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The Effect of Organic and Inorganic Fertilizer on Bioremediation of Crude Oil Polluted Land

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***Abstract* – With the frequent reports of oil spillages in the Niger Delta, there is need to seek for a cost-effective method for mediation of crude oil impacted soils. This particular study focuses on the effect of Nutrient sources: NPK fertilizer and goat droppings on crude oil polluted soil from Afam in Oyigbo LGA of Rivers State. The study lasted 9 weeks due to financial constraint. Laboratory tests were conducted at Ideyi Laboratory, to check for changes in pH, total hydrocarbon (THC), Total Organic Carbon (TOC), Phosphate, Nitrate, Potassium and Moisture Content. The effects of the above mentioned physiochemical properties on seed germination of Beans and maize and their growth variables such as plant height, plant leaf length and leaf width were also investigated. Fertilizer/goat droppings of 1, 5, 10, 20, and 50g were added to contaminate 20 polyethylene bags in random design. The treatment samples were tested at two (2) weeks interval and last test was conducted in one (1) week interval. The planting of beans and maize seedling was conducted after one (1) week of planting i.e 9th week. It was observed on conducting lab test on the 9th week that the application of goat droppings was able to ameliorate the levels of total hydrocarbon from 7568mg/kg to about 439mg/kg as against 500mg/kg produced by NPK fertilizer, indicative of a better remediation in goat droppings application. By this work I developed a model to generate the level of reduction of the Total Hydrocarbon with respect to time in weeks. Result was compared with the known regression model which shows no significant difference in rates of biodegradation of concentration of Total Hydrocarbon on the use of fertilizer (NPK) and goat dropping.**

***Keywords* – Bioremediation, Crude Oil, Effect, Inorganic Fertilizer, Organic Fertilizer, Polluted Land.**

I. INTRODUCTION

The natural environment may be altered or even exterminated by man through a series of agencies and effects. One of the major agencies that have led to habitat destruction and modification (ecosystem alterations) is industrialization and technology, through pollution of air, water and land. In the petroleum industry for example, pollution of the environment may occur through effluent discharges and accidental oil spillages. Environmental studies in Nigerian reveal that the development and production processes in the oil industry require an urgent need to plan, protect and prudently utilize environmental resources for a better environment for man. These studies indicate that subtle changes occur in the Nigeria aquatic and terrestrial ecosystems due to the activities of the oil industry [1]-[10]. Most of the environmental changes occur from the release of crude oil into the environment.
There were about 5334 reported cases of crude oil spillages between 1976 and 1997, with over 2.8m barrels of crude oil released into the environment [7]-[20]. [29], reported that about 400,000 barrels of crude oil was released into the sea off Bayelsa State in the Texaco's Funiwa-5 well blow-out in 1980. About 40,000 barrels of crude oil was also released into the sea on January 12 1998 from Mobil producing Nigeria Unlimited Idaho oil Spill which occurred near Akwa-Ibom state due to a burst on corroded oil pipeline conveying crude oil from Idaho oil field to Qua Iboe Terminal at Mkpanak [11]-[30].

When crude oil is spilled on land, the greasy fraction permeate slowly into the soil and is slowly biodegraded, while the light hydrocarbon fractions evaporate. Some that do not permeate the soil become thicker like tar. All, though, have toxic ingredients. Among the most troublesome are the high molecular weight compounds, especially the polycyclic aromatic hydrocarbons (PAH's) that include many known carcinogens which can combine with common environmental materials to form other carcinogens [15]-[20]. The release of crude oil into the environment may therefore result in habitat fragmentation, destruction and disruption and disruption of ecosystems, intelligence in natural biogeochemical cycles and the loss of plants and animals. [17]-[30], reported that the oil spill incident of 1970 at Ejamah-Ebubu near Eleme. Rivers state rendered farmlands and streams devastated. The NNPC spillage of 1982 at Abudu and Owa in Delta State also rendered the soil totally oil logged, whereas economic crops were scorched to death. The pollutants and toxicants in crude oil may cause deaths of plants and animals, disrupt biochemical pathways, metabolites and enzyme systems in all the cells and tissues of organisms [15]-[25].

For sometime now, Niger Delta region of Nigeria has provided the natural resources to support an extensive and successful petroleum industry. But with continued growth within the industry, there must be an increase in awareness on how to protect the natural resources. Increased petroleum exploration and production increase the potential hazard to ecologically sensitive areas, such as wet lands and forests. This region contains more than 30% of the nation's wetland. Oil production and exploration take place in this environment, and as a result, they are

continually at risk to petroleum contamination, caused by accidental spills, leaks, or discharges [17]-[30]

Hitherto, the prevalent method adopted in curbing oil-spilled on land is by scooping off the polluted top soil and replacing it with another layer of fertile soil. But this approach is expensive and labour-intensive compared to the economical use of fertilizers to restoring fertility of such crude oil-polluted soils [15]-[20]. Hence, the author's interest in comparing the remediation effects of two kinds of fertilizers (Organic and Inorganic) in oil-polluted soil.

