



Effect of Enhanced Natural Attenuation Remediation on Chronically Oil-impacted Soil in some Communities of Ogoniland, Rivers State, Nigeria

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ABSTRACT: Frequent oilspills in the Niger Delta regions have created ecological problems needing solutions. This study therefore investigated the effect of enhanced Natural Attenuation Remediation (ENA) on chronically oil-impacted soil in some communities of Ogoniland, Rivers State, Nigeria. Total petroleum hydrocarbons (THCs) migration was measured at 0.5m soil depth intervals and relevant edaphic variables measured before and after an ENA remediation procedure at 6 sampling locations (OLs). THC contaminants were as high as 40,645.00mg/kg on the surface at OL 1, and undetectable at OL control. Mean concentrations of THC (Sig.value=0.018), C/N ratios (Sig.value=0.050), SO₄²⁻ ions (Sig.value=0.000) and sand compositions (Sig.value=0.040) differed markedly (p<0.05) across the OLs before remediation, while concentrations of pH (Sig.tvalue=0.048), EC and K⁺ ions (Sig.tvalue=0.000 each), Na⁺ ions (Sig.tvalue=0.006), Mg²⁺ ions (Sig.tvalue=0.024), and clay composition (Sig.tvalue=0.020) differed (p<0.05) after remediation. Results indicate effectiveness of the cost-effective ENA technique in the restoration of soil of a Niger Delta area.

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Crude oil has contributed enormously to the Gross Domestic Product of Nigeria, as the product currently generates bulk of the country foreign exchange and serves as energy source and industrial raw materials. Nonetheless, the effects of its extraction on the Niger Delta environment are very damaging. Over the last decade, Eni and Okpiliya (2011) observed that oil exploration and exploitation activities have impacted disastrously on the social and physical environments of oil-bearing communities in the Niger Delta, largely threatening the subsistent peasant economy, the environment, and livelihood, hence the basic survival of the people. The incidences of oil spills in the Niger Delta area of Nigeria have become rampant and are mainly from fractured pipelines due to corrosion or company operational errors in the environment, as

well as from sabotage of pipelines for economic and political reasons (Bob-Manuel and Johnson, 2001). Other remote causes of oil spill are the low-level of technological know-how, the weakness of our laws and their feeble enforcement, the callousness of multinational enterprises participating in the oil business in the country, and the carelessness of various personnel within and outside the industry (Ebuehi *et al.*, 2005). Widespread spillages on soil, in rivers, creeks, ponds and wells in the riverine areas of the country have rendered arable soils and good drinking water scarce, and many victims of the pollution have suffered from diarrhea and dysentery (Albert *et al.*, 2018). Most products from oil are toxic to wildlife, which when incorporated in the food chain will also be poisonous to humans. This knowledge has increased

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scientific interest in studying the distribution, fate and behavior of oil and its derivatives in the environment (Semple *et al.*, 2006). Natural attenuation is the monitoring of natural processes in soil and groundwater environments that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in those media (Jørgensen, 2011). It is a bioremediation method used to treat polluted environments, in which microorganisms contribute to pollutant degradation without deliberate human interventions. For risk assessments and endpoint forecasting, natural attenuation sites are carefully monitored over a long period of time until the contaminated site returns to comparable ambient levels in pollutants loading. On the other hand, when site assessments require rapid removal of pollutants, enhanced natural attenuation bioremediation, categorized into biostimulation (introduction of nutrients and chemicals to stimulate indigenous microorganisms) and bioaugmentation (inoculation with exogenous microorganisms), can be applied. Of the available remediation techniques, the enhanced natural attenuation is the least expensive in environmental management, because the technique could be practiced with little or no expertise and in a natural environment. This study therefore investigated the effect of enhanced Natural Attenuation Remediation (ENA) on chronically oil-impacted soil in some communities of Ogoniland, Rivers State, Nigeria.

Tai, Gokana and Khana LGAs) is located between latitudes 4°36'0" and 4°47'0"N and longitudes 7°16'30" and 7°27'30"E (Figure 1). The area is within the tropical rainforest zone of Nigeria, with surplus rainfall, plain landform, thick natural vegetation and as well as abundant mineral resources. The natural vegetation has been depleted as a result of population growth, persistent farming and rapid socio-economic development, including but not limited to mineral exploitation. This has thus, predisposed the area to high level of natural and man-made environmental hazards such as soil erosion, flooding and oil pollution. The climate is typical of the tropics; with average rainfall of 200 mm, mean ambient temperature of 28°C, and relative humidity oscillating between 88 and 98% (SPDC, 2002). Wet season usually lasts between March and November, while the dry season lasts the remaining four months. The soil is composed mainly of sandy-loam (SPDC, 2002), and economic trees including oil palm (*Elaeis guineensis*) and rubber (*Hevea brasiliensis*) dominate the area. Annual crops, mainly cassavas and maize, as well as pineapples, okra and other vegetables are grown extensively in farm plots. Oil exploration and exploitation activities started in the area in the late 50's and early 60's, and currently, there are several oil wells and pipelines criss-crossing the areas. Several oil-spill incidences occurred over time at various locations in the areas, with many from pipeline vandalism that resulted in the spillage of large quantities of crude oil into several hectares of adjoining farmlands and forest (Plate 1). Following these incidents, locals have engaged in illegal oil bunkering and artisanal refining activities that tend to worsen environmental damages inflicted by spills alone.

