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BIOREMEDIATION POTENTIAL OF ORGANIC POLLUTANTS IN A CRUDE OIL CONTAMINATED LOAMY SOIL IN NIGER DELTA REGION

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ABSTRACT

This study investigated the instigation of organic pollutants in crude oil-contaminated loamy soils in Nigeria. The findings demonstrated that contamination alters soil physico-chemical properties, increases levels of toxic hydrocarbons, and reduces microbial diversity. While hydrocarbon-degrading microbes adapt and proliferate, the persistence of pollutants like PAHs and asphaltenes indicates a long-term ecological challenge. The results emphasize the urgent need for remediation measures and stricter environmental management in oil-producing regions.

Keywords: Bioremediation, Organic, Pollutants, Crude Oil, Contaminated Soil

1.0 INTRODUCTION

Urbanization and industrialization has resulted to a widespread environmental pollution notably in the Niger Delta region of Nigeria. Nigeria happens to fall within the largest oil producing and exporting nation across the world. And the Niger Delta is not an exception within the Nigerian State, arguably the highest producer of oil and gas products which doubles as the economy business and country's hub of mangroves and extraordinary biodiversity (Sam et al., .2016). During the oil extraction and processing activities, massive land abuse evolves resulting in the vulnerability of the soil to contamination of hydrocarbon (Sam et al., 2016). Land affected by oil spill has been identified as a major challenge to livelihood, human and environmental health in the Niger Delta region of Nigeria. These has reiterated the decision makers, opinion seekers, scientists, businesses and individual citizens to generally accept and understand the impacts of air, land and water pollution on human health and environment. However, the impacts of land contamination are very often perceived as a burden for policy makers and public administration as a potential threat to citizens' health and environment (JRC, 2015). Brownfield sites are associated with widespread hydrocarbon contamination in varying degrees of concentration. It could be abandoned or underused industrial properties that pose risk to humans and the environment. In the Niger Delta, the challenges pose from brownfield sites cannot be overemphasized as natural recovery of crude oil from polluted soil is slow and the communities affected by such cases are denied of their agricultural lands for a long time. Therefore, it is imperative that remediation of hydrocarbon polluted sites can be revitalized so that it will not endanger human health, bio-physical environment and socio- economic environment. The released of crude oil has gained a widespread into the environment thereby causing carcinogenic and mutagenic or teratogenic effect. This reflects the inadequate effective statutory laws and regulations as well as lack of regulatory enforcements for environmental protection (Ite et al., 2016). There are still diversities of contaminants that are inevitable in polluted soil which pose ecological risk to health.

The aim of this study is to determine the diversities of contaminants at a contaminated site in a tropical rainforest zone. The Specific objectives of the study are as follows: To determine the physical and chemical properties of the soil, to determine the contaminants concentration of total Petroleum Hydrocarbon (TPH) and metal available in the soil and to evaluate the soil quality index across the sites.

1.1 Brownfield Pollutant

Brownfield sites are abandoned oil and gas exploration site which has high level of TPH, heavy metals like Lead, Mercury, Cadmium etc. and harmful substances like aromatic hydrocarbon (Benzene, Toluene, Xylene, and ethyl benzene) and polycyclic aromatic hydrocarbons (DPR, 2002). These compounds are carcinogenic or mutagenic as they can be environmentally harmful to life (Okparanma *et al.*, 2009). These are due to their abundance in the environment which is traceable to the drilling formation.

Figure 1: Typical brownfield sites in Niger Delta (Source: Getty Image, 2021)

1.2 Impact of Oil Spill in the Niger Delta Region

Soil contaminations in the Niger Delta have become unbearable and have attracted the international community as this have affected the entire region like the local farmer and mangroves whose economic wellbeing is dependent of river and alluvial fertile soil (UNEP, 2011). This was buttressed by Zabbey et al., (2017) that increasing large volumes of toxic organic substances continually enter the coastal environment of the Niger Delta via different routes including leachate and seepage during operations, extraction, transportation, distribution storage, and refining.