Prior to the period of oil boom, the Niger Deltans were predominantly farmers. They provided the nation with most of the agricultural produce like fishes, palm oil, to mention but a few, but now they import these farm produces. This is due to reduced agricultural activities in the area occasioned by the quest for white-collar jobs that are non existent and oil spillages on their waters and farm lands. It is also an obvious fact that in event of spillages, the communities that are affected go after compensation that the oil company concerned will pay rather than the clean up of the mess. Consequently, a lot of spilled sites are left unattended to, thus reducing the available fishing, farming and even building spaces. Again, there are cases of remediation attempts by the soil companies but most of them were inconclusive and abandoned [18]-[25].

Based on the above issues, it is imperative to find a remediation method that will be affordable, and at the same time available to the rural dwellers before oil spillage will turn to a norm in the Niger Delta region.

The significance of this study has made it economically viable to use organic and inorganic fertilizers which are readily available in the market and time efficient to remediate crude oil polluted land.

In my study I used students t = distribution to compare the rates of degradation of the Total Hydrocarbon by both nutrient sources i.e. NPK fertilizer and goat droppings.

The objectives of this study are:

1. To determine the effectiveness of remediation of contaminated soil from Afam-Nta using NPK and Goat droppings under laboratory scale study.
2. To determine the better nutrient supplement Organic fertilizer (Goat dropping) or Inorganic fertilizer (NPK) that can be used to restore rapidly the fertility of Crude Oil polluted soil.

The study was experimental in design and it covered analysis of contaminated soil sample collected from an oil-polluted site in Afam-Nta, Ndoki, in Local Government Area of Rivers State.

The parameters of interest investigated include: pH, moisture content, Total Organic Carbon (TOC), nitrate, phosphate, potassium, Total Hydrocarbon (THC). Secondary parameters investigated: Seed germination, plant growth variables (i.e. Plant Height, leaf Length and Leaf Width)

II. MATERIALS AND METHODS

The experimental site/plot is located in a small village called Afam-Nta in Ndoki community which is in Oyigbo Local Government Area of Rivers State. It is Oil well head site which blew on Saturday 15 may, 2004 Ndoki has a population of about 100,000 people whose major occupation is farming. Majority of the populace there are foreigners working at the Afam power station.

The costal plain sand and clay deposit the topsoil is usually sandy loam and the vegetative cover is the tropical rainforest. The volume of rainfall provides great amount of surface run-offs rivulets and occasional streams which may carry substances like crude oil to nearby lands and rivers.

Equipment and Implement:

Shovel polythene**,** black bag**,** hoe, rainguage**,** distilled water**,** glass beaker**,** Orio research pH meter model 407A**,** organic and inorganic fertilizer**,** bean seed**,** maize seed**,** weighing balance**,** heater (Oven)**,** sieve and dessicator

Measurement of Materials

I used rule to measure the depth of the subsoil to about 15-30"cm" before collecting sample with a shovel and I measured both contaminated and uncontaminated sample on a weighing balance, I use the rule to measure leaf length, leaf width and leaf height.

The remediation study took place from August to November 2004. The soil was divided into twelve (12) polythene bags as presented in Table I

Table I: Experimental Layout of the Site

US	CS	OF_1	OF_2	OF_3	OF_4	OF_5
		IF_1	IF_2	IF_3	IF_4	IF_5

Where:

US - Polythene bag with uncontaminated soil
CS - Polythene bag with uncontaminated soil
OF_1 - Polythene bag with 1.0"g" of organic fertilizer/1kg of contaminated soil
OF_2 - Polythene bag with 5.0"g" of organic fertilizer/1kg of contaminated soil
OF_3 - Polythene bag with 10.0"g" of organic fertilizer/1kg of contaminated soil
OF_4 - Polythene bag with 20.0 "g" of organic fertilizer/1kg of contaminated soil
OF_5 - Polythene bag with 50.0"g" of organic fertilizer/1kg of contaminated soil
IF_1 - Polythene bag with 1.0"g" of Inorganic fertilizer/1kg of contaminated soil
IF_2 - Polythene bag with 5.0"g" of Inorganic fertilizer/1kg of contaminated soil
IF_3 - Polythene bag with 10.0"g" of Inorganic fertilizer/ 1kg of contaminated soil
IF_4 - Polythene bag with 20.0g of Inorganic fertilizer/1kg of contaminated soil
IF_5 -Polythene bag with 50.0"g" of Inorganic fertilizer/1kg of contaminated soil

Soil Test

Some soil physical and chemical properties such as pH, moisture content, organic and organic were determined.

Soil pH

Fifty milliliters (50"ml") of distilled water was added to 20"g" soil samples in a glass beaker. The mixture was

stirred for 10 minutes left to stand for 30"m" minutes and stirred again for 2 minutes. The pH of the supplement liquid was stirred determined using an orion research pH meter 407 A [5].

