

## **COMPUTER SIMULATION OF THE DISPERSION OF OIL SPILL IN SOIL (A CASE STUDY OF OSHIKA VILLAGE IN RIVERS STATE OF NIGERIA)**

**BALOGUN, Ayodeji Timothy**

B. Tech (Chemical Engineering)

Federal University of Technology, Minna, Niger State.

### **ABSTRACT**

The dispersion of pollutants as a result of oil spillage, which has an unfavorable effect on soil, water and general environment in Niger Delta area of Nigeria was identified as the study area. Attempt at computer simulation of dispersion in soil was explored using visual basic programs. Sampling site were delimited at each area by the grid technique and soil samples were collected at top surface 0-15cm and sub-surface up to 45-60cm depth. The factors measured are pH, electric conductivity, total petroleum hydrocarbon, nitrate, nitrite, carbonate, phosphate and BOD. The results from the sites were compared. From soil level of 0-15cm, site A had the highest pH of 5.82 and site B has the least of 5.03, level 15-30cm site A had 6.40 and site B 5.92. It was discovered that in both sites increase in level increases the level of pH. In site A level 45-60 had the highest pH of 7.02 and B had highest pH of 6.75 in the horizontal direction. The electronic conductivity reduces with increase in level of Site A. soil level 0.15 had had the highest conductivity by 2.35ms/cm and level 45 – 60 had the least by 0.68, organic nitrate 0-15 had the highest by 0.32mg/kg and 45-60cm had the least by 0.08, organic phosphate reduces as the level increases, total petroleum hydrocarbon reduces as the level increases, total petroleum hydrocarbon reduces as the level increases, nitrite, carbonate, BOD also reduces as level increases. In site B the trend activities from, pH, electrical conductivity, organic N03, organic P04, TPH, while N03, C03, and BOD show discrepancies level 30-45cm, having the highest values of 0.7, 0.76 and 0.32 respectively. Site A in vertical direction, increase in the level of soil increases the pH and send trend followed in site B. the other factors from electrical conductivity to BOD reduces as the level increases simulation was carried out to validate the experimental results and there was positive agreement between both of them. Conclusion was reached that the result simulation of model developed based on the modified pollutant transport principle showed conformity with experimental result, the quality of the soil with respect to pH is unacceptable when compared to the Federal Environmental Protection Limit. The computer model developed can help in the estimation of environmental impact of an accidental oil spill and to design efficient emergency strategies and recommendation. Effort should be made by the oil exploring host communities to provide instant support to the people of area affected by the spillage in order to alleviate their problem, and advice the oil producing companies operating in these communities to reduce the level of oil spillage. The results indicate that oil-spill has unfavourably affected the nutrient level and fertility status of Oshika soil, necessitating the inclusion of Oshika in the ongoing remediation technique for soil cleaning in Rivers State.

## 1. INTRODUCTION

### 1.1 Background to the Study

Crude oil is naturally occurring oil, bituminous liquid consists predominantly of several organic chemicals. It is found in large quantities underneath the surface of earth and is used as a fuel and as a raw material in the chemical industries. The Fumes are putrid; respiration is impaired; the local says they cannot fish on river; they can neither farm as their land has being devastated (The Guardian, Tuesday August 20, 2002, Debo Adesina, *Oil spill in Niger Delta area*, Guardian News papers limited, Lagos). Such is the story of communities in the Niger delta region of Nigeria. Of all the diverse ways in which the industrialized world's use of energy can damage the natural environment, the most vivid for many people may be oil spills. On a seemingly regular basis, our newspapers and television screens are filled with pictures of listing tankers spilling crude oil (also known as petroleum), and oil soaked sea-birds in various stages of death. While these oil spills may be the most publicized (the Exxon Valdez for example), accidental spills from tankers account for only about 20% of the crude oil discharged into the world's oceans each year. The remaining 80% is largely a result of routine oil tanker activity such as emptying ballast tanks. There are possible methods of reducing the amount of crude oil released into our oceans each year, but as long as vast amounts of oil are routinely transported by sea, there will be some amount of unavoidable spillage over the year. The people have had their aquatic environment contaminated as a result of oil spillage that refuses to dry up after many years of occurrence.

Oil spills vary widely in magnitude, location, and in the degree of soil, debris and water contamination. In addition to accidental spills, oily waters are encountered in the formation of petroleum (produced water), in numerous waste pits, and in manufacturing activity involving lubricating oils. Although each situation calls for a special set of remediation activity, it is useful to develop a generalized approach that can be adapted to specific conditions. This generalized approach can be visualized in terms of a mathematical model.

There is frequent dispersion of crude in the Niger-Delta Area. These dispersions have really become the topic of the day in the Niger-Delta Area owing to the resulting harm from this problem. On completion of this work, certain measure of crude oil dispersed to reach a particular distance could be predicted. As a corollary, the distance that a particular crude dispersion will reach at a given time will also be predicted using a model equation. The model developed can be simulated with the aid of a computer soft ware called Visual Basic Program in addition to spread sheet programmed to analyze the result for its validity. This can then be used for the control of dispersion of crude oil in the concerned areas.

This project is therefore a input towards the sustainability of the environment of the Niger-Delta Area as the model developed can be used to effectively monitor and predict the extent of movement of the spilled oil. This will enhance oils remediation measure to be put in place.

An oil spill is an accidental release of crude oil or petroleum product. According to the Federal Ministry of Environmental (FME); any spilling, leaking, pumping, pouring, emitting, emptying or dumping that allows harmful quantities of oil to enter the water or soil is regarded as

accidental oil discharge. The effects of oil spill are very visible and sometimes devastating. Petroleum products which have been released into the environment are eventually degraded into simple compound of their constituents element by physiochemical or biological agencies, with or without human assistance and becomes innocuous; but in the process, they may cause serious damage to plant and environment and this impede human exploitation of natural resources (Achem, 1998).

Oil dispersion in soil causes the disaggregation of soil matter, such as clays, by the altering of fluid and surface chemistry to create a suitable suspension. Oil dispersion has been shown to cause slop malfunction, increased soil erosion, reduces in soil electrical conductivity, degradation of soil productivity, increased potential for transport of absorbed contaminants, increase in soil pH, decrease in soil biochemical oxygen demand (BOD), degradation of soil nitrates, phosphates and carbonates. An assessment of the consequences of these environmental contaminations requires an understanding of the extent to which it is responsible for changes in organisms' population in the affected area. Much current research on the effects of oil dispersion in soil which results in soil pollution in directed towards finding sensitive biological response factors, which will allow us to evaluate the state of soil organisms and organic matters exposed to oil under experimental conditions.

Therefore, it is the objective of the present study, to preliminarily assess the toxicity characteristics of Nigerian crude oil on a selected list of environmental impact on organism and other soil organic matter in areas that have experienced an oil spill in the Niger Delta using Oshika Village in Rivers State as a case study. The capability of the government of the day and people to quantify the effect of the resultant soil pollution, contaminant and environmental degradation on the environment cum ineffective monitoring of the activities of the oil exploration, drilling, crude oil transportation by pipeline and loading and discharging of oil by concerned oil companies operators, by the appropriate organs have exposed the people in the Niger Delta area to a lot of health hazard. It is therefore, on this note that a mathematical model and computer simulation that can ascertain the concentration of pollutant and contaminant from the oil spill as it disperses from the source to certain depth in soil will be developed.

Modelling and simulation can be carried out with the aid of computer using some packages powerful software like Excel Polymath, MathCAD, SPSS etc (Giwa, 2004). Simulation represents the application of modelling techniques to real system. This enables information on plant characteristic to be gained without constructing or operating the full-scale plants or system under consideration. Simulation methods are of two types namely: Digital Simulation and Analogue Simulation, of these two, Digital Simulation which involves the use of codes and programs are more in use since they can be implemented on modern computer with exceptional speed (William, 1995).

## **1.2 Statement to the Problem**

Oil spillage in the Niger Delta area of Southern Nigeria has become a public concern as a result of its frequent occurrence which has been linked with petroleum exploration and development activities. Crude oil spill affects plants negatively by creating conditions which makes essential

nutrients like nitrogen, oxygen etc needs for plant growth unavailable to them from the spilled affected soil. Therefore, the purpose of this study is to evaluate the effects of oil spillage using computer simulation of oil spillage on soil properties in these areas. The result will give an insight to the level of damage that oil spill has done to the fertility and nutrient status of the community farmland.

### **1.3 Aim of the Study**

The aim of this project is to develop a model and computer simulation of oil dispersion in soil in the Niger Delta area of Nigeria due to oil spillage from the activity of oil companies.

### **1.4 Objectives of the Study**

The objectives of the study are stated below:

1. To present some unfavourable effects of crude oil dispersion in soil and how it affects man and soil organic matter.
2. To study the population dynamics, stock size and survival strategy of the environmental factors affected in the soil i.e. soil porosity, hydrological factors, soil topography, soil pH etc.
3. To develop a productive model that will ascertain dispersion of oil in soil as it dispersed from the source of the spillage.
4. To simulate the developed model equation by computer program using visual basic programming language.

### **1.5 Scope of the Study**

The project focuses on computer simulation of oil dispersion in soil in the Niger Delta are of Nigeria. This will enable us to know actually the economic impact of the spillage on the environment, to know the clean-up strategy for the spill exercise, to also identify the source of the spillage and the legal implications of the spillage when compared with the Federal Environmental Protection Agency (FEPA) and the regulation Act of the Department of Petroleum Agency Resources (DPR) minimum acceptable level of oil spillage dispersion in soil.

## **2. LITERATURE REVIEW**

### **2.1 Introduction**

Crude oil or petroleum (derived from Latin petrus-rock and oleum-oil) or mineral oil is a thick, dark brown or greenish flammable liquid, which, at certain points, exists in the upper strata of Earth's crust. It consists of a complex mixture of various hydrocarbons, largely of the methane series, but may vary much in appearance, composition, and Crude oil properties. It can be shortened to the prefix petro-, as in "petrodiesel"

Oil Spill: An oil spill is the release of crude oil into the natural environment, usually the ocean. An oil spill that occurs near a coastline will always impact more living organisms than one

which occurs in the open ocean. This is simply because coastal areas are home to much more concentrated and diversified populations of marine life than the open ocean. Nevertheless, all oil spills have an impact on marine organisms, and oil from open ocean spills can end up contaminating beaches hundreds of miles away. Oil spills can harm marine life in three different ways, by poisoning after ingestion, by direct contact and by destroying habitats.

## **2.2 Formation of Crude Oil and Types**

Crude oil is a naturally occurring complex mixture of predominantly hydrocarbons and non-hydrocarbon derivative ranging in molecular weight from methane to heavy bitumen. Petroleum or crude oil consists largely of gaseous mixtures of liquids and solid hydrocarbon. It is believed to have been formed by the effect of heat and pressure on decomposing marine organisms. Crude oils from the various part of the world have variable composition i.e. some are predominantly paraffinic (e.g. Nigeria, North America such as Pennsylvania oil), whereas some oils are predominantly Naphthenic (e.g. Soviet Union Oil) while some contain both paraffin and Nap thins as the main constituent, together with some aromatic compounds e.g. Indonesian oils (Edoga, 2003).

## **2.3 Mechanisms of Petroleum Activity**

When oil is found in a well, casings and pipes are sunk, and such a well is linked with other producing oil wells. From the well-head, the crude oil flows to a flow station where oil and gas are separated, the crude oil measured and gases formation gauged. The oil then flows from the flow station to the oil terminal where water is separated and the crude oil is ready for export.

