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Assessment of Total Petroleum HydrocarbonRemediation on Crude Oil Impacted Soil, Nkeleoken, Eleme Rivers State Nigeria.

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Abstract
Background:*This study was aimedat assessing the extent of remediated crude oil polluted soils in Nkeleoken, Eleme, Rivers State, Nigeria. Total Petroleum Hydrocarbon (TPH) is an important group of environmental contaminants that are toxic to human and environmental receptors and can cause safety hazards, ecological harm and human health effects.*
Materials and Methods: *In this study, the Remediated soil samples were collected with the aid of manual hand dug soil auger at the depth of 0 – 30 cm from three (3) sampling locations while the non-remediated soil sample were at the depth of 3 m. Samples were preserved by the addition of 50 ml methanol and were transported to the laboratory for extractions. TPH was analyzed by Petroleum Hydrocarbon Analyzer (Buck Model HC-404).*
Results:*The results of TPH recorded during dry and wet season in Nkeleoken remediated soil were 296.7±10.0, 246.7±26.2; 199.8±9.80, 193.7±8.81 and 248.3±4.50, 220.2±11.9 mg/kg representing the following sample locations* $TPRSEN_a$, $TPRSEN_b$ *and* $TPRSEN_c$ *respectively.The percentage removal of TPH in Nkeleoken ranged from 70.43 – 80.09% in dry season and 74.8 – 80.24 % in wet season while Index of geo-accumulation (I-geo) varied from 0.414 – 0.984 in dry season and 0.369 – 0.718.The TPH varied significantly (P<0.05) at all sampling locations and season.*
Conclusion: *The study revealed that the remediation of the crude oil polluted soils were not uniform at all sample locations and varied from season to season and the values of TPH on the remediated soils were above the permissible limit of 100 mg/kg for cleanup.*
Keywords: *Soil, Pollution, Remediation, Petroleum Hydrocarbon, Crude Oil*

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I. Introduction

Industrial Pollution is one of the ecological problems facing Nigeria, particularly in the Niger Delta Area (Olof and Jonas, 2013). Oil leaksoccurring in the Niger Delta have received less responsiveness in global media, despite significantly greater impacts on human wellbeing and the local ecosystem (UNEP, 2011). Oil spills mainly impact vegetation and wildlife, such as seabirds. Most of the impacts are due to the physical appearances of the oil. The adhesive stuffs lead to reduced agility and suspension of natural fats and waxes on body surfaces, feathers etc. (NRC, 2003; Itopf, 2011a). Certain aromatic petroleum hydrocarbons may also cause direct toxic effects due to ingestion or permeation through body surfaces (Heubeck*et al.*, 2003). Many of the toxic as well as non-toxic hydrocarbons vanish and are degraded by microbes quite speedily (NRC, 2003; itopf, 2011a). However, there may be adversative long-term special effects under particular conditions (Peterson *et al.*, 2003). Aprojected 2 million tons of oil is free into the atmosphereannually from human and natural routes. About half of this comes from natural leakage of oil into the sea and coastal environs from oil deposits on the mainland shelf (NRC, 2003).

Polluted air, water and soil by industrial runoffs are associated with health and disease problem which may be advanced as one reason for the current shorter life expectation in developing countries when compared with the developed countries. Each year, industrial facilities discharge into the environment large amount of chemicals leading to respiratory, neurological, developmental, reproductive disorders and cancer, yet communities close to such facilities, especially in poor nations occasionally know the extent to which these discharges are disturbing their health (Itodo*et al.*, 2019).

The remediation of soils refers to practices of either removing contaminants or converting them into less mobile species; that is, into less bioavailable forms. The selection of a method is generally based on the nature of the contaminants, the soil type, and the characteristics of the contaminated site. Methods for remediating metal-polluted soils have been widely investigated and discussed (Pierzynski*et al.*, 2005;

Kumpiene*et al.,* 2005). Most commonly used remediation technologies **(***in situ* and non *in situ* methods) as outlined by Kabata-Pendias (2011)

II. The Study Area

The study area, Ogoniland is situated in Rivers State in the South-South (Niger Delta) geopolitical zone, Nigeria. River State is located in the area roughly between longitudes 6^o 40' 30"East and latitude 4^o 58' 30"N. Its topography is mainly characterized by rivers, lakes, creeks, lagoons and swamps of varying dimensions. Eleme is one of the local government area of Rivers state. It is one of the settlement with refinery in Ogoniland. It lies between Latitude 4.7874 and longitude 7.1433: The sampling locations covers two community Nkeleoken remediated sites and Ogale-Alode non-remediated sites.

