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Prediction of Soil Nitrogen Depeltion in Crude Oil Contaminated Soil in Southern Nigeria

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Abstract- Oil spillage is a major environmental threat in south-south of Nigeria where most of the oil exploration and exploitation activities take place. If this goes on unchecked or poorly managed, it will lead to the total annihilation of the ecosystem. The objective of this study is to develop a model for the prediction of soil nitrogen depletion in crude oil contaminated soil with time using regression analysis. Each sample containing 10kg of soil were artificially polluted with 0.5, 1.0, 1.5, 2.0, and 2.5 liters of crude oil (Bonny Light). The Soil Nitrogen concentrations were determined using standard methods. Results show that the concentration of residual soil nitrogen in the soil for all the volumes of crude oil introduced into the soil depleted significantly with time when compared to values obtained for the control sample. The residual concentration in the control soil sample was about three times higher than the concentration obtained for other samples. The results obtained from the derived model were very close to the experimental value. The model is suitable for determining Soil Nitrogen content in crude oil polluted sites.

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I. Introduction

In Nigeria, oil spillage in the Niger Delta region, especially on Agricultural Lands, has been a significant issue of concern both to the government and the people in the area. The outcome of this research work can serve as a vital tool in resolving problems associated with oil pollution and bioremediation of affected lands. Oil has hostile effects on the physicochemical properties of soils, plant and, animal community. Beyond 3% concentration, crude oil has been reported to be increasingly deleterious to soil biota and crop growth (Osuji et al., 2006). Unfortunately, available data to manage the ecological spoils of the Niger Delta Region has been found inadequate. Though existing data has found various uses in the Post spill management program of the affected ecosystem and communities, recent advances have shown that such data has been specific to particular sites and incidences, predominantly because of the nature of the crude oil contaminant and possible environmental modifications (Osuji et al., 2006).

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Soil fertility is the result of the interaction between the biological, chemical, and physical properties of soil due to soil type, land use, and effects of climate. Soil chemical properties are related to the supply of plant nutrients that is essential for plant growth. Generally, oil affects the physicochemical properties in plant communities in soil. Oil spill reduces crop yield, land productivity, and grandly decreases farm income. Observation shows that a 10% increase in oil spill reduces crop yield by 1.3% while farm income plummeted to 5% (Odjuwuederhie et al., 2006). According to Shell 1996, half of the volume of the crude oil spill is due to the corrosion of aging facilities mostly flow line. Another 21% happens in the course of operations to produce oil, while about 28% is due to sabotage. The remaining 1% is mainly due to engineering and drilling activities. There have been numerous reports on the impact of crude oil spill on farmland in the Niger Delta region (Osuji and Nworie, 2007; Eneje et al., 2012; Onwuka et al., 2012, Uzoho et al., 2007 and Choron et al., 2010).

Mathematical Models can be used to predict the impacts of crude oil spill on the physicochemical properties of soil to reduce the complaints about polluted farmlands. In predictive modeling, data are collected for relevant predictors (variables that are likely to influence future behavior or results) followed by a model formulation, then predictions are made, and the model is validated. The different approaches to deciding model validity include conceptual model validation and operational validation (Nwaogasi, 2006). A case in which n- control variables X_1, X_2, X_3 to X_n are involved a corresponding linear multiple regression equation is of the form

$$Y = A_0 + A_1X_1 + A_2X_2 + A_3X_3 \ldots + A_nX_n \qquad 1.0$$

The regression coefficient for A_0, $A_1$to A_n can be obtained using Panel Data Computer Software.

II. Methods

They carried out the study over a period of sixteen (16) weeks using different containers measuring 17cm (height) by 18.5cm (diameter). The study area is the research farm of the Federal University of Technology Owerri, located in Owerri, Imo State Nigeria. The soils are derived from coastal plain sands called acid sands – Benin formation (Orajaka, 1975).Samples measuring 10kg polluted soil were placed in each of the

containers and exposed to the same atmospheric and environmental conditions.

Table 1: Layout of experimental design

Polluted Soil Sample	A	B	C	D	E	F
Vol. of crude oil in Liters/kg of soil	0	0.05	0.10	0.15	0.2	0.25
Variable monitored for ABCDEF was:	Soil Nitrogen					

The soil used in the study was collected from the Federal University of Technology Owerri (FUTO) Research Farm from 15cm to 20cm depth with a shovel. It was measured into containers and taken to the laboratory for treatment (greenhouse treatment).

