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FIELD PILOT STUDY ON THE ASSESSMENT OF SELECTED HYDROCARBON REMEDIATION TECHNIQUES

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Abstract —The study discussed the remediation potentials of phytoremediation, land farming treatment and chemico-biological stabilization treatments in degrading Total Petroleum Hydrocarbon (TPH) and Polycyclic Aromatic Hydrocarbon (PAH) in soils polluted with crude oil in varying concentrations. The field pilot study was carried out in Benin city, Nigeria by preparing nine (9) cells with sub-cells attached which serve as control; each cell measures 1.53 m2. Three cells contained 100 kg of artificially contaminated soils at low contamination concentration (3000 mg kg-1), the next three cells contained 100 kg of contaminated soil samples but with medium concentration (5000 mg kg-1), while the last three cells contained 100 kg of spike samples in high concentration (7000 mg kg-1). The sub cells contained 10 kg of soil and left untreated. Each role containing three cells with low, medium and high concentration was treated separately using the three treatment methods. Soil samples to organic amendment ratio for the treatments was 2:1. The results showed over 90% reduction in the initial concentration of TPH and PAH across the different contamination levels with except in the control sub cells were only 30% reduction was recorded. The treated soil was found useful for agricultural purpose. One-way analysis of variance reveals a significant difference at $p \leq 0.05$ in the results obtained in application of the three methods. This implies that the methods effectively degraded the TPH and PAH concentrations. The three different methods of treatments effectively degraded TPH and PAH contaminants with land farming treatment being the best of the three.

***Keywords*:** Contamination, Remediation, Hydrocarbon, Crude oil and Treatment

1.0 INTRODUCTION

Crude oil-hydrocarbons are naturally occurring products of several anaerobic transformation of diverse biomass under extremely high pressure and temperature. The exploration, exploitation, refining, transportation and marketing of the refined products which include petrol (PMS), diesel, kerosene, oil, asphalt and bitumen etc are usually accompanied with uncontrolled spills either through careless handling, facility breakdown or intentional damage of transport systems by vandals in order to syphon the precious fluid [1]. The various medium for transportation of crude oil and its refined product includes pipeline network, rails, cargos, and heavy-duty trucks are all susceptible to sabotage which makes petroleum hydrocarbon pollution very prevalent in surface water, ground water and surficial soils. Crude oil exploration in commercial started in Nigeria in the wake of 1950 in present day Bayelsa state. The entire Niger Delta zone of Nigeria which consists of nine (9) states have several rich oil wells where over two (2) million barrels of crude oil is mined daily. The region alongside the surrounding offshore locations generate about 75% of the nation's foreign earning and have provided several jobs (direct and indirect) for the growing population [2]. The high presence of crude oil infrastructures and oil exploration facilities such as; jetty, platform, flow station, heavy duty trucks, ships, tank farm, underground and surface pipeline network makes the area potential flash point for hydrocarbon contamination [3, 4].

In the last three decades, the Nigerian Petroleum industry (both upstream and downstream) have grown and developed in product handling and marketing but with heavy demand on diesel and fuel for power (energy) generation, the attendant effect of crude oil and it refine product sabotage has also been on the increase thereby posing severe health threat to man and his immediate environment. In the Niger Delta region, several pipeline leakages, indiscriminate dumping of hydrocarbon waste, leakages from transporting vessels/vehicles have been reported by different researchers [5, 6, 7]. Vast land that would have been used for agriculture and surface streams that was once used for fishing adventure have been

destroyed and rendered less useful by the incessant spills in this region. The World Bank and United Nations have joint prevailed on the Federal Government of Nigeria and oil companies doing business in the region to clean up the pollutes sites. The results from the cleanup exercise still left much to be desired due to poor application of recommended methods or weakness on the part of the handlers [8].

Remediation is the process of contentiously managing and observing a pollutant either in-situ of ex-situ in order to mitigate its spread and ameliorate its effects on man, plants and animals. The process when thoroughly monitored can lead to land monitoring and recovery. Remediation of crude oil hydrocarbon and heavy metal polluted sites can either be biological (use of plants and microorganisms), chemical (use of artificial fertilizers) or physical (replacing polluted soil with clean soil). In the past and even presently, phytoremediation, bioremediation, phytostabilization, rhizofiltration, phytovolatization and phytoextraction have been used in remediating polluted lands due to its cost effectiveness, environmentally friendly and effective in decontaminating hydrocarbon contaminated soil [4, 9, 10, 11, 12]. The idea of decontaminating petroleum hydrocarbon whether in soils or water, revolves around availability of air, nutrients and water so as to increase the rate of microbial activities in the soil and in turn degrade the pollutants [13, 14]. According to [15] over 95% bioremediation is achievable in soil polluted with Polycyclic Aromatic Hydrocarbon (PAH). Using bioremediation treatment technique is dependent on site and therefore has its specific terms in each site; therefore, it is imperative to carry out treatability studies before undertaking full scale implementation [16].

This work utilized the traditional method of phytoremediation (using guinea grass) and compared the results with two other methods of chemic-biological stabilization (use of fertilizers and plant) and land farming treatment (use of organic and inorganic fertilizers). The materials for the three separate practice are readily available in abundance although the technology of land farming and chemico-biological stabilization was new in the region (Niger Delta). Phytoremediation involves the cultivation of plants (in this case guinea grass) with roots capable of opening soil pore spaces which allows aeration, increased moisture content and increase in the rate of microbial synthesis. Chemico-biological stabilization is the use of cover plants, organic and inorganic fertilizers in remediating contaminated sites while land farming is the utilization of organic and inorganic fertilizers for the purpose of increasing the nutrient level for microorganism consumption in order to degrade pollutants. The objective of this work is to determine under field pilot study, the efficiency of three remediation approaches (phytoremediation, chemico-biological stabilization and land farming) in the treatment of hydrocarbon contaminated soil in different concentrations. These methods were chosen as a result of the availability of the materials involved and the ease of application of the required procedures.

