MODELLING OF MAJOR SOIL NUTRIENTS DEPLETION IN CRUDE OIL CONTAMINATED SOIL

BY

NWAKWASI, NGOZI LIVINUS, B.Eng. (FUTO), M.Eng. (Benin)

(REG. NO. 20124771968)

POSTGRADUATE SCHOOL

FEDERAL UNIVERSITY OF TECHNOLOGY, OWERRI.

JUNE, 2016.

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JUNE, 2016.

CERTIFICATION

This is to certify that this work, "Modeling of major soil nutrients depletion in crude oil contaminated soil", was carried out by Nwakwasi, Ngozi Livinus (Reg. No. 20124771968) in partial fulfillment of the requirements for the award of the degree of Doctor of Philosophy (Ph.D) in Civil Engineering (Water Resources Engineering) of the Federal University of Technology, Owerri.

____
Engr. Dr. B.C. Okoro
Supervisor
Date 21/06/16

jcagunwamba
Engr. Prof. J.C. Agunwamba
Supervisor
Date 21/06/16

____
Engr. Dr. (Mrs.) B.U. Dike
Supervisor
Date 21/06/16

____
Engr. Dr. (Mrs.) B.U. Dike
HOD, Civil Engineering
Date 21/06/16

____
Engr. Prof. G.I. Nwandikom
Dean, SEET
Date 21/06/16

____
Engr. Prof. (Mrs) K.B. Oyoh
Dean, Postgraduate School
Date ______________

____
External Examinar
21-06-2016

DEDICATION

To the most High God, who makes all things beautiful in His own time.

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ABSTRACT

Modeling of major soil nutrients depletion in crude oil contaminated soil was carried out, using field experimental data generated from Research Farm Soil at the Federal University of Technology, Owerri, Imo State, Nigeria. The main objective of the study was to investigate the variation of nutrients, curde oil concentration and bacteria with time in the laboratory. To develop models for prediction of nutrient depletion with time and see how the models can be applied in field and bioremediation activities. The soil was artificially polluted with crude oil (bonny light) of different volumes/wt (i.e. 0.5, 1.0, 1.5, 2.0 and 2.5 litres per 10kg of soil), equivalent to 629 barrels/hectare, 1258 barrels/ha, 1887 barrels/ha, 2515 barrels/ha and 3144 barrels/ha respectively. Some physicochemical properties that reflects major soil nutrient content and fertility status (Nitrogen, Phosphorous, Potassium, Organic Carbon, Organic Matter and Soil pH) were determined, using standard methods. Results from the different levels of crude oil pollution over time showed that nitrogen content depleted from 0.287 to 0.123 within the first 14 days after pollution. Nitrogen content of the control sample was about three times higher than the values of nitrogen content at other various levels of crude oil pollution (0.021/0.0079) when averaged over a period of time (112 days). Similar results were obtained for phosphorous content which depleted five times over the control value when averaged over a period of time. Potassium content also showed a significant decrease from the control value, and was about 3 times lower when averaged over a period of time. There was, however, a slight increase in the organic carbon and organic matter content, which was about 1.5 times higher than the control value. The model values of major soil nutrients obtained from the various model equations were very close to experimental values. Hence the models are all suitable for determining the various contents of Nitrogen, Phosphorous, Potassium, Organic Matter and Organic Carbon in crude oil polluted site. The agitation/complaints over polluted farm lands in the Niger Delta region can now be resolved within the shortest possible time by utilizing the findings and model equations developed from the study. Hence, the cut-off between what really constitutes a poisonous dose and no-effect or tolerable dose in crude oil contamination can be determined using the models.

Key words: crude oil, pollution, soil nutrient, depletion, contaminated oil, model and soil fertility.

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND OF STUDY

Environmental degradation issues are of topical concern to communities in the Niger Delta region of Nigeria. These issues have also attracted considerable international attention in recent times. In an effort to reconcile the conflict between environment and development processes particularly as they affect communities in the Niger Delta area, an environmental survey was first initiated in February, 1995, by the Shell Petroleum Development Company of Nigeria Limited (SPDC) on behalf of its Joint Venture with the Nigeria National Petroleum Corporation (NNPC), Elf oil company and Agip oil company.

The primary goal of the Niger Delta Environment Survey (NDES) was to provide a good information base, to understand and tackle the enormous environmental and socio economic problems of the region and achieve a development that was environmentally sustainable and people-centered. The Niger Delta region is located in the central part of Southern Nigeria. The Niger Delta region is Africa's largest Delta region covering some 70,000 square kilomelers (NDES, 1995). About one-third of the region is made up of wetlands, and it contains the third largest mangrove forest in the world (HSE-ENV., 2004). It is also home to Nigeria's oil industry. The country is the largest oil producer in Africa and among the world's top 10. Almost all of its production comes from the Delta. About 10 million Nigerians who live in this region bear the brunt of the environmental impact of oil production and pollution on socio-economic activities, which include fishing, agriculture, forest resources exploitation and demographic change (NDES, 1999).

Environmental concern has been growing over this region, both nationally and internationally. In spite of the Delta's resource endowment, its immense potential for economic growth and sustainable development, the region is in a terrible state both economically and environmentally. It is under increasing threat from rapidly deteriorating economic conditions and social tensions which were not addressed by policies and behaviour patterns as observed by Osuji (2001). A study of this region by the World Bank warned that: "an urgent need exists to implement mechanisms to protect the life and health of the regions inhabitants and its ecological systems from further deterioration" (Osuji, et. al., 2006).

In line with this, there are enormous and unique challenges facing oil companies in Nigeria. The Shell Petroleum Development Company alone has 86 flow-stations (East and West) and some 6,200 kilometres of pipelines and flowlines in 31,000 square kilometers of the Niger Delta and one can guess the amount of oil spills expected from such facilities.

Between 1989 and 1996 alone, SPDC recorded an average of 221 oil spills per year in its operational areas. This involved a total of some 7,350 barrels of oil a year. Most of these spills involved volumes of not less than eight barrels ($1.27m^3$) per spill. In 1993 and 1994, 68% of the oil spills were more than eight barrels (Shell, 1996). Figures 1.1 shows the various causes of oil spillage (Shell, 1996).

From Fig. 1.1 it can be seen that half of the volume spilled is due to corrosion of ageing facilities, mostly flowlines. 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 (Shell, 1996).

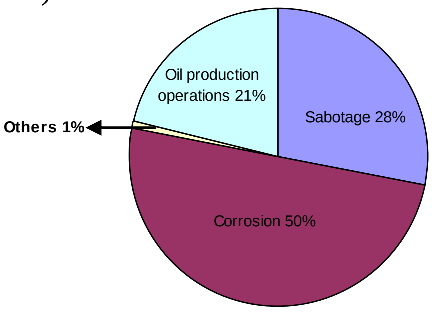


Fig. 1.1: Cause of oil spillage
(Shell Publication, 1996)

The six major causes of oil spills include (a) Production operations and facilities (b) Corrosion of pipelines (c) Flowline replacement (d) Flowstation upgrade (e) Leaking valves and (f) Tampering/sabotage.

Environmental contamination issues are complex problem with worldwide implications. Risk to both human and ecological health as a result of toxic materials present or introduced into the environment are a matter of grave concern to modern society. The effective management of environmental contamination problem has therefore become an important environmental priority that will remain a growing social challenge for years to come. But it has also become evident that the proper management of contamination by petroleum products pose several challenges. Risk assessment seems to be one of the fastest evolving tools that promises a way for developing appropriate strategies to aid environmental management decisions (Kofi, 1998).

Risk assessment is a tool used to organize, structure, and compile scientific information in order to help identify existing hazardous situation or problems (like oil spill in the Niger Della reqion), anticipate potential problems, establish priorities and provide a basis for regulatory controls and/or corrective actions. It may also be used to help gauge the effectiveness of corrective measures or remedial actions. A key underlying principle of risk assessment is that some risks are tolerable-reasonable, and even sensible in a way, considering the fact that nothing is wholly safe. In fact, whereas large amounts of toxic substances may be of major concern, simply detecting a hazardous chemical in the environment should not necessarily be a cause for alarm (Amadi, et. al., 1993).

In order to be able to make a credible decision on the cutoff between what really constitutes a poisonous dose and a no-effect dose or tolerable dose, however, systematic scientific tools - such as those offered by risk assessment - become important in the design of environmental programmes. In this regard, therefore, risk assessment seems to represent an important foundation in the development of effective' environmental management strategies. Indeed, to ensure public health and environmental sustainability, decisions relating to environmental management should be based on systematic and scientifically valid processes, such as via the use of risk assessment. This research work focused on the application of risk assessment concepts and principles in the development of effective environmental management programmes, in relation to petroleum contaminated soils.

1.2 STATEMENT OF PROBLEM

Over the years, there has been strong agitation over pollution farmlands 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 farmlands due to oil pollution. In some cases, compensation for damaged crops and farmlands have been paid to communities affected by the spill and in others nothing has been done. In the event of spill, the best the oil companies can do, is to carry out a clean-up exercise in the affected farmlands and no remedial actions are carried out to the affected farmlands. To this end, no serious work has been done to determine the rate of nutrient depletion in the affected farmlands over a period of time as a result of the pollution. Hence the object of this research work is to determine the rate of nutrient depletion in a crude oil contaminated soil.

1.3 OBJECTIVES OF STUDY

The main objective of the research work is to model the depletion of major soil nutrients in crude oil contaminated soil. The specific objectives are:

i. to characterize soil nutrients and crude oil constituents for use in experimentation;

ii. to investigate the variation of nutrients, crude oil concentrations and bacteria with time in the laboratory;

iii. to develop models for prediction of nutrient depletion with time;

iv. to calibrate the model using experimental data;

v. to apply the model in field bioremediation activities.

1.4 JUSTIFICATION OF STUDY

Implementation of recommendations from this thesis will be beneficial to the society in many ways, especially the Niger Delta region. The result of this research work will provide an understanding of the effect of crude oil spill on mainly farm lands in the Niger Delta region of Nigeria. Remedial actions for crude oil contaminated sites can be properly assessed and compensation duely paid to the affected communities, when the level of pollution or contaminations are determined. The outcomes of the research work will help Government at all levels in taking appropriate decisions on the best way of managing environmental degradation oil contamination affected areas.

The formulated mathematical models, can predict the impact of crude oil spill on physico-chemical properties of similar soil types. The litigation/complaints over polluted farm land can be resolved within the shortest possible time, by using the results of this research work to determine the level of pollution on similar affected lands. The research work will help in appropriate decision making on the cut off between what really constitutes a poisonous dose and a no-effect dose or tolerable dose of pollutants which is important in the design of environmental programmes. The models developed in the research work can be used in the overall engineering management of polluted or contaminated sites of similar soil types.

1.5 SCOPE OF STUDY

The scope of this research work include the following:

i. Laboratory investigation to determine the physico-chemical properties of soil and the variation of nutrients at different levels of crude oil concentrations with time.
ii. Formulation of mathematical models for prediction of nutrient depletion in a crude oil contaminated soil, over a period of time.
iii. Emphasis on contaminated soil types is limited to agricultural farm lands of loamy sand texture.
iv. To see how the result of the this work can assist in tackling bioremediation activities in the Niger Delta region.

CHAPTER TWO

LITERATURE REVIEW

2.1 SOIL DEGRADATION

In order to properly analyse optimality of soil resource use over time, it is important to first understand the nature of the soil degradation problem. Soil is often classified as a slowly renewable resource and can thus be treated as both renewable and exhaustible resources (Barbier, 1986). For example, when the major reason for soil degradation is the depletion of soil nutrients' stock (soil mining), soil quality can be replenished through the natural growth of the soil augmented by the application of external inputs such as inorganic fertilizers or manure. Soil mining can, therefore, occur and drastically affect land productivity without posing an irreversible long-run threat to land productivity since measures are available to compensate for nutrient losses (Brekke and Abdalha, 1999). Soil physical structure on the other hand, can be considered as an exhaustible resource. Over a reasonable time horizon, erosion induced losses of topsoil and damage to soil physical structures are thus irreversible. Although soil nutrient depletion can be countered by application of external inputs, soil mining (nutrient depletion) remains the major limitation to crop productivity. Nutrient depletion is the main from of soil degradation, because the insufficient application of external inputs (e.g. chemical and organic fertilizers) among smallholder farmers cannot compensate nutrient losses due to crop harvest and nutrient lost through erosion of the topsoil. The present study, therefore, focused on soil quality as measured in terms of soil nutrient stock and considered depletion of soil nutrients' stock to be mainly through crude oil contamination.

Although, the need for policies to protect soil and ground water is recognized, strategies for managing contaminated land have moved towards fitness for use. Land contamination remains high on the agenda of environmental and regeneration programmes in most European countries, but at low ebb in developing countries.

2.2 CRUDE OIL SPILL DATA IN THE NIGER DELTA - A TIP OF THE ICE BERG

Oil spillage poses a major threat to the environment of the Niger Delta region. If not checked or effectively managed, it could lead to total annihilation of the ecosystem especially in the Niger Delta. Life in this region is increasingly becoming unbearable due to the ugly effects of oil spills. Available records (Tables 2.1 and 2.2) show that oil spill incidents have occurred in many parts of the Niger Delta since 1970 till date. According to the Directorate of Petroleum Resources (DPR), between 1976 and 1996, a total of 4835 incidents resulted in the spill of approximately 2446322 barrels (388940.735m^3) of oil into the environment. Of this quantity an estimated 1,896,930 barrels 301592.9m^3 comprising 77% were lost to the environment (DPR, 1997).

Table 2.1: Oil Spill Data, in Nigeria (1976 – 1996)

S/No	Year	No. of Spill	Quantity Spilled (barrels)	Quantity Recovered (Barrels)	Net Volume lost to the Environment (Barrels)
1-	1976	128	26.157	7.135	19021.50
2.	1977	104	32879.25	1,703.01	31 176.75
3.	1978	154	489,294.75	391,445	97,849.75
4.	1979	157	694,117.13	63,481.20	630,635.93
5.	1980	241	600,511.02	42.416.83	558,09.19
6.	1981	238	42,722.50	5,470.20	37,252.30
7.	1982	257	42,841	2,171.40	40,669.60
8.	1983	173	48,351.30	6,355.90	41995.40
9.	1984	151	40,209	1,644.80	38,564.20
10.	1985	187	11876.60	1,719.30	10,157.30
11.	1986	155	12.905	552	121358

S/No	Year	No. of Spill	Quantity Spilled (barrels)	Quantity Recovered (Barrels)	Net Volume lost to the Environment (Barrels)
12.	1987	129	31.866	6,109	25,757
13.	1988	208	31,866	1,955	7207
14.	1989	228	5,956	2,153	3,803
15.	1990	166	14,150.35	2,092.55	12,057.80
16.	1991	258	108367.01	2,785.96	105.912.05
17.	1992	378	51 187.90	1,476.70	49,711.20
18.	1993	453	8,105.32	2,937.08	6,632.11
19.	1994	495	35,123.71	2355.93	32,787.78
20.	1995	417	63,677.17	3.110.02	60 568.15
21.	1996	158	39,903.667	1,183.807	38,719.860
	TOTAL	4647	2,369,470.04	549,060.38	1,820 410.50

Source: (Department of Petroleum Resources, 1997).

Table 2.2: Oil Spill Data in Selected Land Locations in the Niger Delta (1997 – 2003)

Date/Year	Location	Causes	Barrels Lost
16/5/92	Assa flare site (cassava farms spray with oil)	Carry over during station closure	152,428
28/3/93	Obigbo North W/R (swamp polluted)	Sabotage suspected	116,553
29/7/93	Bornu 27TFK (Dere area polluted, crude oil collected and burnt)	Corrosion on well's F/C	55,907
10/12/93	Brass terminal	Back pressure on production line	197,204
13/3/94	Oyigbo North (spray of oil on bush and farm)	Sabotage	395,835
15/3/94	Bonny offshore (surface water polluted)	24" submarine hose from Bonny to ship developed hole leak	558,678
28/8/94	Bonny well (mangrove swamp & creek polluted)	Flow line burst	642,206
13/3/95	Lawthrone channel (Fls slot and mangrove swamp	Sabotage	750,593
3/7/96	lbewa (nearby bush & swamp polluted	Bondwall damaged	823,317
10/7/96	Ebegoro (swamp polluted)	Drain valve failure	651,506
12/7/97	TNP/Elelenwa Junction (farm land polluted)	Worn out gasket	758,058

Date/Year	Location	Causes	Barrels Lost
13/10/97	Kolo creek well 20f/1 (water surface & Raffia	Corrosion	766,053
6/7/98	Krakrama (creek polluted)	Carry over during station closure	692,269
11/12/99	Bornu ml/fl (Dere farm land polluted)	Leakage from pipeline flauge connection	842,474
18/12/99	IDU (Creek pollution)	Leakage from pipeline 24"	752,496
19/5/2000	S/L Epkpe (offshore polluted)	Leakage from 16" pipeline	513,622
10/12/2001	Obiakpu (adjacent cassava farm sprayed with oil)	Sabotage	650,876
29/12/2001	Ebegoro No.5 oil field Pollution	Sabotage	438,500
15/3/2002	Ebocha village (Dere farmland polluted)	Leakage from flauge connection	508,000
10/8/2002	Akiri/ODURI (nearby bush and Swamp polluted)	Flow line burst	544,000
28/9/2003	Obagi (bush polluted) a new well head	Misconnection from a new well head	467,574
2/9/2003	Oyigbo North (spray of oil on bush & farm)	Sabotage	112,416

Source: (Department of Petroleum Resources, 2004).

2.3 COMPONENTS OF HYDROCARBONS IN CONTAMINATED SITES

Before further considering the chemistry of hydrocarbons, it is necessary to establish definitions for two commonly-used acronyms. Petroleum hydrocarbons (PHC) is widely used to refer to the hydrogen and carbon-containing compounds that originate from crude oil. Total petroleum hydrocarbons (TPH) refers to the measurable amount of petroleum-based hydrocarbons in an environmental matrix. Thus, whilst PHC deals with an absolute and somewhat intangible quantity, TPH pertains to actual results obtained by sampling and analysis. As mentioned above, in its strictest sense, TPH pertains to a mixture and hence the results of simple TPH analysis are not of great help in terms of risk assessment.

A full discussion of the elementary chemistry associated with hydrocarbons is available in standard organic chemistry textbooks (e.g. Morrison and Boyd, 1973). However, the properties of a range of simple paraffin alkanes, which could be found at contaminated sites are listed in Table 2.3. Also Table 2.4 gives some corresponding physical properties for aromatic molecules that might occur at contaminated sites, while Figure 2.1 is a schematic representation of interaction of hydrocarbons with soil.

Table 2.3: Simple Paraffin Alkanes

Molecular Formula	Name	Boiling Point (°C)	Melting Point (°C)	Density at 20°C
C_6H_{14}	n-Hexane	69	-94	0.658
C_8H_{18}	n-Octane	126	-98	0.702
$C_{10}H_{22}$	n-Decane	174	-32	0.747
$C_{12}H_{26}$	n-Dodecane	215	-12	0.768
$C_{16}H_{34}$	n-Hexadecane	287.5	18	0.775 (at mp)
$C_{20}H_{42}$	n-Eicosane	205	36.7	0.778 (at mp)
$C_{30}H_{62}$	n-Triacontane	449.7	66	0.775
$C_{35}H_{72}$	n-Penta triacontane	490	74.6	0.781

Source: (Sadler and Connels, 2003)

Table 2.4: Some Aromatic Compounds

Molecular Formula	Name	Boiling Point (°C)	Melting Point (°C)
C_6H_6	Benzene	80	5.5
$C_{10}H_8$	Naphthalene	218	80.3
$C_{14}H_{10}$	Phenanthrene	338	100.5
$C_{18}H_{12}$	Chrysene	448	253
$C_{20}H_{12}$	Benzo(a)pyrene	310-312	179
$C_{22}H_{12}$	Benzo(g,h,l)perylene	542	278

Source: (Sadler and Connels, 2003)

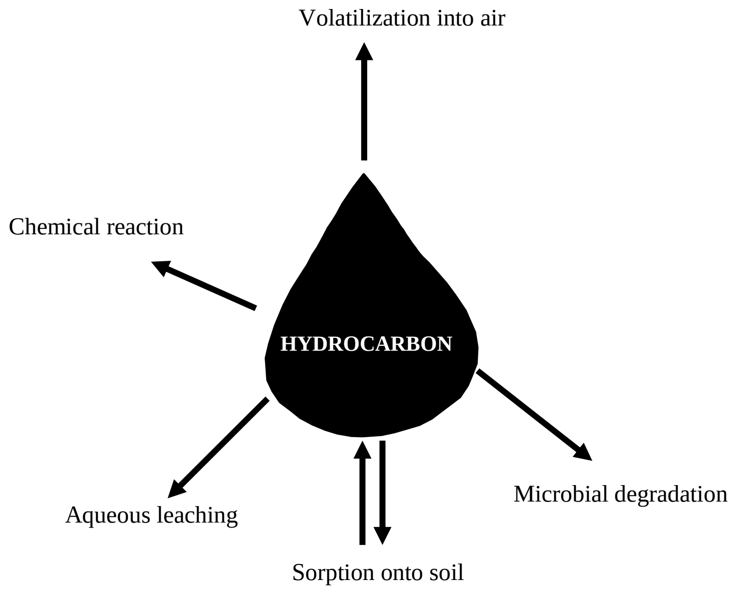


Fig. 2.1: Hydrocarbon Interaction with soil

(Sadler and Connels; 2003)

2.4 FATE OF HYDROCARBONS IN SOIL

The result of these processes is an alteration in the composition of the hydrocarbon discharged into the soil. Clearly, those hydrocarbons that are most strongly sorbed onto soil organic matter will be most resistant to loss or alteration by the other processes (Fig. 2.1). Conversely, the more volatile (soluble) hydrocarbons will be the most susceptible to change by volatilization/reaction/leaching/ biodegradation. The ultimate result will be "weathering" of the hydrocarbon mixture discharged into the soil, with an accompanying change in its composition and a preferential transport of certain fractions to other environmental compartments.

Because of the overall complexity of the problem and of the spectrum of hydrocarbons likely to be encountered, it is impossible to view TPH as a single entity. There have been many approaches to the problem, but the simplest and one most frequently used is the one based on the vapour pressure ranges of the organics in question. This also relates to the sampling methodology employed. The approach consists of sub-dividing the hydrocarbons into the most volatile fraction referred to as gasoline range organics (GRO) and the less volatile fraction. In the case of monitoring of storage tanks, a sub-fraction known as diesel range organics (DRO) is often distinguished amongst the semi-volatile fraction.

These are typical of results that would be obtained if water is spiked with a mixture of the various hydrocarbons. As regards a contaminated soil, this type of analysis is not possible for a number of reasons, most particularly because the various hydrocarbons cannot be extracted from the sample with equal efficiency. In particular, volatiles require special procedures to achieve satisfactory recovery from the matrix. It thus becomes important to distinguish between those compounds that are considered to be volatile and those that rank as semi- or non-volatiles.

2.5 VOLATILE HYDROCARBONS (INCLUDING GROS)

Very few authorities today employ a boiling-point based definition of volatiles, because some volatile substances (e.g. naphthalene) sublime rather than boil, whilst others emit significant quantities of vapour well below their boiling point. Standards Australia (1999) defines a volatile substance as one whose boiling point or sublimation temperature are such that it exists to a significant extent in the gaseous phase under ambient conditions. Table 2.5 lists some common hydrocarbons that are generally considered as volatile. Most (but not all) of these would be considered as GROs.

Table 2.5: Some Commonly Encountered Volatile Hydrocarbons

Aliphatic	Aromatic
Pentanes	Benzene
Hexanes	Toluene
Heptanes	Ethylbenzene
Octanes	Xylenes
Nonanes	Naphthalene
Decanes	Phenanthrene
	Anthracene
	Acenaphthylene

Source: (Minnich, 1993)

As regards the sampling of volatile hydrocarbons in the field, two procedures are generally recommended namely zero headspace and solvent extraction (Minnich, 1993). It should be noted that these two procedures do not necessarily give equivalent results.

Zero heads pace procedures involve the collection of a soil sample with immediate transfer to a container into which the sample fits exactly. The only space for gases is that within the soil pores. The volume of sample collected depends upon the concentration of volatiles in the soil. It is imperative that the container employed can be interfaced directly with the gas chromatograph. Several commercial versions of zero headspace sampling devices are available. The sample is transported to the laboratory at 4°C, where it is analysed directly by purge and trap gas chromatography (US EPA 5035, 1996) or other appropriate techniques such as Vacuum Distillation (US EPA 5032, 1996) or Headspace (US EPA 5021, 1996).

Solvent extraction procedures involve collection of sample by an appropriate device and subsequent immediate placement into a borosilicate glass vessel, which contains a known quantity of ultrapure methanol. The bottle is then transported to the laboratory at 4°C, and the methanol fraction analysed by purge-and-trap gas chromatography (or similar procedure).

In general, the zero headspace procedures are employed when the concentrations of volatiles in the soil are relatively low and the solvent extraction methods are used for more polluted soils (Standards Australia, 1999). Irrespective of which procedure is used, quantification of volatiles in soil is subject to serious errors if sufficient care is not taken with the sampling operation (Siegrist and Jenssen, 1990). Although direct purge-and-trap methods are frequently advocated for determination of volatiles in samples collected by zero headspace procedures, there are certain problems associated with this technique. It has been hypothesised that the procedure really only collects that fraction of the volatile that exists in a free form within the soil pore spaces, or is at least in a facile equilibrium with this fraction. Askari et. al. (1996) compared three methods for extraction of volatiles from soil samples. In addition to the standard direct purge-and-trap and methanol extractions, they also employed a 40°C methanol procedure, in which the vial containing the sample was sonicated to improve efficiency.

Gas chromatography detectors employed for the determination of volatile organics in soil are generally Flame Ionisation Detector (FID), Photoionization Detector (PID) or mass spectrometry. FID detectors will respond to all carbon compounds in the sample, whereas the PID is capable of some sensitivity by virtue of the energy of the lamp employed. A 10.2 or 10.0 eV lamp yields more specific response to unsaturated (including aromatic) hydrocarbons and may also be employed to give a complete BTEX (benzene, toluene, ethyl benzene and xylene) characterisation at sites where this is likely to be an issue. As regards the columns used for the analysis of volatile hydrocarbons, a wide variety can be used. Wide bore capillary columns of length typically about 105 metres are generally employed and they must be capable of resolving 3-methyl pentane from methanol as well as ethyl benzene from the xylenes. There may be some variation in choice of column, however, according to the resolution required by the authority. There is some debate concerning appropriate limits for the gasoline range and this is reflected in disparate legislation amongst various countries. For instance, the upper range of the gasoline organics may be defined by naphthalene or dodecane.

Typical gas chromatography conditions involve an oven temperature ramped between 40°C and 240°C, with a detector maintained at 250°C and an injector at 200°C. There are two methods of calibration for the gas chromatograph. One method consists of analysing a mixture of individual hydrocarbons that bracket the gasoline range and calculating an average response factor from the response for each individual component. The other method involves analyzing a standard that contains one or more gasolines.

2.6 SEMI AND NON-VOLATILE HYDROCARBONS (INCLUDING DROS)

In almost all cases of hydrocarbon contamination, some attention will have to be paid to the presence of semi- and non-volatile hydrocarbons. Even at service station sites, the leakage of diesel and kerosene storage tanks is a possibility and requires checking. A gas chromatography-based finish is generally employed in the analysis of semi-or non-volatile hydrocarbons. However the collection, handling of samples and their ultimate preparation for analysis is entirely different from that used for volatile hydrocarbons. In general, it is not necessary to take such rigorous procedures to prevent loss of analyses following collection, although the procedures should still be verified using appropriate quality control measures (Standards Australia, 1997).

Before analysis of semi- or non-volatile components can proceed, it is necessary that the hydrocarbon components be brought into solution. In a sample from a contaminated site, semi- and non-volatile molecules may exist in the soil pores in the free form within the pore spaces, but are far more likely to be adsorbed by organic matter attached to the soil.

A number of procedures are available to effect this dissolution. These include Soxhlet extraction (US EPA-3540C, 1996 and related methods; most applicable to "heavy hydrocarbons" and PAHs), ultrasonic extraction (US EPA-3550B, 1996), thermal extraction (US EPA-8275A, 1996) and supercritical fluid extraction (US EPA-3560, 1996 and US EPA-3561, 1996). Although these procedures are well documented in these and a number of other references, some of their important details are frequently overlooked, with the result that the extraction is unsatisfactory. In the case of ultrasonic extraction, the method (US EPA-3550B, 1996) clearly stipulates the use of an ultrasonic disrupter of the horn type, with a minimum power of 300 watts. Many laboratories however wrongly interpret this to mean an ultrasonic bath, used for cleaning glassware. Such baths are of far lower energy and are not capable of separating the hydrocarbons from their association with humic material. As regards the use of supercritical fluid extraction, a methanol modifier is required to achieve complete extraction of PAHs, whereas supercritical CO_2 is sufficient to elute normal hydrocarbons (cf. US EPA-3560, 1996 and US EPA-3561, 1996).

Whilst all of the above methods have been accepted by the US EPA, problems have been shown to exist under some circumstances. Although widely used, solvent extraction procedures have been demonstrated as sensitive to such variables as content of humic matter and moisture within samples. Supercritical fluid extraction appears to be a more robust procedure. Banerjee and Gray (1997) compared the effectiveness of thermal extraction techniques with conventional solvent procedures, for a variety of contaminated soils. The efficiency of thermal extraction procedures was sensitive to the size of the soil sample and in some cases, the technique resulted in the cracking of higher hydrocarbons.

In the case of solvent extraction procedures, it is necessary to concentrate and also to clean up the samples. A number of methods of cleanup are available and are further described in US

EPA-3600c. With complex mixtures of semi-volatile hydrocarbons, it is generally advisable to separate the aliphatic and aromatic fractions.

As mentioned above, the most usual analytical finish for hydrocarbon determination is gas chromatography. Depending upon the degree of resolution and level of information required, a number of instrument configurations may be employed. The most common requirement is determination of TPHs and this will often largely consist of DROs. For this purpose, the most normal procedure is GC/FID, according to US EPA method 8015B. Because of the nature of the analyses (boiling point from 170°C to 430°C), higher oven temperatures are required for chromatography of this fraction, compared to GROs. Commonly, fused silica capillary columns of 30 metres length with a 0.53mm internal bore are used, the column being bonded with DB wax at a 1μ film thickness.

The sample is generally introduced by direct injection as the technique is less discriminatory than splitless injection. Temperatures of the injector and detector are maintained at 200°C and 340°C respectively throughout the run and the column temperature ramped from 45°C to 275°C. GC/FID may be used to simply fingerprint the components of a hydrocarbon pollution episode (Bruce and Schmidt, 1994), this strategy being most successful if the pollutant has only recently entered the soil environment. Most frequently however, some attempt is made to quantify the hydrocarbon fractions represented (Whittaker et al, 1995). It is possible to employ both external and internal standards in these determinations. When internal standards are used, they are generally compounds such as hexafluoro-2-propanol, hexafluoro-2-methyl-2-propanol or 2-chloroacrylonitrile. As regards determination of DROs, regulatory authorities vary in terms of the prescribed range. Typically, the DRO range is considered to begin at C_{10} to C_{12} and end at C_{24} to C_{28}. Whatever the range, TPH is taken as the sum of the area within that region of the chromatogram.

More sophisticated detection methods for gas chromatography are also employed in the analysis of hydrocarbons, namely GC/MS (cf. US EPA-827OC, 1996) and GC/FTIR (cf. US EPA-8410, 1994). These procedures have a significant advantage in providing a better characterization of the determinants and are thus of particular use where some environmental modification of the hydrocarbons has taken place subsequent to soil deposition. Quantification by GC/MS, based upon internal standards has been reported as being superior to that based upon external standards (Xie et al, 1999). In addition, they provide the only satisfactory means of resolving PAHs within complex mixtures.

One of the major problems associated with profiling of hydrocarbons at contaminated sites is the phenomenon known as "weathering". This term refers to change in composition of hydrocarbons with time, through the action of volatilisation, leaching, chemical reaction and biotransformation. As regards volatile organics, the most significant process is through volatilisation, resulting in a decrease of overall concentration with time. The longer chain hydrocarbons are however more prone to modification through other processes and it becomes necessary to identify the product of the various transformations. In addition, it is useful to obtain some index of overall weathering.

Such information cannot readily be obtained from simple GC/FlD profiles and hence more sophisticated techniques must be used (Whittaker et. al., 1995). The majority of characterisations have made use of GC/MS. As is well-known, both "hard" (electron impact) ionisation (El) and "soft" (chemical) ionisation (Cl) procedure arc available. Thus, the former procedure produces predominantly fragment ions, whereas the latter produces predominantly parent ions. With complex refractory hydrocarbon samples, chemical ionisation can produce ambiguous results, since many of the analytes have identical parent ion peaks. Thus, GC/EI/MS becomes the method of choice for analysis of most hydrocarbon studies (Altgelt and Boduszynski, 1994). The availability of GC/MS/MS has further enhanced the ability to examine environmental hydrocarbon samples for particular components.

Of particular significance in the study of petroleum weathering are the so-called 'biomarker' molecules. These substances, which include the components of crude oils known as pristane, phytane, the hopanes and steranes. The biomarkers have historically been employed as crude oil signatures in prospecting and characterisation. More recently, they have also been employed in the environmental field, both for the determination of pollutant source and estimation of the degree of weathering. The structures of these biomarker molecules are shown below.

The biomarker molecules are particularly resistant to microbial attack and thus the ratio of other hydrocarbon components to the biomarker will decrease as the crude oil is biodegraded (Wang and Fungus, 1997). In the case of an ongoing oil discharge into the soil, this ratio will be highest nearest the source and will decrease with increasing distance from the source. Thus, the ratio may be used to locate the source of the contaminant (Whittaker et. al., 1995). In a similar manner, expression of biodegradable hydrocarbons as a ratio to high molecular weight PAHs should have potential for fingerprinting purposes. The failure of some attempts to use PAHs for this purpose probably stems from an inappropriate choice of molecules for comparison. Low molecular weight PAHs such a naphthalene or phenanthrene are often selected because of their abundance and relative ease of measurement. Unfortunately, these molecules are also the most prone to biodegradation as well as other forms of attenuation (Sadler and Connell, 2002).

2.7 SCREENING PROCEDURES FOR TOTAL PETROLEUM HYDROCARBON (TPH)

Given the relative complexity (and expense) of the analytical methods described above, it is not surprising that there has been a considerable effort towards devising simplified procedures for determination of TPH. Particular efforts have been expended in terms of finding a satisfactory method for use in the field. Although some promising advance have been made in recent years, laboratory analysis remains the method of choice.

As with laboratory analysis, the major problem lies in the range of compounds covered by the term "hydrocarbons". Again, the most notable variation is in the relative volatility of the substances in question. As regards volatile organics (e.g. GROs), a number of portable devices are used to detect vapours in soil (cf. Standards Australia, 1999). Table 2.6 summarises some of these instruments.

All of these procedures are of use only in the case of volatile analytes and in circumstances where the opportunity exists for sufficient soil gas to accumulate. A more sophisticated approach to the problem involves collection of the contaminated soil and sealing it in a container, where the soil gas can accumulate. This gas is then analysed by one of the above procedures. More often (particularly in the case of PID and FID) the soil is often analysed in situ by direct insertion of the probe into the vadose zone.

Table 2.6: Some Examples of Equipment used for Field Screening of Volatile Substances

Instrument	Principle	Capabilities/Limitations
Portable gas chromatograph	Carrier gas used to move analyte through separation column at elevated temperatures. Detector is usually flame ionisation or photoionisation.	Affords some resolution of mixtures and permits some quantification. The sophistication of these instruments has increased markedly over the past five years.
Photoionisation detector (PID)	Ionization of analyte by ultraviolet radiation.	Detection is generally non- specific and response varies from compound to compound. By using lamps of different energy output, it is possible to limit the range of compounds detected. Presence of moisture may cause artificially high results.
Flame ionisation detector (FID)	Presence of analyte produces ions in an air-hydrogen flame.	Provides non-specific detection, incapable of resolving mixtures and response varies from compound to compound.
Photoacoustic Fourier transform infrared spectrometer	Determination of infrared absorbance.	Analyte must exhibit infrared absorption. Capable of some resolution of mixtures and of partially quantifying components.
Ultraviolet derivative specrometry	Determination of ultraviolet spectra.	Analyte must exhibit ultraviolet absorption. Capable of some resolution of mixtures and of partially quantifying components.