MATERIALS AND METHODS

Description of the Study Area: Ogoniland, comprising four Local Government Areas (LGAs) (viz, Eleme,

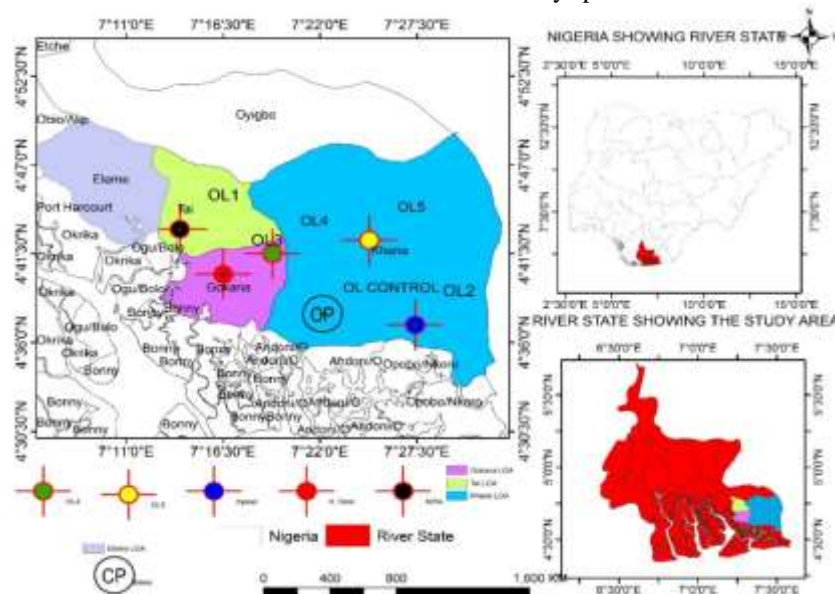


Fig. 1. Map of the Local Government Areas (LGAs) of Ogoniland in Rivers State, Nigeria showing six sampling locations (OL 1-OL Control)

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Research Design/Strategy and Sampling locations:

The research involved the application of bioremediation techniques in the amendment of crude oil-contaminated soil. Quality assurance procedures were strictly adhered to in sample collections and laboratory analyses. The longitudes and latitudes of 5 impacted sampling locations (OL 1-OL 5) and an unimpacted (Control) location (OL Control) are presented in Table 1.

Soil profile sampling: Soil samples were collected at 0.5m depth intervals during a drilling exercise up until the first shallow aquifer was reached during drilling of site monitoring boreholes from the 6 locations; with location 6 (OL Control) sited in a community/location free from oil-spill impacts.



Plate 1. Large volumes of crude oil spilled into the surrounding environment at one of the communities studied in Ogoniland (Source: Robin, 2019)

Table 1. Longitudes and latitudes of the communities serving as sampling locations

Location	Longitude	Latitude	Community	LGA
OL 1	4.6033	7.4674	Kpean	Khana
OL 2	4.7323	7.2596	Bara-Alue Kira	Tai
OL 3	4.6637	7.2836	K. Dere	Gokana
OL 4	4.7304	4.2588	Bara-Alue Kira	Tai
OL 5	4.6045	7.4680	Kpean	Khana
OL Control	4.7460	7.4777	Nyowii Bangha	Khana

Soil Remediation Exercise: At each sampling location, oil-contaminated soils were excavated up to reasonable depths, spread, mixed to a depth of about 0.5 m with plants and animal dungs, and ploughed. Ploughing and tilling were conducted twice with digger and spade, and then homogenized. Composted plants and animal (poultry) dung, as well as nitrate-phosphate-potassium (NPK) fertilizer were added during the homogenization. Windrows (ridges) were constructed and then leveled at alternate times during the entire exercise that lasted 17 weeks.

Laboratory Analyses

Soil Samples: This was in keeping with standard methods of APHA (2002). THC contents were obtained by shaking 10 g of a representative soil sample with 20 mL toluene and oil was extracted. The extracted oil was determined with absorbance at 420nm wavelength in a Spectronic 21-D spectrophotometer. Concentration was then calculated with reference made to the standard curve that was prepared using a known concentration of

hydrocarbons in the extractant. Multiplication was made by the appropriate dilution factor.

The method of Pansu and Gautheyrou (2006) was employed in the determination of soil pH; whereby air-dried soil sample was passed through a 2 mm sieve and afterwards, 20 g of it was placed in a 50 mL beaker. Forty milliliters of distilled water was added to it and the mixture was stirred with glass rod and allowed to stand for 30 minutes. The pH value was read off a Corning pH meter (Model 7).

The Bougoucou hydrometer method, as modified by Pansu and Gautheyrou (2006) was used to determine textural classifications. The soil samples were dispersed with solution of sodium hexametaphosphate (Calgon 44g/L) and sodium carbonate (8g/L). The pH of the solution was maintained at about 8.3, and the textural classes determined using the textural triangular diagram.

For the exchangeable cations, 1 g of soil sample was put into digesting tube following the addition of 10 mL conc. HNO_3 . Sample was placed in the digester for 8 hrs at 96°C with intermittent stirring, and upon complete digestion, it was filtered into 100 mL volumetric flask using Whatman No. 42 filter papers. Sample was made up to 100 mL mark in the volumetric flask with distilled deionized water. The concentrations of K^+ , Ca^{2+} , Mg^{2+} and Na^+ ions in the supernatant solution was determined using Varian Spectr-AA 600 Atomic Absorption Spectrophotometer (AAS), with air acetylene flame connected to it.

