

**DISPERSION OF OIL SPILLAGE ON SOIL**

**(A CASE STUDY OF NIGER-DELTA)**

**BY**

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## DECLARATION

I, ATAH DONATUS UGI, with matriculation number 97/ 5952EH, declare that this thesis; Dispersion of oil spillage on soil, A case study of Niger- Delta area, presented for the award of Bachelor of Engineering in Chemical Engineering, has not been presented for any other degree elsewhere.

  
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Signature

17th OCTOBER 2003  
Date

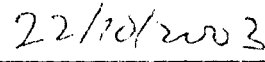
## CERTIFICATION

This is to certify that this project was supervised, moderated and approved by the following underlisted persons on behalf of the Chemical Engineering Department, School of Engineering and Engineering Technology, Federal University of Technology, Minna.



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## **DEDICATION**

This project is specially dedicated to my dearly beloved parents Mr. And Mrs. Atah .C. Ugi who gave me the encouragement and bears the responsibilities of my education and to my most dearly beloved brother and sisters, Henry, Prisca, Felicia and Elizabeth for their loving attention

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## ABSTRACT

An investigation of the effect of oil spillage, multiple regression of result obtained from the polluted area to derive a statistical model equation and also to predict a pH of the soil. The parameters measured are the pH, Electrical Conductivity (EC), Total Petroleum Hydrocarbon (TPH), Organic Nitrate and Nitrite ( $\text{NO}_3$  &  $\text{NO}_2$ ), Carbonate ( $\text{CO}_3$ ), Biological Oxygen Demand (BOD) and the Distance. The samples were collected over the month of February and March 2002. The result obtained shows that in general the Total Petroleum Hydrocarbon, Organic Nitrate, Organic Nitrite, Electrical Conductivity, Biological Oxygen Demand, Carbonate, are within the FEPA standards. But the pH of the soil which dependant on soil quality is unaccepted when compared with the set limit by FEPA (Federal Environmental and Protection Agency). The result of regression model simulated showed a remarkable agreement with the experimental results.

## CHAPTER ONE

### 1.0 INTRODUCTION

Oil has been an important part of the Nigeria economy since vast reserves of petroleum were discovered in Nigeria in the early 1950's [Jerry & Dozie, 1981]. For example, revenues of oil have increased from 219 million Naira in 1979 [Jerry & Dozie, 1981]. Currently oil provides 80% of Nigeria's revenue and 90% of its foreign exchange. The bulk of two billion barrels produced per day are derived from fields in the Niger-delta area [Jerry and Dozie, 1981]. Many developing countries give priority to rapid industrial development in order to improve their economic and society well being. Such development is essential they lead to progress and improved quality of life. However, they caused serious environmental deterioration if not carefully controlled. Environmental pollution has transcended natural boundaries, results to problems like; acid rain, stratospheric ozone depletion, global warming, the green house gas effect, deforestation, mega disaster are some of the various environmental problems attributed to environmental pollution has necessitated global co-operation in order to secure and maintain a live able global environment. Acid rain has the tendency to dispersed from one country to another has lead to political instability between nations. People are begging to recognized that pollutant can affect not just one region but also the entire planet [John & William, 1977]. Modern industrial society creates far more CO<sub>2</sub> than what the planet can consume. As the excess CO<sub>2</sub> rises into atmosphere it acts as an absorptive body, which trap heat reflected from the earth surface [Batsone, R. Smith, J.E & Wilson, 1989].

Oil production in Nigeria has severe environmental and human consequences for the indigenous people who inhabit the areas surrounding oil exploration and exploitation. Spillage of different kinds has been common in recent times in the Niger-delta. Oil spillage is associated with areas where there is oil exploration or along pipelines used for its transportation from one place to another. Oil spillage could be as a result of mechanical failure, sabotage cases or through operational discharges. The mobility of the spilled crude from the surface of the soil and viscosity of the oil [John & Williams, 1977]. The contaminated soil will then exerts its adverse effect on plants by creating certain conditions which makes nutrient unavailable. Oil contamination of the soil, thus results in the soil becoming unsuitable for agricultural purposes.

### **1.1 JUSTIFICATION**

The study was carried out for the purposes of studying the economic and environmental problems, affecting the people in the Niger-delta and also how it affects the soil used for agricultural purposes. These problems will be intensively covered in the result and discussion of result. Possible conclusion will be drawn and recommendations made on the ways of improving the situations

### **1.2 SCOPE OF STUDY**

This project covers the oil-drilling field in the Niger-delta area. The samples were collected from various distances starting from the incidence point. The samples were

used to measure the amount of the following pollutants in the soil, after a spill as occurred;

- (i) pH
- (ii) Electrical Conductivity
- (iii) Organic Phosphate
- (iv) Total Petroleum Hydrocarbon
- (v) Organic Nitrate
- (vi) Carbonate
- (vii) Organic Nitrite
- (viii) Biological Oxygen Demand.

### **1.3 DEFINITION OF OIL SPILLAGE**

Oil spillage can be regarded as the outflow of an identified fluid out of the particular flow paths, channels, container vessels, pipes etc. into the environment in the cause of operations [Porteous, A.1976]

It is sometimes the result of equipment's failure or an act of sabotage.

### **1.4 CLASSIFICATION OF OIL SPILLAGE**

Spills are classified according to a combination of magnitude, actual or potential impact, and the resources required for effective response. The following three categories are recognized [Porteous, A.1976].

#### **1.4.1 MINOR SPILL**

A spill is as a minor spill if the discharge of oil in inland water of less than 25 barrels or less than 250 barrels on soil, coastal or offshore [Porteous, A.1976]. Little or no

## 1.6 AIMS AND OBJECTIVES

The objective of this work is to investigate the concentrations of pollutants in the soil due to oil spillage. This could be achieved via the realization of the following aims;

- Analysis the soil samples collected at various distances away from the point of spilled to determine the concentration of the pollutant in the soil.
- Developed a statistical model from the data to predict the pH of the soil.
- Simulate the model developed by computer program.
- Determination of the nature and degree of environmental impacts caused by the oil spill.

## **1.5 OIL SPILLAGE CONTINGENCY PLAN**

A contingency plan is an organized predetermined course of action to be pursued when oil spillage occurs. This contingency plan outline by oil companies in the Niger- delta area in response to oil spill from wells, pipelines, flowstations, terminal gas plant, ware houses, laboratories etc. The mandatory requirement which provide for the preparation of contingency planning, control and the combating of spill are as follows:[Pickford,J.1977]

- Petroleum regulations 1967 section 101
- Oil pipeline ordinance cap 145 of 1956 as amended by oil pipelines act, 1965, section 17(b) and 31(c) DPR.
- Oil in navigable water act 1968.

Oil contingency has basically three functions [Pickford, J. 1977].

- (i) To ensure that the environment is protected
- (ii) To ensure that the manpower, equipment's and funds are available to effectively contain and contain clean-up oil spills.
- (iii) To ensure that good record keeping is maintained and accurate information concerning the spills are disseminated to the public and government.