Source: (Standard Australia, 1999)

At best, this can only give a rough qualitative idea of the presence of volatile components. In the case of a recent gasoline spill into sandy soil with low organic matter content, such an approximation may be a useful guide. The instrument however gives no information on the presence of non-volatile components and because of differential responses to various compounds, may give misleading information in the case of mixtures. In terms of toxicological assessment of contaminated sites, results of such field monitoring are useless. Naphthalene is by far the most prevalent PAH in coal tar (Johnston et. al., 1993) and will evoke a response from a PID or FID device. It is however the least significant PAH in terms of human health, whereas carcinogenic PAHs such as benzo(a)pyrene will not be detected by the techniques used to sense volatiles.

As a partial compromise between the use of instruments described above and laboratory analysis, a number of investigators have made use of passive sampling procedures, notably the Petrex technique. The underlying principle of these methods is immersion of a passive sampler into the soil and collection of evolved gases, which are adsorbed onto a solid phase support. The sampler is then removed to the laboratory, where the gases are transferred by Curie point desorption, directly into the ion source of an interfaced quadrupole mass spectrometer. The procedures have their origin in the petroleum exploration industry and the samplers can be used at a considerable range of depths (Einhorn et. al., 1992). The most normal procedure for the use of these sampling devices consists of augering a hole to a depth of 45cm, into which the sampler is placed (Fig. 2.2). Once the holes have been sealed, the soil vapours are allowed to equilibrate with the sampler for a time period between several hours to several days, depending upon the nature of the contamination and soil. At the end of this period, the samplers are removed to the laboratory for analysis. Generally, Petrex samplers are placed in a grid pattern over the contaminated site. They have the advantage of may other methods of allowing some collection of semi-volatile hydrocarbons and can achieve detection limits as low as parts per trillion.

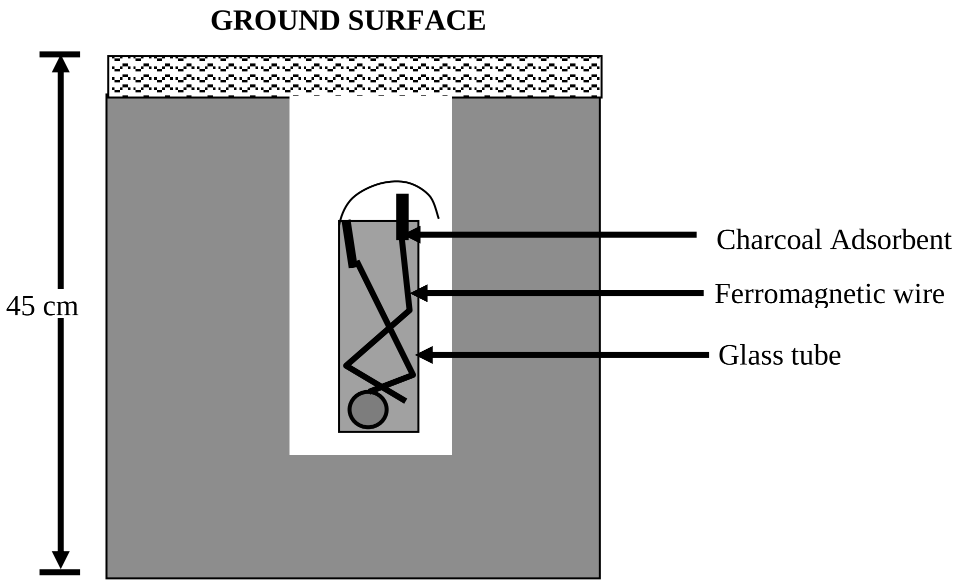


Fig. 2.2: Pretrex Sampler in Soil

A number of procedures based on microanalysis of samples for known physical properties have also been employed. For example, field screening, which uses infrared spectroscopy has been practised, employing a portable version of the well-known laboratory procedure (Kasper et. al., 1991). Unlike other procedures, field turbidometric methods (such as the commercially-available Petro-FLAG) favour the determination of heavy hydrocarbons and are of some use in delineating such pollution within soil (Kahrs et. al., 1999). The fluorescence spectra exhibited by the aromatic components provide the basis for laser-induced fluorescence spectroscopy. This has been used by a number of authors for field screening and in situ techniques have been devised (Apitz et. al., 1992; Lohmannsroben et. al., 1999). They allow detection of polycyclic aromatic compounds and thus are able to take account of a fraction not measured by other field screening techniques. All these procedures have potential application at contaminated site and yet none is free from interference.

A somewhat more specific approach is offered by chemical-based procedures. Immunoassay methods are available for both petroleum hydrocarbons (US EPA-4030) and PAHs (US EPA-4035) and a number of commercial kits are on the market. In the case of petroleum hydrocarbons, the kits are available in a number of ranges, bracketing hydrocarbon concentrations between 5mg kg^{-1} and 500mg kg^{-1}. The PAH kits are generally most sensitive to three and four ring PAHs, although they show some recognition of most larger members of the series. In both cases, the procedure consists of making an extract of the soil and performing the immunoassay test on the extract. Another chemical procedure is the Hanby method, which is based on the production of colour Friedel-Crafts reaction products by aromatic compounds present in the sample. The colour of the reaction product is compared with a standard chart to tentatively identify the contaminant. Commercial test kits, based on this reaction are available (Driscoll et. al., 1992).

In summary, although these procedures are of use in locating possible hydrocarbon contamination, their results are only indicative of the presence of these substances and ultimate confirmation can only come from laboratory analysis.

2.8 CHARACTERIZATION OF SOIL NUTRIENT

2.8.1 Characterization of Soil Nutrient

Soil may be defined as a collection of natural bodies, which has been synthesized in profile form, from a variable mixture of broken and weathered minerals and decaying organic matter which covers the earth in a thin layer and which supplies, when containing the proper amounts of air, water, mechanical support and sustenance for plants.

2.8.2 Cropping Systems for Soil Fertility

Major food crops in humid tropical regions include: plantain, banana, rice and root crops (such as cassava, yam, sweet potato and cocoyam) in the humid zone; sorghum, maize and cowpea in the sub humid zone; and millet and cowpea in the semi-arid zone (Okigbo, 1980; Mudahar, 1986).

Traditional cropping systems vary, since they have evolved in response to prevailing soil and climatic conditions and social and ethnological preferences (Ruthenberg, 1976; Okigbo, 1980; Kang, 1986). Traditional farmers often plant more than one crop species in a small patch of cleared and burnt land after several years of bush fallow. Intercropping, the practice of growing two or more crops simultaneously in the same field, is common throughout the tropics. It is practiced in 80% of the cultivated areas in West Africa (Steiner, 1984). The multi-story homestead gardens, where more than three annual crop and vegetable species are mixed with tree crops, are common in the humid forest regions (Juo, 1989).

Rainfall distribution and solar radiation in the Savannah regions are better suited for a wider range of rainfed agriculture than the forest or semi-arid zones. Most of the sorghum, millet, maize, cowpea, groundnuts and yams are produced on high base-status soils. In the humid region, which is dominated by low-base-status and acid Ultisols and Oxisols, systems based on trees, shrubs and root crops are more stable than cereal crop systems, as shown by the existence of highly successful tree crop plantations of rubber and oil palm (Sanchez, 1976; Kang, 1986; van Wambeke, 1991). Systems based on cassava and plantain are prevalent in the humid region, which is dominated by acid and low-base-status soils. Systems based on maize and millet are more common in high-base-status soils in sub humid and savanna areas (Juo and Ezumah, 1992). Generally, cropping systems in tropical Africa and Latin America may be grouped into five categories:

i. Cassava-based cropping systems are mainly found on sandy soils of the coastal belt (mainly Ultisols) in the humid forest region, where other food crops perform less satisfactorily except for coconuts or oil palm. Cassava is mainly intercropped with maize or upland rice. These fast-growing cereals reduce nutrient loss through leaching, runoff and erosion by utilizing a substantial amount of N mineralized (100 to 300kg N/ha) during the onset of the rainy season (Mueller-Harvey et al. 1985). These systems also recycle nutrients by returning residues to the soil.

ii. Cropping systems based on plantain or starchy banana are common in forested areas. Intercropped with plantain are cocoyam, maize and beans, planted so as to maximize light use efficiency.

iii. Yam-based systems are traditionally inter-cropped with a number of food crops, including cowpea, maize, cassava, vegetables, plantains, and groundnuts. Under upland conditions, cassava is inter-cropped with maize or upland rice during the second year as soil nutrient levels become inadequate to support a yam crop.

iv. Maize-based systems are widely practiced in the humid transitional zone as well as in the subhumid region and tropical highlands. In wetter areas, maize is usually intercropped with cassava, yam or sweet potato. In the subhumid regions, it can be intercropped with cowpea or beans. Commercial maize monoculture is found on volcanic soils and on the more fertile Alfisols in highland areas.

v. Cropping systems based on sorghum and millet are typical of savanna zones and semiarid regions. These cereals are commonly intercropped with groundnut (peanut), cowpea or Bambara groundnut in Africa, and with beans in Latin America. Millet/cowpea intercropping is often found on sandy soils. Sorghum/legume intercropping is usually found on finer-textured soils. In areas where rainfall is less than 600 mm/year, millet monoculture and millet/cowpea intercropping are more common.

2.8.3 Factors Related to Soil Fertility

Soil fertility is the result of the interactions between the biological, chemical and physical properties of soil due to soil type and land use, and the effects of climate. It is related to the potential for the sustainable production of crops and animals and can be assessed and/or described in various ways.

a. Soil colour: Soil colour depends on the type and amount of minerals and organic matter. Black soils are rich in organic matter and often are very fertile, whereas grey soils have little organic matter and poor drainage. Brown soils contain an adequate amount of organic matter, Fe and other minerals, and have good drainage. Red soils have large amounts of oxidized Fe and frequently good drainage but very little organic matter. Yellow soils have both oxidized and reduced Fe with little organic matter and medium drainage.

b. Soil physical properties: Soil physical properties include structure, texture, consistency, porosity and water holding capacity. The structure of a soil is related to the arrangement of mineral particles into aggregates, which influence the air and water content of the soil, its ability to retain water and its drainage characteristics.

i. *Soil texture* is concerned with the size of the mineral particles, which determines the surface area of the soil. At a simple level, according to particle size, there is clay (<0.002 mm), silt (0.002-0.05 mm), sand (0.05-2 mm), and stones (>2 mm). Soils with a large content of clay become hard when dry and sticky when wet,

ii. *Soil consistency* is related to the compression/compaction and plasticity of a soil and influences tillage and other mechanical operations. Soil organic matter has an effect on consistency by helping to bind mineral particles together. The sensitivity of a soil to erosion is related to texture and consistency.

iii. *Soil porosity* refers to the total volume of pores in the soil. Pores (an be filled either with air Dr water. Large pores allow the rapid exchange of air and drainage of excess water. Small pores retain water against drainage and the availability of this water for crops depends on the diameter of the pores. Clay soils are characterized by having many small pores with a large water holding capacity, but not all of this water is available to plants.

c. Soil chemical properties: Soil chemical properties are related to the supply of plant nutrients that are essential for plant growth. Chemical elements are released from clay minerals and organic matter into the soil solution from where they can be absorbed by plant roots or microorganisms. Nutrient adsorption and release are important properties of soils related to the amount of soil organic matter (SOM) and the amount and type of clay minerals and their ability to hold and exchange cations or anions. The cation exchange capacity (CEC) is an important factor in soil fertility. The availability of nutrients to plants depends on soil pH (soil acidity) and the redox-potential. The total salt content measured as electrical conductivity (EC) of soil is of great importance in irrigated agriculture.

i. *Phosphorus (P)* is an essential, irreplaceable element for all living organisms and crop production depends on there being an adequate supply (Johnston, 2000). Crops do not respond to nitrogen (N) when P is deficient. Deficiency of plant-available P can be due to two factors. The first is where P is chemically bound as Fe or Al phosphate, as in sandy acid Ferralsols. The second is the capacity of Fe and AI oxides and some clay minerals to strongly adsorb P added in water-soluble forms, as in loamy Nitosols. This latter process is reversible. The extent of P fixation can be estimated analytically by determining the buffer curve of a soil (Langmuir adsorption isotherms).

Strong P adsorption is minimized when other anions compete with phosphate ions on the sorption sites of Fe and Al oxides and clay minerals, thus making P more available. Such anions include hydroxyl (OH^-) and bicarbonate (HCO_3^-) ions, e.g. following lime applications, and also soluble silicates and organic anions from soil organic matter. Therefore, under the conditions of the humid tropics, P fertilizers that also contain silicates (e.g. basic slag and thermal phosphates) have proved to be superior to water-soluble phosphates (e.g. triple superphosphate, TSP). This is because silicate ions are adsorbed on sites able to adsorb phosphate ions. Some crops are more efficient at this than others, e.g. chickpea, white mustard, white lupin, rape and buck wheat, so called P-efficient plant species, compared to wheat, sorghum and maize . Such P-efficient plants are better able to utilize small amounts of P in soil.

Plant roots also release chelating and reducing substances, such as organic acids, amino acids and phenols. Chelates can solubilize Fe and Al phosphates by producing stable AI and Fe chelates.

Developing P-efficient cultivars would be a more economic approach to cropping that is favourable to small-scale farmers who have to manage their crop production with no, or only small inputs. This benefit, however, has a downside effect because cropping without P inputs will deplete soil P reserves more quickly. But if some part of the extra income generated by the increased yields is used to buy P fertilizer then there should he no problem.

ii. *Base cations* such as potassium (K), Ca and magnesium (Mg) become deficient in the acid soils of the humid tropics. This is due to the small amount in the parent material, the small CEC to retain them against leaching and their removal by erosion. Very large losses of K can occur after forest has been cut and removed (Likens et. al., 1994). Losses through soil erosion greatly exceed those by leaching, highlighting the need to minimize erosion. Burning the above ground vegetation as a part of shifting cultivation, only leads to a short transitory increase in the amount of base cations from the ashes. Growing cash crops, such as vegetables, fruit trees, oil palm, coffee, coconut and tuber plants that have a large requirement for these nutrients quickly results in deficiencies or imbalances. In cases of severe deficiency, soluble compounds of K, Ca and Mg can be applied as foliar sprays and crops will show a rapid response.

iii. *Potassium* has an irreplaceable role in a number of functions in plants but only small amounts are required relative to the much larger quantities needed to fulfill its role as an osmotic regulator in all cells (Johnston et al., 2001). Plants well supplied with K are more resistant to pests and diseases. Furthermore, beneficial effects of K on the chilling tolerance of plants grown in a warm climate and to photo oxidative stress under high light intensity are well documented (IPI, 2003).

iv. *Calcium* is important in cell membrane stabilization and enzyme modulation. Consequently, Ca deficiency exhibits itself as the disintegration and collapse of cell walls, mainly seen in vegetables and fruit trees, which have a large Ca requirement.

v. *Magnesium* is involved in many metabolic processes. Chlorotic or necrotic spots spread over the leaves indicate deficiency. Regular applications of calcitic or dolomitic amendments are required to prevent deficiency.

vi. *Sulphur (S)* deficiency is becoming more frequent due to leaching and to sorption of sulphate ions (SO_4^{2-}) on sesquioxides in the soil, particularly in Perralsols, but also due to desorption as a consequence of increased applications of P fertilizers. The only soil-borne source of S is organic matter after microbial decomposition and mineralization. Oil palm, vegetables, fruit trees and legumes have a particularly large requirement for S. To meet this requirement, S can be applied as ammonium sulphate (AS), ammonium sulphate nitrate (ASN), single superphosphate (SSP), potassium sulphate. (SOP), gypsum ($CaSO_4$) and elemental sulphur. Sulphur-coated urea (SCU) is not only a source of S, but also the S delays the transformation of urea, which may reduce leaching of nitrate (NO_3).

vii. *Micronutrients* can be very important in tropical agriculture because they can be deficient in many soils. Deficiency is due to losses by leaching from the highly weathered soils.

viii. *Liming* by increasing soil pH, drastically decreases Aluminium (Al) and manganese (Mn) toxicity. It also increases the availability of P by both solubilizing Fe and Aluminium (Al) phosphates and desorbing phosphate ions from sesquioxides. Tropical soils are particularly sensitive to overliming, and adding small amounts of lime are usually sufficient to produce good yields. Liming should be done frequently because Ca and Mg ions are not readily retained in many tropical and subtropical soils due to their low buffering capacity. Using dolomitic material supplies both Ca and Mg. Maize and legumes show a good response to liming.

Table 2.7 gives a summary of the essential nutrient elements and their sources.

Table 2.7: Essential Nutrient Elements and their sources

Essential Elements used in relatively large amount		Essential elements used in amounts relatively small
Mostly from Air and Water Carbon, Hydrogen and Oxygen	from soil solids nitrogen, phosphorus, potassium, Calcium, Magnesium, Sulphur	from soil solids iron, copper, manganese, boron, zinc, chlorine, cobalt, and molybdenum

Source: (Amberger, 2006)

d. Biological properties: In a fertile soil there is a large number of living organisms (microflora and microfauna), which vary greatly in size and function. One group is responsible for the decomposition of added and existing organic matter. This process brings plant nutrients in the organic material into inorganic forms that are available for uptake by plant roots. Some bacteria capable of fixing atmospheric N exist in nodules on the roots of legumes (biological nitrogen fixation, BNF); others are free living in the rhizosphere.

Mycorrhizal fungi play an important role in nutrient acquisition in many plant species. A mycorrhiza is d close symbiotic association of a fungus and a root of a higher plant. Two types of association are important for plant nutrition. The arbuscular rnycorrhizae (AM) can invade a root developing an internal mycelium, together with a considerable length of external mycelium that greatly increases the effective length of the root. The ecto-mycorrhizal fungi typically form a dense sheath of hyphae around the root with a web of hyphae between the cortical cells (Tinker, 1980). Most important are the AM that are found in almost all tropical and subtropical crops. All mycorrhizae take carbon compounds fixed by photosynthesis in the leaves from the host plant and, in return, supply it with nutrients, particularly P and micro nutrients, which they take up from the soil solution. This symbiosis is of great importance in soils poor in P and micronutrients, especially zinc (Zn). There are differences between AM genotypes, e.g. between those utilizing Aluminium (Al) phosphates in acid soils and those using hydroxylapatites in neutral/alkaline soils. Mulching with plant residues favours the development of mycorrhizal fungi. The efficiency of AM is constrained by low temperature, water stress and soil pH < 5.0 as well as by salinity, toxic concentrations of Aluminium (Al), Fe and Mn, and also by large additions of soluble P fertilizers.

2.9 BASIC CONCEPTS ON MODELING AND PREDICTION

The word “modeling” may be taken as an imitation of something on a smaller scale. It is a description of nature that can predict things about many similar situations. A model may help to explain a system and to study the effects of different components and to make predictions about behaviour. Therefore, modeling is the process of generating abstract, conceptual, graphical and or mathematical models. 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 constants and adopting such equations for forecasting or predictions. Prediction takes us into the future for decision making as we examine different responses arising from changes in control variables.

2.9.1 Definition of Terms Associated with Modeling and Prediction

i. **Variable**: A variable is a value that may change within the scope of a given problem or set of operations. Variables can be dependent or independent. The **independent variables** are typically the variables representing the value being manipulated or changed. These are variables or quantities available at the start of a process.

ii. **Dependent variables** are the observed results of the independent variable being manipulated. They are those quantities or variables being created by the process. Consider the relationship y = f(x). y is the dependent variable and x is the independent variable if there is some relation specifying y in terms of x.

iii. **Constant:** A constant is a value that remains unchanged though often unknown or undetermined. Constants are non-verifying values. It is however different from mathematical constants which are specified numbers independent of the given problem.

iv. **Statistical model:** is a formalization or relationship between variable in the form of mathematical equations. A model is statistical as the variable are not deterministically but stochastically related (Frigg, 2003).

2.9.2 Model Verification and Prediction

The accuracy of a calibrated model is usually verified before such a model can be made useful in future predictions. Model prediction is an exercise that follows after calibrated and verification. Model prediction of any future even such as peak flow, concentrations of pollutant in time and space and so on is the whole essence of mathematical modeling in engineering practice. It serves best for design and decision making, (Nwaogazie, 2006). Therefore in predictive modeling, data acre collected for relevant predictors – variable factors that are likely to influence future behaviour or result-followed by model formulation, then predictions are made and the model is validated. The mode may employ a simple linear equation or complex equations mapped out by sophisticated softwares.

The different approaches to deciding model validity include conceptual model validation and operational validation. The conceptual model validation involves determining that the theories and the assumptions underlying the conceptual model are consistent with those in the system theories and that the model presentation of the system is reasonable. The operational validation is defined as determining that the model's output behaviour has sufficient accuracy for the model's intended purpose over the domains of the model's intended applicability (Nwagozie, 2006).

2.9.3 Regression Analysis and Models

In statistics, regression analysis includes many techniques for modeling and analyzing several variables when the focus is on the relationship between a dependent variable and one or more independent variables. More specifically, regression analysis helps understand how the typical values of the dependent variable change when any one of the independent variables is varied while other independent variables are held fixed. Most commonly, regression analysis estimates the conditional expectation of the dependent variable given the independent variables. The estimation target is a functional relationship between a scalar variable y and one or more explanatory variables denoted x. A linear regression model (in vector) form is given as:

$$y = a_0 + a_1x \qquad (2.1)$$

where y is the regressand or the dependent variable and x is the regressor or the independent variable. a_0 is a constant which captures all the factors which influence the dependent variable y other than the regessor x, while a_1 is the regression coefficient. When one regressor is used in a regession model, the regression is called single regression. More than one regressor makes for multiple regression.

2.9.4 Correlation Analysis

Correlation may be taken as the degree of relationship between variables which seeks to determine how well a linear or non-linear equation describes the relationships simple correlation, it becomes multiple correlation when more than two variables are involved. When a dependent variable is correlated with all the independent variables in any given situation there will be an absolute or total correlation. Where dependent variable is correlated with only one independent variable with other variable kept constant, the constant, the correlation is partial.

Coefficient of Correlation

Coefficient of correlation, also known a Correlation coefficient, is a measure of how well the predicted values from a forecast model fit with the real life data. It measures the degree to which two things vary together or oppositely. Coefficient of correlation is a number ranging from -1 to 1. A perfect fit gives a correlation of 1. If coefficient is say 0.80 or 0.90, the corresponding variables closely vary together in the same direction; if -0.80 or -0.90, then the corresponding variables vary together in the opposite direction. -1 or 1 means complete dependence. Zero correlation represents complete independence. That means that two variables vary separately and there is no relationship between the predicted values and the actual values. The most common of correlation coefficients is the Pearson correlation coefficient which is sensitive to linear relation between variables. Standard error of estimate is the standard deviation of the differences between the actual values of the dependent variables (results) and the predicted values (Nwagozie, 2006).

2.9.5 Modeling Petroleum Products in Soils

There is a compelling incentive to understand and describe in quantitative terms, the behaviour and effect of petroleum in soils. It is relatively easy to describe the fate of petroleum in soils in merely qualitative terms. For example, it is clear that volatile petroleum such as gasoline experience considerable loss by evaporation, normal alkanes are subject to fairly rapid biodegradation; aromatic hydrocarbons, particularly those of lower molecular weight are very susceptible to dissolution into water and may thus cause contamination of water supplies in the locality. It is however, much more difficult to make rigorous, scientifically justifiable statements in which these processes are described in quantitative terms. In very few cases has it been possible to state, for example that in a period of one year 20% of a particular mass of oil spill was lost by evaporation, 2% by dissolution, and 30% by biodegradation and that 3% was altered by photolysis (Eastcott, 1989). There have been numerous studies and reviews of this issue, including the proceedings of American Petroleum Institute. There are also numerous reports on oil biodegradation in soil, for example Lee and Ward (1985), Jobson and Smart (1972), Walker and Colwell (1976), Westlake and Cook (1984). Table 2.8 shows the list of selected environmental models potentially applicable to soil risk assessment and environmental management problems.

Table 2.8: List of Selected environmental models potentially applicable to risk assessment and environmental management problems

S/N	Environmental compartment	Model name	Model type and description	Model uses/application	Source of model information/developer
1	Soil vadose (unsaturated zone)	SESOIL (seasonal Soil Compartment model)	SESOIL is a seasonal soil compartment model that estimates the rate of vertical chemical transport and transformation in the soil column in terms of mass and concentration distributions among the soil, water and air phases in the unsaturated soil zone. It is designed for long-term environmental fate simulations of pollutant in the vadoze zone. SESOIL is a one diversional unsaturated zone model for both organic and inorganic chemicals	SESoil can be used for assessing risks from handful disposal, accidental leaks or spills on lands e.g. leaking underground storage tanks	Office of toxic substances, explosive evaluation division USEPA, Washington D.C.
2	Multimedia air water and soil	MCPOSSM (monte carlo PCB on-site spill model)	MCPOSSM is chemical spill exposure assessment methodology providing a quantitative frame work for estimating uncertainties of chemical levels associated with spills.	MCPOSSM provides a distribution of concentrations overtime and probabilities of exceeding specific levels (i.e. probability of a work care level), which then forms a basis for the exposure assessment.	EPRI (electric power research institute) Palo, Alto Canada.
3	Multimedia (withio soil zones)	CEMO/Soil	Cemos/soil is a dynamic model used to simulate the transport and accumulation of a chemical in a soil column	CEMOS/soil can be used to calculate the concentration profile of a chemical in soil as well as the fractions of the chemical in the soil-water, the soil-air and the soil-matrix	Institute for environmental systems research, university of Osnabrueke Germany

Source: (USEPA Report, 1997).

2.10 BASIC MICROBIAL KINETIC THEORIES

i. Single Substrate Model

Monod kinetics are often used as a starting-point to relate the transformation rate of a compound to its concentration and microbial concentration

$$-\frac{dC}{dt}=\frac{k\times C}{K+C} \tag{2.2}$$

where

C = substrate concentration

t = time

X = microbial amount

k = maximum specific utilization rate of the substrate and

K = half-saturation constant for the substrate.

This equation is based on the assumption that the substrate is a rate-limiting factor. It is only suitable for a single, nontoxic substrate in solution under steady state conditions. In practice, this assumption is not always true. As a result, the unsuitability of basic Monod kinetics alone hinders process design attempts for biotransformation of chlorinated solvents.

ii. Multisubstrate models

For in situ bioremediation of chlorinated solvents, organic or mineral nutrients often become a limiting factor. Widdowson, et al (1981) proposed a model to simulate organic carbon biodegradation by facultative bacteria using oxygen-based respiration patterns in aerobic conditions and/or nitrate-based respiration patterns in anaerobic conditions. The substrate degradation rate for aerobic patterns is presented according to Monod kinetics as the following:

$$-\left(\frac{dC}{dt}\right)_{so}=k_0 X\frac{C}{K_c+C}\cdot\frac{C_{EA}}{K_{EA}+C_{EA}}\cdot\frac{C_A}{K_A+C_A} \tag{2.3}$$

where

k_0 = maximum specific utilization rate of substrate under aerobic condition

X = microbial amount

K_c = half-saturation constant for substrate

C_{EA} = concentration of electron acceptor

K_{EA} = half-saturation constant for electron acceptor

C_A = nutrient concentration and

K_A = half-saturation constant for nutrient

Similarly, the substrate degradation rate under anaerobic conditions can be expressed as:

$$-\left(\frac{dC}{dt}\right)_{sn} = k_n X \frac{C}{K_c + C} \cdot \frac{C_N}{K_N + C_N} \cdot \frac{C_A}{K_A + C_A} I(C_{EA)} \qquad (2.4)$$

where

k_n = maximum specific utilization rate of the substrate under anaerobic condition

K_N = half-saturation constant for electron donor

C_N = electron donor concentration and

$I(C_{EA})$ = the inhibition effect of oxygen to the anaerobic process

The next rate is the sum of the substrate degradation due to aerobic and/or anaerobic activities in which oxygen may inhibit the anaerobic process to some extent.

iii. Petroleum Hydrocarbon’s Transport model

Ground water contaminant is most frequently conducted on sand filters simulating loose, permeable grounds. In the theoretical models the diffusive transport of hydrocarbons and convection resulting from water flow through aeration sphere are usually taken into account. These models properly describe the transport of hydrocarbons with viscosity $\mu > 2.10^{-6} m^2 \cdot s^{-1}$. To verify the results obtained experimentally, a diffusive model of hydrocarbons' transport (the initial boundary condition) in the sand – hydrocarbon system was proposed (Gawdzik et. al., 2010)

$$R_i = \frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial z^2} - \mu_i C_i \tag{2.5}$$

where

$C_i(z, 0) = 0$ for $0 < z \leq S$;

$C_0 \ell^{\mu_1 t} = C_i(0, t)$ for $t \geq 0$; and

$\frac{\partial C_i}{\partial t} = 0$ for $t > 0$ and $z = S$

The solution of the problem describing the transport of petroleum product in the ground is the Equation 2.6.

$$C_i(z,t) = \frac{C_{0i} \cdot S}{\sqrt{4 \cdot \pi \cdot D_i \cdot R_i^2 \cdot t}} \exp\left\{-\left[\frac{z^2}{4 \cdot D_i \cdot t} + \mu_i \cdot t\right]\right\} \tag{2.6}$$

where

μ_i – hydrocarbon's biodegradation coefficient [s^{-1}]

C_i – concentration of key component "i" in the matrix [$kg \cdot m^{-3}$]

C_{0i} – initial concentration of key component "i" in the matrix [$kg \cdot m^{-3}$]

D_i – equivalent diffusion coefficient of key component "i" [$m^2 \cdot s^{-1}$]

S – the maximum depth of hydrocarbon penetration through the ground [m]

R_i – retardation factor of key component "i" in the matrix

t – migration time [s]

z - direction of hydrocarbon's migration [m]

sand soils usually do not contain matter and their sorptivity is smaller than that of migrating organic contaminants and heavy metal ($R_i \rightarrow 1$) On the basis of coefficients determined for Equation (2.5) and the solution Equation (2.6), the maximum depth of hydrocarbon infiltration into sand soil after time t from the leakage can be calculated. The result shows to what degree hydrocarbons' transport is a menace to underground-water table. Hence, the value we are looking for which is the concentration of hydrocarbons C_i in time t covers a distance z. If z is the distance of contamination source from underground-water table the time of ecological disaster-groundwater contamination can be assessed.

iv. Environmental Requirements

Optimum environmental conditions for the degradation of contaminants are reported in Table 2.9.

Table 2.9: Environmental conditions affecting degradation

Parameters	Condition required for microbial activity	Optimum value for an oil degradation
Soil moisture	25 – 28% of water holding capacity	30 – 90%
Soil pH	5.5 – 8.8	6.5 – 8.0
Oxygen content	Aerobic minimum air-filled pore space of 10%	10 – 40%
Nutrient content	N and p for microbial growth	C:N:P = 100:10:1
Temperature (^{0}C)	15 – 45	20 – 30
Contaminants	Not too toxic	Hydrocarbon 5 – 10% of dry weight of soil
Heavy metals	Total content 2000 ppm	700 ppm
Type of soil	Low clay or silt content	

Source: Vadali (2001)

2.11 REVIEW OF SELECTED LITERATURES ON THE IMPACT OF CRUDE OIL SPILL ON FARM LANDS IN THE NIGER DELTA REGION

Osuji and Nwoye (2007) investigated the impact of petroleum hydrocarbons on soil fertility, the Owaza experience. Major fertility indices such as Nitrogen (N), Phosphorous (P), Potassium (K), Total Organic Carbond (TOC) and Total Organic Matter (TOM) contents were examined against the backdrop of physico-chemical conditions of pH temperature, moisture content and electrical conductivity of soils three months after oil spillage at Owaza in Niger Delta region of Southern Nigeria. Evidence of severe hydrocarbon contamination was provided by high extractable hydrocarbon content of 3.4 × 10^3mg/kg, high soil acidity (low pH of 4.9 – 5.1), low electrical conductivity as well as high temperature and moisture content, all provided evidence of reduced metabolic activities on the affected site which explains the relatively low TOC and TOM values obtained. These conditions generally imply low soil fertility which in turn implies low agricultural productivity and reduced source of livelihood in the affected area. However no modeling was done to determine the level of nutrient depletion.

Omasun et al (2008), investigated the Growth and anatomy of Amaranthus Hybirdus as affected by different crude oil concentration. For growth parameters like plant height, number of leaves, leaf area, plant fresh weight and plant dry weight, the mean values obtained were higher for control (0%) and progressively decreased from (1 – 4%). The 4% concentration lethal to the A hybridus grown on it as they all died within ten days after planning. Crude oil in soil makes the soil condition unsatisfactory for plant growth, due to the reduction in the level of available plant nutrient or a rise in toxic level of certain elements such as iron and zinc. In any case, no model was developed.

Eneje et. al., (2012), investigated the amelioration of chemical properties of crude oil contaminated soil using compost from calapiogonium mucunoides and poultry manure. The study was carried out in green house and laboratory of soil science and Meteorology Department, Michael Okpara University of Agriculture Umudike to compare the effect of a plant; calapoigonium mucunoides and poultry manure at different rates (0%, 0.5%, 1% and

2%) on crude oil polluted solid. Samples were moisturized to 50% field capacity water content amended with organic materials singly and in combination in pots laid out in Completely Randomized Design (CRA). The polluted and amended soils were incubated for a total of three weeks before soil analysis. Standard laboratory techniques were used to analyze the following soil chemical properties; soil pH, total Nitrogen, organic carbon, available phosphorus, exchangeable cations (Na, K, Ca and Mg). The results after pollution and amendments reveal that the 1% and 2% of the amendments applied singly or in combination, enhanced chemical properties of oil polluted soil than 0.5% applied rate. It also increased the values obtained for soil properties such as PH from 4.85 to 6.83. Total Nitrogen from 0.09 to 0.13mg/kg. No model was developed.

Onwuka et. al., (2012) investigated the Determination of Total Petroleum Hydrocarbon (TPH) and some cations (Na^+, Ca^+ and Mg^+) in a crude oil polluted soil and possible Phytoremediation by Cynodon dactylon (Bermuda grass). The soil samples (A B C and D), each weighing 5kg were collected. Samples B, C, D were polluted with crude oil at different concentration (B: 30ml/kg; C: 50ml/kg and D: 100mml/kg). Sample A was unpolluted. Total petroleum hydrocarbon and some cations were determined after seven days of pollution and after two months of phytoremediation by Cynodon dactylon and the result were compared. The result showed that mean TPH concentration decreased after remediation. The result also showed that cynodon dactylon has the ability to clean-up crude oil polluted soil. However, no model was developed to determine the Nutrient depletion.

Alaba and Ifelola (2011) investigated the impact assessment of oil spillage on farmlands of some communities in Ilaje Area of Ondo State. Three farmlands were considered in the course of the study. Two of the three farmlands were within the Ikorigbo and Otumara communities that recently experienced oil spillage and they are about 300m from each other.

While the third farmland was within the Igbokoda community which is geographically similar but has not experienced oil spillage, it was used as control. The farmland was delineated at each area by the grid technique and soil samples were collected at 0 – 20cm depth of the ground. Some physico-chemical properties that reflect soil nutrient content and fertility status (PH, electrical conductivity, moisture content, organic matter, nitrogen phosphorous and cation exchange capacity (CEC) were determined using standard methods and results from the three areas were compared. There was a significant decrease in the calcium (Ca), magnesium (Mg), Potassium (K) and organic matter (OM) as well as a significant increase in the electrical conductivity, moisture content and phosphorous content of the oil spill affected farmlands at Ikorigho and Otumara when compared with the non-affected farmland at Igbokoda. The result show that oil spillage has adversely affected the nutrient level and fertility status of farmlands at Ikorigho and Otunmara communities, which needs urgent remediation.

