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Evaluation of Physico-Chemical Characteristics of Bioremediated Soils in Eleme, Rivers State, Nigeria

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ABSTRACT

Bioremediation is a complex process and exercise with its unique attendant challenges. The issue of residual pollutants and intermediate metabolites, which are occasionally discovered in soils after bioremediation, is one of the major concerns of this complex process, and requires a substantial scientific inventory of in situ hydrocarbons and the physicochemical regime of the soil. Consequently, this study evaluated three selected bioremediated sites at Aleto, Alode, Ebubu and Eteo in Eleme, Rivers State, Nigeria for their physicochemical characteristics and hydrocarbon contents. Seasonal variations of pH, electrical conductivity, total organic content, acidity, effective cation exchange capacity, nitrogen, phosphorus, potassium, exchangeable bases and particle size distribution were analyzed using conventional analytical methods. Total petroleum hydrocarbon, polycyclic aromatic hydrocarbon and heavy metals levels were also examined. The following results were obtained within the wet and dry seasons respectively: pH ranged from (4.35±0.01 to 7.02), electrical conductivity 0.05±0.01 µS/cm to 89.02±0.02 µS/cm, total organic carbon (0.55±0.01% to 3.33±0.01%), effective cation exchange capacity 2.98±0.04 Cmol/kg to14.33±0.01 Cmol/kg, exchangeable bases Ca^{2}+ (8.99±0.01 Cmol/kg), (8.29±0 Cmol/kg); Mg^{2+}(2.39±0.01 Cmol/kg), (5.15±0.01Cmol/kg); K^{+} (0.33±0 Cmol/kg), (0.84±0.01 Cmol/kg); Na^{+}(1.23±0.01Cmol/kg), (1.2±0.01Cmol/kg), nitrogen 0.09±0 % to 2.7±0.01 %, phosphorus 0±0 mg/g to 82.33±0.02 mg/g. The concentrations of Total petroleum hydrocarbon, Polycyclic aromatic hydrocarbon and heavy metals of soil samples in both pre-planting and post planting periods varied significantly (P<0.01). Overall, the results showed a significant correlation between physciochemical parameter in pre-planting period with post-planting period in Eteo (Control), Aleto and Ebubu sites.

Keywords: Bioremediation, Pollution, Contaminants, Physicochemical, Eleme.

1.Introduction

In recent years, the advancement in industrialization, urbanization and exponential growth in global population has resulted in the progression of the petroleum industry. Apparently, this has its associated problems of environmental pollution and degradation which consequently has elicited tremendous attention. The increasing demand for petroleum products has contributed substantially to exacerbate the challenging situation, thus resulting in further contamination of soil and water environment.

Anthropogenic activities of crude oil exploration and exploitation contributes immensely to the enhancement of environmental pollution arising from oil spillages. Crude oil pollution is a global problem which results in significant decline in soil quality and chronic sub-acute toxicological effects within ecosystem (Tanee and Albert 2015).

Additionally, crude oil spills on soil poses a significant deleterious effect on a wide range of living organisms in soil. Osuji et al. (2005) further asserted that oil concentration above 3% exerts harmful effects on soil biota. Similarly, Souza et al. 2014 averred that hydrocarbons are vastly toxic, carcinogenic and mutagenic substances which have negative effects on soil ecosystem integrity. Oil pollution also exerts deleterious effect on plant growth, soil macronutrients, microorganisms and the terrestrial ecosystem in general (Osuji, 2002). According to Khan et al. (2008) the buildup of heavy metals in contaminated soils may have negative health effects.

Abii and Nwosu(2009); Osuji and Nwoye(2007)reported that crude oil contamination causes reduction in soil fertility thus rendering the soils unproductive for agricultural purposes due to depletion in essential nutrients. Adding that oil spills causes adverse impact in the top soil than sub soil. Abosede (2013) reported that crude oil contaminated soils exerts drastic changes on physico-chemical properties of the soil which also leads to non-availability of nutrients in the soil, reduction in soil aeration, infiltration of water into the soil, etc.

