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Quantification of Polycyclic Aromatic Hydrocarbons (PAHs) in Soil Adjacent to the Ogini Flow Station Associated Gas Flare, Delta State, Nigeria

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ABSTRACT

Gas flaring, a common practice in the oil and gas industry, contributes to environmental pollution through the release of pollutants, including polycyclic aromatic hydrocarbons (PAHs). The PAHs levels in soil adjacent to the gas flare in the Ogini flow station were evaluated. The soil samples were analysed using gas chromatography-mass spectrometry (GC-MS) for the determination of 16 PAHs USEPA priority pollutant. The research findings show that the most common contaminant among the 16 priority PAH compounds tested was benzo(g,h,i)perylene with a mean concentration of 39.58 mg/kg at the topsoil layer, followed by indeno(1,2,3-cd)pyrene with a mean concentration of 36.87 mg/kg. However, the samples collected at the shorter distance to gas flare areas (STN 1 to STN 3) recorded high concentrations of PAHs levels in the soil. The values recorded at these stations were above the US EPA Integrated Risk Information System (IRIS) and the intervention value of polluted soil by the Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN). The texture of soil samples in these areas plays a significant role in the retention of PAHs pollutants, as demonstrated at station three (200 m), where total PAHs were significantly high at the topsoil (0–15 cm) due to the sandy-clay-loam texture of the soil, with total PAHs of 278.50 mg/kg and drift drastically to 7.20 mg/kg at the bottom soil (15–30 cm) of loam sand texture, respectively. Hence, the Niger Delta environment needs holistic monitoring of PAHs emissions to prevent negative environmental impacts.

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are persistent organic pollutants and are known to be carcinogenic and mutagenic to humans. The most significant human sources of PAHs are thought to be crude oil and the byproducts of its combustion, while coal has been identified in other studies as an unidentified or unthinkable source of PAHs (Liu *et al*., 2012). These compounds are released into the environment through activities such as burning fossil fuels, vehicle

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emissions, and industrial processes. PAHs can accumulate in soil, water, and air, posing a threat to human health and the environment (Ramesh *et al*., 2011). However, in recent times, global energy demand has led to a significant increase in the exploration and production of oil and gas resources and by extension increase in the amount of gas being flared continuously as the exploration continues. Drilling for crude oil has had a variety of effects on nations that possess such resources, in addition to bringing about sustained economic growth (Akpomedaye and Okposo, 2021). In the Nigerian Niger Delta, gas flaring is a common practice by the oil-producing companies that releases various pollutants into the atmosphere, such as sulphur dioxide, nitrogen dioxide, volatile organic compounds (like benzene, toluene, and xylene), polycyclic aromatic hydrocarbons, hydrogen sulphide, particulates, etc. (Seiyaboh and Izah, 2017). Despite the huge natural resources that Nigeria is endowed with in her reservoir of oil and gas wells around the Niger Delta region, the ineffective transmission and distribution process has resulted in a greater percentage of these energy sources being flared (Anyadiegwu *et al*., 2015). This flaring of the associated gases is usually an incomplete combustion process because of the high moisture and wind that are at the tip of the flare, thereby leading to inefficient burning and the release of harmful pollutants into the atmosphere. These gaseous releases eventually end up in the soil and aquifer (Hawboldt and Adams, 2005). Therefore, the soil is considered the major final receptor and disposal site for this hydrophobic organic contaminant emitted into the atmosphere from several anthropogenic sources (Cheruyiot *et al*., 2015; Enuneku and Kubeyinje, 2019; Omoruwou *et al*., 2023). The features of PAHs, such as their water solubility and air evaporation rates, determine how easily they migrate across the environment. In general, PAHs are difficult to dissolve in water. They cling to the surfaces of tiny solid particles or exist as vapours in the air before they return to Earth as rainfall and urban runoff (Cheruyiot *et al.*, 2015). They can reach bodies of water mainly through wet and dry deposition, road runoff, industrial wastewater, and leaching from petroleum spills. While some PAHs from surface waters evaporate into the atmosphere, the majority of others attach themselves to solid particles and sink to the bottom of rivers and lakes. Underground water can also be contaminated by several PAHs found in soils (Mumtaz and George, 2002).