The soil was air-dried for two weeks and sieved through 2.0cm sieve. The soil samples labeled B, C, D, E, F, each weighing 10kg were polluted with 0.5, 1.0, 2.0, 2.5 liters of crude oil (Bony light), respectively, and thoroughly mixed on a polythene sheet and put in a labeled container.

Sample A was not polluted and was used as the control. To maintain the moisture content of the soil, 50cl of water was sprinkled on each polluted soil sample at two weeks intervals.

The polluted samples were allowed to stay 14 days before the commencement of analysis. The representative samples from (A, B, C, D, E, F) containers were taken at two weeks intervals to the soil science laboratory of Department of Crop, Soil and Pest Management, School of Agriculture and Agricultural Technology, FUTO for analysis to determine the fate of soil nitrogen nutrient with time at various levels of pollution with crude oil. The concentration remaining after 14, 28, 42, 56, 70, 84, 98 and 112 days intervals were obtained.

Ten grams (10g) of air-dried soil sample was introduced into a dry 500ml macro-kjeldahl flask, and 20ml of distilled water was added and allowed to stand for 30 minutes after a little swirling. 30ml of concentrated. H_2SO_4 was annexed into the mixture and heated at low heat at the digestion stand. The mixture was allowed to boil for five hours. The digest was transferred carefully to a clean 750ml flask, and 50ml of H_3BO_3 indicator solution was added and placed under the condenser of the distillation apparatus. As distillation commenced, the condenser was kept cool below 30°C, allowing sufficient cold water to flow through and to regulate heat to minimize fronting and prevent suck-back. 150ml distillate was collected, and the distillation process was stopped. The Nitrogen (NH_4-N) in the distillate was determined by titrating 0.01N standard HCl at 0.1ml intervals, and as the color changes from green to pink. The percentage of Nitrogen (%N) content of the soil was read and recorded. This process was repeated for various levels of crude oil pollution for the soil samples.

The Panel Data Computer Software called Stata 13 version was used to obtain the regression coefficients B_0, B_1, B_2, B_3, and B_4 and the model equation for soil nitrogen using the data obtained from the laboratory. The model equation for the soil nitrogen is expressed as:

$$Y_{it} = B_0 + B_1 C_{vit} + B_2 T_{it} + B_3 T_{it}^{\ 2} + B_4 \sqrt{C_{vit}} + U_{it} \quad (2.0)$$

Where,

Y_{it} = soilnitrogen
B_0 B_1, B_2, B_3 and B_4 = model coefficients
T_{it} = Number of days
C_{vit} = Crude oil volume in litres
U_{it} = Random error of the model
i = crude oil pollution levels (0, 0.5, 1.0, 1.5, 2.0)
t = contact time for pollution (days)

III. Results and Discussions

Table 2: The Variation of soil nitrogen values with time after pollution

Time (days)	Pollution level (liter)/10Kg of soil					
	0	0.5	1	1.5	2	2.5
14	0.287	0.143	0.123	0.115	0.121	0.126
28	0.285	0.148	0.128	0.120	0.127	0.128
42	0.291	0.150	0.133	0.125	0.130	0.134
56	0.300	0.152	0.136	0.128	0.127	0.140
70	0.298	0.154	0.138	0.130	0.134	0.142
84	0.300	0.158	0.14	0.133	0.140	0.143
98	0.300	0.159	0.14	0.134	0.140	0.144
112	0.300	0.159	0.14	0.134	0.137	0.144

Table 2 shows the soil nitrogen remaining in the soil after any given time (t = 14 to 112 days), for values of soil samples with crude oil pollution volume ranging from 0 to 2.5L per 10Kg of soil.

