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Full Length Research Paper

An appraisal of the impact of petroleum hydrocarbons on soil fertility: the Owaza experience

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Major fertility indices - N, P, K, TOC and TOM contents - were examined against the backdrop of physic-cochemical conditions of pH, temperature, moisture content and electrical conductivity of soils three months after oil spillage at Owaza in the Niger Delta region of Southern Nigeria. Evidence of severe hydrocarbon contamination was provided by high extractable hydrocarbon content of 3.4 x 10^3 – 6.8 x 10^3 mg/kg. High soil acidity (low pH of 4.9 – 5.1), low electrical conductivity as well as high temperature and moisture content, all provided evidence of reduced metabolic activities on the affected site which explains the relatively low TOC/TOM values obtained. These conditions generally imply low soil fertility, which in turn implies low agricultural productivity and reduced source of livelihood in the affected area. Based on the results obtained, contingency/remedial measures should include the application of appropriate and sufficient inorganic NPK fertilizer to restore the carbon to nutrient ratios to the optimum required to stimulate and sustain microbial activity; adjustment of the pH to 6.0 – 6.5 by the addition of calcitic lime; stimulation of indigenous microbial growth by cultivating the soil to distribute the nutrients and lime and appropriate aeration of the treatment zone.

Key words: Owaza, petroleum hydrocarbons, oil spillage, primary macronutrients (N, P and K); soil fertility.

INTRODUCTION

The exploration and exploitation of petroleum hydro-carbons have been with Nigerians for decades now and their concomitant effects on the oil producing communities have been quite problematic. These activities, though developmental, have elicited all kinds of impact, ranging from the barely tolerable ones to utterly disastrous effects. For instance, the activities are known to have decimated terrestrial and aquatic biota, which constitute the peoples' major source of livelihood. While much have been written and documented in these areas, soil fertility still remains one of the inextricable effects that has received insufficient attention.

Soil fertility may be defined as the capacity of the soil to support the growth of plants on sustained basis under given conditions of climate and other relevant properties of land (Aina and Adedipe, 1991). Loss of soil fertility through loss of soil organic matter, leaching of nutrients, loss of the nutrient-laden topsoil, changes in soil-pH, reduction in cation exchange capacity, salinization, water logging and other forms of soil degradation are major problems associated with agricultural productivity in the oil producing areas of Nigeria. In a study conducted for NEST/ Ford Foundation in the Niger Delta, NDES (1999) reported that soil fertility loss and declining crop yield, among others, were of "high priority" because these were found to be indirect sources of pressure on natural resources and community structure, especially amongst the poor. The reality of these and other socio-economic effects in areas where oil pollution has already taken place, and their anticipation in areas prone to experience oil spill, have continued to provoke concern in the Niger Delta region.

Oil is known to exert adverse effects on soil properties and plant community. Beyond 3% concentration, oil has been reported to be increasingly deleterious to soil biota and crop growth (Baker, 1976; Amadi et al**.**, 1993; Osuji et al., 2005). Unfortunately, available data to manage the ecological spoils of the Niger Delta region have been found inadequate. Though these data have found various uses in the post-spill management programme of affected ecosystems and communities, recent advances have sh-

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Figure 1. A photographic plate of the cross-sectional view of the spill site at Owaza, Niger Delta (Nigeria).

shown that such data have been specific to particular sites and incidents, largely because of the nature of the crude oil contaminant and possible environmental modify-cations (Osuji et al., 2006a and b).

Consequently, contemporary works have been focused on the monitoring and management of site-specific areas. Seasonal records of hydrocarbon content, for instance, shall enhance our ability to confirm the extent of pollution, by comparing with data from virgin areas or regulatory bodies. In the present study, we have attempted to appraise "soil fertility", a very important index of agricultural productivity. The overriding objective of this study was to provide an impetus towards the effective remediation of the large expanse of farmsteads polluted by the oil spill at Owaza, one of the oil producing communities in the petroliferous Niger Delta.

MATERIALS AND METHODS

Site description

The study site is around the vicinity of Imo River-2 flow station at Owaza in Abia State of Nigeria, located East of Nkali and North of Isimiri flow stations in the Niger Delta Basin. The release was caused by valve failure at the relief pit behind the flow station (Figure 1) and covered over five hectares of arable land. The release occurred September 20, 2003 and sampling was carried out October 12, 2003, allowing a post-impact period of approximately three weeks; samples were put in the refrigerator prior to laboratory analyses on 14th of October 2003. An estimated 30,000 barrels (approximately 4.8 million litres) of crude oil was released.