## CHAPTER TWO

### 2.0 LITERATURE REVIEW

The fluid mineral petroleum (rock oil) is an extra-ordinary unique substance, its history dates back to early civilization. It is a naturally occurring mixtures of hydrocarbons containing some impurities like sulphur, hydrogen sulphide and some mechanical impurities like sand.[Abdulrahman,M.1993]. The initial idea was based on the fact that, methane gas ,an important constituent of hydrocarbon is also highly associated with the atmosphere of the outer planets of the solar system and the satellites[John & Williams, 1977]. Modern theories now suggest that petroleum is of biogenic origin that must have occurred by bacteria activity on the remains of animals and plants buried some years ago. Evidence in support of this includes;

- crude oil highly associated with beds containing the remains of marine organism
- almost all living matter contain liquid fatty acid which could be acted up[on by bacteria to produce parrafinic hydrocarbon.
- The presence in crude oil of certain compounds which would have destroyed in the presence of oxygen also suggest that petroleum must have from the remain of living things.

The biogenic origin can further be explained in terms of element of weather (temperature change, wind and rain) wears away the surface of the rock transport to lower area such as sea beds. The particles are usually deposited where the water transporting then becomes sufficiently calm. These depositional features from the marine sediments in which petroleum is formed [Abdulrahman, M.1993].



Oil spillage is a subject of interest to professional in the field of spill problem. Oil almost since it first formation in geological time, must have been coming to the earth and entering the water. Some of these oil seep took place on soil, the Asphalt lake of Trinidad [U.S Environmental Protection Agency, 1992].

In the early period, developing countries like Nigeria are faced with a lot of problems. One of such problems is pollution of sea and soil due to the activities of processing industries. J. Wardly Smith, 1977, noted that the terrestrial oil spill problem receives less publication or opposed to marine environment. Terrestrial spills on the water frequently occur in isolated region that are faraway from direct view of the health, conservation of natural resources and aesthetic problem.

## **2.1 EFFECT OF OIL IN SOIL**

After the petroleum product is spilled, it migrates downwards under the force of gravity [Marais, G.V, 1994]. The mobility of the oil depends on its viscosity quantity and the permeability of the soil. During its movement through the unsaturated zone, there is absorption and reactions between the oil and the rock matrix tending to immobilized and alternate the oil [Marais, G.V, 1994]. If water table is far enough below the ground surface, the oil maybe immobilized in the unsaturated zone, before it reaches the water table. In the case of shallow water table aquifers, where the oil is not mobilized in the unsaturated zone, the spill will reach the table aquifers. Where oil is not mobilized in the saturated zone, the spill will reach the water table [Stirlon, R.I 19761]. The soluble components will dissolve in the water and vapour will be released which maybe collected forming potential fire or explosion hazards.

Field s and laboratory studies revealed that oil deposited on leaves and reduces transpiration and photosynthesis [Stirlon, R.I 1971]. When the pollution is light the leaves becomes yellow and drop soon after, but under heavy contamination, complete shedding of leaf results. However, the plant could recover if the soil itself is not heavily contaminated. Oil itself on contaminating soil is not toxic to plants. It however, 4exerts it adverse effect on plants indirectly by creating conditions which makes nutrient like Nitrogen, which are essential for plant growth, unavailable to plants [Stirlon, R.I 1971]. Oil contamination of the soil thus results in the soil becoming unsuitable for crop growth.

## **2.2 TREATMENT OF OIL IN SOIL**

It is necessary that operators should respond immediately, an oil spill occurs in order to prevent the spreading of the spilled product. Clean up spills of contaminated environment shall constitute damage to already impacted environment. It is therefore required that an operator adopts an approved method. Clean up by the Oil Company in the Niger –delta area commence within 24 hours of the occurrence of the spill. Before any cleaning is attempted two questions must be considered;

1. Why is cleaning or oil removal required?
2. Will the process damage the environment?

In case of one, to be cleaned, the practice type of cleaning permitted, and the extent of the operation should have decided in advance and included in the method of contingency plan. Movement of people over an area trying to clean it up is sometimes enough to cause damage. For example, vehicles and people crossing sand dunes to reach scene of pollution can so damage the plant cover and expose the sand to a long-term damage.

## **2.3 METHOD EMPLOYED FOR CLEANING**

### **2.3.1 MECHANICAL REMOVAL**

Even if only some of the oil can be taken by this method, it is still the most satisfactory. A sand beach is firm enough to bear vehicles and with access from a road, can be cleaned by removing the minimum amount of oily sand. Which can be collected by mechanical graders or bulldozers and loaded into lorries [Batstone, R. Smith, J.E & Wilson 1989]. To reduce cost this process must be carried out with great care to ensure that only sand is removed. The sand beaches is replenished by the action of tide and waves. Mechanical removal of oil on rocky shore can only be done by hand cleaning. Perhaps, suction from gully erupters to remove oil from pool.

### **2.3.2 USE OF ABSORBENT MATERIAL**

If the ground is smooth as for example a cemented jelly, an Oleophilic material such as Silicon treated sawdust, can be sprinkled over the oil and the whole lot brushed into heaps and removed [John Boardman, 2003]. An alternative use of absorbent materials is to cover the oil with powder to remove its oily properties and to leave the oil and powdered to weather. A great number of powders have been tried for this purpose but none of them are really satisfactory unless very large quantities is used.

### **2.3.3 BURNING**

Oil on the shore is often wet, either because the water is in droplets throughout the body of the oil. That is on the ways to the formation of a water- in- oil emulsion, or because the oil is mixed with seaweed and other wet detritus. It is very difficult even to

ignite oil when it is on the shore and impossible to get many practical disadvantages. Claims have been made that some of the igniting materials used to burn floating oil can be used to burn oil on a beach [John Boardman, 2003]. But although they help in lighting the oil, eventually the fire goes out leaving a path of ground heavily contaminated with unburnt heavy residue.

## **2.4 CAUSES OF OIL SPILLAGE**

A good understanding of the causes of oil spill are important to note. From the numerous investigations of oil spill incidents in Nigeria, the causes of oil spillage are so many and are of various kinds, as stated below:

### **2.4.1 MECHANICAL FAILURE**

This cause maybe further sub-divided into failure attributed to faults in construction and those from defects in materials or compounds. While historically both sources have been responsible for spillage from pipeline in the past, the very high standard of construction and inspection applied by the oil industry have drastically reduced the potential for this type of failure.

### **2.4.2 NATURAL HAZARD**

This can be through flooding, landslides and subsidence such occurrences are in many cases extremely rare and the risk is reduced by careful routine, investigation to avoid possible problem areas, such as in mining region by intelligent observation during periodic inspection. The few-recorded incidents that have cause spillage from pipeline have generally reserved from very sudden and unpredictable freak weather conditions.

