

ASSESSMENT OF ORGANIC POLLUTANTS IN REMEDIATED SOILS FROM KAWA AND KPEAN COMMUNITIES, RIVERS STATE, NIGERIA

¹Daniel D. N., ²Ideriah T. J. K., ¹Yuodewei P. O., and ¹Gobo A.E.,

¹Institute of Geosciences and Environmental Management, Rivers State University, Port Harcourt Nigeria.

²Institute of Pollution Studies, Rivers State University, Port Harcourt, Nigeria dorka.daniel@ust.edu.ng

DOI:10.5281/zenodo.14795167

Abstract

The levels of Total petroleum hydrocarbons (TPH) and Polycyclic Aromatic Hydrocarbons (PAHs) in crude oil remediated soils in Khana LGA, Rivers State, in comparison with noncrude oil impacted soils which served as the control, was carried out in this study to ascertain the impact of the remediation exercise on soil quality. Eight composite soil samples from two different locations were randomly collected at 0 – 15cm and 15 – 30 cm depths using soil auger. The samples were air-dried, ground, sieved and analyzed using standard methods with GC-MS. The results showed TPH levels fell between 3.20876 and 17.51729 ppm at 0 – 15 cm depth and between 4.48214 and 7.03104 ppm at 15 – 30 cm depth. All the stations recorded TPH levels below the target and intervention limits. The total PAH levels at Stations 1 and 2 and the Control station were below the Department of Petroleum Resources (DPR) target and intervention values while Station 3 recorded total PAH level above the target value but below the intervention value. The results obtained revealed that the remediation exercise is efficient in restoring the soil quality. Therefore, the remediation work should be sustained.

Keywords: PAH, TPH, Pollutants, Crude Oil, Remediated Soils, Kawa and Kpean, Nigeria

INTRODUCTION

The Niger Delta of Nigeria, being the center of exploration and exploitation operations of oil industries, is affected by oil spill resulting in massive soil contamination with hydrocarbons (Mnif et al., 2017). The spills usually are due to inadvertent discharge of crude or refined oil and related products onto land or into inland waters, estuaries or Open Ocean. These may be through oil well blow outs, tanker accidents, accidental or deliberate rupture of oil pipelines and dumping of used petroleum products. According to Saravana and Amruta (2013), about 0.08-0.46 % of the total oil produced is continuously being spilled into the environment and this eventually pollutes land and water.

The frequent occurrences of oil spills in the Niger Delta, largely attributed to fractured pipelines, corrosion, operational errors, and sabotage for economic and political motives, have become widespread (Bob-Manuel and Johnson, 2001). Additional factors contributing to oil spills include low technological expertise, weak

enforcement of laws, the indifference of multinational enterprises involved in the oil industry, and negligence by personnel both within and outside the sector (Ebuehi et al., 2005).

The consequential spillages in soil, rivers, creeks, ponds, and wells in the riverine areas of Nigeria have led to the scarcity of arable soils and clean drinking water. Numerous individuals affected by the pollution have suffered from ailments such as diarrhea and dysentery (Albert et al., 2018). Furthermore, the toxicity of oil-derived products poses a threat to wildlife, potentially contaminating the food chain and causing harm to humans. The principal components of the very complex mixtures of crude oil (petroleum) are hydrocarbons, which may be paraffinic, alicyclic or aromatic. Most of the chemical components in petroleum are made up of five main elements with varying weight percentages as shown in Table 1. The elements are combined to form a complex mixture of organic compounds of molecular weight ranging from 16 (Methane, CH₄) to several thousand. Natural attenuation, as defined by Jørgensen (2011), involves the monitoring of natural processes in soil and groundwater environments, acting autonomously to diminish the mass, toxicity, mobility, volume, or concentration of contaminants, without human intervention. It serves as a bioremediation method for treating polluted environments, relying on microorganisms for pollutant degradation without deliberate human interventions.

For sites undergoing natural attenuation, meticulous monitoring occurs over an extended period until the contaminated site reverts to comparable ambient pollutant levels, facilitating risk assessments and endpoint forecasting. Conversely, in situations where swift pollutant removal is imperative, enhanced natural attenuation bioremediation becomes applicable. This involves biostimulation, which entails introducing nutrients and chemicals to stimulate indigenous microorganisms, and bioaugmentation, which involves inoculating with exogenous microorganisms.

This is a major concern not only here in Nigeria but worldwide, as the presence of hydrocarbons pollution in the environment poses great hazard to livelihood, human and environmental health. (Margesin et al., 2003; Mnif et al., 2017). As a result, there are worldwide concern about remediating and restoring the hydrocarbon-polluted environment.

