates in Table-1. Due to background knowledge of the impact of certain industries like refineries and other human on the concentration of polycyclic aromatic hydrocarbons, the sites at Okrika and Mgbuodohia were chosen because the proximity of the Port Harcourt refinery and artisanal is not combustion of crude oil while the site at Chokocho was chosen as a control site because there are not such activities of large scale combustion of crude oil in close proximity.

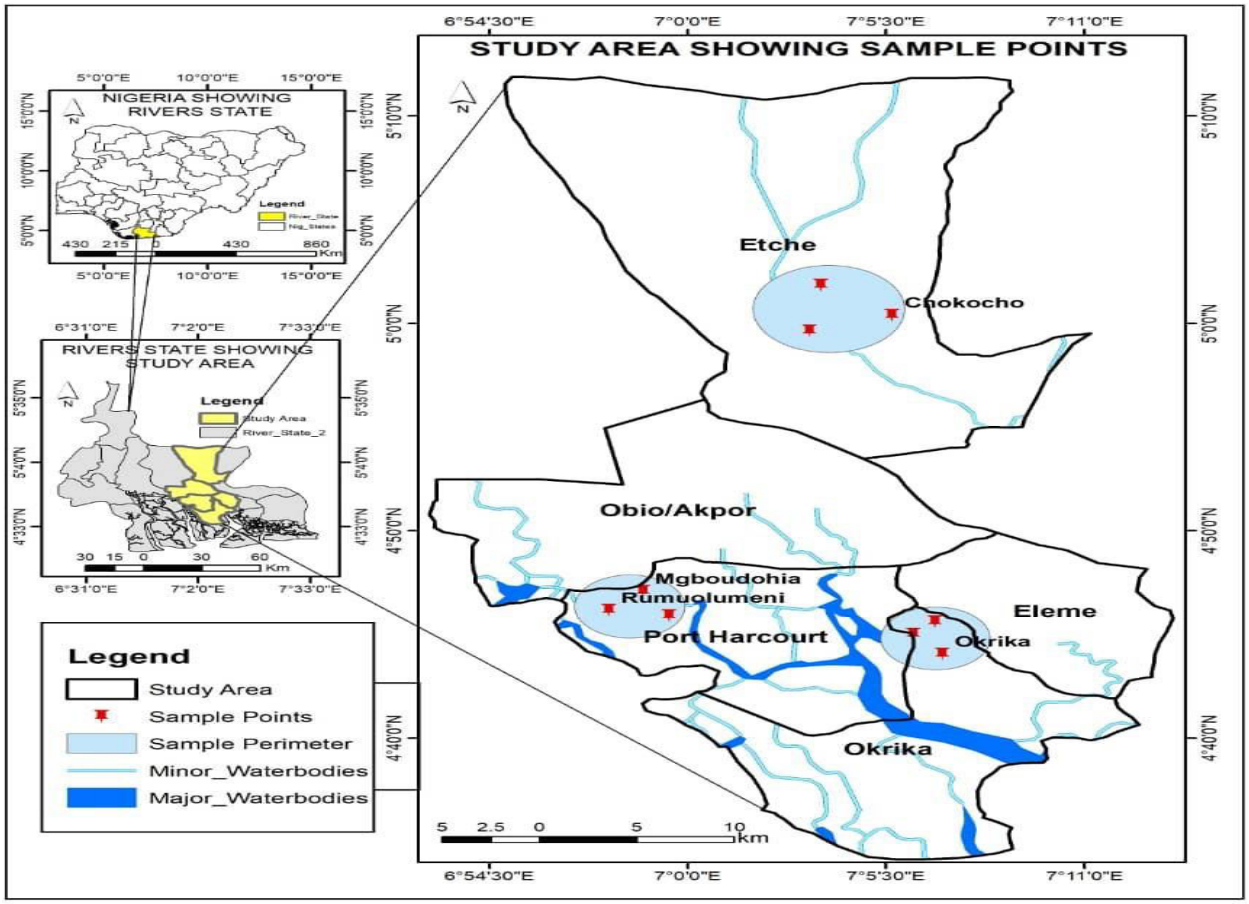

Figure-1. Map showing sampling points in Okrika (Okrika LGA), Mgbuodohia (Obio/Akpor LGA) and Chokocho, (Etche LGA) in Rivers State, Nigeria.

