EFFECT OF PETROLEUM PRODUCTS SPILLAGE ON

ENVIRONMENT (AGRICULTURAL SOIL AND WATER)

A CASE STUDY OF ELUKU/OJUTAYE VILLAGE

BY

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DECLARATION

I hereby declare that this project is a record of research work that was undertaken and written by me. It has not been presented before for any degree or diploma or certificate at any university or institution. Information derived from personal communication, published and unpublished works of others were duly referenced in the text.

....2 - 12 - 2008......

TOLORUNTOMI STEPHEN TOPE   Date

Name of student

CERTIFICATION

This project entitled effect of petroleum products on the environment(Agricultural soil and water) in Eluku/Ojutaiye village in Ilorin East local Government Area of Kwara State by Toloruntomi Stephen tope meets the regulations governing the award of degree of Bachelor of Engineering(B.ENG) of the Federal University Of Technology, Minna, and it is approved for its contribution to scientific knowledge and literary presentation.
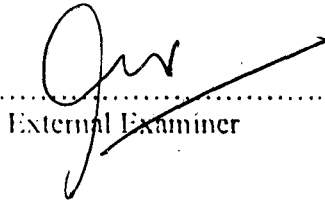
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External Examiner   Date

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DEDICATION

This research work is dedicated to the Almighty God, who has been so wonderful in my life. (Baba ninye).

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My sincere thank and appreciation to the Rock of ages, whom I refer to as Baba ninye, because he is just too much. Words can't express my sincere appreciation to him, he is just working wonders and all I does is just to look (Baba sise mo kan nwo ran nii).

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ABTRACT

At two farm sites in Eluku/Ojutaiye Village in Ilorin Kwara state, all of which were affected by petroleum products spillage due to non replacement of ageing tanks and pipes in the Nigerian National Petroleum Cooperation Depot around there. Soil and water samples were taken from the polluted and unpolluted farms and their heavy metal content, and other chemical and physical characteristics were measured. The pollution altered both chemical and physical soil properties, aggregating soil particles, lowering porosity and increasing resistance to penetration and hydrophobicity. The Manganese, Nickel, Cadmium, Cobalt, Copper, Boron, Arsenic, Barium, Zinc, Mercury. Iron and Chromium contents of polluted soils and water were higher than their unpolluted counterpart and the background concentrations in soil.

Soil pH ranges between 8.5- 9.2 in polluted soils and 8.1 in unpolluted soils. Soil electrical conductivity ranges from between (539-577) $\Omega^{-1}km^{-1}$ in polluted soils and (134) Ω^{-1} km^{-1} in unpolluted soils. The silt and clay content of polluted lower than unpolluted soils, whereas the sand content was higher in the polluted soils than unpolluted soils. The pH and the electrical conductivity of the water samples were also higher in the polluted (pH between 8.7 – 9.1) than unpolluted water (pH 6.4). Electrical conductivity is between (13900 - 17750) Ω^{-1} km^{-1} in polluted water and $2291\Omega^{-1}km^{-1}$ in unpolluted water. The chloride and sulphate ions were also higher in polluted water (276.6 – 474.8) mg/l than in unpolluted water (201) mg/l and between (451 - 523) mg/l in polluted water and 247mg/l in unpolluted water respectively.

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CHAPTER I

1.0   INTRODUCTION

Our environment is a global concern. it transcend all boundaries, including those of wealth, culture and language. Increasingly all nations are recognizing that it is not possible to treat or consider the environment on a national scale.(Bloodworth 2005).

In the past few years man's awareness of the environment has greatly increased, mostly as a result of observing the environmental damage already done. The environment is everything that surrounds us; we are also part of the environment. As such the environment is a huge pull of resources that helps us satisfy our needs and fulfill our wants (knees 1962)

None of the environmental resources is infinitely abundant. Therein, lays the trap into which we have fallen and which had led to our widespread pollution. If man is to survive more than just a few generations, we must re-examine the man- earth relationship and attempt to understand, manage and control, as adequately as possible all our environmental resources.

In re-evaluating the inter relation between man and the environment, one must not forget the dynamic nature of the environment. For instance, 11000-12,000

years ago glaciers covered the area occupied today by the city of Toronto (Canada), 500 years ago, the -North America continent was in a wide, undeveloped state with very few men roaming around.