Therefore, there is an urgent need to evolve viable technologies to combat oil or hydrocarbon pollution that may accompany activities of oil industries. Especially, the frequent spills of crude oil or related products in part of the Niger Delta region demand a refocused attention on the problem of hydrocarbon contaminant in the area.

The impact of crude oil contamination on soil fertility is profound, with repercussions that extend beyond immediate environmental concerns. Crude oil contains a myriad of hydrocarbons and toxic substances that can alter the physical, chemical, and biological properties of the soil (Victor et al., 2020). One of the primary consequences is the disruption of nutrient cycling and availability, leading to imbalances in essential elements crucial for plant growth (Orisakwe, 2021). The presence of hydrocarbons in the soil can impede microbial

activity, inhibiting the microbial communities responsible for breaking down organic matter and releasing nutrients (Cusack et al., 2011). Furthermore, the alteration of soil structure and texture can negatively affect water retention and drainage, compounding the challenges faced by plants (Shaheen et al., 2014). In turn, compromised soil fertility directly impacts agricultural productivity, jeopardizing the livelihoods of communities dependent on agriculture for sustenance and economic well-being. Effective remediation strategies are therefore imperative to mitigate these adverse effects, aiming to restore optimal soil conditions and support sustainable agriculture in regions affected by crude oil contamination.

When there is oil spillage, the released hydrocarbons will invade soil capillaries that will be once filled with water or air, bind to the particle of the earth, or form reservoirs of material within the soil in terrestrial spaces. All of these regions will suffer ecological damage as both air and water become excluded from the soil micro-environment leading to suffocation as hydrocarbon movement will permeate through the soil layers until an impervious horizon such as leg bedrock, water tight clay or aquifer is encountered (Margesin et al., 2003). The flow of hydrocarbon into the body of water likely resulted in two things. low solubility components stay on the surface of water, thereby preventing oxygen penetration, or dissolution and thus leading to elimination of marine life, and the soluble components contaminate the ground water.

Therefore, spillage of oil on the land renders it unproductive for agricultural purpose for example respiratory surfaces of mangroves are readily clogged by oil, which presumably kills the plant by blocking supplies to the roots (Guarino *et al.*, 2017; Taiwo, 2011).

Though relatively small number of the hydrocarbons present in crude oil have been well characterized as toxic, but generally petroleum is classified as toxic. Polluted water bodies have been shown to affect the state of health of the people (Abha and Singh, 2012).

Many reports have demonstrated that due to mutagenic and teratogenic properties of the compositional hydrocarbons, they can damage many organs such as nervous system, circulatory system, immune system, sensory system and kidney of the human body and thus leading to a wide range of diseases and disorder (Abha and Singh, 2012; Nwilo and Badejo, 2005). The damage can be immediate or it may take months or years depending on the nature of the hydrocarbon, and the mode and duration of exposure. There have been reports of death from the site of oil spill in Nigeria, for example the major Texaco spill of 1980 was reported to have led to the death of about 180 people in one community as a result of the pollution (Nwilo and Badejo, 2005). The non-volatile components of crude oil which tend to be absorbed by the soil and persist at the site of spill may cause many harm to living beings by skin contact, and by intake of contaminated water or food.

The naphthenic-aromatics and polyaromatic compounds which are mainly the heavy fraction of the crude oil are carcinogenic and long exposure to them often leads to tumors, cancer, and failure of the nervous system (Abha and Singh, 2012). Therefore, hydrocarbon compounds are important group of environmental pollutants

that have worldwide concern and are the focus of remediation and thus restoring the environment (Bicca *et al.*, 1999). As a consequence of this, there is a strong need to evolve viable technologies not only in the activities of production but also to combat oil or hydrocarbon pollution that may accompany them.

Thus, there is an urgent need to evolve viable technologies to combat oil or hydrocarbon pollution that may accompany activities of oil industries. Especially, the frequent spills of crude oil or related products in part of the Niger Delta region demand a refocused attention on the problem of hydrocarbon contaminant in the area.

Scope of the Study

This study focuses on assessing the impact of crude oil remediation on soil fertility potentials in Khana Local Government Area (LGA), Rivers State. The geographical scope encompasses two selected communities (Kpean and Kwawa) known to be impacted by oil spill within Khana LGA that have been identified as having experienced crude oil contamination. The study investigated the concentration of polycyclic aromatic hydrocarbons (PAH) and Total Petroleum Hydrocarbon (TPH), in the soil samples. The findings of this study contribute valuable insights into sustainable soil management practices, with a particular focus on the local environmental, agricultural, and ecological contexts in Khana LGA.

