Modeling Of Soil Phosphorous Depletion in Crude Oil Contaminated Soil

N. L Nwakwasi¹, B. C Okoro¹, B. U Dike¹, A. N Nwachukwu& J. C. Agunwamba²

¹Department of Civil Engineering, Federal University of Technology Owerri, P. M. B 1526, Owerri, Nigeria ²Department of Civil Engineering, University of Nigeria Nsukka Correspondence: N. L Nwakwasi

Abstract: Environmental degradation issues are of topical concern to communities in the Niger Delta region of Nigeria. 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 phosphorus nutrient 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 perkg 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 phosphorus 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 phosphorus content of the control sample was five (5) times higher than the values of phosphorus content at various level of crude oil pollution (2.59/0.492). The low content of phosphorus mineralization occasioned by toxic and deleterious effects of crude oil on soil organism. Amodel which can be used as a predictive tool to determine the level of soil phosphorus depletion in crude oil polluted soil has been developed.

Keywords: Soil nutrient, Pollution, Phosphorus, depletion model.

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I. INTRODUCTION

Globally there is a growing concern over environmental pollution and it's 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 (Okwuosha, 2000). 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 phosphorus nutrient depletion 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. (Nwaogazie, 2006) 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, calibrate such equations in the way of assigning values of associated constant and adopting such equations for forecasting or prediction. Prediction takes 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 phosphorous 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

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1.0

 $Y = B_0 + B_1 X_1 + B_2 X_2 + B_3 X_3 \dots + B_n X_n$

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

Phosphorus is one of the major soil nutrient needed in crop production. The depletion of this nutrient 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 phosphorus nutrient over a period of time.Other authours whose publications were reviewed in respect to this research work include: Abii, et al., (2009), Akinrede, et al., (2000), Akpan, (2014), Dobermann, et al, (2002), Johnson et al., (2001), Jones, (2001), Krishnakumar, et al.,(2000) and Lewbel, (1979).

1.1 Study Area

The study area is located in Owerri, Imo State and lies between latitude $5^{0}22^{\circ}$ 51.5 N and longitude $6^{0}59^{\circ}39^{\circ}3^{\circ}E$, with an elevation of 61m. It is a humid tropical environment with average annual rainfall of 2400mm. The mean daily temperature is about 27° C. The geological formation in the area shows that the soils are derived from coastal plain sands called acid sands - Benin formation (Orajaka, 1975).

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 1: Layout of experimental design						
Polluted Soil Sample	Α	В	С	D	Е	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: Phosphorus (P)						

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 tabled B, C, D, E, F, each weighing 10kg were polluted with 0.5, 1.0, 2.0, 2.5liters 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 depletion of soil phosphorous 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 the determination of phosphorus, one (1) gramof air-dried soil sample was put into 15m centrifuge tube and 7ml extracting solution was added. The suspension was allowed to centrifuge for 15minutes at 2000.rpm. 5ml distilled water and 2ml of ammonium molybdate solution were added to 2ml of the clear supernatant in a 20ml test tube. One (1) ml of SnCl₂2H₂O dilute solution was added and the content properly mixed. The percentage (%) transmitted on the electro photometer at 660mm wave length was measured after 20minutes. The standard curve within the range 0-1ppm was prepared and plotted against the optical density (OD) standard solution. The content of extractable phosphorous in soil was determined and recorded. This was repeated for various levels of crude oil pollution of 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 phosphorous using the data obtained from the laboratory. The model equation for the soil phosphorous is expressed as:

$$Y_{it} = B_0 + B_1 C_{vit} + B_2 T_{it} + B_3 T_{it}^2 + B_4 \sqrt{C_{vit}} + U_{it}$$
(2.0)
Where,
$$V_{it} = soll phosphorous$$

= soilphosphorous Y_{it} $B_0 B_1, B_2, B_3 and B_4$ = model coefficients = Number of days T_{it} C_{vit} = Crude oil volume in litres Uit = Random error of the model

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i = crude oil pollution levels (0, 0.5, 1.0, 1.5, 2.0)

t = contact time for pollution (days)