The monocalcium phosphate extraction method was used to determination of sulphate in the soil samples (Pansu and Gautheyrou, 2006). Ten grams of air-dried and sieved soil sample was placed in a 50 mL Erlenmeyer flask, exactly 25 mL of monocalcium phosphate extracting solution was added, and the resulting solution shaken at 200 oscillations per min. for 30 minutes. Exactly 0.25 g of charcoal was added to each sample and shaken for an additional 3 mins. The solution was then filtered through a sulphate-free Whatman No. 42 filter paper. Exactly 10 mL of the filtrate was pipetted from the extraction process, transferred into a 50 mL Erlenmeyer flask, and 1 mL of acid "seed" solution added. The solution was swirled and 0.5 g of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ crystals added. The mixture was allowed to stand for 1 minute, and then swirled with magnetic swirler in the flask frequently until the crystals got dissolved. Within the time interval of 3 to 8 minutes, the transmittance was read on a HACH DR 2010 UV-visible spectrophotometer at a wavelength of 420 nm. The absorbance reading was recorded by plotting absorbance against concentration on a linear graph paper. The sulphate concentration from the standard curve for 10g sample of soil sample was calculated as follows:

$$\text{MgSO}_4 \text{ as } \frac{S}{\text{kg}} \text{ of soil} = \text{mg} \frac{S}{L} \times 2.5$$

For available phosphorus, first, the extracting solution was prepared by adding 15 mL of 1M ammonium fluoride and 25 mL of 0.5N HCl to 460 mL distilled water. Then 1g of air-dried and sieved (through a 2mm mesh size) soil sample was weighed into a centrifuge tube and 7 mL of the extracting solution was added. This mixture was shaken for 1 min. and then centrifuged. Two milliliters of the clear supernatant was transferred into a 20 mL test tube, followed by the addition of 5 mL distilled water and 2 mL ammonium solution. To the mixture was added 1 mL of chloride solution. Within 20 minutes, the percent transmittance was measured in a spectrophotometer at 660 nm wavelength. The amount of available PO_4^{3-} ion in

sample was determined from the standard curve prepared with phosphate in soil standard solution (Pansu and Gautheyrou (2006).

The electrical conductivity (EC) of soil samples was determined on the filtrate obtained after filtering the suspension used for pH determination. The Lovibond conductivity meter (Model CM-21 Bridge) was used in measuring conductivities in $\mu\text{S}/\text{cm}$ (Pansu and Gautheyrou (2006).

Total nitrogen was determined by the Macro Kjeldah method as described by Pansu and Gautheyrou (2006). Five grams of a representative soil sample was shaken with 50 mL of 1N K_2SO_4 . Aliquot of the resulting extract was used to determine the nitrogen content by the phenoldisulphonic acid method.

Organic carbon was determined by wet combustion method of Pansu and Gautheyrou (2006). Two grams of soil sample was weighed out in duplicates and transferred to 250mL Erlenmeyer flask. A pipette was used to transfer 10mL of 1N $\text{K}_2\text{Cr}_2\text{O}_7$ solution into the flask and the flask was gently swirled to disperse the soil. Rapid addition of 20mL conc. H_2SO_4 was made using an automatic pipette, directing the stream into the suspension. Immediately the flask was swirled gently until soil and reagents got mixed. Then it was swirled vigorously for 1 minute. The flask was then allowed to stand for 30 minutes on a sheet of asbestos.

After standing for 30 minutes, 100mL of distilled water was added. Four drops of o-phenanthroline-ferrous indicator was added and titration with 0.5N ferrous sulphate solution followed. Approach to end-point of titration was marked by the solution changing from greenish cast to dark green colour. At this point, the ferrous sulphate was added drop-wise until the colour changed sharply from blue to red (maroon colour) in reflected light against a white background. A blank titration was also made without soil sample to standardize the dichromate. Result was computed and organic carbon expressed in percentage.

Statistical Analyses: Descriptive statistics and variation plots were employed to show variations in hydrocarbon levels and other edaphic variables. The one-way ANOVA was used to explore spatial variations in concentrations of hydrocarbon contaminants and other edaphic parameters at the 95% confidence interval. Post-hoc Duncan multiple range test was used to separate means of the parameters spatially. The Student's t-test was used to compare means of the soil parameters before and after remediation exercise.

RESULTS AND DISCUSSION

Petroleum Hydrocarbons contamination across soil profiles: At the contaminated soil surface (0.0 m depth), highest THC concentrations of 40,645.00, 60.00, 30.00, 44.00 and 4,346.00 mg/kg were recorded at OL 1, OL 2, OL 3, OL 4 and OL 5 respectively, and least concentration of 3.30 mg/kg was recorded at the OL control location (Table 2). At 1.0 m soil depth, THCs concentrations of 1,514.00, 30.00, 8.00, 28.00 and 1,412.0 mg/kg were recorded at OL 1, OL 2, OL 3, OL 4 and OL 5 respectively, and 3.20 mg/kg was

recorded at the control location. At 2.0 m depth, THCs concentrations of 1,193.00, 17.00, 124.00, 26.00, 1,003.0 and 10.5 mg/kg were recorded at OL 1, OL 2, OL 3, OL 4, OL 5 and the control respectively. At 3.00 m depth, concentrations were 313.00, 3.38, 3.30, 13.00, 310.00 and 3.30 mg/kg at OL 1, OL 2, OL 3, OL 4, OL 5 and OL Control respectively. At 4.00 m depth, concentrations were 158.00, 3.00, 3.13, 7.00, 150.00 and 3.10 mg/kg were recorded at OL 1, OL 2, OL 3, OL 4, OL 5 and the control locations respectively.