Experimental Methods

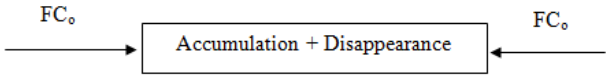
The characteristics of contaminated soil in terms of the physiochemical component such as pH moisture content (%), total organic carbon (%), nitrate ("mg/kg"), phosphate ("mg/kg"), potassium ("mg/kg"), total hydrocarbon ("mg/kg"), organic matter (%), sodium ("mg/kg"), calcium ("mg/kg"), magnesium ("mg/kg") and sodium absorption ratio (SAR) were analyzed using American Society for Testing and Materials [6]-[16] and [10].

Model Derivation and Validation

Model Derivation

The model for computing the rate degradation of concentration of Total Hydrocarbon which is represented by C is given by: Constant stirred tank reactor equation [10].

From first principles



Input of Total hydrocarbon to soil =
Output rate + Disappearance due to biochemical reaction + Accumulation (1)

Input = FC_o (2)

Output = FC_o (3)

Rate of disappearance due to biochemical reaction = RsV (4)

Rate of accumulation = $V\frac{dc}{dt}$ (5)

Substituting (2), (3), (4) and (5) into equation (1) we shall have

$$FC_o = FC + R_sV + V\frac{dc}{dt} \quad (6)$$

Dividing all through of equation (6) by V

$$\frac{FC_o}{V} = \frac{FC}{V} + R_s + \frac{dc}{dt}$$

$$\frac{F}{V}C_o = \frac{FC}{V} - R_s + \frac{dc}{dt}$$

$$\frac{dc}{dt} = \frac{F}{V}(C_o - C_o) - R_s \quad (7)$$

At steady state meaning that at t = 0, C_o = C. Using the above condition into equation (7).

$$\frac{dc}{dt} = \frac{F}{V}(C_o - C_o) - R_s$$

$$\frac{dc}{dt} = -R_s \quad (8)$$

$R_S = K_SC$

Where K_S = rate of degradation

C = concentration

$$\frac{dc}{dt} = -K_sC \quad (9)$$

The equation (9) is the mathematical model representing the process the above model can be solved using the appropriate method to be specific using separation of variable.

$$\frac{dc}{dt} = -K_sC \quad (10)$$

$$\frac{dc}{dt} \bullet \frac{dt}{C} = -K_sC \bullet \frac{dt}{C}$$

$$\frac{dc}{C} = -K_s dt \quad (11)$$

Integrating both sides of equation (5), we have

$$\int_{c_o}^{c} \frac{dC}{C} = -K_s \int_0^1 dt$$

$$\text{In C}\Big|_{C_O}^{C} = -K_s t \int_0^t$$

$$\text{In } C - \text{In C}_o = -K_s(t-0)$$

$$\text{In } C - \text{In C}_o = -K_s$$

$$\text{In } \frac{C}{C_o} = -K_s t \quad (12)$$

Taking exponential on both sides of equation $e^{\text{In}\frac{C}{C_o}} = e^{-K_s t}$

$$\frac{C}{C_o} = e^{-Kt}$$

$$C = C_o e^{-Kt} \quad (13)$$

Determining the rate of biodegradation of the concentration of Total Hydrocarbon

C_o = Initial concentration of Total Hydrocarbon

C = Final concentration of Total Hydrocarbon

K = Rate of degradation of Total Hydrocarbon

t = time in weeks

The above equation (13) shows how the petroleum contaminant reduces in concentration (Abowei et al., 1997).

I conducted lab test at Ideyi consult to find out how the Total hydrocarbon reduces in concentration, from samples collected from spilled sites, then I used t = distribution test to validate result findings.

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Validation

Table II: Showing THC concentration reduction with respect to time in weeks using model for fertilizer. $C = C_o e^{-Kt}$

S/N	Degradation Rate (K_s)	Time In Weeks (t)	Initial Concentration ("mg/kg")	Final Concentration ("mg/kg")
1	55.732	2	7568	6512
2	61.280	2	6512	3860
3	59.841	2	3860	3860
4	54.829	2	839	559
5	50.12	1	459	501

Table III: Percentage Reduction Effect of Fertilizer (F_1) on Total Hydrocarbon (THC) Content of the Contaminated Soil Sample

Duration (WK)	Level Of Fertilizer (g)	1	5	10	20	50
Week 2		86.71	85.86	87.32	82.82	94.5
Week 4		87.05	87.32	88.50	85.47	87.84
Week 6		88.90	89.43	90.14	87.18	89.56
Week 8		90.62	89.96	91.94	88.24	91.41
Week 9		91.62	91.94	92.73	91.53	93.39

Table IV: Percentage Reduction Effect of Goat Dropping (F_2) on Total Hydrocarbon (THC) Content of the Contaminated Soil Sample.