METHODOLOGY

The Study Area

The research was conducted in two communities: Kpean and Kwawa Communities in Khana Local Government Area (LGA) of Rivers State, situated approximately between Latitude 4° 33' 30" N to 4° 49' 22" N and Longitude 7° 19' 11" E to 7° 31' 09" E. Khana LGA is one of the four local governments areas in Ogoni, sharing boundaries with Oyigbo, Opobo-Nkoro, Akwa-Ibom, and Gokana in the North, South, East and West respectively. With a total area of about 575km², Khana is the largest local government in Ogoni covering approximately 56% of the total land area of Ogoni. The area consists of nearly level land with gentle and undulating slopes intersected by shallow valleys that carry water intermittently (Needam *et al.*, 2020).

The selection of Kpean and Kwawa Communities within Khana Local Government Area of Rivers State for the study is deliberate, given their status as flashpoints of soil pollution resulting from recurrent oil spillages in the area. These two communities have been disproportionately affected by environmental degradation due to the oil spillage, making them pertinent focal points for investigation. Kpean and Kwawa Communities serve as emblematic examples of the environmental challenges faced by communities in the region, highlighting the urgent need for comprehensive research and remediation efforts. By focusing on these specific locales, the study aims to shed light on the impacts of oil spillage on soil quality and explore strategies for mitigating pollution in similar vulnerable communities across the Niger Delta.

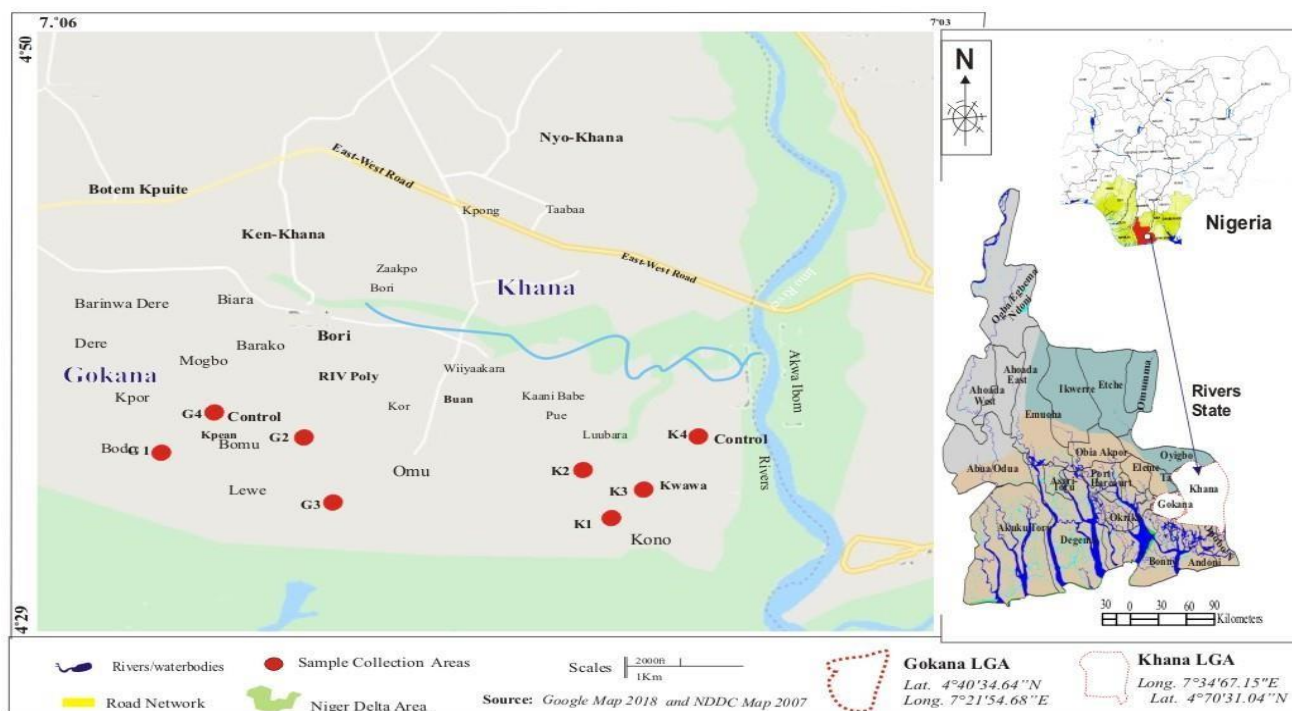


Figure 3.1: Map of the Study Area

Polycyclic Aromatic Hydrocarbons (PAHs) (Using APHA 6440B Method)

First, we selected a representative soil sample, typically ranging from 10 to 20 grams, which was air-dried and finely ground. Next, we performed a Soxhlet extraction, placing the soil sample into a thimble within the Soxhlet extractor. The Soxhlet extractor were filled with a suitable solvent, such as a mixture of dichloromethane and acetone. We conducted the extraction for an extended period, often 24 hours, to ensure thorough extraction of PAHs from the soil. After extraction, we concentrated the extract using a rotary evaporator and further purify it if necessary, using silica gel or column chromatography. The purified extract was then analyzed using Gas Chromatography-Mass Spectrometry (GC-MS) equipped with a suitable column for PAH separation. We identified and quantified PAH compounds based on their retention times and mass spectra, comparing them with standard reference materials if available. Quality control measures, including blank and spiked samples, were utilized to validate the accuracy of our method. Throughout the procedure, we adhered strictly to safety protocols, including proper handling of solvents and chemicals, and disposal of waste according to laboratory safety guidelines.