2.0 MATERIAL AND METHODS

The project site is located in Ologbo, Ikpoba Okha local government area of Edo state that lies between longitude 05° 38' 36.47"E to 05°4' 26.56" E and latitude 06° 4' 28.17"N to 06° 4' 33.79"N which is 32 km south-west of Benin City, Nigeria. The location of the project is almost 18 km from NPDC link road which is off Benin-Sapele Road. There are several oil wells in this area and spill is quite common especially during peak production. Soil samples were collected in this location while the crude oil for the artificial contamination was taken from Ologbo flow station located within the community. The map of Ikpoba Okha LGA showing Ologbo where the study was carried out is shown in Figure 1. The field where the research was carried out is known as Ologbo oil field; it is used to carry out crude oil development researches and cleanup innovations.

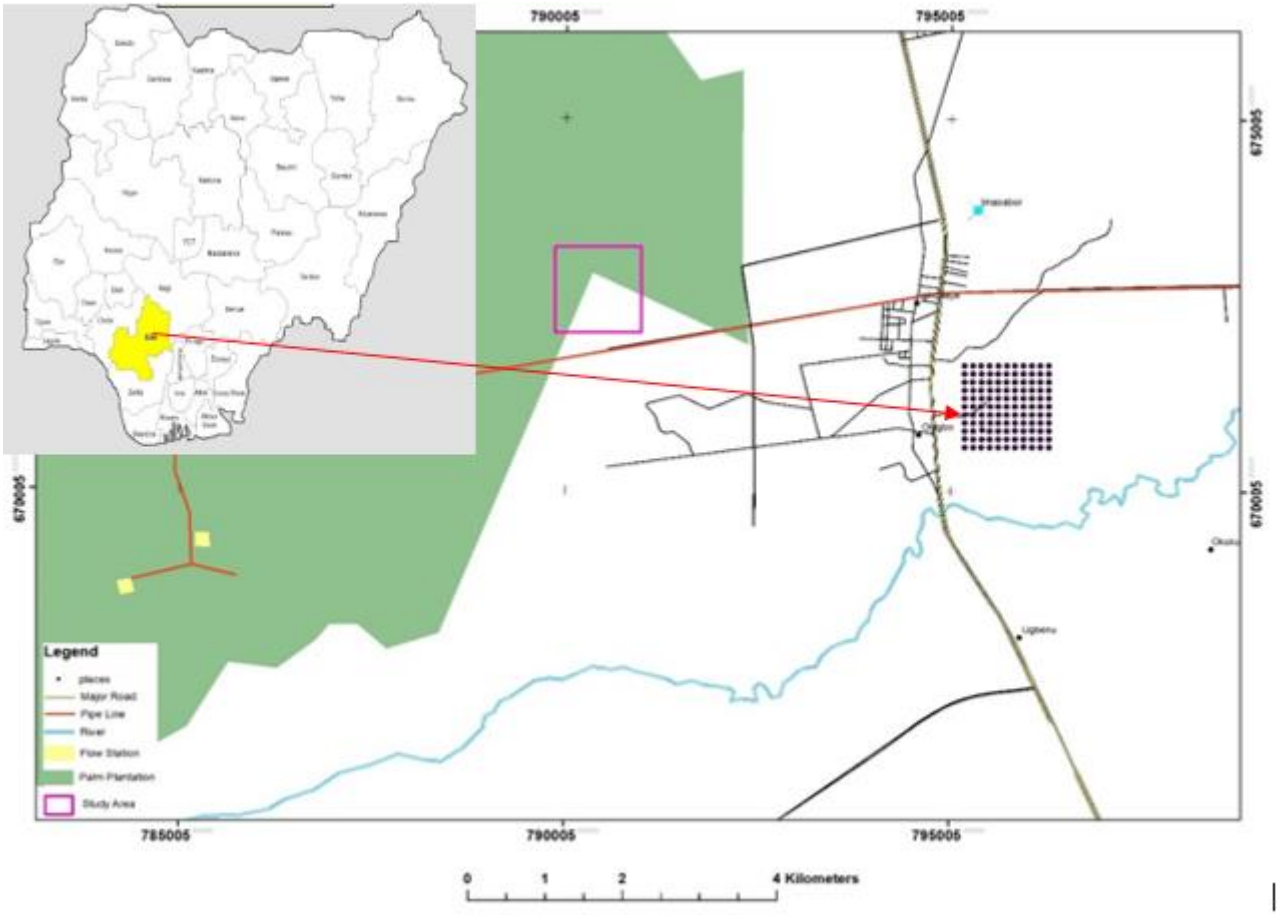

Figure 1 Map of the field pilot study area

2.1 SOIL RECOVERY AND PREPARATION

Soil was taken at the project location with depth not greater than 45 cm using calibrated hand auger and the coordinates of the locations were obtained using handheld GPS. Sampling was systemic so as to ensure that only topsoil was taken as it affects plants growth the most. The recovered soil samples were placed in cellophane bags and transported to University of Benin Geotechnical Laboratory where it was dried, pulverized, sieved and preserved before taken to Chemistry Laboratory for the determination of the baseline TPH concentration levels. The results revealed TPH values in the soil samples were below detection level hence artificial contamination was carried out.