Other industrialised nations have devised several means of flaring and venting petroleum-associated gas, which has drastically reduced atmospheric organic pollutants. For instance, Norway implemented carbon pricing and enacted a carbon tax that penalises businesses for gas venting or flaring (Braun *et al*., 2014; Romsom and Mcphail, 2021). Nonetheless, Nigeria appears to have excessively lenient penalties for gas flaring and venting, making it difficult to stop the practice or reduce emissions (Odionu, 2018; Okafor and Aniche, 2015). An alternate method of disposal might be the liquefaction of natural gas for energy supply or the re-injection of associated natural gas into the ground for possible future harvesting (Ite and Ibok, 2013; Odumugbo, 2010). The environment has been directly affected by gas flares's temperature, leading to depletion of the ozone layer, global warming, and acid rain, which elevates soil pH, causes infertility, and ruins roofing sheets in communities where the gas is flared (Akpomedaye and Okposo, 2021).

2. MATERIALS AND METHODS

2.1 Sampling Technique

Soil samples were collected around the flare stack of the Ogini flow station for the evaluation of polycyclic aromatic hydrocarbons (PAHs). Ten sampling points were marked out and geo-referenced at intervals of one hundred meters (100m), totaling one thousand meters (1km) from the flare stack. The control sample was collected in a farm area about 1500 meters (1.5 km) away from the flare site, The rotated soil auger was used for sampling at different depths of 0-15cm and 15-30cm respectively.

2.2 Extraction and Analysis of Samples

Analysis of samples was carried out using the standard reference method employed in the analysis of PAHs as outlined by US EPA 8240. The samples were homogenized and extracted with freshly prepared extracting solution (1:1 mixture of acetone and methylene chloride) to 10g of each sample and 10g of sodium sulphate was added (to remove moisture) and was extracted with 100ml of the extracting solution (mix solvent) in two portions of 50ml each time with ultra-sonication for 25 minutes. The extracts were concentrated with a rotary evaporator to about 1ml. Finally, the PAHs fractions were separated from the concentrated extracts in silica gel-packed column cartridges utilizing a methylene chloride for elution. An Agilent 6890 series GC system with a mass selective detector (MSD), the purified PAH extracts were analyzed using a calibrated capillary GC-MSD, adhering to the fundamental GC parameters for the detection of polycyclic aromatic hydrocarbons (Beaton and Suuberg, 2017).

2.3 Quality Assurance and Quality Control Measures

Laboratory blanks, spiked blanks and duplicate samples were analyzed along with the soil samples and extraction of samples was carried out in a three-stage extraction process for recovery of more components of PAHs. The cleanup procedure was carried out in a separate extraction-packed column to avoid cross-contamination during the cleanup process. The recoveries of surrogate standards were kept between 90% and 130% in all of the spiked samples; otherwise, a repeated analysis of the sample was performed.

2.5 Description of sampling station

Table 1: Sampling Distance, Location code, Coordinates and Activities

S/N	Distance	Location code	Coordinates	Activities
1	10m. away	STN 1	5.568896°N 6.305152°E	Flare point
2	100m	STN 2	5.569125°N 6.304192°E	Flow station area
3	200m	STN 3	5.570407°N 6.304054°E	Flow station area
4	300m	STN4	5.569788°N 6.303317°E	Flow station area

5	400m	STN5	5.568828°N 6.303306°E	Flow station area
6	500m	STN6	5.568122°N 6.302629°E	Back of fence
7	600m	STN7	5.571035°N 6.303640°E	Bike areas
8	700m	STN8	5.570839°N 6.302808°E	Bush around F/S
9	800m	STN9	5.572147°N 6.302877°E	Flow Station Road
10	1000m	STN10	5.572881°N 6.301130°E	Roadside Bush
11	1500m	CTRL	5.573790°N 6.296754°E	Cassava Farmland