### **2.4.3 SABOTAGE CASES**

It refer to deliberate human intervention of a normal operation of an oil facility either for the purpose of venting their anger, or to get monetary compensation from oil companies concerned. Apart from these categories spills could also be due to accident from third party like road construction and even unknown causes.

An analysis of oil soil between 1976 to 1986 showed the following statistics; For period under review, sabotage accounted for 21% of spill incidents about 3.2% of the total quality spilled [Jerry & Dozie, 1981]. Most of the sabotage involved in pipeline damages, the rest high level of occurrence is well heads.

### **2.4.4 OPERATION DISCHARGES**

Discharges of oil are very common by its by nature, some oil is expected to escape in small quantities during oil operations e.g. when changing connections or transferring oil from one container to another. At industrial sites, such little drops could build upon to, a substantial quantity which then poses a problem of disposal [Jerry & Dozie, 1981].

### **2.5 INLAND OIL SPILLS**

When oil spill on ground, it will spread out and will almost inevitably sink through the surface of the permeable soil. The volume of the spilled oil and the viscosity of oil in the soil. The volume of the spilled oil and the viscosity of the oil spill on soil, immediate action should be taken to limit and stop the escape oil and to prevent the oil from reaching a water coarse or entering sewers, should be put as soon as possible. While inlets to drainage system can be covered by using materials such as tarpaulins blankets and plastic sheets.

## **2.6 PREVENTION OF OIL SPILLAGE**

Since oil spillage is of global concern, environmental scientist have been and are still carrying out researches on how spillage could be prevented in oil industries. Some of these measures are;

### **2.6.3 CORROSION**

- (i) Wrapping of pipelines**
- (ii) Cathodic prevention**
- (iii) Replacement of aging flowlines (maximum of 15 years old)**
- (iv) The use of coated pipes**

### **2.6.4 PRODUCTION OPERATIONS**

**(Equipment failure / operation maintenance error)**

- (i) Proper assets management**
- (ii) Good design and operating procedures**
- (iii) Safety device**
- (iv) Good drainage systems e.g. oil / water separation**

### **2.6.5 SABOTAGTE**

- (i) Surveillance**
- (ii) Improve community relations**
- (iii) Community education via open for a**

### **2.6.6 HUMAN ERROR**

**(For engineering, drilling and others)**

- (i) Continuous staff / contractors personnel training
- (ii) Adherence to procedures
- (iii) Constant vigilance
- (iv) Pipelines and flowlines inspection
- (v) Making use of proper valves in various pressure measuring points.

## 2.7 MATHEMATICAL MODELLING

A model is nothing more than a mathematical abstraction of a real process. The equation or sets of equations that comprise the model are best an approximate to the true process. Hence, the model cannot incorporate all of the features, both microscopic and macroscopic of the real process. The engineering normally must seek a compromise involving the cost of obtaining. The model, that is, the time and effort required to obtain and verify [Lugben, 1995].

In a broader view, model is a simplified representation of a system intended to enhance our ability to understand, explain change, predict and possibly control the behaviour of a system [Abdulkareem, 2001]. Modeling is thus the presence of establishing inter-relationship between entities of a system. Models are represented in terms of goals performance criteria and constraints [Xavier, 1983].

A mathematical model of a system only represents the mathematical aspects of a process or process or system of interest. It gives the description of the process both the physical and chemical phenomenon taking place there in [Abdulrahman, 2001]. A model retains the physical properties of the system, it is therefore aimed at providing the

simplest possible description of a system, which is an exact time retain its physical characteristics [Lugben, 1995].

The purpose of studying systems through the modeling approach is to achieve different goals, without actually constructing or operating real processes. These goals of modeling may include the following;

- (a) To predict system behaviour is different situation where any level of predictive ability represents a benefit.
- (b) To improve understanding of some mechanism in the studied process.
- (c) To enable the design and evaluation of synthesized control system.
- (d) To estimate the process variable which are not directly measurable.
- (e) To test the sensitivity of system parameter.
- (f) To optimize system behaviour and efficient fault diagnosis
- (g) To verify models obtained in some other ways.

## **2.8 MODELING TECHNIQUES**

Model can be considered in three different classification, depending on how they are derived [Lugben, 1995].

1. The critical models developed using the principles of chemistry and physics.
2. Empirical models obtained from a mathematical (statistical) analysis of process operating data.
- 3 Semi-empirical models that are a compromise between 1 and 2 with one or more parameters to be evaluated from plant data.



Though ,a variety of modeling techniques tool exist neither the computer nor the tool can completely replace human decision, judgement and experience which still plays a significant role in determining the validity and usefulness of models for practical applications (Xavier,1983). Modeling which serve as a tool of control becomes important in this project because constant monitory of the effect of oil spillage required to evaluate the extent of the spillage in soil. Modeling could eliminate the time and material wastage in carrying out experimental work.

The modeling technique used in this study is empirical model (mathematical model). It is used because of its advantages over other methods. Mathematical model can be useful in process analysis and control in the following ways [Abdulrahman, 2001].

- (a) To design the control strategy for a new process.
- (b) To improve understanding of the process
- (c) To optimize process operating conditions.
- (d) To design the control law.
- (e) To train plant operating personnel.
- (f) To select controller settings.

The modeling technique used i.e. the empirical as stated above is used due to the reasons earlier started which would be seen the result discussions.

## CHAPTER THREE

### 3.0. ANALYTICAL AND EXPERIMENTAL

#### 3.1. SAMPLE (S) TEST

The degree or amount of contamination of the soil by petroleum crude was tested using oil detector pan.

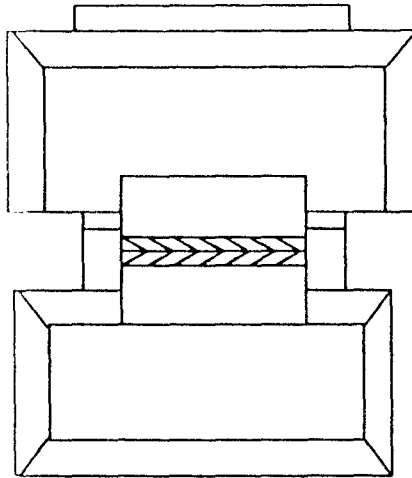


Fig. 1. Detector Pan

0.05 litre of water was poured in both pan A and B, and 200gm of the suspected contaminated sandy soil were added into the water in pan. The water in pan A and the added soil sample were mixed up thoroughly using a small stick or iron steel rod. After mixing, wait for 1 – 3 minutes, then the water in pan A was allowed to flow to pan B. much attention was paid to colour changes and behaviour the floating layer. Thick floating area was observed making the layer with anti-reflection plate coming out with a blue colour, which signifies diesel or fuel oil. The pan was then washed and rinsed

for another test. Three (3) test was carried out in the spilled area (i.e. the suspected site) to confirm the present of fuel oil in it (Jackson M.L., 1997).

