Modeling Soil Organic Carbon in Crude Oil Contaminated Soil in the Niger Delta

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***Abstract*—Oil is known to exert adverse effects on soil properties and plant community. Over the years, there has been strong agitation over polluted farm lands in the Niger Delta region by oil companies operating in the area. This is as a result of oil exploration and exploitation in the region. The people in the region can no longer expect good harvest from their farm lands due to oil pollution. This paper is set to investigate the effect of crude oil pollution on soil organic carbon with time. The soil sample collected from the university research farm was artificially polluted with 0.05, 0.1, 0.15, 0.2, and 0.25 liters per kg of soil. The polluted soils were tested using standard methods at 14days interval. The panel Data Regression model (PDRM) was used to analyze the data. The result reveal that the soil organic carbon content of the soil at various level of crude oil pollution varied with time. This can be attributed to mineralization and immobilization processes in the polluted soil environment. Over time, the soil organic carbon content of the control sample was two (2) times lower than the values of soil organic carbon content at various level of crude oil pollution. The high soil organic carbon at various crude oil pollution level could also be due to presence of the increase carbonaceous substance, their proliferation did not adequately cope with the business of breaking down the excess carbonaceous substrate. A model which can be used as a predictive tool to determine the level of soil organic carbon fate in crude oil polluted soil has been developed.**

***Index Terms*—Crude Oil; Pollution; Soil Organic Carbon; Model; Fluctuation.**

I. Introduction

Globally there is a growing concern over environmental pollution and its management. The three major areas of environmental pollution include water, air and land. One of the major causes of this environment pollution in Nigeria especially the Niger Delta region is as a result of hydrocarbon exploration and exploitation [1]. This has led to the degradation of farm lands, pollution of air, surface and ground waters due to gas flaring. The natural recovery of crude oil polluted land is slow. Communities affected are denied meaningful and economic use of their lands a long time. Hence modeling soil organic carbon fate over time as a result of oil pollution has become imperative. The prediction will help to determine the level of degradation and possible bioremediation work to be carried out. A model may help to explain a system and to study the effect of different component and to make predictions about behavior. Modeling is a process of generating abstract, conceptual, graphical and or mathematical model. Reference [2] defined modeling as the act of constructing or fashioning a model of something or finding a relationship between variables. The trend in modeling is to collect existing records (data), establish relations through mathematical equations, and calibrate such equations in the way of assigning values of associated constant and adopting such equations for forecasting or prediction. Prediction takes us into the future for decision making as we examine different responses arising from changes in control variables. The panel data multiple regression analysis was chosen after considering some other engineering tools like finite element method, finite differences, neural network and Matlab due to its capacity to analyze data with several variables. It also gives the researcher a large number of data points by increasing the degree of freedom and reducing the collinearity among explanatory variables hence improving the capacity to produce the expected results in this research work. Analysis of the linear regression can be extended to cover situations in which the dependent variable is affected by several controlled variables (independent variables). In this case, the question is how soil organic carbon is affected by crude oil pollution at various levels in the soil during the duration of pollution.

Given n sets of measurements,

$(Y_1, X_{11}, X_{21}, X_{31})$ ---- $(Y_n, Y_{1n}, X_{2n}, X_{3n})$, the multiple regression equation is of the form

$$Y = B_0 + B_1X_1 + B_2X_2 + B_3X_3 \dots + B_nX_n \quad (1)$$

The least square estimates for B_0, B_1 and B_3 can be obtained using Panel Data Computer Software.

The fate of soil organic carbon over time as a result of oil pollution is now a growing concern in the Niger Delta region of Nigeria. The objective of the study is to carry out a laboratory investigation using crude oil and soil samples collected from the region to determine the effect of crude oil pollution on the soil organic carbon over a period of time [6]. Other authors whose publications were reviewed in respect to this research work include: [3]-[11].