Duration (WK)	Level Of Fertilizer (g)	1	5	10	20	50
Week 2		84.67	81.63	78.45	64.64	12.95
Week 4		87.05	85.10	83.62	80.44	43.71
Week 6		91.15	88.50	86.65	86.79	79.52
Week 8		93.26	89.83	87.98	82.07	89.43
Week 9		94.20	93.39	92.07	95.38	94.72

Table V: Summary of the Models for THC Remediation Using NPK Fertilizer (F_1)

	REGRESSION MODEL	R^2
1	Y = 55.732x + 1157.20	0.9583
5	Y = -61.28x + 1195.40	0.9608
10	Y = -59.841x + 1094.30	0.9947
20	Y = -82.829x + 1460.60	0.9379
50	Y = -88.84x + 1321.30	0.9817

Table VI: Summary of the Models for THC Remediation Using Goat (F_2)

Level Of Nutrient Application (g)	Regression Model	R^2
1	Y = -106.82x + 1370.90	0.9847
5	Y = -113.48x + 1576.20	0.9558
10	Y = -131.27x + 1839.60	0.9526
20	Y = -310.76x + 3023.60	0.9379
50	Y = -894.89x + 7910	0.9459

$Y = a_0 + a_i x$

Where Y = total hydrocarbon (THC) remaining in soil (mg/kg)

X = time (week)

R = correlation coefficient

Using Student's t - = distribution to Compare the rates of degradation of THC by both nutrient sources (Fertilizers and Goat Dropping)

Table VII: Rates of Degradation = Slope from Regression Equation

Level Of Nutrient Application (g)	Degradation Rate X_1 (Fertilizer)	X_2 (Goat Dropping)
1	55.732	106.82
5	61.28	113.48
10	59.841	131.27
20	82.829	310.76
50	88.84	894.89
	$\sum X_1 = 348.523$	$\sum X_2 = 1557.22$

Table VII: Cont.

X_1^2	X_2^2
3106.056	11410.512
3755.238	12877.710
3580.945	17231.813
6860.643	96571.778
7892.723	800828.112
$\sum X^2_1 = 17302.883$	$\sum X^2_2 = 938919.925$

Let X_1 and X_2 represent the rate of degradation of THC by fertilizer and goat dropping respectively.

Then the null and alternative hypothesis is given as:
H_0: $X_1 = X_2$: There is no significant difference in both rates of degradation of THC
H_1: $X_1 \neq X_2$: There is significant difference in the rate of degradation of THC between fertilizer and goat dropping

$$SSX_1 = \sum X^2_1 - \frac{(\sum x_1)^2}{N}$$
$$= 17302.883 - \frac{(121468.2815)}{5}$$
$$= 17302.883 - 24293.656$$
$$= -6990.773$$

$$SSX_2 = \sum X_2^2 - \frac{(\sum X_2)^2}{N}$$
$$= 938919.925 - \frac{2424934.128}{5}$$
$$= 938919.925 - 484986.826$$
$$= 453933.099$$

Variance for fertilizer

$$V_{x_1} = \frac{SSX_1}{N-1}$$
$$\frac{-6990.773}{4}$$
$$= -1747.693$$

Variance for goat dropping

$$VX_2 = \frac{SSX_2}{N-1}$$
$$= \frac{453933.099}{4}$$
$$= 113483.275$$

Mean of fertilizer

$$\bar{X}_1 = \sum X_1 = \frac{348.523}{5}$$
$$= 69.705$$

Mean of goat dropping

$$\bar{X}_2 = \frac{\sum x_2}{N} = \frac{1557.22}{5}$$
$$= 311.444$$

Variances of means
For fertilizer,

$$V\bar{X}_1 = \frac{Vx1}{Nx_1} = \frac{-747.693}{5}$$
$$= -349.539$$

For Goat dropping

$$V\bar{X}_2 = \frac{Vx_2}{Nx_2} = \frac{-747.693}{5}$$
$$= 22696.655$$

Therefore, the t-test

$$T(Nx_{1-1} + Nx_{2-1}) = \frac{\bar{X}_1 - \bar{X}_2}{\sqrt{VX_1 - +VX_2}}$$
$$= \frac{69.705 - 311.44}{\sqrt{-349.539 + 22696.655}}$$
$$= \frac{241.739}{\sqrt{22347.116}} = \frac{-241.739}{149.490}$$
$$= 1.617$$

$\therefore$ /t/ = 1.617

From the t-table, the percentage point for the two-tailed test at 5% level and eight degree of freedom is $t_{0.025.}$ 8 = 2.31. As the computed value of t-taken in absolute value (/t/) is less than $t_{0.025}$. 8, the result is not significant at 5% level. Thus, we conclude that there is no significant difference in both rates of degradation of total hydrocarbon and therefore we accept the null hypothesis, H_0.

III. Results and Discussions

Results of investigation as shown below indicate soil characteristics and outcome of the various treatment employed viz. physical and biological treatments.

Table VIII: Characteristics of Contaminated Soil Before Nutrient Application

S/No	Parameter	Control Sample	Contaminated Sample
1	Ph	5.42	6.33
2	Moisture content %	1.55	3.077
3	Total organic carbon %	0.068	0.104
4	Nitrate “Mg/kg”	4.034	0.041
5	Phosphate “mg/kg”	2.90	0.97
6	Potassium “mg/kg”	6.93	4.54
7	Total hydrocarbon “mg/kg”	<1	7568
8	Organic matter %	0.1176	0.1799
9	Sodium “mg/kg”	25	29.10
10	Calcium “mg/kg”	9.23	11.08
11	Magnesium “mg/kg”	33.16	42.50
12	Sodium absorption ratio (SAR)	0.87	0.90

Initial Condition of Soil Sample before Remediation

Examination of composite contaminated soils (Table VIII) revealed high concentrations of total hydrocarbon 7568 “mg/kg”, Nitrate 0.041”mg/kg” Phosphate (0.97”mg/kg”) and potassium 4.54”mg/kg”.