Oil terminals in Nigeria include Bonny, Forcados-Brass, Escarvos and Qua Iboe. Drilling of crude oil wells may be either on land (Onshore drilling) or under the sea (Offshore drilling). Millions of Naira is incurred in the search for formation of crude oil (Nwafor, 2002).

## **2.4 Pollution**

### **2.4.1 Sources of Oil Pollution in Soil**

As long as petroleum exploration, formation, refining and transportation continue, there will always be dangers of an accidental release of oil. In general, known sources of soil spillage in Nigeria includes:

- i. Onshore and Offshore exploration and formation activities.
- ii. Petroleum (crude oil) refining activity
- iii. Transportation of oil activities i.e. spills from tankers such as loading and discharging activity.
- iv. Bunkering activities: this normally occurs in Port or at Oil terminals.
- v. Indiscriminate dumping of waste oil by companies and individuals utilizing petroleum products.

## **2.5 Classification of Oil Spill**

### **2.5.1 Minor Spill**

This refers to a spill or release of oil less than 25 barrels on land, offshore or coastal water that does not pose a serious threat to the health of the public (Asunmo, 2003).

### **2.5.2 Major Spill**

This refers to a spill or release of oil over 2500 barrels on land, offshore and coastal water. Any spills that pose a serious threat to the health and welfare of the public may be classified as medium or major spill depending upon its degree of impact on environmental lives (Asunmo, 2003).

## **2.6 Causes of Oil Spillage**

The causes of oil spills are many. They are mistakes or carelessness from people, break down of equipment, natural disasters such as hurricanes, deliberate acts by terrorists, countries at war and vandals, or illegal dumpers. Whatever the cause, most spills can be prevented by proper engineering practices, equipment and procedures.

The main causes of oil spill in the Nigerian Petroleum Industry are not entirely different from what exists in other parts of the world. However, Nwakwo 1983 observed that there are a few peculiarities characteristic of the Nigerian situation. According to him, the main causes are:

- i. Burst/Rupture/Corrosion of flow line/pipelines;
- ii. Over pressure malfunctions/overflow of process equipment components;
- iii. Sabotages of oil well heads and flow lines;
- iv. Hose malfunction on the tanker loading system i.e. accidental discharge;
- v. Oil well blowout.

Pipeline leakage or canalizations have accounted for over 30% of the total occurrence of oil spillage, and added to well over 50% of oil spilled. Pollution arising from sabotage appears to be peculiar to Nigeria. The motivation for these acts can be attributed to three major reasons, namely:

- i. A wrong sense of revenge on the action of certain oil operator
- ii. Theft, and
- iii. Manoeuvres of claim compensations probably because of the apparent lack of sensitivities, for the welfare of the people in the contaminated area on the part of the operating companies. From the numerous investigation of oil spills incident in Nigeria, the causes of oil as pillage can be broadly classified into oil well blowout, accidental discharge, sabotage and natural causes.

## **2.7 Oil Well Blowout**

An oil well blowout occurs when formation fluid (oil and gas) flow uncontrolled out of the well bore. This can only occur when an oil or gas well is being drilled, it could result from

human error or equipment malfunction and the consequences could be very disastrous as huge volumes of oil and gas may spew out of the well bore with probability of damage to the drilling rig and personnel as well as the equipment. Example includes Texaco's Funiwa – 5 well blowouts in 1980 and Shell's Apará well blowout in 1963. To prevent well blowouts, only the best equipment in addition to the best oil field practices is employed in drilling activity (Oladipo, 2000).

## **2.8 Accidental Discharges**

Tanker accidents which have mostly been traced to human error is another cause of oil spillage e.g. Torray Canyon Spill in 1957. Accidental causes may also be due to equipment malfunction apart from human error. Equipment malfunction could be due to malfunctioning, age, overloading, corrosion, or abrasion of part of the facilities and equipment malfunction (Achem, 1998).

## **2.9 Operational Discharges**

By the nature of oils, some oil is expected to escape in small quantities during oil activities e.g. when changing connection or transferring oil from one vessel or container to another. At industrial sites, such little drops could build up to a substantial measure which then poses a serious treat or problem of disposal (Achem, 1998).

## **2.10 Sabotage**

Sabotage cases refer to deliberate obstruction of normal activities of oil facilities. These may be pipeline vandalization, revenge by individuals or community for an act of a particular oil operator or to get some monetary compensation from the oil concerned.

## **2.11 Natural Causes**

Natural causes such as wind hurricane, cyclone, storm, flood etc also added to to oil spillage on land, offshore and coastal water.

## **2.12 Environmental effect of Oil Spill on Soil**

The environmental effects of discharges from pollutant of oil spillage have great effect on human health, aquatic and terrestrial plant. The catastrophic events that are associated with oil exploration and formation that introduces large amount of oil into the environment, induces the well blowout account for the largest single source of oil entering the environment.

## **2.13 Effect of Oil Spill on Crop Performance**

When oil spill is on land, it has potential to impair the contaminated soil for farming. Spilled oil may prevent the germination of growth of crops. Plants exchange the gases involved in respiration and photosynthesis through small pores, mostly on their leaves, anaerobic soil also transport air from the soil pores to their roots, improving the soil condition locally (Jackson, 1958). The soil pores may be readily penetrated by thin oil, a process which is usually

demonstrated by a darkening of the plant leaves as its air-spaces become filled with the oil. Once it has received a significant covering of active oil, an individual leaf invariably dies.

Oil percolation into the soil around the root may interfere with its uptake of water or causes the release of substances to the plant. In soil affected by oil spills, processes like nitrification, denitrification, nitrogen fixation, sulphate reduction, phosphate uptake and photosynthesis did not occur at sufficient levels compared to the control site where there is no oil spillage (Achem, 1998).

#### **2.14 Economic Hazards of the Oil Spill**

1. There is reduction in food formation from the area that their land is covered by oil.
2. When oil is spilled on water, fishing and fish farming which are economic activities and which constitute a major source of labour and revenue for many communities are affected. Spillage of oil can destroy these economic activities with potential unquantifiable results.
3. When oil is spilled on land, it has the potential to impair the contaminated soil for farming and dwelling. This has an impact on the income and choice of place to live by the affected parties.
4. Tourism in beaches and diving in coral reefs are both economic and recreational activities that are affected by oil spillage.

#### **2.15 Economic Cost of Oil Spill**

The economic cost of the above hazards is enormous and is never fully quantified by the stakeholders in an oil spill event. For example, the economic losses arising from an oil spill via a pipeline rupture includes:

1. The values of the oil spilled are not recovered (i.e. the volume of the spilled oil multiplied by the crude oil price on the international market).
2. The loss of formation for the duration that the pipeline is shut down for use.
3. The actual cost of repairing the pipeline including the cost of transporting men, materials and equipment to site and the manpower cost.
4. Cost of settling the affected communities as parts of compensation.
5. The cost of clean-up of the oil spill, etc (Oladipo, 2000).

#### **2.16 Strategy for Combating Oil Spill**

There will always be dangers of an accidental release of oil as long as petroleum is produced and transported and until there are possibilities for human error or equipment breakdown. The behaviour of oil at sea or land and the possibility of stopping a given spill depend, on the nature of the petroleum product, on hydro-geo-meteorological conditions and on large numbers of other factors.



### **2.17 Anti-Pollution Strategy**

To be efficiently prepared means that one has planned the organization and the general course of anti-pollution activity. So, three objectives must be studied; viz.

- i. Establishment of a contingency plan
- ii. Training of available personnel
- iii. A good knowledge of the tactics and techniques in the flight against oil pollution.

### **2.18 Contingency Plan (CP)**

Each emergency situation necessitates prompt, accurate and efficient response. In the case of an oil spillage, and particularly a major one, much time can be lost during the first hours after the accident. The loss of time is generally due to lack of:

- i. Precise organization scheme, allocating responsibilities and duties.
- ii. Knowledge of available resources of manpower and equipment.
- iii. Environmental data on affected areas.

Then, the objective of the CP is to provide adequate response in case of an incident causing or likely to cause an oil spillage. This plan must clearly define;

- i. Policy statement
- ii. Organization charts
- iii. The role of each unit involved in the intervention
- iv. A plan of command
- v. A transmission network
- vi. The available means of personnel and equipments
- vii. Operational procedures

Here, there must be a person, usually called On-scene commander or On-Scene-coordinator (OSC) who will be responsible for all actions taken during the entire response activities. Some times OSC will be responsible for general policy, operational decisions and strategy at the same time. Since one person cannot physically cope with all the requirements of an oil spill response activity, a team of specialists who work as his assistants will support the OSC. This command team will usually include:

1. Legal adviser,
2. Technical manager,
3. Public relations officer,
4. Financial officer,
5. Record keeper and any other specialist considered necessary by the OSC. The principal function of a command team will include:
  - i. Surveillance, monitoring and analysis
  - ii. Decision taking on appropriate counter measures
  - iii. Communications co-ordination of assistance

- iv. Government liaison
- v. Relations with mass media
- vi. Scientific advice (ecological, geological, biological, etc)
- vii. Legal advice
- viii. Log keeping
- ix. Preparation of indemnification claims (Abdel, 1999)

Spill response teams including work teams and support teams will carry out the OSC and his command team. The functions of work teams include:

- i. Oil containment
- ii. Oil recovery
- iii. Application of chemicals
- iv. Application of other treatment products
- v. Shore clean-up
- vi. Storage and transportation
- vii. Disposal of collected material

The logistic support provided by support teams is extremely primal for the smooth running of activity and it includes:

- i. Provision of equipment and products
- ii. Provision of fuel
- iii. Catering services (food and drinks)
- iv. Provision of accommodation
- v. Transport of personnel and equipment
- vi. Maintenance of vehicles, vessels and equipment

Oil spill response activity can only start once the local or national authority responsible for oil pollution control is informed about the occurrence of an accident. The discussion made and the type of size of the response activity will depend directly on the contents of information received by the concerned authority and the designed OSC.

## **2.19 Personnel Training**

The 1990 international conference on oil pollution preparedness and response adopted resolution 7 stipulating that the capability of the state to respond to an oil pollution incident rely on the response personnel. The conference agreed that there is a need for an increased global effort by all those concerned with the land and maritime transport of oil and its environmental impact towards the development of a global training program in oil pollution preparedness and response. In general, three levels could be identified for training purposes namely:

- i. Senior government and private sector management personnel responsible for high level decision-making. They require training including demonstrations of clean-up equipment and facilities for operational control.
- ii. Middle management personnel responsible for the preparation of contingency and response action plans and conduct effective activity. They require courses of longer duration and greater frequency.
- iii. Operational staff in charge of clean-up activity on site. They need to know the basic oil spill combating and preventing or limiting techniques including the use of booms, skimmers, sprays, pumps dispersants etc on site.

Personnel familiar with different techniques and antipollution equipment will considerably improve the quality and the speed of an operational response (Abdel, 1999).

## **2.20 Anti-Pollution Tactics and Techniques**

It is difficult to bring a readymade solution to all the problems which result from an oil spill, but rather, it is possible to apply a method which allows an analysis of the situation in order to best use the available means. A statistical analysis of the major land oil spill has shown that 30 59 70% of the released petroleum washes up on the shore.

Two major tactics of intervention are conceivable

- i. To stop or decrease the source of pollution as quickly as possible.
- ii. To combat and reduce the pollution when it occurs. The effectiveness of the first tactic limits the quantities of pollutant, which must be treated by the second tactic.

The choice between the two tactics, which are obviously not mutually exclusive, is due to various circumstances, which are called the factors of the incident.