Table 3: Regression Model Coefficient for the proposed model

L RESULTS				Number of Obs = 48		
source	ss	df	Ms	F(4, 43) = 599.75		
Model	0.172198	4	0.43049	Prob > F = 0.0000		
Residual	0.004704	43	0.00011	R- Squared = 0.9824		
Total	0.176902	47	0.00376	Adj R-Squared = 0.9808		
				Root MSE = 0.06255		
N	Coef	Std Err	t	P > |t|	95% Conf.	Interval
Conc	0.112373	0.005989	18.76	0	0.100294	0.1244519
time	0.000414	0.000217	1.91	0.063	-2.3E-05	0.0008518
$time^2$	-2.01E-06	1.68E-06	-1.2	0.237	-5.40E-06	1.38E-06
$conc^{1/2}$	-0.27537	0.009769	-28.29	0	-0.29507	-0.25567
_cons	0.1927	0.006827	40.39	0	0.261974	0.2895091

The R^2 for the determination of the proposed model is 0.9824, with a root mean square error of 0.06255, as shown in table 3. The root mean square error is small; hence the adopted model fits (Chang, 2015). The P-value of 0.00 shows that there is a strong relationship between soil nitrogen and concentration of crude oil spilled at any given time. The equation for prediction of soil nitrogen fate in crude oil contaminated soil is therefore

$$N = 0.1927 + 0.1124C_{vit} + 0.0009T_{it} - 2.102eT_{it}^2 + 0{,}2754\sqrt{C_{vit}} + 0.06255$$

The model was checked and adjusted using another set of experimental data. The model validation is represented in fig 1 and table 4, respectively. The values indicate the closeness of the predicted values with the observed values, thus confirming the validity of the model developed (Essington, 2005).

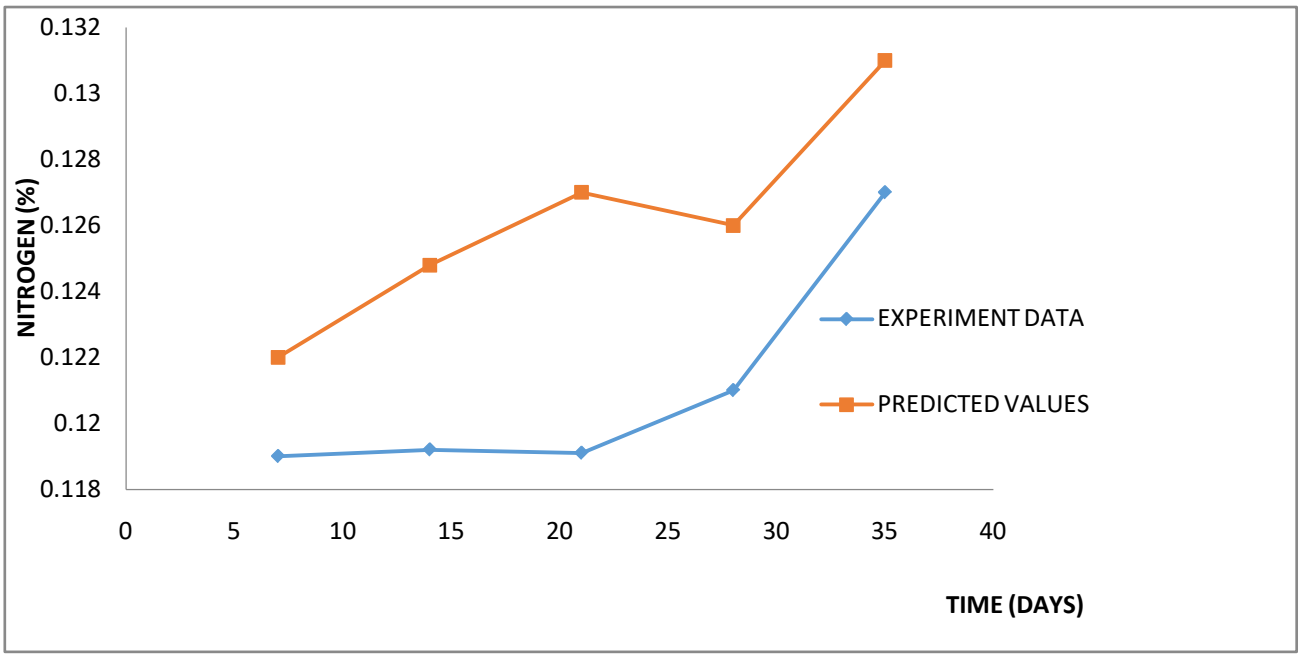

Fig. 1: Experimental and predicted soil nitrogen over time

Table 4: Experimental and Predicted Values for Soil nitrogen over Time

Time/Day	Experimental Data (ED)	Predicted Value (PV)	Percentage Difference
7	0.119	0.122	2.50
14	0.1192	0.1248	5.10
21	0.1191	0.1270	4.40
28	0.1210	0.1260	4.10
35	0.1270	0.1310	1.50