Total Petroleum Hydrocarbon (TPH) Analysis of Soil Samples

To determine the total petroleum hydrocarbon (TPH) content in soil samples, we began by selecting representative soil samples, typically ranging from 10 to 20 grams, which were airdried and finely ground. Subsequently, we performed a solvent extraction method such as Soxhlet extraction or sonication, using a suitable solvent such as hexane or a mixture of hexane and acetone. This extraction process was conducted for a specified period to ensure the efficient extraction of TPH from the soil matrix. Following extraction, we concentrated the extract using a rotary evaporator and further purify it if necessary, using techniques such as column chromatography or solid-phase extraction. The purified extracts were then analyzed using Gas Chromatography with Flame Ionization Detection (GC-FID) or Gas Chromatography-Mass Spectrometry (GC-MS). We identified and quantified the TPH compounds present in the soil samples based on their retention times and characteristic mass spectra. Quality control measures, including the use of blank and spiked samples, was employed to ensure the accuracy and reliability of the analytical results. Throughout the entire procedure, strict adherence to safety protocols were maintained, including proper handling of solvents and chemicals, and disposal of waste in accordance with laboratory safety guidelines.

RESULTS

Polycyclic Aromatic Hydrocarbons

Levels of PAHs across all sampling stations at the 0 – 15 cm and 15 – 30 cm depths are shown in Tables 1 and 2. At the 0 – 15 cm depth, Naphthalene levels fell between 0.000164 and 0.000274 ppm, Acenaphthylene levels fell between 0.000089 and 0.000800 ppm, Acenaptene levels fell between 0.000110 and 0.000691 ppm, Fluorene levels was fell 0.000067 ppm, Anthracene level was 0.000067 ppm, Pyrene levels fell between 0.000094 and 0.000151 ppm, Benzo(a)anthracene levels fell between 0.000022 and 0.000098 ppm, Crysene level was 0.000097 ppm, Benzo(b)fluorantene level was 0.000020 ppm while total PAH levels fell between 0.000939 and 0.001439 ppm.

At the 15 – 30 cm depth, Naphthalene levels fell between 0.000145 and 0.000293 ppm, Acenaphthylene levels fell between 0.000103 and 0.000866 ppm, Acenaptene level was 0.000805 ppm, Fluorene levels was fell 0.000073 ppm, Anthracene level was 0.000097 ppm, Pyrene levels fell between 0.000046 and 0.000187 ppm, Benzo(a)anthracene levels fell between 0.000040 and 0.000072 ppm, Crysene level was 0.000102 ppm, Benzo(b)fluorantene level was 0.000036 ppm while total PAH levels fell between 0.000842 and 0.001669 ppm.

Total Petroleum Hydrocarbons (TPH)

Levels of TPHs across all sampling stations at the 0 – 15 cm and 15 – 30 cm depths are shown in Tables 3 and 4. At the 0 – 15 cm depth, TPH levels fell between 3.20876 and 17.51729 ppm while TPH levels fell between 4.48214 and 7.03104 ppm at the 15 – 30 cm depth.

PAH COMPONENT (ppm)	0-15 cm depth							
	KWAWA ST1	KWAWA ST2	KWAWA ST3	KWAWA ST4 (CONTROL)	KPEAN ST1	KPEAN ST2	KPEAN ST3	KPEAN ST4 (CONTROL)
Naphtalene	0.000242	0.000216	0.000242	0.000249	0.000235	0.000274	0.000241	0.000164
Acenaphthylene	0.000733	0.000800	0.000689	0.000702	0.000660	0.000089	0.000703	0.000416
Acenaphthene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000691	0.000000	0.000110
Fluorene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000067	0.000000	0.000000
Phenanthrene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
Anthracene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000069	0.000000	0.000000
Fluoranthene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
Pyrene	0.000143	0.000081	0.000094	0.000094	0.000089	0.000104	0.000121	0.000151
Benzo(a)anthracene	0.000000	0.000047	0.000000	0.000022	0.000000	0.000028	0.000000	0.000098
Chrysene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000097	0.000000	0.000000
Benzo(b)flourant hene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000020	0.000000	0.000000
Benzo(k)Flouran thene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
Benzo(a)Pyrene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000