3.0 Results and Discussions

PHORUS (P)						
Pollution (uays)	level (Li ບ	iter/10k U.5	g of soi	il) 1.5	2	2.5
14	35.500	6.7500	5.650	4.570	5.450	7.060
28	35.980	7.4552	6.420	5.340	6.200	7.720
42	36.230	8.5142	6.870	6.000	6.550	8.351
56	37.600	8.4350	7.340	6.300	7.200	8.702
70	37.200	8.6524	7.590	6.460	7.220	9.000
84	36.900	8.7871	7.680	6.670	7.251	9.000
98	37.260	8.7282	7.540	6.690	7.120	9.100
112	26.940	8.5124	7.310	6.450	7.121	8.710

Table 2: The Variation of phosphorous values (ppm) with time after pollution.

Table 2 shows the phosphorus value in parts per million (ppm) 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.

ESULTS			Number of Obs = 48			
source	SS	df	Ms	F(4, 43) = 147.45		
Model	5349.146	4	1337.28	Prob > F = 0.0000		
Residual	258.1359	43	6.00316	R- Squared = 0.9321		
Total	5607.272	47	119.304	Adj R-Squared = 0.9257		
			Root MSE = 0.15309			
•	_			a		
۲	Coef	Std Err	t	P > [t]	95% Conf.	Interval
Conc	Coef 19.71109	Std Err 1.403061	τ 14.05	P > t 0	95% Conf. 16.88155	Interval 22.54063
P Conc time	Coef 19.71109 0.068644	Std Err 1.403061 0.050821	t 14.05 1.35	P > [t] 0 0.184	95% Conf. 16.88155 -0.03385	Interval 22.54063 0.1711335
Conc time time ²	Coef 19.71109 0.068644 -0.000415	Std Err 1.403061 0.050821 0.000394	t 14.05 1.35 -1.05	P > [t] 0 0.184 0.299	95% Conf. 16.88155 -0.03385 -0.00121	Interval 22.54063 0.1711335 0.0003801
Conc time time ² conc ^{1/2}	Coef 19.71109 0.068644 -0.000415 -48.46306	Std Err 1.403061 0.050821 0.000394 2.288342	t 14.05 1.35 -1.05 -21.18	P > [t] 0 0.184 0.299 0	95% Conf. 16.88155 -0.03385 -0.00121 -53.0779	Interval 22.54063 0.1711335 0.0003801 -43.84818

Table 3: Regression Model Coefficient for the proposed model

The R² for the determination for the proposed model is 0.9321 with a root mean square error of 0.15309 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 phosphorus and concentration of crude oil spilled at any given time. The equation for prediction of phosphorous depletion in crude oil depleted soil is therefore $p = 30.1 + 19.71C_{vit} + 0.0686T_{it} - 0.0004T_{it}^2 - 48.4\sqrt{C_{vit}} + 0.15309$

The model was checked and adjusted using another set of experimental data. The model validation is represented in fig 1 and table 3 respectively. The values indicate 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 phosphorus over time

Table 3: Experimental and Predicted Values for Soil Phosphorous (ppm) over Time

Time/Day	Experimental Data (ED)	Predicted Value (PV)	Percentage Difference
7	6.526	6.302	3.55
14	6.852	6.724	1.86
21	7.145	7.2	0.769
28	7.380	7.440	0.81
35	7.820	7.953	1.98