Historical antecedence and geo-characteristics of soils

Over twenty-eight soil types from various soil zones of the Niger Delta have been identified. The study site soils fall within the Agbada-1 and Agbada-2 prospect areas of the Niger Delta Basin and, are believed to have been derived from the quartenary Warri – Sombreiro plains; the major underlying bedrock of the area (Ilaco, 1966). This plain appears on either side of the recent alluvial plain and was deposited in the Late Pleistocene to Early Holocene time. It occupies an area similar to the present day delta but was mostly eroded away during the ice ages when the sea level was lower. The sediments occur as grey to dark grey/brown clayey-silty sands. These sediments likely retard vertical infiltration to a shallow aquifer around the Agbada flow station thereby limiting contamination to the near surface horizon.

Climate

The study area lies in the wet equatorial climatic region, with high cloud cover characterized by limited sunshine, extended high cloud cover, low sunshine hours and very high relative humidity most of the year. The study area records a mean daily temperature of 26^{o}C and monthly rainfall of 180 mm respectively; rain falls every month of the year with a short dry spell in the months of January to March (NDES, 1999).

Sampling design and soil collection

Sampling plots were erected at both the oil spill impacted site and unimpacted (control) sites by grid system (Figure 2). An impacted area was delimited by reconnaissance with the area of heaviest spill as the epicenter. A sampling area of 200 x 200 m^2 was divided into 100 grid plots, each measuring 20 x 20 m^2 and ⅓ of this (that is, 33 grid plots) was randomly selected. Soil samples were taken from three replicate quadrats of the oil-impacted and control plots.

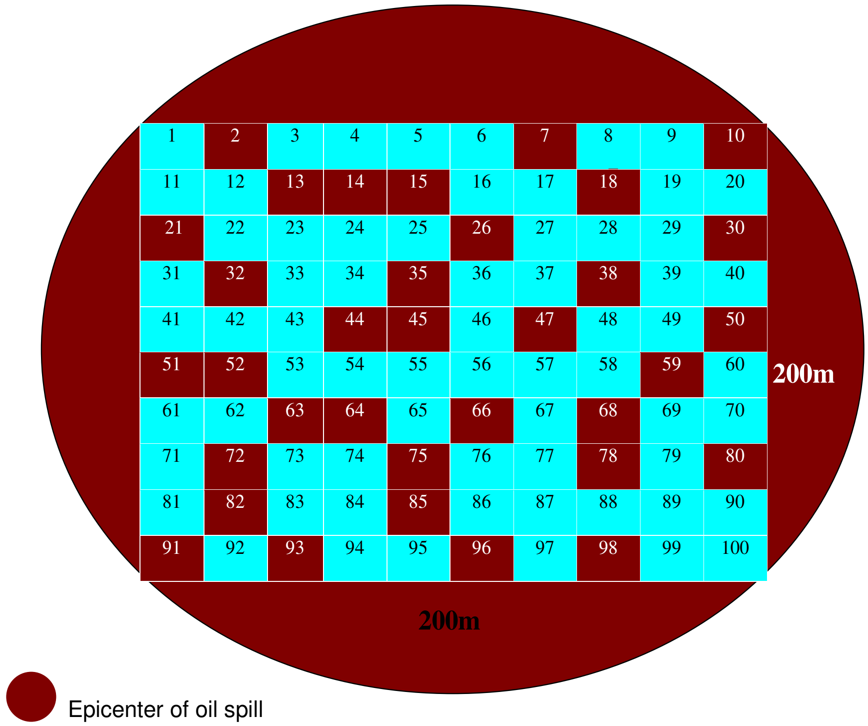

Figure 2. A schematic diagram showing grided areas and randomly sampled plots at Owaza oil spillage site in Niger Delta, Nigeria.

Soil samples were collected at surface (0 – 15 cm) and subsurface (15 – 30 cm) depths. The soil samples were put in aluminum foil paper bags, labeled and taken to the laboratory.