Uzoho et. al., (2007) investigated the fertility status under land use types on soil of similar lithology. Fertility status under six land use types (fallow, cassava, plantain, cocoyam, bamboo and oil palm) in Mbaitoli and (oil palm, industrial site, cocoyam, bamboo, plantain and cassava) in Ikeduru were evaluated. Triplicate soil samples (0 – 15cm) collected along a transverse on each land use were characterized. Wide variability in soil pH, organic matter, P,N, C/N ratio, CEC, Fe and Zn occurred under various landuses with performance in cocoyam being better than others for both Mbaitoli and Ikeduru.

Choron et. al., (2010) researched on the bioremediation of a crude oil polluted soil by application of fertilizers. The soils were kept in 30^0C and 60% of field capacity condition for 5 to 10 weeks. To provide the necessary aeration the soils were tilled twice a week by shovel. Soil samples were analysed for hydrocarbon – degrading heterotrophic bacteria count and some soil chemical properties. The results indicate that the applied fertilizer increased the degradation of the hydrocarbon compared with the control.

Zulfiqar and Safia (2012) investigated the degradation of petroleum hydrocarbons by oil field isolate bacterial consortium. A mixed conservive was prepared with 15 bacteria isolated by enrichment technique from the sample collected from an oil contaminated site. This consortium was incubated with crude oil to investigate the metabolic capacity of bacteria. The degration efficiency of the isolates in consortium was checked with 2% crude oil by shake flask transformation in mineral salt medium at 37^0C for 24 days. Total removal of aliphatic and aromatics was 94.64% and 93.75% respectively. The ability of degrading long chain n-alkanes and crude oil at high concentrations makes the consortium potentially useful for bioremediation and microbial enhanced oil recovery.

Okiemien and Okiemien (2005) investigated the bioremediation of crude oil polluted soil – effects of poultry droppings and natural rubber. Laboratory biomediation experiments were carried out on crude oil polluted soil samples by applying various amounts of poultry droppings and natural rubber processing sludge as nutrient supplements at 29^0C and using slurry-phase and solid-phase biodegradation techniques. Changes in the total hydrocarbon content of the soil were determined using a spectrophotometric technique as a function of time. It was found that the extent of crude oil degradation in untreated soil samples was markedly lower (by up to 100%) than in the soil samples treated with nutrients supplement.

Chang and Ibrahim (2011) researched on laboratory scale bioremediation of Tapis crude oil contaminated soil be bioaugmentation of Acinetobacter baumannic T30C. Microbial degregation of Tapis crude oil contaminated soil by Acinetabacter baumannic T30C was conducted to evaluate the efficiency of the selected potential hydrocarbon degrader in stimulating bioremediation of crude oil contaminated soil with differential treatment units in microcosms with 2.5kg soil. The reduction of residual hydrocarbons in the soil was observed for a period of about 35 days. The study showed that amendment of nutrients was needed for stimulating the growth of A banumanic T30C and indigenous micro organism in assisting the degradation of residual hydrocarbons in the soil.

Lauo and Fochit (2005) investigated the development of relevant ecological screening criteria (RESC) for petroleum hydrocarn contaminated sites. The research seeks to address two deficiencies of ecological risk-based decision making for petroleum contaminated sites namely;

1. the lack of a relevant ecological screening criteria (RESC) for petroleum-contaminated soils and
2. reliance on the use of generic chemical criteria based on total, not bioavailable chemical levels.

The goal of the study was to develop a test data set for screening petroleum contaminated sites that included the responses of an array of soil macro invertebrates, plants and microganisms as effects assessment end point and measures of bioavailable petroleum hydrocarbon (BPH) and total petroleum hydrocarbon (TPH) as exposure measures. No model was also developed.

Hossner and Juo (2001) investigated soil Nutrient management for sustained food crop production in upland farming systems in the tropics. Sustainable soil nutrient-enhancing strategies involve the wise use and management of inorganic and organic nutrient sources in econologically sound production system (Janssen, 1993). The primary goal of integrated nutrient management (INM) is to combine old and new methods of nutrient management into economically sound and economically viable farming systems that utilize available organic and inorganic sources of nutrients in a judicious and efficient way. Integrated nutrients management optimizes all aspects of nutrient cycling. It attempts to achieve tight nutrient cycling with synchromy between nutrient demand by the crop and nutrient release in the soil, while minimizing losses through leaching runoff, volatilization and unmobilization.

Odjuvwuederhe et al (2006), evaluated the effect of oil spillage on crop yield and farm income in Delta state, Nigeria. Using samples of 262 crop farmers drawn randomly from 10 communities and five (5) Local Government Areas in the oil producing agro ecological zones of Delta state, the negative impact of oil spill on crop production was accentuated. Oil spill reduced crop yield, land productivity and greatly depressed farm income as a 10% increase in oil spill reduced crop yield by 1.3% while farm income plummeted to 5%. In order to halt the continual degradation of the Niger Delta environment. the authors recommended the enactment and enforcement of stringent environmental laws to protect the area and the people.

Aikpokpodwin (2010) investigated the nutrients dynamics in cocoa soils, leaf and Beans in Ondo State, Nigeria. Soil samples, young but matured foliage and cocoa beans were collected from the farms of some cocoa farmers across Idanre, Owema and Bamikenw in Ondo state. Samples were prepared according to standard procedure and analyzed chemically in the laboratory to determine the nutrient status of the samples. Result showed that the soils were deficient in magnesium and phosphorous. Foliar samples had some of the vital nutrients below critical levels. Potassium (K) was found limiting in the foliage which is at variance with K content in the soil. The findings showed that old cocoa soils in the study area were depleting in some vital soil nutrients which is a consequence of continuous mining of nutrients from the soil by cocoa without replacement. However, to connect the nutrient deficiency in the investigated soils for optimal cocoa yields and quality farmers within the area were of the opinion to adopt the use of inorganic fertilizer which must be applied according to recommendation.

Thapa and Kumar (2012), researched on the Review of Bioremediation of Petroleum Hydrocarbon contaminants in soil. The review article illustrates the pro and cons of using bioremediation process for the remediation of petroleum contaminants in soil. Bioremediation along with other processes have been used to remediate petroleum hydrocarbon contaminants in soil in the past. The major constituents of most crude oil are biodegradable, so bioremediation has proven to be cheap and efficient than other techniques. Different micro organisms like Pseudomonas, Aeromonas, Moraxella, Beijerinckia, F. Lavobacteria, chrobacteria, nocardia corynebacteria, atinetobacter, mycobacteria, modococci, streptomyces, Bacilli, Arthrobacter and cyanobacteria re employed to degrade petroleum hydrocarbon, using various techniques of bioremediation contaminated soil. However, bioremediation can be considered one of the best technologies to deal with petroleum product contaminated soil.

Sadler and Connel (2003) investigated the analytical methods for the determination of total petroleum Hydrocarbons in soil. The research stated that hydrocarbons may enter the soil environment from a number of sources and thus widely different spectro of these molecules appear at contaminated site. Hydrocarbon interaction with soil contaminants is important both in terms of their toxicology and also their accessibility by analytical methods. There is no simple procedure that will give an overall picture of hydrocarbons present at contaminated sites. This is largely because the molecules are present in two separates categories – voilatile and non-volatile. These two categories require significantly different sample techniques. Given the wide variety of hydrocarbons contamination that can potentially enter and exist in the soil environment a need exist for methods that satisfactorily quantitate these chemical.

Formally, the idea of total hydrocarbon determination in soil was seen as providing a satisfactory tool for assessing contaminated sites. Modern assessment methodology for contaminated sites, however, dictates a risk-based approach and hence quantitation of particular hydrocarbon species is required.

Amberger (2006) investigated soil fertility and plant nutrition in the tropics and subtropics. The publication was jointly published by the author and International Fertilizer Industry Association (IFA). It discusses the possibilities and constraints to food production on the many different soil types found in the tropical and subtropical countries. By indicating ways in which crop nutrition and hence crop production can be increased on these soils in developing countries, the author shows ways to ensure food security and improve livelihoods. No model development was involved.

Oil spillage in the Niger Delta region, especially on agricultural lands has been a major issue of concern both to government and the people in the region. The outcome of this research work can serve as a vital tool in resolving problems associated with oil pollution and bioremediation of affected lands.

CHAPTER THREE

MATERIALS AND METHODS

3.1 MATERIALS

Soil and crude oil were the two materials used in the study. The soil sample was collected from a rich humus farmland (loamy sand by textural classification) of the School of Agriculture and Agricultural Technology, Owerri. The crude oil used for the experiment was obtained from Shell Petroleum Development Company (SPDC) flow station, Opuawa, Bayelsa State. Six plastic containers (17cm x 18.5cm) labeled A, B, C, D, E, F were used to store the soil samples.

3.2 METHODS

3.2.1 Study Site and Location Description

This study was done by carrying out a laboratory test on the impact of crude oil pollution on the physico-chemical properties of soil by determining major soil nutrients depletion with time. The results of the field data were compared with the formulated mathematical models at various levels of crude oil pollution. The experiment was carried out as an ex-situ treatment of polluted soil obtained from the Federal University of Technology, Owerri (FUTO) Research Farm, Imo State Nigeria. The study area is located in Owerri, Imo State and lies between Latitude $5^o22'$ 51.1''N and Longitude $6^o59'$ 39.3''E with an elevation of 61mast obtained with Global Positioning System (GPS) Receiver (Germiu Ltd Kansas, USA). It is a humid tropical environment with average annual rainfall of 2400mm and three distinct months of dryness (December – February). The mean daily temperature is about 27^oC. The soils are derived from coasted plain sands called acid sands – Benin Formation (Orajaka, 1975).

3.2.2 Textural Characterisation of the Soil

Texture is the most nearly permanent soil attribute or characteristic and is based upon the arbitrary division of the soil into three size fractions of sand, silt and clay. Fifty-one grams (51.0g) of air-dry soil which has been passed through a 2mm sieve was weighed and transferred to the mix cup of the milkshaker machine. 50ml of 5% calgon (dispersing agent) and 100ml of distilled water were added and the mixture was stirred and allowed to set for 30 minutes. The soil hydrometer was placed into the suspension and allowed to slide slowly until the hydrometer is floating. The first reading on the hydrometer and the thermometer were taken at 40 seconds after the cylinder was set down. The amount of sand and clay in the suspension were recorded. The second hydrometer and temperature readings after 3 hours is generally taken to indicate the percentage of silt in suspension.

Mathematically, the percentages of sand, clay and silt in the suspension were calculated as follows:

$$\% \text{ sand} = 100.0 - [H_1 + 0.2(T_1 - 68) - 2.0] \times 2 \qquad 3.1$$

$$\% \text{ clay} = [H_2 + 0.2(T_2 - 68) - 2.0] \times 2 \qquad 3.2$$

$$\% \text{ silt} = 100.0 - (\%\text{sand} + \%\text{clay}) \qquad 3.3$$

Where,

H_1 = Hydrometer reading at 40 seconds

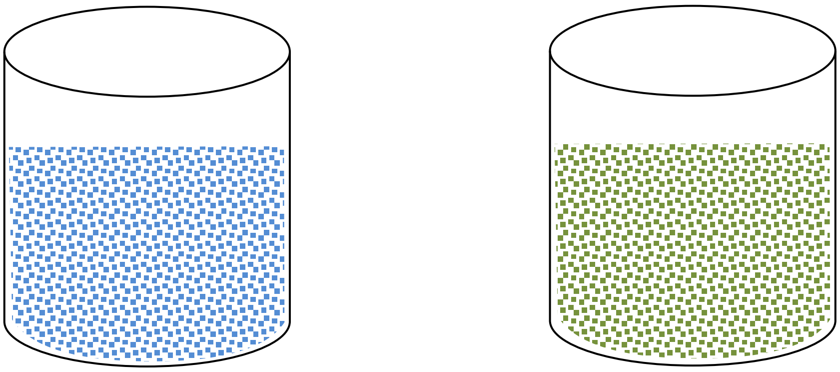
T_1 = Temperature at 40 seconds

H_2 = Hydrometer reading at 3 hours

T_2 = Temperature reading at 3 hours

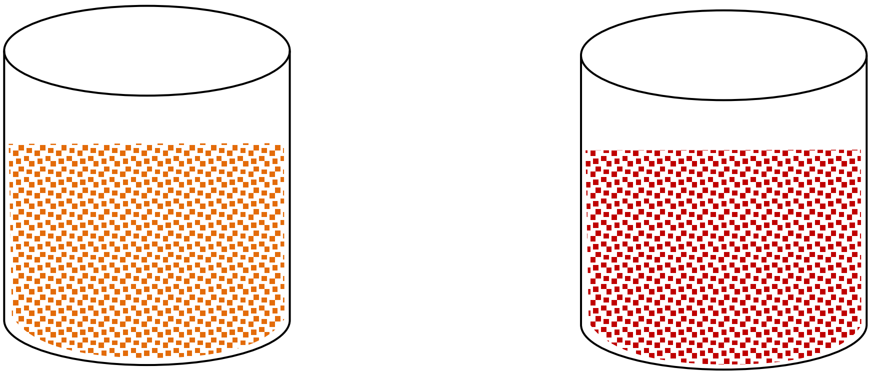
3.2.3 Pollution Process of the Soil Samples

The study was done for a period of sixteen (16) weeks, between April 18th to August 16th 2014. The soil sample was air dried under room temperature for two weeks and sieved through 2.0mm sieve. The soil samples (A, B, C, D, E, F), each weighed 10kg. Crude oil was added to samples B, C, D, E and F at different concentration and thoroughly mixed on a polythene sheet. That is B: 0.5 litres/10kg; C: 1.0 litre/10kg; D: 1.5 litres/10kg; E: 2.0 litres/10kg; F: 2.5 litres/10kg. Sample A was unpolluted and was used as the control sample. To maintain the moisture content of the soil, 50cl of water each was sprinkled on the polluted soil samples at two weeks interval. The polluted soil samples for laboratory analysis and layout of the experimental design are shown in Fig. 3.1 and Table 3.1 respectively.



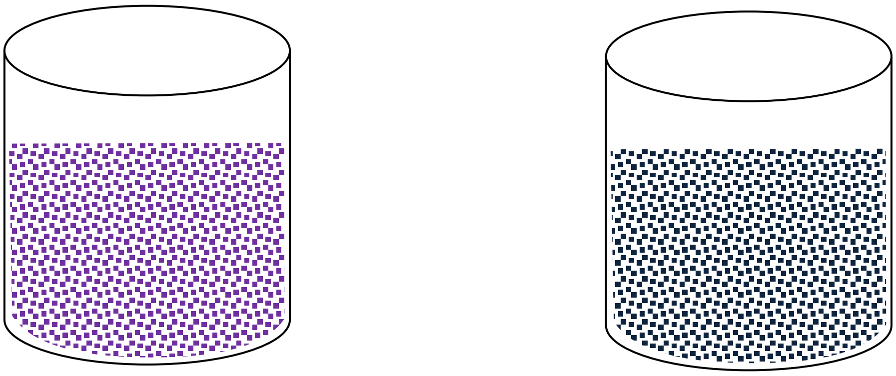
A: Control sample

B: 0.5 litres pollution to 10kg soil



C: 1.0 litres pollution to 10kg soil

D: 1.5 litres pollution to 10kg soil



E: 2.0 litres pollution to 10kg soil

F: 2.5 litres pollution to 10kg soil

Fig. 3.1: Polluted soil samples for Lab Analysis

A = Control sample

B = 0.5 litres pollution to 10kg soil (equivalent to 629 barrels/hectare)

C = 1.0 litres pollution to 10kg soil (equivalent to 1258 barrels/hectare)

D = 1.5 litres pollution to 10kg soil (equivalent to 1887 barrels/hectare)

E = 2.0 litres pollution to 10kg soil (equivalent to 2515 barrels/hectare)

F = 2.5 litres pollution to 10kg soil (equivalent to 3144 barrels/hectare)

Note: 2,000,000kg of soil (farrow slice) = one hectare.

Source: (Pete Landschoot, 2010).

Table 3.1: Layout of the Experimental Design

Polluted Soil Sample	A	B	C	D	E	F
Vol. of crude oil in (litres)/10kg of soil	0	0.5	1.0	1.5	2.0	2.5
Variables monitor for A, B, C, D, E and F were:	N, P, K, OM, OC, pH					

3.2.4 Laboratory Analysis of Soil Samples

The representive samples (A, B, C, D, E, F) where taken at two weeks intervals to the Soil Science Laboratory of Department of Crop, Soil and Pest Management, School of Agriculture and Agricultural Technology, Federal University of Technology, Owerri for analysis to determine the following parameters, Nitrogen, Phosphorous, Potassium, Organic matter, Organic carbon and Soil pH.

3.2.4.1 Soil pH

Twenty grams (20g) of air-dried soil sample was put into 50ml beaker and 20ml of distilled water was added. The lump of the soil was stirred to form a homogenous slurry. The pH meter (3020 model) probe was immersed into the sample and allowed to stabilize at 25°C. The pH values was taken and recorded.

3.2.4.2 Nitrogen

Ten grams (10g) of air-dried soil sample was introduced into a dry 500ml macro-kjeldahi flask and 20ml of distilled water was added, and allowed to stand for 30 minutes after a little swirling. 30ml of conc. H_2SO_4 was added into the mixture and heated at a low heat at the digestion stand. The mixture was allowed to boil for five hours. The digest was carefully transferred 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 in order 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 colour changes from green to pink. The percentage Nitrogen (%N) content of the soil was read and recorded.

3.2.4.3 Phosphorous

One gram (1g) of air-dried soil sample was put into a 15ml centrifuge tube and 7ml of extracting solution was added. The suspension was allowed to centrifuge for 15 minutes 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 ml (1.0ml) of $SnCl_22H_2O$ dilute solution was added and the content properly mixed. The percentage (%) transmittance on the electrophotometer at 660mμ wave length was measured after 20 minutes. The standard curve within the range of 0 – 1ppm was prepared and plotted against the optical density (OD) standard solution. The content of extractable phosphorous in soil was determined and recorded.

3.2.4.4 Potassium

Five grams (5g) of air-dried soil sample was put into 100ml volumetric flask and 30ml of NH_4OAC was added and agitated for two hours (2hrs) on a mechanical shaker. The clear supernatant was carefully centrifuged for 10 minutes at 2000 rpm and another 30ml of NH_4OAC solution added and agitated for 30 minutes. The value of soil potassium in Cmol/kg was determined using the Flame photometer and recorded.

3.2.4.5 Organic carbon and organic matter

Half a gram (0.5g) of each air-dried soil sample was put into a conical flask and 2.5ml of 1N potassium dichromate solution $K_2Cr_2O_7$ was added and swirled gently to disperse the sample in the solution. 5ml of concentrated tetraoxosulphate (VI) acid was added rapidly into the flask and swirled gently until sample and reagents were mixed and finally swirled vigorously for about a minute. The flask was allowed to stand in a fume cupboard for 30 minutes. Five (5) drops of the indicator were added to $FeSO_4$ solution until the colour changes to maroon colour. A blank determination was carried out to standardize the dichromate (Nelson and Sommers, 1982). Organic carbon (OC) and organic matter (OM) contents were calculated as follows:

$$\mathrm{OC}(\%) = \frac{\left(\mathrm{MeqK_2Cr_2O_7} - \mathrm{MeqFeSO_4}\right) \times 0.003 \times 100 \times 1.3}{\text{Weight of sample(g)}} \qquad 3.4$$

where $MeqK_2Cr_2O_7$ = 1N × 2.5ml

$MeqFeSO_4$ = 0.5N × Vol. of titrant in ml

0.003 = Milliequivalent weight of carbon

1.30 = correction factor

OM(%) = C(%) × 1.724

where 1.74 = conversion factor

3.2.4.6 Total Petroleum Hydrocarbon Concentration (THC)

Two grams (2g) of air-dried soil sample was put into 100ml conical flask and 50ml chloroform was added and mixed vigorously for 3 minutes. Standard curve of the absorbance of different known concentrations of petroleum hydrocarbons in the extract was derived using fresh crude oil appropriately diluted with the solvent and was used to read off petroleum hydrocarbon content. Mathematically, petroleum hydrocarbon concentration in soil was then calculated after reading the absorbance of the petroleum hydrocarbons in the extract from the spectrophotometer. The Total Hydrocarbon Content (THC) was obtained as described in Equation 3.4:

$$\mathrm{THC}(\mathrm{mg/kg\ soil}) = \frac{(\mathrm{Absorbance} \times \mathrm{DF} \times 50)}{\mathrm{Weight\ of\ soil\ used}} \qquad 3.5$$

where DF is dilution factor 50 is the initial extraction volume.

3.2.5 Consideration of Some Engineering Tools for Prediction

1. Finite element method: this deals more with structural elements that have shapes and dimensions, hence can not be used in soil physico-chemical analysis.
2. Finite differences: this also has something to do with space and dimensions. That is, a defined area extent has to be established for the tool to work well. The design of this study does not align with this tool.
3. Nueral network: this involves a large array of data as an input, which is beyond the scope of this work.
4. The panel data multiple regression analysis was chosen due to its capacity to analyse complex data with several variables as in the case of physico-chemical properties of soil and its increasing popularity among science and engineering researchers. 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 work.

3.2.6 Panel Data Regression Model (PDRM)

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 are Nitrogen (N), Phosphorous (P), Potassium (K), Organic matter (OM), Organic carbon (OC) and Soil pH, affected by crude oil pollution at various levels in the soil and at time intervals during which the pollution lasted. A case in which three controlled variables x_1, x_2 and x_3 are involved, a corresponding linear but multiple regression equation is of the form:

$$y = a_0 + a_1 x_1 + a_2 x_2 + a_3 x_3 \qquad 3.6$$

Equation (3.5) is a linear regression equation of y on x_1, x_2 and x_3. Because the dependent variable y varies partially due to variation in x_1, x_2 and x_3, respectively, the coefficient a_1, a_2 and a_3 represents partial regression coefficients of y or x, with x_2 and x_3 held constant; y on x_2 with x_1 and x_2 held constant, and y on x_3 with x_1 and x_2 held constant, respectively.

Given n sets of measurements, (y_1, x_{11}, x_{21}, x_{31}) … (y_n, y_{1n}, x_{2n}, x_{3n}) the least square estimates of a_0, a_1, a_2 and a_3 can be obtained using panel data computer software. In this work the panel data computer software called stata 13 version was used to generate the coefficients B_0, B_1, B_2, B_3 and B_4 and the model equations for Nitrogen, Phosphorous, Potassium, Organic matter, Organic carbon and Soil pH. This was achieved by keying in the input data of polluted soil analysis for various soil parameters (N, P, K, OM, OC, pH) as shown in Tables 4.1 – 4.6.

Therefore, the computer generated model equation is expressed as

$$Y_{it} = B_0 + B_1 C_{v_{it}} + B_2 T_{it} + B_3 T_{it}^2 + B_4 \sqrt{C_{v_{it}}} + U_{it} \qquad 3.7$$

where,

Y_{it} = Variables of soil characteristics (N, P, K, OC, OM)

(B_0, B_1, B_2, B_3 and B_4) = Estimated parameters of the model

T_{it} = Number of days

$C_{v_{it}}$ = Crude oil Volume in litres

U_{it} = Randon error of the model

i = Treatment levels of crude oil (i.e. 1, 2, 3, …, 19 panel)

t = Time dimension of experimental (t = 14, 28, …, 308 days)

Note: for the main experimental data collection

i: begin from 1 – 6 (0, 0.5, 1.0, 1.5, …, 2.5 litres)

t: begin from 14 – 112 (14, 28, 42, …, 112 days)

For out of sample predictions

i: starts from 7 – 19 (same crude oil pollution levels extended up to 19 panels)

t: starts from 126 – 308 (days)

The detail of this is found in the computer generated values in Appendix H.

3.2.7 Calibration of Model using Experimental Data

The data generated from a final year student project in Civil Engineering of similar work in 2014 was used to calibrate the model. This is shown in Tables 4.23 to 4.28. The accuracy of any model that can be used for future predictions happens only when the model has been calibrated.

3.2.8 Application of the Model in Bioremediation Operations

The following steps can be applied in using the model for field bioremediation activities:

i. Identify crude oil spillage in an area, especially on a farm land and estimate the quantity of oil spill in the affected area and the area extent.

ii. Collect soil samples from the affected oil spill area after two (2) to three months (3 months) of the spill.

iii. Analyse the soil samples in a good soil laboratory to determine the physico-chemical properties of the soil and total hydrocarbon concentration.

iv. Select the major soil nutrients parameters like Nitrogen (N), Phosphorous (P), Potassium (K), Organic Carbon (OC), Organic Matter (OM) and Soil pH from the data and record their values.

v. Check whether the values obtained for the major soil nutrient parameters are above or below the critical levels for tropical soils (Enwezor et. al., 1990). If the values obtained for the major soil nutrients parameters are below the critical levels, that means, that the soil is deficient of major soil nutrients and need bioremediation work.

vi. Mathematically, the model equations developed for the various major soil nutrients parameters (N, P, K, OC, OM, and pH) can be used to estimate values knowing the volume of crude spilled, the land area and observation time.

3.2.9 Computer Program for the Panel Data Analysis

To ease the use of the equations derived for predicting the values of the major soil nutrients depletion, a computer programme was written using stata 13 version. The programme is user friendly. The program are for all the cases considered are shown in Appendix B.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 RESULTS

It is pertinent at this point to introduce the results of the experimental works and findings in terms of tables and figures and in line with the objectives of the study.

4.1.1 Soil Characterization

The percentage of size fractions were combined to determine the texture using the standard soil textural triangle as shown in Appendix A. The laboratory result showed that the soil sample consist of; % sand = 82.20, % clay = 8.60 and that of silt = 9.2%. The dominant fraction of the grain size composition of the soil was used to derive or establish the textural class of the soil, using the triangle. In this case, the textural class of the soil used was loamy sand.

4.1.2 Physico-chemical Properties of polluted Soil Samples

Tables 4.1 to 4.8 show the results of physico-chemical properties of the polluted soil samples at various pollution levels at 14 days intervals, up-till the 112 days experimental period. Table 4.9 shows the mean values of various physico-chemical parameters as against the various pollution levels of soil samples with crude oil. Fig. 4.1 to Fig. 4.6 show the values of the major soil nutrient parameters (nitrogen, phosphorous, potassium, organic carbon, organic matter and pH) at various crude oil pollution levels with time, when compared with the values of the control sample respectively. Table 4.10 and Fig. 4.7 also show the results of how total petroleum hydrocarbon concentration in the soil changes with time at various crude oil pollution levels.

Table 4.1: Physico-chemical Properties of the Polluted soil samples after 14 days (Soil Nutrient Parameters)

	Ph	OC	OM	N	P	Ca	Mg	K	Na	Al	TEA	ECEC	%BS	%Sand	%Clay	%Silt
Control 1 A	6.23	1.34	2.31	0.287	38.90	2.725	0.899	0.057	0.046	0.55	0.85	4.531	81.10	82.20	8.60	9.20
0.5L B	7.30	1.995	3.439	0.143	6.75	0.974	0.30	0.022	0.018	0.52	0.76	2.085	63.50	89.15	4.65	6.20
1.0L C	7.35	2.015	3.474	0.123	6.59	0.98	0.29	0.021	0.018	0.50	0.73	2.039	64.20	89.20	4.65	6.15
1.5L D	7.42	2.035	3.508	0.115	5.96	0.976	0.287	0.02	0.017	0.47	0.71	2.019	65.60	88.95	4.70	6.35
2.0L E	7.47	2.075	3.577	0.121	5.45	0.975	0.285	0.02	0.016	0.45	0.68	1.976	65.60	89.10	4.75	6.15
2.5L F	7.49	2.095	3.612	0.119	4.70	0.974	0.279	0.018	0.014	0.43	0.67	1.955	65.70	89.15	4.75	6.10

Ph = soil acidity; OC = % organic carbon; OM = % Organic Matter; N = % Total Nitrogen; P = Phosphorous (ppm); Ca = Calsium (cmol/kg); Mg = Magnesium (cmol/kg); K = Potassium (cmol/kg); Na = Sodium (cmol/kg); Al = Aluminium (meg/100g); TEA = Total Exchange Acid (meg/100g); ECEC = Effective Cation Exchange Capacity (meg/100g); BS = % Base Saturation.

Table 4.2: Physio Chemical Properties of the Polluted soil samples after 28 days (Soil Nutrient Parameters)

	Ph	%OC	%OM	%N	$P_{mg/kg}$	Ca	Mg	K	Na	Al	TEA	ECEC	%BS	Sand	Clay	Silt
Control 2	6.21	1.335	2.302	0.285	37.40	2.63	0.91	0.06	0.047	0.70	0.86	4.507	80.90	89.50	4.65	5.85
0.5L	7.20	1.995	3.439	0.129	7.20	0.895	0.288	0.025	0.019	0.50	0.75	2.065	63.70	89.18	4.76	6.06
1.0L	7.33	2.01	3.465	0.136	6.88	0.973	0.28	0.022	0.018	0.49	0.74	2.155	65.70	89.20	4.68	6.12
1.5L	7.40	2.033	3.505	0.131	6.54	0.91	0.275	0.022	0.018	0.50	0.70	1.925	63.60	89.16	4.65	6.19
2.0L	7.42	2.076	3.579	0.127	6.20	0.97	0.25	0.02	0.017	0.44	0.66	1.917	65.60	89.20	4.69	6.11
2.5L	7.45	2.092	3.607	0.123	5.90	0.895	0.268	0.019	0.017	0.43	0.67	1.869	64.20	89.05	4.69	6.26

Table 4.3: Physio Chemical Properties of the Polluted soil samples after 42 days (Soil Nutrient Parameters)

	Ph	%OC	%OM	%N	$P_{mg/kg}$	Ca	Mg	K	Na	Al	TEA	ECEC	%BS	Sand	Clay	Silt
Control 3	6.18	1.33	2.293	0.291	38.00	2.75	0.90	0.058	0.045	0.64	0.96	4.713	79.60	90.00	4.77	5.30
0.5L	7.20	1.99	3.431	0.138	7.68	0.976	0.31	0.025	0.021	0.57	0.80	2.144	64.10	89.10	4.75	6.15
1.0L	7.25	2.008	3.462	0.133	7.30	0.98	0.302	0.023	0.02	0.55	0.77	2.095	63.20	89.05	4.75	6.20
1.5L	7.30	2.03	3.499	0.129	6.90	0.973	0.294	0.023	0.018	0.50	0.70	2.008	65.10	89.10	4.80	6.10
2.0L	7.35	2.069	3.567	0.13	6.55	0.977	0.295	0.022	0.019	0.45	0.69	2.008	65.50	89.05	4.65	6.30
2.5L	7.36	2.088	3.599	0.124	6.45	0.976	0.29	0.022	0.017	0.42	0.68	1.985	65.70	89.15	4.56	6.29

Table 4.4: Physio Chemical Properties of the Polluted soil samples after 56 days (Soil Nutrient Parameters)

	Ph	%OC	%OM	%N	$P_{mg/kg}$	Ca	Mg	K	Na	Al	TEA	ECEC	%BS	Sand	Clay	Silt
Control 4	6.10	1.35	2.327	0.30	37.60	2.698	0.869	0.062	0.044	0.62	0.92	4.513	79.60	88.94	4.66	6.40
0.5L	7.00	1.992	3.434	0.14	8.00	0.98	0.299	0.026	0.022	0.60	0.69	2.031	64.30	89.20	4.70	6.10
1.0L	7.20	2.00	3.448	0.138	7.64	0.987	0.308	0.024	0.021	0.54	0.70	2.04	65.70	89.15	4.69	6.16
1.5L	7.27	2.021	3.484	0.132	7.30	0.984	0.299	0.024	0.02	0.53	0.70	2.027	65.50	89.30	4.80	5.90
2.0L	7.29	2.057	3.546	0.127	7.20	0.982	0.292	0.023	0.018	0.44	0.69	2.005	65.60	89.40	5.00	5.60
2.5L	7.30	2.073	3.574	0.128	6.93	0.98	0.293	0.023	0.021	0.46	0.68	1.997	65.90	89.50	5.02	5.48

Table 4.5: Physio Chemical Properties of the Polluted soil samples after 70 days (Soil Nutrient Parameters)

	Ph	%OC	%OM	%N	$P_{mg/kg}$	Ca	Mg	K	Na	Al	TEA	ECEC	%BS	Sand	Clay	Silt
Control 5	6.06	1.32	2.276	0.298	37.20	2.29	0.901	0.06	0.047	0.59	0.87	4.168	79.10	89.30	4.65	6.05
0.5L	6.96	1.972	3.399	0.142	9.08	0.986	0.305	0.024	0.025	0.58	0.70	2.05	65.90	89.20	4.90	5.90
1.0L	7.16	1.994	3.438	0.139	8.74	0.992	0.303	0.024	0.023	0.57	0.67	2.012	66.70	89.40	4.95	5.65
1.5L	7.23	2.024	3.489	0.137	8.46	0.993	0.299	0.023	0.022	0.56	0.65	1.987	67.30	90.10	5.00	4.90
2.0L	7.24	2.059	3.549	0.134	7.22	0.986	0.299	0.023	0.02	0.56	0.62	1.952	68.20	89.15	5.05	5.80
2.5L	7.25	2.078	3.582	0.131	7.22	0.986	0.296	0.022	0.0202	0.54	0.60	2.106	71.50	89.90	5.10	5.00

Table 4.6: Physio Chemical Properties of the Polluted soil samples after 84 days (Soil Nutrient Parameters)

	Ph	%OC	%OM	%N	$P_{mg/kg}$	Ca	Mg	K	Na	Al	TEA	ECEC	%BS	Sand	Clay	Silt
Control 6	6.02	1.33	2.30	0.30	36.90	2.30	0.89	0.06	0.05	0.62	0.85	4.13	78.40	90.20	4.70	5.10
0.5L	7.15	1.96	3.39	0.14	9.89	0.99	0.30	0.03	0.02	0.58	0.68	2.04	66.70	89.40	4.95	5.65
1.0L	7.18	1.99	3.43	0.14	9.46	1.00	0.30	0.03	0.02	0.56	0.65	2.00	67.60	90.20	4.95	4.85
1.5L	7.19	2.03	3.50	0.14	9.45	1.00	0.30	0.03	0.02	0.54	0.62	1.97	68.50	89.20	5.00	5.80
2.0L	7.21	2.05	3.53	0.14	7.59	0.99	0.30	0.03	0.02	0.53	0.59	1.96	70.00	89.10	5.03	5.87
2.5L	7.23	2.07	3.57	0.13	7.59	0.99	0.30	0.02	0.02	0.46	0.55	1.88	70.80	89.20	5.05	5.80

Table 4.7: Physio Chemical Properties of the Polluted soil samples after 98 days (Soil Nutrient Parameters)

	Ph	%OC	%OM	%N	$P_{mg/kg}$	Ca	Mg	K	Na	Al	TEA	ECEC	%BS	Sand	Clay	Silt
Control 7	5.98	1.319	2.274	0.30	37.26	2.187	0.892	0.061	0.045	0.60	0.86	4.045	78.40	90.10	4.55	5.90
0.5L	7.13	1.968	3.393	0.14	9.91	0.994	0.31	0.025	0.025	0.55	0.69	2.054	66.70	89.10	4.85	6.05
1.0L	7.15	1.99	3.431	0.14	9.54	1.002	0.307	0.025	0.024	0.50	0.68	2.038	66.60	89.75	4.90	5.60
1.5L	7.16	2.031	3.501	0.14	9.15	1.001	0.302	0.024	0.023	0.47	0.66	2.01	68.20	89.40	4.94	5.65
2.0L	7.18	2.044	3.516	0.14	7.94	0.994	0.30	0.024	0.022	0.46	0.63	1.973	68.10	89.30	5.00	5.70
2.5L	7.20	2.057	3.546	0.13	7.94	0.994	0.297	0.023	0.022	0.44	0.60	1.936	69.00	89.20	5.06	5.74

Table 4.8: Physio Chemical Properties of the Polluted soil samples after 112 days (Soil Nutrient Parameters)