The Nigerian economy is monolithic which depends strictly on crude oil earnings derived predominantly from the Niger Delta. Eleme community is a

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hub of the Oil and Gas business in the Niger Delta region of Nigeria that has experienced significant adverse effect of oil pollution. The intervention of the United Nations Environment programme (UNEP) culminated in the Ogoni Clean-up exercise which is currently been implemented by the Hydrocarbon Remediation Pollution Project (HYPREP).

Hydrocarbon Remediation Pollution Project (HYPREP) had chosen to conduct the cleaning up of Eleme – Ogoniland through bioremediation technique because it is an environmental clean-up technology option that is economical, eco-friendly and effective in enhancing petroleum hydrocarbon degradation. Bioremediation is a biological process which basically involves the application of micro-organisms and plants to remediate contaminated environment. The primary objective in bioremediation is to reinstate the site to its pristine status.

However, recent studies including that of Jason-Ogugbueet al. (2019) confirmed that most bioremediated soils harbour some residual contaminants and intermediate metabolites derived from crude oil. An effective removal of these residual contaminants from the soil requires a multi-dimensional approach. This is because no single method can be expected to work equally well on all constituents of a diverse mixture; a combination of remediation approaches may therefore represent the most cost-effective solution among several practicable ones (Mmom andIgbuku 2015).

The presence of crude oil in the soil environment interferes with both physico-chemical and the biological parameters of the soil (Amadi et al. 1993). Thus the physicochemical characteristics of soil serve as a reflection of the soil nutrient content and fertility status. Agricultural productivity therefore depends upon physico-chemical parameters of the soil. Soil quality includes mutually interactive attributes of physical, chemical and biological properties, which affect many processes in the soil that make it suitable for agricultural practices and other purposes (Rakesh et al. 2012). The above development necessitates the assessment of the physicochemical properties of soils as it usually acts as a pointer of soil health and quality.

This study is therefore aimed at assessing the physicochemical profiles of bioremediated soil samples obtained from HYPREP sites in Eleme Rivers State, Nigeria.

2.Materials and Methods

Description of Study Area:

The study area was in Eleme Local Government located at the western end of Ogoniland in Rivers state in the Niger Delta region of Nigeria. It lies between the coordinates of latitude: 5° 04' 60.00" North and Longitude: 6° 38' 59.99" East. Soil samples were obtained from Hydrocarbon Pollution Remediation Project (HYPREP) sites. The project is a brain child of the Federal Government of Nigeria under the supervision of the Ministry of Environment to clean up Ogoniland of hydrocarbon pollution. The sites are located in Aleto, Alode and Ebubu, all in the Eleme, Local Government Area of Rivers State. Eteorepresented the control without hydrocarbon contamination. Eleme is situated in the tropical rain forest zone of Nigeria and is characterized by two distinct seasons, the dry and rainy seasons which occurs between November - March and April - October respectively. The annual mean rainfall ranges between 160-298 mm and the annual mean temperature range is between 28-33°C (UNEP Report, 2011). The vegetation is typical of rain forest vegetation, characterized by covers of primary forest, forest regrowths/ bush fallow and farm lands. The people are predominantly subsistent farmers. According to the 2006 National population census, Eleme has a population of 190,884.The study area enjoys the hot monsoon climate due to its latitudinal position, and the relief is lowland with average elevation between, 20 m and 30m above sea level. The geology of the area comprises alluvial sedimentary basin and basement complex.