TIME	COV	ED for P	PV for P	% Difference
14	0	35.500	34.34120941	3.264202998
28	0	35.980	35.05882645	2.560238194
42	0	36.230	35.61418533	1.699736867
56	0	37.600	36.00727844	4.235957703
70	0	37.200	36.2381134	2.585718656
84	0	36.900	36.30668259	1.607910338
98	0	37.260	36.21299362	2.809996637
112	0	26.940	35.95703888	-33.47081725
14	0.5	6.7500	6.73	0.296296296
28	0.5	7.4550	7.2	3.420523139
42	0.5	8.5124	8.465	0.556834735
56	0.5	8.4350	8.513	-0.924718435
70	0.5	8.6524	8.6737	-0.246174472
84	0.5	8.7871	8.8012	-0.160462496
98	0.5	8.7282	8.7715	-0.496093123
112	0.5	8.5124	8.6123	-1.173582069
14	1	5.650	5.589241505	1.075398315
28	1	6.420	6.306860447	1.762300086
42	1	6.870	6.862217426	0.113283737
56	1	7.340	7.25531292	1.153773139
70	1	7.590	7.486145973	1.368271005
84	1	7.680	7.554717541	1.63128251
98	1	7.540	7.461027145	1.047384839
112	1	7.310	7.205074787	1.435056814
14	1.5	4.570	4.552961826	0.372827389
28	1.5	5.340	5.270580769	1.299984902
42	1.5	6.000	5.825937748	2.901052968
56	1.5	6.300	6.219032764	1.285197204
70	1.5	6.460	6.449866295	0.15686909
84	1.5	6.670	6.518437862	2.272295916
98	1.5	6.690	6.42474699	3.966352867
112	1.5	6.450	6.168794632	4.359774279
14	2	5.450	5.226278782	4.104973123
28	2	6.200	5.943898201	4.130671228
42	2	6.550	6.49925518	0.77473296
56	2	7.200	6.892350197	4.272911397
70	2	7.220	7.123183727	1.340942739
84	2	7.251	7.191754818	0.817062435
98	2	7.120	7.098064423	0.308084753
112	2	7.121	6.842112064	3.916410183
14	2.5	7.060	6.992114067	0.961556856
28	2.5	7.720	7.709733009	0.13299223
42	2.5	8.351	8.265089989	1.028738982
56	2.5	8.702	8.658185005	0.503504686
70	2.5	9.000	8.889019012	1.232891838
84	2.5	9.000	8.957590103	0.471222764
98	2.5	9.100	8.863899231	2.59452007
112	2.5	8.710	8.60794735	1,171667893

Table 4: Experimental and Predicted Values of Soil Phosphorus at Various Pollution Levels Using Model

 Equation



Fig 2: Soil Phosphorus content at various crude oil levels with time

Figure 2 shows the graph of the control sample in comparism with the soil phosphorus content at various levels of crude oil pollution with time

The phosphorous content of the soil at various level of crude oil pollution varied with time of pollution as shown in Fig. 2. For the control (sample), soil phosphorous decreased with time after 28 days the value increased and was best at 96 days (37.5ppm). The fluctuation in values also could be attributed to mineralization and immobilization processes in the soil. For the sample containing 0.5 litres of crude oil level (equivalent to 629 barrels per hectare), the phosphorous content increased gradually and was best at 84 days with a value of 8.787ppm. For the samples with 1.0 and 1.5 litres pollution level respectively, the phosphorous value increased gradually and was best at 112 days (9.990ppm). Similarly, the phosphorous of soil content for samples containing 2.0 and 2.5 litres of crude oil, phosphorus values increased with time and was best at 112 days with a value of 8.400ppm.

Generally, the highest phosphorous content recorded for various crude oil pollution levels was obtained for the control sample (38.90pp) while the lowest values of P was recorded at concentration level of 2.5 litres/10kg of soil at 14 days (4.70ppm). On the average the phosphorous content of the control sample was five (5) times higher than values of phosphorous content at various levels of crude oil pollution (2.59/0.492). The low content of phosphorous at various crude oil pollution levels could be due to reduced microbial activity and depressed phosphorous mineralization, occasioned by toxic and deleterious effects of crude oil on soil organism. The deleterious influence decreased with time, resulting to improved phosphorous concentration with time.

Soil phosphorous content at all levels of crude oil pollution and time were also below the critical limit (8 – 12mg/kg) for tropical soils (Enwezor et. al., 1990). This showed that crude oil pollution at various levels affected the phosphorous content of the soil so badly that P-values obtained can hardly sustain crop Production. 4.0 Conclusion

The impact of crude oil pollution on the physcio-chemical properties of soil in relation to soil fertility in the Niger Delta Region of Nigeria has been reviewed. Modelling of phosphorus nutrient depletion in crude oil contaminated soil over a period of time was carried out. Thesoil phosphorus content for various crude oil levels of pollution increased with time being highest (8.787ppm)at 84days. However over time, the phosphorus content of the control sample was about five (5) times higher than the value of phosphorus content at various levels of crude oil pollution. The phosphorus content of soil contaminated with crude oil over time loses its phosphorus content and thereby deficient for crop production in tropical soils.

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