In the subsoil on the other hand, the subsoil of the control sample recorded 1 “mg/kg”, 0.034“mg/kg”, 0.90“mg/kg”, and 3.93“mg/kg”, for Total hydrocarbon,

Nitrate, phosphate and potassium respectively. The pH of uncontaminated and contaminated soil samples were 5.42 and 6.33 respectively indicating slightly acidic condition.

Effects of the Nutrient (Fertilizer F_1 and Goat Dropping F_2) On Some of the Physiochemical Parameters of the Soil.

The results of the remediation effects of the two kinds of fertilizers on the contaminated soil with respect to some parameter Viz. pH, Total Hydrocarbon (THC) e.t.c at different stages of remediation are shown on the tables IX - X.

Table IX: Result of the effect of remediation with one gramme (1 "g") of Nutrient at week 9

S/No	Parameter	Fertilizer (F_1)	Goat Dropping(F_2)
1	pH	4.84	5.88
2	Moisture content (%)	3.76	4.60
3	Total organic carbon (%)	1.26	2.04
4	Nitrate (Mg/kg)	148	133
5	Phosphate (mg/kg)	10.74	9.90
6	Potassium (mg/kg)	70.60	18.90
7	Total hydrocarbon (mg/kg)	634	439

Table X: Result of the effect of fertilizer (F_1) on pH of the contaminated soil sample (Level of fertilizer ("g")).

DURATION	1	5	10	20	50
Week 2	6.99	7.81	7.78	7.07	7.17
Week 4	7.01	7.76	7.72	6.97	7.01
Week 6	6.89	7.82	7.75	7.17	6.90
Week 8	7.03	7.90	7.78	6.89	7.21
Week 9	4.84	7.50	7.50	6.66	6.29

Table (XI): Result of the effect of Goat dropping (F_2) on pH of the contaminated soil sample (Level of Goat dropping ("g")).

DURATION	1	5	10	20	50
Week 2	7.94	6.67	6.80	7.22	7.82
Week 4	7.60	6.60	6.90	7.01	7.60
Week 6	7.80	6.80	6.81	6.90	7.71
Week 8	7.91	6.70	6.85	7.20	7.50
Week 9	5.88	6.70	6.80	7.05	7.68

Table XII: Result of the effect of Goat dropping (F_2) on the Total Hydrocarbon (THC) content of the contaminated soil sample (Level of goat dropping ("g")).

DURATION	1	5	10	20	50
Week 2	1006	1070	960	1300	1170
Week 4	980	960	870	1100	920
Week 6	840	800	746	970	790
Week 8	710	760	610	890	650
Week 9	634	610	550	641	500

Table XIII: Result of the effect of Goat dropping (F_2) on the total hydrocarbon (THC) content of the contaminated soil sample (Level of goat dropping ("g")).

DURATION	1	5	10	20	50
Week 2	1158	1390	1631	2676	6588
Week 4	980	1060	1240	1480	4260
Week 6	670	870	1010	1000	1550
Week 8	510	770	910	600	800
Week 9	439	500	600	350	400

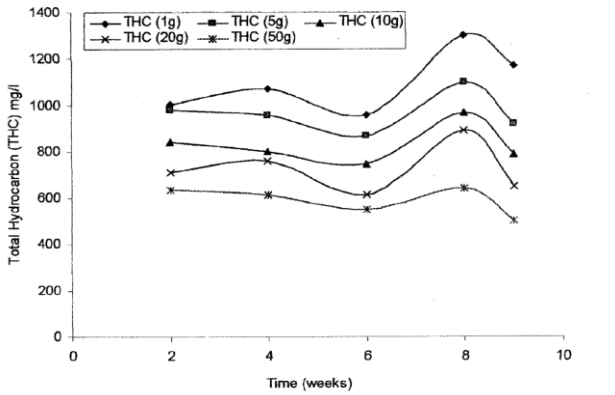

Fig.I. Total hydrocarbon concentration for fertilizer application (F_1) against time

50 grams of fertilizer nutrient added to contaminated soil brought about the greatest reduction of the total hydrocarbon concentration from 7568mg/kg to 500mg/kg unlike the 1g application which shows that the greater the application the better the remediation because the nitrogen supply from NPK fertilizer, the micro organisms that break down the substrate needed it for speedy remediation.