Research Article

Indeno(1,2,3c,d) pyrene	0.00000	0.000000	0	0.000000	0.000000	0.000000	0.000000	0.000000
Dibenz(a,h)anthr acen e	0.00000	0.000000	0	0.000000	0.000000	0.000000	0.000000	0.000000
Benzo(g,h,i)pyrel ene	0.000000	0.000000	0.000000	0.000000	0.000000			0.000000
Total PAH	0.001118	0.00114	0.001025	0.001067	0.000984			0.000939
	4							

Table 2: Levels of Polycyclic Aromatic Hydrocarbons at 15 – 30 cm depth

PAH COMPONENT (ppm)	15-30 cm depth							
	KWAW A ST1	KWAW A ST2	KWAW A ST3	KWAW A ST4 (CONTR OL)	KPEAN ST1	KPEAN ST2	KPEAN ST3	KPEAN ST4 (CONTROL)
Naphtalene	0.000226	0.000259	0.000228	0.000260	0.000252	0.000293	0.000221	0.000145
Acenaphthylene	0.000709	0.000866	0.000599	0.000731	0.000555	0.000103	0.000609	0.000394
Acenaphthene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000805	0.000000	0.000094
Fluorene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000073	0.000000	0.000000
Phenanthrene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
Anthracene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000097	0.000000	0.000000
Fluoranthene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
Pyrene	0.000127	0.000180	0.000087	0.000121	0.000046	0.000118	0.000108	0.000137
Benzo(a)anthrace ne	0.000000	0.000060	0.000000	0.000040	0.000000	0.000042	0.000000	0.000072
Chrysene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000102	0.000000	0.000000
Benzo(b)fluorant hene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000036	0.000000	0.000000
Benzo(k)Flourant hene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
Benzo(a)Pyrene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000

Indeno(1,2,3c,d)pyrene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
Dibenz(a,h)anthracene	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
Benzo(g,h,i)pyrene	0.000000	0.000000	0.000000	0.000000	0.000000			0.000000
Total PAH	0.001062	0.001365	0.000914	0.001152	0.000853			0.000842

Table 3: Levels of Total Petroleum Hydrocarbons at 0 – 15 cm Depth

TPH COMPONENT	KWAW A ST1	KWAW A ST2	KWAW A ST3	KWAWA ST4 (CONTROL)	KPEAN ST1	KPEAN ST2	KPEAN ST3	KPEAN ST4 (CONTROL)
n-Nonane (C9)	0	0.02156	0	0	0	0	0	0
n-Decane (C10)	0	0	0	0	0	0	0	0
n-Undecane (C11)	0.05976	0.2821	0.03962	0.08592	0.08718	0.25084	0.14935	0.1476
n-Dodecane (C12)	0.43167	0.03582	0.40709	0.28751	0.26533	0.18828	0.16839	0.4125
n-Tridecane (C13)	0.02186	0.01301	0.01904	0.00136	0.01393	0.01469	0.01186	0.01916
n-Tetradecane (C14)	2.22458	0.19053	2.11511	1.452	1.9229	0.94728	1.17753	2.10358
n-Pentadecane (C15)	0.32753	0.0271	0.57774	0.26013	0.17909	0.12511	0.07625	0.30533
n-Hexadecane (C16)	3.13679	0.3598	2.99317	3.00061	2.57408	1.10132	1.43863	2.80812
n-Heptadecane (C17)	0.37866	0.0502	0	0	0	0.03615	0	0.35031
n-Octadecane (C18)	2.94465	0.0106	2.72213	0.62031	2.53237	1.33208	1.37624	2.83667