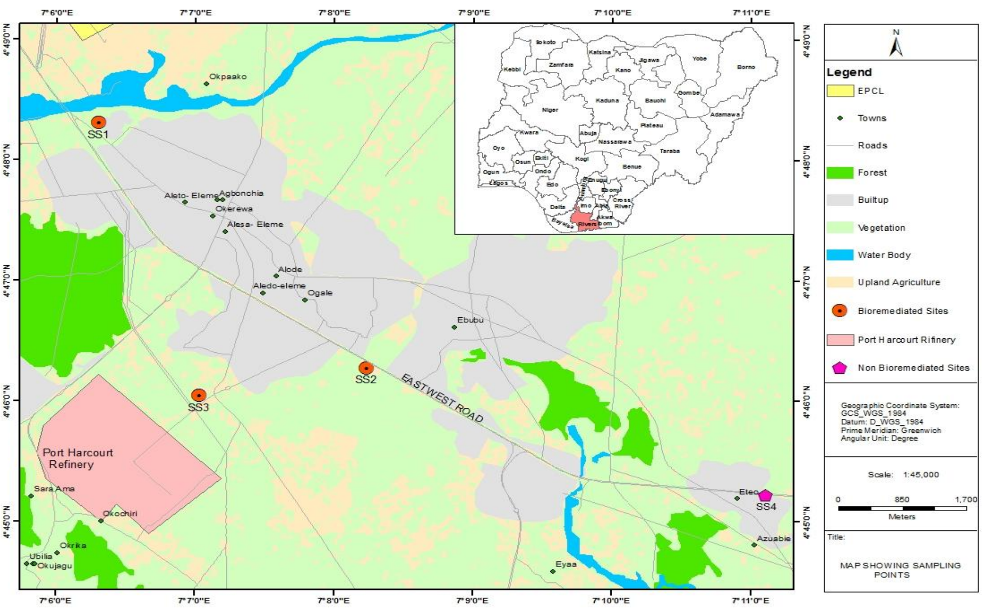

Fig.1: Map of Eleme showing delineated sampling sites (HYPREP bioremediated Sites)

Sample Design, Collection and Preparation:

Sampling plots were selected from HYPREP bioremediated Lotsand uncontaminated sites. The grid technique was implored in designing the plots where the soil samples were collected. A perimeter sampling area of 100×100 m^2 was marked out from where 24 samples were randomly collected from each site. The samples were collected from surface depth of 0- 30cm with the aid of a soil auger. The soil samples upon collection were placed in polythene bags, tightly tied and labeled. They were subsequently homogenously mixed to form composite samples. The representative samples were air dried for one week, ground into fine particles and sieved to pass through 2mm aluminum mesh, then preserved before they were conveyed to laboratory for soil analysis (Boulding 1994; Nomeda 2004).

Determination of Physico-chemical characteristics

Physicochemical characterization of the study soil samples (bioremediated crude oil contaminated soils and those from control site) were determined. This was conducted pre-planting and post planting in both the wet and dry seasons.

The physico-chemical parameters determined include pH, electrical conductivity, exchangeable cation, cation exchange capacity, total organic content, acidity, nitrogen, phosphorus and Potassium, magnesium, calcium, iron, zinc, copper, aluminium and particle size distribution.

Sample Analysis:

$_P$H determination was conducted with the use of pH meter (Hanna HI98103). This was done using 1:1 soil to water mixture ratio. Total Organic Carbon (TOC) was determined by Walkley-Black method (1934) while Effective Cation Exchange Capacity (ECEC) was determined using the Kjeldahl distillation and titration method. Exchangeable bases (Calcium, Magnesium, Potassium, Sodium, Aluminium) of soil samples were determined by extracting solution (1N NH4OAc) of pH 7.0. The extracted solution is then analyzed by Atomic Absorption Spectrophotometer for the soil cations. K and Na were determined on the Flame Photometer.

Electrical conductivity meter was used to determine Electrical Conductivity (EC). Total acidity (H^{++}, Al^{3+}) was determined using the barium chloride triethanolamine (BaCl2-TEA) method while Total Nitrogen was analyzed using Micro-Kjeldahl method (Bremner et al 1983). Phosphorus was determined using BRAY-1 Method of Bray and Kurtz while Potassium and sodium in soil was determined by flame photometric method. Particle Size Distribution was determined through the use of Bouocousou Hydrometer method.

Total petroleum hydrocarbons present in the soil samples were determined using the Varian CP 3800 gas chromatography (GC) in line with ASTM D5765, EPA 1625 and USEPA 8270B while Polycyclicaromatic hydrocarbons in soil samples were determined using ASTM D7363.

Data obtained were subjected to statistical analysis using the one-factor Analysis of Variance (ANOVA) to determine if there are significant differences between data obtained from different sites.