Nine (9) cells with sub cell attached, each measuring 170 cm x 90 cm was prepared for the remediation research. Cellophane bags were placed at the base of each cell so as to prevent the samples from contaminating the ground. The prepared soil samples were divided into three groups with each group having about 300 kg of soil and delineated as low, medium and high. The low samples were spiked with 6.1 kg of crude oil sample an equivalent of 3000 mg kg-1 concentration, the medium samples were spiked with 12.2 kg of crude oil an equivalent of 5000 mg kg-1 concentration while the high samples were contaminated with 18.3 kg of crude oil samples an equivalent of 7000 mg kg-1 concentration respectively. Samples from the three concentration (low, medium and high) were taken to the laboratory for the quantification of TPH, PAH and their components. The values are shown in Tables 1 - 2. The low concentration samples were further divided into three (100 kg each) and delineated as a, b, c; medium concentration samples were also divide into three (100 kg each) and delineated as d, e, f; the same was done for high concentration and delineated as g, h, i, respectively. This made a total of nine (9) samples with same mass but in three different concentrations of low, medium and high. Samples a, d and g were

treated using phytoremediation (guinea grass and cow dung); samples b, e and h were treated using chemico-biological stabilization (Brachiaria humidicola, commonly known as humidicola grass, calcium oxide (CaO) and palm kernel husk) while samples c, f and i were treated using land farming method (NPK fertilizer and cow dung). Figures 2 and 3 show the pictures of the cells and the layout of the experiment during the study.

The composition of the Polycyclic Aromatic Hydrocarbon (PAH) present in the crude oil used for the study and their quantities were determined as shown in Table 2. Four out of the seventeen constituents namely Naphthalene, Benzo(a)pyrene, Benzo(a)anthracene and Dibenzo(a,h)anthracene (which are carcinogenic) had values higher than WHO and USEPA permissible limits in soils. The effect of the various treatment methods on these four constituents was therefore monitored to ascertain their degradation.

Figure 2 Cell Preparation

Figure 3 Experimental layout

Table 1 Summary of Total Petroleum Hydrocarbon Found in Spiked Samples

TPH Components	Low Concentration (mg kg^{-1})	Medium Concentration (mg kg^{-1})	High Concentration (mg kg^{-1})
$C_5 - C_{10}$	154.16±0.18	542.67±0.07	962.17±0.15
$C_{11} - C_{15}$	254.44±0.55	796.58±0.12	747.61±0.09
$C_{16} - C_{27}$	451.36±0.07	857.94±0.07	1326.91±0.16
$C_{28} - C_{35}$	149.26±0.05	828.40±0.81	1986.67±0.21

Table 2 Summary of Polycyclic Aromatic Hydrocarbons Found in Spiked Samples

COMPOUND	HIGH CONC. MEAN VALUE (mg kg^{-1})	MEDUIUM CONC. MEAN VALUE (mg kg^{-1})	LOW CONC. MEAN VALUE (mg kg^{-1})	USEPA LIMIT (mg kg^{-1})
2-Methylnaphthalene	0.17±0.22	0.11±0.007	0.08±0.002	<1
Acenaphthene	0.36±0.20	0.14±0.004	0.12±0.17	<1
Acenaphthylene	0.89±0.16	0.66±0.45	0.19±0.001	<1
Anthracene	0.53±0.31	0.51±0.003	0.22±0.004	-
Benzo*(a)*anthracene	1.53±0.45	1.22±0.21	1.01±0.003	<1
Benzo*(a)*pyrene	1.72±0.03	1.42±0.005	1.26±0.13	<1
Benzo*(a)*fluoranthene	0.13±0.97	0.07±0.003	0.02±0.18	-
Benzo*(k)*fluoranthene	0.02±0.001	0.005±0.55	-	-
Benzo(*g, h, i*)perylene	0.38±0.64	0.008±0.002	-	-
Chrysene	0.25±0.002	0.038±0.001	-	-
Dibenzo*(a,h)*anthracene	1.43±0.63	1.39±0.08	1.10±0.07	<1
Fluoranthene	0.20±0.62	0.006±0.001	-	
Fluorene	0.43±0.11	0.21±0.73	-	
Indeno(1,2,3-c,d)pyrene	0.27±0.61	0.005±0.01	-	
Naphthalene	1.66±0.93	1.48±0.89	1.35±0.66	<1
Phenanthrene	0.16±0.09	0.003±0.7	-	-
Pyrene	0.08±0.52	-	-	-
Total PAHs Compound	10.22±6.49	7.28±3.65	5.35±1.20	

2.2 SOIL TREATMENT

The cow dung, palm kernel husk, crude oil samples, soil samples, organic and inorganic fertilizers used for the soil treatment were first taken to Chemistry Laboratory at the University of Benin for characterization, and determination of physical and chemical properties. Values obtained are shown in Tables 3 - 5 respectively. The summary of the treatments are:

1. Phytoremediation Treatment:100 kg of soil sample + 50 kg organic amendment (cow dung) + 10 number Guinea Grass. 10 kg of contaminated samples were also placed in the sub cell but were not treated, this was used as control (natural attenuation).
2. Land Farming Treatment: 100 kg of soil sample + 25 kg NPK fertilizer + 25 kg organic amendment (cow dung). 10 kg of contaminated samples were also placed in the sub cell but were not treated, this was used as control (natural attenuation).
3. Chemico-biological Stabilization: 100 kg of soil samples+ 25 kg CaO + 25 kg organic amendment (palm kernel husk) + 10 number humidicola grass (Brachiaria humidicola). 10 kg of contaminated samples were also placed in the sub cell but were not treated, this was used as control (natural attenuation).

The initial moisture content of 20% was maintained at the commencement of the study. The research was carried out for a period of 150 days while samples were taken to the laboratory every 30 days for determination of residual TPH.