Laboratory analyses

Oil extraction and estimation of THC

Five grams (5 g) of each soil sample was weighed out and transferred into a 500 ml volumetric flask. Into this was added 50 ml of xylene. The xylene/soil mixture was shaken vigorously for five minutes and filtered into 400 ml cylinder. The volumetric flask and solid materials were rinsed properly with 500 ml xylene and filtered again into the cylinder. The xylene-oil extract was thereafter placed in cuvette wells and its absorbance was determined using Hack DR/2010 Particle Data Logging Spectophotometer. A calibration curve was obtained by measuring the absorbance of dilute standard solutions of lease oil (Bonny Light/Bonny Medium crude oils), prepared by diluting 2.5, 5.0, 10.0, 20.0, 25.0, and 30.0 microlitres of the lease oil with 50 ml xylene solution. Total hydrocarbon content (THC) was calculated after reading the absorbance of the extract from the spectrophotometer at a wavelength of 425 nm.

Determination of moisture content

A constant weight of watch glass was obtained and thereafter, 20 g of sample was weighed into the watch glass, and transferred into the oven for 1 h at 110°C. The samples were cooled inside a desiccator for 30 min before a constant weight of the sample and watch glass after heating and cooling was recorded. Moisture content was estimated as:

$$\% \text{ Moisture Content} = \frac{[W_1-(W_3-W_2)]}{W_1} \text{X100}$$

Where W1 = weight of sample;
W_2 = Constant weight of watch glass; and
W_3 = Weight of sample + watch glass after heating and cooling.

Determination of soil-pH and electrical conductivity (EC)

To five grams (5.0 g) of each soil sample (in a sample cell) was added 50 ml of distilled water. The lump of the soil was stirred to form homogenous slurry, then pH meter (Jenway 3015 model) and EC meter (Jenway 4010 model) probes were immersed respectively into the sample and allowed to stabilize at 25°C and pH of sample was recorded.

Total organic carbon (TOC) and total organic matter (TOM) contents

Half a gram (0.5 g) of each air-dried soil sample was put into a conical flask and 2.5 ml of 1N potassium dichromate solution $K_2Cr_2O_7$ was added and swirled gently to disperse the sample in the solution. 5 ml of concentrated tetraoxosulphate (VI) acid was added rapidly, into the flask and swirled gently until sample and reagents were mixed and finally swirled vigorously for about a minute. The flask was allowed to stand in a fume cupboard for 30minutes. Five to ten (5 to 10) drops of the indicator were added and the solution titrated with 0.5N $FeSO_4$ to maroon colour. A blank determination was carried out to standardize the dichromate (Nelson and Sommers, 1982). TOC and TOM contents were calculated as follows:

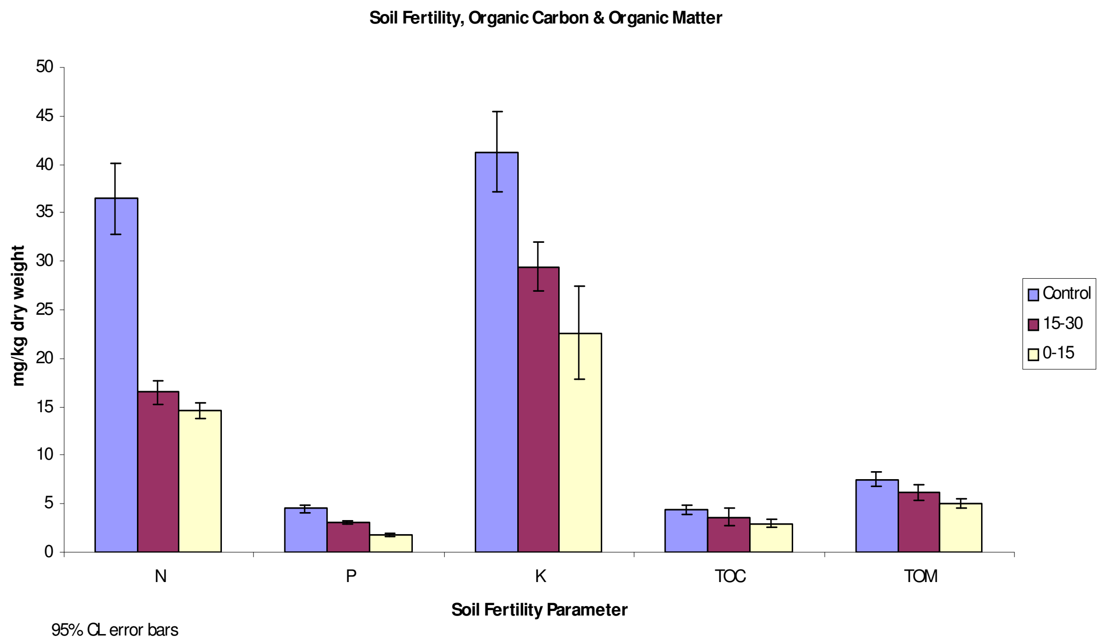

Figure 3. Mean concentration of soil fertility indices (± Standard Error at 95% Confidence Level) in oil impacted and control soils from Owaza, Niger Delta, Nigeria.

Table 1. Total extractable hydrocarbon content and physico-chemical properties of oil-affected and unaffected soils.

Nature/Depth of Soil	Nature/Depth of Soil	Nature/Depth of Soil	Nature/Depth of Soil	Nature/Depth of Soil
Oil-affected Surface Soil (0-15cm)	6,800±900	30.8±2.3	430±5	4.9±0.1
Oil-affected Subsurface Soil (15-30 cm)	3,400 ±202	30.0±1.7	688±16	5.1±0.1
Control	0.6±0.0	9.5±0.4	1,890±2328	5.6±0.1

$$TOC\ (\%) = \frac{(\text{meq } K_2Cr_2O_7 - \text{meq } FeSO_4) \times 0.003 \times 100 \times 1.3}{\text{Weight of sample (g)}}$$

Where: meq $K_2Cr_2O_7$ = 1N X 2.5 ml

meq $FeSO_4$ = 0.5 N X Volume of titrant in ml
0.03 = Milliequivalent weight of carbon
1.30 = Correction factor

TOM (%) = TOC (%) x 1.724

Where: 1.724 = Conversion Factor; **[i.e. %TOM = %TOC x 100 / 58; since TOC is 58% of TOM]**

Statistical analysis

Standard Error (±SE) was given as: $SE = SD / N^{1/2}$

Where SD is standard deviation and N, number of replicates. SE was estimated at 95% Confidence Limit (CL) by multiplying by 1.96

RESULTS AND DISCUSSION

Table 1 shows total extractable hydrocarbon content, and the physico-chemical properties of the oil-impacted and their background control soils. Some indices of gross fertility measured from the Owaza soils are summarized in Table 2.

Total hydrocarbon content (THC)

Hydrocarbon content of 3,400 – 6,800 mg/kg (no overlap in standard errors at 95% confidence limit), represents a high level of hydrocarbon contamination on the site. A review of existing data on the Niger Delta by NDES (1999), Osuji (2001) and Osuji et al (2004) affirms that such high hydrocarbon levels affect both above-ground and subterranean flora and fauna, which are essential adjuncts in the biogeochemical cycle that affects availability of plant nutrients. In general, plants require 16 essential elements for growth, 13 come from the soil, three of which (N, P, and K) constitute the primary macro-nutrients. The concentration of macronutrients in both the study and control areas are inherently low (Table 2 and Figure 3) compared to acceptable ranges of 15,000, 2,000 and 10,000 mg/kg for N, P, and K respectively (HSE-ENV, 2004) recommended for agricultural soils. The con-

Table 2. Mean level of soil fertility indices of oil affected and unaffected soils.

Nature/Depth of Soil	Mean Concentrations (±S. E @ 95% C.L) (mg/kg)				
	NO_3^-N	PO_4^-P	K	TOC	TOM
Oil-affected Surface(0-15cm)	14.6 ± 0.8	1.8 ± 0.2	22.6 ± 4.8	3.0 ± 0.4	5.1 ± 0.5
Oil-affected ubsurface (15-30cm)	16.5 ± 1.2	3.1 ± 0.2	29.4 ± 2.5	3.6 ± 0.9	6.1 ± 0.8
Control	36.5 ± 4.2	4.5 ± 0.8	41.3 ± 9.0	4.4 ± 0.6	7.5 ± 1.0