1.3 Impact Assessment of Niger Delta Region

The Niger Delta has been reported as one of the most heavily oil-impacted regions in the world due to over five decades of oil exploitation activities, coupled with poor management practices that have led to the contamination of soil and groundwater resources. Since the inception of the Nigerian oil sector, 13 million tonnes of hydrocarbons have been reported as spilled in the Niger Delta (Kadafa, 2012) as a result of sabotage, pipeline vandalism (individuals that break pipeline during oil theft), well blowout, and engineering failure (e.g. pipeline rupture) (Konnet, 2014). Considerable oil contamination of the land has been reported and recent estimates suggest that over 2000 land-based oil-contaminated sites exist (lte et al., 2013).

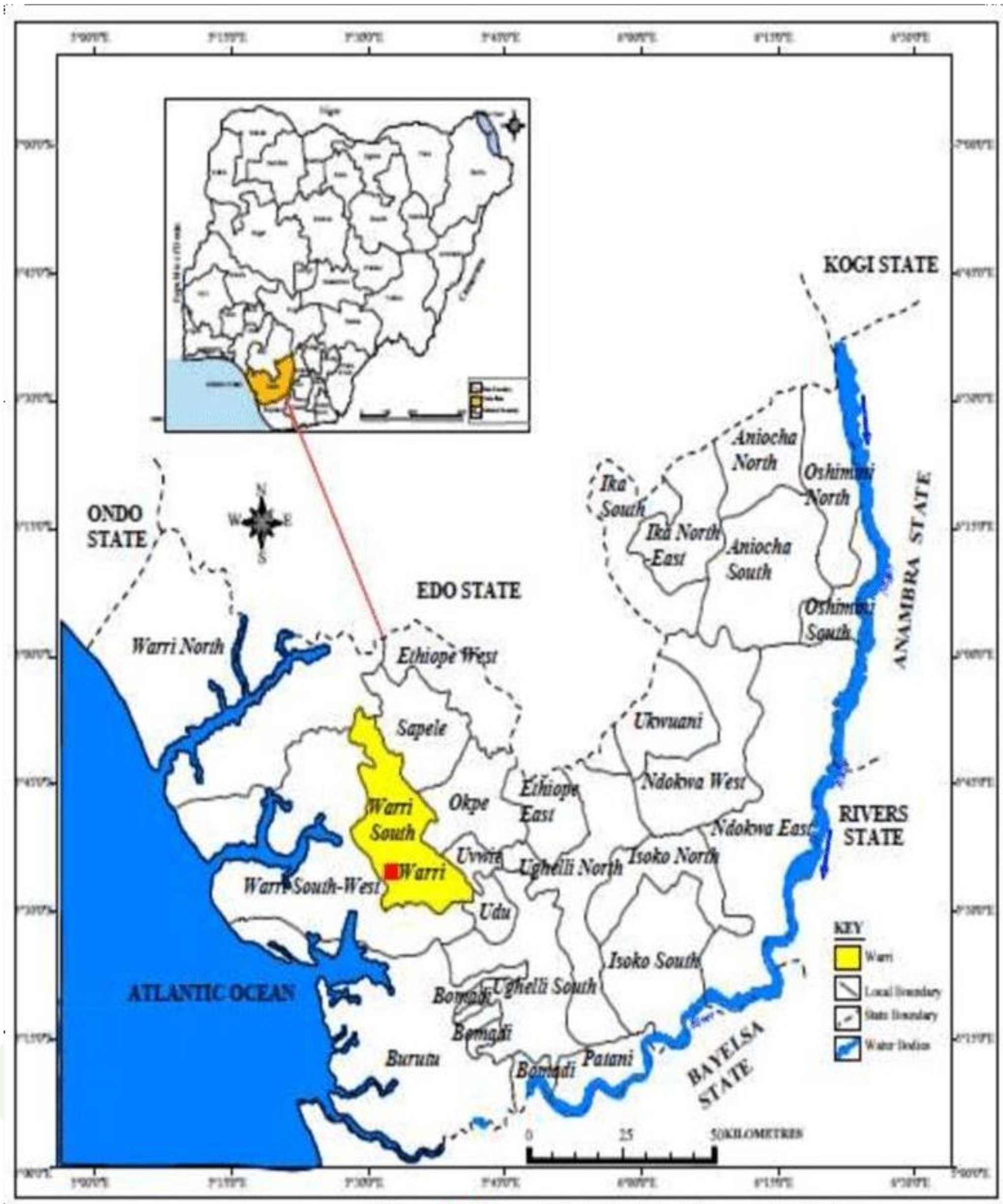

Figure 2: Map of Nigeria showing the Niger Delta region and satellite view of sampling locations indicated with yellow place marks (2016 Google Earth)

In Nigeria, there are large numbers of hydrocarbon contaminated sites mainly in the Niger Delta region where most of the arable land are been affected by crude oil and natural gas activities. Few attempts has been made to clean up oil-related contaminated land and the most common approach used was remediation by enhanced natural attenuation (RENA) (UNEP, 2011). RENA is a land farming treatment bioremediation method whereby contaminated media (e.g. soil and sediments) are periodically tilled to provide aeration (Ebuehi et al., 2005).

1.3 Integrated Risk Assessment Framework

Integrated risk assessments provide greater opportunity for engagement between risk assessors, decision makers, regulators, experts, operators and the public, because of the multiple information inputs. Risk assessment is a systematic approach to identify, evaluate, manage and communicate the likelihood