	Ph	%OC	%OM	%N	$P_{mg/kg}$	Ca	Mg	K	Na	Al	TEA	ECEC	%BS	Sand	Clay	Silt
Control 8	5.92	1.326	2.286	0.30	26.94	1.92	0.896	0.06	0.046	0.63	0.83	3.754	81.70	89.50	4.60	5.90
0.5L	7.12	1.96	3.379	0.144	10.07	1.01	0.314	0.026	0.026	0.56	0.64	2.014	66.20	89.40	4.95	5.65
1.0L	7.14	1.994	3.438	0.14	9.99	1.01	0.311	0.02	0.025	0.53	0.62	1.979	68.50	89.30	4.98	5.60
1.5L	7.16	2.031	3.483	0.137	9.17	1.11	0.308	0.02	0.024	0.56	0.62	1.979	68.70	89.40	5.10	5.50
2.0L	7.19	2.031	3.501	0.137	8.40	1.00	0.306	0.02	0.023	0.43	0.60	1.952	69.30	89.10	5.10	5.80
2.5L	7.21	2.045	3.526	0.135	8.40	1.00	0.304	0.02	0.023	0.41	0.59	1.935	69.50	89.40	5.15	5.45

Table 4.9: Mean Values of different concentrations against physico-chemical parameters

Parameter	A	B	C	D	E	F
	Control (Mean)	Mean of 0.5L Conc.	Mean of 1.0L Conc.	Mean of 1.5L Conc.	Mean of 2.0L Conc.	Mean of 2.5L Conc.
Ph	6.088	7.133	7.220	7.266	7.294	7.311
%OC	1.331	1.979	2.000	2.029	2.058	2.075
%OM	2.296	3.413	3.448	3.496	3.546	3.577
%N	0.295	0.137	0.137	0.1331	0.132	0.127
$P_{mg/kg}$	36.275	8.573	8.268	7.810	7.069	6.891
Ca cmol/kg	2.438	0.974	0.991	0.980	0.984	0.974
Mg cmol/kg	0.895	0.303	0.300	0.296	0.291	0.291
K cmol/kg	0.061	0.025	0.024	0.023	0.023	0.021
Na cmol/kg	0.046	0.022	0.021	0020	0.019	0.019
Al	0.619	0.556	0.530	0.512	0.470	0.449
TEA	0.875	0.714	0.695	0.670	0.645	0.630
ECEC	4.295	2.060	2.045	1.765	1.967	1.958
% BS	79.863	65.138	66.025	66.563	67.238	67.788
% Sand	89.593	89.213	89.406	89.326	89.175	89.318
% Clay	4.648	4.814	4.819	4.874	4.908	4.923
% Silt	5.538	5.970	5.791	5.799	5.916	5.765

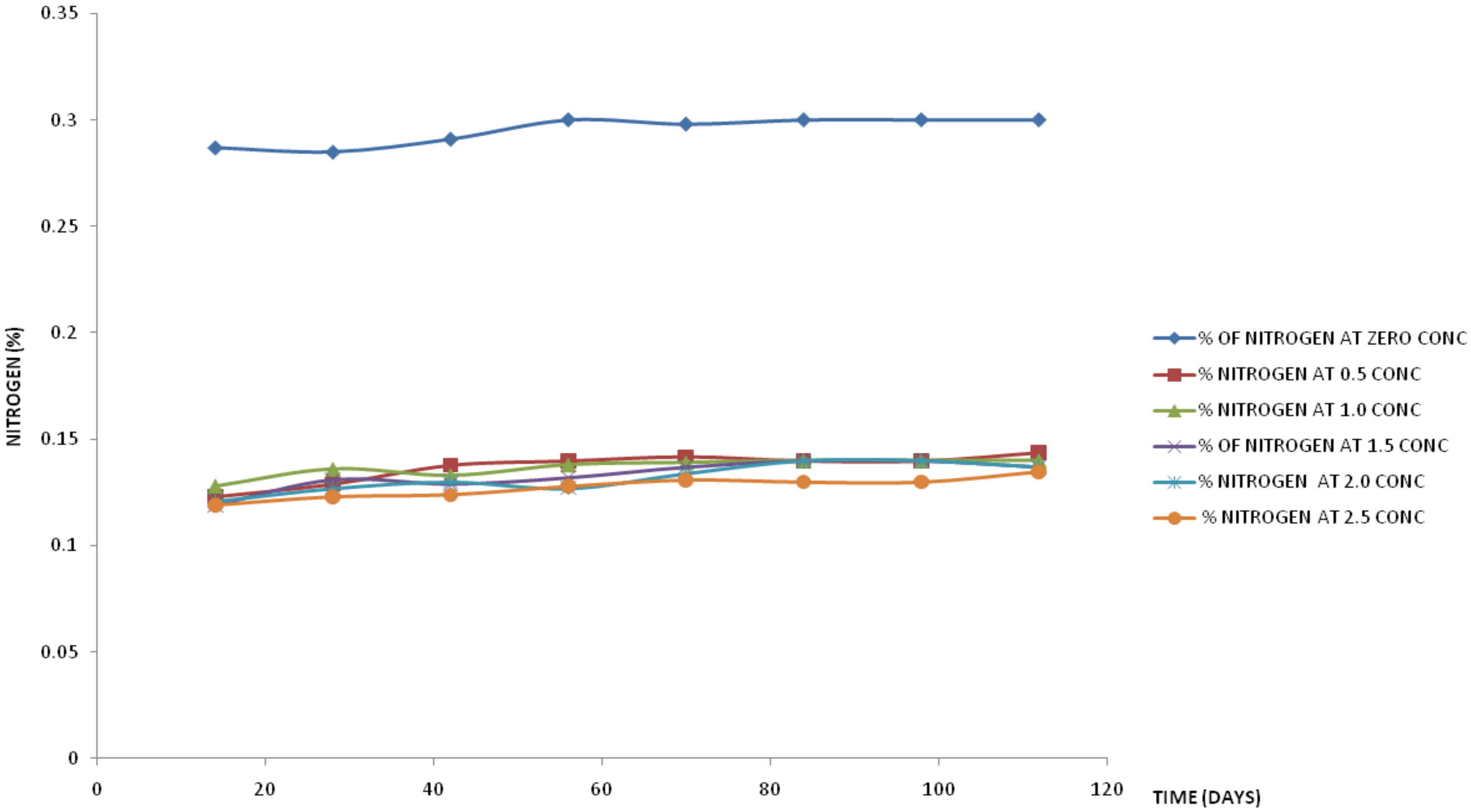


Fig. 4.1. Soil Nitrogen Content at various crude oil levels with Time

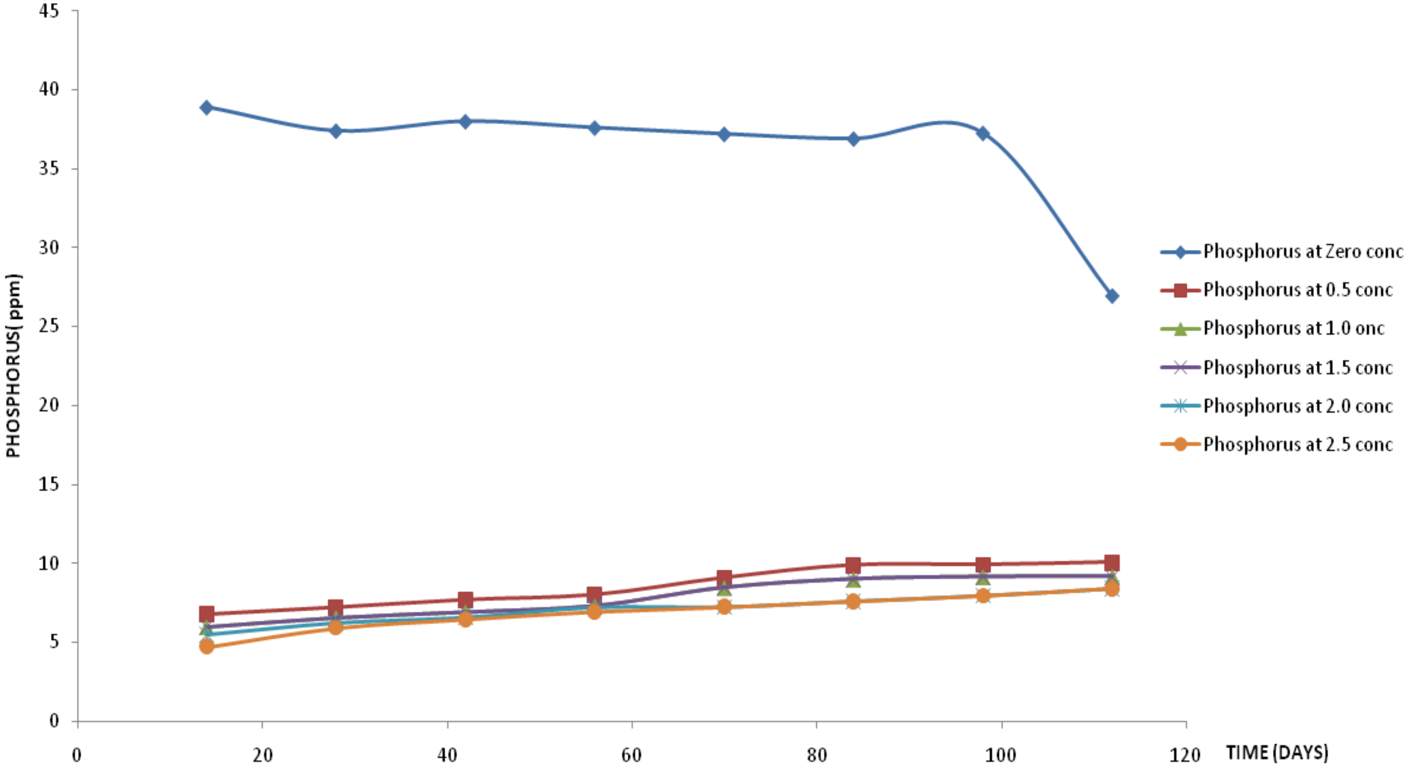


Fig.4.2. Soil Phosphorus content at various crude oil levels with Time

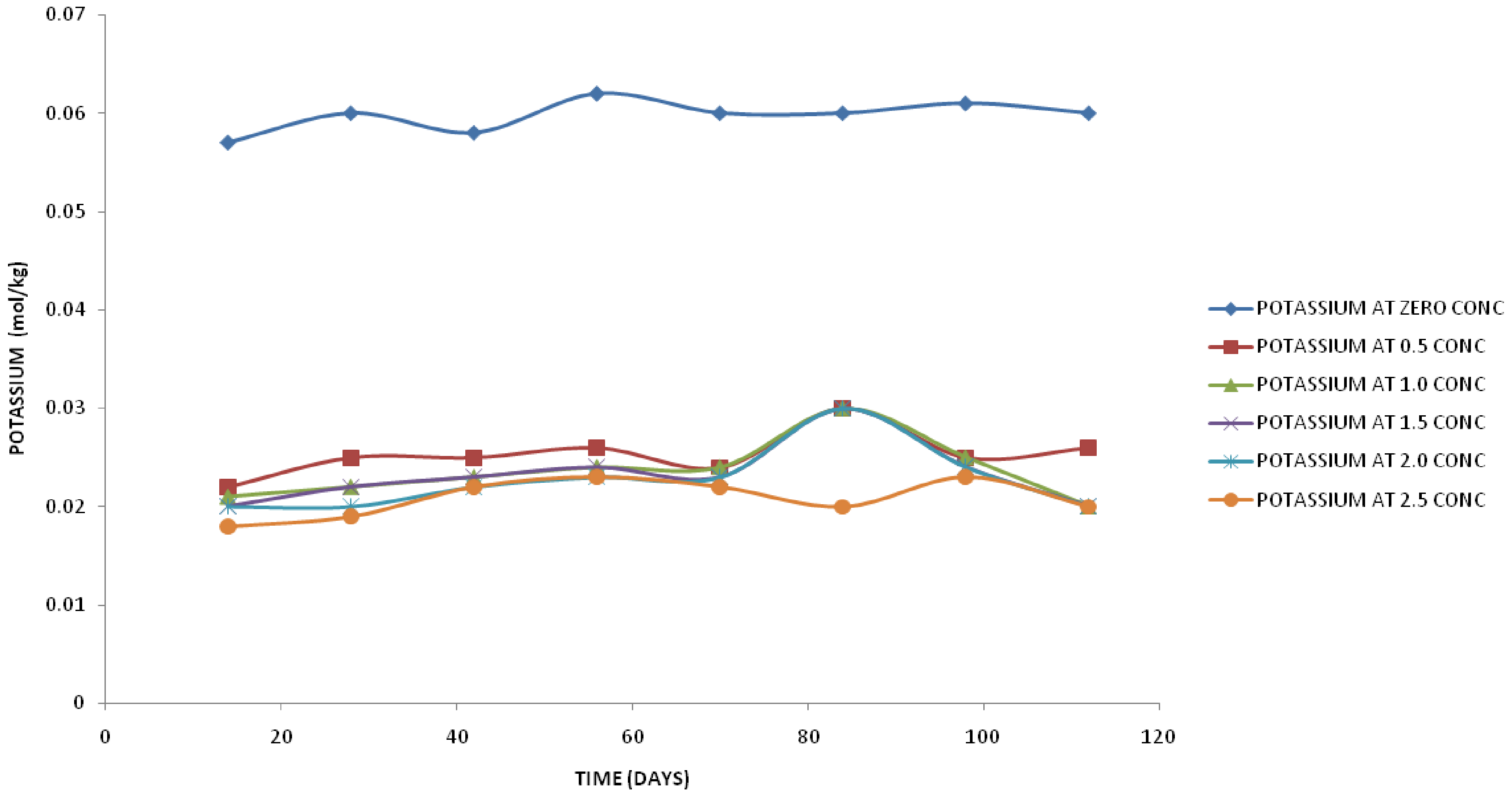


Fig. 4.3. Soil Potassium content at various crude oil levels with Time

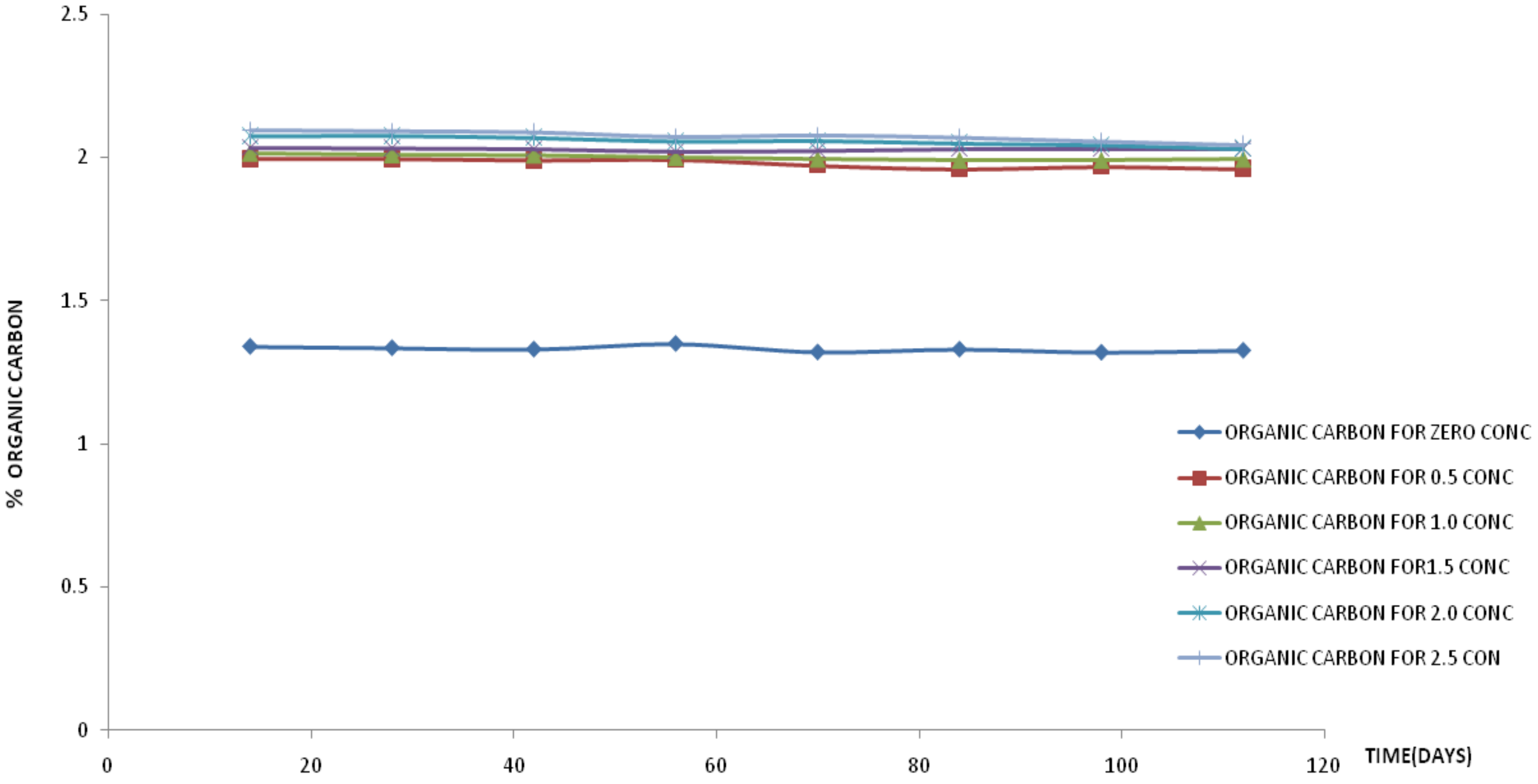


Fig. 4.4. Soil Organic Carbon at various crude oil levels with Time

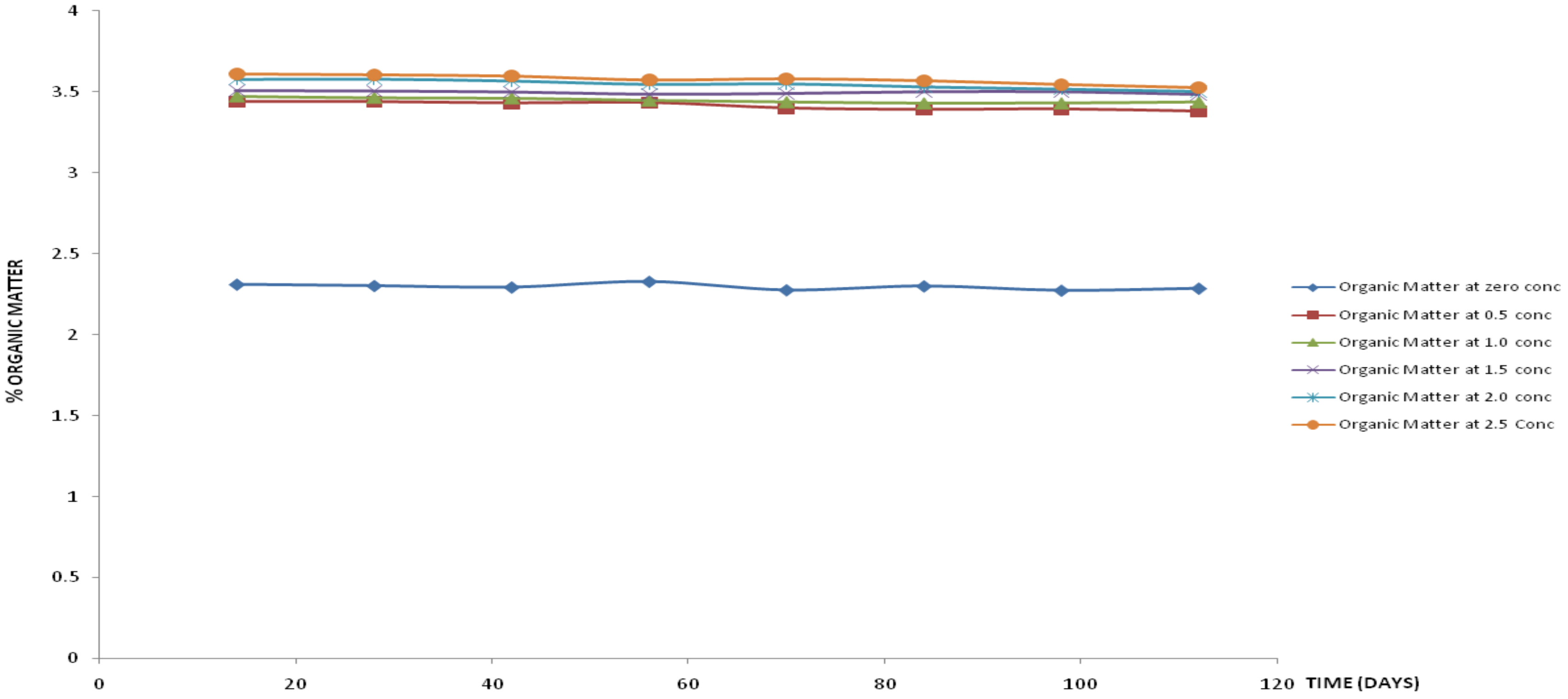


Fig. 4.5. Organic Matter at various crude oil levels with Time

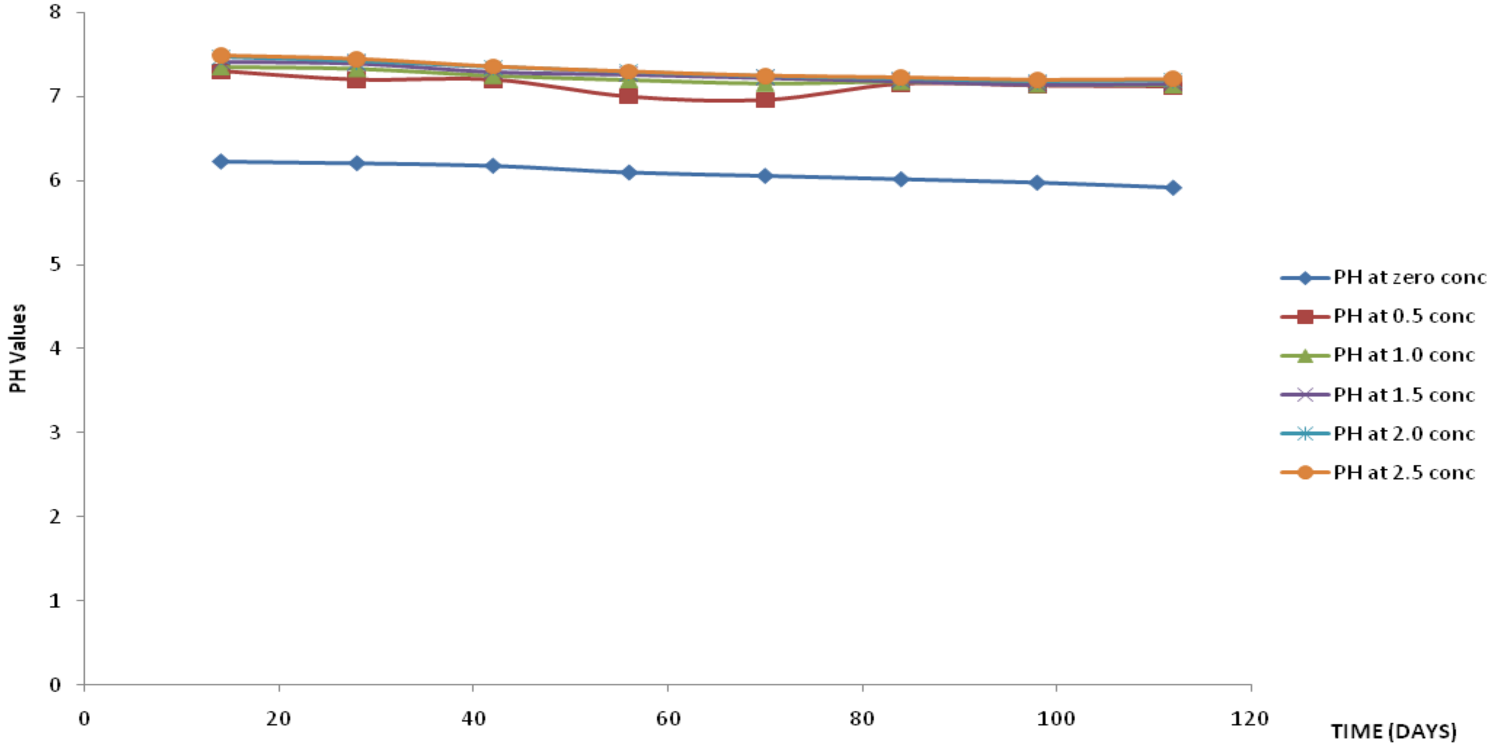


Fig. 4.6. Soil PH at various crude oil levels with Time

Table 4.10: Total Petroleum Hydrocarbon Concentration in mg/kg with time

Time in Days	**Control 0**	**Crude oil pollution levels in litres**				
		0.5	**1.0**	**1.5**	**2.0**	**2.5**
14	1.620	5520	14480	22360	30040	32640
28	1.582	4400	13940	21520	28400	31732
42	1.463	4100	13000	20780	27200	30650
56	1.366	3600	12300	20280	26200	29540
70	1.274	3420	11380	19600	25180	28775
84	1.241	3040	10200	19200	24600	27450
98	1.140	2952	9860	18360	23740	26300
112	0.987	2450	8750	17840	22941	25660

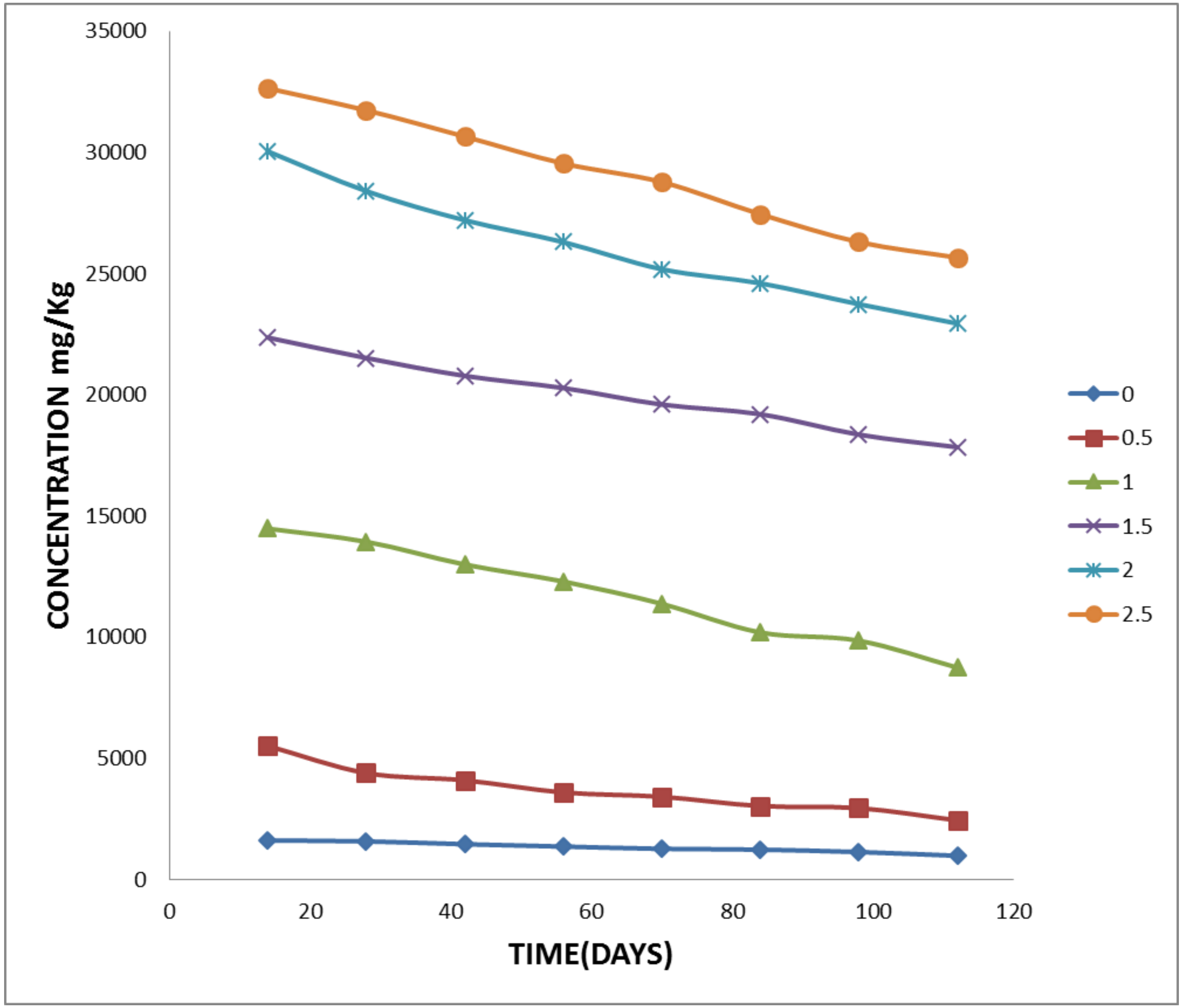


Figure 4.7: Total Petroleum Hydrocarbon concentration against time

4.1.3 Panel Data Regression Models

Table 4.11 to 4.16 shown the panel data regression model results for soil nitrogen, phosphorous, potassium, organic carbon, organic matter and soil pH respectively. The tables also contain the experimental data that were used to generate the model results indicating R^2 of 0.9824, 0.9321, 0.9540, 0.9807, 0.9734 and 0.9830 for nitrogen, phosphorous, potassium, organic carbon, organic matter and pH respectively. Tables 4.17 to 4.22 show the experimental and predicted values of the major soil nutrients parameters (N, P, K, OC, OM and pH) respectively, at various pollution levels. The percentage difference between experimental and predicted values are also indicated. Figs. 4.8 to 4.12 show the correlation between the experimental and predicted values of the major soil nutrients parameter where the blue lines indicate the experimental, the red lines indicates the predicted and the green lines indicates the standard error of the prediction.

Table 4.11 Panel Data Regression Model Results for soil Nitrogen

NITROGEN (N)

Time (days)	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

MODEL 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

NOTE: E -06 Means, X10^{-6} **WHERE, X IS ORDINARY MULTIPLICATION**

Table 4.12 Panel Data Regression Model Results for soil Phosphorus

PHOSPHORUS (P)

Time (days)	0	0.5	1	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

MODEL RESULTS

source	ss	df	Ms	Number of Obs = 48 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

P	Coef	Std Err	t	P > |t|	95% Conf.	Interval
Conc	19.71109	1.403061	14.05	0	16.88155	22.54063
time	0.068644	0.050821	1.35	0.184	-0.03385	0.1711335
time^2	-0.000415	0.000394	-1.05	0.299	-0.00121	0.0003801
conc$^{1/2}$	-48.46306	2.288342	-21.18	0	-53.0779	-43.84818
_cons	30.1	1.599236	20.92	0	30.23616	36.68649

NOTE: E -06 Means, X10 $^{-6}$ **WHERE, X IS ORDINARY MULTIPLICATION**

Table 4.13 Panel Data Regression Model Results for soil Potassium

POTASSIUM (K)

Time (days)	0	0.5	1	1.5	2	2.5
14	0.0570	0.026	0.019	0.018	0.018	0.019
28	0.0600	0.0278	0.022	0.020	0.020	0.021
42	0.0580	0.03	0.023	0.022	0.022	0.023
56	0.0620	0.031	0.024	0.024	0.023	0.023
70	0.0600	0.0302	0.024	0.023	0.023	0.024
84	0.0600	0.03	0.025	0.023	0.023	0.025
98	0.0610	0.0301	0.024	0.022	0.023	0.023
112	0.0600	0.0289	0.023	0.020	0.020	0.023

MODEL RESULTS.

source	ss	df	Ms	Number of Obs = 48
				F(4, 43) = 222.76
Model	0.008942	4	0.02235	Prob > F = 0.0000
Residual	0.003518	43	8.18E-06	R- Squared = 0.9540
Total	0.009293	47	0.0002	Adj R-Squared = 0.9497
				Root MSE = 0.00286

K	Coef	Std Err	t	P > |t|	95% Conf.	Interval
Conc	0.023563	0.001638	14.38	0	0.02026	0.0268664
time	0.000214	5.93E-05	3.61	0.001	9.44E-05	0.0003337
time^2	-1.47E-06	4.60E-07	-3.2	0.003	-2.40E-06	-5.46E-07
conc$^{1/2}$	-0.059987	0.002672	-22.45	0	-0.06538	-0.0546
_cons	0.048	0.001867	28.36	0	0.049186	0.567171

NOTE: E -06 Means, X10 $^{-6}$ **WHERE, X IS ORDINARY MULTIPLICATION**

Table 4.14 Panel Data Regression Model Results for soil Organic Carbon

ORGANIC CARBON (OC)

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	1.960	1.990	2.030	2.050	2.070
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

MODEL RESULTS

				Number of Obs = 48		
source	**ss**	**df**	**Ms**	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	**-0.427626**	0.022206	-19.26	0	-0.47241	-0.382844
time	-0.00036	0.000803	-0.45	0.657	-0.00198	0.0012625
time^2	3.34E-07	6.23E-06	0.05	0.957	-1.2E-05	0.0000129
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

NOTE: E -06 Means, X10 $^{-6}$ **WHERE, X IS ORDINARY MULTIPLICATION**

Table 4.15 Panel Data Regression Model Results for soil Organic Matter

ORGANIC MATTER (OM)

Time (days)	0	0.5	1	1.5	2	2.5
14	2.310	3.439	3.4740	3.508	3.577	3.612
28	2.302	3.439	3.4650	3.505	3.579	3.607
42	2.293	3.431	3.4620	3.499	3.567	3.599
56	2.327	3.434	3.4480	3.484	3.546	3.574
70	2.276	3.399	3.4380	3.489	3.549	3.582
84	2.300	3.390	3.4300	3.500	3.530	3.570
98	2.274	3.393	3.4310	3.501	3.516	3.546
112	2.286	3.379	3.4380	3.483	3.501	3.526

MODEL RESULTS

source	**ss**	**df**	**Ms**	Number of Obs = 48 F(4, 43) = 393.52 Prob > F = 0.0000
Model	9.572077	4	2.39302	R- Squared = 0.9734
Residual	0.194609	43.000	0.00453	Adj R-Squared = 0.9709
Total	9.766686	47	0.2078	Root MSE = 0.01046

OM	**Coef**	**Std Err**	**t**	**P > |t|**	**95% Conf.**	**Interval**
Conc	-0.729008	0.038524	-18.92	0	-0.8067	-0.651317
time	-0.000441	0.001395	-0.32	0.754	-0.00325	0.0023735
$time^2$	-7.70E-07	1.08E-05	-0.07	0.943	-2.3E-05	0.000021
$conc^{1/2}$	1.912686	0.062832	30.44	0	1.785974	2.039398
_cons	2.349435	0.043911	53.5	0	2.260881	2.43799

NOTE: E -06 Means, X10 $^{-6}$ **WHERE, X IS ORDINARY MULTIPLICATION**

Table 4.16 Panel Data Regression Model Results for soil pH

Time (days)	PH 0	0.5	1	1.5	2	2.5
14	6.230	7.300	7.350	7.420	7.470	7.490
28	6.210	7.200	7.330	7.400	7.420	7.450
42	6.180	7.200	7.250	7.300	7.350	7.360
56	6.100	7.000	7.200	7.270	7.290	7.300
70	6.060	6.960	7.160	7.230	7.240	7.250
84	6.020	7.150	7.180	7.190	7.210	7.230
98	5.980	7.130	7.150	7.160	7.180	7.200
112	5.920	7.120	7.140	7.160	7.190	7.210

MODEL RESULTS

source	ss	df	Ms	Number of Obs = 48 F(4, 43) = 620.95 Prob > F = 0.0000
Model	9.393115	4	2.34828	R- Squared = 0.9830
Residual	0.16261645	43.000	0.0037818	Adj R-Squared = 0.9814
Total	9.55573099	47	0.2033134	Root MSE = 0.615

OM	Coef	Std Err	t	P > |t|	95% Conf.	Interval
Conc	-0.7080021	0.0352156	-20.1	0	-0.779021	-0.6369832
time	-0.0062861	0.0012756	-4.93	0	-0.0088585	-0.0037137
time^2	2.86E-05	9.88E-06	2.89	0.006	8.67E-06	0.0000485
conc$^{1/2}$	1.857124	0.0574353	32.33	0	1.741294	1.972953
_cons	6.355381	0.0401394	158.33	0	6.274432	6.43633