- i. The origin of pollution
- ii. The cause of pollution
- iii. The characteristics
- iv. The weather and climate conditions
- v. Location
- vi. Resources

An understanding of these factors will allow the adoption of a preventive tactic, if pollution has not yet taken place or a corrective tactic, if a pollutant is already discharged. The second tactic, which consists of fighting and reducing pollution, can be applied from the sea (fight at sea) or from the land (fight on land) (Abdel, 1999).

## **2.21 Oil Spill Cleaning-Up Techniques**

These techniques are essential in either mechanical and/or chemical treatments. Leave alone action can also be considered as method of clean-up.

### 2.21.1 Cleaning up Technique at Sea

Clean-up techniques at sea can be mechanical or chemical treatments techniques.

**Mechanical Technique (Spill Containment and Oil Recovery):** Booms are used for oil collection, deflection, containments, protection and prevention of the spread of oil over the sea surface, oil skimmers are used for the collection and recovery of oil spilled on water and come in wide range in shapes and sizes. Skimmers are used to collect oil from the surface of the water, however, their efficiency depend on several factors such as:

- i. Oil thickness
- ii. Oil viscosity or degree of emulsification
- iii. States of the sea
- iv. Weather conditions (air temperature, sea surface temperature, wind etc).

Many skimmers do not operate effectively in shallow shoreline areas of on beaches; one type of skimming device that has been widely used for picking up oil in shallow shoreline waters or directly from beaches in the vacuum system. There are three main types of vacuum systems used in oil spill cleanup activities, they fall into one the following categories.

- i. Vacuum tankers – high vacuum/low air flow rate
- ii. Air conveyors-low vacuum/low air flow rate
- iii. Portable vacuum system (intermediates vacuum and flow rate)

**Chemical Treatment (Sorbents):** Sorbents act by adsorbing oil floating on the surface, because of their very low density, they continue to float when they are impregnated with oil, and they can be harvested by mechanical process.

### 2.21.2 Dispersants

Oil spill dispersants are used according to the following conditions.

- i. To decrease the interfacial tension between the oil and the soil water
- ii. To prevent coalescence of oil droplets after dispersion
- iii. To rapidly disperse the oil mainly on the lowering oil concentration
- iv. To enhance the biodegradation process.

Moreover, it is always difficult to decide whether to use dispersant or not, the decision will be taken, according to the authorities' approval, but we should known that there are many disadvantages in using dispersants if it is acceptable (Abdel, 1999).

## 2.22 Cleaning-UP Techniques on Land and Shores

When a large spill of oil occur in land area or near the coast where oil reaches the shore, several techniques can be used to clean up the land soil or the coastline, the coastline, the selection of the type of treatment on the land soil or shore will depend on the following:

- i. The type of oil and the amount of oil on the land soil or shore.

- ii. The nature of the land or coast
- iii. The depth of oil penetration into land soil or shore sediments
- iv. The accessibility and traffic capability of the land area or shoreline environment.

In general, the cleaning up techniques on land and shores may be classified into:

1. Mechanical pick-up
2. Hydraulic cleaning and sand blasting

Common clean-up methods on land include in-situ bioremediation, natural attenuation, pump, excavation and incineration and soil washing.

### 3. MATERIALS AND METHODS

#### 3.1 Introduction

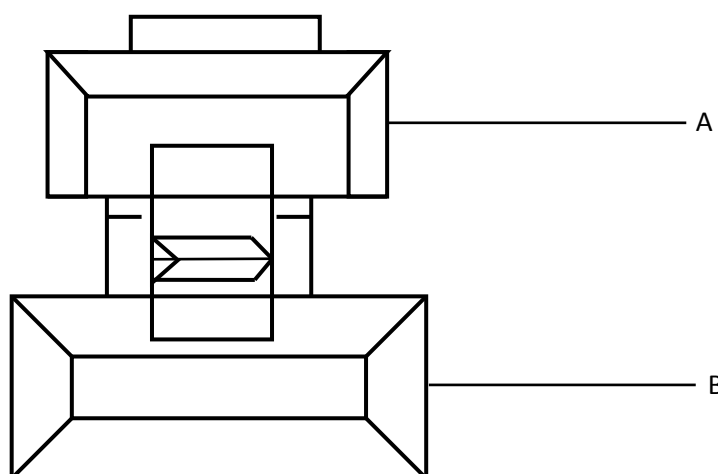
The study area, Oshika, is located in Rivers State in the Southern part of Nigeria. The Study was carried out between 2008 and 2010.

#### 3.2 Sample Collection and Method

Samples were randomly collected at the depth of 0-15cm, 15-30cm, 30-45cm up to 45-60cm, the respective samples were taken to the laboratory, air dried, sieved through 2mm sieve and stored in plastic bags for analysis. The sample site was delimited at each area by grid technique and the soil samples were collected and the factors measured were pH, electric conductivity, total petroleum hydrocarbon, nitrate, nitrite, carbonate, phosphate and BOD. These were ascertained using standard method.

#### 3.3 Experimental Procedure

The presence of the components to be analyzed and contamination of the land by crude oil was tested using the oil detector pan shown below:



**Fig. 3.1: Detector pan used to Measure the Contaminated or Spilled Oil**

0.5 liters of water was poured into both pan A and B and 3200 grams of the suspected oil contaminated soil mixture which is sandy soil was added into the water in Pan A. the soil sample were mixed up together using a small iron rod. After mixing the mixture was left for about 1-3 minutes, then the water in pan A was allowed to flow into pan B. serious attention was paid to the color changes and the behaviors' of the floating layer. Thick floating layer was observed, observation with anti-reflection plate makes the layer thinner coming out with a blue color, with indicates diesel or fuel oil. The pans was then washed and rinsed for next use. Three (3) tests were carried out in the spilled area to confirm the presence of fuel oil in it (Jackson, 1958).

All these samples were air dried, sieved and analyzed for pH, electrical conductivity, organic nitrates, total petroleum hydrocarbon (TPH), biodegradable oxygen demand (BOD), carbonates and particulate organic phosphates.

### 3.4 Measuring Porosity

Several methods can be employed to measure porosity:

1. Direct methods (determining the bulk volume of the porous sample, and then determining the volume of the skeletal material with no pores (pore volume = total volume – material volume).
2. Optical methods (e.g., determining the area of the material versus the area of the pores visible under the microscope). The "areal" and "volumetric" porosities are equal for porous media with random structure.
3. Computed tomography method (using industrial CT scanning to create a 3D rendering of external and internal geometry, including voids. Then implementing a defect analysis utilizing computer software.
4. Imbibition methods, i.e., immersion of the porous sample, under vacuum, in a fluid that preferentially wets the pores.
5. Water saturation method (pore volume = total volume of water – volume of water left after soaking).

### 3.5 Determination of Biodegradable Oxygen Demand (BOD)

This is the amount of oxygen required by the bacteria to reduce some of the organic matter in a composite (waste) under standard condition. The BOD serves as the useful measures of the quality of biodegradable matters, which serve as food for bacteria. This is defined as the difference in values of dissolved oxygen at day 1 and 5 of the sample.

#### 3.5.1 Procedure for BOD Determination

The impacted soil sample was collected at the site of the oil spillage, it was placed in an ambered (dark) colour glass bottle with screw cap, and the sample was filled to the brim in the glass bottle and was taken to the laboratory. Sample from each site was duplicated.

The dissolved oxygen (DO) meter probe, after proper calibration was inserted into each bottle containing impacted soil sample; the reading observed was recorded as DO1. The sample after the reading was immediately transferred to an incubated and left there for 5<sup>th</sup> days on the sample gave a reading of DO5 (Jackson, 1958).

BOD (mg/kg) =

Where, DO1 – dissolved oxygen after sample preparation i.e. day 1 in mg/kg.

DO5 – Dissolved oxygen of dilute sample after 5 days of incubation in mg/kg.

P – Decimal volumetric fraction of the sample used.

### 3.6 pH Determination

The pH values usually serve as the measure of acidity of alkalinity of a substance and it is the usual measure or means of expressing the hydrogen ion concentration of a substance. From the pH scale, the pH less than values of 7 indicate acidic, pH of 7 indicates neutral while the pH greater than 7 indicates alkaline substance.

$\text{pH} = -\log_{10}(\text{H}^+)$

where,  $(\text{H}^+)$  – the hydrogen ion concentration.

### 3.7 Procedure for pH Determination

Log of air-dried soil sample were collected and weighed accurately into two beakers. 250ml of distilled water was added and stirred for period of time with the aid of magnetic stirrer. This was then allowed to settle for 5 – 10 minutes, before the Oion Model 1260 pH meter is used to take the pH of the soil. The meter was calibrated prior to use with buffer standards of 4 & 7. Samples were analyzed by dipping the probe of the meter into the soil and water suspension of 1:1 ration (Jackson, 1958).

### 3.8 Electrical Conductivity Determination

Electrical conductivity is the numerical expression of the capability of an aqueous solution to conduct an electric current in the system. This capability of the aqueous solution rely on the presence of ions, their total concentration, valence and relative concentration and as well as temperature of measurement of solution of relatively good conductors, while molecules of organic compounds that do not dissolve in aqueous solution conduct current very poorly. The electrical conductivity determination serves a very useful purpose in chemical analysis and in the estimation of total solids.

### 3.9 Procedure for Electrical Conductivity Determination

It was ascertained electrically with conductivity meter (Orion 150) in accordance with American Public Health Association (APHA) 2501B. The equipment was calibrated with potassium chloride of 0.01m and 0.1 m at two ranges of 12g/cm and 1413mg/cm. the

conductivity probe was immersed in the soil with water suspension of ratio 1:1 and its reading was noted and recorded (Ekpeta et al., 1964).

### **3.10 Determination of Total Petroleum Hydrocarbon (TPH)**

#### **3.10.1 Procedure**

These are ascertained calorimetrically in accordance with the water operational guide 1987, using Unicam Ultraviolet/Visible spectrometer. Soil samples were extracted with sodium acetate while extracts for NO<sub>3</sub> were analyzed using brucine (2.5%) in the presence of concentrated sulphuric acid at 470nm. Meanwhile, NO<sub>2</sub> was analyzed using sulphuric acid with dissolved 30% acetic acid with alpha Naphthylamine in acid solution at 520nm (Silverstein et al., 1950).

### **3.11 Determination of Phosphate**

#### **3.11.1 Procedure**

Phosphate was ascertained in accordance with stannous chloride reduction methods by the American Public Health Association (APHA), 42AE-using UNICAM ULTRAVIOLET/VISIBLE SPECTROMETER. Soil samples are extracted with 25% acetic acid and the extract was run on the ultraviolet at a wavelength of 700nm (Silverstein et al., 1950).

### **3.12 Determination of Carbonate (CO<sub>3</sub><sup>2-</sup>)**

#### **3.12.1 Procedure**

0.05M Sodium hydroxide solution (NaOH), 2cm<sup>3</sup> of concentrated HCL diluted to 1000cm<sup>3</sup> in a volumetric flask and methyl red indicator are the reagents needed for the determination of Carbonates. 10g of the soil sample were placed in 30cm<sup>3</sup> of distilled water in a beaker. Filter paper was used to filter the sample. 25cm<sup>3</sup> of the filtrate was pipette into a conical flask and two drops methyl red indicator was added. The sample was then titrated with the acid i.e. HCl. The volume of the acid was noted and the average volume of the acid used was ascertained. The concentration of carbonates in the filtrate was ascertained.

### **3.13 Mathematical Modelling and Computer Simulation**

Mathematical modelling and simulation are relatively new analytical tools available to the engineer concerned with the analysis, design or activities of control systems. Mathematical modelling and simulation can result in an increase in the fundamental knowledge about a system since it usually involves a considerable analysis of the system.