n-Nonadecane (C19)	0.64441	0.82419	0.36396	2.27665	0.2227 7	0.0594 4	0.0276 1	0.55519
n-Eicosane (C20)	1.92029	0.07019	1.70376	0.70341	2.1060 7	0.6611 7	0.6369 7	1.7986 9
n-HeneiCosane (C21)	0.82554	0.11008	0.30731	0.4001	0.2715 6	0.1513 2	0.0138 5	0.64483
n-Docosane (C22)	1.08794	0.32011	1.30786	1.5902	0.9308 1	0.3640 8	0.2732	0.97138
n-Tricisane (C23)	0.798	0.05031	0.26886	0.40004	0.6909 3	0.1449 7	0.0433 3	0.22799
n-Tetracosane (C24)	0.58599	0.23343	0.63632	1.1324	0.5969 4	0.1323 7	0.0638 8	0.50878
n-Pentacosane (C25)	0.82319	0.15331	0.79321	0.40001	0.8090 8	0.1872 5	0.0875 4	0.65975
n-Hexacosane (C26)	0.26072	0.1379	0.27628	0.4852	0.2423 1	0.0384	0.0177 7	0.23603
n-Heptacosane (C27)	0.22036	0.09702	0.22889	0.55335	0.3437 1	0.0490 6	0.0325 8	0.17209
n-Octacosane (C28)	0.54378	0.051	0.52574	0.09542	0.2066 7	0.2553 7	0.2732	0.57524
n-Nonacosane (C29)	0.06156	0.03554	0.06747	0.20753	0.5430 6	0.0876 3	0.1820 5	0.03675
n-Triacontane (C30)	0.00907	0.01779	0.02253	0.51114	0.4097 2	0.0438 7	0.1111 7	0.01178
n-Hentriacontane(C31)	0.02111	0.00742	0.02596	0.05406	0.2945 6	0.0108 8	0.0088 9	0.02339
n-Dotriacontane (C32)	0.00188	0.01153	0.01482	0.00531	0.1814 6	0.0045 5	0.0139 9	0.00246
n-Tritriacontane (C33)	0.02013	0.00541	0.01743	0.01603	0.1411 3	0.0143 4	0.0105 9	0.01126

Research Article

n-Tetratriacontane (C34)	0.0054	0.0025	0.00754	0.00284	0.06378	0.0108	0.00458	0.01023
n-Pentatriacontane (C35)	0.00858	0.00491	0.00872	0.00912	0.02761	0.03081	0.05796	0.12657
n-HexaTriacontane (C36)	0.1334	0.00494	0.1154	0.00224	0.13641	0.0105	0.02167	0.01254
n-Heptatriacontane (C37)	0.00558	0.05532	0.01389	0.0045	0.00615	0.00525	0.00385	0.00543
n-Octatriacontane (C38)	0.00579	0.00622	0.00664	0.06394	0.00873	0.00403	0.00494	0.00942
n-Nonatriacontane (C39)	0.00615	0.00649	0.00512	0.00011	0.00724	0.00299	0.00684	0.0073
n-Tetracontane(C40)	0.00292	0.00152	0.00497	0.00602	0.00506	0.0027	0.00333	0.00304
n-Hentetracontane(C41)	0	0.00484	0	0.00594	0	0	0	0

n-Dotetracontane(C42)	0	0.00607	0	0.00222	0	0	0	0
TOTAL	17.51729	3.20876	15.59658	14.63562	15.82064	6.26753	6.29804	15.59341

Table 4: Levels of Total Petroleum Hydrocarbons at 15 – 30 cm Depth

TPH COMPONENT	KWAW A ST1	KWAW A ST2	KWAW A ST3	KWAWA ST4 (CONTRO L)	KPEA N ST1	KPEA N ST2	KPEA N ST3	KPEAN ST4 (CONTRO L)
n-Nonane (C9)	0	0.02998	0	0	0	0	0	0
n-Decane (C10)	0	0	0	0	0	0	0	0
n-Undecane (C11)	0.05796	0.37275	0.01782	0.1191	0.0416 7	0.1534 2	0.0845 3	0.1354
n-Dodecane (C12)	0.33271	0.07691	0.40012	0.47611	0.1540 1	0.1378 2	0.1190 1	0.40412
n-Tridecane (C13)	0.021028	0.01351	0.00501	0.02075	0.0050 1	0.0082 4	0.0004 7	0.00427
n-Tetradecane (C14)	1.86923	0.49029	2.013	2.26698	1.3529	0.6285 3	1.0354 1	2.00173
n-Pentadecane (C15)	0.173	0.14287	0.501	0.32122	0.0518	0.1139	0.0550 2	0.10023
n-Hexadecane (C16)	3.10011	0.43312	2.8765	3.01475	2.4431 1	1.0520 1	1.2900 1	2.5492
n-Heptadecane (C17)	0.35001	0.09578	0	0	0	0.0061	0	0.32101
n-Octadecane (C18)	0.3008	0.9612	0.5409	2.98399	0.1600 1	0.0821 9	0.3001 2	0.15028
n-Nonadecane (C19)	2.64432	0.13253	1.99843	0.40817	2.4137 4	1.2228	1.3091 4	2.52801
n-Eicosane (C20)	0.5923	0.42634	0.62519	1.79782	0.5800 1	0.2441	0.2179	0.7214
n-HeneiCosane (C21)	0.61032	0.10604	0.23801	0.41429	0.106	0.0551	0.0094	0.03802
n-Docosane (C22)	1.90011	0.36614	1.46102	1.15596	2.0008	0.429	0.6000 3	1.77701