of occurrence and consequences of harm resulting from land contamination (Defra, 2011). In addition, specific measures are put in place for e.g. assessment of exposure and effects and impacts on local populations, identification of contaminant fate and transport and pollutant linkages, assessment of effects on multiple species/target organisms, toxicological organisms, toxicological endpoint identification, and socio-technical assessment. A significant step in the risk assessment process is the development of the conceptual site model (CSM), which is used to establish the links between source-pathway-receptors. Within the risk assessment framework, social, environment, and economic values are often considered to provide a holistic perspective (Sam et al., 2016).

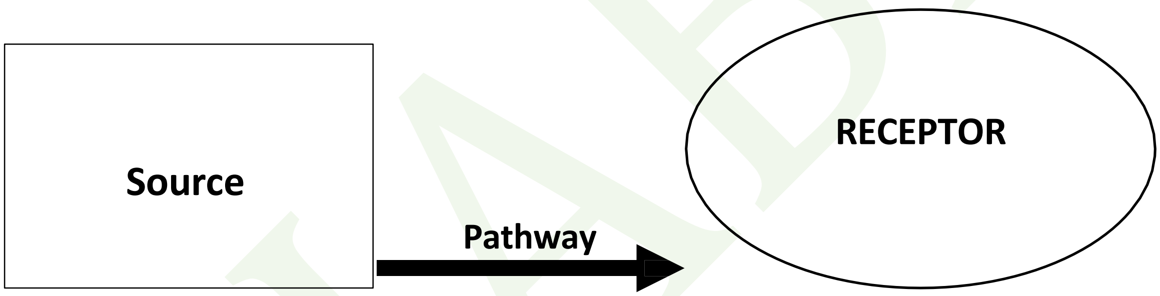

Figure 3: Contaminant linkage and risk management options (Cundy et al., 2013).
Source: "Control" Pathway Receptor Protection Management

2.0 THEORETICAL ANALYSIS

2.2 Soil Sampling Plot

The sampling locations was in K-Dere well which comprises of Site A (4.390N; 7.150E), Site B (4.390N; 7.21oE), and Site C (4.390N; 7.230E). Surface and subsurface soil samples were collected from different random spot per site using a hand dug auger capable of obtaining uniform cores of equal volume to desired depth of Ocm, 15cm, 30cm and 45cm respectively for the background check. The samples were then put into amber colored glass vials with no headspace to preserve the integrity of the sample in other to prevent volatilization, stored in a cooler containing sufficient ice blocks, and transported to the laboratory for analysis.

2.2 Testing Methods

To evaluate the ecological health risk, selected parameters were tested such as TPH, metals concentration, pH and soil quality index (SQI) were used to determine the percentage of contaminants in soil.