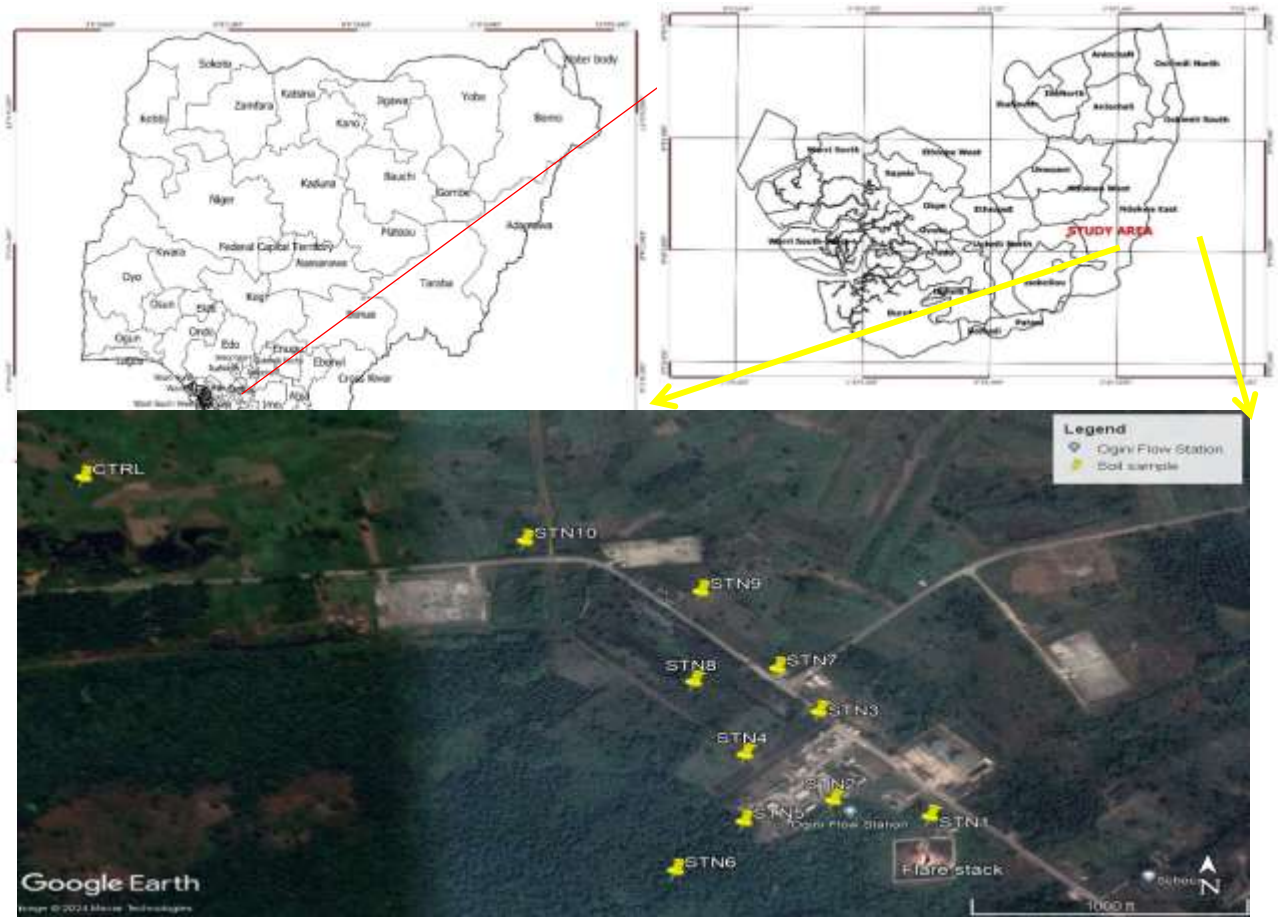

Figure: 1.0 Map of (a) Nigeria indicating Delta State (b) Delta State indicating the Sampling (c)

3. RESULTS AND DISCUSSION

Table 2: PAHs and particle size analysis results of the sampling area

SAMPLE CODE	*PAH (mg/kg)*	*% Sand*	*% Silt*	*% Clay*	*Texture*
STATION1/SS1/0-15cm	2025	81.0	4.0	15.0	*SANDY LOAM*
STATION1/SS1/15-30cm	1418	72.0	16.0	12.0	*SANDY LOAM*
STATION2/SS2/0-15cm	1114	82.0	1.0	17.0	*SANDY LOAM*
STATION2/SS2/15-30cm	946.90	82.0	1.0	17.0	*SANDY LOAM*
STATION3/SS3/0-15cm	278.50	68.0	9.0	23.0	*SANDY CLAY LOAM*
STATION3/SS3/15-30cm	7.20	84.0	2.0	14.0	*LOAM SAND*
STATION4/SS4/0-15cm	131.65	68.0	9.0	23.0	*SANDY CLAY LOAM*
STATION4/SS4/15-30cm	27.65	80.0	7.0	13.0	*SANDY LOAM*
STATION5/SS5/0-15cm	83.04	70.0	9.0	25.0	*SANDY CLAY LOAM*
STATION5/SS5/15-30cm	4.24	81.0	4.0	15.0	*LOAM SAND*
STATION6/SS6/0-15cm	4.61	86.0	2.0	12.0	*LOAM SAND*
STATION6/SS6/15-30cm	0.69	87.0	4.0	9.0	*LOAM SAND*
STATION7/SS7/0-15cm	1.74	85.0	1.0	14.0	*LOAM SAND*
STATION7/SS7/15-30cm	0.73	85.0	1.0	14.0	*LOAM SAND*
STATION8/SS8/0-15cm	0.68	87.0	1.0	12.0	*LOAM SAND*
STATION8/SS8/15-30cm	0.29	88.0	1.0	11.0	*LOAM SAND*
STATION9/SS9/0-15cm	0.68	88.0	1.0	11.0	*LOAM SAND*
STATION9/SS9/15-30cm	0.24	82.0	1.0	17.0	*SANDY LOAM*
STATION10/SS10/0-15cm	0.52	85.0	3.0	12.0	*LOAM SAND*
STATION10/SS10/15-30cm	0.18	83.0	2.0	15.0	*SANDY LOAM*
CTRL/SS11/0-15cm	0.09	85.0	3.0	12.0	*LOAM SAND*
CTRL/SS11/15-30cm	0.00	85.0	3.0	12.0	*LOAM SAND*