3.Results

$_P$H (Hydrogen ion concentration):

The pH of Aleto, Alode and Ebububioremediated soil samples and Eteo – Control (uncontaminated) soil were determined. The results of the Wet season at pre-planting revealed a range of 4.35 – 5.43. The uncontaminated soil from Eteo (control) recorded the highest $_P$H of 5.43 while the bioremediated soil of Aleto had the least $_P$H value of 4.35. The post planting results had a range of 4.36 – 6.75. Similarly, Eteo (control) recorded the highest $_P$H results of 6.75 while Aleto had the least value of 4.36. In the dry season, the $_P$H range for pre-planting was 5.45 – 5.82. Alode recorded the highest value of 5.82 while Aleto had the least value of 5.45. For post planting, Alode recorded the highest value of 7.02 while Aleto had the least value of 6.68.

Total Organic Carbon:

The range of Total Organic Carbon in the soils for Wet season pre- planting is 0.55% – 1.22%. Ebubu had the highest Total Organic carbon of 1.22 % while Eteo (control) recorded the least value of 0.55%. For post planting, the range was between 1.2% – 1.48%. Eteo (control) recorded a maximum value of 1.48% while Ebubu recorded minimum value of 1.2%. In the dry season, the TOC range for pre-planting was 2.74% - 3.33%. Eteo recorded an elevated value of 3.33% while Aleto had the least value of 2.74%. For post planting, Eteo (control) had the highest value of 2.95% while Aleto recorded the least value of 1.95%.

Effective Cation Exchangeable capacity (ECEC):

The range of Effective Cation exchangeable capacity (ECEC) at Pre-planting in wet season was 4.33 Cmol/kg – 4.97Cmol/kg. Ebubu recorded the least value of 4.33 Cmol/kg while Eteo (control) had the highest value of 4.94 Cmol/kg.

At post planting in wet season, the range of ECEC was 2.98 Cmol/kg – 12.05 Cmol/kg. Aleto recorded the least value of 2.98 Cmol/kg while Eteo (control) had an elevated value of 12.03 Cmol/kg. The total range of ECEC for the wet season was 2.98Cmol/kg – 12.05Cmol/kg.

In the dry season, the range of Effective Cation exchangeable capacity (ECEC) at pre-planting was 7.23Cmol/kg – 7.98 Cmol/kg. Aleto recorded the least value of 7.23 Cmol/kg while Eteo (control) had the highest value of 7.98Cmol/kg.

At post planting in dry season, the range of ECEC was 12.27 Cmol/kg – 14.33 Cmol/kg.

The total range of ECEC for the dry season was 7.23Cmol/kg – 14.33Cmol/kg. An increase in ECEC values was obtained in all soil samples in the dry season study.

Electrical Conductivity:

The range of Electrical conductivity (EC) in the soils for pre- planting in the Wet season is 0.05 µS/cm to 0.47µS/cm. Eteo (control) had the highest value of 0.47µS/cm while Aleto and Alode recorded an equal least value of 0.05µS/cm. For post planting, the range was between 22µS/cm – 89µS/cm. Alode recorded an elevated value of 89µS/cm while Eteo recorded the least value of 22µS/cm. In the dry season, the EC range was 0.36µS/cm– 34.15µS/cm. For Pre-planting, Ebubu recorded the highest value of 0.45µS/cm whereas Alode had the least value of 0.36µS/cm. For post planting, Ebubu had the highest value of 34.15µS/cm while Eteo (control) recorded the least value of 13.05µS/cm.

Nitrogen:

Total Nitrogen range for the Wet season is 0.09% – 2.05%. For pre planting, Eteo (control) recorded the highest value of 2.05% while Ebubu had the least value of 0.12% respectively. Post planting in wet season Ebubu and Eteo (control) recorded equal maximum value of 0.11%. Similarly, Aleto and Alode had equal least value of 0.09%. In the dry season, the % Nitrogen range was 0.19% - 2.7%. For Pre- planting, Eteo (control) recorded the highest value of 2.7% whereas Alode and Ebubu had equal least value of 1.34%. For post planting, Eteo (control) had the highest value of 0.23% while Ebubu and Alode recorded equal least value of 0.19%.