Table 5: Experimental and Predicted values of Soil Nitrogen at various pollution levels using model equation

TIME	COV	ED for N	PV for N	% Difference
14	0	0.287	0.281146199	2.039652249
28	0	0.285	0.285761297	-0.267122925
42	0	0.291	0.289586693	0.485675427
56	0	0.300	0.292622387	2.459208073
70	0	0.298	0.294868439	1.050861862
84	0	0.300	0.29632479	1.225074084
98	0	0.300	0.296991438	1.002858043
112	0	0.300	0.296868414	1.043866037
14	0.5	0.143	0.142616615	0.268103978
28	0.5	0.148	0.147231698	0.653370589
42	0.5	0.150	0.151057094	-0.704961653
56	0.5	0.152	0.154092804	-1.376844432
70	0.5	0.154	0.156338841	-1.518724677
84	0.5	0.158	0.157795191	0.129626446
98	0.5	0.159	0.158461854	0.338457064
112	0.5	0.159	0.15833883	0.540932135
14	1	0.123000002	0.118149087	3.943833426
28	1	0.128000001	0.12276417	4.090492609
42	1	0.133000001	0.126589566	4.819875774
56	1	0.135999997	0.129625276	4.687294834
70	1	0.137999986	0.131871313	4.441067734
84	1	0.140000001	0.133327663	4.765955445
98	1	0.140000001	0.133994326	4.289767554
112	1	0.140000001	0.133871317	4.377631186
14	1.5	0.115	0.112447582	2.219496083
28	1.5	0.120	0.117062658	2.447762651
42	1.5	0.125	0.120888054	3.289551246
56	1.5	0.128	0.123923771	3.192116903
70	1.5	0.130	0.126169801	3.020902324
84	1.5	0.133	0.127626151	4.040488128
98	1.5	0.134	0.128292814	4.259094149
112	1.5	0.134	0.128169805	4.422214726
14	2	0.121	0.116460115	3.751970786
28	2	0.127	0.121075191	4.665207292
42	2	0.130	0.124900587	3.922621935
56	2	0.127	0.127936304	-0.737243726
70	2	0.134	0.130182341	2.849001867
84	2	0.140	0.131638691	5.972364094
98	2	0.140	0.132305354	5.496176202
112	2	0.137	0.13218233	3.516543661

14	2.5	0.126	0.126680404	-0.619859946
28	2.5	0.128	0.131295487	-2.574596719
42	2.5	0.134	0.135120884	-0.836495537
56	2.5	0.140	0.138156593	1.316723681
70	2.5	0.142	0.14040263	1.124906562
84	2.5	0.143	0.141858965	0.867246761
98	2.5	0.144	0.142525643	1.092511955
112	2.5	0.144	0.142402619	1.109295959

Where
COV = Crude oil Volume
ED for N = Experimental Data for soil Nitrogen
PV for N = Predicted value for soil Nitrogen