Sample Collection

The emission source for the Okrika study area is the river that receives the effluents from the Eleme refinery. The source for Mgbuodohia is also a mini stream that is very close to where local distillation of crude oil is carried out. The river Otamiri and its environ in Chokocho Etche local government area served as a control area, as there is no nearby activity of a petrochemical or refining company. Soil samples were collected using composite sampling after setting a grid. At each location in each of the three communities, the soil auger, which was marked to explore different depths, was used to collect topsoil (depth 0-15cm) and subsoil (depth 15-30cm). By the simple action of turning the soil auger in the clockwise direction, the soil auger gets to the depth of interest. On reaching the depth, it was slowly pulled up and its content discharged into a clean plate. For each sampling point, three samples were taken from the same area, discharged into a clean plate, and thoroughly mixed to obtain a composite homogenous mixture. A spoon was used to scoop some of the mixture into amber coloured sample bottles. The bottle was filled to the brim to leave little or no room for air before it was covered with a lid and stored in a cooler that contained ice packs. The samples were clearly labelled, dated and positions indicated and then placed in a cooler containing ice packs needed to keep the soil samples cool. The soil samples were transported and on reaching the laboratory were kept in a refrigerator at a very low temperature, again to minimize loss of the analyte.

Extraction of PAHs from Soil

Soil sample was removed from the soil jar. The soil sample was homogenized thoroughly by mixing properly in a container. The whole soil was transferred into a beaker. The soil is thoroughly homogenized by thorough mixing. 15 g of soil was weighed and transferred into another beaker. This is taken into the fume cupboard as the solvent to be used is toxic. Organic solvent used to extract the organics is dichloromethane. 30 ml of the solvent was added, and the mixture stirred using a stirring rod or by swirling. This process was carried out for soil samples collected from Mgbuodohia and Chokocho because they are loose soils. Soil samples from Okrika sampling sites was clay soil. Anhydrous sodium sulphate was added to break up the soil and to allow for greater interaction between solvent and the soil thereby facilitating better extraction of all organics. A settling time of about 3-15 minutes was given to allow for the extraction of all hydrocarbons. A separation assembly comprising of funnel, filter paper and silica gel which basically removed all polar compounds was set up in the extraction chamber. The filtrate obtained (silica gel treatment) comprised of non-polar compounds of polycyclic aromatic hydrocarbon, was collected in a vial. The content of the vial was taken for identification and quantification in the GC-FID instrument.

Quality Assurance Quality Control (QAQC)

To ensure the utmost integrity of each sampling point, quality assurance quality control measures put in place include thoroughly washing with detergent and rinsing the soil auger with plenty of water between any two sample points. Disposable gloves used at a sampling point were disposed and fresh ones used at another sampling point. The plate used for homogenization of the soil sample was covered with polyethylene bags, which are changed for each sampling point. These significantly reduced cross-contamination. In addition, different clean containers were also used to house the soil samples collected per point after thorough homogenization. The sampling containers for these organics were made of glass. Ice packs in coolers kept the sample cool.

PAHs Analysis

The polycyclic aromatic hydrocarbons present in the extracted samples of soil, were passed in for analysis using the GC-FID. The basic GC parameters are as follows; The injector temperature was 270 ^{o}C while the detection temperature was 320 ^{o}C. The GC was heated for 1 minute to a temperature of 65^{o}C. The temperature was ramped at 25 ^{o}C/min to 140 ^{o}C at 0 minutes and later at 10 ^{o}C/minute to 290 ^{o}C at 11 minutes. The injection volume of standards and samples was 1 to 2 µL. Standards used for the calibration of the instrument were of industrial grade.