### 3.14 **Basis of Fundamental Laws**

The basis for mathematical model is fundamental physical and chemical laws, which are obtainable from physical sciences. They includes the law of conservation of energy and matter/mass, the law of conservation of momentum, the law of mass and material transport phenomena, mass and material balance equations etc. stated in their time derivative forms. Factors, which are included, are mass transfer coefficient, hydraulic conductivity, manning's roughness coefficient, effective porosity etc that are either obtained experimentally or from process operating databank.

### 3.15 **Assumptions**

For effective engineering and scientific prediction, provable assumption has to be made in order to simplify the system while modelling. A simple model need many assumption and yield an approximate result quickly while a more complicated model of the same system need fewer assumptions and yield a more accurate answer by more advanced mathematical techniques. During the assessment of result obtained, all assumption made in the modelling procedure must be carefully considered.

### 3.16 **Mathematical Consistency of the Model**

There must be a greater consistency in the unit of term of the equations used in the model. Consistency checks are essential as they save many hours/days of frustration, confusion and wasted computing time. Great care must be taken not to under specify or over specify the numbers of variable or equation describing the system because in order to obtain a solution, the numbers of variable must be equal to the number of equation i.e. the "degree of freedom" of the system must be zero" (William, 1990).

### 3.17 **Model Equation Solution**

Solution techniques are tools that must be kept in mind whenever a model is being developed. Possible approximations for the defining equation, boundary and initial condition as well as an acceptable final solution are considered in the search for a method of model equations' solution.

### 3.18 **Verification of the Model Results**

The validity of a model is a primal part of a mathematical modelling and there is a need to prove such validity. One way of achieving this objective of verifying a model is by comparing average experimental result for similar activities condition to that of the computer result. Usually, verification of model result is very tedious using manual method, but with the aid of computer, model verification is made easy and simple and requires little time for completion.

### 3.19 **Simulation**

Simulation involves subjecting models to various changes in such a way as to explore effects of these changes on the real system. "Simulation of a system is the activities of a model which

would be impossible, to expensive or impracticable to perform on the real system it portrays” as defined by Martin Shubik.

Simulation can be carried out with the aid of the computer using some packages powerful software like excel, polymath, MathCAD, SPSS etc. Simulation is very primal in that:

- i. It results in considerable saving of both time and money
- ii. It can result in an increase in the fundamental knowledge about a system since it usually involves considerable analysis of the system.
- iii. It gives greater understanding and insight into the behaviour of the physical system and the principle upon which its design is based.
- iv. It provides a convenient, inexpensive and time saving means of gaining understating and a variety of activities condition.
- v. When it is impractical to experiment with the real system. Simulation can be used to explore the effect of changes on a system.

### 3.20 Process Simulation

Process of simulation could be described as a three-step process

1. A mathematical model is first created to describe the behaviour of the system being studied.
2. The mathematical model is manipulated wherever possible and practicable to give the desired information concerning the system.
3. Whenever conventional mathematical manipulation is impractical the analogue/digital computer may be used to simulate the mathematical model (Asunmo, 2003).

### 3.21 Simulation Procedure

The procedure for carrying out the manipulations stated above as follows:

- i. Data collection
- ii. Problem analysis
- iii. Simulation model specification
- iv. Model programming
- v. Model verification
- vi. Simulation experimentation
- vii. Assessment and interpretation of simulation results
- viii. Report generation (Aunmo, 2003).

### 3.22 Programming Language

Programming is defined, as the process of converting broad system specifications into usual machine instructions that produces desired results. The act of giving instructions to a computer is made possible through the use of programming languages. Simply put, a programming language is the medium of communicating with computers. It is the form of an artificially

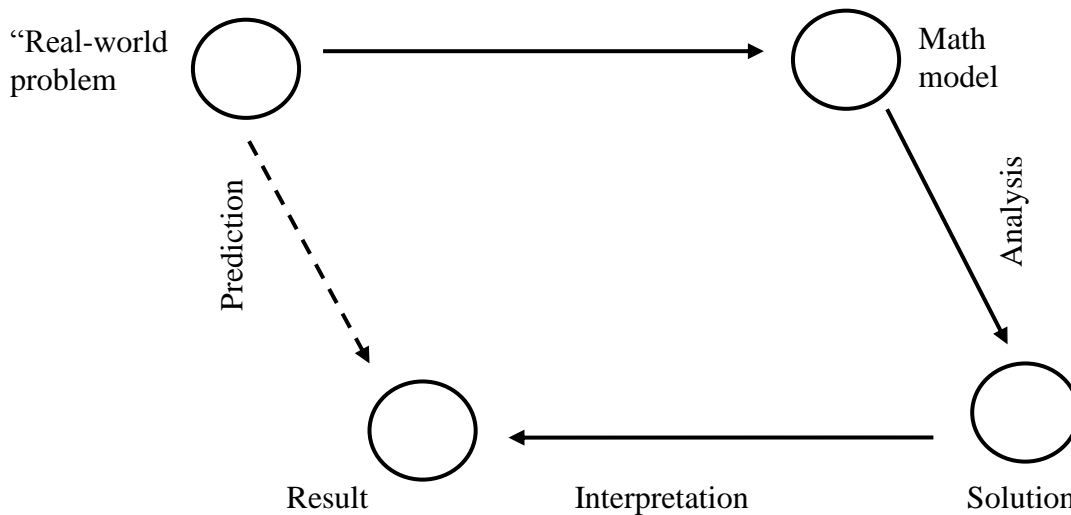
defined set of characters, symbols and words plus the rules for combining these characters, symbols and words into meaningful communication.

In the course of developing the computer software for the “computer simulation of oil dispersion in soil”, in his project work, the Visual Basic (VB) programming language is employed, through there are other programming languages such as Q basic, D base III etc.

### 3.23 Oil Dispersion Modeling

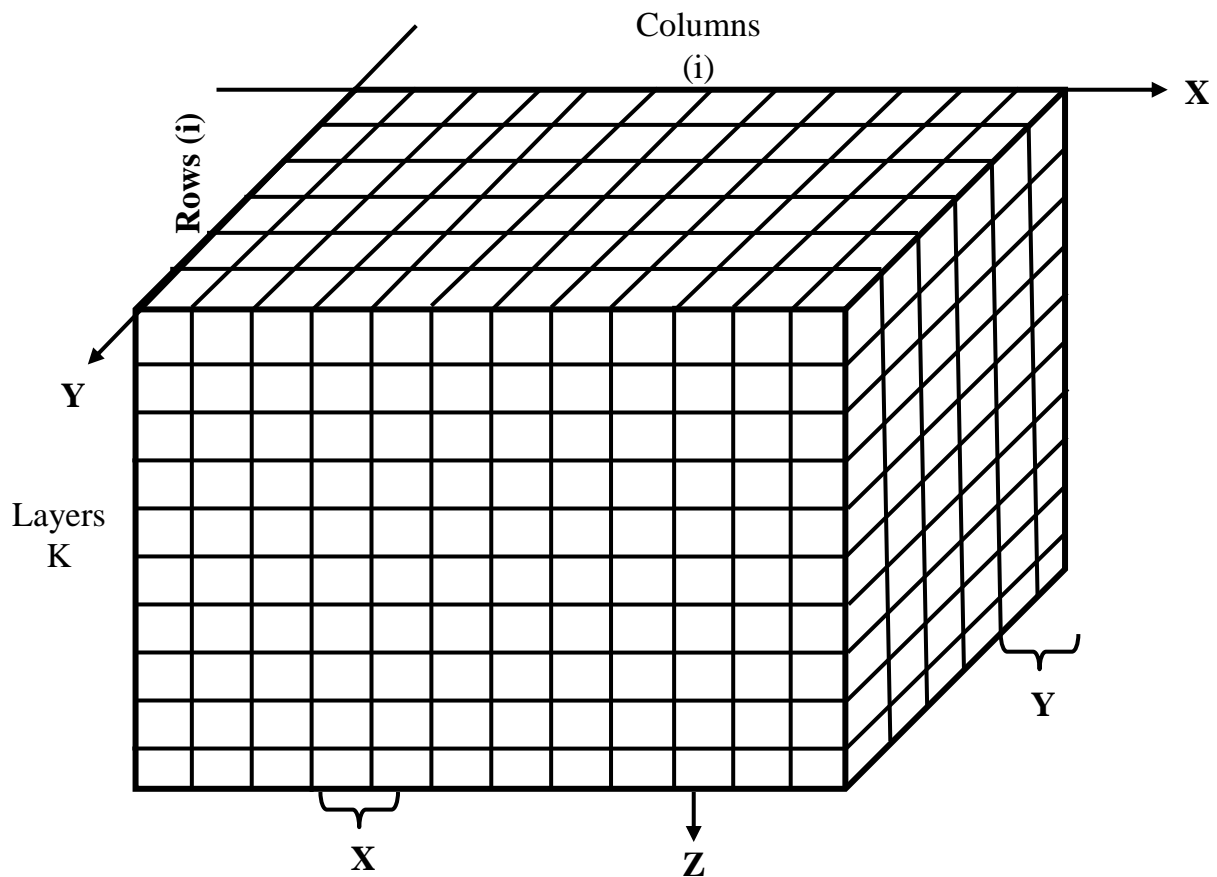
Many authorities have prepared all spill contingency plans, a primal element in these plans in the use of computer to predict the movement of spilled oil and its possible impact. Modeling of oil spills requires combining several components some of which are interrelated. The two main components: hydrodynamics and the physiochemical aspects of the oil. The capability to predict oil spills movement will assist in the assessment of damage. Computer modeling in the best way to predict the oil spill movement (Beer *et al.*, 1983). Models for predicting the transport of oil spills were done by Cuesta *et al.*, 1990, using the continuity and momentum conservation equation and by Shankar *et al.*, 1996, using the 2.D depth averaged transport dispersion equation (Mohammed, 1999).

A mathematical model of a physical system is a portrait in the symbolic language of mathematics. Like all portraits, the model will emphasize some feature of the original and ignore or distort others. Thus, the modeling process is as much an art as it is a logical process as shown below:



(Robert L. *et al.*, 1992).

**Figure 3.2: The Modeling Process**



**Figure 3.3: Block Diagram of Oil Spill Dispersion Along X, Y And Z Direction**

----- Aquifer Boundary

- i. Active cell
- ii. Inactive cell

### 3.24 Assumption

1. The equilibrium controlled linear or non-linear sorption and order irreversible are reaction are involved in the chemical reaction.
2. The velocity of dispersion of oil is the same as the velocity of ground water.
3. The movement of oil along the x, y axes are uniform
4. Hydrodynamic coefficients are constant and,
5. X, Y, and Z coordinate axes are oriented along the row, column and layer directions, respectively. The origin of the Cartesian coordinate is located at the upper top, left corner of the cell at the first row, first column and first layer or cell (1, 1,1) as illustrated in the Fig 2.1

### 3.25 Fundamentals of Transport Model

#### 3.25.1 Governing Equation

The partial differentiation equation describe three-dimensional transports of contaminant in groundwater can be written as follows (Javandel *et al.*, 1984).

$$\frac{\delta c}{\delta t} = \frac{\partial}{\partial x} Dy \frac{\delta c}{\delta x_j} - \frac{\delta}{\delta x_t} (V_t C) + \frac{q}{\theta} C + \sum_{k=1}^N R_k \quad 3.1$$

Where;

C is the concentration of contaminant dissolved in groundwater, kg/m<sup>3</sup>

t is time; s

x<sub>j</sub> is the distance along the respective Cartesian coordinate axis, m

Dy is the hydrodynamic dispersion coefficient, m<sup>2</sup>/s

V<sub>t</sub> is the seepage or linear pore water velocity, m/s

q<sub>s</sub> is the volumetric flux of water per unit volume of aquifer representing sources (positive) and sinks (negative), s<sup>-1</sup>.