NOTE: E -06 Means, X10 $^{-6}$ **WHERE, X IS ORDINARY MULTIPLICATION**

Table 4.17: 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

Table 4.18 : EXPERIMENTAL AND PREDICTED VALUES OF SOIL PHOSPHORUS AT VARIOUS POLLUTION LEVELS USING MODEL EQUATION

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 4.19 : EXPERIMENTAL AND PREDICTED VALUES OF SOIL POTASSIUM AT VARIOUS POLLUTION LEVELS USING MODEL EQUATION

TIME	COV	ED for K	PV for K	% Difference
14	0	0.0570	0.055660103	2.350697391
28	0	0.0600	0.057791054	3.681574099
42	0	0.0580	0.059344627	-2.318325294
56	0	0.0620	0.060320817	2.708358194
70	0	0.0600	0.060719624	-1.199375865
84	0	0.0600	0.060541052	-0.901756207
98	0	0.0610	0.059785102	1.991637884
112	0	0.0600	0.058451768	2.580384471
14	0.5	0.026000099	0.025024053	3.75400919
28	0.5	0.027800373	0.027155004	2.321436832
42	0.5	0.03	0.028708577	4.304742932
56	0.5	0.031000001	0.029684767	4.242688344
70	0.5	0.030200002	0.030083576	0.385516095
84	0.5	0.029999999	0.029905004	0.316649682
98	0.5	0.0301	0.029149054	3.159291503
112	0.5	0.02891	0.02781572	3.785126042
14	1	0.019	0.019235618	0.385182637
28	1	0.022	0.02136657	2.879226088
42	1	0.023	0.022920141	0.347213252
56	1	0.024	0.023896333	0.431947406
70	1	0.024	0.024295142	-1.229757122
84	1	0.025	0.02411657	3.572290305
98	1	0.024	0.023360617	2.664095432
112	1	0.023	0.022027284	4.229014261
14	1.5	0.018	0.017535226	2.582051253
28	1.5	0.020	0.019666178	2.158317072
42	1.5	0.022	0.021219751	3.546587167
56	1.5	0.024	0.022195941	7.516913982
70	1.5	0.023	0.02259475	1.761957028
84	1.5	0.023	0.022416178	2.326020904
98	1.5	0.022	0.021660227	1.544422168
112	1.5	0.020	0.020326894	-1.129049676
14	2	0.018	0.017950971	0.823363962
28	2	0.020	0.020081922	-0.409614304
42	2	0.022	0.021635493	1.656848269
56	2	0.023	0.022611685	1.688325855
70	2	0.023	0.023010494	-0.045626708
84	2	0.023	0.022831922	0.730771897
98	2	0.023	0.02207597	4.017523802
112	2	0.020	0.020742636	-3.713183188
14	2.5	0.019	0.019719029	-3.784366577
28	2.5	0.021	0.021849982	-3.554422148
42	2.5	0.023	0.023403553	-1.754580059
56	2.5	0.023	0.024379743	-4.14243151
70	2.5	0.024	0.024778554	-3.243976413
84	2.5	0.025	0.024599982	1.992084435
98	2.5	0.023	0.02384403	-3.669694383
112	2.5	0.023	0.022510696	2.551079832

Table 4.20 : EXPERIMENTAL AND PREDICTED VALUES OF SOIL ORGANIC CARBON AT VARIOUS POLLUTION LEVELS 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

Table 4.21 : EXPERIMENTAL AND PREDICTED VALUES OF SOIL ORGANIC MATTER AT VARIOUS POLLUTION LEVELS USING MODEL EQUATION

TIME	COV	ED for OM	PV for OM	% Difference
14	0	2.310	2.343113899	-1.433504644
28	0	2.302	2.336486816	-1.498122065
42	0	2.293	2.329554319	-1.594170816
56	0	2.327	2.32231617	0.201277747
70	0	2.276	2.314772606	-1.703540537
84	0	2.300	2.306923389	-0.301019011
98	0	2.274	2.29876852	-1.089208078
112	0	2.286	2.290308237	-0.188461229
14	0.5	3.439	3.331082582	3.138043391
28	0.5	3.439	3.324455738	3.330740239
42	0.5	3.431	3.317523241	3.307395903
56	0.5	3.434	3.310285091	3.602647738
70	0.5	3.399	3.302741528	2.831962456
84	0.5	3.390	3.294892311	2.805539554
98	0.5	3.393	3.286737442	3.131813999
112	0.5	3.379	3.278277159	2.980846147
14	1	3.4740	3.526791334	-1.519613051
28	1	3.4650	3.520164251	-1.592044402
42	1	3.4620	3.513231754	-1.479834278
56	1	3.4480	3.505993605	-1.681950441
70	1	3.4380	3.498450041	-1.758291963
84	1	3.4300	3.490600824	-1.766785901
98	1	3.4310	3.482445955	-1.499445091
112	1	3.4380	3.473985672	-1.04670473
14	1.5	3.508	3.592153549	-2.398906917
28	1.5	3.505	3.585526705	-2.297477538
42	1.5	3.499	3.578593969	-2.274761224
56	1.5	3.484	3.571356058	-2.507350498
70	1.5	3.489	3.563812256	-2.144229638
84	1.5	3.500	3.555963039	-1.598943983
98	1.5	3.501	3.547808409	-1.337003204
112	1.5	3.483	3.539348125	-1.61780318
14	2	3.577	3.590043306	-0.364646463
28	2	3.579	3.583416462	-0.123399435
42	2	3.567	3.576483965	-0.265883176
56	2	3.546	3.569245815	-0.655550238
70	2	3.549	3.561702251	-0.357910018
84	2	3.530	3.553853035	-0.675724186
98	2	3.516	3.545698166	-0.844656803
112	2	3.501	3.537237883	-1.035074431
14	2.5	3.612	3.544815063	1.860047766
28	2.5	3.607	3.538187981	1.907738557
42	2.5	3.599	3.531255484	1.882314363
56	2.5	3.574	3.524017334	1.39850446
70	2.5	3.582	3.51647377	1.82932012
84	2.5	3.570	3.508624554	1.719198339
98	2.5	3.546	3.500469685	1.283990952
112	2.5	3.526	3.492009401	0.963999471

Table 4.22 : EXPERIMENTAL AND PREDICTED VALUES OF SOIL PH AT VARIOUS POLLUTION LEVELS USING MODEL EQUATION

TIME	COV	ED for PH	PV for PH	% Difference
14	0	6.230000019	6.272980213	-0.689890754
28	0	6.210000038	6.201789379	0.132216731
42	0	6.179999828	6.141809464	0.617967086
56	0	6.099999905	6.093039513	0.114104789
70	0	6.059999943	6.055480003	0.07458646
84	0	6.019999981	6.029130936	-0.15167699
98	0	5.980000019	6.013991833	-0.568424976
112	0	5.920000076	6.010063171	-1.521336046
14	0.5	7.300000191	7.232163906	0.929264149
28	0.5	7.199999809	7.160973549	0.542031408
42	0.5	7.199999809	7.100993156	1.375092437
56	0.5	7	7.052223206	-0.746045794
70	0.5	6.960000038	7.014663696	-0.785397383
84	0.5	7.150000095	6.988314629	2.261335169
98	0.5	7.130000114	6.973175526	2.199503314
112	0.5	7.119999886	6.969247341	2.117311051
14	1	7.349999905	7.422101974	-0.980980555
28	1	7.329999924	7.35091114	-0.285282632
42	1	7.25	7.290931225	-0.564568618
56	1	7.199999809	7.242161274	-0.585575914
70	1	7.159999847	7.204601765	-0.622931819
84	1	7.179999828	7.178252697	0.024333306
98	1	7.150000095	7.163113594	-0.183405574
112	1	7.139999866	7.159184933	-0.268698412
14	1.5	7.420000076	7.485479832	-0.882476479
28	1.5	7.400000095	7.414289474	-0.193099715
42	1.5	7.300000191	7.354309082	-0.743957396
56	1.5	7.269999981	7.305539608	-0.488853194
70	1.5	7.230000019	7.267980099	-0.525312304
84	1.5	7.190000057	7.241630554	-0.718087574
98	1.5	7.159999847	7.226491928	-0.928660365
112	1.5	7.159999847	7.222563267	-0.873790792
14	2	7.46999979	7.483345509	-0.178657547
28	2	7.420000076	7.412155151	0.10572675
42	2	7.349999905	7.352174759	-0.029589855
56	2	7.289999962	7.303404808	-0.183879921
70	2	7.239999771	7.265845299	-0.356982437
84	2	7.210000038	7.239496231	-0.409101148
98	2	7.179999828	7.224357605	-0.617796347
112	2	7.190000057	7.220428944	-0.423211212
14	2.5	7.489999771	7.43934536	0.676293897
28	2.5	7.449999809	7.368155003	1.098588037
42	2.5	7.360000134	7.30817461	0.70415112
56	2.5	7.300000191	7.259405136	0.556096624
70	2.5	7.25	7.221845627	0.388336182
84	2.5	7.230000019	7.195496082	0.477232872
98	2.5	7.199999809	7.180357456	0.272810466
112	2.5	7.210000038	7.176428795	0.46562057

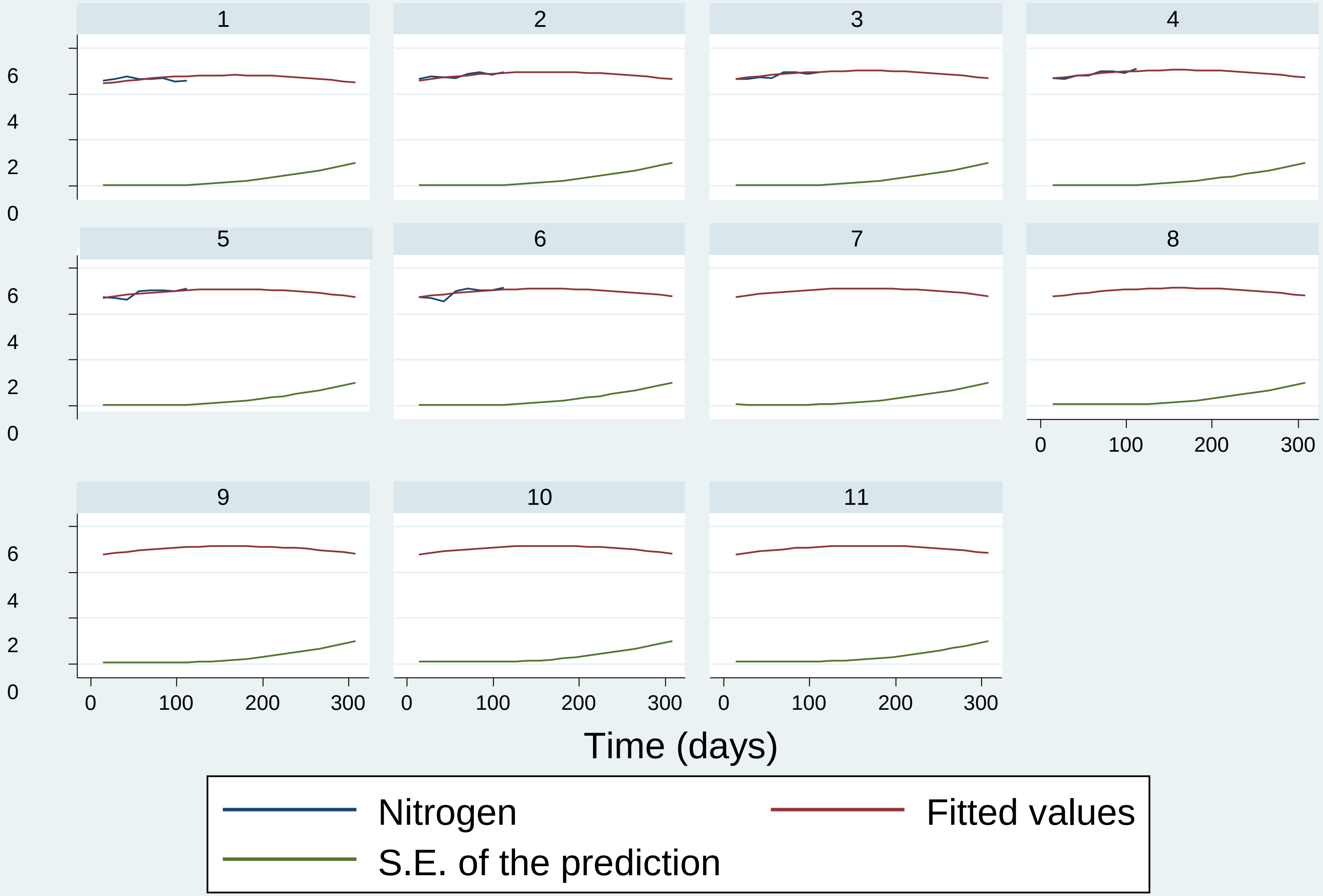


Fig 4.8: Correlation between the experimented and predicted values of the soil Nitrogen

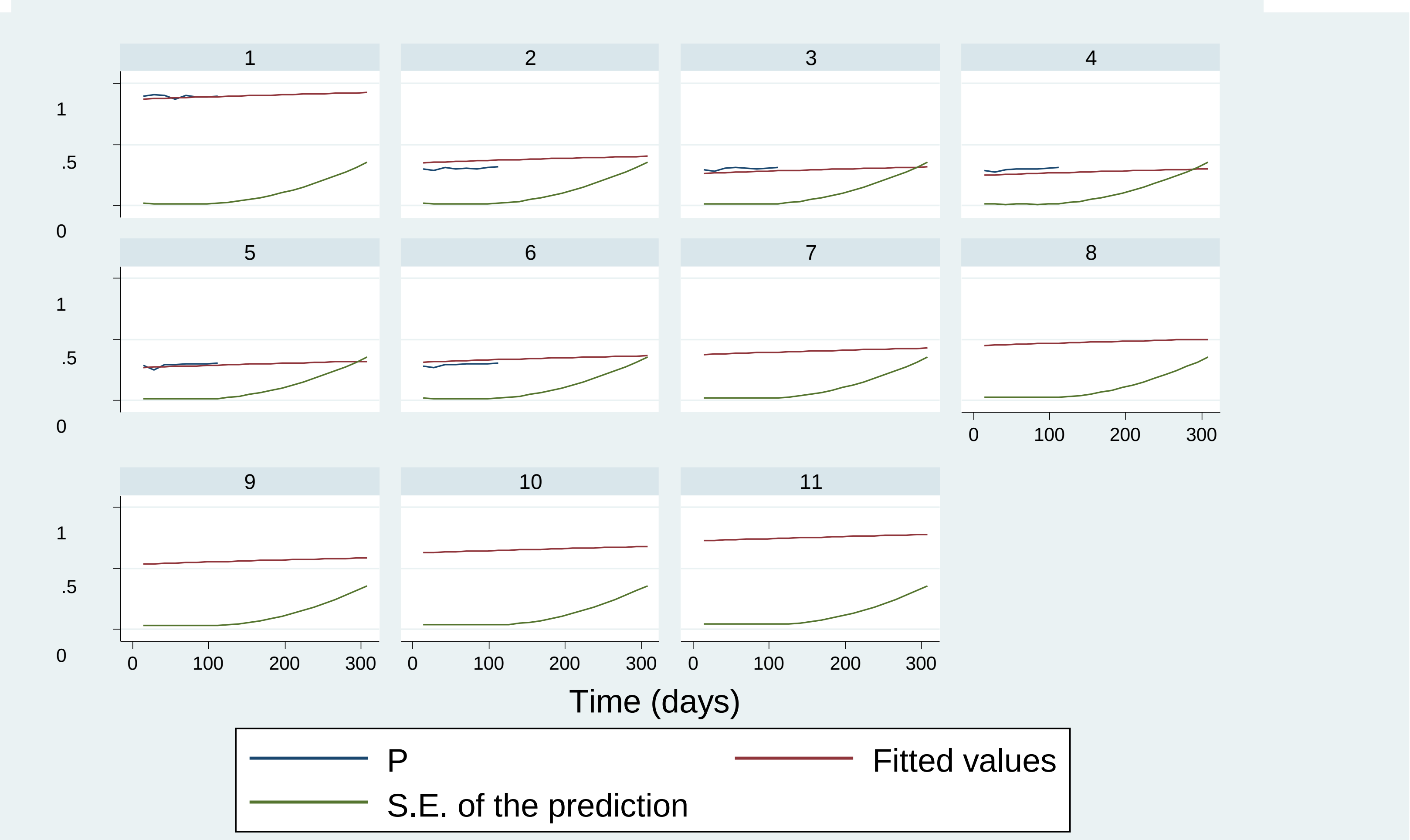


Fig 4.9: Correlation between experimented and predicted values of the soil Phosphorus

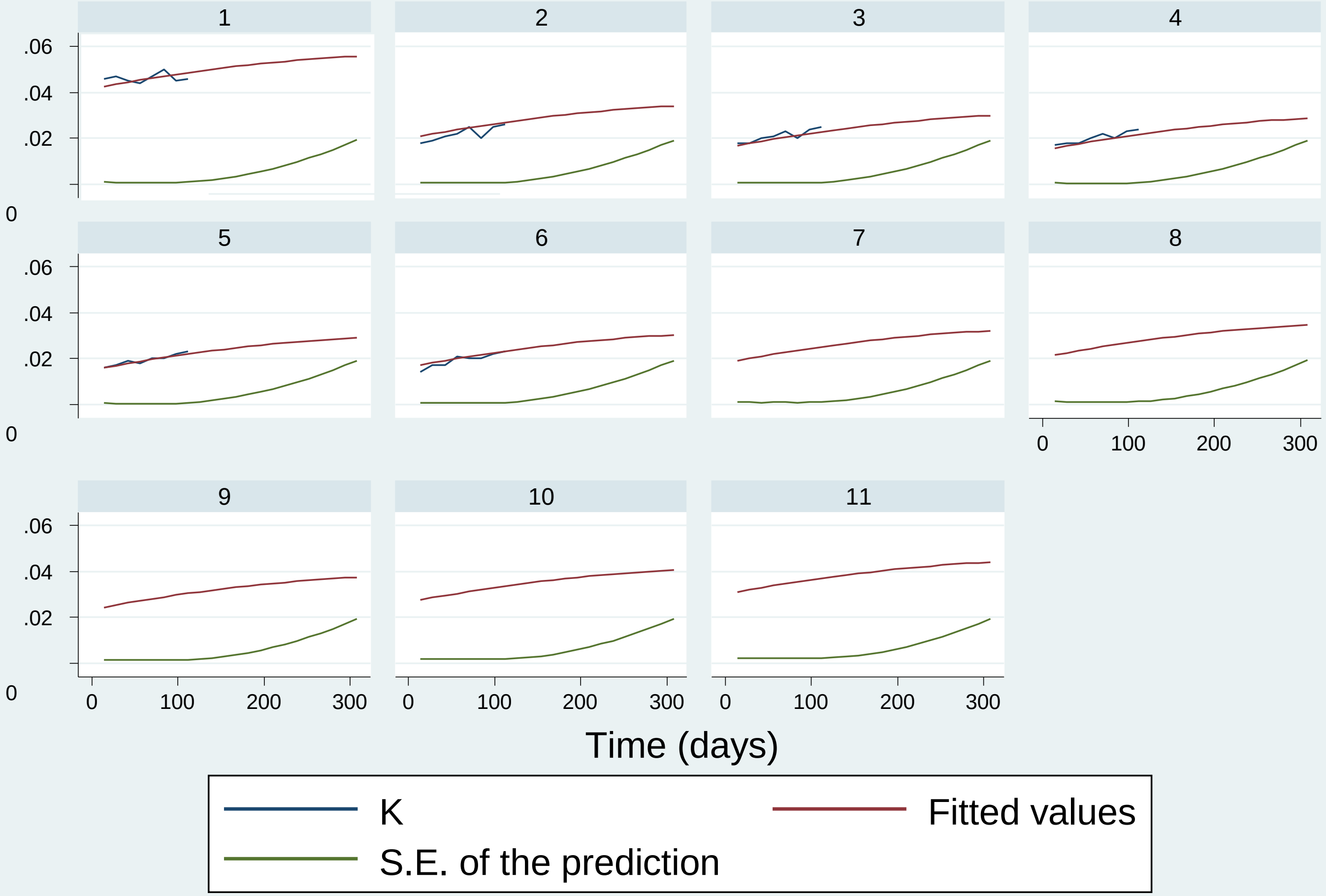


FIG 4.10: Correlation between experimented and predicted values of the soil Potassium(K)

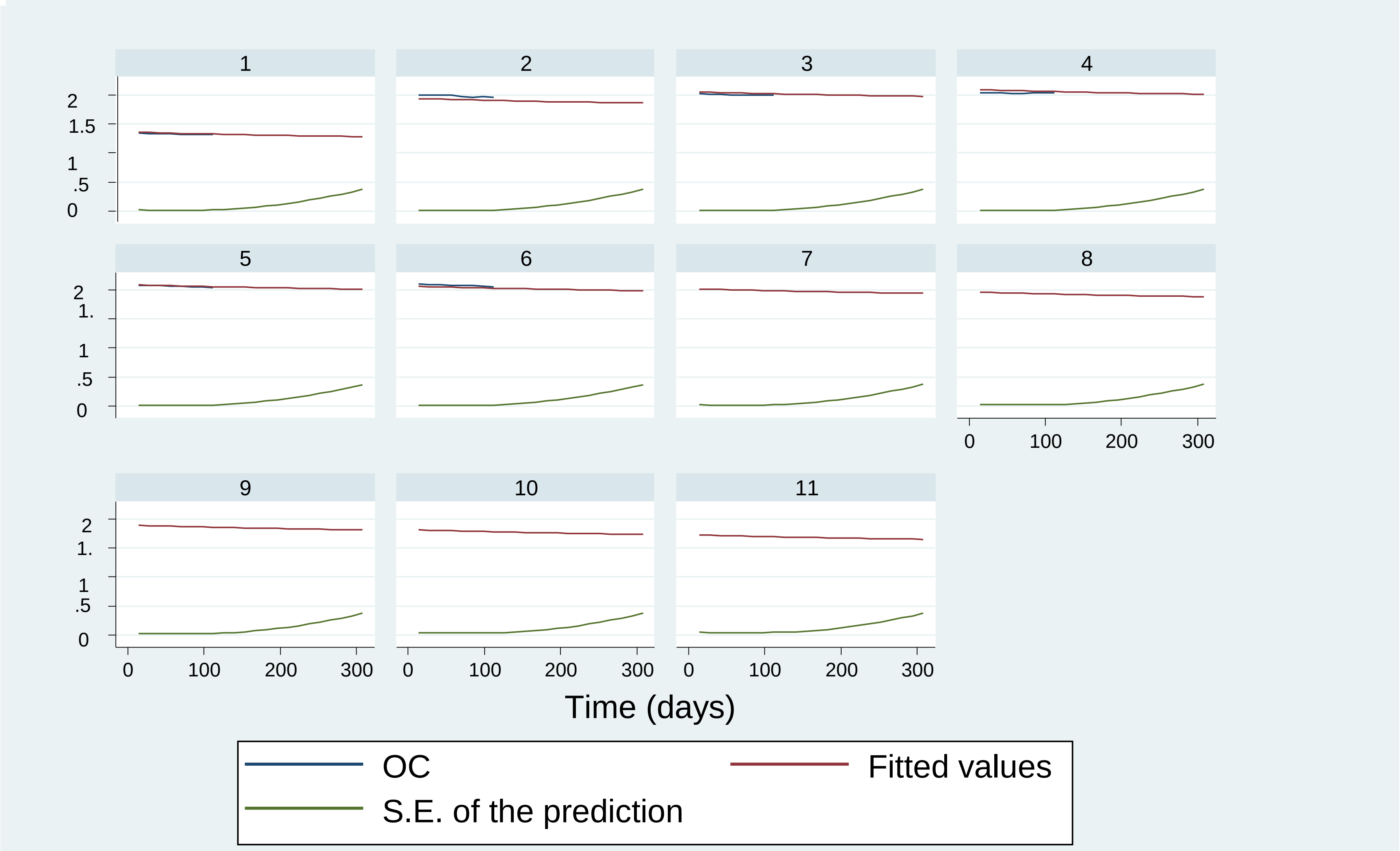


Fig 4.11: Correlation between experimented and predicted values of the soil Organic carbon

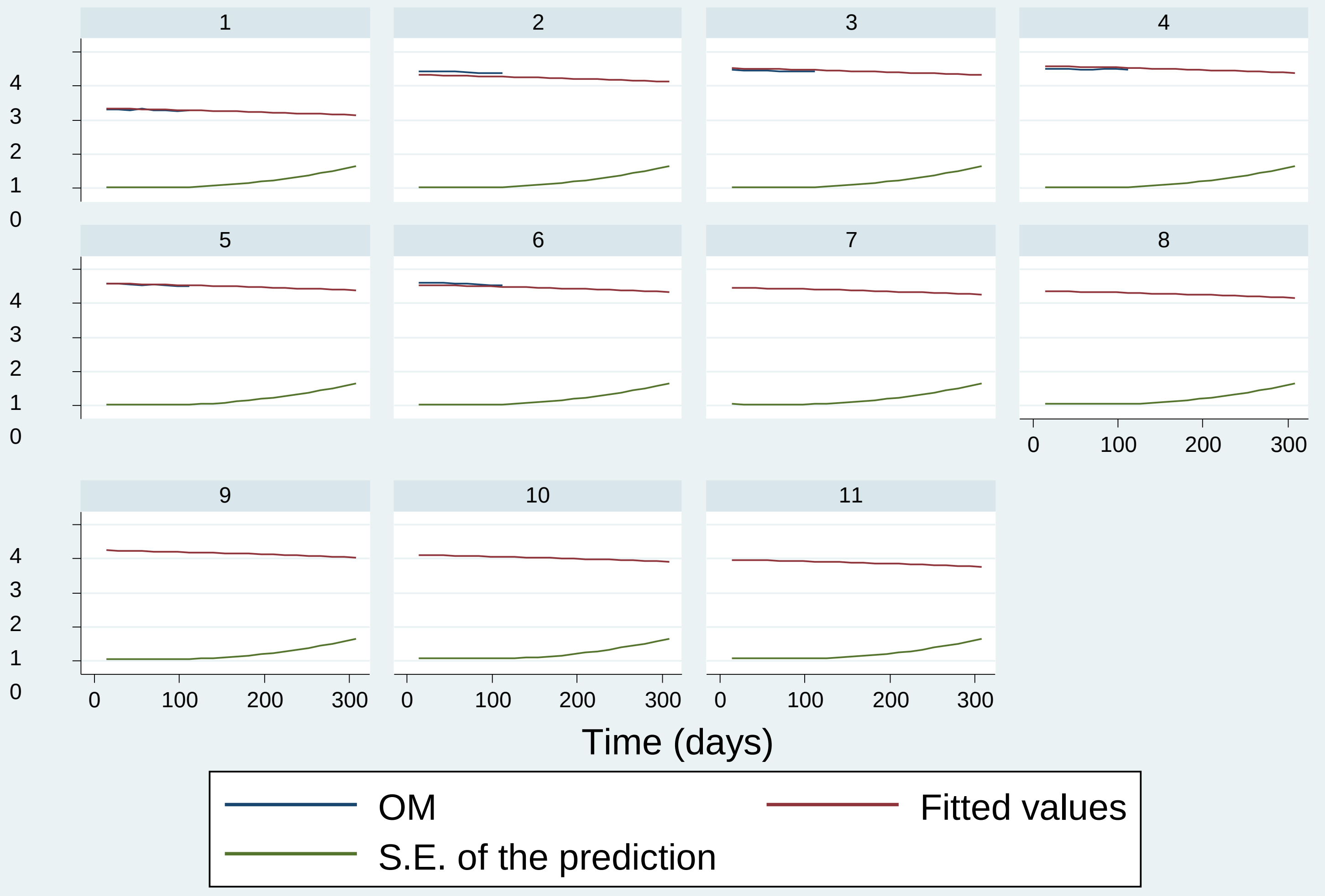


Fig 4.12: Correlation between experimented and predicted values of the soil Organic Matter

4.1.4 MODEL EQUATIONS FOR THE MAJOR SOIL NUTRIENT PARAMETERS (N, P, K, OM, OC AND pH)

Equations 4.1 to 4.7 were the computer generated model equations for predicting major soil nutrients depletion in crude oil contaminated soil, namely nitrogen, phosphorous, potassium, organic carbon, organic matter and soil pH.

$$Y_{it} = B_0 + B_1 C_{V_{it}} + B_2 T_{it} + B_3 T_{it}^2 + B_4 \sqrt{C_{V_{it}}} + U_{it} \quad \ldots \tag{4.1}$$

(i) For Nitrogen (N)

$$N = 0.1927 + 0.1124 C_{V_{it}} + 0.0004 T_{it} - 2.01 e T_{it}^2 - 0.2754 \sqrt{C_{V_{it}}} + 0.0655 \quad \ldots \tag{4.2}$$

(ii) For Phosphorous (P)

$$P = 30.100 + 19.71 C_{V_{it}} + 0.0686 T_{it} - 0.0004 T_{it}^2 - 48.46 \sqrt{C_{V_{it}}} + 0.15309 \quad \ldots \tag{4.3}$$

(iii) For Potassium (K)

$$K = 0.0480 + 0.0236 C_{V_{it}} + 0.0002 T_{it} - 1.47 e T^2 - 0.0599 \sqrt{C_{V_{it}}} + 0.0028 \quad \ldots \tag{4.4}$$

(iv) For Organic Carbon (OC)

$$OC = 1.3100 - 0.4276 C_{V_{it}} - 0.0004 T_{it} + 3.34 e T_{it}^2 + 1.1214 \sqrt{C_{V_{it}}} + 0.1043 \quad \ldots \tag{4.5}$$

(v) For Organic Matter (OM)

$$OM = 2.3494 - 0.7290 C_{V_{it}} - 0.00044 T_{it} - 7.70 e T_{it}^2 + 1.9126 \sqrt{C_{V_{it}}} + 0.01046 \quad \ldots \tag{4.6}$$

(vi) For Soil pH (pH)

$$pH = 6.310 - 0.7080 C_{V_{it}} - 0.0063 T_{it} + 2.86 e T_{it}^2 + 1.857 \sqrt{C_{V_{it}}} + 0.0387 \quad \ldots \tag{4.7}$$

where

T_{it} = Number of days

$C_{V_{it}}$ = crude oil volume in litres

e = x 10^{-6}

4.1.5 Calibration of Soil Nutrient Parameters

The data of major soil nutrient parameters used in the calibration of the model over time are shown in Tables 4.23 to 4.28, while Fig. 4.13 to. 4.18 show the model of the various soil nutrient parameters after calibration. The computer generated values for panel data regression model is in Appendix B.

4.1.6 Calibration/Validation of the Model using Experimental Data

Calibration of the major soil nutrients parameters was done and the results for the experimental and predicted values are shown in Tables 4.29 to 4.34:

$$Y_{it} = B_0 + B_1 CV_{it} + B_2 T_{it} + B_3 T_{it}^2 + B_4 \sqrt{C_{V_{it}}} + U_{it} \qquad (4.1)$$

(i) Nitrogen (N) (where T = 7 days, $C_{V_{it}}$ = 0.5 litres)

$N = 0.1927 + 0.1124 \times 0.5 + 0.0004 \times 7 - 2.01 \times 14 \times 10^{-6} \times 7 \times 7 - 0.2754 \times 0.707 + 0.0655$

N = 0.122 as against 0.119 (Exp. data)

(ii) Phosphorous (P)

$P = 30.100 + 19.71 \times 0.5 + 0.0686 \times 7 - 0.0004 \times 7 \times 7 - 48.46\sqrt{0.5} + 0.15309$

$= 30.100 + 9.855 + 0.480 - 0.0196 - 34.266 + 0.15309$

P = 6.302 as against 6.526 (Exp. data)

(iii) Potassium (K)

$K = 0.0480 + 0.0236 \times 0.5 + 0.0002 \times 7 - 1.4 \times 10^{-6} \times 7 \times 7 - 0.0599\sqrt{0.5} + 0.0028$

$= 0.0480 + 0.0118 + 0.0014 - 0.000068 - 0.42 + 0.0028$

K = 0.0219 as against 0.0209 (Exp. data)

(iv) Organic Carbon (OC)

$OC = 1.310 + 0.4276 \times 0.5 + 0.0004 \times 7 + 3.34 \times 10^{-6} \times 7 \times 7 + 1.1214\sqrt{0.5} + 0.1043$

$= 1.310 - 0.2138 - 0.0028 + 0.00016 + 0.792 + 0.1043$

Table 4.23: Nitrogen values at various levels of crude oil pollution

Time (days)	0.5	1.0	1.5	2.0
7	0.1190	0.096	0.088	0.084
14	0.1176	0.092	0.086	0.083
21	0.1186	0.095	0.086	0.079
28	0.121	0.089	0.079	0.077
35	0.129	0.097	0.080	0.088

Table 4.24: Phosphorous values at various levels of crude oil pollution

Time (days)	0.5	1.0	1.5	2.0
7	6.526	2.140	1.112	1.520
14	6.852	2.744	1.450	1.340
21	7.145	2.850	1.650	1.450
28	7.380	3.100	1.946	2.100
35	7.800	3.220	2.145	2.136

Table 4.25: Potassium values at various crude oil pollution

Time (days)	0.5	1.0	1.5	2.0
7	0.0209	0.0133	0.0126	0.0100
14	0.0219	0.0137	0.0133	0.0152
21	0.0227	0.0142	0.0136	0.0180
28	0.0232	0.0146	0.0142	0.0214
35	0.0259	0.0156	0.0148	0.0273

Table 4.26: Organic Carbon values at various levels of crude oil pollution

Time (days)	0.5	1.0	1.5	2.0
7	1.889	1.972	2.114	2.125
14	1.844	1.984	2.117	2.129
21	1.869	1.988	2.124	2.133
28	1.920	1.999	2.130	2.137
35	1.912	2.100	2.127	2.134

Table 4.27: Organic Matter values at various levels of crude oil pollution

Time (days)	0.5	1.0	1.5	2.0
7	3.294	3.495	3.588	3.599
14	3.296	3.493	3.582	3.594
21	3.290	3.488	3.562	3.589
28	3.285	3.490	3.579	3.590
35	3.280	3.491	3.516	3.592

Table 4.28: pH values at various levels of crude oil pollution

Time (days)	0.5	1.0	1.5	2.0
7	7.150	7.392	7.499	7.500
14	7.147	7.389	7.492	7.497
21	7.135	7.381	7.489	7.492
28	7.119	7.375	7.473	7.483
35	7.00	7.370	7.472	7.481