Table 3 Physical and Chemical Properties of the Crude oil used in the study

Parameters	Value
Water Content (% Vol.)	0.50
Specific Gravity @ 15/15 ˚C	0.8966
Dry Specific Gravity @ 15/15 ˚C	0.8961
*API@15/15 ˚C	26.4
Kinematic Viscosity	10.45
Appearance	Dark Brown Liquid

** API- American Petroleum Institute*

Table 4 Properties of Organic and Inorganic Fertilizers used in the Study

Parameters	Cow Dung	Oil Palm Husk Ash	NPK Fertilizer
pH	8.27	6.14	9.62
Organic Carbon (%) $*10^{-1}$	137.40	7.53	463.23
Total Nitrogen (%)	40.65	21.86	58.40
Phosphate (mg kg^{-1})	23.68	124.66	26.07
Potassium (mg kg^{-1})	17.49	10.03	7.83
Magnesium (mg kg^{-1})	5.88	14.72	11.35
Calcium (mg kg^{-1})	1.42	2.84	37.55
Sodium (mg kg^{-1})	1.94	6.75	1.06

The three fertilizers used (organic and inorganic) have high Nitrogen content which makes them suitable for remediation operations.

Table 5 Physical and Chemical Properties of the soil used in the study

Properties	Value
pH (1:1 soil-water)	5.72
Nitrogen (mg kg^{-1})	8.83
Phosphorus (mg kg^{-1})	11.73
Organic Carbon (g kg^{-1})	47.8
Gradation Analysis	
Sand (%)	79.4
Silt (%)	14.5
Clay (%)	6.1
Textural Class	Sandy Loam
Specific Gravity	2.5

2.3 SAMPLES ANALYSIS AND INSTRUMENTATION

Samples recovered for monthly analysis were placed in plastic bags and put into a glass jar with seal. Each sample was labelled differently and stored in a refrigerator at 4 °C. Sample extraction was carried out using extraction procedure detailed in USEPA method 3540 and ASTM method D5369 with little adjustments on flask size, choice of solvent, volume of solvent and extraction time. Pestle and mortar were used to pound samples to get fine texture before extraction was carried out. Pebbles and stones were also removed in the process of pounding. Hydrocarbons in the soil samples were then determined using Agilent 6890 Gas Chromatograph fitted with a split injection auto sampler. Samples were injected and separated on a HP-5MS/DB-5MS column of 0.25 mm diameter, 30 m long and is 0.25 μm film thick while placed in a 2 ml chromatographic vial. Carrier gas was Nitrogen with a makeup flow of 25 ml min-1 while temperature throughout the chromatographic operation was 80 °C for 3 minutes, 20 °C /minute until 280 °C was obtained and hold for 20 minutes and the detector flame was set at 300 °C.

2.4 TOTAL HETEROTROPHIC MICROBIAL ENUMERATION

The determination of the amount of bacteria populations was evaluated using plate counting technique. A popular method is ‘spread plate method’, it is quite easy and most frequently used to enumerate useful microorganism in soil [17, 18]. The process was carried out by the preparation of serial dilution (as1:10-1:100 of soils samples, aliquot of dilution was spread on the surface of Trypticase Soya Agar (TSA) plate and brooding the plate (TSA) under adequate conditions.

Physiological saline solution, about 99 ml and l g of polluted soil samples was positioned in a 250 ml materialized flask to produce 1:100 dilutions. Then 1 ml of suspension was conveyed into a 15 ml sterilized test tube containing 9 ml physiological saline to produce a dilution 1:103. The same procedure was continued until the desired dilution is ascertained. The busked dilution was spread on TSA plates and brooded in the presence of oxygen at 26 °C for two (2) days. A mean number of colonies, similar to

dilutions within 30 and 300 per plate was calculated using equation 3.1. It is expressed as number of colony form unit (cfu).

$$\text{No of } \frac{\text{cfu}}{\text{g}} \text{ of soil } = \frac{\text{Mean quantity of colonies} * \text{dilution factor}}{\text{Initial weight of soil}} \quad (1)$$

2.5 ANALYSIS OF DATA

The design of experiment suits split-split pilot in Complete Randomized Design (CRD) while the responses will be decrease in TPH (including it aliphatic groups) and PAH components concentrations in the soil for 150 days. One-way Analysis of Variance (ANOVA) was carried out on the results in order to ascertain the variation in the responses of the applied treatments. The percentage amount of hydrocarbon removed from each treatment cell within all the carbon ranges for a period of 150days was calculated using [19] mathematical expression given in equation 2.

$$\% \, q = \frac{C_o - C_e}{C_o} \quad (2)$$

Where C_o is initial concentration, C_e is final concentration while %q is percentage degradation.

3.0 RESULTS AND DISCUSSION

Results obtained from the field pilot study for TPH and PAH degradation monitoring using phytoremediation, land farming and chemico-biological stabilization in low, medium and high concentrations are presented in Figures 4 - 13. The result showed gradual reduction in TPH and PAH values in all the concentrations examined using the treatment methods. In the first 30days of the treatment, about 20% of TPH was lost in low concentration, 15% was lost in medium concentration, 22% was lost in high concentration while the natural attenuation (control) lost only 5% of TPH.