### **3.1.2 COLLECTION OF SAMPLE (S)**

These samples were first collected at the incident point. Then with the help of a tape rule, 15cm was measured horizontally away from the incident point and another were collected at this 15cm mark. With the help of the tape rule 30cm was measured horizontally from the incident point. These steps were done repeatedly on 3 more points. Also from the incident point 15cm was measured downward (Vertically) and it was dug downward with the aid of a shovel. The step was done continuously for 3 more points and samples were collected respectively. (Head K.H. 1989). The collections were done on two (2) months.

## **3.2. DETERMINATION BIOLOGICAL OXYGEN DEMAND (B.O.D)**

This is the amount of oxygen required by the bacteria to reduce some of the organic matter in a waste under standard condition. The B.O.D. serves as the useful measure of the quality of biodegradable matter, which serves as food bacteria.

This is defined as the difference in values of dissolved oxygen at day 1 and day 5 of the sample.

### **3.2.1. PROCEDURE**

1. The impacted soil sample 10g was collected at the site was placed in an amber (dark brown) glass bottle screwed cap.

2. The sample was filled to the brim in the glass bottle and taken to the laboratory.
3. Sample from each site was duplicated.
4. The dissolved oxygen (D.O) meter probe after due calibration is inserted into each bottle containing the impacted soil sample. The reading observed was recorded as  $DO_1$
5. The sample in (4) above after reading is immediately transferred to an incubator and left for five days to incubate at a temperature of  $36.4^{\circ}C$ .
6. The repetition of (4) above after five days on the same sample gives a reading of  $DO_5$  (Jackson M.L., 1997)

### **CALCULATION**

$$BOD \text{ in mg/l} = \frac{DO_1 - DO_5}{P}$$

Where

$DO_1$  = Dissolved oxygen ( $O_2$ ) after sample preparation in mg/l

$DO_5$  = Dissolved oxygen ( $O_2$ ) of diluted sample after 5 days of incubation at  $20^{\circ}C$

P = Decimal volumetric fraction of sample used.

### **3.3 DETERMINATION OF pH**

The pH value usually serve as measure of acidity or alkalinity of a substance and it is usually measure or means of expression the hydrogen ion concentrated of substance. Wastewater with an adverse concentration of hydrogen ion is difficult to treat biologically and if the concentration is not

altered prior to its disposal it may alter the concentration of the receiving water and as such can affect the aquatic life.

### **3.3.1 PROCEDURE**

10g of air-dried soil sample were collected and weigh accurately into two (2) beakers. 250ml of distilled water were added and stirred. This was then allowed to settle for 5 – 10 minutes. The Orion model 1260-meter in. the meter is calibrated prior to use with buffer standard of 4,7 and 10 at temperature. Samples were analysed by dipping of the probe of meter into soil and water suspension of 1:1 ratio. (Jackson M.L. 1997)

### **3.4 DETERMINATION OF ELECTRICAL CONDUCTIVITY**

This is the numerical expression of the ability of an aqueous solution to conduct electric current in the system. This ability depends on the presence of ion, their total concentration, valency, and relative concentration and as well as temperature of measurement. Solution of relatively good conductors while molecule of organic compounds that do not dissolve in aqueous solution conduct current very poorly. The electrical conductivity determination serves as a very useful purpose in chemical analysis and also in the estimate of total solid.

#### **3.4.1. PROCEDURE**

It is determined electronically with a conductivity meter (ORION 150) in accordance wit APIHA 2501B. the equipment is calibrated with potassium chloride of 0.01m at two ranges of 12.9 ms/cm and 1413 ms/cm. The

### **3.6. DETERMINATION OF NITRATE/NITRITE (NO<sub>3</sub> & NO<sub>2</sub>)**

#### **3.6.1 PROCEDURE**

There are determined calorimetrically in accordance with the water operational guide 1987, using unican ultraviolet/visible spectrometer. Soil samples were extracted with sodium acetate while extracts for NO<sub>3</sub> were analysed using brucine (25%) in the presence of concentrated sulphuric acid at 470nm. Meanwhile, NO<sub>2</sub> was analysed using sulphuric acid dissolved 30% acetic acid with alpha-naphthylamine in acetic acid solution at 520nm. (R.M. Silverstein, L.R. Perthel, 1950).

### **3.7. DETERMINATION OF SULPHATE**

#### **3.7.1. PROCEDURE**

PO<sub>4</sub> is determined in accordance with stannous chloride reduction method as described in America Public Health Association (APHA), 42AE using unican ultraviolet/visible spectrophotometer. Soil samples are extracted with 25% acetic acid and the extract was run on the ultraviolet at a wavelength of 700nm. (R.M. Silverstein & R. Perthel, 1950)

### **3.6 DETERMINATION OF NITRATE & NITRITE (NO<sub>3</sub> & NO<sub>2</sub>)**

#### **3.6.1 PROCEDURE**

There are determined calorimetrically in accordance with the water operational guide 1987, using unican ultraviolet / visible spectrometer. Soil samples were extracted with Sodium Acetate while extracts for NO<sub>3</sub> were analyzed using Brucine (25%) in the presence of concentrated Sulphuric Acid dissolved 30% Acetic Acid with Alpha – Naphthylamine. Meanwhile, NO<sub>2</sub> was analyzed using Sulphuric Acid dissolved 30% Acetic Acid with Alpha-Naphthylamine in acetic acid solution at 520Nm. (R. M Siverstein, L.R.Perthel, 1950)

### **3.7 DETERMINATION OF PHOSPHATE**

#### **3.7.1 PROCEDURE**

PO<sub>4</sub> is determined in accordance with stannous Chloride reduction method as described in America Public Health Association (APHA), 42AE using Unican Ultraviolet / Visible spectrometer. Soil samples were extracted d with 25% Acetic Acid and the extract was run on the Ultraviolet at a wavelength of 700Nm. (R.M.Silverstein & R. Perthel, 1950)

### **3.8 DETERMINATION OF CARBONATE (C<sub>03</sub>)**

#### **3.8.1 REAGENTS AND PROCEDURES**

- (1) 0.05m sodium hydroxide (NaOH).
- (2) 20cm<sup>3</sup> concentrated HCL-Dilute to 1000cm<sup>3</sup> volumetric flask.
- (3) 10g of the sample were dissolved in 30cm<sup>3</sup> of distilled water it was filtered with the help of a filter paper. To separate the solute from the soil sample.
- (4) Pipette 25cm<sup>3</sup> of the sample in a conical flask and two drops of methyl/indicator.
- (5) Titrate with the acid i.e. HCL
- (6) Take the volume used and find average (Jackson, M.L 1997).