Table 2. Distribution of Total Petroleum Hydrocarbons (THCs) across soil profiles impacted by oilspill at locations in Ogoniland

Depth (m)	THC concentrations (mg/kg) at the sampling locations (OLs)					
	OL 1	OL 2	OL 3	OL 4	OL 5	OL Control
0.0	40,645.00	60.00	30.00	44.00	4,346.00	3.30
0.5	1,679.00	55.00	3.32	32.00	1,569.00	4.00
1.0	1,514.00	30.00	8.00	28.00	1,412.00	3.20
1.5	1,778.00	33.00	74.00	24.00	978.00	2.20
2.0	1,193.00	17.00	124.00	26.00	1,003.00	10.50
2.5	252.00	5.00	190.00	19.00	350.00	3.38
3.0	313.00	3.38	3.30	13.00	310.00	3.30
3.5	419.00	3.00	3.00	8.00	350.00	3.12
4.0	158.00	3.00	3.13	7.00	150.00	3.10
4.5	75.00	3.20	3.20	3.00	70.00	1.50
5.0	140.00	4.11	27.6	6.00	88.00	1.20
5.5	69.00	8.20	3.50	5.00	70.00	1.20
6.0	55.00	3.30	11.70	7.00	65.00	0.50
6.5	50.00	3.00	4.00	4.00	50.00	0.50
7.0	42.00	3.00	2.80	2.00	40.00	0.20
7.5	22.00	3.38	3.00	3.00	36.00	ND
8.0	13.00	3.30	2.60	2.00	12.00	ND
8.5	11.00	3.10	2.10	2.10	10.00	ND
9.0	8.00	2.70	3.38	1.30	7.00	ND

ND=Not Detectable

At the depth of 5.0 m, THCs concentrations of 140.00, 4.11, 27.60, 6.00, 88.00 and 1.20 mg/kg were recorded at OL 1, OL 2, OL 3, OL 4, OL 5 and the control locations, and at 6.0 m soil depth, they were 55.00, 3.30, 11.70, 7.00, 65.00 and 0.50 mg/kg at the respective locations. At 7.0 m depth, concentrations at OL 1, OL 2, OL 3, OL 4, OL 5 and the control locations were 42.00, 3.00, 2.80, 2.00, 40.00 and 0.20 mg/kg respectively. At 8.0 m depth, concentrations of 13.00, 3.30, 2.60, 2.00 and 12.00 mg/kg were recorded at the OL 1, OL 2, OL 3, OL 4 and OL 5 locations respectively. However, THCs concentrations were undetected at the control location. At the 9.0 m depth where the first shallow aquifer was reached, THCs concentrations of 8.00, 2.70, 3.38, 1.30 and 7.00 mg/kg were recorded. Again, THCs were undetected at the control location at this depth (Table 2).

Edaphic variability and oil spill remediation: Variability were also observed in the soil parameters measured at the oil impacted locations before and after remediation exercise. Mean pH had decreased from 6.0 (± 0.1) before Remediation (B_{Rem}) to 5.0 (OL 1)

After Remediation (A_{Rem}), 5.3 (± 0.2) B_{Rem} to 5.0 A_{Rem} (OL 4) and from 5.7 (± 0.01) B_{Rem} to 5.2 A_{Rem} (OL Control). However, it had increased from 5.4 (± 0.1) B_{Rem} to 5.5 A_{Rem} (OL 2), and 4.7 (± 0.01) B_{Rem} to 5.1 A_{Rem} (OL 3) (Fig. 2). pH was unchanged (5.4) at OL 5 (Fig. 2). EC had increased from 53 (± 8.5) B_{Rem} to 85 $\mu S/cm$ A_{Rem} (OL 1), 55 (± 2.0) B_{Rem} to 90 $\mu S/cm$ A_{Rem} (OL 2), 28 (± 3.0) B_{Rem} to 88 $\mu S/cm$ A_{Rem} (OL 3), 48 (± 6.0) B_{Rem} to 82 $\mu S/cm$ A_{Rem} (OL 4), 55 (± 3.4) B_{Rem} to 88 $\mu S/cm$ A_{Rem} (OL 5) and 33 (± 0.5) B_{Rem} to 86 $\mu S/cm$ A_{Rem} (OL Control) (Fig. 2). Carbon-Nitrogen (C/N) ratios had increased from 17.0 (± 1.6) B_{Rem} to 26.0 A_{Rem} at OL 1, 16.0 (± 3.0) B_{Rem} to 23.0 A_{Rem} at OL 4, and 9.0 (± 0.4) B_{Rem} to 60.0 A_{Rem} at OL Control. C/N ratios had decreased from 64.0 B_{Rem} to 37.5 A_{Rem} at OL 2, 66.0 B_{Rem} to 28.25 A_{Rem} at OL 3 and 64.0 B_{Rem} to 33.5 A_{Rem} at OL 5 (Fig. 2). THC had decreased from 351.7 (± 97.5) B_{Rem} to 161.4 mg/kg A_{Rem} at OL 1, 5035.30 (± 61.8) B_{Rem} to 2587.3 mg/kg A_{Rem} at OL 2, 2990.7 (± 37.8) B_{Rem} to 497.4 mg/kg A_{Rem} at OL 3, 305.55 (± 26.9) B_{Rem} to 150.0 mg/kg A_{Rem} at OL 4, 5035.30 (± 51.1) B_{Rem} to 158.6 mg/kg A_{Rem} at OL 5, and 65.96 (± 9.9) B_{Rem} to 37.5 mg/kg A_{Rem} at OL