In low, medium and high contaminations levels, THP values were 1016.82±19.96, 3029.87 ± 14.39 and 5033.67±146.89; total PAH values were 5.35±1.20, 7.28±3.65 and 10.22±6.49. After 150 days of treatment, residual TPH in low concentration was 96.23 ± 5.25 for phytoremediation, 59.24 ± 9.53 for land farming, 65.49 ± 4.93, for chemico-biological stabilization; while only about 25% of TPH was degraded under natural attenuation (control). The residual TPH in medium concentration was 102.64 ± 10.63 for phytoremediation treatment, 105.56 ± 5.22 for land farming, and 106.18 ± 3.14 for chemico-biological stabilization while only about 42% was degraded under natural attenuation (control). In high concentration, residual TPH was 388.85 ± 77.87 for phytoremediation, 260.32 ± 32.34 for land farming, 242.08± 50.97 for chemico-biological stabilization while about 36% was degraded under natural attenuation (control). Total PAH was reduced by over 90% in all concentrations using the various treatment methods with natural attenuation (control) being the only exception with an average of 31% degradation. One factor that could be responsible for the gradual loss of TPH and PAH is the interaction between the soil particles, hydrocarbon and the treatment which makes the hydrocarbon to be available thereby increasing efficiency of extraction. Although the treatment applied across various concentrations reduced TPH in the soil, the residual levels in the soil was still above WHO allowable limit of 100 mg kg-1. In Table 5, the seventeen components of PAH of the crude oil sample used in the study were presented; four of the components namely Naphthalene, Benzo(a)pyrene, Benzo(a)anthracene and Dibenzo(a,h)anthracene and had values that exceeded the USEPA allowable limits in soil hence, it was necessary to investigate/monitor the effect of the treatments on these toxic components. The results revealed that the treatments effectively reduced the carcinogenic components below detection level. This implies that although the residual TPH value is high, its toxicity has been completely mineralized. This observation is similar to the findings of [20], where biostimulants were used to biodegrade TPH and PAH in soils around Gulf of Mexico. The various aliphatic components were also degraded by the various treatments irrespective of the residual concentration.

Based on the level of chemical nearness of the n-alkane chains, they were sub-divided into five groups as; C5-C10, C11-C16, C17-C27 and C28- C35. The results revealed degradation of the various groups of alkanes across the concentrations using the treatment methods with the highest degradation recorded in the class of C28- C35. The obtained results are in line with that of some researchers like [21, 22, 23]; they discovered that in fertilized and cultivated soils, virtually all the alkane groups were degraded up to 85% while the control portion (natural attenuation) showed less than 50% degradation. The less degradation in the control portion is an indication of lack of hydrocarbonic degrader which are usually heterotrophic microbes responsible for degradation of single normal alkanes. The impact of guinea grass, humidicola grass and NPK fertilizer in the degradation of hydrocarbon degraded soil is almost the same as the results of [24, 25, 26, 27], they reported high levels of biodegradation of hydrocarbon in vegetative soils. The results from this study also agrees with the suggestions of [28] that guinea grass should be cultivated in crude oil polluted areas because of its efficiency in remediating hydrocarbon polluted soils.

The process of hydrocarbon removal by guinea grass occurs by either polymerization, bacteria or fungi/plant interactions roots exudates production by plants which are sources of nitrogen, phosphorous and carbon, required by hydrocarbon degrading microbes.

The design of experiment suits split-split pilot in Complete Randomized Design (CRD) while the responses will be decrease in TPH (including it aliphatic groups) and PAH components concentrations in the soil for 150 days. One-way Analysis of Variance (ANOVA) was carried out on the results in order to ascertain the variation in the responses of the applied treatments. The percentage amount of hydrocarbon removed from each treatment cell within all the carbon ranges for a period of 150days was calculated using [19] mathematical expression given in equation 2.