Phosphorus:

Total range of Phosphorus for the Wet season is 0±0 mg/g – 82.33 mg/g. For pre planting, Ebubu recorded the highest value of 82.33mg/g whereas Eteo (control) had the least value of 32.27mg/g. At the end of planting (post planting) Eteo (control) and Aleto obtained equal highest value of 0.09mg/g respectivelywhereasEbubu had no trace of phosphorus.

Total range of Phosphorus for the dry season is 0.13 mg/g – 0.55mg/g. For pre planting in dry season Ebubu and Alode had equal least value of 0.42mg/g while Eteo (control) recorded the highest value of 0.55mg/g. At the end of planting (post planting) Eteo (control) obtained the highest value of 0.19mg/g while Ebubu had the least value of 0.13mg/g.

Potassium:

Total range of Potassium for the wet season is 0.11Cmol/kg – 0.33Cmol/kg. For pre planting, Alode recorded the highest value of 0.18Cmol/kg whereas Eteo (control) had the least value of 0.11Cmol/kg. At the end of planting (post planting) Alode recorded maximum value of 0.33Cmol/kg and Eteo (control) recorded the least value of 0.14Cmol/kg. Total range of Potassium for the dry season is 0.12Cmol/kg – 0.84Cmol/kg. For pre planting in dry season Eteo (control) had the least value of 0.12 Cmol/kg while Aleto recorded the highest value of 0.17 Cmol/kg. For post planting in the dry season, Alode recorded the highest value of 0.84Cmol/kg while Eteo (control) obtained the least value of 0.16Cmol/kg.

Particle Size Distribution:

The particle size is characterized into sand, silt and clay. Results obtained shows that there is significant difference ($p < 0.01$) in the percentages of sand, silt and clay between all the locations in both wet and dry seasons.The results of the mean values reveal that Sand fraction ranged 64.65±0.07% to 89.9±0.14%, Silt ranged from 3.43±0.04% to 9.45±0.07 % while the Clay ranged from 4.81±0.01% to 32.03±0.04%.

Total Petroleum Hydrocarbon (TPH) and Polycyclic aromatic hydrocarbon

Results of Total Petroleum Hydrocarbon (TPH) and Polycyclic aromatic hydrocarbon are indicated below in Table 1.

Correlation Analysis:

Pearson correlation result revealed that physcio-chemical parameter in pre-planting period is significantly correlated with post-planting period in Eteo (CTL), Aleto and Ebubu with a correlation coefficient of 0.69, 0.53 and 0.54 respectively during the wet season but was not significant in Alode, however it was significant in all sample with correlation coefficient of 0.97, 0.96, 0.93 and 0.97 respectively during the dry season. More so, the relationship between the parameters in pre and post-planting was weak in wet season and very strong in the dry season.

Consequently, the physcio-chemical parameter during wet season is significantly correlated with dry season in all sampled locations in the pre and post-planting period. Again, in the pre-planting period, the correlation between wet and dry season was weak, while in post-planting period the correlation was strong (see Table 2).

Table 1 Mean of concentrations of Total Petroleum Hydrocarbon (TPH) and Polycyclic aromatic hydrocarbon

	TPH (D5765)				PAH (D7363)			
	Wet		Dry		Wet		Dry	
	Pre-Planting	Post-Planting	Pre-Planting	Post-Planting	Pre-Planting	Post-Planting	Pre-Planting	Post-Planting
DPR LIMIT	5000.04±0.06e	5000.04±0.06e	5000.04±0.06d	5000.04±0.06e	40.01±0.01d	40.01±0.01e	40.01±0.01d	40.01±0.01e
Eteo (CTL)	0±0a	0±0a	0±0a		0±0a	0±0a	0±0a	0±0a
Aleto (P1)	72.32±0.12b	8.66±0.01c	57.75±0.01b	22.57±0.02d	39.47±0.1c	2.86±0b	27.62±0.01c	2.13±0.01b
Alode (P2)	82.94±0.09c	11.21±0.01d	57.66±0.01b	21.08±0.03c	29.61±0.13b	3.17±0.01c	22.56±0.05b	2.51±0.01c
Ebubu (P3)	238.24±0.01d	3.79±0.01b	157.15±0.07c	11.94±0.01b	61.48±0.04e	3.23±0.01d	43.39±0.01e	3.83±0.01d
ANOVA (p-value)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Decision	Significant	Significant	Significant	Significant	Significant	Significant	Significant	Significant