Control (Fig. 3). Available phosphorus contents had decreased from 13.1 (± 8.2) B_{Rem} to 12.52 $\mu\text{g/g}$ A_{Rem} at OL 1, 34.00 (± 1.35) B_{Rem} to 10.7 $\mu\text{g/g}$ A_{Rem} at OL 2, 38.9 (± 7.3) B_{Rem} to 7.5 $\mu\text{g/g}$ A_{Rem} at OL 3, increased from 13.0 (± 2.2) B_{Rem} to 13.2 $\mu\text{g/g}$ A_{Rem} at OL4, and decreased 34.00 (± 2.2) B_{Rem} to 10.50 $\mu\text{g/g}$ A_{Rem} at OL 5, and 15.8 (± 1.7) B_{Rem} to 11.25 $\mu\text{g/g}$ A_{Rem} at OL Control (Fig. 3). K⁺ ion contents had decreased from 64.1 mg/kg (± 14.1) B_{Rem} to 2.51 $\mu\text{g/g}$ A_{Rem} at OL 1, 75.6 (± 7.7) B_{Rem} to 1.79 $\mu\text{g/g}$ A_{Rem} at OL 2, 71.8 (± 1.3) B_{Rem} to 1.42 $\mu\text{g/g}$ A_{Rem} at OL 3, 63.8 (± 0.00) B_{Rem} to 2.50 $\mu\text{g/g}$ A_{Rem} at OL 4, 75.6 (± 5.1) B_{Rem} to 1.70 $\mu\text{g/g}$ A_{Rem} (OL 5) and 59.0 (± 1.3) B_{Rem} to 0.87 $\mu\text{g/g}$ A_{Rem} at OL Control (Fig. 3).

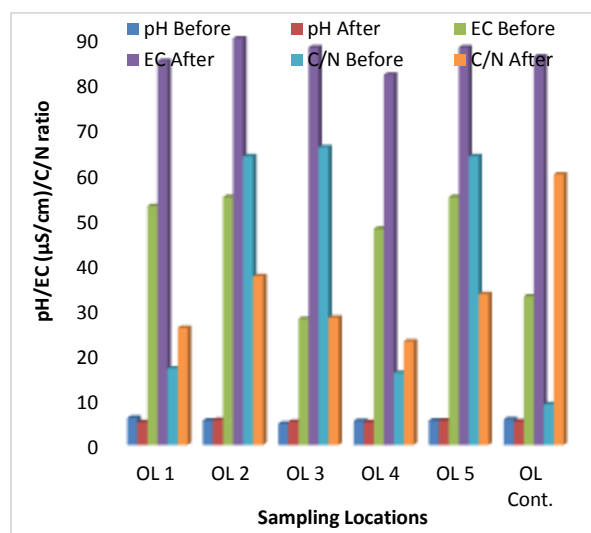


Fig. 2. Variations in pH, Electrical conductivity and C/N ratios in oil-impacted soil before and after remediation

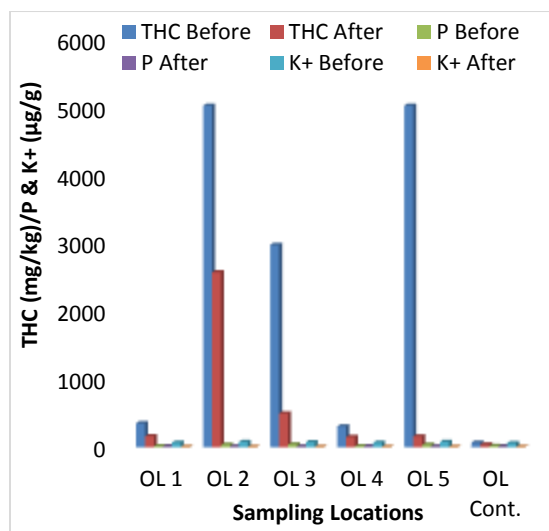


Fig. 3. Variations in levels of Total Petroleum Hydrocarbons, available P and K ions in oil-impacted soil before and after remediation

Organic carbon contents had decreased from 3.22 (± 1.24) B_{Rem} to 1.50 % A_{Rem} (OL 2), 3.62 (± 0.23) B_{Rem} to 1.13 % A_{Rem} (OL 3), and 3.22 (± 0.18) B_{Rem} to 1.45 % A_{Rem} (OL 5), and increased from 0.97 (± 0.22) B_{Rem} to 1.56 % A_{Rem} at OL 1, 0.94 (± 0.02) B_{Rem} to 1.46 % A_{Rem} at OL 4 (Fig. 3). Sulphate ion concentrations had increased from 8.5 (± 0.4) B_{Rem} to 9.0 $\mu\text{g/g}$ A_{Rem} (OL 1), 3.3 (± 0.3) B_{Rem} to 4.0 $\mu\text{g/g}$ A_{Rem} (OL 2), 5.0 (± 0.3) B_{Rem} to 6.0 $\mu\text{g/g}$ A_{Rem} (OL 3), decreased from 8.3 (± 0.3) B_{Rem} to 8.0 $\mu\text{g/g}$ A_{Rem} (OL 4), and increased from 3.3 (± 0.4) B_{Rem} to 4.0 $\mu\text{g/g}$ A_{Rem} (OL 5), and then decreased from 6.2 (± 0.2) B_{Rem} to 5.0 $\mu\text{g/g}$ A_{Rem} (OL Control) (Fig. 3).