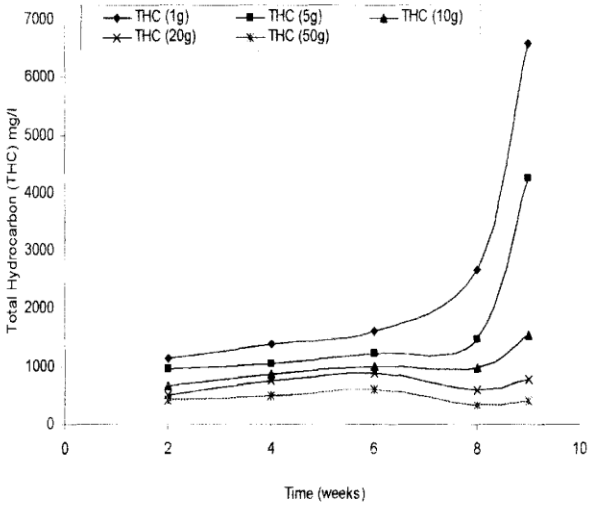

Fig. II. Total hydrocarbon concentration for goat droppings application (F_2) against time

50"g" of goat droppings nutrient added to contaminated soil brought about the greatest reduction of the total hydrocarbon concentration from 7568"mg/kg" to

400“mg/kg” unlike the 1“g” application which shows that the greater the application the better the remediation because the nitrogen supply from goat droppings, the micro organisms that breaks down the substrate needed it for speedy remediation.

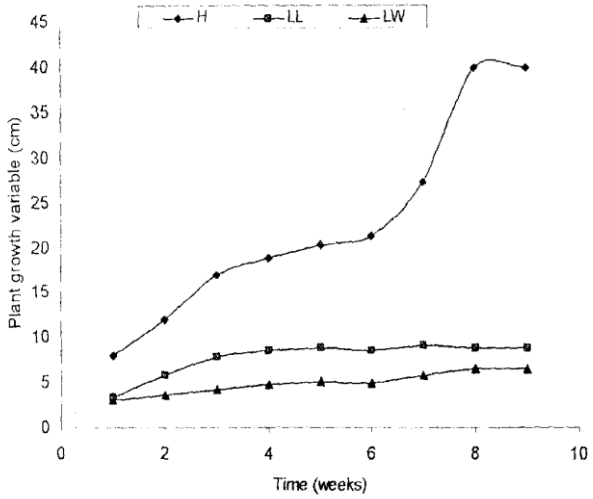

Fig.III. Plant growth variables for contaminated and uncontaminated soil (F_1 = Fertilizer) against time (1g application).

The bean seed recorded growth in height from sixth week to the ninth week due to the breaking down of the total hydrocarbon, allowing growth to occur.

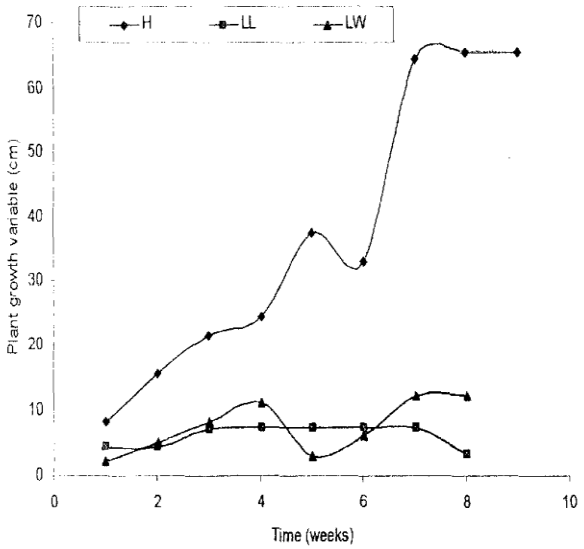

Fig.IV. Plant growth variables for contaminated and uncontaminated soil (F_2 = Goat dropping) against time (5g application).

The bean seed recorded growth in height from sixth week to the ninth week due to the breaking down of the total hydrocarbon, allowing growth to occur.

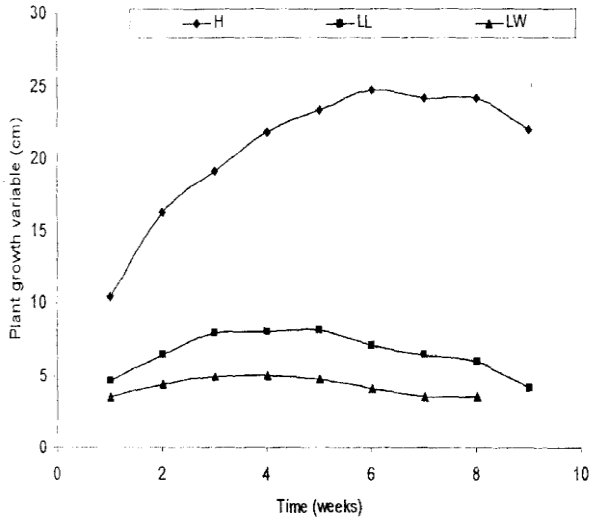

Fig. IV. Plant growth variables for contaminated and uncontaminated soil (F_2 = Goat dropping) against time (20“g” application).

The bean seed recorded growth in height to the sixth week and starting decreasing to the ninth week due to over-flooding of moisture which did not allow for aeration which makes for speeding remediation.