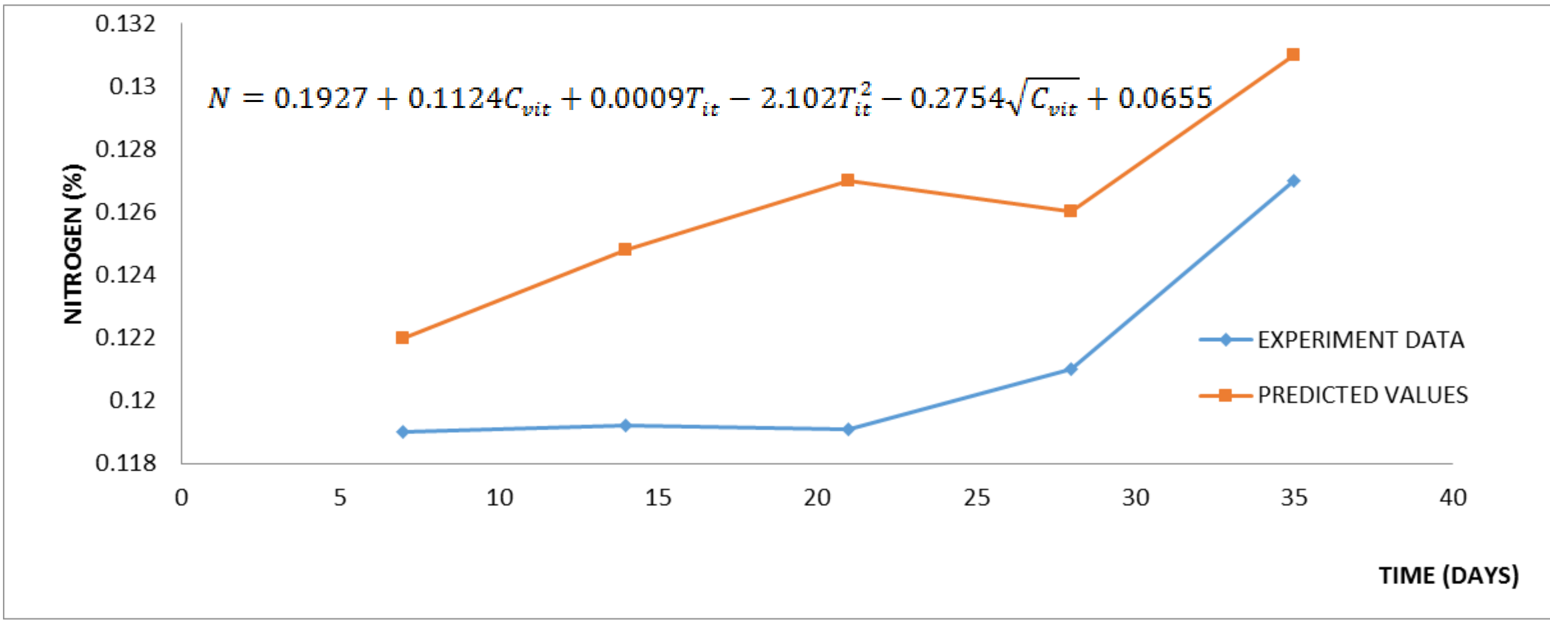


Fig. 4.13: Model for Soil Nitrogen

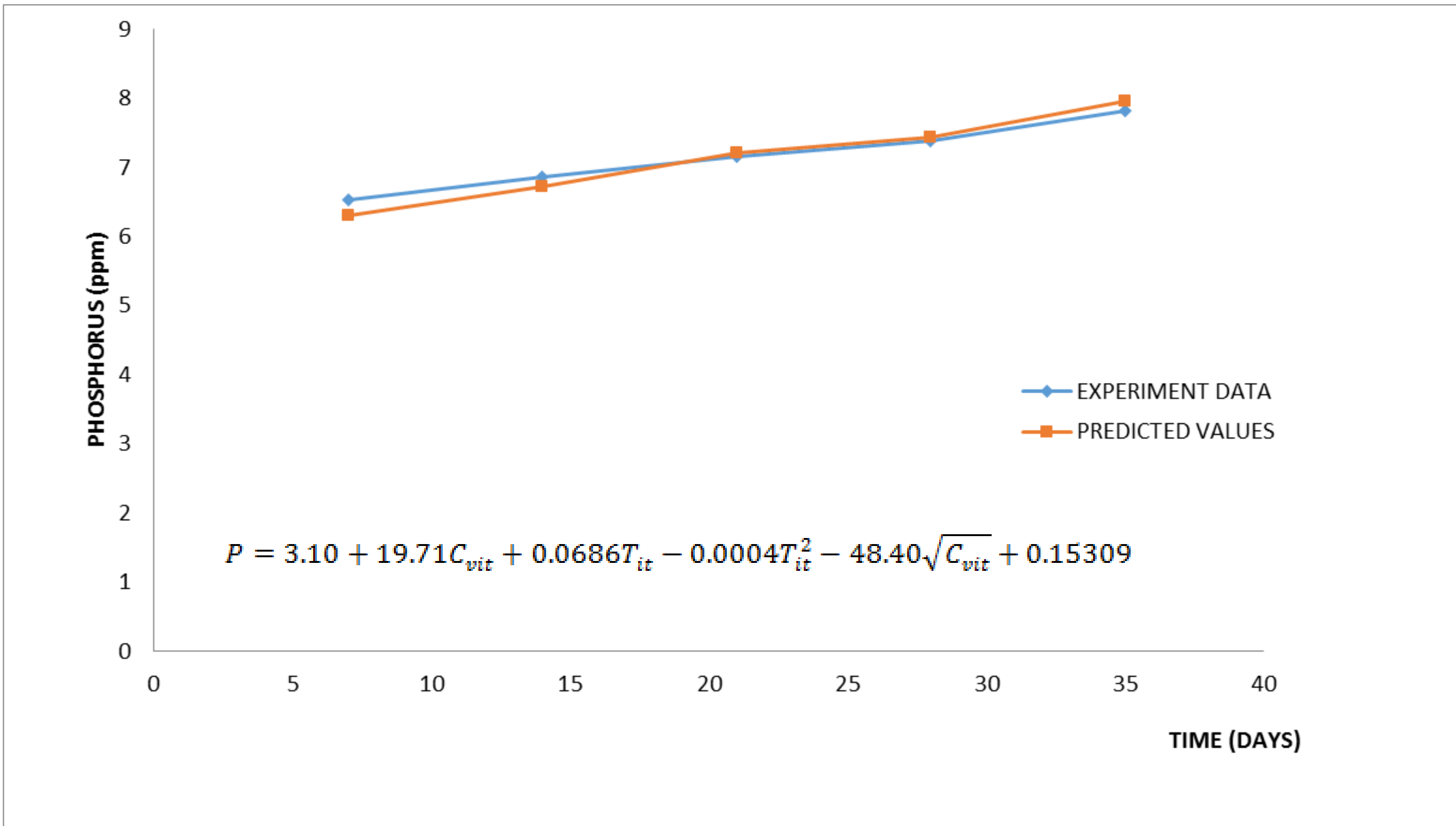


Fig. 4.14: Model for Soil Phosporus

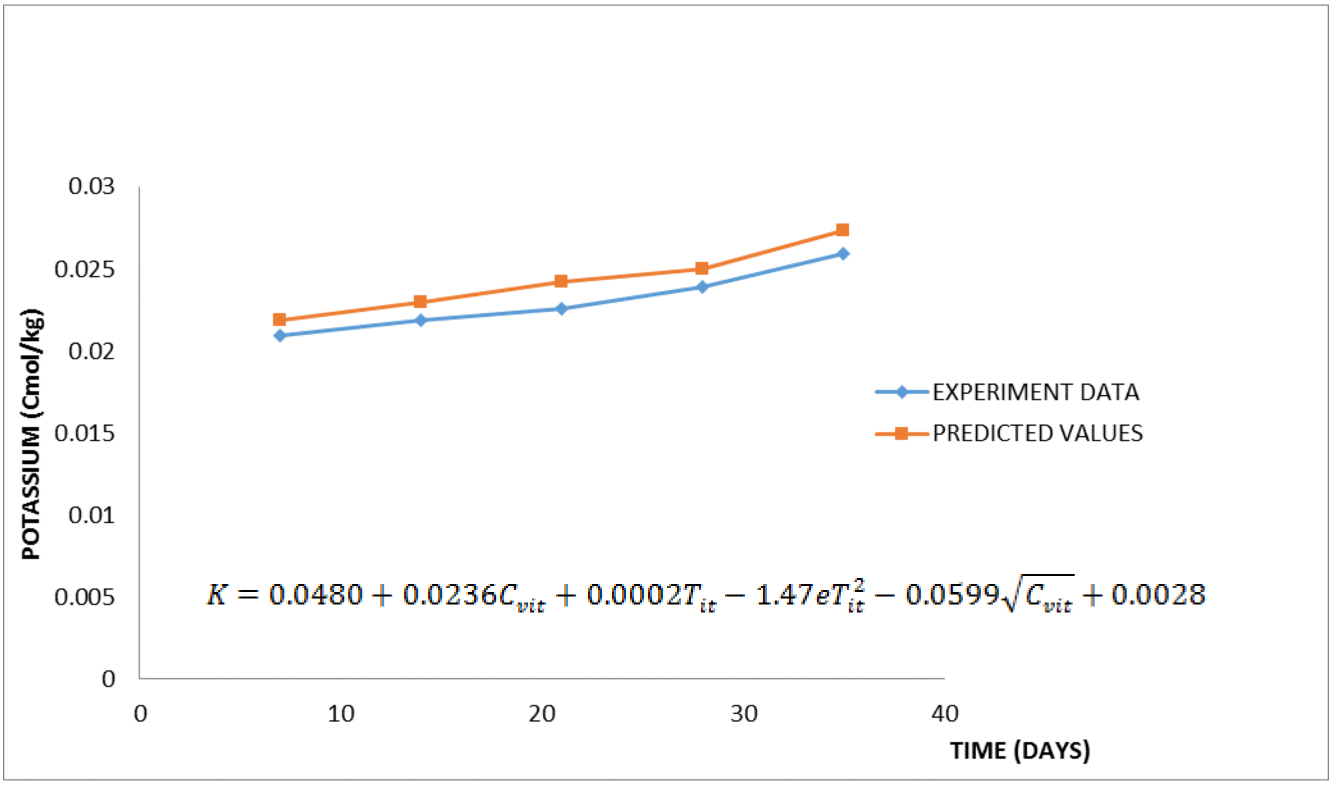


Fig. 4.15: Model for Soil Potassium

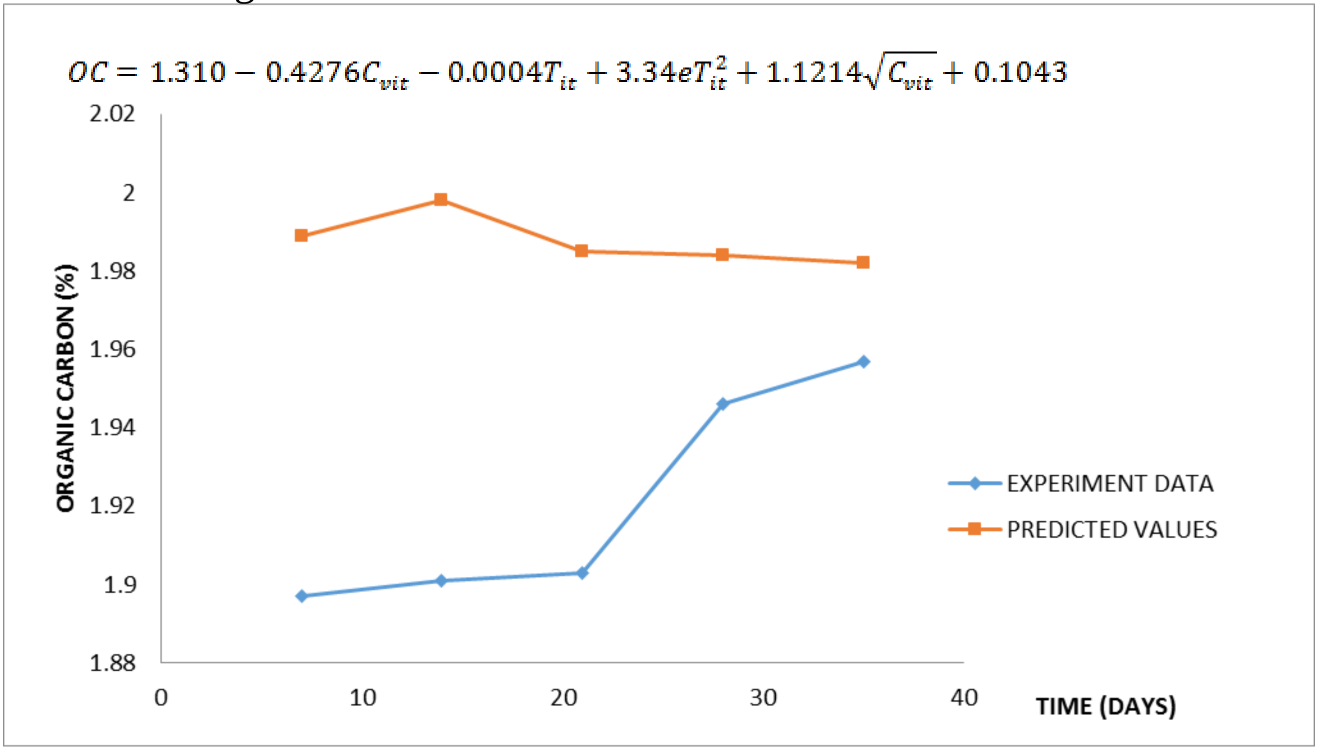


Fig. 4.16: Model for Soil Organic Carbon

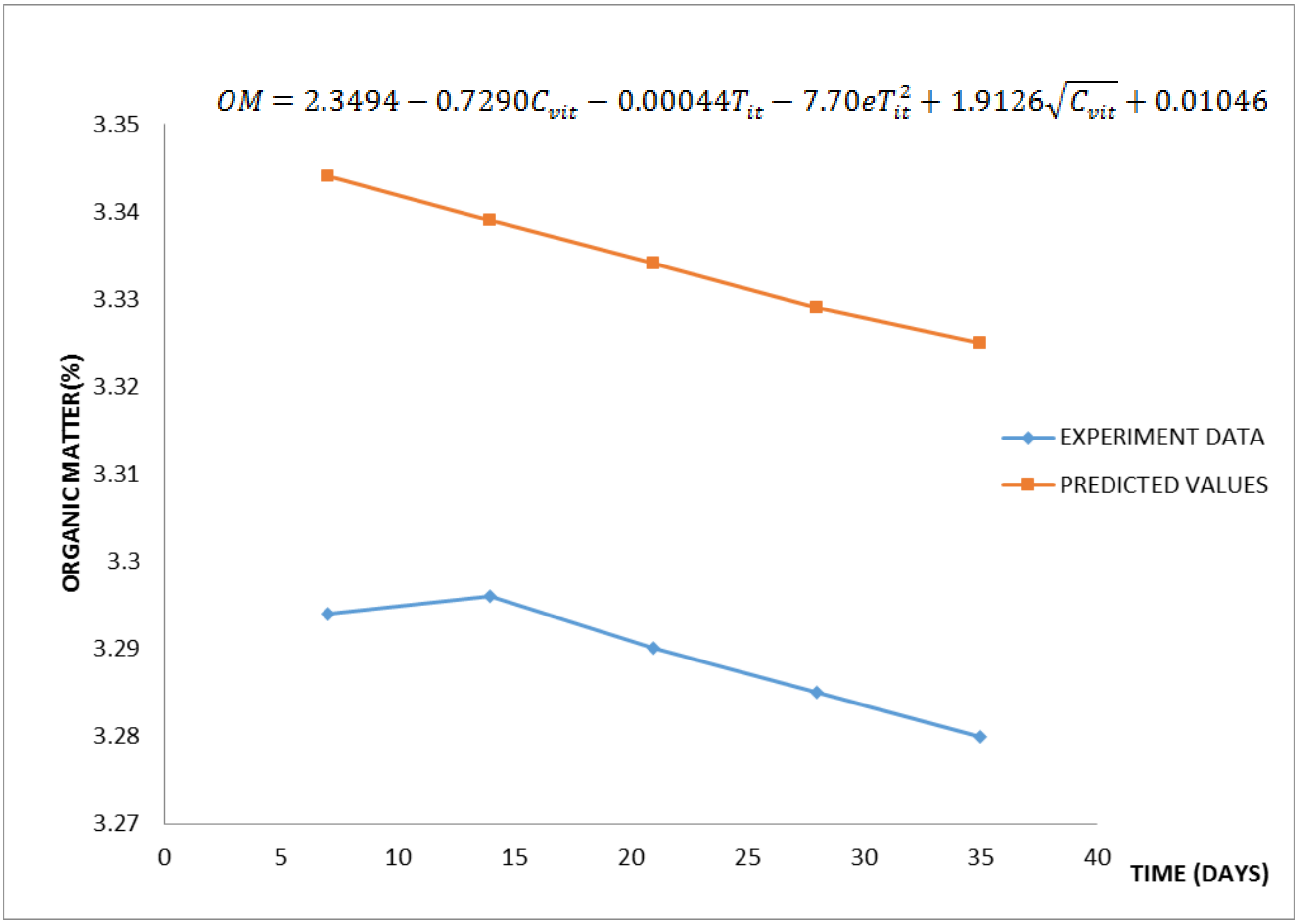


Fig. 4.17: Model for Soil Organic Matter

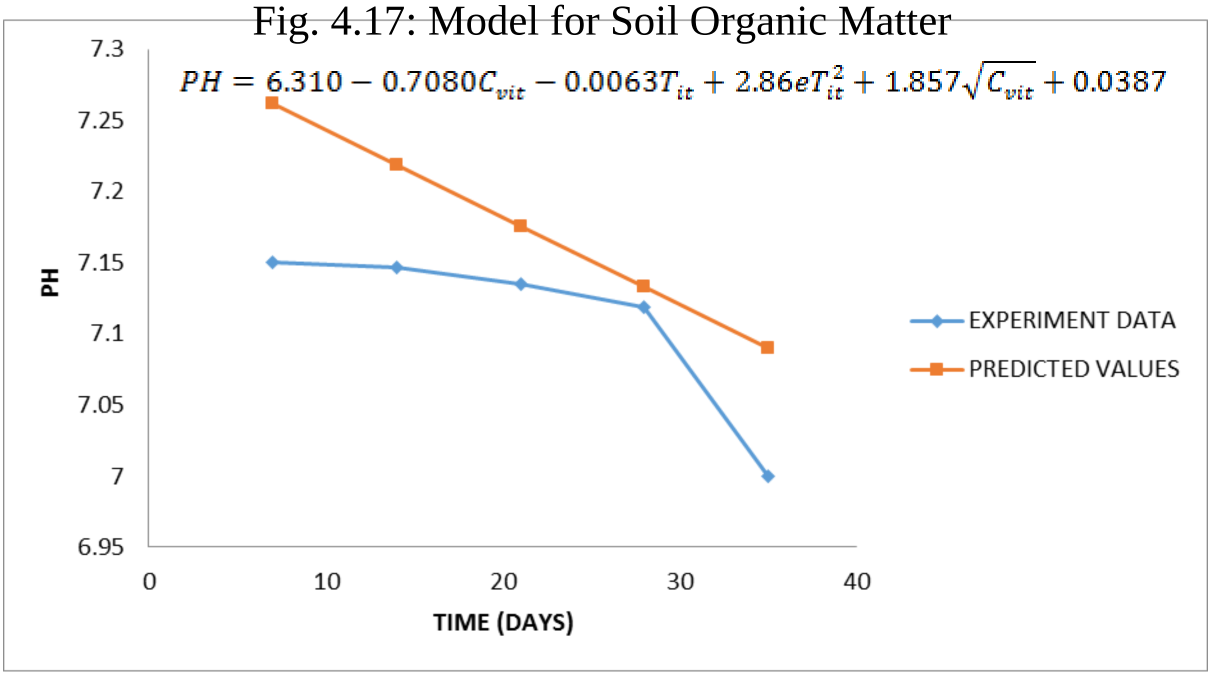


Fig. 4.18: Model for Soil PH

OC = 1.989 as against 1.897 (Exp. data)

(v) Organic Matter (OM)

$$OM = 2.349 - 0.7290 \times 0.5 - 0.00044 \times 7 - 7.70 \times 10^{-6} \times 7 \times 7 + 1.9126\sqrt{0.5} + 0.0104$$

$$= 2.349 - 0.364 + 0.0031 - 0.00037 + 1.352 + 0.0104$$

OM = 3.344 as against 3.294 (Exp. data)

(vi) Soil pH (pH)

$$pH = 6.310 + 0.7080 \times 0.5 + 0.0063 \times 7 + 2.86 \times 10^{-6} \times 7 \times 7 + 1.857 \times 0.707 + 0.0387$$

$$= 6.310 - 0.354 - 0.044 + 0.00014 + 1.312 + 0.0387$$

pH = 7.262 as against 7.150 (Exp. data)

Table 4.29: Experimental and Predicted Values for Soil Nitrogen (%) over Time

Time/Day	Experimental Data (ED)	Predicted Value (PV)	Percentage Difference $PD = \left\| \frac{PV - ED}{PV} * 100 \right\|$
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 4.30: Experimental and Predicted Values for Soil Phosphorous (ppm) over Time

Time/Day	Experimental Data (ED)	Predicted Value (PV)	Percentage Difference $PD = \left\| \frac{PV - ED}{PV} * 100 \right\|$
7	6.526	6.302	8.43
14	6.852	6.724	1.86
21	7.145	7.200	0.769
28	7.380	7.440	0.81
35	7.820	7.953	1.98

Table 4.31: Experimental and Predicted Values for Soil Potassium (Cmol/kg) over Time

Time/Day	Experimental Data (ED)	Predicted Value (PV)	Percentage Difference $PD = \left\| \frac{PV - ED}{PV} * 100 \right\|$
7	0.0209	0.0219	4.7
14	0.0219	0.0231	5.0
21	0.0226	0.0242	2.47
28	0.0239	0.0250	4.4
35	0.0259	0.0273	5.4

Table 4.32: Experimental and Predicted Values for Soil Organic Carbon (%) over Time

Time/Day	Experimental Data (ED)	Predicted Value (PV)	Percentage Difference $PD = \left\| \frac{PV - ED}{PV} * 100 \right\|$
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 4.33: Experimental and Predicted Values for Soil Organic Matter (%) over Time

Time/Day	Experimental Data (ED)	Predicted Value (PV)	Percentage Difference $PD = \left\| \frac{PV - ED}{PV} * 100 \right\|$
7	3.294	3.344	1.5
14	3.296	3.339	1.3
21	3.29	3.334	1.3
28	3.285	3.329	1.3
35	3.28	3.325	1.3

Table 4.34: Experimental and Predicted Values for Soil pH over Time

Time/Day	Experimental Data (ED)	Predicted Value (PV)	Percentage Difference $PD = \left\| \frac{PV - ED}{PV} * 100 \right\|$
7	7.15	7.262	1.5
14	7.147	7.219	1.0 (approx.)
21	7.135	7.175	0.5
28	7.119	7.133	0.19
35	7	7.09	1.3

4.2 DISCUSSION OF RESULTS

Oil is known to exert adverse effects on soil physico-chemical properties and plant community. Beyond 3% concentration, crude oil had been reported to be increasingly deleterious to soil biota and crop growth (Baker, 1976; Amadi et. al., 1993; Osuji et. al., 2005). Unfortunately available data to manage the ecological spoils of the Niger Delta Region have been found inadequate. Though these data have found various uses in the post-spill management programme of affected ecosystem and communities, recent advances have shown that such data have been specific to particular sites and incidents, largely because of the nature of the crude oil contaminant and possible environmental modifications (Osuji et. al., 2006).

Consequently, contemporary works have been focused on the monitoring and management of site-specific areas. Seasonal records or time lag of hydrocarbon content for instance, shall enhance our ability to confirm the extent of pollution by comparing with data from vergin areas or regulatory bodies. In the present study, we have attempted to model major soil nutrient depletion in crude oil contaminated soil, a very important index of agricultural productivity.

4.2.1 Soil Nitrogen

Nitrogen content of the soil at various level of crude oil pollution varied with time of pollution (Fig. 4.1). In the 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 pollution. 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 litres (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 litre rate of pollution was an increase to 84 days and a second decrease up till 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 litres of crude oil pollution increased with time up till 84 days after pollution till 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, 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 litres 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 more than 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 deleterious effects of crude oil on soil organism. This deleterious 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 and time were 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 level, the nitrogen content of the soil was low and could hardly sustain crop production.

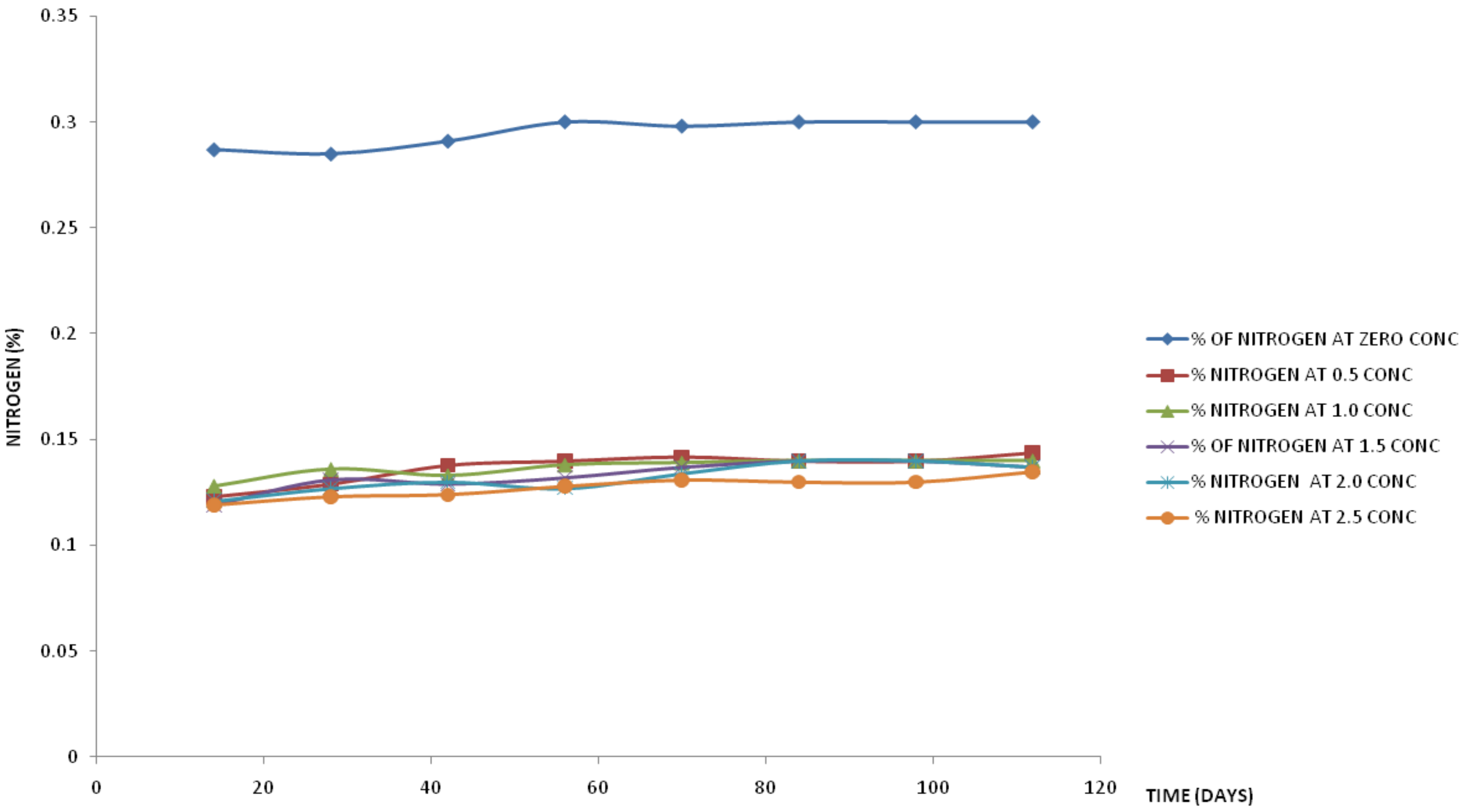


Fig. 4.1. Soil Nitrogen Content at various crude oil levels with Time

4.2.2 Soil Phosphorous

The phosphorous content of the soil duration at various level of crude oil pollution varied with time of pollution as shown in Fig. 4.2. For the control (sample), soil phosphorous decreased with time up till 28 days and later increased and was best at 96 days (37.5). The fluctuation in values also could be attributed to mineralization and immobilization processes in the soil. For 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. The trend for 1.0 and 1.5 litres pollution level (equivalent to 1258 and 187 barrels per hectare) respectively, the phosphorous value increased gradually and was best at 112 days (9.990). Similarly, the values of phosphorous content for 2.0 and 2.5 litres of crude oil rates (equivalent to 2515 and 3144 barrels per hectare) increased with time after pollution and was best at 112 days with a value of 8.400ppm. Fluctuation in phosphorous content with time for various crude oil pollution levels could also be attributed to mineralization and immobilization processes in the soil environment, due to pollution.

Generally, the highest phosphorous content recorded for various crude oil pollution levels was obtained for the control sample (38.90) 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 (Enwezer 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 pollution.

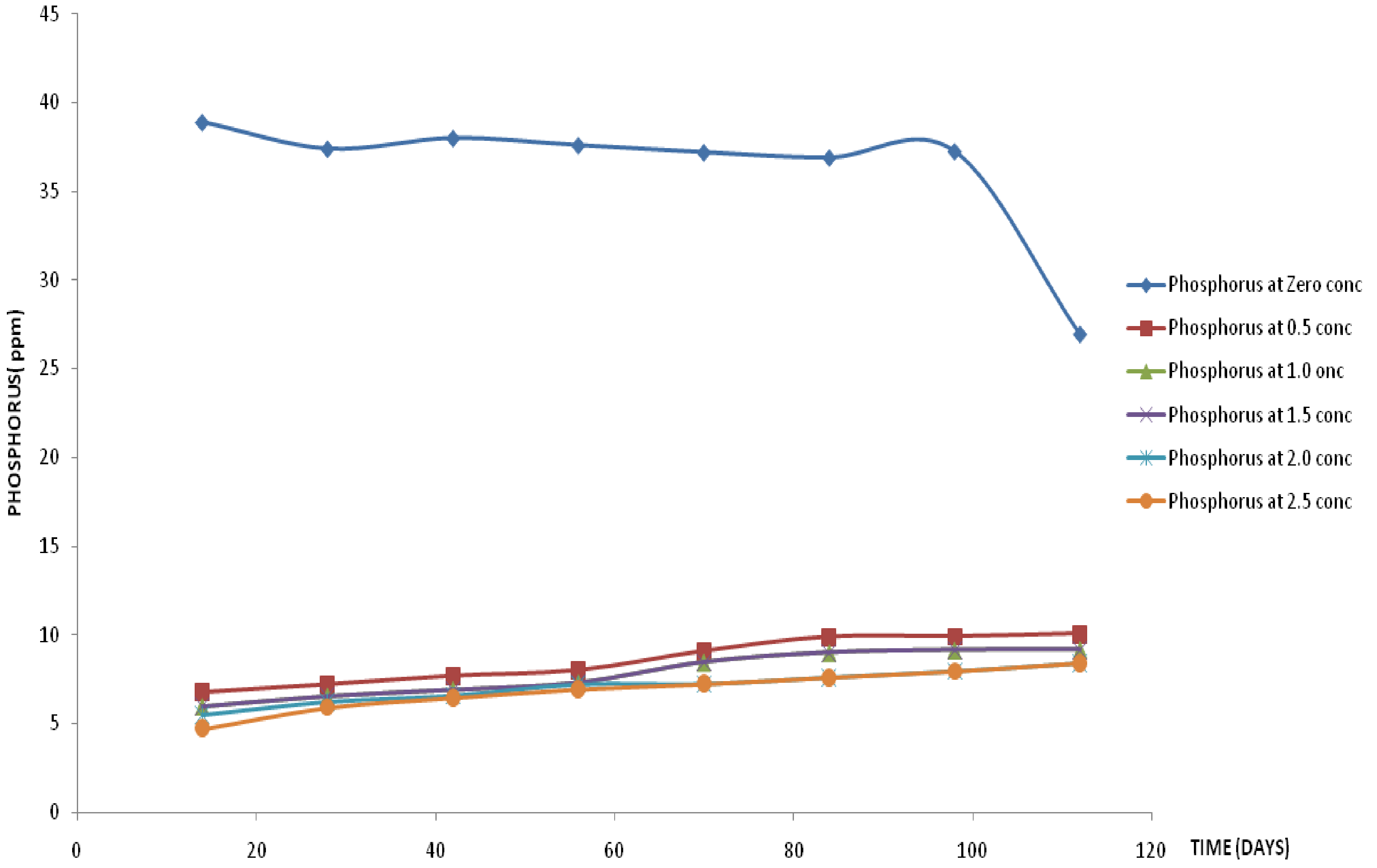


Fig.4.2. Soil Phosphorus content at various crude oil levels with Time

4.2.3 Soil Potassium

The variation of soil potassium content at various crude oil levels with time is presented in Fig. 4.3. In 14days, the potassium content reduced from 0.0570ppm to 0.0200ppm, after pollution of the soil sample. However, the potassium content at various levels of crude oil pollution increased with time being best at 84 days with a value of (0.030ppm). The highest potassium content at different periods was obtained for the control sample (0.0620ppm), while the least potassium value 0.018pm occurred for pollution rate of 2.5 litres/10kg (3144 barrels/hectare) of soil at 14 days.

On the average, the potassium content of the control sample was about 3 times higher than the values of potassium content for various levels of crude oil pollution ranging from 0.0043 – 0.0015ppm. This could be attributed to the depletion of potassium content in the soil as a result of increased hydrocarbon content. The potassium content at various levels of crude oil pollution were below the critical value (0.2cmol/kg) for tropical soils (White and Reddy, 1999; Isieimah et. al., 2003). This indicates high potassium deficiencies and low soil fertility for plant growth.

There was however, distinct difference between potassium content at various pollution levels of crude oil with time. Potassium is responsible for plants growing thick and round. It has an irreplaceable role in a number of functions in plant but only small amounts are required, relative to the much longer quantities needed to fulfill its role as an osmotic regular in all cells (Johnson et al, 2001).

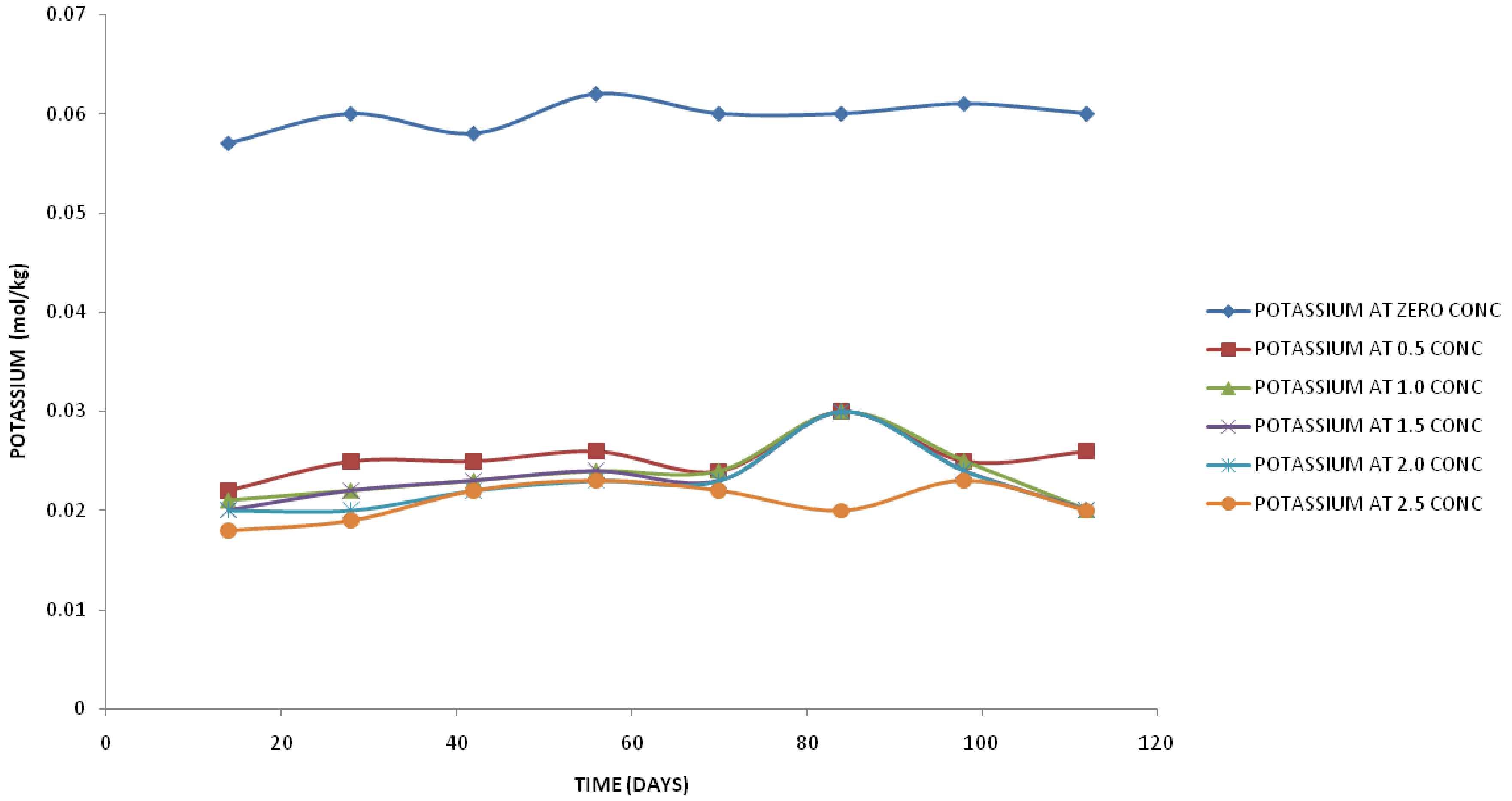


Fig. 4.3. Soil Potassium content at various crude oil levels with Time

4.2.4 Soil Organic Matter and Organic Carbon

Fig. 4.4 and Fig. 4.5 present soil organic carbon and soil organic matter contents at various levels of crude oil pollution with time. Total organic carbon and total organic matter contents were slightly higher than the 1.340% and 2.310% percent obtained for the control soils after the first 14 days of pollution respectively. Organic matter 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 organism 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 (Osuji et. al., 2006). From the study the values of total organic carbon content and that of organic matter, when averaged over a period of time were found to be about 2 times higher than the values obtained for control samples. There was also distinct differences between organic carbon and organic matter content at various crude oil levels with time. The values of organic matter content at various levels of crude oil pollution were slightly above the critical levels (1.5 – 2.0%) for tropical soil. This slight increase might be utilized by micro organism for their survival and not sufficient to be released for plant growth, thereby resulting to deficiencies of organic carbon and organic matter contents in the soil (Osuji et. al., 2006).