n-Tricisane (C23)	0.80013	0.17461	0.3009	0.4065	0.2156 6	0.0901 4	0.0019	0.55241
n-Tetracosane (C24)	1.00405	0.15035	1.228	0.66192	0.9100 1	0.3143 3	0.218	0.75442
n-Pentacosane (C25)	0.771442	0.2138	0.2557	0.84462	0.6888	0.1180 1	0.0222 1	0.21229
n-Hexacosane (C26)	0.51511	0.06138	0.6011	0.29492	0.5000 2	0.0700 4	0.0445 1	0.4831
n-Heptacosane (C27)	0.81144	0.03935	0.61058	0.24933	0.8	0.0510 9	0.0433 4	0.5539
n-Octacosane (C28)	0.20511	0.02642	0.23518	0.50157	0.1500 4	0.3004 3	0.0050 1	0.2214
n-Nonacosane (C29)	0.2106	0.02378	0.14632	0.06358	0.3224 6	0.0446	0.0186 3	0.14892
n-Triacontane (C30)	0.5321	0.01628	0.39913	0.00664	0.2108	0.2409 3	0.1832 1	0.38713
n-Hentriacontane(C31)	0.04721	0.01126	0.06253	0.02473	0.5290 2	0.0744 1	0.0964 2	0.03523
n-Dotriacontane (C32)	0.00761	0.00572	0.22224	0.00551	0.4046 8	0.0410 9	0.1100 2	0.01058
n-Tritriacontane (C33)	0.02004	0.00712	0.01863	0.01813	0.2640 1	0.0070 2	0.0069 5	0.0152
n-Tetratriacontane (C34)	0.00109	0.00849	0.00376	0.00426	0.0695 1	0.0016 3	0.0061	0.002
n-Pentatriacontane (C35)	0.01721	0.05553	0.00633	0.00652	0.0742 1	0.0031 9	0.0062 2	0.01005
n-HexaTriacontane (C36)	0.00297	0.00835	0.00512	0.09849	0.0397 7	0.006	0.0026 1	0.00111
n-Heptatriacontane (C37)	0.00721	0.00834	0.00201	0.01003	0.0108 2	0.0107 2	0.0551 2	0.11903

n-Octatriacontane (C38)	0.11318	0.01086	0.11103	0.00632	0.11314	0.00093	0.01426	0.0091
n-Nonatriacontane (C39)	0.00335	0.00636	0.00512	0.00757	0.0053	0.00472	0.00336	0.00524
n-Tetracontane(C40)	0.00384	0.00668	0.00539	0.00326	0.00599	0.00261	0.00286	0.00831
n-Hentetracontane(C41)	0.00375	0	0.00312	0	0.00469	0.00177	0.00623	0.00571
n-Dotetracontane(C42)	0.0017	0	0.00297	0	0.00301	0.0015	0.00301	0.00215
TOTAL	17.03104	4.48214	14.90216	16.19304	14.631	5.51837	5.87101	14.26796

DISCUSSION PAH Contents of Soil

Total Polycyclic Aromatic Hydrocarbon (PAH) levels at the KWAWA ST1 and KWAWA ST2 stations were higher than the KWAWA ST4 (control) station at the 0 – 15 cm depth while the KWAWA ST4 (control) recorded higher total PAH levels than all the remediation site stations at the 15 – 30 cm depth. The KPEAN remediation site stations recorded higher PAH levels than the KPEAN ST4 (control) station at the 0 – 15 cm depth while at the 15 – 30 cm depth, the KPEAN ST4 (control) site recorded lower PAH level than the remediation site stations. The DPR (2002) Target and Intervention values of the Total PAH in soil are 1 ppm and 40 ppm respectively. Stations 1 and 2 and the Control station recorded total PAH levels below the target and intervention values while Station 3 recorded total PAH level above the target value but below the intervention value. Thus, only Station 3 had total PAH levels above the desired level and no potential treats of PAH toxicity was observed across all stations as they were below the intervention value.

TPH Contents of Soil

KWAWA ST1 and KWAWA ST2 stations recorded higher TPH levels than the KWAWA ST4 (control) station at the 0 – 15 cm depth while only KWAWA ST1 recorded TPH level higher than the control at the 15 – 30 cm depth. The KPEAN ST2 and KPEAN ST3 stations had lower TPH level than the KPEAN ST4 (control) station at the 0 – 15 cm depth while only KPEAN ST1 had TPH level higher than the control at the 15 – 30 cm depth. The DPR (2002) Target and Intervention values of the total petroleum hydrocarbons (TPH) in soil are 50 mg/kg and 5000 mg/kg respectively. All the stations recorded TPH levels below the target and intervention limits. The

highest levels of 17.51729 and 17.03104 mg/kg were recorded at KWAWA ST1 at the 0 – 15 and 15 – 30 cm depths respectively while the lowest levels of 3.20876 and 4.48214 were recorded at KWAWA ST2 at the 0 – 15 and 15 – 30 cm depths respectively.