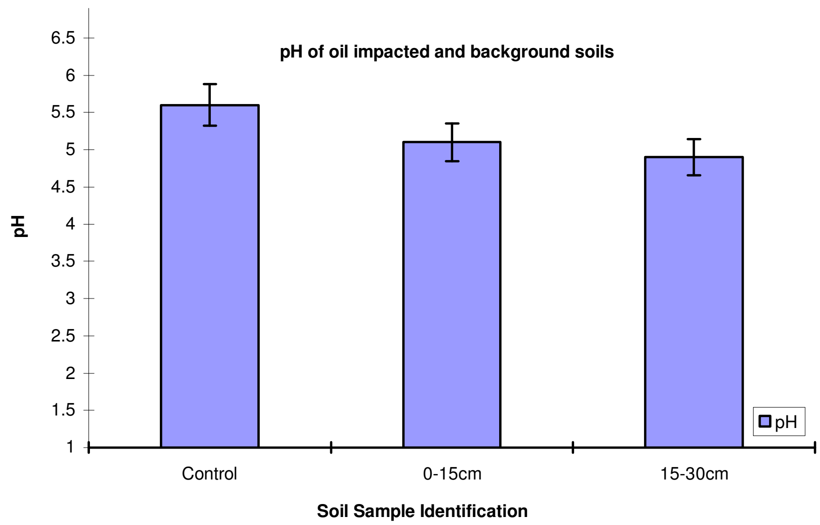

Figure 4. pH (± Standard Error at 95% Confidence Level) of oil impacted and control soils from Owaza in Niger Delta, Nigeria.

centrations of extractable macronutrients N, P and K in the oil-impacted area were significantly lower than in adjacent control plots. This may be due to interference with the extraction analysis due to free hydrocarbon in the soil but more likely to utilization/complexation of the nutrients by resident microflora. It is unlikely that the oil release is directly responsible for loss of macronutrients. However the intense infusion of degradable hydro-carbon likely stimulated aerobic and anaerobic microbial metabolism. As oxygen becomes limiting, utilization of alternate electron acceptors produces an increasingly reducing environment. Direct utilization of nitrate as a terminal electron acceptor would explain the dramatic differences in concentrations between the control plot and hydrocarbon impacted area. Because the concentrations of macronutrients are well below those recommended for agriculture, supplemental applications are required. Furthermore, the introduction of degradable hydrocarbon has altered the carbon to nutrient ratio well beyond recommended for balanced soil nutrition. The C:N, C:P and C:K ratios can be adjusted with the application of additional inorganic NPK fertilizers.

Moisture content

The higher moisture content of 30.8 ± 2.3% and 30 ± 1.7% in oiled surface and subsurface soils (*cf*: Table 1) can be attributed to insufficient aeration of the soil that might have arisen from the displacement of air in the soils; this probably encouraged water logging and reduced rate of evaporation. Partial coating of soil surfaces by the hydrophobic hydrocarbons might reduce the water-holding capacity of the soil due to some significant reduction in the binding property of clay. Usually, such "partial coats" lead to a breakdown of soil structure and the dispersion of soil particles, which reduce percolation and retention of water. Soils develop severe and persistent water repellency following contamination with crude oil (Osuji et al., 2006a). High moisture content might reduce microbial activities not as a result of the water itself but rather by the indirect hindrance to the movement of air which would reduce oxygen supply.

Soil-pH

The pH of the oil-impacted soils at both depths was significantly lower than the background soils but differences between the two depths were not significant (Figure 4).

Oiling must have discouraged the leaching of basic salts which are responsible for raising pH in the control. The binding of the oil with soil particulate matter in the affected area probably posed a major resistance to the removal of such basic ions. While the oil may have had

Table 3. Total extractable hydrocarbon content and physico-chemical properties of oil-affected and unaffected soils.

Nature/Depth of Soil	THC (mg/kg)	Moisture Content (%)	Conductivity (μScm^{-1})	pH
Oil-affected Surface Soil (0-15cm)	6,800±900	30.8±2.3	430±5	4.9±0.1
Oil-affected Subsurface Soil (15-30 cm)	3,400 ±202	30.0±1.7	688±16	5.1±0.1
Control	0.6±0.0	9.5±0.4	1,890±2328	5.6±0.1

some direct impact in lowering the pH, it is more likely that production of organic acids by microbial metabolism is responsible for the difference. The pH of the soil should be adjusted by aeration to complete the microbial mediated oxidation of organic acids while agricultural lime may be added to provide some buffering capacity to the soil.