## CHAPTER FOUR

### 4.0 CONCEPTUALIATION OF MODELLING TECHNIQUES FOR SOIL COMPOSITION USING pH CRITERIA

The pH of a solution is a reflection of the resultant effects of TPH, BOD, NO<sub>3</sub>, NO<sub>2</sub>, distance, electrical conductivity can be determine by the empirical method of the least square method (Carnahan et al. 1969, Himmelblau,

1987). Mathematically,

$$\text{pH} = f(\text{EC}, \text{NO}_3, \text{PO}_4, \text{TPH}, \text{NO}_2, \text{CO}_3, \text{BOD}, \text{DIST}) \quad \text{-----1}$$

Let

Electric\_conductivity = EC

Organic\_nitrates = NO<sub>3</sub>

Phospahtes = PO<sub>4</sub>

Total\_petroleum\_hydrocarbons = TPH

Nitrates = NO<sub>2</sub>

Carbonates = CO<sub>3</sub>

Biodegradable\_ocygen\_demand = BOD

Distance = DIST

then equation 1 above becomes

$$\text{pH} = f(a\text{EC} + b\text{NO}_3 + c\text{PO}_4 + d\text{TPH} + e\text{NO}_2 + f\text{CO}_3 + g\text{BOD} + h\text{DIST}) - 2$$

**where X1=EC, X2=NO<sub>3</sub>, X3=PO<sub>4</sub>, X4=TPH, X5=NO<sub>2</sub>, X6=CO<sub>3</sub>, X7=BOD, X8=DIST  
therefore equation 2 also can be written as**

$$y = ax_1 + bx_2 + cx_3 + dx_4 + ex_5 + fx_6 + gx_7 + x_8$$

= 0

where the pH is the dependent variable in the equation and a, b, c, d, e, f, g and h are the coefficients (constants) which need to be determined and EC, NO<sub>3</sub>, PO<sub>4</sub>, TPH, NO<sub>2</sub>, CO<sub>3</sub>, BOD and DIST are the independent variables for the desired pH. Let I represent the square of the error between the observed pH and its predicted value (P), using the experimentally obtained data of EC, NO<sub>3</sub>, PO<sub>4</sub>, TPH, NO<sub>2</sub>, CO<sub>3</sub>, BOD and DIST

$$I = P - (aEC + bNO_3 + cPO_4 + dTPH + eNO_2 + fCO_3 + gBOD + hDIST) \quad \text{-----3}$$

**For n experimental values of P and EC, NO<sub>3</sub>, PO<sub>4</sub>, TPH, NO<sub>2</sub>, CO<sub>3</sub>, BOD and DIST**

$$nI = \sum (P_i - aEC - bNO_3 - cPO_4 - dTPH - eNO_2 - fCO_3 - gBOD - hDIST)^2 \quad \text{-----4}$$

To minimize nI with respect to the coefficients a, b, c, d, e, f, g and h using the first partial derivatives of nI with respect to these constants and equating these to zero we obtain the necessary condition for a minimum, so from equation 4;

$$\frac{\partial nI}{\partial a} = \left[ -2 \cdot \sum EC_i \cdot (P_i - aEC - bNO_3 - cPO_4 - dTPH - eNO_2 - fCO_3 - gBOD - hDIST)^2 \right] = 0$$

$$\frac{\partial nI}{\partial b} = \left[ -2 \cdot \sum NO_{3,i} \cdot (P_i - aEC - bNO_3 - cPO_4 - dTPH - eNO_2 - fCO_3 - gBOD - hDIST)^2 \right] = 0$$

$$\frac{\partial nI}{\partial c} = \left[ -2 \cdot \sum PO_{4,i} \cdot (P_i - aEC - bNO_3 - cPO_4 - dTPH - eNO_2 - fCO_3 - gBOD - hDIST)^2 \right] = 0$$

$$\frac{\partial nI}{\partial d} = \left[ -2 \cdot \sum TPH_i \cdot (P_i - aEC - bNO_3 - cPO_4 - dTPH - eNO_2 - fCO_3 - gBOD - hDIST)^2 \right] = 0$$

$$\frac{\partial nI}{\partial e} = \left[ -2 \cdot \sum NO_{2,i} \cdot \left[ (P_i - aEC - bNO_3 - cPO_4 - dTPH - eNO_2 - fCO_3 - gBOD - hDIST)^2 \right] \right] = 0$$

$$\frac{\partial nI}{\partial f} = \left[ -2 \cdot \sum CO_{3,i} \cdot (P_i - aEC - bNO_3 - cPO_4 - dTPH - eNO_2 - fCO_3 - gBOD - hDIST)^2 \right] =$$

$$\frac{\partial nI}{\partial g} = \left[ -2 \cdot \sum BOD_i \cdot (P_i - aEC - bNO_3 - cPO_4 - dTPH - eNO_2 - fCO_3 - gBOD - hDIST)^2 \right] =$$

$$\frac{\partial nI}{\partial h} = \left[ -2 \cdot \sum DIST_i \cdot (P_i - aEC - bNO_3 - cPO_4 - dTPH - eNO_2 - fCO_3 - gBOD - hDIST)^2 \right] =$$

When rearranged, these sets of linear equations become;

$$\sum EC_i \cdot P_i = a \cdot \sum (EC)^2 + b \cdot \sum EC_i \cdot NO_{3i} + c \cdot \sum EC_i \cdot PO_{4i} + d \cdot \sum EC_i \cdot TPH + e \cdot \sum EC_i \cdot NO_2 + f \cdot \sum EC_i \cdot CO_{3i} + g \cdot \sum EC_i \cdot BOD_i + h \cdot \sum EC_i \cdot DIST_i \quad \text{-----13}$$

$$\sum NO_{3i} \cdot P_i = a \cdot \sum NO_{3i} \cdot EC + b \cdot \sum (NO_{3i})^2 + c \cdot \sum NO_{3i} \cdot PO_{4i} + d \cdot \sum NO_{3i} \cdot TPH + e \cdot \sum NO_{3i} \cdot NO_{2i} + f \cdot \sum NO_{3i} \cdot CO_{3i} + g \cdot \sum NO_{3i} \cdot BOD_i + h \cdot \sum NO_{3i} \cdot DIST_i \quad \text{-----14}$$

$$\sum PO_{4i} \cdot P_i = a \cdot \sum PO_{4i} \cdot EC + b \cdot \sum PO_{4i} \cdot NO_{3i} + c \cdot \sum (PO_{4i})^2 + d \cdot \sum PO_{4i} \cdot TPH + e \cdot \sum PO_{4i} \cdot NO_{2i} + f \cdot \sum PO_{4i} \cdot CO_{3i} + g \cdot \sum PO_{4i} \cdot BOD_i + h \cdot \sum PO_{4i} \cdot DIST_i \quad \text{-----15}$$

$$\sum TPH_i \cdot P_i = a \cdot \sum TPH_i \cdot EC + b \cdot \sum TPH_i \cdot NO_{3i} + c \cdot \sum TPH_i \cdot PO_{4i} + d \cdot \sum (TPH_i)^2 + e \cdot \sum TPH_i \cdot NO_{2i} + f \cdot \sum TPH_i \cdot CO_{3i} + g \cdot \sum TPH_i \cdot BOD_i + h \cdot \sum TPH_i \cdot DIST_i \quad \text{-----16}$$