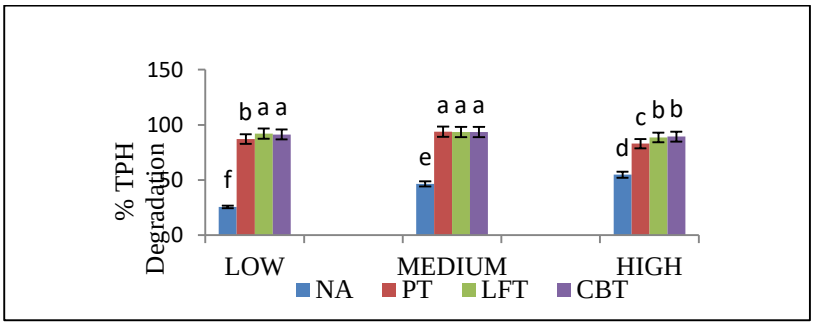

Figure 4 TPH Reduction in Different Concentration in 150 days

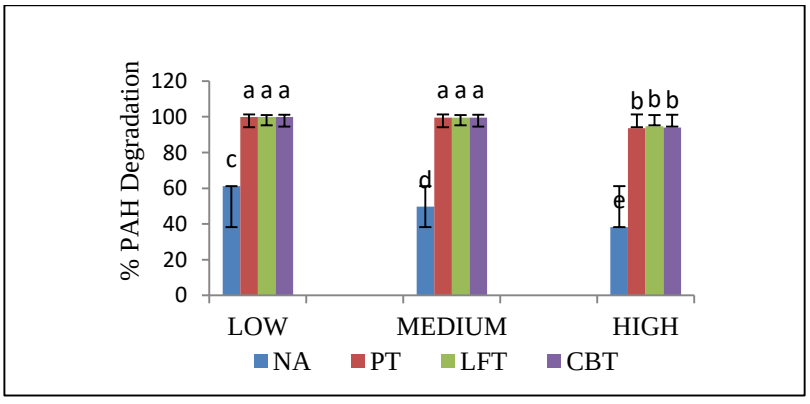

Figure 5 PAH Reduction in Different Concentration in 150 days

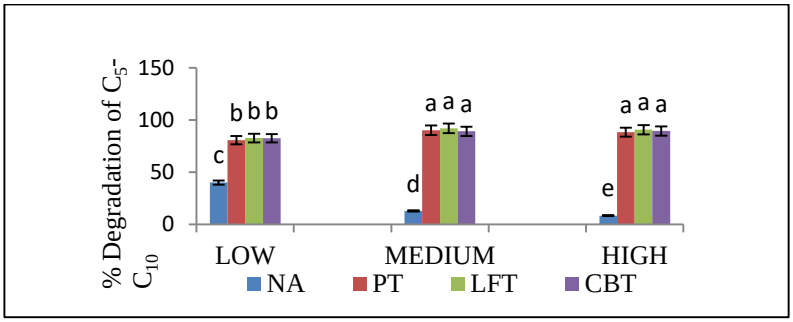

Figure 6 Degradation of C5-C10 in Different Concentrations in 150 days

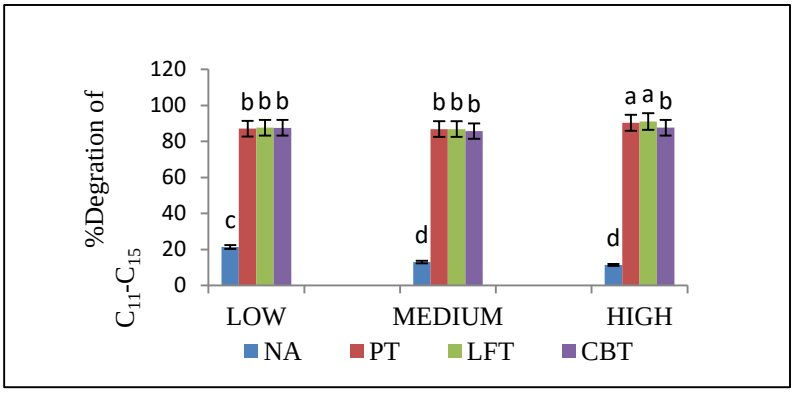

Figure 7 Degradation of C11-C15 in Different Concentrations in 150 days

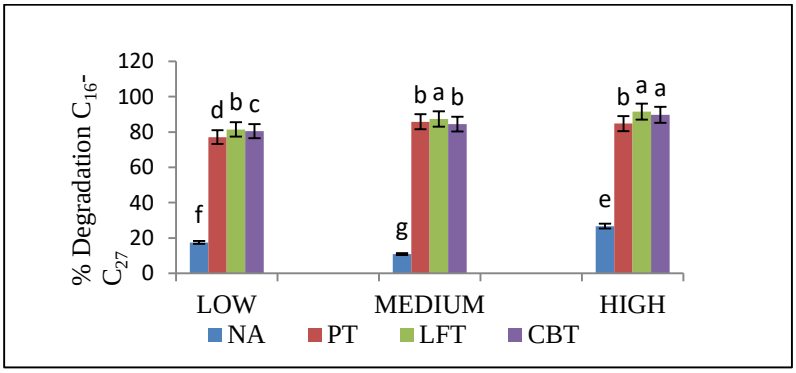

Figure 8 Degradation of C16-C27 in Different Concentrations in 150 days

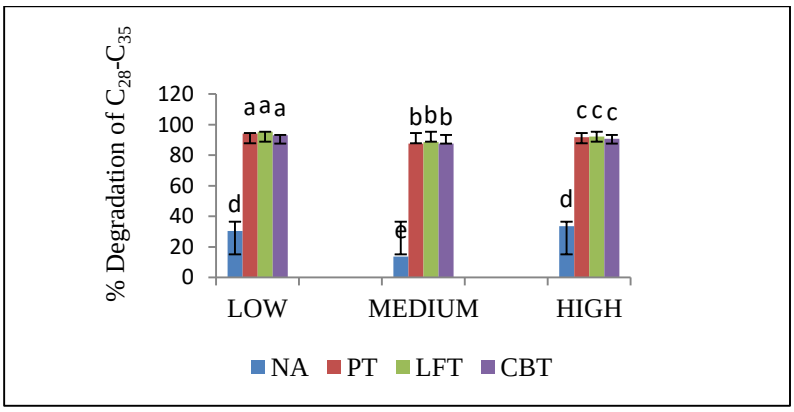

Figure 9 Degradation of C28-C35 in Different Concentrations in 150days

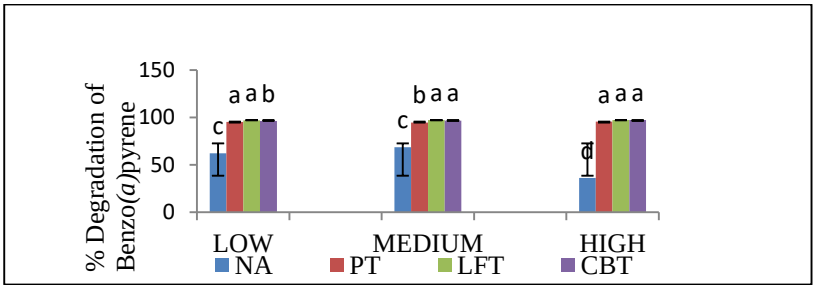

Figure 10 Degradation of Benzo(a)pyrene in Different Concentrations in 150 days

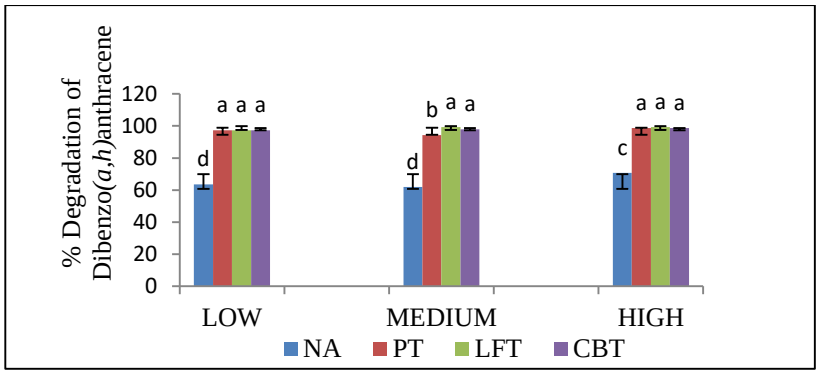

Figure 11 Degradation of Dibenzo(a,h)anthracene in Different Concentrations in 150days