Table 2 Relationship between Pre and Post-Planting Period in Wet and Dry Season

Samples	Correlation Coefficient	Wet	Dry	PRE	POST
		PRE vs POST	**PRE vs POST**	**WET vs DRY**	**WET vs DRY**
Eteo (CTL)	**r**	0.694	0.969	0.816	0.804
	p-value	0.000	0.000	0.000	0.000
Aleto	**r**	0.531	0.958	0.647	0.813
	p-value	0.000	0.000	0.007	0.000
Alode	**r**	0.414	0.928	0.514	0.800
	p-value	0.110	0.000	0.042	0.000
Ebubu	**r**	0.543	0.968	0.796	0.815
	p-value	0.030	0.000	0.000	0.000

Discussion

$_P$H:

The $_P$Hof virtually all soil samples are reasonably acidic varying from 4.35±0.01 to 6.82±0.03 with exception of Alodein dry season (post planting) which is 7.02 (almost neutral). The above result is likely as most tropical soils range from acidic to slightly neutral (Alloway and Aryes 1997; Atlas 1981). Again, the result is in accordance with the findings of Abii and Nwosu (2009) which posited that Eleme soils are generally slightly acidic and also that the acidity cannot be ascribed entirely to crude oil pollution because even the uncontaminated (control) soils are also acidic. This corroborates the assertion of James and Wild (1975) that soils of southern part of Nigeria are generally acidic. Aprile (2012) also asserted that tropical soils are generally acidic. This status can be attributed to heavy rainfall which culminates into increase in the rate of soil leaching(Chytry,´et al 2007).

The high $_P$H values witnessed in the dry season might be attributed to low precipitation and high evaporation that also reduces the loss of base forming cations. Additionally, the high $_P$H may probably be due to high values of exchangeable calcium (Feyesa et al. 2011).

The mean values of $_P$H of all soil samples in both dry and wet seasons vary significantly (P< 0.01). This could infer that bioremediation exerted a significant effect on the pH of soil. With exception of Alode and Ebubu wet season, all other samples experienced similar trend in $_P$H dynamics with an increase in their corresponding post planting periods. The elevation in the $_P$H could be relatively due to the organic supplements that were applied to the soil before planting. This corroborates the findings of Naramabuye and Haynes (2006); Ogbonna et al.(2018). Again, the upsurge in $_P$H values in the dry season could be attributed to the microbial activities in the conversion of residual hydrocarbons to organic acids in the bioremediated soils. This is in conformity with the findings of Jason- Ogugbue et al. (2019). The higher soil pH values obtained in the dry season may also be attributed to the release of higher basic cations during organic matter decomposition (Oyedele et al. 2008).

pH is a crucial soil characteristic that has a significant impact on the concentration and uptake of solutes in soil (Akpoveta et al. 2010). Several factors, such as the fact that many plants and soil life prefer either alkaline or acidic conditions or the pH's effect on the soil's ability to hold nutrients, make it an important factor in agricultural output as well (Pandeeswari and Kalaiarasu, 2012; Imran et al 2010).

The Particle size distribution (PSD):

The trend in particle size distribution is sand > silt > clay. The proportion of sand in all the soil samples was consequently greater than double that of silt and clay, indicating that all the soil samples were sandy loam. This result synchronizes with the result of previous work of Abii and Nwosu (2009). FDALR(1987) reported that the high sand content of the soils is characterized by sand formed on unconsolidated coastal plain sand and sandstones. All the soil samples are similar because they are all of same origin. This finding is supported by the assertion of Oyedele et al. (2008) that the textural class of a particular soil is mainly inherited from the soil forming materials.

Total Organic carbon:

Dry season recorded higher Organic carbon values. This could be attributed to the effect of natural attenuation and an increase in organic matter materials (litter fall) probably released by plants growing on all the soils. The relatively low value of organic carbon witnessed at the onset of the wet season may be ascribed to the lack of vegetative cover in the site. Earlier studies by Brady and Weil (2002) confirm this assertion.