RESULT AND DISCUSSIONS

The result in Table-2 shows that for both dry and wet seasons, there were no significant difference in PAHs in soil between depth 0-15 cm and 15-30 cm ($P>0.05$). In Okrika, and during the dry season, about 37% of detected PAHs show an increase in concentration with depth. This decreases to about 12% during the wet season with only 2 of the detected PAHs showing an increase in concentration with depth. Results in Table-3 show that for both dry and seasons, there was no significant difference in PAHs in soil between depth 0-15 cm and 15-30 cm ($P>0.05$). Table 4 in dry season, about 70% of the detected PAHs show increase in the concentration of PAHs with depth. In comparison, only about 30% of the detected PAHs show an increase in the level of PAHs in the soil from Mgbuodohia in the wet season. The result in Table 4 shows that for both dry and seasons, there were no significant difference in PAHs in soil between depth 0-15 cm and 15-30 cm ($P>0.05$) with the exception of Acenaphthene which was significantly higher during at 0-15 cm than 15-30 cm during dry season ($P<0.05$).

Table-2. Concentration of PAHs (mg/kg) in soil at different depth in Okrika.

	Dry		Wet	
	0-15 cm	**15-30 cm**	**0-15 cm**	**15-30 cm**
Naphthalene	3.21±2.72	2.14±2.07	36.67±14.89	11.78±5.28
Acenaphthylene	3.22±1.82	4.49±4.30	59.28±22.23	24.39±13.53
Acenaphthene	10.22±5.93	9.75±9.35	53.70±20.87	18.38±6.39
Fluorene	8.60±4.59	7.91±5.52	34.95±12.25	19.41±8.00
Phenanthrene	28.83±14.47	21.18±17.97	100.01±43.79	30.40±16.81
Anthracene	10.17±5.15	7.95±5.71	26.50±9.07	10.75±5.73
Fluoranthene	21.37±13.20	12.84±8.97	62.45±27.49	23.03±10.25
Pyrene	22.22±12.93	7.63±4.81	53.20±16.14	29.24±15.50
Benzo(a)anthracene	16.42±9.45	11.10±10.00	42.18±19.57	27.96±13.36
Chrysene	11.07±6.92	5.36±3.59	38.05±17.45	10.02±6.81
Benzo(b)fluoranthene	4.31±3.01	4.36±2.89	54.54±27.91	6.44±3.05
Benzo(k)fluoranthene	3.88±0.60	4.73±0.81	21.25±13.48	8.20±4.08
Benzo(g,h,l)perylene	0.29±0.22	0.64±0.25	9.40±5.82	4.24±2.89
Benzo(a)pyrene	0.49±0.23	0.80±0.31	8.69±3.89	4.87±4.14
Dibenzo(a,h)anthracene	0.81±0.59	0.42±0.20	5.05±2.51	13.12±11.22
Indo(1,2,3)pyrene	0.21±0.14	0.36±0.24	1.16±1.02	0.17±0.11

*Significant higher at 5% (P<0.05), **Significant higher at 5% (P<0.01).

Table-3. Concentration of PAHs (mg/kg) in soil in different depth in Mgbuodohia.