Nkeleoken remediated site is an NNPC and SPDC Trunk lines with UNEP Reference Code: 002 – 002. The sampling coordinates are (E291066, N527226); (E291075, N527217); (E291039, N527162) while the Non-remediated site is an SPDC Well in Ogale-Alode with UNEP CODE: 005 – 001. The coordinates of the sample locations are (E295804, N2955341); (E295758, N533914).

Sample Collection and Preparation

Soil samples were collected from the selected sites in Eleme Local Government Areas where remediation had taken place and those that have not been remediated. Remediated sites were designated as a, b and c while the non remediated sites designated as x, y, and z. The samples were collected in March, 2021 while samples for wet season were collected in October, 2021.

Stratified and systematic sampling technique was applied for soil sample collectionaccording to Xie and Cheng (2001) with little modification. Under this sampling technique, the remediated site, Nkeleoken in Eleme. The site was divided into three sub-populations labelled a, b and c. The non-remediated siteOgale-Alodewasalso divided into x, y and z. Samples were taken randomly in individual sub-population at a distance of 150 meters from each other to enable detailed study on individual sub-population and increases the precision and accuracy of the estimate over the entire sites. In each sub-population, approximately 10 – 20 g soil samples were randomly collected at the depth of 0 –15 cm for remediated soil and 5 m for non-remediated soil with manual auger. The 10-20 g sample units of approximately equal size were pooled together to form composite sample for the location.

The soils samples were preserved by the addition of 50 ml methanol to prevent the escape of the organic pollutants. The samples were kept in an ice container which were taken to the laboratory and stored at -4° C until further analyzed (*Edore et al.,* 2020).

III. Materials and Methods

TPH analysis

Total Petroleum Hydrocarbon (TPH): Method according to USEPA 8240 adopted from Ihejirika*et al.,* (2019) with little modifications in choice of solvent and extraction time was used. A 20 g of soil sample was weighed into a 100 mL glass sample bottle and 20 g of Na_2SO_4 anhydrous was added followed by a mixture of 2:1 n – hexane and dichloromethane (40 mL n-hexane and 20 mL dichloromethane, DCM). The mixture was shake for 1 hour with mechanical shaker and then centrifuged (10 min at 150 rpm). The organic layer (extract) was filtered into a vial through 5 g anhydrous Na_2SO_4 stored for further analysis. The analyte were analyzed by Total Hydrocarbon Analyzer (Buck Model HC-404).

Statistical Analysis

Data was subjected to statistical tests of significance using the one way analysis of variance (ANOVA) to assess significant variation in the concentration levels of the TPH in all the sample across the sampling sites and season. Probability less than 0.05 ($p < 0.05$) was considered statistically significant. All statistical analyses was done by SPSS 17.0 for windows.

III. Results and Discussion

Concentrations of TPH.

The results of the total petroleum hydrocarbon in Nkeleoken remediated and Ogale-Alodenon-remediated sites were presented in figure 1 below.