$$\sum NO_{2i} \cdot P_i = a \cdot \sum NO_{2i} \cdot EC + b \cdot \sum NO_{2i} \cdot NO_{3i} + c \cdot \sum NO_{2i} \cdot PO_{4i} + d \cdot \sum NO_{2i} \cdot TPH + e \cdot \sum EC_i \cdot NO_{2i} + f \cdot \sum NO_{2i} \cdot CO_{3i} + g \cdot \sum NO_{2i} \cdot BOD_i + h \cdot \sum NO_{2i} \cdot DIST_i \quad \text{-----17}$$

$$\sum CO_{3i} \cdot P_i = a \cdot \sum CO_{3i} \cdot EC + b \cdot \sum CO_{3i} \cdot NO_{3i} + c \cdot \sum CO_{3i} \cdot PO_{4i} + d \cdot \sum CO_{3i} \cdot TPH + e \cdot \sum CO_{3i} \cdot NO_{2i} + f \cdot \sum (CO_{3i})^2 + g \cdot \sum CO_{3i} \cdot BOD_i + h \cdot \sum CO_{3i} \cdot DIST_i \quad \text{-----18}$$

$$\sum \text{BOD}_i \cdot P_i = a \cdot \sum \text{BOD}_i \cdot \text{EC}_i + b \cdot \sum \text{BOD}_i \cdot \text{NO}_{3i} + c \cdot \sum \text{BOD}_i \cdot \text{PO}_{4i} + d \cdot \sum \text{BOD}_i \cdot \text{TPH} ..$$

$$+ e \cdot \sum \text{BOD}_i \cdot \text{NO}_{2i} + \left[ f \cdot \sum \text{BOD}_i \cdot \text{CO}_{3i} + g \cdot \sum (\text{BOD}_i)^2 + h \cdot \sum \text{BOD}_i \cdot \text{DIST}_i \right]$$

$$\sum \text{DIST}_i \cdot P_i = a \cdot \sum \text{DIST}_i \cdot \text{EC} + b \cdot \sum \text{DIST}_i \cdot \text{NO}_{3i} + c \cdot \sum \text{DIST}_i \cdot \text{PO}_{4i} + d \cdot \sum \text{DIST}_i \cdot \text{TPH} .$$

$$+ e \cdot \sum \text{DIST}_i \cdot \text{NO}_{2i} + f \cdot \sum \text{DIST}_i \cdot \text{CO}_{3i} + g \cdot \sum \text{DIST}_i \cdot \text{BOD}_i + h \cdot \sum (\text{DIST}_i)^2$$

where  $\Sigma = \sum_{i=1}^n$  and  $n = 16$  and the sum is obtained from the experimental

data using basic program. The output of summation is as generated from the table below

T :=

	1	2	3	4	5	6	7	8	9
1	5.85	2.35	0.32	12.35	82.88	0.12	0.56	0.15	15.00
2	6.40	1.20	0.22	2.15	44.50	0.08	0.32	0.12	30.00
3	6.95	0.97	0.13	0.88	25.00	0.05	0.14	0.09	45.00
4	7.02	0.68	0.08	0.37	14.89	0.01	0.07	0.05	60.00
5	5.53	1.12	0.32	10.10	34.33	0.09	0.42	0.75	75.00
6	6.42	1.00	0.10	2.00	20.03	0.08	0.19	0.30	90.00
7	6.98	0.88	0.69	0.98	12.08	0.06	0.07	0.21	105.00
8	7.00	0.57	0.32	0.34	0.45	0.05	0.01	0.10	120.00
9	5.03	0.52	0.21	2.62	13.02	0.08	0.24	0.62	135.00
10	5.92	0.40	0.14	2.05	0.01	0.08	0.15	0.53	150.00
11	6.23	0.31	0.09	1.76	1.98	0.70	0.76	0.32	165.00
12	6.95	0.19	0.02	1.21	0.46	0.50	0.10	0.09	180.00
13	4.23	0.34	0.18	0.15	5.20	0.06	0.12	0.09	195.00
14	5.40	0.30	0.20	0.10	3.14	0.03	0.09	0.07	210.00
15	6.32	0.27	0.26	0.06	1.20	0.02	0.07	0.04	225.00
16	7.12	0.12	0.30	0.02	1.00	0.01	0.03	0.02	240.00

A := T <1> := T <2> := T <3> := T <4> := T <5> := T <6> T <7> = T <8> T <9>

pH := A EC := B NO<sub>3</sub> := C PO<sub>4</sub> := D TPH := E NO<sub>2</sub> := F CO<sub>3</sub> := G BOD := H DIST := I

$$\sum \overrightarrow{(B)^2} = 12.57; \sum \overrightarrow{(B \cdot C)} = 2.8; \sum \overrightarrow{(B \cdot D)} = 50.13; \sum \overrightarrow{(B \cdot E)} = 362.537 \sum \overrightarrow{(B \cdot F)} = 1.117$$

$$\sum \overrightarrow{(B \cdot G)} = 3.14 \sum \overrightarrow{(B \cdot I)} = 924.9 \sum \overrightarrow{(C)^2} = 1.16; \sum \overrightarrow{(C \cdot D)} = 9.874 \sum \overrightarrow{(C \cdot E)} = 67.318$$

$$\sum \overrightarrow{(B \cdot H)} = 2.715$$

$$\sum \overrightarrow{(C \cdot F)} = 0.28 \sum \overrightarrow{(C \cdot G)} = 0.68 \sum \overrightarrow{(C \cdot H)} = 0.81 \sum \overrightarrow{(C \cdot I)} = 441. \sum \overrightarrow{(D)^2} = 280.807$$

$$\sum \overrightarrow{(D \cdot E)} = 1.585 \times 1 \sum \overrightarrow{(D \cdot F)} = 5.071 \sum \overrightarrow{(D \cdot G)} = 14.87 \sum \overrightarrow{(D \cdot H)} = 14.029$$

$$\sum \overrightarrow{(D \cdot I)} = 2.631 \times \sum \overrightarrow{(E)^2} = 1.163 \times 10^4 \sum \overrightarrow{(E \cdot F)} = 23.442 \sum \overrightarrow{(E \cdot G)} = 89.966$$

$$\sum \overrightarrow{(E \cdot H)} = 64.6 \sum \overrightarrow{(E \cdot I)} = 1.465 \times 10^4 \sum \overrightarrow{(F)^2} = 0.802 \sum \overrightarrow{(F \cdot G)} = 0.783$$

$$\sum \overrightarrow{(F \cdot H)} = 0.511 \sum \overrightarrow{(F \cdot I)} = 286.2 \sum \overrightarrow{(G)^2} = 1.35 \sum \overrightarrow{(G \cdot H)} = 1.0 \sum \overrightarrow{(G \cdot I)} = 349.2$$

$$\sum \overrightarrow{(H)^2} = 1.545 \sum \overrightarrow{(H \cdot I)} = 408.45 \sum \overrightarrow{(I)^2} = 3.366 \times 10^5$$

$$\sum \overrightarrow{(A \cdot B)} = 69.54; \sum \overrightarrow{(A \cdot C)} = 22.4 \sum \overrightarrow{(A \cdot D)} = 219.0; \sum \overrightarrow{(A \cdot E)} = 1.589 \times 10^3$$

$$\sum \overrightarrow{(A \cdot F)} = 12.737 \sum \overrightarrow{(A \cdot G)} = 20.064 \sum \overrightarrow{(A \cdot H)} = 20.89 \sum \overrightarrow{(A \cdot I)} = 1.251 \times 10^4$$