C<sub>s</sub> is the concentration of the sources of sinks, kg/m<sup>3</sup>

θ is the porosity of the porous medium dimensionless,

$\sum_{k=1}^n R_k$  is a chemical reaction term. ML<sup>-3</sup> T<sup>-1</sup>

From assumption (1) equilibrium controlled linear or non-linear sorption and first irreversible rate reactions are involved in the chemical reactions, the chemical reaction term in equation (3.1) can be express as: (Grove and Stollenwerk, 1984).

$$\sum R_k = \frac{\rho_b}{\theta} \frac{\delta c}{\delta t} - \lambda \left( C + \frac{b}{\theta} C \right) \quad 3.2$$

Where;

ρ<sub>b</sub> is the bulk density of the porous (kg/m<sup>3</sup>)

Ĉ is the concentration of contaminants sorbed on the porous medium (kg/kg)

λ Is the constant of first order rate reactions (s<sup>-1</sup>)

by rewriting the  $\frac{\rho_b}{\theta} \frac{\delta \bar{c}}{\delta t}$  term as  $\frac{\rho_b}{\theta} \frac{\delta \bar{c}}{\delta t} = \frac{\rho_b}{\theta} \frac{\delta C}{\delta t} \frac{\delta \bar{c}}{\delta C}$  3.3

Substituting equation (3.2) and (3.3) into equation (3.1), we have;

Rearranging equation (3.3) by moving the fourth term on the right hand side of equation (3.3) to the left hand side, the equation (3.3) becomes;

$$R \frac{\delta C}{\delta t} = \frac{\delta}{\delta x} \left( D_y \frac{\delta C}{\delta x} \right) - \frac{\delta}{\delta x} (V_t C) + \frac{q^s}{\theta} C_s - \lambda \left( C + \frac{\rho_b}{\theta} C \right) \quad 3.4$$

Where R is called the Retardation factor, defined as:

$$R = 1 + \frac{\rho_b}{\theta} \frac{\delta \bar{C}}{\delta C} \quad 3.5$$

The equation (3.5) is the governing equation underlying in the transport model. The transport equation is linked to the flow equation through the relationship;

The hydraulic head is obtained from the solution of the three-dimensional groundwater flow equation:

$$\frac{\delta}{\delta x} \left( K_H \frac{\delta h}{\delta x} \right) + q_s = S_s \frac{\delta h}{\delta t} \quad 3.6$$

Where  $S_s$  is the specific storage of the porous materials,  $m^4$

### 3.26 Advection

The second term on the right-hand side of equation (3.5) i.e.  $\frac{\delta}{\delta x} \left( \frac{V}{t} C \right)$  is referred to as the advection term.

The advection term describes the transport of miscible contaminate at the same velocity as the groundwater, the advection term above dominates. To measure the degree of advection domination, a dimensionless Peclet number is defined as;  $P = \frac{V/L}{D}$  3.7

Where

$V$  is the magnitude of the seepage velocity vector,  $ms^{-1}$ ,

$L$  is a characteristic length, commonly taken as the grid cell width,  $m$ ;

$D$  is the dispersion coefficient,  $m^2/s$ .

In advection-dominated problems, also referred to as sharp front problem, the Peclet number has a large value. For pure advection problems, the Peclet number becomes infinite.

### 3.27 Dispersion

#### 3.27.1 Dispersion Mechanism

Dispersion in porous media refers to the spreading of contaminants (oil) over a greater region than would be predicted solely from the ground water velocity vector. As described by (Anderson, 1984), dispersion is caused by mechanical dispersion, a result of deviations of actual velocity on a micro scale from the average ground water velocity, and molecular diffusion, a result of concentration variations. The molecular diffusion effect is generally secondary and negligible compared to the mechanical dispersion effect and only becomes primal where groundwater velocity is low. The sum of the mechanical dispersion and the molecular diffusion is termed *hydrodynamic dispersion*.

The first term on the right-hand side of equation (3.5) i.e.

$$\frac{\partial}{\partial x} \left( D_y \frac{\delta c}{\delta x} \right)$$

is referred to as the dispersion terms

It represents a pragmatic approach through which realistic transport calculations can be made without fully describing the heterogeneous velocity field, which of course, is impossible to do in practice. While many different approaches and theories have been developed to represent the dispersion process, equation (3.5) is still basis for most practical simulation.

#### 3.28 Dispersion Coefficient

The hydrodynamic dispersion tensor for isotopic porous media is defined, according to (Bear, 1979) in the following component forms:

$$D_{xx} = aL \frac{V_x^2}{|V|} + aT \frac{V_y}{|V|} + \frac{V_x^2}{|V|} D \quad 3.8a$$

$$D_{yy} = aL \frac{V_y^2}{|V|} + aT \frac{V_x}{|V|} + \frac{V_y^2}{|V|} D \quad 3.8b$$

$$D_{zz} = aL \frac{V_z^2}{|V|} + aT \frac{V_x}{|V|} + \frac{V_y^2}{|V|} D \quad 3.8c$$

$$D_{xy} = D_{yx} = (aL - aT) \frac{V_x V_y}{|V|} \quad 3.8d$$

$$D_{yx} = D_{zx} (aL - aT) \frac{V_x V_y}{|V|} \quad 3.8e$$

$$D_{yz} = D_{zy} (aL - aT) \frac{V_y V_z}{|V|} \quad 3.8f$$

Where

$\alpha_L$  is the longitudinal dispersivity, L:

$\alpha_T$  is the transverse dispersivity, L:

$D^*$  is the effective molecular diffusion coefficient,  $m^2 S^{-1}$ ;

$V_x, V_y, V_z$  are components of the velocity vector along the x, y and z axes,  $ms^{-1}$

$|V| = (V_x^2 + V_y^2 + V_z^2)^{1/2}$  is the longitudinal dispersivity, L:

Equation (3.8a) to (3.8f) become equivalent to equation (3.8a) to (3.8f) when the two transverse dispersivities are set equal.

### 3.29 Sinks and Sources

The third term on the right hand side of equation (3.5) i.e.  $\frac{q}{\theta}Cs$  is the sink/source term, which represents solute mass dissolved in soil water entering the simulated domain through sources, or solute mass dissolved in soil water leaving the simulated through sinks. Sinks or sources may be classified as a really distributed or point sinks or sources. The point sinks or sources include wells, drains and rivers.

### 3.30 Chemical Reactions

The chemical reactions include in the MT3D transport model are equilibrium controlled linear or non-linear sorption and first order irreversible rate reactions most commonly, radioactive decay or biodegradation.

### 3.31 Linear or Non-Linear Sorption

Sorption refers to the mass transfer process between the contaminants dissolved in groundwater (solution phase) and the contaminants sorbed on the porous medium (solid phase).

It is generally assumed that equilibrium conditions exist between the solution-phase and solid phase concentrations and that the sorption reaction is fast enough relative to groundwater velocity so that it can be treated as instantaneous. The functional relationship between the dissolved and sorbed concentration is called the Sorption Isotherm.

Sorption isotherms are generally incorporated into the transport model through the use of the retardation factor (e.g. Goode and Konikow, 1989). Three types of Sorption isotherms are considered in the MT3D transport model, linear Freundlich and Langmuir (Zheng, 1990).

The linear sorption isotherm assumes that the sorbed concentration (C)

is directly proportional to the dissolved concentration (C); i.e.  $C_s = K_d C$ .

Therefore  $C_s = K_d C$  3.9

Where  $K_d$  is called the distribution coefficient,  $m^3/s$ . The retardation factor is defined as:



$$R = 1 + \frac{\rho b}{\theta} \frac{\delta \dot{C}}{\delta C} = 1 + \frac{\rho b}{\theta} K_d \quad 3.10$$

The Freundlich isotherm is a non-linear isotherm, expressed in the following form:

$$C = K_f C^a \quad 3.11$$

Where;  $K_f$  is the Freundlich constant ( $m^3 kg^{-1}$ )<sup>a</sup>

$a$  is the Freundlich exponent, dimensionless.

Both ' $K_f$  and  $a$ ' are empirical coefficients. When ' $a$ ' is equal to 1, the Freundlich isotherm is equivalent to the linear isotherm. The retardation factor for the Freundlich isotherm is defined accordingly as:

$$R = 1 + \frac{\rho b}{\theta} \frac{\rho b}{\theta} = 1 + \frac{\rho b}{\theta} a K_f C^{a-1} \quad 3.12$$

Another non-linear Sorption isotherm is the Langmuir isotherm, described by:

$$\dot{C} = \frac{K_1 S C}{1 + K_1 C} \quad 3.13$$

Where;  $K_1$  is the Langmuir constant,  $m^3/kg$

$S$  is the total concentration of sorption sites available,  $kg/kg$

The retardation factor for the Langmuir isotherm is defined as:

$$R = 1 + \frac{\rho b}{\theta} \frac{\sigma \dot{C}}{\sigma C} = 1 + \frac{\rho b}{\theta} \left[ \frac{K_1 S C}{1 + K_1 C^2} \right] \quad 3.14$$

### 3.32 Radioactive Decay or Biodegradation

The first-order irreversible rate reaction term is included in the governing equation  $-\lambda(c + \frac{\rho b}{\theta} \bar{C})$  represents the mass loss of both the dissolved phase ( $C$ ) with the same rate constant ( $\lambda$ ).

The rate constant is usually given in terms of the half-life;  $\lambda = \frac{\ln 2}{t_{1/2}}$  3.15

Where;  $t_{1/2}$  is the half life of radioactive or biodegradable materials, or the time required for the concentration to decrease to one-half of the original value.

For certain types of biodegradation, the rate constant for the dissolved and sorbed phases may be different. Thus, in the MT3D model, two general rate constants are used; one for the dissolved phases ( $\lambda_1$ ) and the other for the sorbed ( $\lambda_2$ ) as shown below:

$$-\lambda(c + \frac{\rho b}{\theta} \bar{C}) = \lambda_1 \bar{C} - \lambda_2 \frac{\rho b}{\theta} C \quad 3.16$$

The two constants should be set equal if the rate of reaction simulated is radioactive decay, since radioactive decay generally occurs at the same rate in both phases. If the simulated reaction is biodegradation, two rate constants can be entered as different values.

It should be noted that the biodegradation process in the subsurface is complex and often does not follow the first-order rate reaction equation (e.g. Suflita, *et al.*, 1987).

### 3.33 Eulerian-Lagrangian Equations' Solution

According to the chain rule, the advection term in the in the governing equation (3.5) can be expanded to:

$$\frac{\delta}{\delta x} \left( \frac{V C}{t} \right) = \frac{V}{t} \frac{\delta}{\delta x} + \frac{\delta V_t}{\delta x} = \frac{V}{t} \frac{\delta C}{\delta x} + C \frac{q}{\theta} \quad 3.17$$

Substituting equation (3.19) into equation (3.5) and dividing both sides by the retardation factor, the governing equation becomes:

$$\frac{\delta C}{\delta t} = \frac{1}{R} \frac{\delta}{\delta x} \left( D_y \frac{\delta C}{\delta x} \right) - \frac{V}{t} \frac{\delta C}{\delta x} - \frac{q_s}{R\theta} (C - C_t) - \frac{\lambda}{R} \left[ C + \frac{\rho}{\theta} C \right] \quad 3.18$$

Where,  $\bar{V}_t = \frac{V_t}{R}$  represent the “retarded” velocity of a contaminated particle.