Table 3: Mean concentration of 16 priority PAHs components across the sampling area

PAH COMPONENTS (mg/kg)	TOP SOIL RANGE (0 - 15cm)	MEAN VALUE	BOTTOM SOIL RANGE (15 - 30cm)	MEAN VALUE
Naphthalene	ND	0.00	ND	0.00
Acenaphthylene	0 - 160.34	26.17	0 - 112.23	17.22
Acenaphthene	0 - 162.79	26.57	0 - 113.95	17.48
Fluorene	0 - 202.52	33.08	0 - 141.76	21.79
Phenanthrene	0 - 111.31	18.18	0 - 77.91	11.99
Anthracene	0 - 178.14	29.1	0 - 124.69	19.18
Fluoranthene	0 - 76.67	12.52	0 - 53.66	8.23
Pyrene	0 - 62.28	10.18	0 - 43.59	6.69
Benz(a)anthracene	ND	0.00	ND	0.00
Chrysene	0 - 112.03	18.31	0 - 78.42	12.13
Benzo(b)fluoranthene	0.01 - 52.36	8.56	0 - 36.65	5.63
Benzo(k)fluoranthene	0 - 9.22	1.5	0 - 6.45	0.99
Benzo(a)pyrene	0.01 - 215.90	35.29	0 - 151.13	23.3
Dibenz(a,h)anthracene	0.02 - 211.25	34.59	0 - 147.87	22.98
Indeno(1,2,3-cd)pyrene	0.03 - 226.36	36.87	0 - 158.45	24.52
Benzo(g,h,i)perylene	0 - 244.29	39.58	0 - 171.00	26.53

ND: Non detected

The distribution and toxicity of sixteen (16) US EPA priority PAHs in the soil around the gas flaring of the Ogini flow station and its environs showed that contaminants are predominated in a shorter distance of 10 meters to 100 meters away from the flare point and declined in concentration with an increase in sampling distance as expressed in the graphs below.