Seed Germination and plant Growth in the Contaminated Soil Sample

Growth of bean plants in contaminated and uncontaminated soil amended with fertilizer and goat dropping. Bean seeds were planted in seven levels (1 “g”, 5“g”, 10“g”, 20“g”, and 50“g”) of both fertilizer and goat dropping, and the effect of varying levels on the growth of bean plants (i.e. plant height, leaf length, leaf width and number of leaves) were noted.

Effect of the Nutrient (Fertilizer F, and Goat Dropping F_2) on the Physiochemical Parameter of the Soil.

1. The Soil pH

The pH values for the original soil samples were 5.42 and 6.33 for control uncontaminated samples respectively, which indicate that both soils are acidic. On application of the nutrients, there were some changes in the pH value at various level of nutrient application, the values fluctuated between 7.91 and 4.84, sec Tables II-IV. It was observed that the pH values for NPK fertilizer levels of 5“g” and l0“g” of soil remained within the neutral pH range whereas goat dropping levels of 20“g” and 50“g” of soil remained within the neutral pH throughout the study duration. See Table III. From the results of the tests, it was observed that oil Stills on land alters the pH from its natural state. The spilt shifted the soil pH from more acidic to less acidic zone. The magnitude of the shift is dependent on the degree of pollution that occurs in the given soil environment [20]. The pH Values observed in Sq and log soil of NPK fertilizer and 20“g” and 50“g” of soil of goat dropping fall within the optimum pH for rapid decomposition of waste which is usually in the range of 6.5 to 8.5 [7]-[18]

2. Moisture Content

Moisture content values of 1.55 and 3.077 were observed for control and contaminated samples respectively before remediation was initiated. The reason for the difference is not far fetched; it was due to the saturation of the contaminated site with crude oil. After remediation with 1“g” each of the nutrients, there was an increment in the moisture content in both cases i.e. 3.76 and 4.60 for NPK fertilizer and goat droppings respectively. Both values are higher than the initial value of 3.077. However the goat dropping has a higher impact on the moisture content than the fertilizer.

3. Nitrate

Nitrate concentration in both control and contaminated soils were 4.034“mg/kg” and 0.041 mg/kg respectively. After 9 weeks of remediation with 2 tonnes/ha each of the nutrients, there was an increase in the values to 148“mg/kg” (fertilizer) and 133“mg/kg” (goat droppings). Increment to fertilizer application was higher than that of goat dropping, because of the presence of nitrogen in the inorganic fertilizer composition [2].

4. Phosphate

Phosphate values of 2.90 and 0.97 were recorded for control and contaminated samples respectively prior to treatment. At the end of 9 weeks of treatment with 1“g” each of nutrients, there was increase in the values to 50 “mg/kg” (fertilizer) and 30“mg/kg” (goat droppings). Fertilizer has a higher effect than goat dropping application of fertilizer the different levels recorded a percentage reduction in THC concentration as follows: 1g (86.70%), 5“g” (8.86%), l0“g” (87.32%), 20g (82.82%), 50g (84.54%) whereas that of goat dropping is as follows: 1g (84.69%), 5“g” (12.95%). The difference in the level of THC degradation can be attributed to the fact that fertilizer readily provided Nitrogen, phosphorus and potassium to the inherent microbial population unlike the goat dropping which does not readily release these same minerals until after mineralization of the goat droppings.

At the end of the study, fertilizer recorded the following percentage in THC concentration: 2tonnes/ha (91.62%), l0tonnes/ha (91.94%), 20tonnes/ha (92.73%), 20“g” (91.53%), 50“g” (93.39%) while that of goat dropping is as follows: 1“g” (94.20%), 1“g” (93.39%), l0“g” (92.07%), 20g (95.38%). 50“g” (94.71%). As can be observed from the result recorded at the last stage of the study, goat dropping recorded higher percentage reduction in THC concentrations than fertilizer. This could probably be attributed to the fact that the fertilizer (NPK) applications ability to readily release nitrogen, phosphate and potassium exposed the elements to leaching effect. Thereby depriving the microorganisms of the nutrients they require functioning effectively in the degradation of the hydrocarbon in the soil. The phenomenon is graphically reflected in Figure I as indicated by the chair-like conformation of fertilizer (NPK) applications. Figure II shows L-like curve for goat dropping indicative of continuous release of nutrients, increase in microbial population and reduction in THC level in the soil. Models for both nutrient sources are shown in Appendix 2. Using student’s t-distribution, it was found that there was no significant difference in both (fertilizer and goat dropping) rate of degradation of Total hydrocarbon.

Seed Germination and Plant Growth

There was seed germination in both controls A (i.e. contaminated soil unamended with nutrients) and control B (i.e. uncontaminated soil unlamented with nutrients) as can be seen in Figure III, crude oil affect germination and plant growth in diverse ways.

It may directly kill the plant or inhibit continued growth of already established vegetation. Growth may be indirectly affected through the creation of nutrient-deficient conditions by microbial immobilization [25]-[28]. At high levels of pollution, the seeds are destroyed while at lower levels, germination is retarded [26]. Therefore the rate of germination ha san inverse relationship with the dose of oil in contamination [8] reported that the poor levels of seed germination is due to poor soil wettability, aeration and toxic effect of oil.