Magnesium ions decreased from 1.2 (± 0.2) B_{Rem} to 0.30 mg/kg A_{Rem} (OL 1), 2.5 (± 0.1) B_{Rem} to 0.5 mg/kg A_{Rem} (OL 2), 3.4 (± 0.2) B_{Rem} to 0.2 mg/kg A_{Rem} (OL 3), 1.0 (± 0.1) B_{Rem} to 0.2 mg/kg A_{Rem} (OL 4), 2.5 (± 0.1) B_{Rem} to 0.5 mg/kg A_{Rem} (OL 5), and 2.1 (± 0.3) B_{Rem} to 0.5 mg/kg A_{Rem} (OL Control) (Fig. 3). Total nitrogen contents decreased slightly from 0.05 (± 0.01) B_{Rem} to 0.04 % A_{Rem} (OL 2), 0.06 (± 0.01) B_{Rem} to 0.04 % A_{Rem} (OL 3), 0.06 (± 0.01) B_{Rem} to 0.05 % A_{Rem} (OL 4), and 0.06 (± 0.01) B_{Rem} to 0.02 % A_{Rem} (OL Control) (Fig. 4). Sodium ion showed slight increases from 0.8 (± 0.01) B_{Rem} to 1.09 mg/kg A_{Rem} at OL 1, 0.9 (± 0.01) B_{Rem} to 1.13 mg/kg A_{Rem} at OL 3, 0.7 (± 0.02) B_{Rem} to 1.08 mg/kg A_{Rem} at OL 4, and 0.9 (± 0.01) B_{Rem} to 1.17 mg/kg A_{Rem} at OL Control, but had slightly decreased from 1.2 (± 0.0) B_{Rem} to 1.08 mg/kg A_{Rem} (OL 2), and 1.2 (± 0.05) B_{Rem} to 1.08 mg/kg A_{Rem} (OL 5) (Fig. 4). Calcium ions had increased from 0.8 (± 0.02) B_{Rem} to 1.4 mg/kg A_{Rem} (OL 2), 1.2 (± 0.05) B_{Rem} to 1.3 mg/kg A_{Rem} (OL 3), and 0.8 (± 0.0) B_{Rem} to 1.2 mg/kg A_{Rem} (OL 5), and decreased from 1.8 (± 0.3) B_{Rem} to 1.1 mg/kg A_{Rem} (OL 1), 1.7 (± 0.02) B_{Rem} to 1.0 mg/kg A_{Rem} (OL 4), and 0.9 (± 0.0) B_{Rem} to 0.8 mg/kg A_{Rem} (OL Control) (Fig. 4).

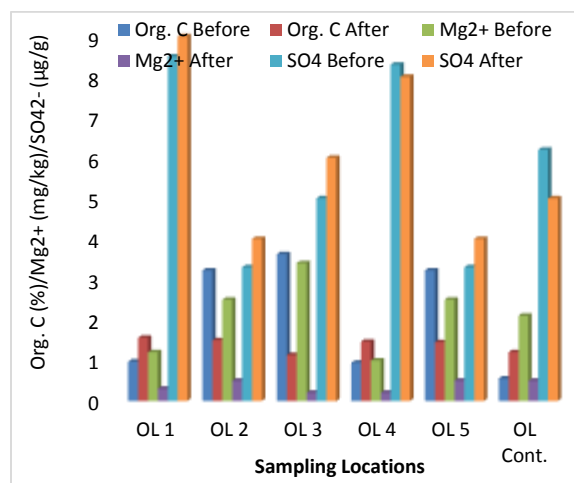


Fig. 3. Variations in levels of Organic C, Magnesium and Sulphate ions in oil-impacted soil before and after remediation

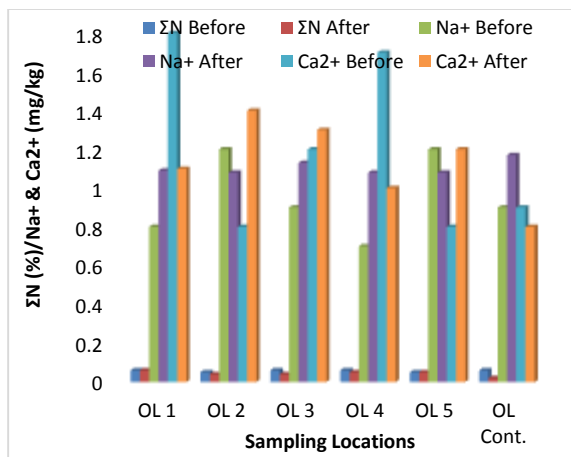


Fig. 4. Variations in levels of Total Nitrogen, Sodium and Calcium ions in oil-impacted soil before and after remediation