Equation (3.18) is an Eulerian expression in which the partial derivative  $\left( \frac{\delta C}{\delta t} \right)$  indicates the rate of change in solute concentration (c) at a fixed point space. Equation (3.18) can also be expressed in the language form as:

$$\frac{DC}{Dt} = \frac{1}{R} \frac{\delta C}{\delta x} \left( D_y \frac{\delta C}{\delta x} \right) = \frac{q}{R\theta} (C - C_t) - \frac{\lambda}{R} = \left[ C + \frac{\rho}{\theta} C \right] \quad 3.19$$

Where substantial derivative,  $\frac{DC}{D} = \frac{\delta C}{\delta t} + V_t \frac{\partial C}{\partial x}$  indicates the rate of change in solute concentration (C) along the path line of a contaminant particle for a contaminant particle (or a characteristic curve of the velocity field).

By introducing the finite-difference algorithm, the substantial derivative in equation (3.19) can be approximated as:

$$\frac{DC}{D} = \frac{C_m^{n+1} - C_m^{n*}}{\Delta t} \quad 3.20$$

So that equation (2.3) becomes

$$C_m^{n+1} = C_m^{n*} + \Delta t \times \text{THS} \quad 3.21$$

Where:

$C_m^{n+1}$  is the average solute concentration for cell m at the new time level (n + 1).

$C_m^{n*}$  is the average solute concentration for cell m at the new time level (n + 1) due to advection alone, also referred to as the intermediate time level (n\*).

$\Delta t$  is the time increment between the old time level (n) and the new time level (n + 1); RHS represents the finite-difference approximation to the terms on the right hand side of equation (2.3). The finite – difference approximation is explicit if the concentration at the old time level  $C^n$  is used in the calculation of RHS; it is implicit if the concentration at the new time level  $C^{n+1}$  is used.

Equation (3.5) constitutes the basic algorithm of the mixed Eulerian Lagrangian method used in the MT3D transport model. In this method, the term  $C^{n*}$  in equation (3.5) which accounts for the effects of advection is solved with Lagrangian method on a moving co-ordinate, while the second term in equation (3.5) which accounts for the effects of dispersion, sink/source, missing and chemical reactions, is solved with a finite-difference method on the fixed Eulerian grid.

### 3.34 Assessment of the Dispersion Term

After completing the assessment of the cell concentration due to pure advection at the intermediate time level, or  $C_{i,j,k}^{n*}$

$$C_{i,j,k}^{n*} = w C_{i,j,k}^{n*} + (1 + w)C_{i,j,k}^{n*} \quad 3.22$$

The weighted concentration  $C_{i,j,k}^{n*}$  is then used to calculate the changes in concentration due to dispersion, sink/source mixing, and/or chemical reaction with the explicit finite difference method. This is done because the process of dispersion, sink/source mixing, and/or chemical reaction occur neither at the beginning of step, but throughout the step. The weighted concentration, thus, represents an averaged approach.

The concentration change due to dispersion alone can be written as

$$\begin{aligned} \frac{DC_{DSP}}{Dt} &= \frac{1}{R} \frac{\delta}{\delta x} \left( D_y \frac{\delta}{\delta x} \right) \\ &= \frac{1}{R} \left[ \begin{aligned} &\frac{\delta}{\delta x} \left( D_{xx} \frac{\delta c}{\delta x} \right) + \frac{\delta}{\delta x} \left( D_{xy} \frac{\delta c}{\delta y} \right) + \frac{\delta}{\delta x} \left( D_{xz} \frac{\delta c}{\delta z} \right) + \frac{\delta}{\delta y} \left( D_{yx} \frac{\delta c}{\delta x} \right) + \\ &\frac{\delta}{\delta y} \left( D_{yy} \frac{\delta c}{\delta x} \right) + \frac{\delta}{\delta y} \left( D_{yz} \frac{\delta c}{\delta z} \right) + \frac{\delta}{\delta z} \left( D_{zx} \frac{\delta c}{\delta z} \right) + \frac{\delta}{\delta z} \left( D_{zy} \frac{\delta c}{\delta y} \right) + \frac{\delta}{\delta z} \left( D_{zz} \frac{\delta c}{\delta z} \right) \end{aligned} \right] \quad 3.23 \end{aligned}$$

#### 4. RESULTS AND DISCUSSION

**Table 4.1: Horizontal Physico-Chemical Properties of Spilled Soil at Site A**

S/N	Depth (cm)	Matrix	pH	E/cond. (ms/cm)	Org. NO <sub>3</sub> Mg/kg	Org. PO <sub>4</sub> mg/kg	TPH mg/kg	NO <sub>2</sub> mg/kg	CO <sub>3</sub> Mg/kg	BOD mg/kg
1.	0-15	Soil	5.82	2.35	0.32	12.35	82.88	0.12	0.56	0.15
2.	15-30	Soil	6.40	1.20	0.22	2.15	44.50	0.08	0.32	0.12
3.	30-45	Soil	6.95	0.97	0.13	0.88	25.00	0.05	0.14	0.09
4.	45-60	Soil	7.02	0.68	0.08	0.37	14.87	0.01	0.17	0.05

**Table 4.2: Vertical Physico-Chemical Properties of Spilled Soil at Site A**

S/N	Depth (cm)	Matrix	pH	E/cond. (ms/cm)	Org. NO <sub>3</sub> Mg/kg	Org. PO <sub>4</sub> mg/kg	TPH mg/kg	NO <sub>2</sub> mg/kg	CO <sub>3</sub> Mg/kg	BOD mg/kg
1.	0-15	Soil	5.83	0.32	0.32	10.10	34.33	0.9	0.42	0.75
2.	15-30	Soil	6.42	0.10	0.10	2.0	20.03	0.08	0.19	0.30
3.	30-45	Soil	6.98	0.67	0.67	0.98	12.08	0.06	0.07	0.21
4.	45-60	Soil	7.00	0.32	0.32	0.34	0.45	0.05	0.01	0.10

**Table 4.3: Horizontal Physico-Chemical Properties of Spilled Soil at Site B**

S/N	Depth (cm)	Matrix	pH	E/cond. (ms/cm)	Org. NO <sub>3</sub> Mg/kg	Org. PO <sub>4</sub> mg/kg	TPH mg/kg	NO <sub>2</sub> mg/kg	CO <sub>3</sub> Mg/kg	BOD mg/kg
1.	0-15	Soil	5.03	0.52	0.21	2.62	13.02	0.08	0.24	3.50
2.	15-30	Soil	5.92	0.40	0.14	2.05	5.17	0.08	0.15	1.80
3.	30-45	Soil	6.23	0.31	0.09	1.76	1.98	0.7	0.76	0.32
4.	45-60	Soil	6.75	0.19	0.02	1.21	0.46	0.5	0.10	0.09

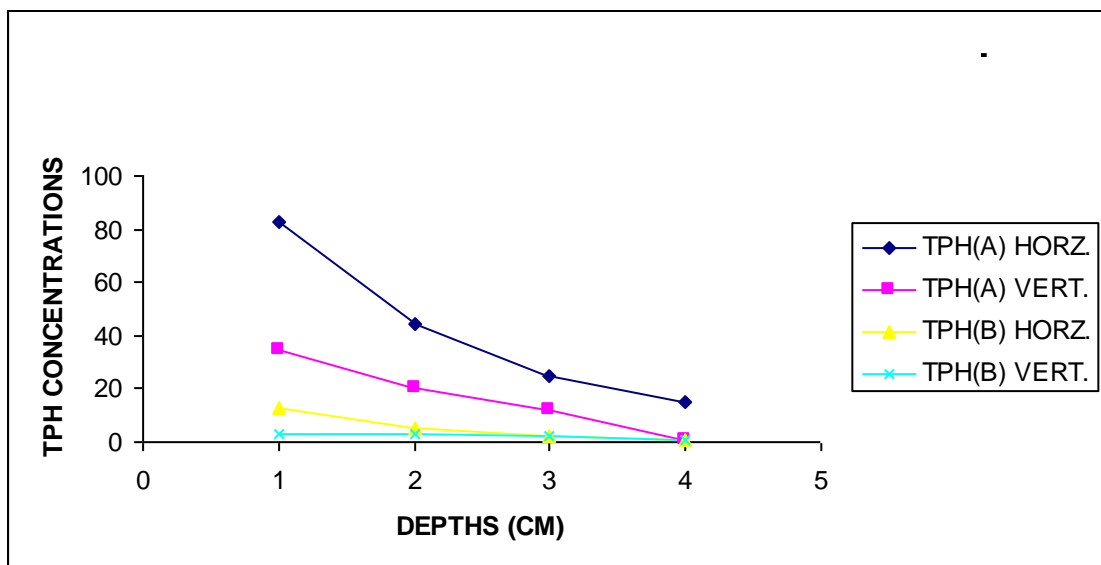
**Table 4.4: Vertical Physico-Chemical Properties of Spilled Soil at Site B**

S/N	Depth (cm)	Matrix	pH	E/con d. (ms/cm)	Org. NO <sub>3</sub> Mg/kg	Org. PO <sub>4</sub> mg/kg	TPH mg/k g	NO <sub>2</sub> mg/k g	CO <sub>3</sub> Mg/k g	BOD mg/k g
1.	0-15	Soil	5.23	0.34	0.18	0.15	5.20	0.06	0.12	10.00
2.	15-30	Soil	5.40	0.30	0.20	0.10	3.14	0.03	0.09	8.30
3.	30-45	Soil	6.32	0.27	0.26	0.06	1.98	0.02	0.07	6.00
4.	45-60	Soil	7.12	0.12	0.30	0.02	1.00	0.01	0.03	4.97

#### 4.1 Simulation Results

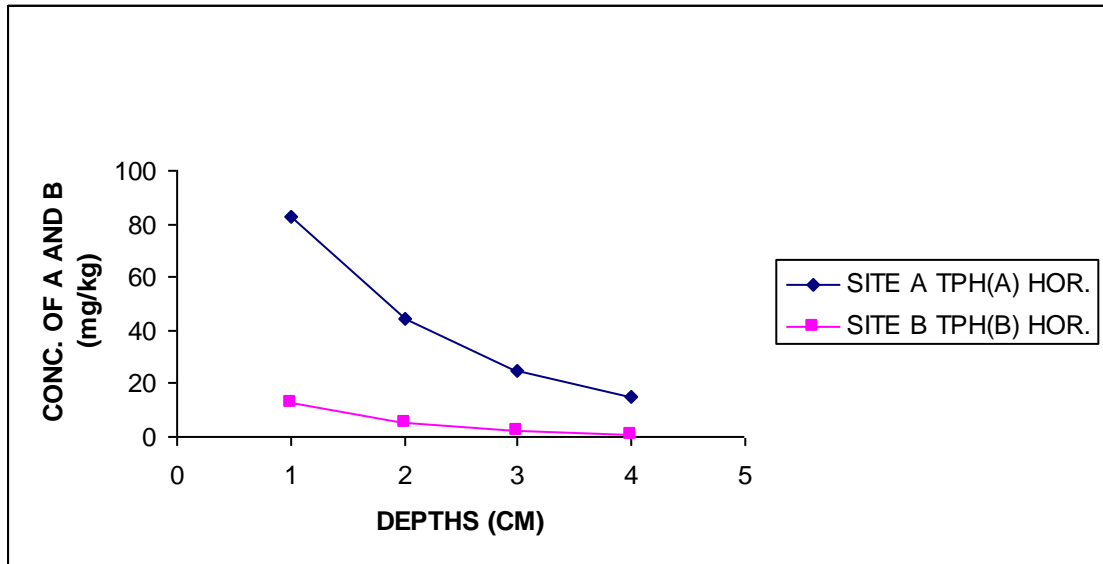
Simulation of the model means the use of computer codes to show the activities and behaviour of the system in reality. The model equation was simulated using V-Basic program. The result of the computed concentration in g/m<sup>3</sup> of the total petroleum hydrocarbons for 100m<sup>3</sup>, 150m<sup>3</sup> and 200m<sup>3</sup> of oil spilled at various distance, porosity and time with corresponding effective concentration are shown in table 4.1 to 4.4. The effective concentration is calculated using the