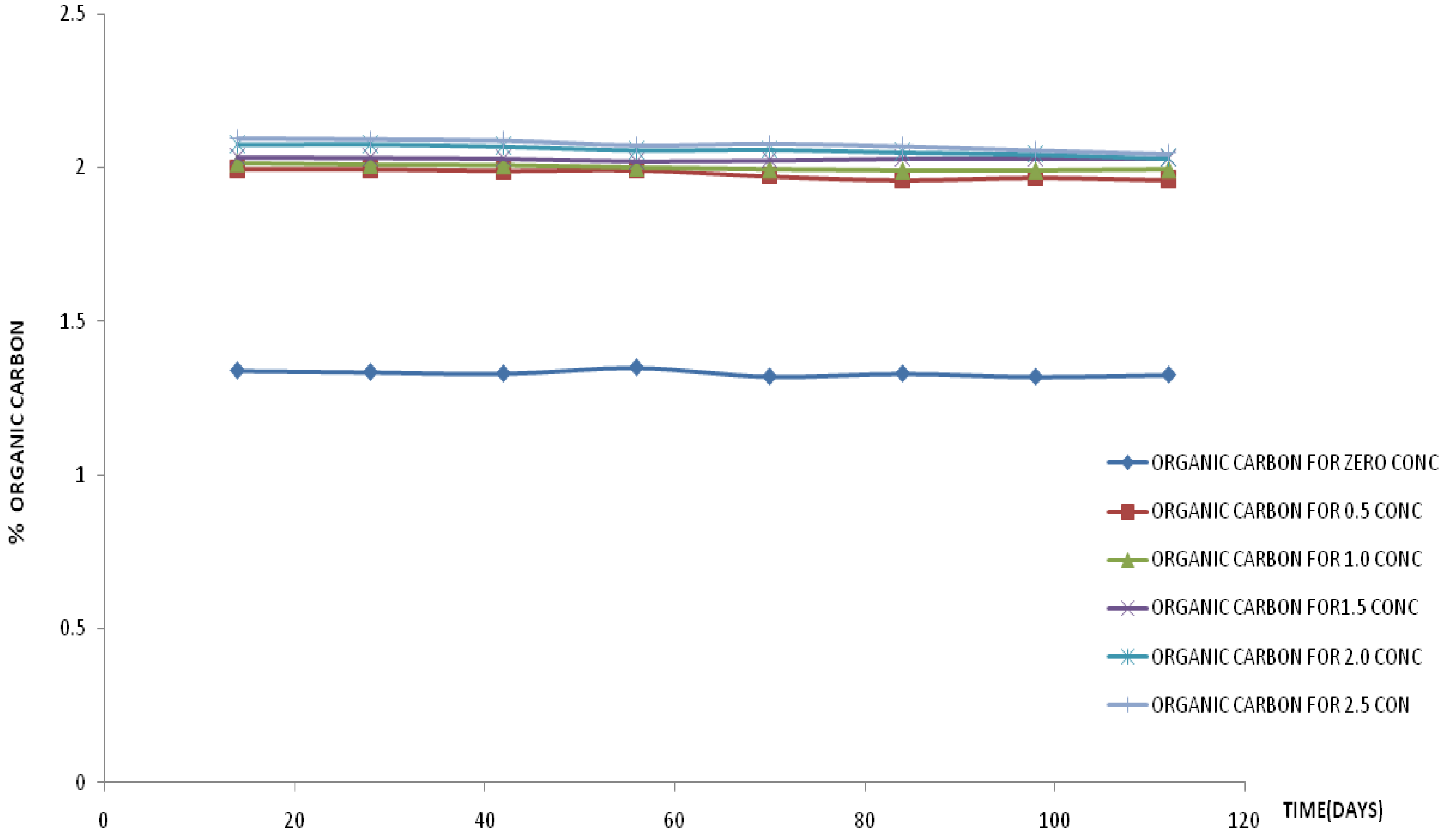


Fig. 4.4. Soil Organic Carbon at various crude oil levels with Time

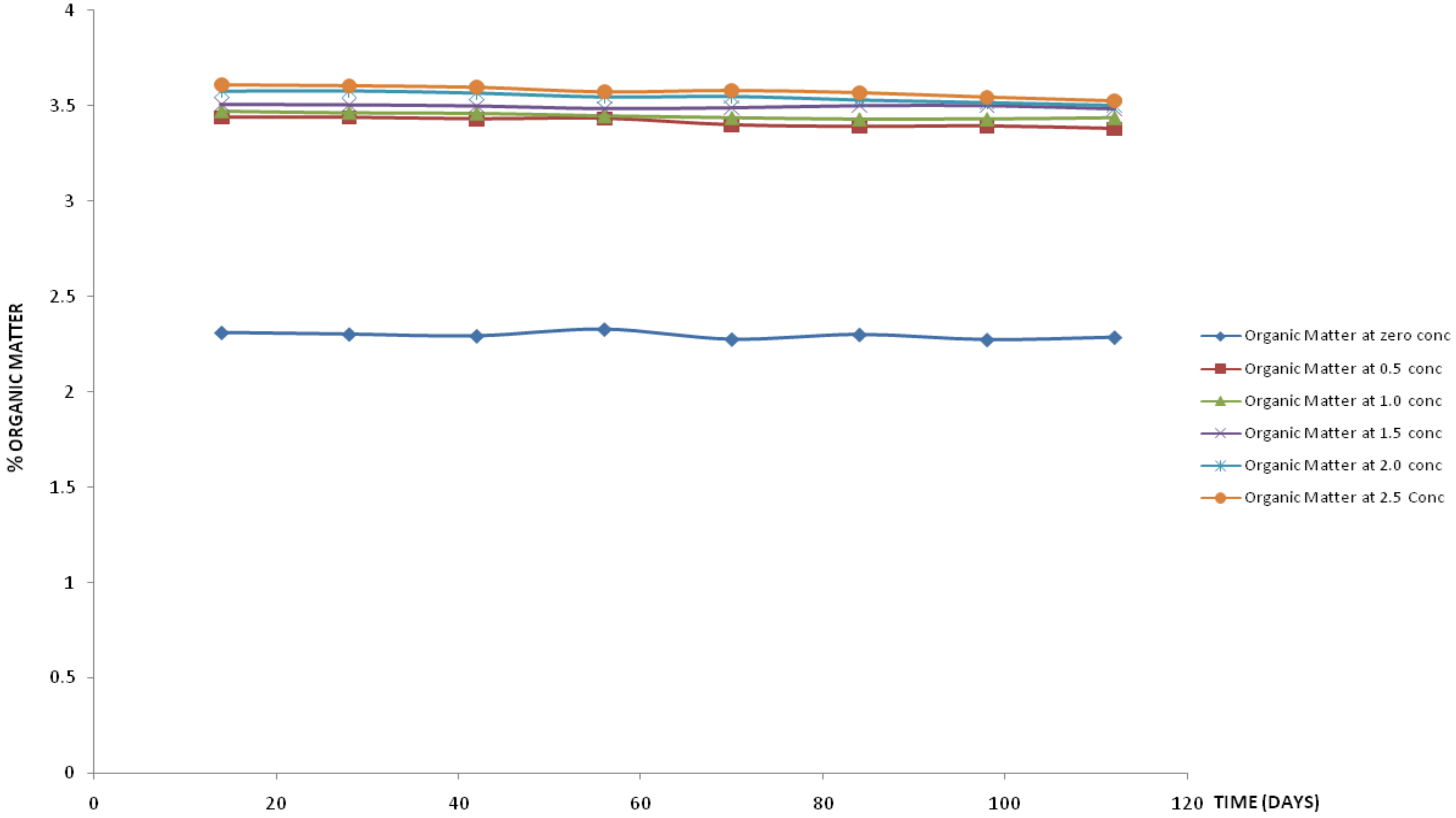


Fig. 4.5. Organic Matter at various crude oil levels with Time

4.2.5 Soil pH

Fig. 4.6 presents the soil-pH at various crude oil levels with time. The soil pH is not only essential for determining the availability of many soil nutrients, but also in determining the fate of many soil pollutants, their breakdown and possible movement through the soil. In other words pH measures the acidic and alkaline condition of soil and availability of micro and macronutrients to plants. The pH value increased slightly over a period of time being lowest at 56 days after pollution for 0.5l pollution level. The increase in pH value was attributed to the alkalinity of soil as a result of the carbonaceous substances in the crude oil.

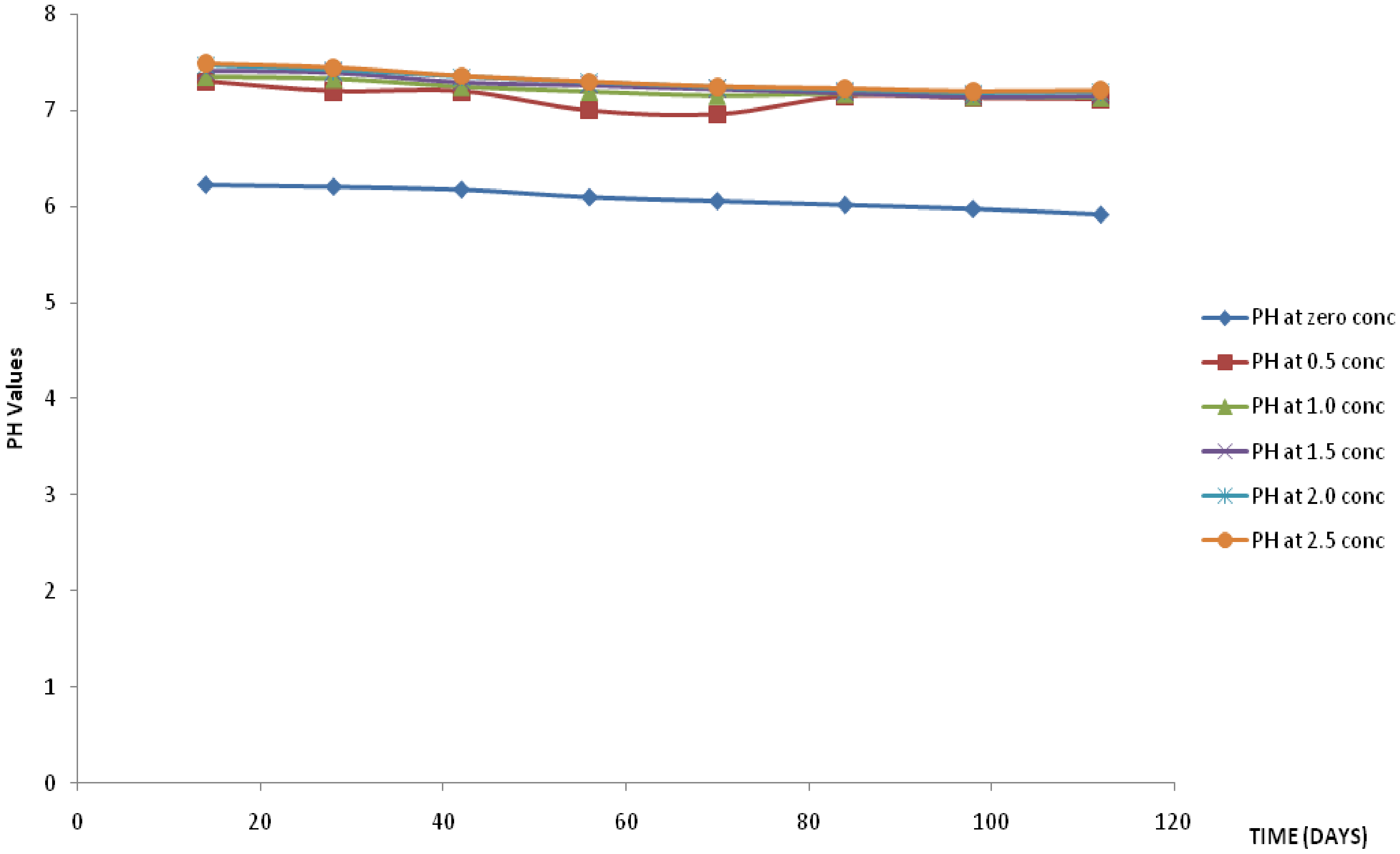


Fig. 4.6. Soil PH at various crude oil levels with Time

4.2.6 Panel Data Regression Model Results

Tables 4.11 and 4.12 presents, the panel data regression model results for Nitrogen and phosphorous. The R^2 value for Nitrogen stands as 0.9824 and the mean square error is 0.6255. The computer generated coefficients for the Nitrogen as a parameter is stated in model results. The coefficients stands for the crude oil volume in litres, time in days and the constant. However, the coefficients were utilized in the formulation of the model equations. The R^2 also for phosphorous is 0.9321 and the mean standard error stand as 0.15309. This is an indication that prediction tool is in order. The model equations were shown in Equations 4.2 and 4.3. Tables 4.13 and 4.14 presents also the panel data regression model results for potassium and organic carbon. The R^2 for both are 0.9540 and 0.9807 respectively. The model equations for the potassium and that of organic carbon are shown in Equations 4.4 and 4.5.

Similarly, Tables 4.15 and 4.16 presents the panel data regression mode results for organic matter and soil pH, with R^2 of 0.9734 and 0.9830 respectively. From the Tables, the value of the mean standard error for organic matter and soil pH were 0.01046 and 0.0387. The model equations for the organic matter and soil pH are expressed in equations 4.6 and 4.7 respectively.

4.2.7 Total Petroleum Hydrocarbon Concentration

Total Petroleum Hydrocarbon Concentration with time for various crude oil pollution levels is presented in Fig. 4.7. In the control sample, the concentration was at very low level as shown in Fig. 4.7. However, as soon as the pollution rates increased, the concentration values began to increase from 5520 to 3264 mg/kg for crude oil pollution levels of 0.5 and 2.5 litres, respectively at 14 days after pollution.

At 112 days after pollution, the concentration of total petroleum hydrocarbon concentration in the polluted soils, decrease from 5520 to 2450 mg/kg at the pollution level of 0.5 litres and 3264 to 25660 mg/kg at the 2.5 litres respectively. It is important to note that, as total petroleum hydrocarbon concentration continue to decrease with time, the major soil nutrients like nitrogen continue to increase with time. This was shown in Fig. 4.19 for crude oil pollution level of 2.5 litre. However, organic carbon and organic matter content of the polluted soil decreases as the total petroleum hydrocarbon concentrations decreases.

Table 4.11 Panel Data Regression Model Results for soil Nitrogen

NITROGEN (N)

Time (days)	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

MODEL RESULTS

source	ss	df	Ms	Number of Obs = 48 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

NOTE: E -06 Means, X10 $^{-6}$ **WHERE, X IS ORDINARY MULTIPLICATION**

Table 4.12 Panel Data Regression Model Results for soil Phosphorus

PHOSPHORUS (P)

Time (days)	0	0.5	1	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

MODEL RESULTS

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

P	Coef	Std Err	t	P > |t|	95% Conf.	Interval
Conc	19.71109	1.403061	14.05	0	16.88155	22.54063
time	0.068644	0.050821	1.35	0.184	-0.03385	0.1711335
time^2	-0.000415	0.000394	-1.05	0.299	-0.00121	0.0003801
conc$^{1/2}$	-48.46306	2.288342	-21.18	0	-53.0779	-43.84818
_cons	30.1	1.599236	20.92	0	30.23616	36.68649

NOTE: E -06 Means, X10 $^{-6}$ **WHERE, X IS ORDINARY MULTIPLICATION**

Table 4.13 Panel Data Regression Model Results for soil Potassium

POTASSIUM (K)

Time (days)	0	0.5	1	1.5	2	2.5
14	0.0570	0.026	0.019	0.018	0.018	0.019
28	0.0600	0.0278	0.022	0.020	0.020	0.021
42	0.0580	0.03	0.023	0.022	0.022	0.023
56	0.0620	0.031	0.024	0.024	0.023	0.023
70	0.0600	0.0302	0.024	0.023	0.023	0.024
84	0.0600	0.03	0.025	0.023	0.023	0.025
98	0.0610	0.0301	0.024	0.022	0.023	0.023
112	0.0600	0.0289	0.023	0.020	0.020	0.023

MODEL RESULTS.

source	ss	df	Ms	Number of Obs = 48 F(4, 43) = 222.76
Model	0.008942	4	0.02235	Prob > F = 0.0000
Residual	0.003518	43	8.18E-06	R- Squared = 0.9540
Total	0.009293	47	0.0002	Adj R-Squared = 0.9497
				Root MSE = 0.00286

K	Coef	Std Err	t	P > |t|	95% Conf.	Interval
Conc	0.023563	0.001638	14.38	0	0.02026	0.0268664
time	0.000214	5.93E-05	3.61	0.001	9.44E-05	0.0003337
$time^2$	-1.47E-06	4.60E-07	-3.2	0.003	-2.40E-06	-5.46E-07
$conc^{1/2}$	-0.059987	0.002672	-22.45	0	-0.06538	-0.0546
_cons	0.048	0.001867	28.36	0	0.049186	0.567171

NOTE: E -06 Means, X10 $^{-6}$ **WHERE, X IS ORDINARY MULTIPLICATION**

Table 4.14 Panel Data Regression Model Results for soil Organic Carbon

ORGANIC CARBON (OC)

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	1.960	1.990	2.030	2.050	2.070
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

MODEL RESULTS

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	**-0.427626**	0.022206	-19.26	0	-0.47241	-0.382844
time	-0.00036	0.000803	-0.45	0.657	-0.00198	0.0012625
time^2	3.34E-07	6.23E-06	0.05	0.957	-1.2E-05	0.0000129
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

NOTE: E -06 Means, X10 $^{-6}$ **WHERE, X IS ORDINARY MULTIPLICATION**

Table 4.15 Panel Data Regression Model Results for soil Organic Matter

ORGANIC MATTER (OM)

Time (days)	0	0.5	1	1.5	2	2.5
14	2.310	3.439	3.4740	3.508	3.577	3.612
28	2.302	3.439	3.4650	3.505	3.579	3.607
42	2.293	3.431	3.4620	3.499	3.567	3.599
56	2.327	3.434	3.4480	3.484	3.546	3.574
70	2.276	3.399	3.4380	3.489	3.549	3.582
84	2.300	3.390	3.4300	3.500	3.530	3.570
98	2.274	3.393	3.4310	3.501	3.516	3.546
112	2.286	3.379	3.4380	3.483	3.501	3.526

MODEL RESULTS

Number of Obs = 48

F(4, 43) = 393.52

source	ss	df	Ms	Prob > F = 0.0000
Model	9.572077	4	2.39302	R- Squared = 0.9734
Residual	0.194609	43.000	0.00453	Adj R-Squared = 0.9709
Total	9.766686	47	0.2078	Root MSE = 0.01046

OM	Coef	Std Err	t	P > |t|	95% Conf.	Interval
Conc	-0.729008	0.038524	-18.92	0	-0.8067	-0.651317
time	-0.000441	0.001395	-0.32	0.754	-0.00325	0.0023735
$time^2$	-7.70E-07	1.08E-05	-0.07	0.943	-2.3E-05	0.000021
$conc^{1/2}$	1.912686	0.062832	30.44	0	1.785974	2.039398
_cons	2.349435	0.043911	53.5	0	2.260881	2.43799

NOTE: E -06 Means, X10 $^{-6}$ **WHERE, X IS ORDINARY MULTIPLICATION**

Table 4.16 Panel Data Regression Model Results for soil pH

PH

Time (days)	0	0.5	1	1.5	2	2.5
14	6.230	7.300	7.350	7.420	7.470	7.490
28	6.210	7.200	7.330	7.400	7.420	7.450
42	6.180	7.200	7.250	7.300	7.350	7.360
56	6.100	7.000	7.200	7.270	7.290	7.300
70	6.060	6.960	7.160	7.230	7.240	7.250
84	6.020	7.150	7.180	7.190	7.210	7.230
98	5.980	7.130	7.150	7.160	7.180	7.200
112	5.920	7.120	7.140	7.160	7.190	7.210

MODEL RESULTS

source	**ss**	**df**	**Ms**	Number of Obs = 48 F(4, 43) = 620.95 Prob > F = 0.0000
Model	9.393115	4	2.34828	R- Squared = 0.9830
Residual	**0.16261645**	43.000	**0.0037818**	Adj R-Squared = 0.9814
Total	**9.55573099**	47	**0.2033134**	Root MSE = 0.615

OM	**Coef**	**Std Err**	**t**	**P > |t|**	**95% Conf.**	**Interval**
Conc	**-0.7080021**	**0.0352156**	**-20.1**	0	**-0.779021**	**-0.6369832**
time	**-0.0062861**	**0.0012756**	**-4.93**	0	**-0.0088585**	**-0.0037137**
$time^2$	2.86E-05	**9.88E-06**	**2.89**	**0.006**	**8.67E-06**	**0.0000485**
$conc^{1/2}$	1.857124	**0.0574353**	**32.33**	0	**1.741294**	**1.972953**
_cons	6.355381	**0.0401394**	**158.33**	0	**6.274432**	**6.43633**

NOTE: E -06 Means, X10 $^{-6}$ **WHERE, X IS ORDINARY MULTIPLICATION**

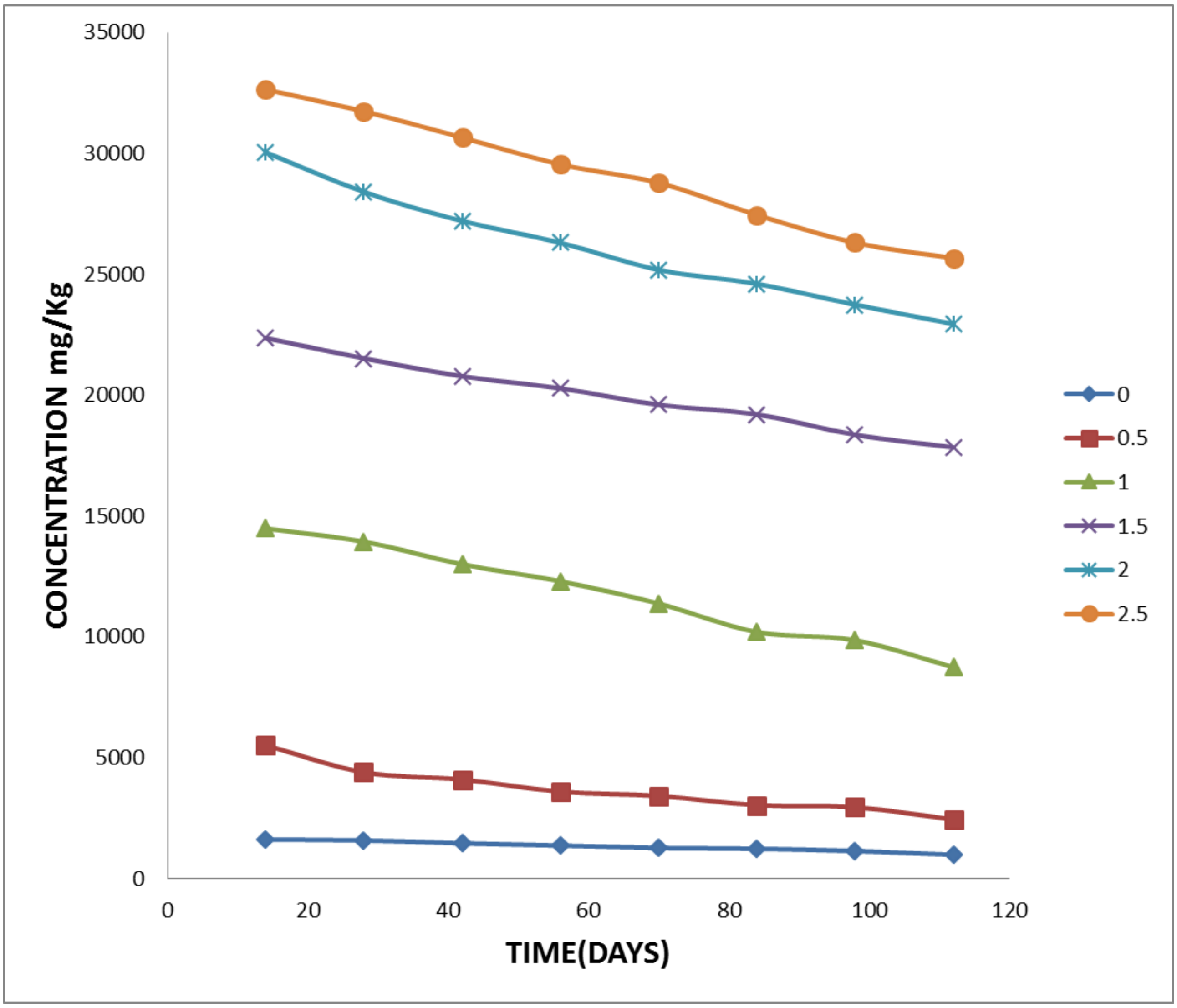


Figure 4.7: Total Petroleum Hydrocarbon concentration against time

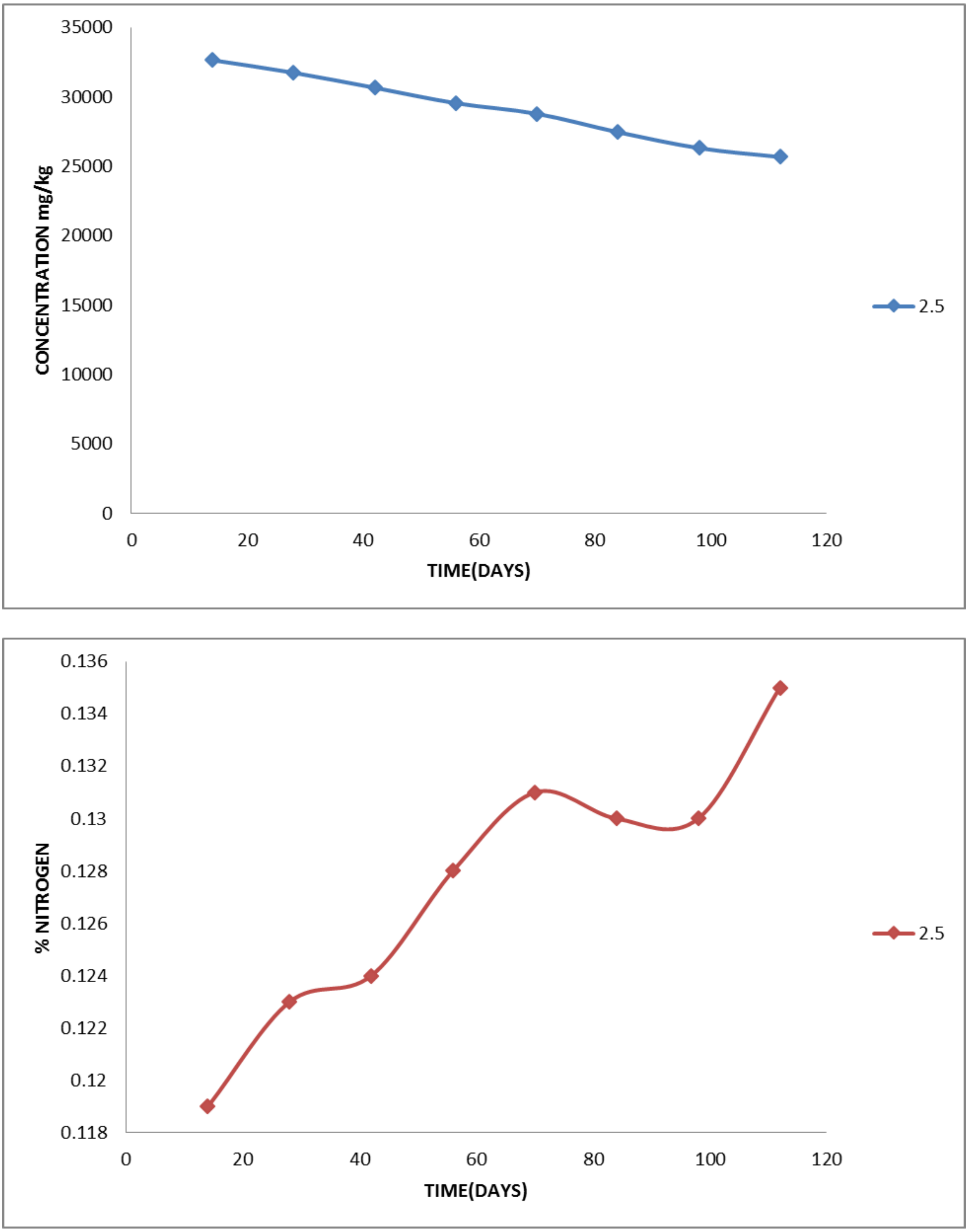


Figure 4.19: Total petroleum hydrocarbon concentration against nitrogen content over time.

4.3 APPLICATION OF MODEL TO FIELD AND BIOREMEDIATION

In 2012, precisely on 18th of October 2012, there was an oil spill in the range of 1000 barrel on a cassava farmland about one hectare in size, in Abacheke Community Ohaji/Egbema Local Government of Imo State. After one month, soil sample from the spill site was collected to determine the impact of crude oil on the physico-chemical properties of the soil in the laboratory. The result of that study is shwon in Appendix C. Now, using this as a case study, the mathematical model equations developed for the various major soil nutrient parameters, can be used to determine the values of Nitrogen, Phosphorous, Potassium, etc. in the affected site. In line with this, the percentage (%) nitrogen content in crude oil impacted site of 1000 barrels of crude oil spill, on one hectare of land, after 30days of oil spill can be deduced as follows:

One (1) barrels of crude oil = 159 litres

2,000,000kg of soil (furrow slice) = 1 hactare

Note,

1000 barrels = 159,000 litres of crude

2,000,000kg of soil = 159000 litres

$\therefore$ 10kg of soil = $\frac{159000}{2000000} \times 10$

= 0.795 litres of crude.

For $C_{V_{it}}$ = 0.795 litres and T = 30days, the equation developed for Nitrogen can be utilized.

$$N = 0.1927 + 0.1124 C_{V_{it}} + 0.0004T_{it} - 2.01e T_{it}^2 - 0.2754 \sqrt{C_{V_{it}}} + 0.0655$$

$$= 0.1927 + 0.1124 \times 0.795 + 0.0004 \times 30 - 2.01 \times 10^{-6} \times 30 \times 30 - 0.2754 \sqrt{0.795} + 0.0655$$

$$N = 0.1927 + 0.089 + 0.012 - 0.0018 - 0.245 + 0.0655$$

$$N = 0.112\%$$

This value (0.112%) below the critical level of (0.15%) for tropical soils, hence the soil is deficient of Nitrogen content and needs bioremediation works to improve the nitrogen content of the soil for crop production.

Similarly, the values of phosphorous, potassium, organic carbon, organic matter and pH contents can be computed using the various equations developed for each of the parameters.

For $C_{v_{it}} = 0.795$ litre; T = 30days

(ii) Phosphorous (P)

$$P = 30.100 + 19.71 C_{V_{it}} + 0.0686T_{it} - 0.0004 T_{it}^2 - 48.46 \sqrt{C_{V_{it}}} + 0.15309$$

$$= 30.100 + 15.66 + 2.058 - 0.36 - 43.20 + 0.15309$$

P = 4.41(ppm)

(iii) Potassium (K)

$$K = 0.0480 + 0.0236 C_{V_{it}} + 0.0002T_{it} - 1.4e T_{it}^2 - 0.0599 \sqrt{C_{V_{it}}} + 0.0028$$

$$K = 0.0480 + 0.0236 \times 0.795 + 0.0002 \times 30 - 1.4 \times 10^{-6} \times 30 \times 30 - 0.0599 \sqrt{0.795} + 0.0028$$

$$= 0.0480 + 0.018 + 0.006 - 0.00126 - 0.053 + 0.0028$$

K = 0.020(cmol/kg)

(iv) Organic Carbon (OC)

$$OC = 1.310 - 0.4276 C_{V_{it}} - 0.0004T_{it} + 3.34e T_{it}^2 + 1.1214 \sqrt{C_{V_{it}}} + 0.1043$$

$$= 1.310 + 0.4276 \times 0.795 - 0.0004 \times 30 + 3.34 \times 10^{-6} \times 30 \times 30 + 1.1214 \sqrt{0.795} + 0.1043$$

$$= 1.310 + 0.339 - 0.012 + 0.003 + 0.999 + 0.1043$$

OC = 2.74%

(v) Organic Matter (OM)

$$OM = 2.349 + 0.729\, C_{V_{it}} + 0.00044T_{it} - 7.70e\, T_{it}^{2} - 1.913\sqrt{C_{V_{it}}} + 0.0105$$

$$= 2.349 - 0.729 \times 0.795 - 0.00044 \times 30 - 7.7 \times 10^{-6} \times 30 \times 30 + 1.913\sqrt{0.795}$$

$$+ 0.0105$$

$$OM = 2.349 - 0.579 - 0.013 - 0.0069 + 1.705 + 0.0105$$

$$OM = 3.479\%$$

(vi) Soil pH (pH)

$$pH = 6.310 - 0.7080\, C_{V_{it}} + 0.0063T_{it} - 2.86e\, T_{it}^{2} - 1.857\sqrt{C_{V_{it}}} + 0.0387$$

$$pH = 6.310 - 0.7080 \times 0.795 - 0.0063 \times 30 + 2.86 \times 10^{-6} \times 30 \times 30 + 1.857\ \sqrt{0.795}$$

$$+ 0.0387$$

$$pH = 6.310 - 0.562 - 0.189 + 0.0025 + 1.655 + 0.0387$$

$$pH = 7.25$$

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

(i) The impact of crude oil pollution on the physico-chemical properties of soil in relation to soil fertility in the Niger Delta region of Nigeria has been reviewed. Modeling of major soil nutrients depletion in crude oil contaminated soil over a period of time was carried out. The major soil nutrients considered in this study were Nitrogen (N), Phosphorous (P), Potassium (K), Organic Matter (OM) and Organic Carbon (OC) and soil pH.

(ii) Nitrogen content of the polluted soil sample depleted from 0.287 to 0.123 percent within the first fourteen (14) days of observation. However, the nitrogen content at various levels of crude oil pollution increased with time and was highest at 112 days (0.144). The highest nitrogen content at different periods was distained with the control sample (0.300%) while the least was at the highest pollution rate of 2.5 litres/10kg at 98 days (0.130%), equivalent to 3144 barrels per hectare. On the average for 112 days, the nitrogen content of the control sample was about three (3) times higher than the values of nitrogen content at various levels of crude oil pollution. Nevertheless, total nitrogen content at various levels of crude oil pollution were below 0.15%, the critical value for tropical soils indicating high nitrogen deficiencies.

Similarly, phosphorous content showed a sign of decline from 38.9 (control) to 6.75 parts per million (ppm) (at 0.5 litre pollution) within the first 14 days. The phosphorous content at various crude oil levels increased with time being highest at 84 days (8.787). On the average the phosphorous content of the control sample was about five (5) times higher than the values of phosphorous content at various levels of crude oil pollution. In other words, phosphorous content was depleted by five (5) times when compared with the control sample. With the exception of the control sample and that of 0.5 litres pollution level, the values of phosphorous contents in the study fell below 8 – 12mg/kg critical range for tropical soils. Potassium in a similar way depleted about three (3) times when compared with the control sample when averaged over a periods of time. However, organic matter and organic carbon contents slightly increased over time.