Of the textural classes, the composition of sand, silt and clay increased very slightly from 49 (±2) B_{Rem} to 51 % A_{Rem} at OL 2, 49 (±0.5) B_{Rem} to 50 % A_{Rem} at OL 5, and 64 (±0.5) B_{Rem} to 65 % A_{Rem} at OL Control (Fig. 5). However, they decreased from 60 (±1.5) B_{Rem} to 47 % A_{Rem} at OL 1, 74 (±1.3) B_{Rem} to 63 % A_{Rem} at OL 3, and 59 (±0.3) B_{Rem} to 55 % A_{Rem} at OL 4 respectively. Silt composition increased from 17 (±1.0) B_{Rem} to 34 % A_{Rem} at OL 1, 9 (±0.5) B_{Rem} to 26 % A_{Rem} at OL 3, 18 (±1.1) B_{Rem} to 32 % A_{Rem} at OL 4, 27 (±0.1) B_{Rem} to 28 % A_{Rem} at OL 5, and 14 (±0.4) B_{Rem} to 28 % A_{Rem} at OL Control (Fig. 5). Clay composition decreased from 23 (±1.0) B_{Rem} to 19 % A_{Rem} at OL 1, 25 (±1.2) B_{Rem} to 23 % A_{Rem} at OL 2, 17 (±0.5) B_{Rem} to 11 % A_{Rem} at OL 3, 23 (±1.2) B_{Rem} to 13 % A_{Rem} at OL 4, 24 (±1.1) B_{Rem} to 22 % A_{Rem} at OL 5, and 22 (±0.3) B_{Rem} to 7 % A_{Rem} at OL Control (Fig. 5).

The One-way ANOVA test revealed that the concentrations of THC (Sig._{value}=0.018), C/N ratios (Sig._{value}=0.050), SO₄²⁻ ions (Sig._{value}=0.000) and sand compositions (Sig._{value}=0.040) all differed markedly across the sampling locations at p<0.05. A mean separation technique with the Duncan Multiple Range test (Table 3) revealed that the observed difference in THCs was mainly between OL 1=OL 4=OL Control

and the other locations; that in C/N ratios was between OL 4 and the rest locations; that in SO₄²⁻ ions was between OL 1=OL 4, OL 2=OL 5 and OL 3=OL Control; while that in Sand composition was between OL 5 and the rest locations. However, there were also slight significant differences observed in pH mostly between OL 3 and the other sampling locations, and in organic carbon mainly between OL Control and the rest locations. A pair-wise comparison in concentrations of the edaphic variables measured using the Student's t-test revealed that mean concentrations of pH (Sig._{value}=0.048), EC and K⁺ ions (Sig._{value}=0.000 each), Na⁺ ions (Sig._{value}=0.006), Mg²⁺ ions (Sig._{value}=0.024), and the composition of clay (Sig._{value}=0.020) all differed significantly before and after the remediation exercise.

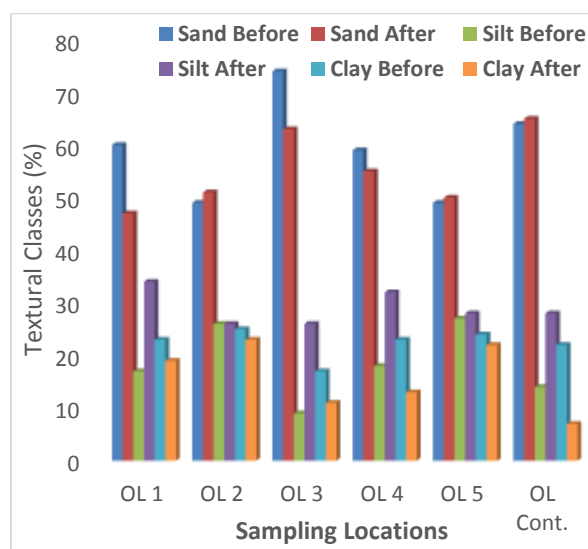


Fig. 5. Variations in Sand, Silt and Clay compositions of oil-impacted soil before and after remediation

Table 3. Mean separation in edaphic variables impacted by oilspill in Ogoniland using Duncan Multiple Range Test (p<0.05)

Parameters	Sampling Locations					
	OL 1	OL 2	OL 3	OL 4	OL 5	OL Control
pH	5.63b	5.43ab	4.83a	5.20ab	5.40ab	5.53ab
EC	63.66a	66.33a	48.00a	59.33a	65.66a	50.66a
THC	288.31a	4219.29a	2159.60ab	253.70a	3409.73b	56.47a
Organic C	1.16ab	2.64ab	2.78b	1.11ab	2.62ab	0.76a
ΣN	0.06a	0.04a	0.05a	0.05a	0.05a	0.04a
C/N ratio	19.66ab	54.83b	53.41b	18.00a	53.50b	26.00ab
Av. P	12.90a	26.20a	28.40a	13.03a	26.13a	14.28a
SO ₄ ²⁻	8.63c	3.53a	5.33b	8.20c	3.53a	5.80b
K ⁺	43.57a	50.99a	48.34a	43.33a	50.96a	39.62a
Na ⁺	0.86a	1.16a	0.97a	0.82a	1.16a	0.95a
Ca ²⁺	1.53a	0.96a	1.20a	1.46a	0.90a	0.86a
Mg ²⁺	0.86a	1.83a	2.33a	0.73a	1.83a	1.53a
Sand	55.33ab	49.66a	70.00b	57.66ab	49.33a	64.33ab
Silt	23.00a	26.00a	14.66a	22.66a	27.33a	18.66a
Clay	21.66a	24.33a	15.33a	19.66a	23.33a	17.00a

Values with same superscript along same row are not significantly different at p<0.05; EC=Electrical conductivity; THC=Total Petroleum Hydrocarbons; Av. P=Available phosphorus