$$C_E = \sqrt{C_x^2 + C_y^2 + C_z^2}$$



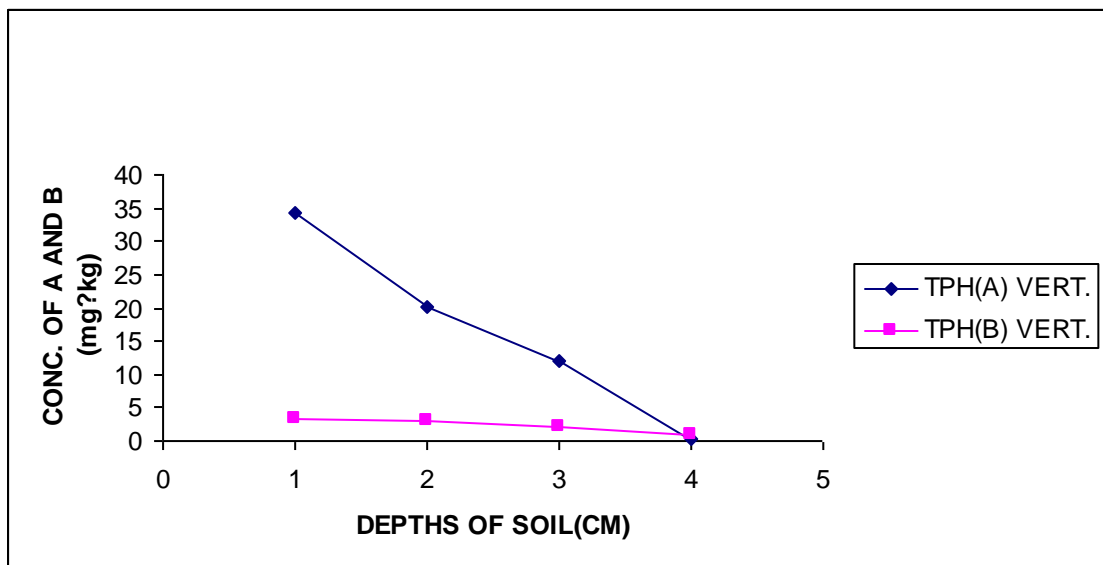
**Fig. 4.1: Site A and B in X and Y Against Depths of Soil**

Figure 4.1 above shows the effect of soil depth on the concentration of total petroleum hydrocarbon. The graph shows that as the depth of the soil increases, the total petroleum hydrocarbon decrease. Site A decrease faster than others horizontal and vertical while site B reduces shortly in the both horizontal and vertical axis. This is due to the rate of diffusion of the crude oil on soil.



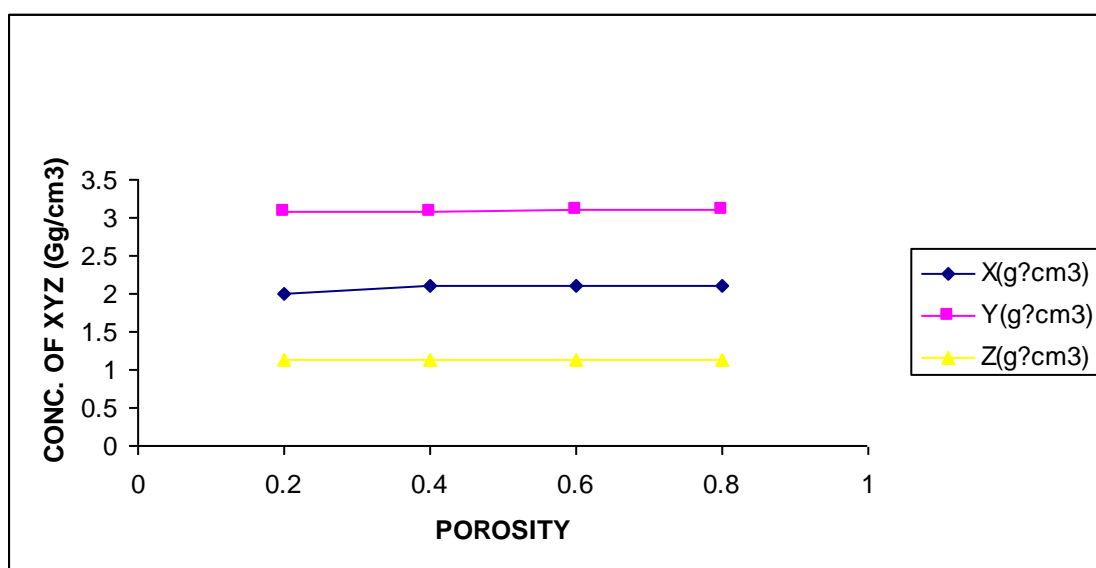
**Fig. 4.2: Concentration of Site A and B Horizontally Against Depths of Soil**

Figure 4.2 above shows the effect of soil depth on the concentration of total petroleum hydrocarbon. The graph shows as the soil depth increases the total hydrocarbon petroleum reduces as a result of the rate of diffusion being slowed down into the soil.



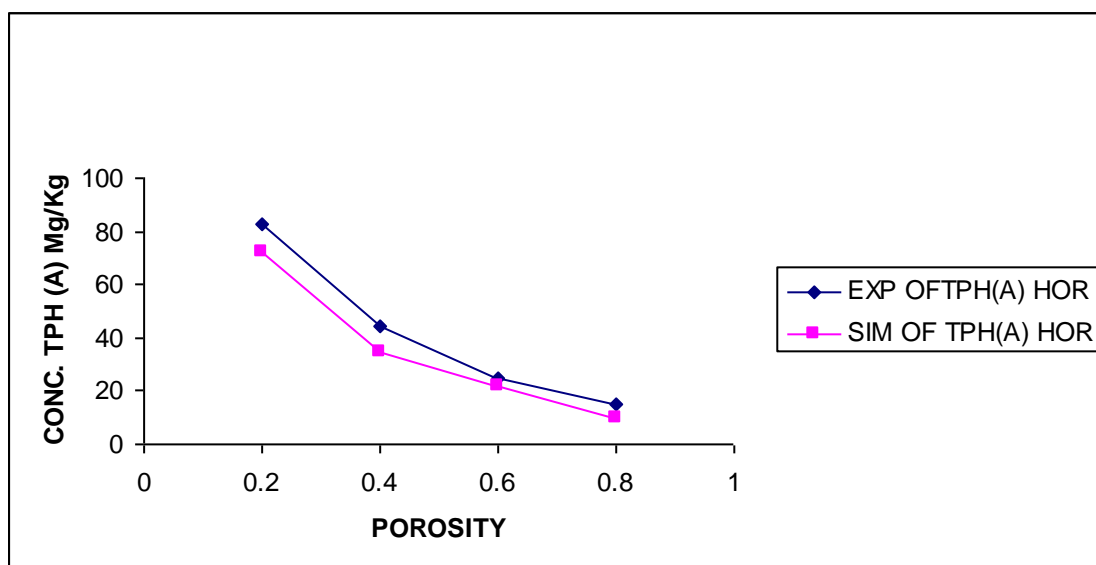
**Fig. 4.3: Concentration of TPH(A) and B Vertically Against Depths of Soil**

Figure 4.3 above shows that site A reduces sharply with increase in depths than site B vertically and the reason is because of the spillage.



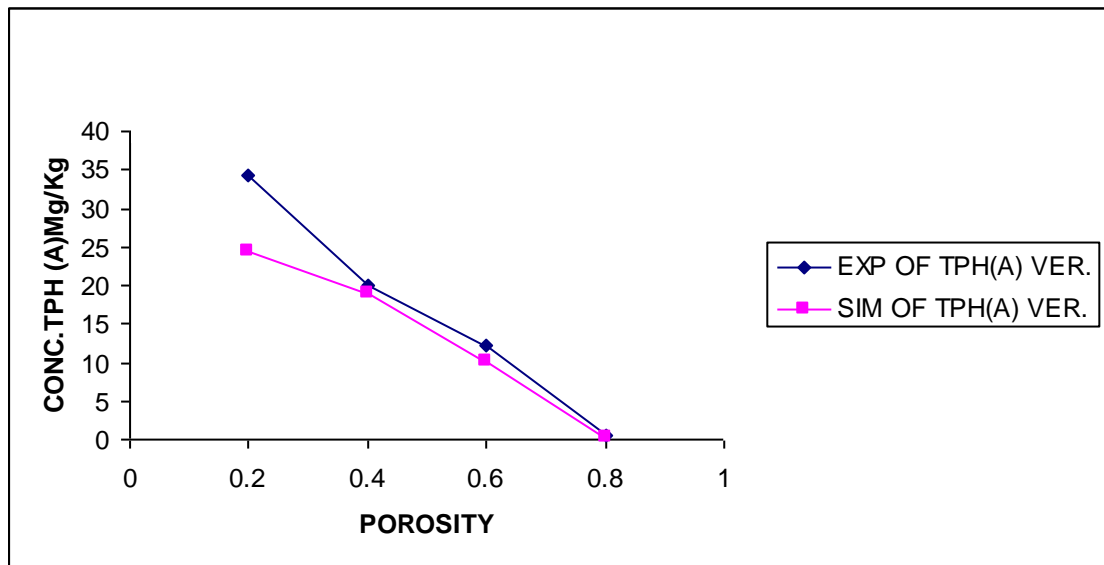
**Fig. 4.4: Concentration of XYZ Directions Against Porosity**

Figure 4.4 above shows that increase in porosity increases the concentration of TPH in X, Y and Z directions, but indicate that X has the highest concentration followed by Y and finally Z.



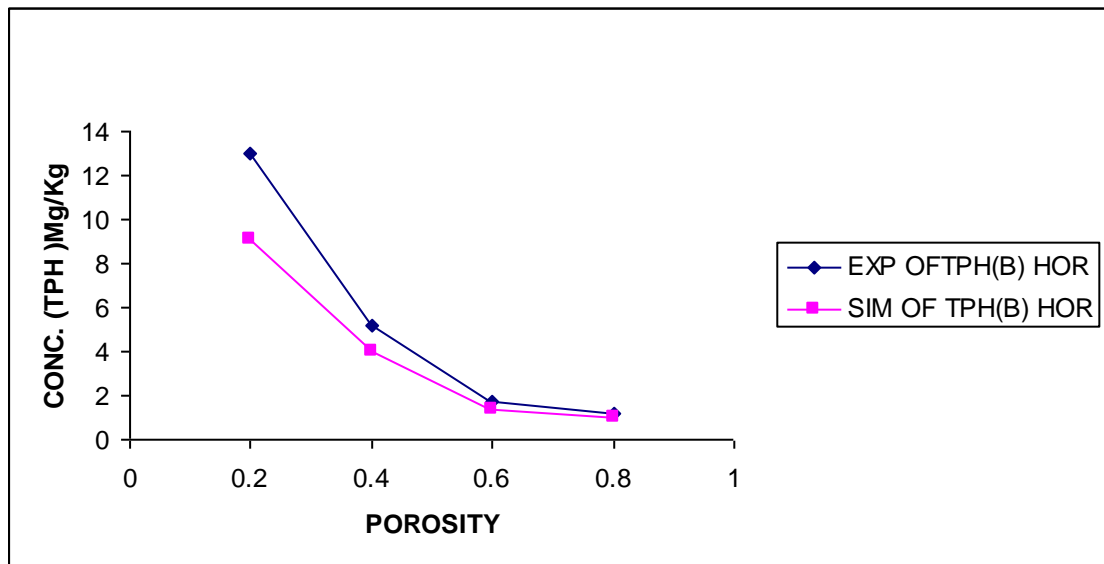
**Fig. 4.5: Comparison between Experimental and Simulation**

Figure 4.5 above shows that there is agreement between the experimental and simulation results in the horizontal directions of site A as porosity increases the concentration of the total hydrocarbon into soil also increases.