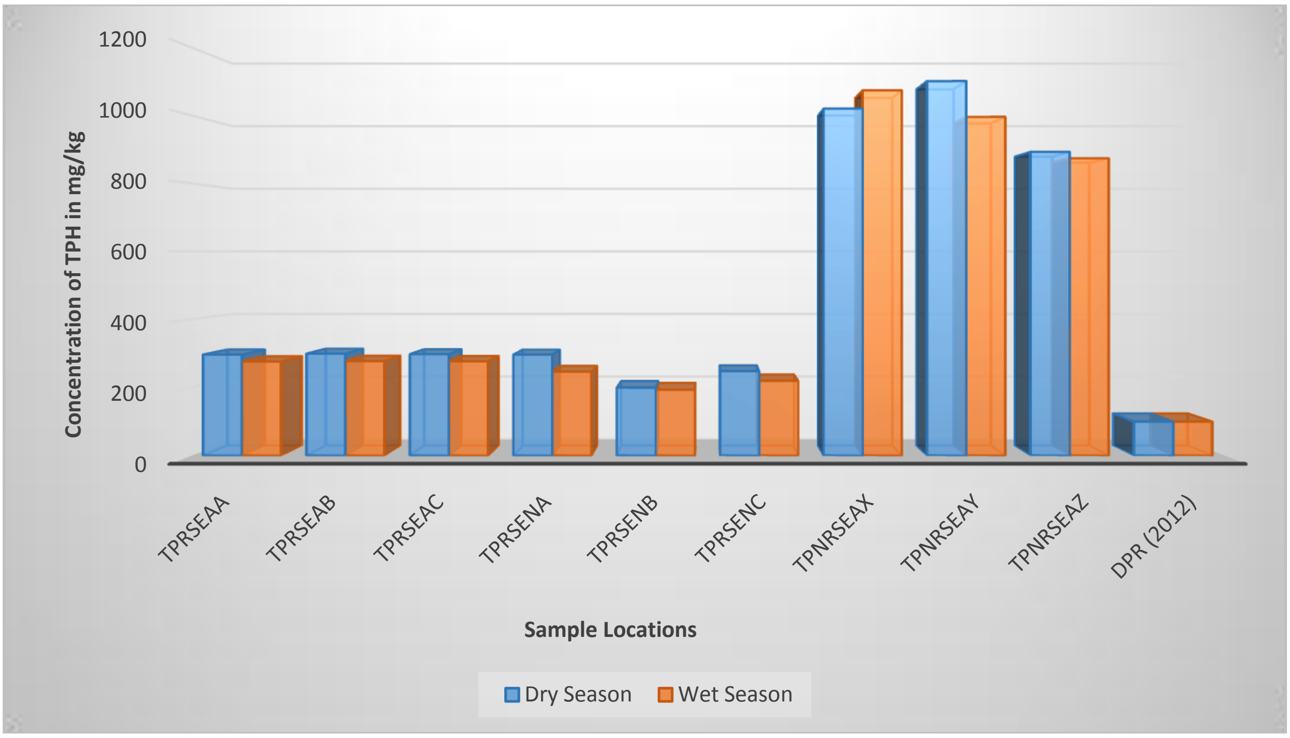

Fig. 1: Concentrations of Total Petroleum Hydrocarbon (mg/kg) in Eleme, Nkeleoken Remediated and Non-remediated Soil.

The mean concentrations of the hydrocarbon in Nkeleoken remediated during dry and wet season were 296.7±10.0; 246.7±26.2, 199.8±9.80; 193.7±8.81 and 248.3±4.50; 220.2±11.9 mg/kg representing the following sample locationsTPRSEN$_{a,}$ TPRSEN$_b$ and TPRSEN$_c$ respectively. It is noticeable that sample location TPRSENa had the highest concentration of hydrocarbons in both seasons followed by TPRSEN$_c$ while TPRSEN$_b$ had the least concentrations as indicated in the figure above. However, hydrocarbon concentrations in the non-remediated sites (TPNRSEA$_A$ - TPNRSEA$_C$) ranged from 892 to 1099 mg/kg in the dry season and 873 to 1072 mg/kg during the wet season.

The results showed that the concentrations of the hydrocarbon at various remediated sites were above the permissible limit of 100 mg/kg for petroleum hydrocarbon recommended by the Nigeria Department of Petroleum Hydrocarbon (DPR, 2012) for cleanup site.