2.3 TPH Analysis

The TPH-is the summation of the aliphatic (CI0 - C40) plus the summation of the 16 United States Environmental Protection Agency (USEPA) priority polycyclic aromatic hydrocarbons (PAHs). TPH was determined by (EPA, 1994a, b) methods 8270 and 8270B, respectively. 5-h water bath sonication method was used to extract TPH compounds from the soils samples. Sample clean-up was done with a silica gel-on-glass wool chromatographic column. Analysis of TPH was carried with a 7890B gas chromatograph (GC) coupled to a 5977 mass selective detector (MSD) (Agilent Technologies Inc., USA) operated at 70 eV in positive ion mode. The GC-MSD is equipped with a G4513A auto sampler, and a 10 mm chromatographic column. The oven temperature was programmed from 60°C, hold time of 1min -290°C at 8 "C Imin. Samples were injected in a split-splitless mode with the relay open at 20 S. Injector and detector temperatures were 285 and 315°C respectively. Hydrogen acted as the fuel gas at 2-3 ml/min, helium as the carrier gas at 2-3 ml/min at a linear velocity of 50 crn/s, and air as the oxidizer and make-up gas at 400 ml/min and 30 ml/min respectively.

Data was processed with Chemstation® software. TPH compounds were quantified by the external standard method. Before then, two different 5-level calibration curves were developed each for PAH and alkane quantitation with different calibration solution mixes. As quality control measures, 1 mg/ml alkane mix standard and 1 mg/ml PAH mix standard after every bath of 20 samples, one duplicate sample, solvent (DCM) blank, and method (clean soil sample) blank in every bath of 60 samples were also analysed.

2.3 Metals Analysis

Nitric-perchloric acid digestion of the samples was carried out before metal content determination. A 2g sample of treated (or untreated) drill cuttings was transferred into PO instruments-AA500 spectrophotometer in line with ASTM D1688D methods. A 10ml of the digestion mixture comprising three parts concentrated nitric acid and two parts concentrated perchloric acid were put into equipment. The metals have different wavelengths and the concentration of each metal was obtained via a previous stored calibration with certificate materials using a specific standard and lamp unique for each metals and a linear graph is generated prior to analyzing the selected metals namely, As, Cr, Cu, Ni, Pb and Zn by a flame atomic absorption procedure according to APHA (1998). Results were calculated automatically as the necessary sample details were computed.

2.4 Soil Quality Index (SQI) Determination

A significant portion of the soil sample was oriented towards evaluating if soil contamination exists and to what degree in the tropical rainforest. Composite soil samples from the surface and subsurface were collected to confirm or deny that impact has occurred above the appropriate regulatory standard by DPR. To determine the level of contamination and ecological health risk within the study sites, three factors were put into consideration as proposed by CCME (2007) including scope (Fl), frequency (F2), and amplitude (F3). Where, F1 is the percentage of contaminants that did not meet their respective soil quality guidelines, F2 is the percentage of individual tests of contaminants that did not meet their respective soil quality guidelines and F3 is the amount by which the contaminants did not meet their respective soil quality guidelines as described in recent publication (Okaranma et al., 2017).

2.5 Quality Assurance and Quality Control for TPH

In the evaluation of methods for analysis of hydrocarbons in environmental samples, the quality of method is not judged by the percentage of fat extracted alone, but also by a number of factors like reproducibility, ease of application of method, cost and time of the analysis (Etchie et a1., 2011**).** The loss of some hydrocarbons of interest cannot be ruled out. To this end, the extent to which the compound of interest is recovered also plays a vital role in conjunction with the factors earlier mentioned.