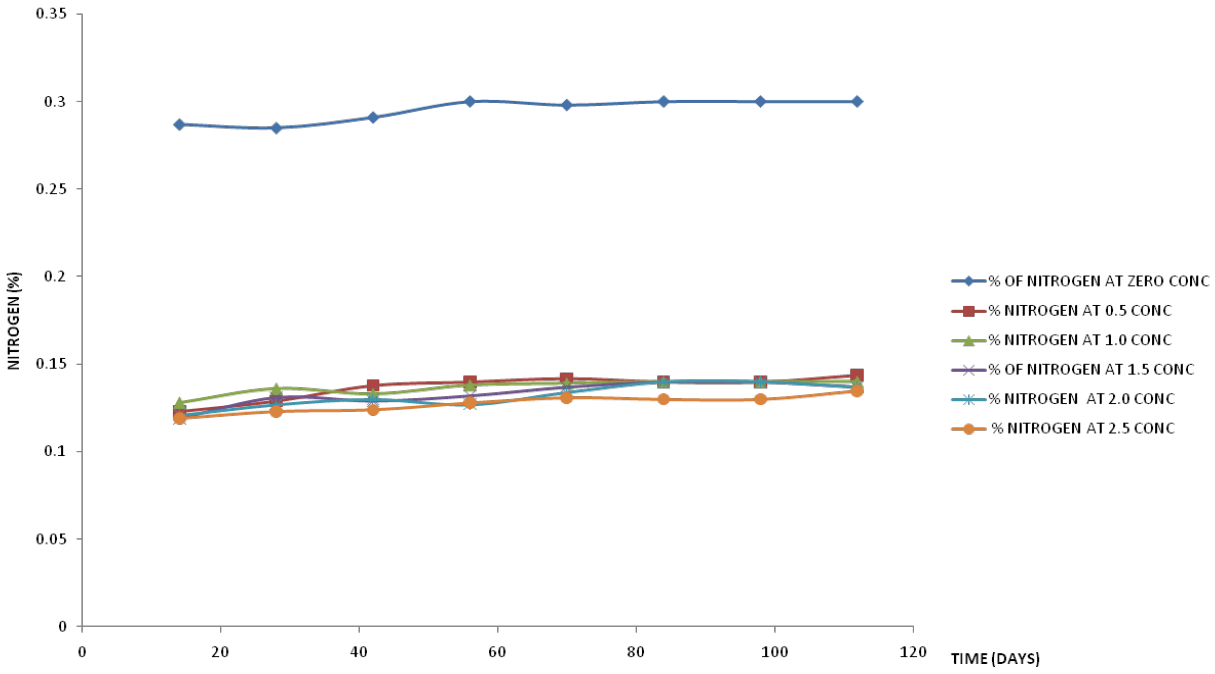

Fig. 2: Soil Nitrogen at various crude oil levels with time

Figure 2 shows the graph of the control sample in comparison with the soil nitrogen at various levels of crude oil pollution with time.

Nitrogen content of the soil at various levels of crude oil pollution varied with time of pollution as shown in Fig. 2. In control (no crude oil added), soil nitrogen increased with time of pollution up till sixty (60) days and remained almost constant till 112 days after. Best soil nitrogen concentration at 60 days of pollution was 0.315%, with the fluctuation in value before and after this time (60 days). This could be ascribed to Nitrogen transformation processes, especially mineralization and immobilization (Catherine et al., 2004).

At 0.5 liters (equivalent to 629 barrels per hectare), of crude oil pollution, N concentration increased with time up till 70 days and then decreased, before a second increase at 112 days. The trend for the 1.0-liter rate of pollution was an increase to 84 days and a second decrease up to 112 days. Values of Nitrogen (N) for the 14, 28, 42, 84 and 112 days of pollution were 0.12, 0.13, 0.13, 0.14, 0.135% respectively. The nitrogen content at 1.5 liters of crude oil pollution increased with time up till 84 days after pollution until a decrease from the 84 to the 112 days of pollution. Values of Nitrogen (N) varied as 0.12, 0.13, 0, 0.135, 0.129, 0, 0.132, 0.137, 0.140, and 0.136 at 14, 28, 42, 56, 70, 84, 98 and 112 days after pollution respectively. Values of N at 2.0 and 2.5 liters of crude oil pollution increased with time of crude application.

Fluctuations in Nitrogen (N) content with time for various crude oil pollution rates could be attributed to differences in Nitrogen mineralization and immobilization

processes. Generally, soil nitrogen content, averaged over time of crude oil pollution, was three times higher at the control than other rates of crude oil pollution. The low concentrations of N at various crude oil application could be due to reduced microbial activity and depressed nitrogen mineralization, occasioned by toxic and damaging effects of crude oil on soil organism. This bad influence decreased with time of application resulting to improved nitrogen concentration with time.

The percentage of soil nitrogen content at all levels of crude oil pollution with time was below 0.15%, which is the critical nitrogen limit for soils of southeastern Nigeria (Enwezor et al., 1990). This shows that despite crude oil pollution at various levels, the nitrogen content of the soil was low and could hardly sustain crop production.

IV. Conclusion

The impact of crude oil pollution on the physicochemical properties of soil about soil fertility in the Niger Delta Region of Nigeria has been reviewed. Modeling of soil nitrogen in crude oil contaminated soil over a period was carried out. The soil nitrogen value for various crude oil levels of pollution increased with time being lowest at 14days.

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