Study Area

The study area is located in Owerri, Imo State and lies between latitude $5^0 22' 51.5''$ N and longitude $6^0 59' 39'3''$ E, with an elevation of 61m. It is a humid tropical environment with average annual rainfall of 2400mm. The mean daily temperature is about 27^0C. The geological formation in the area shows that the soils are derived from coastal plain sands called acid sands – Benin formation [12].

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II. Methods

The study was carried out over a period of sixteen (16) weeks using different containers measuring 17cm (height) by 18.5cm (diameter). Samples measuring 10kg polluted soil were placed in each of the containers and exposed to the same atmospheric and environmental conditions.

TABLE I: 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 organic carbon					

The soil used in the study was collected from the Federal University of Technology Owerri (FUTO) Research Farm from 15cm to 20cm depth with shovel. The soil 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 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 soil organic carbon 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.

For determination of soil organic carbon, half a gram (0.5g) of each air dried soil sample was put in a conical flask and 2.5ml of 1N $K_2Cr_2O_7$ solution was added and swirled gently to disperse the sample in solution. 5ml of Concentrated Tetraoxosulphate (VI) H_2SO_4 was added rapidly into the flask and swirled gently until the sample and reagent were mixed and finally swirled vigorously for about a minute. The flask was allowed to stand in a fume cupboard for 30min. five (5) drops of the indicator were added to FeSO4 solution until the color changes to maroon color. A blank determination was carried out to standardize the dichromate [14] organic carbon content were calculated as follows:

$$OC(\%) = \frac{(M_{eq}K_2Cr_2O_7 - M_{eq}FeSO_4)\ x\ 0.003\ x\ 100\ x\ 1.3}{weight\ of\ sample\ (g)} \quad (2)$$

Where $M_{eq}K_2Cr_2 = 1N\ x\ 2.5ml$
$M_{eq}FeSO_4 = 0.5N\ x\ vol.of\ titrant\ in\ ml$
$0.003 = Milliequivalent\ weight\ of\ Carbon$

This was repeated for various levels of crude oil pollution in the soil sample.

The panel data computer software called stata 13 version was used to obtain he regression coefficient B0, B1, B2, B3 and B4 and the model equation for the soil organic carbon using the data obtained from the laboratory. The model equation for the soil organic carbon is expressed as

$$Y_{it} = B_0 + B_1 C_{vit} + B_2 T_{it} + B_3 T_{it^2} + B_4 \sqrt{C_{vit}} + U_{it} \quad (3)$$

Where
$Y_{it} = Soil\ Organic\ Carbon$
$B_0, B_1, B_2, B_3\ and\ B_4 = model\ coefficients$
$T_{it} = Number\ of\ days$
$C_{vit} = Crude\ oil\ volume\ in\ liters$
$U_{it} = Random\ error\ of\ the\ model$
$i = crude\ oil\ pollution\ level\ (0, 0.5, 1.0, 1.5, 2.0)$
$t = contact\ time\ for\ pollution$

III. Results and Discussions

TABLE II: The Variation Of Soil Organic Carbon Values With Time After Pollution.

	Pollution level (Litre)/10Kg of Soil					
Time (days)	**0**	**0.5**	**1**	**1.5**	**2**	**2.5**
14	1.340	1.995	2.015	2.035	2.075	2.095
28	1.335	1.995	2.010	2.033	2.076	2.092
42	1.330	1.990	2.008	2.030	2.069	2.088
56	1.325	1.992	2.000	2.021	2.057	2.073
70	1.320	1.972	1.994	2.024	2.059	2.078
84	1.320	1.972	1.994	2.024	2.059	2.078
98	1.319	1.968	1.990	2.031	2.044	2.057
112	1.312	1.960	1.994	2.031	2.031	2.045

Table II shows the soil organic carbon 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 III: Regression Model Coefficient For The Proposed Model

Source	**SS**	**DF**	**MS**	**Number of Obs** = 48 **F(4, 43)** = 221.71
Model	3.287431	4	0.82186	**Prob > F** = 0.0000
Residual	0.06466	43	0.0015	**R - Squared** = 0.9807
Total	3.352092	47	0.07132	**Adj R-Squared** = 0.9789
				Root MSE = 0.10432