2.6 Contamination Factor

Contamination factor (CF) is used to assess contamination level in relative to average concentration of the respective heavy metals in the environment. CF is often expressed based on the formula previously described by Hakanson (1980) and have been applied by Izah et al., (2017).

$$CF = \frac{\text{Concentration of respective metal in the concentrates soil (cm)}}{\text{Background values form similar geological area (BM)}} \ldots\ldots\ldots\ldots\ldots\ldots 1$$

2.7 Pollution Index and Nemerow Integrated Pollution Index

Pollution index (PI) and Nemerow integrated pollution index (NIPI) is another type of indices used to assess extent of pollution in an industrial area. NIPI considers the overall level of soil pollution, taking into account the concentration of the various heavy metals under concentration (Izah et al., 2017).

$$PI = \frac{\text{Concentration ofindividual metals}}{\text{Background values}} \ldots\ldots\ldots\ldots\ldots\ldots 2$$

2.8 Pollution Index (Contamination Index)

Pollution index (contamination index) (PIICI) is often used in identifying pollution in priority areas (locations) (Sarala and Sabitha, 2012). According to Sarala and Sabitha (2012), PI/CI requires several measurements in the same sampling site. PI/CI was developed by Ott (1978) and has been applied by Sarala and Sabitha (2012). Detailed can be found in Izah et al., (2017).

$$^{PI}/_{CI} = \sum_{w}^{1} x\, C \ldots\ldots\ldots\ldots\ldots 3$$

2.9 Total Petroleum Hydrocarbon (TPH)

10g of each soil samples were extracted by the ultrasonic extraction method using 20ml dichloromethane according to the USEPA 3550C. The extracts were then cleaned and concentrated. 1µl was injected into the Agilent 6890GC for analysis according to USEPA 8015 method. The concentration in mg/kg was deduced from the calibration graph.

3.0 MATERIALS AND METHODS

3.1 Materials and Chemicals

Anhydrous sodium sulphate and extraction solvent dichloromethane (DCM) (99%) were supplied by Loba chemie, Mumbai (India). The TPH mixed standard used was purchased from Accustandard Inc (New Haven, CT.USA.)

3.2 Moisture Content

The method used for determining moisture content in soil was based on ASTM D2216-90. This is a simple weight loss technique obtained at temperature range of 105 to 115^{o}C with the moisture content result expressed in percentage.

3.3 Metals

Acid digestion of the soil samples was conducted prior to analysis. 5g of each section of a sample was accurately weighed and transferred into a boiling tube. Aqua Regia preparation was made by adding the ratio of 3:1 conc. hydrochloric acid and conc. nitric acid. 15ml of the aqua Regia was then added into the boiling tube containing the measured samples and set to heat for 1 hour in the fume cupboard. After heating, the mixture was allowed to cool and then filtered into a 50ml volumetric flask and filled up to mark with distilled water. The concentration of each metal in the samples obtained after digestion was determined using Atomic Absorption Spectrophotometer (ASTM) methods. These were carried out using PG instrument AAS (Model: AA500PCF). Prior to the analysis, calibration was done with each metal standard of known concentrations. Concentration of each metal was ascertained from the data generated by the AAS and expressed in mg/kg.

3.4 Chemical and Reagents:

Hydrochloric acid, Nitric Acid, Distilled water

3.4.1 For Leachable Lead:

The soil samples were grounded to increase the surface area for extraction. The soil was then extracted with acetic acid solution by agitation for about 18 hours. The solution is then filtered and analyzed with using Atomic Absorption Spectrophotometer according to USEPA 1311.

3.5 Hydrocarbon Utilizing Bacteria and Fungi

These were carried out using vapor phase transfer technique adopting spread plate method. The soil (1g) samples to be analyzed were mixed thoroughly. With sterile pipette, a tenfold –serial dilutions of the sample were carried out using a sterile diluent (Normal saline). 0.1ml of the sample dilutions were transferred to corresponding pre-poured solidified culture medium (Mineral Agar) in duplicate Petri-dishes. Using a sterile hockey stick (glass rod spreader), the inoculums were uniformly spread over the surface of the agar medium. Using sterile forceps, filter paper (90mm) was soaked in crude oil and placed inside the upper lid of the Petri dish cover. The plates were incubated at 25°C–30°C for 7–14 days and observed for colony formation. The bacterial/fungi colonies were counted using a colony counter and reported as colony forming unit (cfu) /g of the sample. Single colonies shall thereafter be selected from different media plates and sub-cultured for characterization and identification.