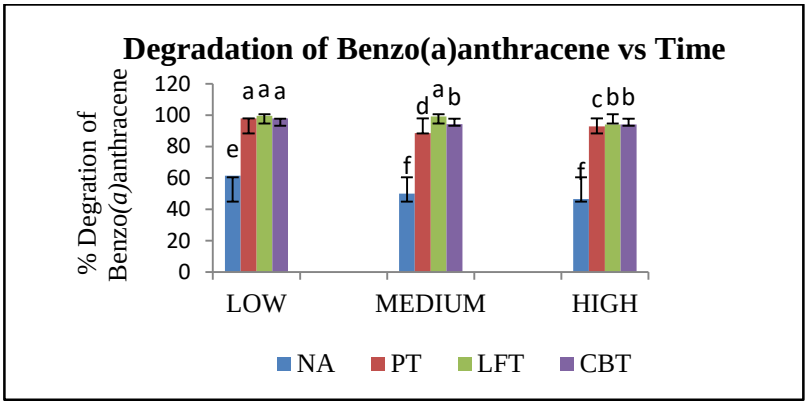

Figure 12 Degradation of Beno(a)anthracene in Different Concentrations in 150 days

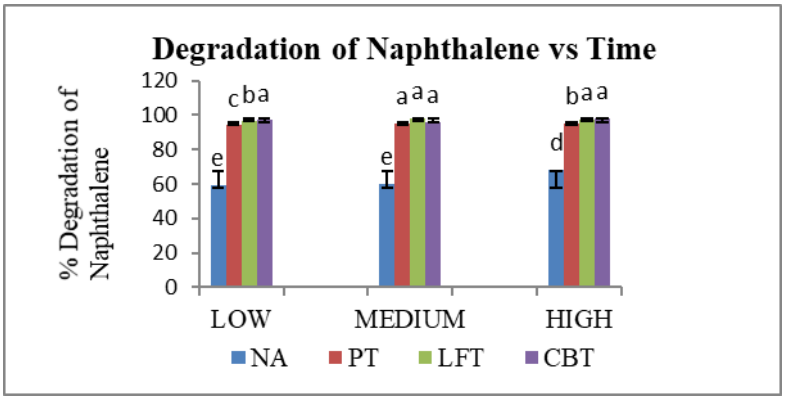

Figure 13 Degradation of Naphthalene in Different Concentrations in 150 days

The error bars indicate the standard deviation of the means (n = 3). Bars with same Letters indicate no significant differences at p levels of <0.05. NA is Natural Attenuation (control), PT is Phytoremediation Treatment, LFT is Land Farming Treatment and CBT is Chemico Biological Treatment.

The hydrocarbon degrading heterotrophic microbes in the treated plots increased remarkably from 0.55E-01 to 3.62E+07 in low concentration, 1.84E-01 to 4.82E+08 in medium concentration and 2.08E-02 to 3.47E+08 in high concentration respectively. This confirmed the biostimulation of indigenous soil bacteria by the application of the treatments which resulted in the accelerated degradation of the crude oil polluted soil. The hydrocarbon degrading microbes found in the soil are; chromobacter, serratia, Bacillus. Figures 14 - 16 shows the graph of Total Heterotrophic Bacteria Count, THBC using the various treatment methods at different concentrations.