OC	**COEF**	**STD ERR**	**T**	**P>|t|**	**95% Conf.**	**Interval**
Conc	-0.42763	0.022206	-19.26	0	-0.47241	-0.38284
time	-0.00036	0.000803	-0.45	0.657	-0.00198	0.001263
time^2	3.34E-07	6.23E-06	0.05	0.957	-1.20E-05	1.29E-05
conc$^{1/2}$	1.121438	0.036217	30.96	0	1.048399	1.194477
cons	1.31	0.025311	53.68	0	1.307639	1.409728

The R^2 for the determination of the proposed model is 0.9807 with a root mean square error of 0.10432 as shown in Table III. The root mean square error is small, hence the adopted model fits. The P value of 0.00 shows that there is a strong relationship between soil organic carbon and concentration of crude oil spilled at any given time. The equation for prediction of soil organic carbon fate in crude oil depleted soil is therefore $OC = 1.310 - 0.4276C_{vit} - 0.0004T_{it} + 3.34eT_{it}^2 + 1.1214\sqrt{C_{vit}} + 0.01043$.

The model was checked and adjusted using another set of experimental data. The model validation is represented in Fig. 1 and Table III respectively. The values indicate closeness of the predicted values with the observed values, thus confirming the validity of the model developed.

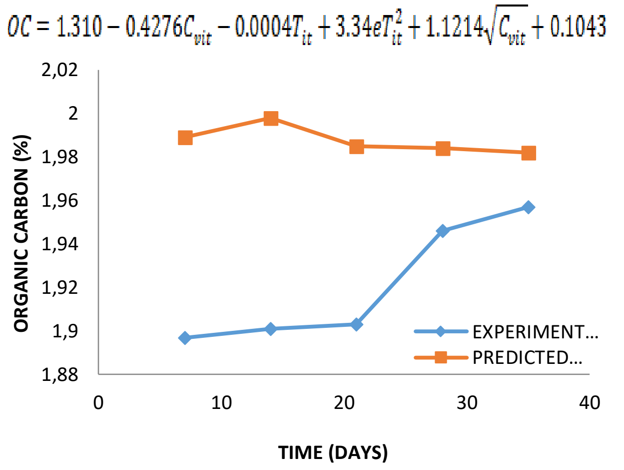

Fig. 1. Experimental and predicted soil organic carbon over time

TABLE IV: EXPERIMENTAL AND PREDICTED VALUES FOR SOIL ORGANIC CARBON (PPM) OVER TIME

Time/ Day	Experimental Data (ED)	Predicted Value (PV)	Percentage Difference
7	1.897	1.989	4.6
14	1.901	1.998	4.8
21	1.903	1.985	4.1
28	1.946	1.984	1.96
35	1.957	1.982	1.50