	Dry		Wet	
	0-15 cm	**15-30 cm**	**0-15 cm**	**15-30 cm**
Naphthalene	0.10±0.07	0.07±0.03	0.26±0.23	0.57±0.57
Acenaphthylene	0.14±0.06	0.06±0.03	1.51±0.61	1.72±0.81
Acenaphthene	0.19±0.09	0.07±0.04	0.41±0.25	0.33±0.17
Fluorene	0.43±0.30	0.51±0.18	1.74±0.63	1.11±0.33
Phenanthrene	1.59±0.64	3.76±2.00	0.71±0.16	1.13±0.33
Anthracene	0.54±0.19	1.11±0.61	0.30±0.16	0.18±0.11
Fluoranthene	2.36±1.30	2.14±0.79	1.49±0.71	0.92±0.41
Pyrene	1.30±0.44	2.14±0.95	1.22±0.42	0.87±0.34
Benzo(a)anthracene	1.38±0.79	0.43±0.29	0.34±0.11	0.30±0.11
Chrysene	0.65±0.31	0.70±0.48	0.68±0.25	0.52±0.18
Benzo(b)fluoranthene	0.61±0.24	1.03±0.48	0.50±0.25	0.56±0.35
Benzo(k)fluoranthene	2.55±0.30	3.23±1.40	6.11±1.85	5.70±2.14
Benzo(g,h,l)perylene	0.51±0.12	0.81±0.30	0.28±0.11	0.27±0.17
Benzo(a)pyrene	0.65±0.12	0.71±0.25	0.34±0.12	0.23±0.13
Dibenzo(a,h)anthracene	0.22±0.07	0.31±0.14	0.13±0.08	0.12±0.09
Indo(1,2,3)pyrene	0.85±0.22	0.98±0.42	0.10±0.08	0.41±0.21

*Significant higher at 5% (P<0.05), **Significant higher at 5% (P<0.01).

Table-4. Concentration of PAHs (mg/kg) in soil in different depth in Chochoko.

	Dry		Wet	
	0-15 cm	15-30 cm	0-15 cm	15-30 cm
Naphthalene	0.09±0.08	0.01±0.01	0.25±0.11	0.25±0.17
Acenaphthylene	0.13±0.08	0.02±0.01	2.04±0.69	0.60±0.20
Acenaphthene	0.11±0.05*	0.01±0.01	0.32±0.14	0.41±0.19
Fluorene	0.31±0.25	0.07±0.07	0.78±0.42	0.29±0.14
Phenanthrene	0.62±0.43	0.17±0.17	1.07±0.26	1.14±0.49
Anthracene	0.16±0.11	0.03±0.03	0.36±0.18	0.19±0.13
Fluoranthene	0.48±0.31	0.17±0.17	2.16±0.82	1.80±0.66
Pyrene	0.23±0.03	0.25±0.05	0.49±0.09	0.78±0.27
Benzo(a)anthracene	0.09±0.06	0.00±0.00	8.90±8.80	0.07±0.03
Chrysene	0.08±0.05	0.00±0.00	0.68±0.46	0.37±0.15
Benzo(b)fluoranthene	0.24±0.24	0.00±0.00	0.16±0.06	0.10±0.05
Benzo(k)fluoranthene	1.29±0.12	1.18±0.18	3.38±0.50	4.04±0.38
Benzo(g,h,l)perylene	0.11±0.11	0.20±0.09	0.07±0.04	0.10±0.05
Benzo(a)pyrene	0.15±0.15	0.24±0.09	0.10±0.08	0.00±0.00
Dibenzo(a,h)anthracene	0.08±0.08	0.03±0.03	3.11±3.02	0.09±0.06
Indo(1,2,3)pyrene	0.16±0.11	0.14±0.09	0.00±0.00	0.00±0.00

*Significant higher at 5% (P<0.05), **Significant higher at 5% (P<0.01).

The total concentration of PAHs in soil sample taken from Okochiri community in Okrika at depths of 0-15 cm and 15-30 cm was found to be 145.32 mg/kg and 101.6 mg/kg during the dry season respectively but in the wet season the total concentration was found to be 607.08 mg/kg and 242.46 mg/kg at the two depths. In Mgbuodohia, the dry season result for the two depths, showed a total concentration of 14.68 mg/kg and 27.33 mg/kg and, 16.12 mg/kg and 14.94 mg/kg in the wet season. In Chokocho, the result showed a total concentration of 4.33 mg/kg and 252 mg/kg in the dry season and 23.87 mg/kg and 10.23 mg/kg in the wet season. Result showed, except for that of the dry season result in Mgbuodohia, that there was always a higher concentration of PAHs in the tops soil (0- 15 cm) compared to the subsoil at the depth of 15-30 cm. Overall the total PAHs concentration was consistently higher in the wet season compared to the dry season. The result corroborates the findings of Ortiz *et al*., (2013) and Gong *et al.*, (2018) who also found the concentration of PAHs to be higher in the wet season compared with the dry season. The dry season result from the soil samples taken from Mgbuodohia community showed the only variation where the concentration of PAHs at the depth of 15-30 cm. This variation is traceable to the higher incidence of artisanal combustion of crude oil about the time of samples and the nature of the soil.