Petroleum Hydrocarbon contamination across soil profile: Obviously, higher concentrations of the Total Petroleum Hydrocarbons (THCs) were detected at the topsoil profile at the oil-impacted locations. This reveals the surface spills that occurred at these locations over time, as already reported by Albert *et al.* (2018), among many other authors. More contaminations at these top soil profiles were recorded at sampling locations 1 and 5, indicating that more volumes of crude oil were spilled at those locations than the others during the period. As soil depths increased, THCs contaminations rather decreased. This indicates seepage and contaminant migration patterns often observed in soil profile, whereby less and less contaminant is transported deeper down the soil pores by both gravity and capillarity forces. This observation had also been made by other authors, including Daniel-Kalio and Braide (2004) and Ebuehi *et al.* (2005) in the Niger Delta area. THCs were also detected at the control borehole because the study area is within the oil-rich Niger Delta region, where many soil samples have traces of hydrocarbons. Other Researchers, including Ridderhof (2013) have made similar observation in the oil-rich Deltas of Nigeria. However, at about 7.5m and more soil depth, THCs contaminant was undetected at the control borehole, confirming the absence of surface spill and contaminant migration there.

Effect of remediation on edaphic variables: Similar to the work of Bello and Anobeme (2015) in a Nigerian Delta area, the current work revealed high concentrations of petroleum hydrocarbons in soil, and drastic decreases after remediation. There was a general decrease in the soil-oil contaminant by up to 50.41% at OL 2 after 17-week remediation. Similar to this outcome, Liu *et al.* (2010) had observed total petroleum hydrocarbon content reduction by 58.2% in treated plots after bioremediation for 360 days. The current observation rightly corresponded with appreciable improvement of carbon-nitrogen ratio, which got progressively lowered as the remediation proceeded, and with the decay and release of more organic nitrogen in the soils. The work of Essien and John (2010) in alluvial soils of the coastal plains of the Qua Iboe river wetlands in Akwa Ibom State also revealed similar trend. Wang *et al.* (2013) stated that naturally organic carbon in soil is generally derived from biota, such as peat formation with time, plant fine roots turnover, microbial biomass and others. However, crude oil contamination in oilfield soils might also contribute to the total organic carbon in the soil. The high concentration of THC in the oil-impacted soil might have resulted to the elevated total organic carbon content recorded. Wang *et al.* (2010) had reported that oil contamination significantly

increased the total organic carbon contents most probably because of the much higher THC concentration in spilled sites. The current work reveals both slight spatial increases and decreases in pH of soil after remediation. The results of previous studies on oilfields in China also showed that oil pollution raised soil pH (Jia *et al.*, 2009; Wang *et al.*, 2010). The higher pH values in crude oil-polluted soil in this study might be caused by two factors: first, the hydrophobic nature of crude oil might induce a potential drought in the surface and subsurface layers of polluted soil (Njoku *et al.*, 2009), which could aggravate salinization, and thus raise the pH values compared with that in the control location. Second, oil pollution in soil has been shown to be associated with the accumulation of exchangeable base (such as Ca^{2+} and Na^{+}) and a reduction in exchangeable acidity and effective cation exchange capacity (Osuji *et al.*, 2006; Agbogidi *et al.*, 2007). These mechanisms might also underpin the increases of pH values in the crude oil polluted soil. However, the mechanisms may not have operated in locations where decreases in pH were recorded in the current work. Across the sampling locations, the levels of petroleum hydrocarbons, carbon-to-nitrogen ratios, SO_4^{2-} ions, and sand composition, as well as pH levels and organic carbon contents all improved significantly after the remediation. Edaphic properties that showed significant decreases in their concentrations after remediation include THC, and Mg^{2+} ions, as well as sand and clay compositions. However, electrical conductivity, sodium and potassium ion concentrations showed increases in their concentrations after remediation. These all contributed to improved soil quality in the area. Results of previous study showed that oil contamination could decrease available phosphorus concentration in soil by various degrees (Wang *et al.*, 2010). A field study on the Momoge wetlands in China showed that the concentration of available phosphorus decreased with increasing time of oil exploration and production (Wang *et al.*, 2010). Similar decreases were however observed in the current work only after remediation. In another experimental oil study, the concentration of available phosphorus in crude oil-contaminated soil decreased as much as 66% compared with the control site when the content of crude oil reached 30 mg/kg (Eneje *et al.* 2012). However, Liu *et al.* (2010) reported that available phosphorus concentrations are not significantly affected by oil contamination. In the present study, lowered available phosphorus concentrations after remediation in all the impacted locations may have been enhanced by two reasons. First, THC in the soil could increase the carbon concentration, which might affect the equilibrium of nutrients in the soil. Microbes in soils, which utilize THC as a carbon source, could utilize considerable

amounts of available phosphorus when they degrade the hydrocarbons (Wang *et al.*, 2013). Second, phosphorus solubility is maximized at near-neutral pH, and higher pH values in some locations of the work may have also lowered the available phosphorus concentration compared with the concentration in the control location. Phosphorus is one of the most important macro-nutrients for plants and soil microorganisms. The decrease of available phosphorus concentrations in impacted locations could change the structure of vegetation and soil microorganisms, and reduce soil ecosystem services and values.

Conclusion: In its aim to employ conventional enhanced natural attenuate (=landfarming) technique in the remediation of an oil-impacted soil, this study reveals the effectiveness of bioaugmentation with simple, locally-available manure, as well as synthetic fertilizer (NPK) in the restoration of the productivity of arable soil in Ogoniland in the Delta area.

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