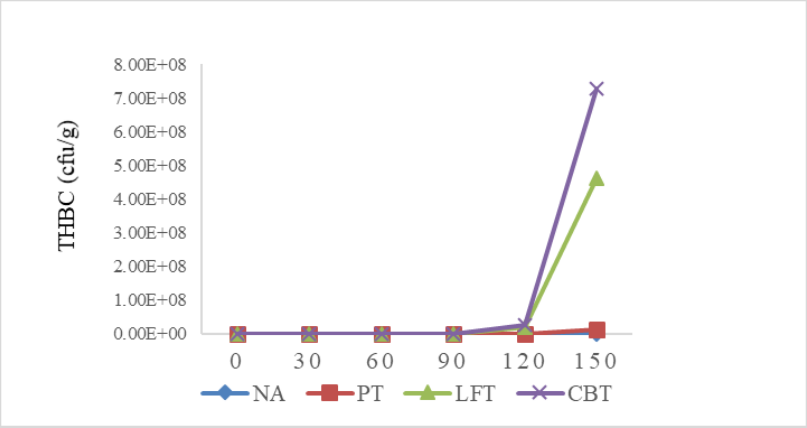

Figure. 14 THBC in Low Concentration under Different Treatment

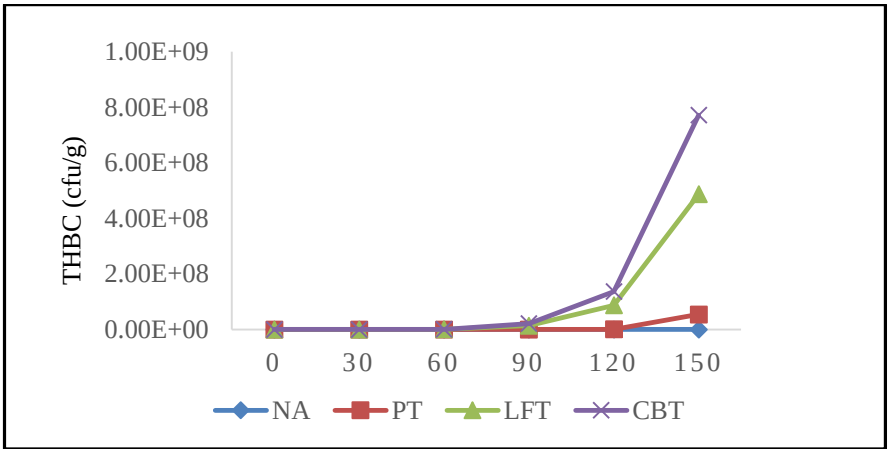

Figure 15 THBC in Medium Concentration under Different Treatment

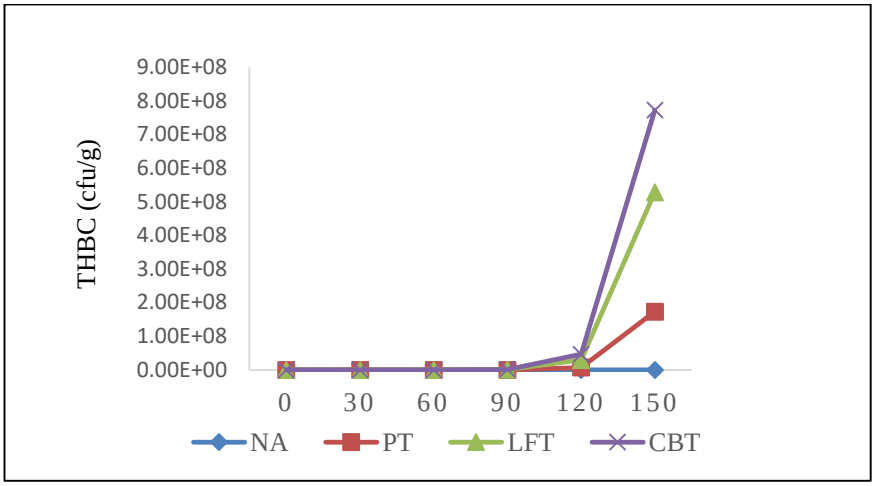

Figure. 16: THBC in High Concentration under Different

The whole product analysis method which gives the yielding concentration of TPH was used in determining the hydrocarbon degradation as opposed to the individual hydrocarbon fractionalization Analysis of variance (ANOVA) was carried out to evaluate the responses of the treated samples to the three treatments applied after 150days. Results obtained are shown in Tables 6 - 8.

Table 6: ANOVA of TPH Responses to Treatments Methods in Low Hydrocarbon Contamination

Sources of Variation	Sum of Squares	d.f.	MSS = $\frac{S.S.}{d.f.}$	Variance Ratio	F Pr. <0.05
Treatment (Soil)	8091.97	2	4045.96	0.0943	3.89
Error	514798.44	12	42899.87		
Total	522890.41	14			

Table 7: ANOVA of TPH Responses to Treatments Methods in Medium Hydrocarbon Contamination

Sources of Variation	Sum of Squares	d.f.	MSS = $\frac{S.S.}{d.f.}$	Variance Ratio	F Pr. <0.05
Treatment (Soil)	26346.17	2	13173.09	0.03505	3.89
Error	4510532.74	12	375877.73		
Total	4536878.91	14			

Table 8: ANOVA of TPH Responses to Treatments Methods in High Hydrocarbon Contamination

Sources of Variation	Sum of Squares	d.f.	MSS = $\frac{S.S.}{d.f.}$	Variance Ratio	F Pr. <0.05
Treatment (Soil)	45636.54	2	22818.27	0.01358	3.89
Error	20168521.37	12	1680710.11		
Total	20214157.91	14			

The results in Tables 6 - 8 shows high percentage degradation in TPH concentration in the soil in responses to the three treatment methods applied. The result showed significant difference in the responses obtained on the application of the three treatment methods at $p \leq 0.05$, this implies that all the methods degrade (reduced) the original TPH concentration in the soil.

Table 9: ANOVA of PAH Responses to Treatments Methods in Low Hydrocarbon Contamination.

Sources of Variation	Sum of Squares	d.f.	MSS = $\frac{S.S.}{d.f.}$	Variance Ratio	F Pr. <0.05
Treatment (Soil)	12.501	2	0.0648	0.0628	3.89
Error	0.1296	12	1.0312		
Total	12.3744	14			

Table 10: ANOVA of PAH Responses to Treatments Methods in Medium Hydrocarbon Contamination

Sources of Variation	Sum of Squares	d.f.	MSS = $\frac{S.S.}{d.f.}$	Variance Ratio	F Pr. <0.05
Treatment (Soil)	20.079	2	0.02675	0.0160	3.89
Error	0.0535	12	1.668775		
Total	20.0253	14			

Table 11: ANOVA of PAH Responses to Treatments Methods in High Hydrocarbon Contamination

Sources of Variation	Sum of Squares	d.f.	MSS = $\frac{S.S.}{d.f.}$	Variance Ratio	F Pr. <0.05
Treatment (Soil)	60.519	2	0.03135	0.006223	3.89
Error	0.0627	12	5.0380		
Total	60.4563	14			

The results of PAH reduction as shown in Tables 9 - 11 exhibited similar pattern with that of TPH; at $p \leq 0.05$ there was significant difference in the responses obtained from the three treatment procedures used. Similar results in TPH and PAH degradation was also reported by [19]; he ascertained that higher hydrocarbon degradation was achieved by the utilization of plants, organic and inorganic fertilizers in variant proportion.

4.0 CONCLUSION

This study has shown the application of phytoremediation, land farming and chemico-biological stabilization can degrade TPH and PAH concentration in soils. The results obtained indicates that residual TPH and PAH found in the soil after treatment was below USEPA limit; the implication is that the soil can be used for agricultural purpose. The rate of degradation is a function of the correct application of the intended method. For effective result in phytoremediation using guinea grass, the ratio of soil samples to organic amendment should be 2:1 with a minimum of 10 number plants in an area of 1.53 m2. Land farming treatment ratio of soil samples to organic and inorganic amendment should be 2: 0.5: 0.5 while chemico-biological stabilization treatment ratio should be 2: 0.5: 0.5 with 10 number cover plants. These recommendations can be tried in laboratory scale before full scale implementation in any intended cleanup site.

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