Ihejirika*et al.*, (2019) also reported higher concentration levels on crude oil spilled remediated soil in the Ikwerre, Rivers State.The concentrations of hydrocarbon in the non-remediated soil were 3 times greater than the remediated soils. The high level of TPH recorded affirm the report of Jebeli et al., (2019) that TPH is the main pollutant in oily wastes collected from treatment plants which was higher in concentration than the acceptable clean up levels for TPH. Also Tambeke and Augustine (2022) reported very high concentrations of TPH on waste from soil remediated sites

The results obtained for TPH in this study suggest the relative potential for human exposure, and therefore, the relative potential for human health effects. According to Agency for Toxic Substance and Disease Registry (ATSDR, 2000) TPH can also affect the blood, immune system, liver, spleen, kidney, developing foetus and lungs. Certain TPH compounds can be irritating to the skin and eyes.The results shows that p-value (0.727) > 0.05, which means there is no significant difference in the two seasons for Nkeleoken Remediated site.

Percentage Removal of TPH

Percentage Removal of Total Petroleum Hydrocarbon (TPH)

The formula below was used to calculate the efficiency of TPH removal where X_1 is the concentration of non-remediated soil, X_2 is the concentration of TPH on the remediated soil (Sylvia, 2018).

$$\frac{X1-X2}{X1} \text{ X } 100 = \% \text{ TPH removal.} \qquad (1).$$

The results of percentage removal of TPH on crude oil contaminated soils are shown in the table below. The percentage removal of TPH in Nkeleoken ranged from 70.43 – 80.09% in dry season and 74.8 – 80.24 % in wet season.

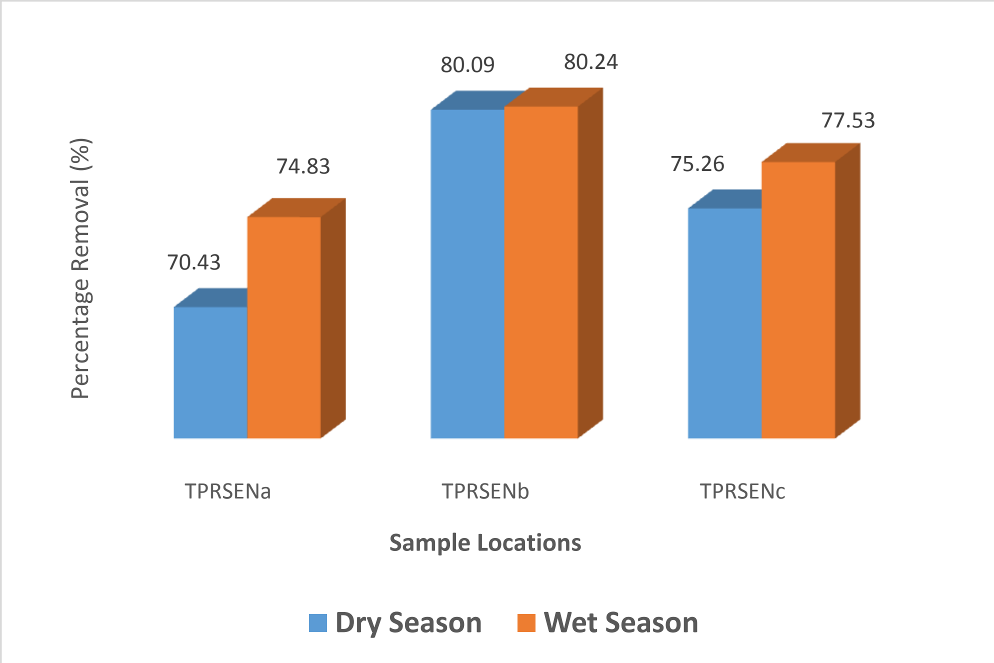

Fig. 2: Percentage Removal of TPH in Nkeleoken Remediated Soil

However, the highest percent removal of TPH were observed in sample locations RSENbin both seasons.it could be observed that percentage removal of TPH was higher in wet season than dry season, this variation may be attributed to the low concentration levels in the wet season in which organic matter decomposition were low as a result of high pH.

Interestingly, the removal was above 50 % but their mean concentration were still above the 100 mg/kg acceptable standard for cleanup soil (DPR 2012).