The use of NPK fertilizer (20:10:10) in the pre planting remediation of crude oil-polluted soil inhibited germination of both beans and maize seeds. See Figures IV and V on the other hand, there was germination in both contaminated and uncontaminated soils amended with goal droppings. See Figures IV -V

The use of goat dropping provided some benefit to the seeds and seedlings. This is hinged on its moderate solubility, balanced macro and micro-nutrients, gradual but steady release of these nutrient into soil, its tendency of increasing the humus level, its non - toxicity to the soil biota, and finally, its slight alkaline pH [1]-[10]. On the other hand, NPK fertilizer did not encourage the germination of seeds beyond 1g level which is primarily due to over-nitration of the soil, its high solubility, water-logging capacity, and its toxic nature to the soil biota. Moreover, the water-logging effect observed in the use of NPK fertilizer is a contributory factor to the observed inhibited growth of plants, because of its potentials in displacing available soil- air-which is otherwise, important to the planted seeds and soil microbes [8]-[20]. However, beans seed was used in the study because of the bulky nature of maize seedlings.

In terms of plant growth variables, leaf length, leaf height etc control B (uncontaminated soil) showed better growth variables than control A (contaminated soil) see Figure 3. On application of 1g of the nutrients, fertilizer showed better growth variables on uncontaminated soil than goat dropping whereas goat dropping showed better growth variables on contaminated soil than fertilizer. (See Figures IV and V).

The highest plant height was recorded in uncontaminated soil when 50“g” of goat dropping was applied whereas the highest plant height was recorded in contaminated soil when 20g of goat droppings was applied [10]-[15].

IV. CONCLUSION

1. Both contaminated and control soils are slightly acidic at the start of the study and still maintained the status at the end. This means that the soil of Afam is acidic in nature.
2. Fertilizer encouraged plant growth better than goat dropping in uncontaminated soil, whereas goat dropping encouraged plant growth better than fertilizer in contaminated soil.
3. Fertilizer application above 1g inhibited germination whereas goat dropping encouraged germination during the remediation period.
4. Fertilizer application up to 20g encouraged germination in the initially inhibited soil after nine weeks of nutrient application.
5. Goat dropping recorded a higher percentage reduction THC concentration than fertilizer but the t-test proved that the difference is insignificant.
6. Increment in NPK level in the soil as a result of fertilizer application is higher than that of goat dropping, showing that fertilizer improves the NPK value in the soil than goat dropping. However, the NPK appear to leach out with time.
7. Both nutrients have the same effect on the pH of the soil i.e. the pH fluctuated within the optimum pH range fro rapid decomposition of waste: 5 to 8.5 [9].

Goat dropping has a higher organic content than fertilizers and is able to sustain nutrient level of a longer period than fertilizer.

The present study has demonstrated that the crude oil polluted soil from SPDC well head site at Afam in Gyibo Local Government Area of Rivers State call be remediate with both organic fertilizer (Goat droppings) and inorganic fertilizer (NPK), considering the effects both nutrients had on the Total Hydrocarbon content of the original soil sample.

Generally, remediation with fertilizers (organic or inorganic) is advantageous in replenishing the lost nitrogen, phosphorus and potassium (in form of nitrate, phosphate and potash) of the polluted soils. Inorganic fertilizer releases more of the elements at a faster rate than its organic counterpart, but the organic fertilizer is able to sustain its nutrient for a longer period. Integration of the results showed that organic fertilizer (goat dropping) is preferable in the pre-planting remediation of crude oil polluted soil. This is mainly because its actions in the soil have 110 toxic or negative effects on the ecological flora and fauna both in the short and long runs. On the other hand, inorganic fertilizer remediated soil call only be cultivated three months after the remediation was initiated. Finally, with increasing awareness and interest in animal husbandry, goat, sheep and cattle droppings can be collected from different farms at no or little cost which at the end of the day will be insignificant compared to the cost of inorganic fertilizer.

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ABBREVIATIONS

PAH'S	Polycyclic Aromatic Hydrocarbons
TOC	Total Organic Carbon
THC	Total Hydrocarbon
SVE	Soil Vapour Extraction
VOC	Volatile Organic Compounds
SVOC	Semi-Volatile Organic Compounds
OF	Organic Fertilizer
IF	Inorganic Fertilizer
RCS	Relatively Clean Soil
DAP	Days After Planting
B	Beans Seedling
H	Plant Height
LL	Leaf Length
LW	Leaf Width
NL	Number of Leaves
F_1	Fertilizer
F_2	Goat droppings
UNEP	United Nations Environmental Programme
WHO	World Health Organization
EX-SITU	Away from the Sport
IN-SITU	On the Spot
Incinerate	To destroy something completely by burning to ashes
Recalcitrance	Resisting necessary action
Remediation	The act of correcting, changing or improving something undesirable
Through put	Output, amount of material put through a process

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