(iii) The mathematical models/equations developed for predicting major soil nutrients depletion are all suitable for determining the various contents of Nitrogen, Phosphorous, Potassium, Organic Matter and Organic Carbon in a crude oil polluted site. The model values of major soil nutrients obtained from the various model equations were very close to experimental values, especially at 14 – 84 days, with percentage differences ranging from 0 to 0.07. The model equations were calibrated using the experimental data and the values obtained for various major soil nutrients where close to that of laboratory values.

(iv) A computer program was developed using STATA 13 version for easy computation of major soil nutrients parameters due to crude oil pollution.

5.2 RECOMMENDATIONS

The following recommendations are hereby proffered on the basis of the findings from this study.

(ii) The oil companies should stop flouting environmental regulations in their areas of operations and pay more attention to environmental protection regimes that would help to abate oil spill. The Government on its part should show commitment in enforcing the minimal environmental laws and regulations designed to control pollution.

(i) Research is required to determine the impact of crude oil spill on the minor soil nutrients like calcium, magnesium, sulphur, sodium, zinc, iron, total exchangeable acids, moisture content and electrical conductivity to ascertain the level of depletion as a result of crude oil contamination for various soil types and not only for similar soil characteristics of the Niger Delta Region.

(iii) Efforts should be made in the utilization of results obtained from both modeling of major soil nutrients depletion and that of minor soil nutrients depletions in carrying out bioremediation of crude oil impacted sites in the Niger Delta Region of Nigeria and other soil types.

5.3 CONTRIBUTIONS TO KNOWLEDGE

(i) The formulated mathematical models can with the aid of a computer, predict the depletion of major soil nutrients in crude contaminated soils over time.

(ii) The models so developed can be applied in field and Bioremediation operations in the Niger Delta region of Nigeria.

(iii) This work has not only confirmed previous work on the impact of crude oil spill on agricultural lands, but has also provided insight knowledge on the use of Panel data Regression model in the analysis of physico-chemical properties of soils polluted with crude oil over time.

(iv) This work will help in making credible decision on the cut-off between what really constitutes a poisonous dose and a no-effect dose or tolerable dose, which is important in the design of environmental programme.

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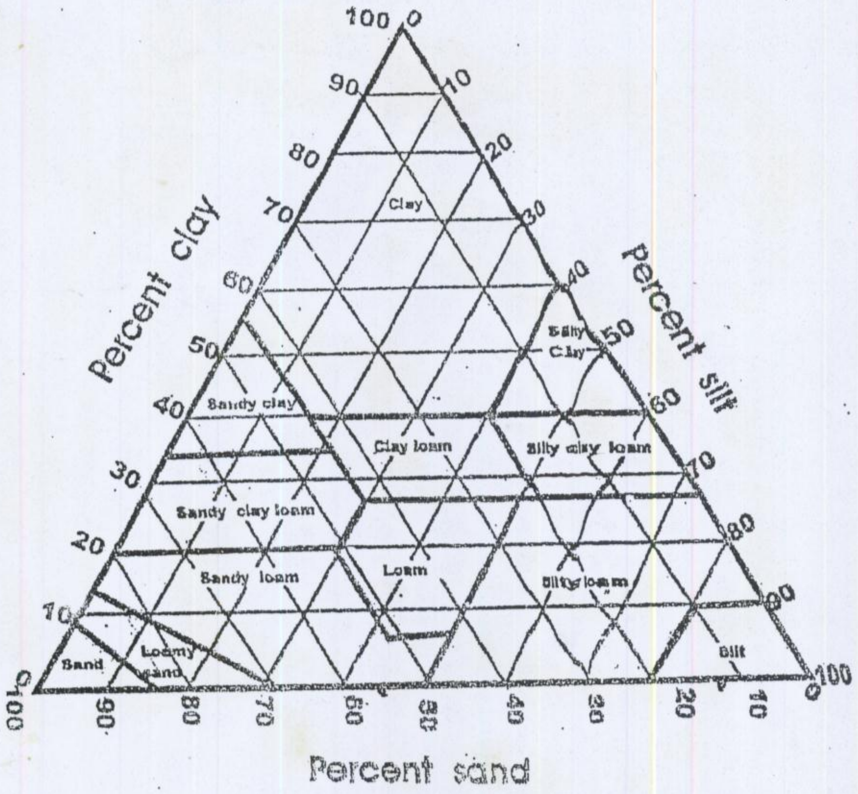
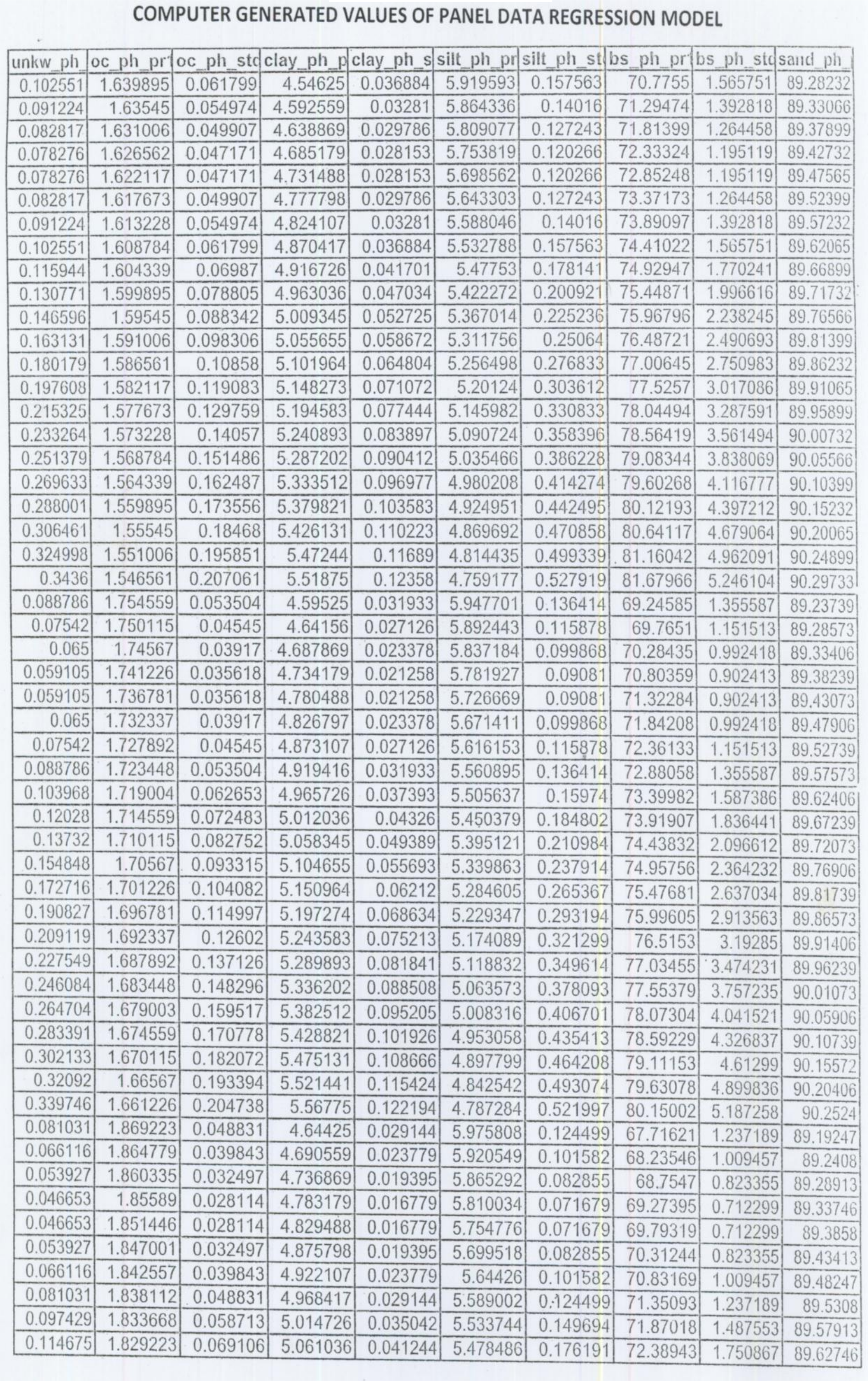
APPENDICES

APPENDIX A



SOIL TEXTURAL TRIANGLE (USDA)

APPENDIX B



COMPUTER GENERATED VALUES OF PANEL DATA REGRESSION MODEL

unkw_ph_	oc_ph_pr	oc_ph_st	clay_ph_p	clay_ph_s	silt_ph_pr	silt_ph_st	bs_ph_pr	bs_ph_st	sand_ph_
0.102551	1.639895	0.061799	4.54625	0.036884	5.919593	0.157563	70.7755	1.565751	89.28232
0.091224	1.63545	0.054974	4.592559	0.03281	5.864336	0.14016	71.29474	1.392818	89.33066
0.082817	1.631006	0.049907	4.638869	0.029786	5.809077	0.127243	71.81399	1.264458	89.37899
0.078276	1.626562	0.047171	4.685179	0.028153	5.753819	0.120266	72.33324	1.195119	89.42732
0.078276	1.622117	0.047171	4.731488	0.028153	5.698562	0.120266	72.85248	1.195119	89.47565
0.082817	1.617673	0.049907	4.777798	0.029786	5.643303	0.127243	73.37173	1.264458	89.52399
0.091224	1.613228	0.054974	4.824107	0.03281	5.588046	0.14016	73.89097	1.392818	89.57232
0.102551	1.608784	0.061799	4.870417	0.036884	5.532788	0.157563	74.41022	1.565751	89.62065
0.115944	1.604339	0.06987	4.916726	0.041701	5.47753	0.178141	74.92947	1.770241	89.66899
0.130771	1.599895	0.078805	4.963036	0.047034	5.422272	0.200921	75.44871	1.996616	89.71732
0.146596	1.59545	0.088342	5.009345	0.052725	5.367014	0.225236	75.96796	2.238245	89.76566
0.163131	1.591006	0.098306	5.055655	0.058672	5.311756	0.25064	76.48721	2.490693	89.81399
0.180179	1.586561	0.10858	5.101964	0.064804	5.256498	0.276833	77.00645	2.750983	89.86232
0.197608	1.582117	0.119083	5.148273	0.071072	5.20124	0.303612	77.5257	3.017086	89.91065
0.215325	1.577673	0.129759	5.194583	0.077444	5.145982	0.330833	78.04494	3.287591	89.95899
0.233264	1.573228	0.14057	5.240893	0.083897	5.090724	0.358396	78.56419	3.561494	90.00732
0.251379	1.568784	0.151486	5.287202	0.090412	5.035466	0.386228	79.08344	3.838069	90.05566
0.269633	1.564339	0.162487	5.333512	0.096977	4.980208	0.414274	79.60268	4.116777	90.10399
0.288001	1.559895	0.173556	5.379821	0.103583	4.924951	0.442495	80.12193	4.397212	90.15232
0.306461	1.55545	0.18468	5.426131	0.110223	4.869692	0.470858	80.64117	4.679064	90.20065
0.324998	1.551006	0.195851	5.47244	0.11689	4.814435	0.499339	81.16042	4.962091	90.24899
0.3436	1.546561	0.207061	5.51875	0.12358	4.759177	0.527919	81.67966	5.246104	90.29733
0.088786	1.754559	0.053504	4.59525	0.031933	5.947701	0.136414	69.24585	1.355587	89.23739
0.07542	1.750115	0.04545	4.64156	0.027126	5.892443	0.115878	69.7651	1.151513	89.28573
0.065	1.74567	0.03917	4.687869	0.023378	5.837184	0.099868	70.28435	0.992418	89.33406
0.059105	1.741226	0.035618	4.734179	0.021258	5.781927	0.09081	70.80359	0.902413	89.38239
0.059105	1.736781	0.035618	4.780488	0.021258	5.726669	0.09081	71.32284	0.902413	89.43073
0.065	1.732337	0.03917	4.826797	0.023378	5.671411	0.099868	71.84208	0.992418	89.47906
0.07542	1.727892	0.04545	4.873107	0.027126	5.616153	0.115878	72.36133	1.151513	89.52739
0.088786	1.723448	0.053504	4.919416	0.031933	5.560895	0.136414	72.88058	1.355587	89.57573
0.103968	1.719004	0.062653	4.965726	0.037393	5.505637	0.15974	73.39982	1.587386	89.62406
0.12028	1.714559	0.072483	5.012036	0.04326	5.450379	0.184802	73.91907	1.836441	89.67239
0.13732	1.710115	0.082752	5.058345	0.049389	5.395121	0.210984	74.43832	2.096612	89.72073
0.154848	1.70567	0.093315	5.104655	0.055693	5.339863	0.237914	74.95756	2.364232	89.76906
0.172716	1.701226	0.104082	5.150964	0.06212	5.284605	0.265367	75.47681	2.637034	89.81739
0.190827	1.696781	0.114997	5.197274	0.068634	5.229347	0.293194	75.99605	2.913563	89.86573
0.209119	1.692337	0.12602	5.243583	0.075213	5.174089	0.321299	76.5153	3.19285	89.91406
0.227549	1.687892	0.137126	5.289893	0.081841	5.118832	0.349614	77.03455	3.474231	89.96239
0.246084	1.683448	0.148296	5.336202	0.088508	5.063573	0.378093	77.55379	3.757235	90.01073
0.264704	1.679003	0.159517	5.382512	0.095205	5.008316	0.406701	78.07304	4.041521	90.05906
0.283391	1.674559	0.170778	5.428821	0.101926	4.953058	0.435413	78.59229	4.326837	90.10739
0.302133	1.670115	0.182072	5.475131	0.108666	4.897799	0.464208	79.11153	4.61299	90.15572
0.32092	1.66567	0.193394	5.521441	0.115424	4.842542	0.493074	79.63078	4.899836	90.20406
0.339746	1.661226	0.204738	5.56775	0.122194	4.787284	0.521997	80.15002	5.187258	90.2524
0.081031	1.869223	0.048831	4.64425	0.029144	5.975808	0.124499	67.71621	1.237189	89.19247
0.066116	1.864779	0.039843	4.690559	0.023779	5.920549	0.101582	68.23546	1.009457	89.2408
0.053927	1.860335	0.032497	4.736869	0.019395	5.865292	0.082855	68.7547	0.823355	89.28913
0.046653	1.85589	0.028114	4.783179	0.016779	5.810034	0.071679	69.27395	0.712299	89.33746
0.046653	1.851446	0.028114	4.829488	0.016779	5.754776	0.071679	69.79319	0.712299	89.3858
0.053927	1.847001	0.032497	4.875798	0.019395	5.699518	0.082855	70.31244	0.823355	89.43413
0.066116	1.842557	0.039843	4.922107	0.023779	5.64426	0.101582	70.83169	1.009457	89.48247
0.081031	1.838112	0.048831	4.968417	0.029144	5.589002	0.124499	71.35093	1.237189	89.5308
0.097429	1.833668	0.058713	5.014726	0.035042	5.533744	0.149694	71.87018	1.487553	89.57913
0.114675	1.829223	0.069106	5.061036	0.041244	5.478486	0.176191	72.38943	1.750867	89.62746

sand_ph_	tea_ph_pr	tea_ph_st	ecec_ph_	ecec_ph_	na_ph_pr	na_ph_std	al_ph_pr1	al_ph_std	mg_ph
0.102124	0.857768	0.016921	3.36983	0.240678	0.03197	0.002383	0.590863	0.012935	0.6046
0.090844	0.84378	0.015052	3.327884	0.214096	0.032828	0.00212	0.594613	0.011506	0.6074
0.082472	0.829792	0.013665	3.285938	0.194365	0.033685	0.001924	0.598363	0.010446	0.6102
0.07795	0.815804	0.012915	3.243991	0.183707	0.034543	0.001819	0.602113	0.009873	0.6130
0.07795	0.801815	0.012915	3.202045	0.183707	0.0354	0.001819	0.605863	0.009873	0.6158
0.082472	0.787827	0.013665	3.160098	0.194365	0.036258	0.001924	0.609613	0.010446	0.6187
0.090844	0.773839	0.015052	3.118152	0.214096	0.037115	0.00212	0.613363	0.011506	0.6215
0.102124	0.759851	0.016921	3.076205	0.240678	0.037973	0.002383	0.617113	0.012935	0.6243
0.115461	0.745863	0.01913	3.034259	0.272111	0.03883	0.002694	0.620863	0.014624	0.627
0.130226	0.731875	0.021577	2.992312	0.306908	0.039688	0.003038	0.624613	0.016494	0.6299
0.145986	0.717887	0.024188	2.950366	0.34405	0.040545	0.003406	0.628363	0.01849	0.632
0.162452	0.703899	0.026916	2.90842	0.382855	0.041403	0.00379	0.632113	0.020575	0.6355
0.179429	0.689911	0.029729	2.866473	0.422865	0.042261	0.004186	0.635863	0.022726	0.6383
0.196785	0.675923	0.032605	2.824527	0.463769	0.043118	0.004591	0.639613	0.024924	0.641
0.214428	0.661934	0.035528	2.78258	0.505349	0.043976	0.005003	0.643363	0.027158	0.6440
0.232293	0.647946	0.038488	2.740634	0.547452	0.044833	0.00542	0.647113	0.029421	0.6468
0.250332	0.633958	0.041477	2.698688	0.589965	0.045691	0.005841	0.650863	0.031706	0.6496
0.26851	0.61997	0.044489	2.656741	0.632807	0.046548	0.006265	0.654613	0.034008	0.6524
0.286801	0.605982	0.047519	2.614795	0.675914	0.047406	0.006691	0.658363	0.036325	0.6552
0.305185	0.591994	0.050565	2.572848	0.719238	0.048263	0.00712	0.662113	0.038653	0.6580
0.323645	0.578006	0.053624	2.530902	0.762743	0.049121	0.007551	0.665863	0.040991	0.6609
0.342169	0.564018	0.056693	2.488955	0.8064	0.049978	0.007983	0.669613	0.043338	0.6637
0.088416	0.816161	0.014649	3.019948	0.208373	0.027866	0.002063	0.558685	0.011198	0.517
0.075106	0.802173	0.012444	2.978002	0.177004	0.028724	0.001752	0.562434	0.009513	0.5200
0.064729	0.788185	0.010725	2.936055	0.152549	0.029582	0.00151	0.566185	0.008198	0.5228
0.058858	0.774196	0.009752	2.894109	0.138714	0.030439	0.001373	0.569935	0.007455	0.5256
0.058858	0.760208	0.009752	2.852163	0.138714	0.031297	0.001373	0.573685	0.007455	0.5284
0.064729	0.74622	0.010725	2.810216	0.152549	0.032154	0.00151	0.577435	0.008198	0.531
0.075106	0.732232	0.012444	2.76827	0.177004	0.033012	0.001752	0.581185	0.009513	0.5340
0.088416	0.718244	0.014649	2.726323	0.208373	0.033869	0.002063	0.584935	0.011198	0.5368
0.103535	0.704256	0.017154	2.684377	0.244004	0.034727	0.002416	0.588684	0.013113	0.53
0.119779	0.690268	0.019846	2.64243	0.282287	0.035584	0.002795	0.592435	0.015171	0.5425
0.136748	0.67628	0.022657	2.600484	0.322279	0.036442	0.003191	0.596185	0.01732	0.5453
0.154203	0.662292	0.025549	2.558537	0.363416	0.037299	0.003598	0.599935	0.019531	0.548
0.171996	0.648304	0.028498	2.516591	0.405349	0.038157	0.004013	0.603685	0.021784	0.5509
0.190033	0.634315	0.031486	2.474645	0.447856	0.039014	0.004434	0.607435	0.024069	0.5537
0.208249	0.620327	0.034504	2.432698	0.490786	0.039872	0.004859	0.611185	0.026376	0.5565
0.226601	0.606339	0.037545	2.390752	0.534038	0.04073	0.005287	0.614935	0.0287	0.5593
0.24506	0.592351	0.040603	2.348805	0.57754	0.041587	0.005718	0.618685	0.031038	0.5622
0.263602	0.578363	0.043675	2.306859	0.621239	0.042445	0.00615	0.622434	0.033387	0.5650
0.282211	0.564375	0.046759	2.264912	0.665096	0.043302	0.006584	0.626185	0.035744	0.5678
0.300875	0.550387	0.049851	2.222966	0.709082	0.04416	0.00702	0.629935	0.038107	0.5700
0.319584	0.536399	0.052951	2.18102	0.753174	0.045017	0.007456	0.633685	0.040477	0.5734
0.338331	0.522411	0.056057	2.139073	0.797355	0.045875	0.007894	0.637435	0.042851	0.5762
0.080694	0.774554	0.01337	2.670066	0.190173	0.023763	0.001883	0.526506	0.01022	0.4297
0.06584	0.760565	0.010909	2.62812	0.155168	0.02462	0.001536	0.530256	0.008339	0.4325
0.053702	0.746577	0.008898	2.586173	0.126561	0.025478	0.001253	0.534006	0.006802	0.4353
0.046459	0.732589	0.007698	2.544227	0.10949	0.026336	0.001084	0.537756	0.005884	0.438
0.046459	0.718601	0.007698	2.50228	0.10949	0.027193	0.001084	0.541506	0.005884	0.4410
0.053702	0.704613	0.008898	2.460334	0.126561	0.028051	0.001253	0.545256	0.006802	0.4438
0.06584	0.690625	0.010909	2.418387	0.155168	0.028908	0.001536	0.549006	0.008339	0.44
0.080694	0.676637	0.01337	2.376441	0.190173	0.029766	0.001883	0.552756	0.01022	0.4494
0.097023	0.662649	0.016075	2.334495	0.228658	0.030623	0.002264	0.556506	0.012289	0.4522
0.114198	0.648661	0.018921	2.292548	0.269133	0.031481	0.002664	0.560256	0.014464	0.4550

mg_ph_st	k_ph_pr1	k_ph_stdp	ppmp_ph_	ppmp_ph_	ca_ph_pr1	ca_ph_std	om_ph_pr	om_ph_st	n_ph_pr1
0.057908	0.042348	0.003401	22.52202	2.738165	1.79108	0.148534	2.833063	0.105481	0.213526
0.051512	0.042747	0.003025	22.75286	2.435743	1.777812	0.132129	2.82552	0.093831	0.215772
0.046765	0.043146	0.002746	22.98369	2.211268	1.764545	0.119952	2.817976	0.085184	0.218018
0.044201	0.043545	0.002596	23.21452	2.090009	1.751277	0.113375	2.810432	0.080513	0.220264
0.044201	0.043943	0.002596	23.44536	2.090009	1.738009	0.113375	2.802889	0.080513	0.22251
0.046765	0.044342	0.002746	23.67619	2.211268	1.724741	0.119952	2.795345	0.085184	0.224756
0.051512	0.044741	0.003025	23.90702	2.435743	1.711473	0.132129	2.787802	0.093831	0.227002
0.057908	0.04514	0.003401	24.13786	2.738165	1.698205	0.148534	2.780258	0.105481	0.229248
0.065471	0.045539	0.003845	24.36869	3.095775	1.684937	0.167933	2.772714	0.119257	0.231494
0.073843	0.045938	0.004336	24.59952	3.491657	1.67167	0.189408	2.765171	0.134508	0.23374
0.08278	0.046336	0.004861	24.83036	3.914215	1.658402	0.21233	2.757627	0.150786	0.235986
0.092116	0.046735	0.005409	25.06119	4.355693	1.645134	0.236279	2.750083	0.167793	0.238232
0.101743	0.047134	0.005975	25.29202	4.810884	1.631866	0.260971	2.74254	0.185328	0.240478
0.111585	0.047533	0.006553	25.52286	5.276242	1.618598	0.286215	2.734996	0.203255	0.242724
0.121589	0.047932	0.00714	25.75369	5.749297	1.60533	0.311876	2.727452	0.221478	0.24497
0.131719	0.04833	0.007735	25.98452	6.228296	1.592062	0.33786	2.719909	0.23993	0.247216
0.141948	0.048729	0.008336	26.21536	6.711967	1.578795	0.364097	2.712365	0.258562	0.249462
0.152256	0.049128	0.008941	26.44619	7.199367	1.565527	0.390536	2.704821	0.277338	0.251708
0.162627	0.049527	0.00955	26.67702	7.689788	1.552259	0.41714	2.697278	0.296231	0.253954
0.173051	0.049926	0.010162	26.90786	8.182688	1.538991	0.443878	2.689734	0.315218	0.2562
0.183519	0.050324	0.010777	27.13869	8.677642	1.525723	0.470727	2.68219	0.334285	0.258446
0.194023	0.050723	0.011394	27.36952	9.174319	1.512455	0.49767	2.674647	0.353419	0.260692
0.050135	0.036559	0.002944	18.18238	2.370633	1.582598	0.128597	3.028799	0.091323	0.189054
0.042588	0.036958	0.002501	18.41321	2.013752	1.56933	0.109238	3.021255	0.077575	0.1913
0.036704	0.037357	0.002155	18.64405	1.735528	1.556062	0.094145	3.013712	0.066857	0.193546
0.033375	0.037755	0.00196	18.87488	1.578129	1.542795	0.085607	3.006168	0.060794	0.195792
0.033375	0.038154	0.00196	19.10571	1.578129	1.529527	0.085607	2.998625	0.060794	0.198038
0.036704	0.038553	0.002155	19.33655	1.735528	1.516259	0.094145	2.991081	0.066857	0.200285
0.042588	0.038952	0.002501	19.56738	2.013752	1.502991	0.109238	2.983537	0.077575	0.202531
0.050135	0.039351	0.002944	19.79821	2.370633	1.489723	0.128597	2.975994	0.091323	0.204777
0.058708	0.039749	0.003448	20.02905	2.776	1.476455	0.150587	2.96845	0.106939	0.207023
0.067919	0.040148	0.003988	20.25988	3.211545	1.463187	0.174213	2.960906	0.123717	0.209269
0.077542	0.040547	0.004554	20.49072	3.666529	1.44992	0.198894	2.953363	0.141244	0.211515
0.087439	0.040946	0.005135	20.72155	4.134539	1.436652	0.224282	2.945819	0.159273	0.213761
0.097529	0.041345	0.005727	20.95238	4.611612	1.423384	0.250161	2.938275	0.177651	0.216007
0.107756	0.041743	0.006328	21.18321	5.095201	1.410116	0.276394	2.930732	0.19628	0.218253
0.118085	0.042142	0.006934	21.41405	5.583616	1.396848	0.302889	2.923188	0.215095	0.220499
0.128492	0.042541	0.007545	21.64488	6.075691	1.38358	0.329582	2.915644	0.234051	0.222745
0.138958	0.04294	0.00816	21.87571	6.570605	1.370312	0.356429	2.908101	0.253117	0.224991
0.149472	0.043339	0.008778	22.10655	7.06776	1.357045	0.383397	2.900557	0.272269	0.227237
0.160025	0.043738	0.009397	22.33738	7.566717	1.343777	0.410464	2.893013	0.29149	0.229483
0.170608	0.044136	0.010019	22.56821	8.067139	1.330509	0.43761	2.88547	0.310767	0.231729
0.181217	0.044535	0.010642	22.79905	8.56877	1.317241	0.464821	2.877926	0.330091	0.233975
0.191847	0.044934	0.011266	23.02988	9.071411	1.303973	0.492087	2.870383	0.349454	0.236221
0.045756	0.03077	0.002687	13.84274	2.16358	1.374116	0.117365	3.224535	0.083347	0.164583
0.037334	0.031168	0.002192	14.07357	1.765325	1.360848	0.095762	3.216991	0.068005	0.166829
0.030451	0.031567	0.001788	14.30441	1.439873	1.34758	0.078107	3.209448	0.055468	0.169075
0.026344	0.031966	0.001547	14.53524	1.245659	1.334313	0.067572	3.201904	0.047986	0.171321
0.026344	0.032365	0.001547	14.76607	1.245659	1.321045	0.067572	3.19436	0.047986	0.173567
0.030451	0.032764	0.001788	14.9969	1.439873	1.307777	0.078107	3.186817	0.055468	0.175813
0.037334	0.033163	0.002192	15.22774	1.765325	1.294509	0.095762	3.179273	0.068005	0.178059
0.045756	0.033561	0.002687	15.45857	2.16358	1.281241	0.117365	3.171729	0.083347	0.180305
0.055016	0.03396	0.003231	15.6894	2.601414	1.267973	0.141116	3.164186	0.100213	0.182551
0.064754	0.034359	0.003803	15.92024	3.061894	1.254705	0.166095	3.156642	0.117952	0.184797

n_ph_stdp	unkw_ph_	unkw_ph_	oc_ph_pr2	oc_ph_std	clay_ph_p	clay_ph_s	silt_ph_pr	silt_ph_st	bs_ph_
0.015255	6.27298	0.028824	1.353715	0.018175	4.46631	0.048897	5.740541	0.217711	77.897
0.01357	6.201789	0.023679	1.348878	0.014931	4.531667	0.040169	5.692128	0.178849	78.259
0.01232	6.141809	0.023036	1.344171	0.014526	4.590675	0.039079	5.641433	0.173996	78.673
0.011644	6.09304	0.023679	1.339596	0.014931	4.643334	0.040169	5.588457	0.178849	79.139
0.011644	6.05548	0.023679	1.335152	0.014931	4.689643	0.040169	5.533199	0.178849	79.659
0.01232	6.029131	0.023036	1.330838	0.014526	4.729603	0.039079	5.475659	0.173996	80.230
0.01357	6.013992	0.023679	1.326656	0.014931	4.763215	0.040169	5.415838	0.178849	80.855
0.015255	6.010063	0.028824	1.322604	0.018175	4.790476	0.048897	5.353735	0.217711	81.532
0.017247	6.017345	0.040139	1.318683	0.025311	4.811389	0.068093	5.28935	0.303181	82.261
0.019453	6.035837	0.057113	1.314894	0.036014	4.825953	0.096888	5.222683	0.431389	83.043
0.021807	6.065539	0.078952	1.311235	0.049785	4.834167	0.133934	5.153735	0.596337	83.878
0.024267	6.106452	0.105193	1.307707	0.066332	4.836032	0.178451	5.082504	0.794546	84.765
0.026803	6.158575	0.135606	1.30431	0.08551	4.831548	0.230044	5.008992	1.024261	85.705
0.029395	6.221909	0.170071	1.301045	0.107242	4.820714	0.288509	4.933199	1.284577	86.698
0.032031	6.296452	0.208521	1.29791	0.131488	4.803532	0.353736	4.855123	1.574998	87.743
0.0347	6.382206	0.250918	1.294906	0.158223	4.78	0.42566	4.774766	1.895236	88.840
0.037394	6.47917	0.297241	1.292033	0.187432	4.750119	0.504242	4.692127	2.245117	89.991
0.04011	6.587345	0.347473	1.289291	0.219107	4.713889	0.589456	4.607206	2.62453	91.193
0.042842	6.70673	0.401605	1.28668	0.253241	4.671309	0.681286	4.520004	3.0334	92.44
0.045588	6.837325	0.45963	1.2842	0.289831	4.622381	0.77972	4.43052	3.471678	93.757
0.048345	6.979131	0.521544	1.28185	0.328872	4.567103	0.884752	4.338753	3.939327	95.117
0.051113	7.132146	0.587344	1.279632	0.370364	4.505476	0.996375	4.244706	4.436325	96.530
0.013207	7.232164	0.024294	1.932878	0.015319	4.608842	0.041213	6.045862	0.1835	65.124
0.011219	7.160974	0.017891	1.928041	0.011282	4.674199	0.030351	5.997449	0.135135	65.486
0.009669	7.100993	0.017032	1.923334	0.01074	4.733207	0.028893	5.946755	0.128643	65.900
0.008792	7.052223	0.017891	1.918759	0.011282	4.785866	0.030351	5.893779	0.135135	66.367
0.008792	7.014664	0.017891	1.914315	0.011282	4.832175	0.030351	5.838521	0.135135	66.886
0.009669	6.988315	0.017032	1.910001	0.01074	4.872136	0.028893	5.780982	0.128643	67.458
0.011219	6.973176	0.017891	1.905819	0.011282	4.905747	0.030351	5.72116	0.135135	68.082
0.013207	6.969247	0.024294	1.901767	0.015319	4.933009	0.041213	5.659057	0.1835	68.759
0.015466	6.976529	0.037021	1.897846	0.023345	4.953921	0.062803	5.594672	0.27963	69.489
0.017892	6.995021	0.054967	1.894057	0.034661	4.968485	0.093246	5.528005	0.415176	70.271
0.020427	7.024724	0.077413	1.890398	0.048815	4.976699	0.131324	5.459056	0.584715	71.105
0.023035	7.065636	0.104043	1.88687	0.065607	4.978564	0.1765	5.387826	0.785861	71.993
0.025693	7.117759	0.134716	1.883473	0.084949	4.97408	0.228534	5.314314	1.017539	72.933
0.028387	7.181092	0.169362	1.880208	0.106795	4.963246	0.287307	5.238521	1.279224	73.92
0.031108	7.255636	0.207943	1.877073	0.131123	4.946064	0.352756	5.160445	1.570635	74.970
0.033849	7.34139	0.250438	1.874069	0.15792	4.922532	0.424846	5.080088	1.891612	76.068
0.036607	7.438354	0.296836	1.871196	0.187177	4.892651	0.503555	4.997449	2.242059	77.218
0.039376	7.546529	0.347126	1.868454	0.218889	4.856421	0.588868	4.912528	2.621914	78.421
0.042156	7.665914	0.401305	1.865843	0.253052	4.813841	0.680777	4.825325	3.031137	79.676
0.044944	7.796509	0.459368	1.863363	0.289666	4.764913	0.779276	4.735841	3.4697	80.984
0.047739	7.938314	0.521313	1.861014	0.328727	4.709635	0.884361	4.644075	3.937585	82.345
0.050539	8.091331	0.587139	1.858795	0.370234	4.648008	0.996028	4.550028	4.434777	83.758
0.012054	7.422102	0.023155	2.047527	0.014601	4.657839	0.039281	6.07396	0.174898	63.595
0.009835	7.350911	0.016311	2.042689	0.010285	4.723196	0.02767	6.025547	0.123201	63.957
0.008022	7.290931	0.015363	2.037983	0.009688	4.782204	0.026063	5.974853	0.116043	64.371
0.00694	7.242161	0.016311	2.033407	0.010285	4.834863	0.02767	5.921876	0.123201	64.837
0.00694	7.204602	0.016311	2.028963	0.010285	4.881172	0.02767	5.866619	0.123201	65.357
0.008022	7.178253	0.015363	2.024649	0.009688	4.921133	0.026063	5.809079	0.116043	65.928
0.009835	7.163114	0.016311	2.020467	0.010285	4.954743	0.02767	5.749258	0.123201	66.553
0.012054	7.159185	0.023155	2.016415	0.014601	4.982006	0.039281	5.687154	0.174898	67.230
0.014493	7.166467	0.036284	2.012495	0.02288	5.002918	0.061553	5.622769	0.274062	67.959
0.017059	7.184959	0.054473	2.008705	0.034349	5.017482	0.092409	5.556103	0.411446	68.741

Appendix c

Result of the Physico-chemical properties of polluted cassava farmland in Abacheke Community, Ohaji/Egbema LGA Imo State (December, 2012)

Soil sample Depth 0 – 4cm	
Sand %	89.4
Silt %	7.2
Clay %	8.4
Textural class	Loamy sand
Moisture content (m.c %)	2.0
Bulk density (cm^3)	1.21
Iron (Fe) %	5.4
Volumetric moisture content m^3/cm^3	24.20
Organic Carbon %	3.42
Organic Matter %	4.62
pH (H_2O) 1:2.5	6.52
Phosphorous (PPM)	7.33
Total Nitrogen %	0.120
Sodium (Na) cmol/kg	1.0
Potassium (K) cmol/kg	0.031
Calcium (Ca) cmol/kg	13.88
Manganese (Mg) cmol/kg	0.12
H^+ Hydrogen cmol/kg	0.10
Aluminium Al^{+++} meq/1000 soil	0.15
Exchangeable Acidity cmol/kg	0.25
Cation exchange capacity	16.11
Effective cation exchange capacity	16.36