Effective Exchangeable Cation Capacity:

Effective cation exchange capacity (ECEC) refers to the total sum of exchangeable cations i.e. exchangeable bases (calcium, magnesium, potassium and sodium) including exchangeable Aluminum, Manganese and Hydrogen ions in the soil. The maximum mean value was recorded in Alode post planting in dry season while the minimum mean value was recorded in Aleto post planting in the wet season. Generally, dry season recorded higher values than the wet season. This could be attributed to the increase in temperature as well as the presence of higher organic matter in the dry season which also stimulates microbial activity. This result corroborates the findings of Salem et al. (2020).

Electrical Conductivity:

Electrical Conductivity is used to determine the concentration of soluble salts in the soil. Electrical conductivity values were substantially higher in the wet season. Control (uncontaminated soils) obtained the lowest values in post planting periods for both wet and dry seasons. Electrical Conductivity values increased in all post planting seasons. This is attributed to the application of organic supplements. This furthermore is in agreement with the findings of Azeez and Van Averbeke(2012) that electrical conductivity of soil significantly increases with the application of poultry, cattle and goat manures.

Nitrogen Concentration:

Higher mean values were recorded in the Pre-planting periods of both wet and dry seasons. The relatively lower values obtained in the post planting periods of both seasons might probably be due to the nitrogen uptake by the experimental plants. Results showed that the values were not significantly different in the post-planting in wet season. The introduction of organic amendments in the post planting enhances the biodegradation of residual pollutants through the activities of micro-oorganisms. This development consequently leads to decrease in nitrogen in post planting periods. This is consistent with similar findings of Atlas etal. (1981); Obire and Nwaubeta(2002).

Total Phosphorus:

The analytical results showed that the total amount of phosphorus concentration of the soils ranged from 0±0mg/g to 82.33±0.02 mg/g. Ebubu post – planting and pre – planting in the wet season recorded the least and the highest values respectively. Except pre planting wet season the other planting periods recorded values that were almost below detectable levels. Similar observation was reported by (Obire and Nwaubeta 2002) in a previous study.

Total Potassium:

The range of available potassium in all soil samples in this study vary from 0.11cmol/kg to 0.84 cmol/kg. Alode post planting in dry season recorded the highest value whereas control (Eteo) pre planting recorded the least value. Post planting values were higher than their corresponding pre planting values. This may be attributed to the introduction of organic supplements in the post planting periods.

Exchangeable Bases:

Statistical analysis revealed that there was significant difference in mean values distribution of exchangeable bases Ca^{2+}, Mg^{2+}, K^+ and Na^+ between studied soil samples in all locations in both wet and dry seasons. Ca^{2+} and K^+distribution was higher in post planting periods in both wet and dry seasons conversely Na^+had higher mean values in the pre planting periods of both wet and dry seasons. However Mg^{2+} recorded higher values in the dry season than in the wet season.

Total Petroleum Hydrocarbon:

Laboratory results revealed that there was no trace of total petroleum hydrocarbons (TPH) detected in the Eteo (control) uncontaminated soil samples in both seasons. The bioremediated soil samples of Aleto, Alode and Ebubu had a total petroleum hydrocarbon (TPH) range varying from 3.79±0.01 mg/kg to 238.24±0.01 mg/kg.

There was significant difference in TPH contents of soil samples in both pre planting and post planting periods in all studied sites. All the TPH values recorded were belowDepartment of Petroleum Resources (DPR) intervention level of 5,000 mg/kg. However, some samples also recorded values above target level of 50 mg/kg. These are: Aleto pre-planting in wet season 72.32±0.12mg/kg, Aleto pre-planting indry season 57.75±0.01mg/kg, Alode pre-planting in wet season 82.94±0.09mg/kg,Alode pre-planting in dry season 57.66±0.01 mg/kg, Ebubu pre-planting in wet season 238.24±0.01mg/kg and Ebubu pre-planting in dry season 157.15±0.07mg/kg.