Pollution Indices

Geoaccumulation Index of TPH

The extent of Total Petroleum Hydrocarbon (TPH) pollution at different locations in Nkeleoken remediated site were evaluated in terms of seven (7) contamination classes in order of increasing value of the index as presented in Table 2 (Matini*et al.*, 2011). It was applied to ascertain the Total Petroleum Hydrocarbon (TPH) at the different sample locations.

I-geo = $\log_2(Cn/1.5Bn)$ (2)

Where Cn was the concentration of the Total Petroleum Hydrocarbon in the contaminated sample and Bnis background value of TPH in the geochemical reference. Concentrations of geochemical background are multiplied each time by the constant 1.5 in order to allow content fluctuations of a given substance in the environment as well as very small anthropogenic influences (Yebpella*et al.*,2019).

Table 1: classification of geo-accumulation index

Category	Value of Soil Quality
<0	Unpolluted
0-1	Unpolluted to moderately polluted
1-2	Moderately polluted
2-3	Moderately polluted to highly polluted
3-4	Highly polluted
4-5	Highly polluted to very highly polluted
>5	Very highly polluted

Source: (Matini*et al.*, 2011)

Table 2. Geoaccumulation index of TPH

Locations/Seasons	Dry Season	Wet Season
$TPRSEN_a$	0.984	0.718
TPRSENb	0.414	0.369
$TPRSEN_c$	0.727	0.554

The results of the I-geo for contaminants were presented in Table 2. I-geo for TPH varied from 0.414 – 0.984 in dry season and 0.369 – 0.718 for all the sample locations. I-geo TPH was highest at points TPRSENa and TPRSENc (0.984, 0.718; 0.727,0.554) for dry and wet seasons respectively and the lowest was at TPRSENb (0.414, 0.369). I-geo for TPH in the studied locations was 0 – 1 which means the remediated soil is still moderately polluted by the hydrocarbons. (Very highly polluted).

Contamination Factor for Total Petroleum Hydrocarbon

The second approach was the application of Contamination factor (Cf) and the degree of contamination. In calculating Cf, the Equation (2) suggested by Hakanson (1980) was used.

$$Cf = C^{i}_{0-1}/C^{i}_{n} \qquad (2)$$

Where C^{i}_{0-1} was the mean content of individual metals or Total Petroleum Hydrocarbon (TPH) from the 6 sample sites and Cin was the pre-anthropogenic concentration of individual metals or Total Petroleum Hydrocarbon (TPH). Cf was used to differentiate between the metals or Total Petroleum Hydrocarbon (TPH) originating from anthropogenic activities and those from natural processes and to assess the degree of anthropogenic influence (Table 3).

Table 3: Categories of contamination factors

Contamination factor	**Category**
$Cf<1$	Low contamination factor
$1 <Cf<3$	Moderate contamination factor
$3<Cf< 6$	Considerable contamination factor
$6<Cf$	Very high contamination factor
3-4	Highly polluted
4-5	Highly polluted to very highly polluted
>5	Very highly polluted

Source: (Hakanson,1980)

Table 4: Contamination Factor of TPH

Locations/Season	Dry Season	Wet Season
$TPRSEN_a$	2.917	2.467
TPRSENb	1.996	1.937
$TPRSEN_c$	2.483	2.202

The results of the calculation of the Contaminant factor (Cf) to assess the impact ofcrude oil spillage after remediation of polluted soils were as presented in Table 4. The Cf value for TPH at TPRSENa had the highest value of 2.917 in dry season and 2.467 in the wet season, followed by TPRSENcwhich recorded 2.483 and 2.202 in dry and wet season respectively while the least was observed at TPRSENb. The results indicates that the level of the contamination after remediation was varied from low to moderate contamination. This is evidence in the percentage removal which range between 70.43 – 80.24% representing an average removal of TPH.The results revealed that the p-value (0.323)> 0.05 means there is no significant difference in the contamination factor for both dry and wet seasons in Nkeleoken remediated site.

IV. Conclusions

The study showed that the remediation of the crude oil polluted soils were not completely effective. Hence, require proper remediation technique for the complete removal of TPH or reduce to the acceptable permissible limit for cleanup soil.

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Conflicts of Interest

The authors declare no conflict of interest

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