Of the three sites, the concentration of PAHs in samples of topsoil and subsoil was highest in Okochiri community in Okrika in the wet season compared with the dry season. Concentration was higher in the topsoil compared with the subsoil. Though the concentration obtained for this study was higher, the reverse was the case of the result that was obtained by Emoyan *et al.*, (2020) who found the concentration of topsoil was higher in the subsoil at a range of 0.1499 mg/kg - 5.3219 mg/kg compared to the concentration of PAHs in topsoil found at a range of 0.3658 mg/kg - 1.0658 mg/kg. In the dry season, this study found the concentration of PAHs in topsoil was higher than that found in subsoil. Again, with topsoil and subsoil concentration found to be 0.0664 mg/kg - 0.2693 mg/kg and 0.2121 mg/kg - 1.3425 mg/kg respectively, Emoyan *et al.,* (2020) concluded that the concentration of PAHs in the subsoil is higher than that of topsoil. Texture of the soil could possibly be a contributory factor to the concentration of PAHs found at different soil depths. As Xu, *et al.,* (2014) pointed out fine soil (with larger surface area) particle distribution is a measure of adsorption of contaminants such as PAHs. This could account for the variation in the concentration of PAHs with soil depth - mostly decrease in concentration with depth. However, with respect to the individual sixteen PAHs, there was no regular pattern of increase or decrease in the concentration of PAHs with depth of soil.

Cancer Risk Assessment of PAHs in Soil

Several studies have shown the impact of PAHs on human health. Of the sixteen PAHs identified by USEPA as a standard, seven are well known carcinogens. The cancer risk for adult and child was calculated using

relevant equation. Table-5 and Table-6 gives the result of the cancer risk of the seven polycyclic aromatic hydrocarbons for the three communities during the wet and the dry season.

Table-5. Cancer risk assessment in dry season for the three communities for children and adult for PAHs in soil.

PAHs	Okrika		Mgbuodohia		Chokocho	
	Child	Adult	Child	Adult	Child	Adult
BaA	0.557	2.125	0.039	0.150	0.001	0.005
Chy	1.628	1.2471	0.032	0.122	0.004	0.015
BbF	0.863	0.669	0.115	0.438	0.050	0.188
BkF	0.857	0.665	0.867	3.303	0.256	0.974
BaPry	1.842	3.132	1.057	4.030	0.211	0.803
DbA	12.306	9.543	0.036	0.139	0.005	0.022
IP	0.0574	0.044	0.039	0.150	0.001	0.005

Table-6. Cancer risk assessment in wet season for the three communities for children and adult for PAHs in soil.

PAHs	Okrika		Mgbuodohia		Chokocho	
	Child	Adult	Child	Adult	Child	Adult
BaA	1.421	5.415	0.013	0.049	0.182	0.693
Chr	4.765	3.631	0.023	0.090	0.020	0.078
BbF	6.071	4.708	0.021	0.081	0.005	0.020
BkF	2.932	2.273	0.239	0.911	0.150	0.573
BaPyr	19.429	33.041	0.365	1.393	0.065	0.248
DbA	180.93	140.3	0.510	1.945	6.485	24.707
IP	0.132	0.102	0.0103	0.039	8.1E-05	0.0004

Table-5 shows the cancer risk assessment for PAHs in the three communities in the dry season. For both preschoolers and adults, and with reference to concentration, PAHs in Okrika was found to be significant most in Okrika compared to the other two communities. The PAHs concentration was significantly higher in Mgbuodohia than in Chokocho. Table 6 shows that the cancer risk in the wet season is high for Okrika community but this is even compared with dry season. This result is somewhat in agreement with the study conducted by Ortiz *et al.,* (2011) and other researchers.