3.6 Nutrients (Nitrate and Phosphate)

A sample cell was filled with 10ml of the sample (extract) and the contents of one Nitrate reagent and Phosphate reagent powder pillows were added respectively (to the prepared sample). A second sample cell was filled with the sample (the blank) used in zeroing the equipment. The prepared sample was then placed into the cell holder and result in mg/kg being read. The equipment used is PG T60 UV spectrophotometer.

4.0 RESULTS AND DISCUSSION

4.1 Result Analysis of Physico-Chemical Properties and Discussion

The physico-chemical analysis of the contaminated loamy soils showed significant differences when compared with uncontaminated (control) soils essential nutrients like nitrogen, phosphorus, and potassium declined sharply. The drop in pH indicates acidification of the soil, which negatively impacts plant growth and microbial activity.

Table 1: Physico-Chemical Properties of Soil Samples

Parameter	Control Soil	l Contaminated Soil	% Change
pH	6.8	5.4	-20.5%
Organic Carbon (%)	1.45	3.85	+165.5%
Nitrogen (%)	0.28	0.11	-60.7%
Phosphorus (mg/kg)	17.5	8.9	-49.1%
Potassium (mg/kg)	220	120	-45.4%
Crude oil contamination increased		soil organic carbon content due to hydrocarbon deposition, while	

4.2 Identification of Organic Pollutants:

Analysis using GC-MS revealed the presence of various hydrocarbons in the contaminated loamy soil.

Table 2: Detected Organic Pollutants in Contaminated Soil

Compound Type	Examples Detected	Concentration (mg/kg)
Alkanes (C10–C28)	Decane, Hexadecane	180.5
Polycyclic Aromatic		
Hydrocarbons (PAHs)	Naphthalene, Anthracene, Benzopyrene	95.2
Aromatic	Hydrocarbons Toluene, Xylene, Benzene	72.8
Resins and Asphaltenes	Complex hydrocarbons	210.3

The presence of carcinogenic PAHs such as Benzopyrene highlights the ecological and health risks associated with crude oil pollution. High levels of asphaltenes and resins confirm persistence and low biodegradability of these compounds in the soil.

4.3 Effect on Soil Microbial Activity

Microbial plate count revealed significant differences between control and contaminated soils.

Table 3: Microbial Load in Soil Samples

Soil Sample	Total Heterotrophic Bacteria (CFU/g)	Hydrocarbon-Degrading Bacteria (CFU/g)
Control Soil	2.4×10^6	1.2×10^5
Contaminated Soil	7.5×10^4	3.6×10^5

Total heterotrophic bacterial count decreased drastically in contaminated soils, showing crude oil's toxicity to general soil microbes. However, the hydrocarbon-degrading bacterial population increased, suggesting adaptive selection of organisms capable of metabolizing hydrocarbons.

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusions

Altered Soil Chemistry: Crude oil pollution significantly acidifies loamy soil, increases organic carbon, but reduces key nutrients (NPK), leading to poor fertility.

Persistence of Pollutants: Hydrocarbons, particularly PAHs and resins, were found in high concentrations, confirming their persistence and environmental danger.

Microbial Shift: While general microbial diversity declined, specialized hydrocarbon-degrading bacteria thrived, indicating a natural but slow bioremediation process.

Environmental Impact: Contamination reduces soil productivity, affects crop growth, and poses long-term risks through leaching into groundwater and bioaccumulation in the food chain.

5.2 Recommendations

Bioremediation Approaches: Employ bioaugmentation and biostimulation strategies using indigenous hydrocarbon-degrading microbes to enhance natural cleanup.

Nutrient Supplementation: Fertilizer amendments (N and P) should be introduced to boost microbial activity and restore soil fertility.

Continuous Monitoring: Regular monitoring of soil and groundwater in oil-impacted areas should be enforced by environmental agencies.

Policy Enforcement: Stricter regulations should be placed on oil companies regarding spill prevention, with penalties for non-compliance.

Community Awareness: Local communities should be educated on the risks of farming and using contaminated soils and supported with alternative livelihoods

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