TABLE V: EXPERIMENTAL AND PREDICTED VALUES OF SOIL ORGANIC CARBON AT VARIOUS POLLUTION LEVEL USING MODEL EQUATION

TIME	COV	ED for OC	PV for OC	%Difference
14	0	1.340	1.353715062	-1.023509584
28	0	1.335	1.348877788	-1.039531764
42	0	1.330	1.344171405	-1.0655159
56	0	1.325	1.339596033	-1.101583765
70	0	1.320	1.335151553	-1.147840917
84	0	1.320	1.330838084	-0.82106298
98	0	1.319	1.326655507	-0.580401921
112	0	1.312	1.322603941	-0.808224423
14	0.5	1.995	1.932878137	3.113878094
28	0.5	1.995	1.928040862	3.356347996
42	0.5	1.990	1.923334479	3.350026627
56	0.5	1.992	1.918758988	3.676756827
70	0.5	1.972	1.914314628	2.925221863
84	0.5	1.960	1.91000104	2.550969269
98	0.5	1.968	1.905818582	3.159627595
112	0.5	1.960	1.901767015	2.971072528
14	1	2.015	2.047526598	-1.614217934
28	1	2.010	2.042689085	-1.626323119
42	1	2.008	2.037982702	-1.493167669
56	1	2.000	2.03340745	-1.670372486
70	1	1.994	2.028962851	-1.753404878
84	1	1.990	2.024649382	-1.741174469
98	1	1.990	2.020466805	-1.530994715
112	1	1.994	2.016415358	-1.124142428
14	1.5	2.035	2.085750818	-2.49389338
28	1.5	2.033	2.080913544	-2.356790532
42	1.5	2.030	2.076207161	-2.276216267
56	1.5	2.021	2.07163167	-2.505282724
70	1.5	2.024	2.067187309	-2.1337639
84	1.5	2.030	2.06287384	-1.619402434
98	1.5	2.031	2.058691263	-1.36343504
112	1.5	2.031	2.054639578	-1.163942892
14	2	2.075	2.084414959	-0.453730653
28	2	2.076	2.079577684	-0.172336669
42	2	2.069	2.074871302	-0.283774573
56	2	2.057	2.070295811	-0.646372844
70	2	2.059	2.06585145	-0.332755447
84	2	2.050	2.061537981	-0.562830682
98	2	2.044	2.057355404	-0.653399909
112	2	2.031	2.053303719	-1.098169412
14	2.5	2.095	2.057798147	1.775746105
28	2.5	2.092	2.052960873	1.866115432
42	2.5	2.088	2.04825449	1.903523377
56	2.5	2.073	2.043678999	1.414421415
70	2.5	2.078	2.039234638	1.865516322
84	2.5	2.070	2.034921169	1.694626333
98	2.5	2.057	2.030738592	1.276681121
112	2.5	2.045	2.026686907	0.895509477

Where
COV = Crude Oil Volume
ED for P = Experimental Data for Organic carbon
PV for p = Predicted value for Organic carbon

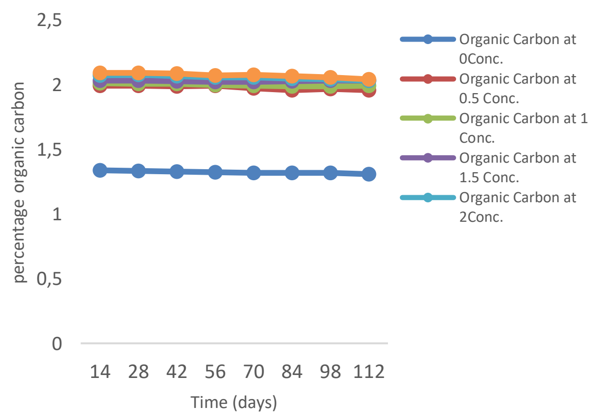

Fig. 2. Soil Organic carbon content at various crude oil levels with time

Fig. 2 shows the graph of the control sample in comparison with the soil organic carbon content at various levels of crude oil pollution with time

Fig. 2 present soil organic carbon contents at various levels of crude oil pollution with time. Total organic carbon contents were slightly higher than the 1.340% obtained for the control sample after the first 14 days of pollution. Organic carbon content should normally increase following the addition of such levels of carbonaceous substances by the polluted soils. The most plausible connection perhaps might be that the crude oil increased the metabolic processes that facilitated the agronomic addition of organic carbon from the petroleum hydrocarbons, thereby increasing the carbon-mineralizing capacity of the microflora.

However, it is most likely that while these organisms might have been stimulated by the presence of the increased carbonaceous substances, their proliferation did not adequately cope with the business of breaking down the excess carbonaceous substrate. Perhaps due to various factors that might include the environmental conditions of weathering and climatic predispositions as well as the physico-chemical properties of the soil [12]. From the study

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the values of total organic carbon content, when averaged over a period of time was found to be about 2 times higher than the values obtained for the control sample. The values of organic carbon content at various levels of crude oil pollution were slightly above the critical levels (1.5 – 2.0%) [13] for tropical soil. This slight increase might be utilized by microorganism for their survival and not sufficient to be released for plant growth, thereby resulting to deficiencies of organic carbon content in the soil [12].

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