The aforementioned development may likely leave many in doubt on the efficacy of the bioremediation exercise. This observation is consistent with the findings of Jason-Ogugbue et al. (2019). Similar observation of the presence of residual contaminants in bioremediated soils was made by UNEP in their report in respect of a bioremediated site in Ejama-Ebubu. UNEP reported that significant hydrocarbon content was found forty years after an oil spill occurred, despite repetitive remediation efforts (UNEP, 2011).

TPH results in a previous study by Jason-Ogugbue et al.(2019) showed greater values than those found in this present investigation. Though the soils used in the previous study were obtained from older bioremediated soils in Ogoni land. Generally, it is expected that due to the effect of natural attenuation the soils should have recorded lower TPH values.

Furthermore, TPH values of pre-planting periods recorded relatively higher values than their associated post planting periods. This may be attributed to the active uptake of total petroleum hydrocarbon by the plants. The consequent bio-accumulation of petroleum hydrocarbons in agricultural products poses threat to human health. The reduction in TPH value witnessed in the post planting in wet season against the dry season could be attributed to the age of the site. Time might have played a contributory role in the depletion of TPH in the studied sites considering the fact that effects of crude oil on the environment often wane with time (Umoren et al. 2019). The findings of Rhykerd et al.(1999) also corroborate the above assertion stating that TPH degradation occurs naturally by indigenous microorganisms with high degradation rate after several months of contamination.

Furthermore, the results obtained from GC-MS analysis in the wet season revealed the presence of some short chain alkanes ($C8 - C11$),aliphatic hydrocarbon fractions ($C12 – C32$) and long chain alkanes ($C33 - C40$). While in the dry season short chain alkanes ($C8 - C11$) were not detected. Somealiphatic hydrocarbon fractions ($C12 – C23$) were also not available.

Polycyclicaromatic Hydrocarbon:

Results of the concentration of polycyclic aromatic hydrocarbonsinvestigated showed a range of 2.13mg/kg to 61.48mg/kg. Ebubu pre-planting in the wet season recorded the highest value whereas Aleto post planting in the dry season recorded the least value. Pre-planting periods in both wet and dry seasons recorded higher values than post planting periods. A greater percentage of the soil samples recorded values that are below the DPR limit of 40mg/kg. However, Ebubu pre-planting in wet season and Ebubu pre-planting in dry season recorded values beyond the DPR permissible limit. The trend of low values recorded in the post planting periods are attributed to PAH accumulation by the experimental plants.Several authors have asserted that plants grown in PAH-contaminated soils can become contaminated with PAHs due to their absorption. This development is of serious concern in agricultural production because PAH is potentially toxic, carcinogenic, mutagenic, recalcitrant, persistent and consequently may pose threat to human and animal health (Zhan et al. 2010).

Heavy Metals:

The concentrations of the Heavy Metals(nickel, cadmium, chromium, lead, zinc and copper) in the studied soil samples varied significantly with the seasons. There was no trace of cadmium in the soils. Other heavy metals such as lead, nickel, chromium, Zinc and Copper were found in varying concentrations in different seasons. This is due to the fact that some heavy metals are associated with petroleum andare usually found at crude oil contaminated sites. The results obtained show the following order of heavy metal concentration in both wet and dry seasonsZn>Cu>Cr>Pb>Ni>Cd. All the heavy metals content fall below DPR limits.

Conclusion:

The study indicated significant variation of physicochemical parameters between wet and dry seasons. The Studied soils (bioremediated) were acidic, typical of the soils of southern Nigeria. The total petroleum hydrocarbon status of the bioremediated soils samples varied significantly from the uncontaminated soil (control). All the TPH values recorded were belowDPR intervention level of 5,000 mg/kg. However, six samples also recorded values above target level of 50 mg/kg.The above scenario indicates that the bioremediated soils conditions are unsatisfactory for crop production. Thus there is need for the introduction of multi-dimensional remedial approach other than the use of single land farming technique. The locations may once again require further time for natural attenuation to increase microbial breakdown of residual pollutants. This is necessary to forestall the transfer of these toxic residual contaminants to humans through crops grown at these locations.

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