CONCLUSION

The levels of PAH and TPH contents of the soil samples from two crude oil remediated sites, in comparison with control sites, in the study areas have been determined in this study. The highest levels of 17.51729 and 17.03104 mg/kg were recorded at KWAWA ST1 at the 0 – 15 and 15 – 30 cm depths respectively. Only Station 3 had total PAH levels above the desired level and no potential treats of PAH toxicity was observed across all stations as they were below the intervention value. Thus the effect of the remediation work, as it reflects on the soil quality, is positive and should be maintained and improved on.

REFERENCES

- Abha, S. & Singh, C. S. (2012). Hydrocarbon Pollution: Effects on Living Organisms, Remediation of Contaminated Environments, and Effects of Heavy Metals Co-Contamination on Bioremediation, *Journal of Biology, Agriculture and Healthcare*, 6(12), 185-206 Albert, ON; Amaratunga, D; Haigh, RP. (2018). Evaluation of the Impacts of Oil Spill Disaster on Communities and its influence on restiveness in Niger Delta, Nigeria. *Proc. Engr.*212: 1054-1061.
- Bicca, F.C., Fleck, L.C. and Ayub, M.A.Z. (1999): Production of biosurfactant by hydrocarbon degrading *Rhodococcus rubber* and *Rhodococcus erythropolis*. *Revista de Microbiologia* 30, 31-37.
- Bob-manual, KDH; Johnson, KT. (2001). Oil Spill clean-up techniques for sustainable environmental protection in the Niger Delta. *NSE Techn. Trans.* 36: 2.
- Cusack, D. F., Silver, W. L., Torn, M. S., Burton, S. D., & Firestone, M. K. (2011). Changes in microbial community characteristics and soil organic matter with nitrogen additions in two tropical forests. *Ecology*, 92(3), 621-632.
- Ebuehi, OAT; Abibo, IB; Shekwolo, PD; Sigismund, KI; Adoki, A; Okoro, IC. (2005). Remediation of Crude Oil Contaminated Soil by Enhanced Natural Attenuation Technique. *J. Appl. Sci. Environ. Mgt.* 9(1): 103-106.

- Guarino, C., Spada, V. and Sciarrillo, R. (2017). Assessment of three approaches of bioremediation (natural, Attenuation, Landfarming and Bioaugmentation) for a petroleum hydrocarbons contaminated soil. *Chemosphere*, 170, 10-16.
- Jørgensen, KS. (2011) Comprehensive Biotechnology. M. Moo-Young (Ed.) (Second Edition), Science Direct Publications/Elsevier B.V.
- Margesin, R., Labbe, D., Schinner, F., Greer, C.W. and Whyte L.G. (2003). Characterization of Hydrocarbon-Degrading Microbial populations in contaminated and Pristine Alpine Soils. *Applied and Environmental Microbiology*, 69, 3085-3092.
- Mnif, S., Chebbi, A., Mhiri, N., Sayadi, S. and Chamkha, M. (2017). Biodegradation of phenanthrene by a bacteria consortium enriched from Sercina oilfield. *Process Safety and Environmental Protection*, 107, 44-53.
- Needam, B. G., Wokocha, C. C., & Kamalu, O. J. (2020). Land use Change Detection of Khana Local Government Area of Rivers State Using Remote Sensing and GIS. *International Journal of Advances in Scientific Research and Engineering* 6(12), 1-8.
- Nwilo, C.P. and Badejo, T.O. (2005). Oil spill problems and management in the Niger Delta.
- Orisakwe, O. E. (2021). Crude oil and public health issues in Niger Delta, Nigeria: Much ado about the inevitable. *Environmental research*, 194, 110725.
- Saravana K. P. and Amruta S. R. (2013) Analysis of biodegradation pathway of crude oil by *Pseudomonas* sp. isolated from marine water sample. *Archives of Applied Science Research*, 5(4), 165-171.
- Shaheen, S. M., Hooda, P. S., & Tsadilas, C. D. (2014). Opportunities and challenges in the use of coal fly ash for soil improvements—a review. *Journal of environmental management*, 145, 249-267.
- Taiwo, M. A. (2011). Composting as a sustainable waste management technique in developing countries. *Journal of Environmental Sciences and Technology*, 4, 93-102
- Victor, I. A., Iwok, E. O., Archibong, I. A., Effiom, O. E., Okon, E., & Andem, A. B. (2020). The biochemical mechanisms of petroleum degradation by bacteria. *Int. J. Eng. Res*, 11, 1258-75.