Diagnostic Ratios and Source Apportionments of PAHS from the Three Communities

Diagnostic ratios were computed to ascertain an identify the possible sources of the PAHs that were detected in the soil samples collected from the three communities.

Table-7. Source apportionment of PAHs in the dry season.

Number of Rings	Diagnostic Ratios	Okrika	Mguodohia	Chokocho
3	An/(An+Phe)	0.266	0.239	0.702
4	Fl/(Fl+Py)	0.534	0.577	0.548
5	BaA/(BaA+Chr)	0.626	0.592	0.507
6	IP/(IP+BgP	0.382	0.586	0.472

Table-8. Source apportionment of PAHs in the wet season.

Number of Rings	Diagnostic Ratios	Okrika	Mgbuodohia	Chokocho
3	An/(An+Phe)	0.222	0.207	0.200
4	Fl/(Fl+Pyr)	0.509	0.535	0.926
5	BaA/(BaA+Chr)	0.593	0.348	0.921
6	IP/(IP+BgP)	0.089	0.482	0.024

The source analysis of 2 - 3 ring PAHs in soils during the dry season showed values of 0.266, 0.2389 and 0.709. The values obtained show that the sources of PAHs obtained in Okrika and Mgbuodohia is petrogenic while that of Chokocho is pyrogenic. The source analysis for 2 - 3 rings PAHs in Okrika, Mgbuodohia and Chokocho during the wet season showed values of 0.222, 0.207 and 0.200. These values indicate that the source of PAH in soil is mainly petrogenic. In the case of four ring PAHs the diagnostic ratios computed Fl/(Fl+Pyr) for Okrika, Mgbuodohia and Chokocho showed values of 0.534, 0.577 and 0.548 in the dry season and 0.509, 0.535 and 0.926 in the wet season - all values pointing to pyrogenic source of PAHs. The diagnostic evaluation of 5 members ring PAHs (BaA/BaA+Chr) showed the values 0.626, 0.92 and 0.507 in the dry season and 0.593, 0.348 and 0.921 in the wet season. For the six-member ring PAHs, the source analysed (IP/IP+BgP) showed values such as 0.382, 0.586 and 0.472 in the dry season and 0.089, 0.482 and 0.025 in the wet season. These values showed that the sources are majorly petrogenic, while a few are pyrogenic. These values indicative of the possible sources of PAHs are similar to the findings of Ekpete et al., (2019) who examined the concentration of PAHs from selected dumpsites in Port harcourt. Majority of the sources point to petrogenic sources, clearly showing the impact of such factors as proximity of refinery as in the case of Okrika which is very close to the Port Harcourt refinery, as well as the illegal activities that leads to the spillage of crude oil in the environment.

CONCLUSIONS

This study was conducted to determine the concentration of polycyclic aromatic hydrocarbons in soils at two depths over two seasons. The study revealed that the soils were heavily polluted especially those in areas near a petrochemical industry as well as area with high incidence of artisanal combustion of crude oil products. There is a prevalence of petrogenic PAHs compared with pyrogenic PAHs and other sources of PAHs in the three locations under study.

RECOMMENDATION

The high values of the concentration of PAHs calls for corresponding action of relevant government parastatals, individuals, traditional rulers in communities where there are illegal activities that impact the release of these toxic chemicals into the environment, as well as health professionals who bear the brunt of professional care and education of people when they take ill. Communities could be educated on the possible dangers that lurk around freely in their environment. Steps could also be taken to promulgate laws that will limit the extent of pollution via effluent from the industries

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