**Fig. 4.6: Comparism Between Experimental and Simulation**

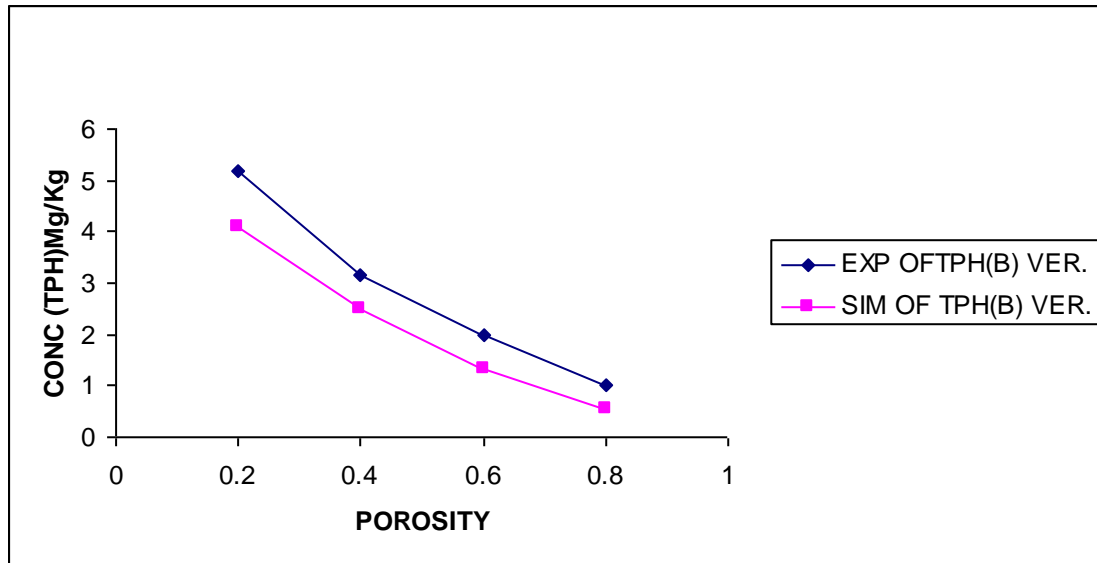
Figure 4.6 above shows that there is agreement between the experimental result and simulation in the vertical direction of site A as porosity increases the concentration of total hydrocarbon increases.



**Fig. 4.7: Comparism Between Experimental and Simulation**

Figure 4.7 shows that there is agreement between the experimental result and simulation of site B in the horizontal direction, because, as the porosity increases the concentration of total petroleum hydrocarbon (TPH) also increases





**Fig. 4.8: Comparism Between Experimental and Simulation**

Figure 4.8 show that the agreement between the experimental result and simulation in the vertical direction as porosity increases the total petroleum hydrocarbon reduces.

## 5. CONCLUSION AND RECOMMENDATIONS

From the experimental values shown in tables 4.1 to 4.2, the concentration of oil pollutant in soil varies from distance to distance. The simulated result presented in appendix 4.3 to 4.4, show that concentration of pollutant in soil varies as the volume of oil spill change with measured either as the volume of oil pollutant, or as pollutant units in unit volume of oil is spilled.

The pH of the soil investigated is observed to be in the range of 5.23 to 7.12 and the Federal ministry of Environment recommends limit is within the range of 6.5 to 8.5. This shows that the soil is acidic and it is an indication that the people in Niger-Delta area are exposed to danger as a result of continuous pollution of soil due to oil spillage.

The slight differences (variations) between the experimental and modeling simulation result could be attributed to some of the assumptions made at the initial stage of modeling and the fact that experimental values are a measure of soil pollution because of the possibility of accumulation while the simulation results is an instantaneous values i.e. It measures the possible amount of total petroleum hydrocarbon (TPH) that that could be dispersed at a given period of time.

## 5.1 Conclusion

From this project research work, the following conclusion can be deduced:

- i. It can be concluded that the result of simulation of model developed based on the modified pollutant transport principle showed conformity (though with negligible difference) with the experimental results.
- ii. The dispersion pattern of oil showed that the extent of spread is dependent on the volume of oil spilled (the higher the volume, the concentration of pollutants in the soil), the soil porosity (the higher the volume, the efficiency of soil retardation capability, the lower the pollutants infiltration I the soil).
- iii. It can be concluded that the quality of the soil with respect to its physic-chemical factors such as pH is unacceptable when compared to Federal Environmental Protection Agency limit.
- iv. The computer model developed in this study may assist in the estimation of environmental impact of an accidental oil spill and to design efficient emergency strategies.

## 5.2 Input to Knowledge

This project is therefore an input towards the sustainability of the environment of the Niger-Delta Area as the model developed can be used to effectively monitor and predict the extent of movement of the spilled oil. This will enhance oils remediation measure to be put in place.

- i. This study enables prediction of environmental danger from potential hydrological sceneries such as normal and extreme maximum or minimum.
- ii. The study also shows the use of computer simulations as a tool to measure the impact of such accident and serves as a input.
- iii. The study of models is highly relevant to predict damages to aquatic fauna and water quality, and generate information simulating scenarios of environmental pollution and the effect of mitigation measures on the quality of water resources.

## 5.3 Recommendations

Federal, State and local governments of oil exploring host communities should provide instant succor to the people affected by oil spillage in order to alleviate their problem. Government should also provide social and infrastructural amenities for the people of Niger-Delta area because of poor farming and fishing due to contamination of soil and rivers by oil. Oil exploring companies and other oil operators should include oil collection/clean-up facilities to all new pipeline installation which links the oil station to process industries. Loading and discharging of oil into/from tankers should be given strict monitoring to avoid spillage of oil.

- i. The government of Nigeria should muster the political will to exact stricter respect for environmental laws and regulations by oil companies and a penalty plan established

that require oil companies whose activities cause excessive pollution or are ill-equipped to forfeit their licenses.

- ii. Multinational and indigenous oil companies should ensure regular and constant inspection and maintenance of oil facilities to avoid accidental release or spillage of oil and other petroleum products.
- iii. The current compensation regime in Nigeria has to be reviewed for it to be fair and adequate to meet the emergency needs and concern of those affected by pollution.

## REFERENCES

- Abdulawahab, G. (2004). Student Industrial Work Experience Scheme (SIWES) Report. Department of Chemical Engineering, Faculty of Engineering, Federal University of Technology, Minna, Niger State.
- Abulkaem, A.S. (2000). Mathematical Modeling of Pollutant Migration from Gas Flaring in Niger-Delta. Unpublished. M. ENG Project, Department of Chemical Engineering, Faculty of Engineering, Federal University of Technology, Minna, Niger State.
- Achem, M. (1998). Impact of Oil on Soil in Niger-Delta, Unpublished. B.ENG. Project, Department of Chemical Engineering, Faculty of Engineering, Federal University of Technology, Minna, Niger State.
- Adeyemo, A. M. (2002). The Oil Industry Extra-Ministerial Institution and Sustainable Agricultural Development. A Case Study of Okirika, LGA of Rivers State, in *Nigeria Journal of Oil and Politics*, 2(1), 1-10.
- Ameej, A. (2004) Oil of Poverty in Niger Delta. A Publication of the African Network for Environment and Economic Justice. Retrieved from [www. www.naturalspublishing.net](http://www.naturalspublishing.net) 1<sup>st</sup> July, 2016.
- Anifowose, B. (2008) Assessing the Impact of Oil and Gas Transport on Nigeria's Environment Uzi Postgraduate Research Conference Proceedings University of Birmingham, UK.
- Asunmo, A. A. (2003). Pollutant Dispersion Assessment from Oil Spillage, A Case Study of Niger-Delta, Unpublished. B.ENG. Project, Department of Chemical Engineering, Faculty of Engineering, Federal University of Technology, Minna, Niger State.
- Bear, J. (1979). *Hydraulics of Groundwater*, New York: McGraw Hill.
- Christopher, G. K. (1988). *Mathematical Models in Coastal Engineering*, London: Pentech Press.
- Frank, J. (2014). Computer Simulation of Oil Dispersion in Rivers in Brazil Following a Spill: A Case Study of Involving the Berigol and Iguacu Rivers. Retrieved from [www.naturalspublishing.net](http://www.naturalspublishing.net) 11<sup>th</sup> December, 2017.
- Jackson, M.L (1958). *Soil Chemical Analysis, Incorporation Eaglewood*, New Jersey: Prentice Hall.
- James, D. J. G., McDonald, J. J. & Stanley, H. (1981). *Case Study in Mathematical Modeling*. New York: John Wiley Inc.
- Jandel, I., Doughty C. T. & Sang C. F. (1984). *Ground Water Transport: Handbook of Mathematical Models*. American Geophysical Union Water Resources Monogram 10.

- Mohammed, A. T. (2003). Oil Spillage Dispersion in Soil: A Case Study of Niger-Delta Area, B Unpublished. ENG Project. Department of Chemical Engineering, Faculty of Engineering, Federal University of Technology, Minna, Niger State.
- Nwafor, J. (2002). Assessment of Oil Spill on Some Aquatic Life in Rivers State, A Case Study of Oshika Village Unpublished. B.ENG. Project, Department of Chemical Engineering, Faculty of Engineering, Federal University of Technology, Minna, Niger State.
- Oladipo, M. O. (2000). Environment Impact Assessment of Oil Spillage in Atypical Area of Niger-Delta Unpublished. B.ENG. Project Department of Chemical Engineering, Faculty of Engineering, Federal University of Technology, Minna, Niger State.
- Robert, L. B. Courtney S. Coleman & William, E. Boyce (1992). Differential Equation Laboratory Workbook. New York: John Wiley & Son Inc.
- Sassen, D. S. (2004). Oil Field-Brine-included Colloidal Dispersion: A Case Study of Southeast, Texas. A Paper Presentation to the South-Central-38<sup>th</sup> Annual Meeting, Texas A & M University.
- Debo, A. (2002). The Guardian, Oil Spill in Niger Delta area, *Guardian News Papers Limited*, Lagos. Tuesday August 20<sup>th</sup>.
- William, L. L. (1995). Process Modeling, Simulation and Control for Chemical Engineering, U.S.A: McGraw Hill International.
- Zheng, C. (1990). A Modula Three-Dimensional model, for Simulation of Advection, Dispersion and Chemical Reaction of contaminants in Ground Water System. S.S. Maryland: Papadopoulos & Associates, Incorporation.
- Zheng, C. (1980). PATH 3D – A Ground Water Path and Travel Time Simulator, Version 2.0 User's Manual. U.S.A., S.S. Maryland: Papadopoulos & Associates, Incorporation.