Substituting these items into 13 to 20 yields

$$12.575a + 2.869b + 50.133c + 362.587d + 1.117e + 3.141f + 924.9g + 4.746h = \text{-----}21$$

$$2.864a + 1.167b + 9.874c + 67.318d + 0.283e + 0.687f + 1.621g + 441.3h = 22. \text{-----}22$$

$$50.133a + 9.824b + 280.807c + 1585d + 5.071e + 14.874f + 24.187g + 2631h = \text{-----}23$$

$$362.573a + 67.318b + 1585c + 11630d + 23.242e + 89.966f + 102.379g + 14650h = \text{-----}24$$

$$1.117a + 0.283b + 5.071c + 23.442d + 0.802e + 0.783f + 0.846g + 286.5h = 12. \text{-----} -25$$

$$3.141a + 0.682b + 14.874c + 89.966d + 0.783e + 1.354f + 1.917g + 349.2h = 20.064 \text{-----} -26$$

$$924.9a + 1.621b + 24.187c + 102.379d + 0.846e + 1.917f + 16.383g + 1007h = 43. \text{-----} -27$$

$$4.746a + 441.3b + 2637c + 14650d + 286.5e + 349.2f + 1007g + 336600h = 12570 \text{-----} -28$$

Equation 21 to 28 forms a 8 x 8 symmetric matrix. A computer software called MathCAD is used to solve the equation to obtain the constant coefficients.

$$ABU := ( 69.53 \quad 22.418 \quad 219.019 \quad 1589 \quad 12.737 \quad 20.064 \quad 20.89 \quad 12570 )^T$$

$$TAK := \begin{pmatrix} 12.575 & 2.869 & 50.133 & 362.537 & 1.117 & 3.141 & 2.715 & 924.9 \\ 2.869 & 1.167 & 9.874 & 67.318 & 0.283 & 0.687 & 0.819 & 441.3 \\ 50.133 & 9.864 & 280.807 & 1585 & 5.071 & 14.874 & 14.029 & 2631 \\ 362.537 & 67.318 & 1585 & 11630 & 23.442 & 89.966 & 64.611 & 14650 \\ 1.117 & 0.283 & 5.071 & 23.442 & 0.802 & 0.783 & 0.511 & 286.5 \\ 3.141 & .682 & 14.874 & 89.966 & 0.783 & 1.354 & 1.027 & 349.2 \\ 2.715 & 0.819 & 14.029 & 64.611 & 0.511 & 1.027 & 1.545 & 408.45 \\ 924.9 & 441.3 & 2631 & 14650 & 286.5 & 349.2 & 408.45 & 336600 \end{pmatrix}$$

$$CONSTANTS := \text{lsolve}(TAK, ABU) \quad M := \overline{CONSTANTS} \quad N := \overline{CONSTANTS}$$

$$M = ( 6.17 \quad -0.107 \quad -0.459 \quad -0.012 \quad 5.645 \quad -4.587 \quad 3.057 \quad 0.021 )$$

$$a := N_1 \quad b := N_2 \quad c := N_3 \quad d := N_4 \quad e := N_5 \quad f := N_6 \quad g := N_7 \quad h := N_8$$

$$pH_M := a \cdot EC + b \cdot NO_3 + c \cdot PO_4 + d \cdot TPH + e \cdot NO_2 + f \cdot CO_3 + g \cdot BOD + h \cdot DIST$$

Therefore, solving these equations gives

$$a = 6.17 \quad b = -0.107 \quad c = -0.459 \quad d = -0.012 \quad e = 5.645$$

$$f = -4.587 \quad g = 3.057 \quad h = 0.021$$

The model equation obtained can be represented as

$$\text{PH}_M = 6.17\text{EC} - 0.107\text{NO}_3 - 0.459\text{P0}_4 - 0.0121\text{TPH} + 5.6458\text{NO}_2 - 4.587\text{CO}_3 \\ + 3.057\text{BOD} + 0.021 \text{Dist}$$

#### 4.1 SIMULATION

Simulation of the model is the use of computer code to show the operation and behaviour of the system. The regression model equations were simulated using the MathCAD. The coefficient of correlation is represented below.

$$R^2 = \frac{\sum (\text{pHM} - \text{mean (pH)})^2}{\sum (\text{pH} - \text{mean (pH)})^2} = 0.962$$

## CHAPTER FIVE

### 5.0 RESULTS

#### 5.1 EXPERIMENTAL RESULTS

**Table 1: Results of Soil Analysis for February taken (horizontally) Om.**

Depth cm	Matrix	PH	E/cond. ms/cm	Org. NO <sub>3</sub> mg/kg	Org. PO <sub>4</sub> mg/cm	TPH mg/kg	Org. NO <sub>2</sub> mg/kg	CO <sub>3</sub> mg/kg	BOD mg/kg
0-15	Soil	5.85	2.35	0.32	12.35	82.88	0.12	0.56	0.15
15-30	Soil	6.40	1.20	0.22	2.15	44.50	0.08	0.32	0.12
30-45	Soil	6.95	0.97	0.13	0.88	25.00	0.05	0.14	0.09
45-60	Soil	7.02	0.68	0.08	0.37	14.89	0.01	0.07	0.05

**Table 2: Results of Soil Analysis for February (vertically) 10m from spill site.**

Depth cm	Matrix	PH	E/cond. ms/cm	Org. NO <sub>3</sub> mg/kg	Org. PO <sub>4</sub> mg/cm	TPH mg/kg	Org. NO <sub>2</sub> mg/kg	CO <sub>3</sub> mg/kg	BOD mg/kg
0-15	Soil	5.53	1.12	0.32	10.10	34.33	0.04	0.42	0.75
15-30	Soil	6.42	1.10	0.10	2.00	20.03	0.08	0.19	0.30
30-45	Soil	6.98	0.88	0.69	0.98	12.08	0.06	0.07	0.21
45-60	Soil	7.00	0.57	0.32	0.34	0.45	0.05	0.01	0.10



**Table 3: Results of Soil Analysis for March (horizontally) 0m from spill site.**

Depth cm	Matrix	P <sup>H</sup>	E/cond. ms/cm	Org. NO <sub>3</sub> mg/kg	Org. P0 <sub>4</sub> mg/cm	TPH mg/kg	Org. NO <sub>2</sub> mg/kg	C0 <sub>3</sub> mg/kg	BOD mg/kg
0-15	Soil	5.03	0.52	0.21	2.62	13.02	0.08	0.24	0.62
15-30	Soil	5.92	0.40	0.14	2.05	0.01	0.08	0.15	0.53
30-45	Soil	6.23	0.31	0.09	1.76	1.48	0.70	0.76	0.32
45-60	Soil	6.95	0.19	0.02	1.21	0.46	0.90	0.10	0.09