Similarly, soil-pH might have affected nutrient availability. The pH is not only essential for determining the availability of many soil nutrients but also in determining the fate of many soil pollutants, their breakdown and possible movement through the soil. Therefore, pH in the range of 4.9 – 5.1 might have implications on nutrient availability in the oil-polluted soils. Such pH ranges, for instance, might have affected the solubility of minerals. It is known that strongly acidic soils (pH 4–5) usually have high concentrations of soluble aluminium and manganese, which are toxic to many plants; nitrogen fixation and decomposition activities are also known to be hindered in strongly acidic soils (Alexander, 1969; Obi, 1976; Manahan, 1994).

Electrical conductivity (EC)

Electrical conductivity (EC) is a measure of ionic concentration in the soils and is therefore related to dissolve solutes. EC was significantly lower in the oil-affected soils than in the control soils (Table 3). It is not likely that the released oil was directly responsible for the observed changes in EC since organic compounds like crude oil cannot conduct electrical current very well. However, it is possible that the anoxic biodegradation mechanism through direct dehydrogenation allowed the anaerobic metabolism of hydrocarbons in the presence of an electron acceptor such as nitrate ion, which may be partially responsible for the observed differences in EC. It is likely that the EC for the control site was different from the contaminated site prior to contamination.

Nitrate-nitrogen (NO_3-N) content

The reduction in the concentration of NO_3-N in the contaminated site suggests that the process of nitrification might have reduced following the incidence of oil spillage. According to Odu et al (1985), oil degrading or hydrocarbon-utilizing microbes such as *Azobacter* spp normally become more abundant while nitrifying bacteria such as *Nitrosomonas* spp become reduced in number. This probably explains the relatively lower values of NO_3-N obtained for the contaminated soils. Enrichments capable of the degradation of hydrocarbon fractions like toluene under anoxic denitrifying conditions have also been reported in agricultural soils, compost, aquifer material, and contaminated soils from various geographic regions of the world (Fries et al., 1994; Atlas and Bartha, 1997).

Total organic carbon (TOC) and total organic matter (TOM) contents

Total organic carbon and total organic matter contents were slightly lower than the 4.4 ± 0.6 and 7.5 ± 1.0 mg/kg obtained for the control soils. Organic matter content should normally increase following the addition of such levels of carbonaceous substances but results obtained herein show that there is rather a reduction in organic carbon and organic matter contents of the polluted soils (Table 2). The most plausible connection perhaps might be that the spilled-oil impaired the metabolic processes that would have facilitated the agronomic addition of organic carbon from the petroleum hydrocarbons by reducing the carbon-mineralizing capacity of the microflora (Osuji and Onojake, 2004; Osuji and Ukale, 2005). Thus, two decomposition processes are of significance to the present discussion: the decomposition of the soil organic matter and the decomposition of the added petroleum hydrocarbons. Both decomposition processes are however the prerogative of heterotrophic organisms. It is most likely that while these organisms might have been stimulated by the presence of the spilled-oil on site, their proliferation did not adequately cope with the business of breaking down the excess carbonaceous substrate, perhaps due to various factors that might include the environmental conditions of weathering and climatic predispositions as well as the physico-chemical properties earlier discussed (Osuji et al., 2006a).

Conclusion

The high hydrocarbon levels extracted from the Owaza oil spill affected plots have provided evidence of severe hydrocarbon contamination on the site. These conditions generally imply low soil fertility, which in turn implies low agricultural productivity and reduced source of livelihood in the affected area. The following clean up measures should be implemented immediately:

1. Application of appropriate and sufficient inorganic NPK fertilizer to restore the carbon to nutrient ratios to the optimum required to stimulate and sustain microbial activity (though the fact that 15ppm of nitrate remain in the soil suggests that adding more N may not have as much effect unless oxygen is added).
2. Adjustment of the soil pH to 6.0-6.5 by the addition of lime.
3. Stimulation of the indigenous microbial growth by cultivating the soil to distribute the nutrients and lime and to aerate the treatment zone.