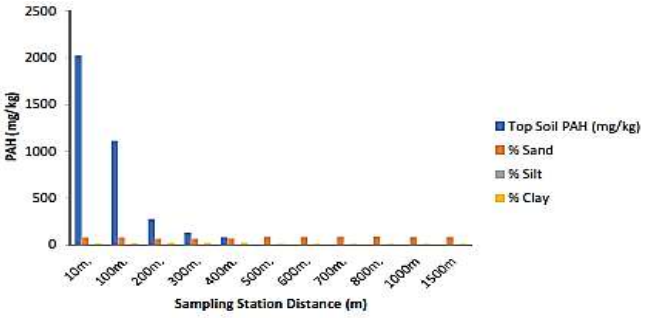

Figure 2: Topsoil mean concentration

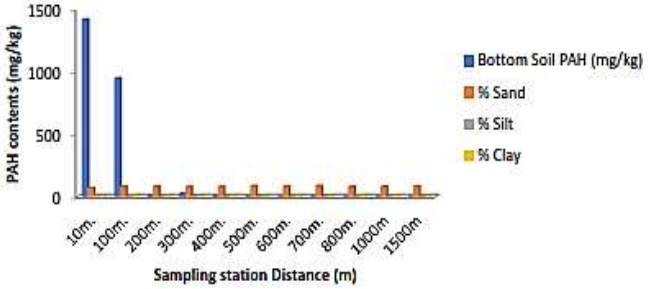

Figure 3: Bottom soil mean concentration

The most common contaminant among the 16 PAHs compounds tested was benzo(g,h,i)perylene with a mean concentration of 39.58 mg/kg at the topsoil layer, followed by indeno(1,2,3-cd)pyrene with a mean concentration of 36.87 mg/kg, respectively. The concentration of PAHs at the bottom of the of the soil also demonstrated a similar trend in their composition, but a declining PAHs value was observed at station three of the flow station area. The texture of soil samples in this area plays a significant role in the deposition and retention of PAHs pollutants. The sandy-clay-loam characteristic of this station recorded significant PAHs values of 278.50 mg/kg for topsoil and drifted drastically to 7.20 mg/kg at the bottom soil with loam-sand soil texture. This variance could be attributed to the high percentage of clay content observed at this sampling point, as clay soil usually tends to retain PAHs or any organic contaminants near the surface and restricts the movement of water, which will further contribute to the retention or accumulation of contaminants on the surface. More so, organic contaminants like PAHs have a high affinity for organic matter because clay particles have a large surface area and strong negative charges that will effectively attract and bind PAHs molecules, stopping them from penetrating further into the bottom soil. While sandy soil will facilitate the seepage of pollutants deep into the soil due to its high permeability characteristics. Hence, it could be inferred that clay-rich soils will retain contaminants near the surface, while sandy soils allow for deeper penetration. This highlights the importance of soil composition in determining the movement and retention of contaminants in the environment. Also, the distance and direction of the wind are principal factors in the amount of contaminants that may be deposited on the soil from the gaseous emissions of the flare. These results are consistent with those of Ali and Khodakarami, (2014) who found that the PAHs concentration decreased with increasing distance from the source of gaseous emission. In general, The values recorded at these stations were above the US EPA Integrated Risk Information System (IRIS) (Verbruggen, 2012) and intervention value of polluted soil by Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN) (Olawuyi and Tubodenyefa, 2018). Crude oil exploration and gas flaring activity significantly contributes to the PAHs load of (Benzo (g,h,i)perylene) and other high pollutants while pollutants like Naphthalene and Benzo(a)anthracene were not detected in all the sampling points. The non-detection of Naphthalene could be due to the volatility of the low molecular PAHs over time as opined by various researchers (Ali and Khodakarami, 2014; Nwaichi *et al*., 2017). The concentration of the PAHs found in the control sample was in traces perhaps from natural or pyrogenic sources and none were detected at the bottom soil (15-30cm) of the control sample. According to Nayebzadeh and Vahedpour, (2017), atmospheric conditions affect the presence of PAHs in the ambient air. The prevailing wind direction is a significant factor in determining the areas most affected by air pollution that is deposited in soil environments.

4. CONCLUSION

This research study showed a distinct spatial deposition of high molecular weight PAHs of Benzo(g,h,i)perylene, Indeno(1,2,3-cd), benzo (a) fluoranthene (BbF), chrysene (Chr) and fluoranthene (Fluo) in higher concentrations than low molecular weight like naphthalene respectively. The three types of soil tested in the study area were subjected to these mutual petro-genic

contaminants and there is a tendency for these contaminants to leach over time from the affected zone to the agricultural farmland. The concentration of PAHs in the topsoil was higher than that in the deep soil, and over time, the high molecular weight PAHs will tend to migrate down to the deep soil. These levels of PAHs measured appear to be influenced by incomplete combustion processes of fossil fuel from gas flaring activities around the flow station. The contaminants will not only pollute the surrounding surface soil but also influence the lower depths of the soil. As a result, groundwater is threatened by the potential risk of PAHs over the long-term impact. The data generated did not compare satisfactorily with the sixteen USEPA priority PAHs as only a few of the pollutants were below the limit recommended by various regulatory bodies. This has called for holistic monitoring of the PAHs emission into the air from various flow stations across the Niger Delta environment, as exposure to these organic pollutants causes varieties of negative health effects such as reproduction defects.

It is however recommended that the regulatory bodies should establish stringent rules that will be followed strictly by the corporate bodies and implement an effective remediation technique to mitigate and restore the soil to a non-polluted state. Also, the government and the policymakers to implement policies to make communities and those residents around the vicinity of the gas flaring activity keep a minimum of 2000 meters (2 kilometres) away from the flare point.

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