**Table 4: Results of Soil Analysis for March (vertically) 10m from spill site.**

Depth cm	Matrix	PH	E/cond. ms/cm	Org. NO <sub>3</sub> mg/kg	Org. P0 <sub>4</sub> mg/cm	TPH mg/kg	Org. NO <sub>2</sub> mg/kg	C0 <sub>3</sub> mg/kg	BOD mg/kg
0-15	Soil	4.23	0.34	0.18	0.15	5.20	0.06	0.12	0.09
15-30	Soil	5.40	0.30	0.20	0.10	3.14	0.03	0.09	0.07
30-45	Soil	6.32	0.27	0.26	0.06	1.20	0.02	0.07	0.04
45-60	Soil	7.12	0.12	0.30	0.02	1.00	0.01	0.03	0.02

## RESULTS OBTAINED FROM A MAJOR SPILL AROUND THE AREA

**Table 5: Results of Analysis at Maintenance Workshop**

Sampling pt	Depth	pH mg/kg	TPH mg/kg	BTEX mg/kg	Cal mg/kg	Pb mg/kg	Ni mg/kg	NO <sub>3</sub> mg/kg	PO <sub>4</sub> <sup>2-</sup> mg/kg	Hydrocarbon Degradar (cfn/0)
Point I	0-15	6.07	4008	0.015	1.00	5.00	18.00	5.68	8.18	5.23 x 10 <sup>5</sup>
	15-30	3.30	644	0.012	1.00	1.25	7.50	4.60	3.00	1.32 x 10 <sup>5</sup>
Point II	0-15	5.96	3160	0.014	1.25	3.75	7.00	10.39	8.14	6.76 x 10 <sup>6</sup>
	15-30	5.10	3344	0.026	0.50	0.63	4.00	9.97	6.26	4.84 x 10 <sup>5</sup>
Point III	0-15	6.85	7824	0.011	0.75	3.13	9.00	15.86	7.18	4.56 x 10 <sup>5</sup>
	15-30	4.82	496	0.032	1.50	0.63	26.00	11.42	2.35	3.76 x 10 <sup>5</sup>
Point IV	0-15	6.28	5520	0.814	5.00	3.75	32.00	11.42	18.68	4.86 x 10 <sup>0</sup>
	15-30	6.03	1456	0.311	3.00	5.00	24.00	9.43	1.50	4.74 x 10 <sup>5</sup>
Point V	0-15	6.33	4312	0.432	4.00	3.75	22.00	9.16	2.66	4.31 x 10 <sup>5</sup>
	15-30	5.97	356	0.007	3.00	6.25	26.00	14.06	7.12	6.36 x 10 <sup>6</sup>

**Table 6: Results of FEPA standard of Industrial Effluent Discharge**

Substance	Max. Concentration (mg/l)
B.O.D	10 - 20
pH	6.5 - 8.5
NO <sub>3</sub>	25
NO <sub>2</sub>	20

## 5.4

**Table 7: Result of the Simulated Values**

$P^H$	$P^H_M$ (simulated)
5.85	6.707
6.4	5.85
6.95	6.129
7.02	4.984
5.53	4.277
6.42	7.383
6.98	7.616
7	6.368
5.03	5.895
5.92	6.026
6.23	5.959
6.95	7.005
4.43	6.082
5.4	6.101
6.32	6.207
7.12	5.677

## 5.5 DISCUSSION OF RESULT

From the result of the analysis of the soil samples it can be observed that; the pH increases with an increase in distance in distance or depth. Also comparing the result in table 1 to 4 with that of table 5, which is the result obtained from the analysis conducted after a major spill. The pH value also increases with increase in distance, this could be attributed to the decomposition rates for species is lower on sites with pH less than 4.5. Then on sites with higher pH values (Hosper, 1989). It can be said that, after spillage the pH values also increases with increase in the depth. 80% of the aerobic bacteria in dip peat could not grow or mobilized nutrient at a lower pH of about 5.5 (Hosper, J. 1989). Using this to analyzed table 5 results, it can be said that, at some site, the plant nutrients will be very poor e.g. pH of 2.90 obtained for the subscription.

The soil component of  $\text{NO}_2$ ,  $\text{NO}_3$ ,  $\text{CO}_3$ , BOD, TPH,  $\text{PO}_4$  and electrical conductivity also decreases with increase in distance or depth as shown in Table 1 to 4. It could also be observed from table 1 to 5 that organic matter increases. This can be attributed to high level of the Organic Hydrocarbon in the soil. Previous studies of oil impacted soil have found that plants growth in such soil were much (Stirlon, R.I.1971). But more crop growth studies of about 2-3 generation and including reproductive characteristics are necessary to establish the quality of crops produced in such soil. Table 6, which show the FEPA allowable standards, shows that, the research in Table 1 to 5 is within the range. This will not have more effect on the crop survival and performance.

Regression modeling of pH in terms of others parameters gives the generation shown below;

$$\text{PH} = 6.17\text{EC} - 0.107\text{NO}_3 - 0.459\text{PO}_4 - 0.0121\text{TPH} + 5.6458\text{NO}_2 - 4.587\text{CO}_3 + 3.057\text{BOD} + 0.021\text{Dist.}$$

From the simulation pH is a function of NO<sub>2</sub>, NO<sub>3</sub>, CO<sub>3</sub>, BOD, Electrical conductivity, PO<sub>4</sub> and TPH and Distance reasonable predicted the observed values of the variance which was determine to be 0.996, for the soil samples. The variation obtained between experimental and computed values could be attributed to the presence of more components in the soil, which are not considered among the components used in the experimental. It can also be attributed to error due to human and experimental procedure.

## 5.6 CONCLUSION

From this model equation the following conclusion can be deduced;

1. The concentration rate of the species in the soil decreases with increase in distance. Hence it will be logical to conclude that the chemical composition of an oil-impacted soil mostly affected is the pH constants.
2. A model equation for predicting the pH, which is a measure of soil quality, has also been developed this equation should be useful in evaluation of effect and quality of the soil after spillage.

## 5.7 RECOMMENDATION

1. There should be an environmental inventory of soil where oil exploration is to commence. This will help access the actual impact of the project on the soil.
2. There is need for the development of monitory sites or units, so that chemical-biological and nutrient pollutants loads are measured along the sites operations continuously.
3. There should be containment pits, which should be properly lined to reduce the effect of the oil on the environment.
4. The pipeline should be change after every ten years, this will minimized spillage due to corrosion of the pipelines.
5. Government should make it as a point of duty to provide amenities and adequately compensate communities within the oil exploration zone, this level help minimized agitation and sabotage.

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