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REFERENCES

Aina EOA, Adedipe NO (1991). Ed., The Making of the Nigerian Environmental policy. Federal Environmental Protection Agency, Lagos. p. 329.
Alexander M (1961). Introduction to Soil Microbiology. John Wiley and Sons Inc. New York and London. pp. 402–421.
Amadi A, Dickson A, Maate GO (1993). Remediation of oil polluted soils: 1.Effect of organic and inorganic nutrient supplements on the performance of maize (Zea may L.). Water Air Soil Pollut. 66: 59–76.
Atlas RM, Bartha R (1997). Microbial Ecology Fundamentals and Principles, 4th Ed. Benjamin/Cummings Science Publishing Company, Menlo Park, CA, USA. pp. 511–573.
Baker JM (1976). Ed., Marine Ecology and Oil Pollution. Applied Science Publishers Ltd., Essex England pp. 483–536.
Fries N, Zhai J, Chee-Sanford J, Ticdje JM (1994). Isolation, charaterization, and distribution of denitrifying toluene degraders from a variety of habitats. Appl. Environ. Microbiol. 60: 2802–2810.
HSE-ENV (2004). Accompanying guidelines for SPDC EIA process – Data collection. Vol. III.HSE-ENV, SPDC 2004 – 0002712
Ilaco NV (1966). NEDECO Report on the soil investigations in the Niger Delta Special Area. Main Report. The Hague, The Netherlands. p.162.
Manahan SE (1994). Environmental Chemistry. CRC Press, Inc. Florida. p.811.
NDES (1999). Niger Delta Environmental Survey Phase 1 Report, Vol.1 Environmental and Socio – Economic Characteristics (Revised Edition). Technical report submitted by Environmental Resource Managers Limited, Lagos. pp. 101 – 116
Nelson DW, Sommers LE (1982). Total carbon, organic carbon and organic matter. In: Page, A.L., Miller, R.H. and Keeney DR. (Eds.), Methods of Soil Analysis, Part *2.* American Society of Agronomy, Madison. pp. 539 - 579.
Obi AO (1976). Relative effects of different N. fertilizers on soil pH and crop yield in a Western Nigerian soil. Niger. Agric. J. 13: 95-101.
Odu CTI, Nwoboshi LC, Esuruoso OF (1985). Environmental studies (soils and vegetation) of the Nigerian Agip Oil Company operation areas. In: Proceedings of an International Seminar on the Petroleum Industry and the Nigerian Environment, NNPC, Lagos, Nigeria. pp. 274–283.
Osuji LC (2001). Total hydrocarbon content of soils, fifteen months after Eneka and Isiokpo oil Spills. J. Appl. Sci. Environ. Mgt. 5(2): 35-38.
Osuji LC, Adesiyan SO (2005). The Isiokpo oil-pipeline leakage: Total organic carbon/organic matter contents of affected soils, Chem. Biodiv. 2: 1079 – 1085.
Osuji LC, Adesiyan SO (2005). Extractable hydrocarbons, nickel and vanadium contents of Ogbodo-Isiokpo oil spill polluted soils in Niger Delta, Nigeria. Environ. Monit. Assess. 110: 129-139.
Osuji LC, Adesiyan SO, Obute GC (2004). Post impact assessment of oil pollution in the Agbada west plain of Niger Delta Nigeria: Field reconnaissance and total extractable hydrocarbon content. Chem. Biodiv. 1(10): 1569-1577.
Osuji LC, Iniobong DI, Ojinnaka CM (2006a). Preliminary investigation of Mgbede-20 oil-polluted site in Niger Delta, Nigeria. Chem. Biodiv. 3: 568-577.
Osuji LC, Onojake CM (2006). Field reconnaissance and estimation of petroleum hydrocarbon and heavy metal contents of soils affected by the Ebocha- 8 oil spillage in Niger Delta, Nigeria. Journ. Environ. Mgt. 79: 133-139.
Osuji LC, Egbuson EJG, Ojinnaka CM (2005). Chemical reclamation of crude-oil- inundated soils from Niger Delta, Nigeria. Chem. Ecol. 21(1): 1-10.
Osuji LC, Inimfon AU, Ogali RE (2006b). Attenuation of petroleum hydrocarbons by weathering: A case study. Chem. Biodiv. 3: 422-431.