We cannot expect to return the environment to such condition, Nor can we attempt to preserve (as some pseudo-ecologist try to make us believe) the

world in a state of pristine, immutable beauty What man can do and should is recognize himself as an important geological agent and attempt to be aware of the environmental side effect to which each of his decisions leads.

At the root of the problem lies environmental pollution and waste. By pollution we mean any undesirable degradation of the environment be it natural or man-made, while waste we mean any undesirable substance accumulated as a result of our inefficient utilization of the environmental resources. Action must be taken now to solve not only our present problem but to anticipate and prevent future pollution difficulties (George G. Evans).

It is not just about the future, but also about the past. We already have a legacy of environmental problems. The former Soviet Union of Kazakhstan has plan to build a new capital city Astana which will be supplied by portable water from River Nura (Bloodworth 2005).

However during the Soviet era through mismanagement approximately 100tonnes of mercury found its way into the silt at the bottom of River Nura. Moreover, studies made after large oceanic spills have shown that the ecological damage of oil and its product spill can be intense.

Because oil and oil products in the environment can cause harm, we need to prevent problems when we can. We all share both the responsibility for creating the problem of the spill and the responsibility for finding ways to solve the problem.

The world summit on sustainable development has committed us all to halving the number of people without descent sanitation by 2015(Bloodworth 2005)

An estimated 2.4 billion people, 40% of the world population lack access to hygienic sanitation facilities. Our commitment as engineers is to provide a safe environment to 1.2 billion people by 2015!

Mankind has basically two choices, either to keep the planet healthy or die with it. If we continue to operate(as we have done in the past) on the principle of super abundance of resources the last alternative will be inevitably accelerated.

However, if we apply our technology and management techniques wisely to our environmental resources, we can assure that many coming generations will enjoy the fruit of our wisdom. Planning is the key to our problem and such planning must be started now. It is obvious that we need to achieve a healthy balance between

mineral resource extraction and the environment. Man's aim should be to attain economic growth such as to satisfy our needs and desires while at the same time preserving the environment.

Researches are still on regarding the effect of pollution on the environment. In Nigeria, there has been reported cases of petroleum and it's product spillage on soil and water, which had lead to water shortages and loss of Agricultural land. Examples of which includes the peculiar case of Ikot ada udo village in Ikot Abasi local Government area of Akwa Ibom state, and Ikarama and Kalaba communities in Yenegoa L.G.A of Bayelsa state.

Of particular interest is the case of people of Eluku/Ojutaye village in Ilorin east L.G.A of Kwara state, who are now counting their losses sequel to the oil spill from the ruptured NNPC tanks. The spill got into the soil and the River which serves as source of irrigation for the farms in the village, lot of

vegetable farms were destroyed, due to non-replacement of ageing tanks and pipeline.

The people of Eluku/Ojutaiye are engage in subsistence farming mostly vegetable to earn out a living. The land was fertile and the people also had access to water, which serves as source of irrigation for their farm . The farmland sustained several families as they use the agricultural products to meet their household needs by keeping some of the harvest for domestic

consumption as well as for sale. All that change when the Nigerian National Petroleum Corporation came around the area. The people can no longer enjoy the full benefit of their God given land, as petroleum product spillage has reduced several farm lands to ruins.

1.1 Aim of Study

The aim of this study is to:-

(i) Find out about the effect of petroleum and its products on soil and water.

(ii) The constituent of the soil and water affected by the spillage.

(iii) The effect of soil and water affected on irrigation on farming.

1.2 Justification of the Study

Petroleum and its product have been playing, a vital role in many industries of the world, it obviously contributes greatly to the economy advancement several Nations, especially in the Middle East and some African countries:

However, its spillage has a destructive effect on agricultural soil and water, having in mind that the agricultural sector contributes about 40% of the Gross Domestic product of most of these countries (NTA

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INTERNATIONAL JUNE 29, 2008) and over 98% of the Gross Domestic Product in the case of the people of Eluku/Ojutaiye.

Therefore, it is high time: a greater attention is paid to oil spillage and its effect on Agricultural Soil and Water. Since this study is about oil spillage and its effect on Agricultural soil and water as it affects plants, it will surely go along way in helping the Agricultural/Environmental Engineers in site allocation for Agricultural purposes.

Moreover, it will also help in the kind of water treatment/method to be adopted, and will also help the government in the area of planning concerning water and land, and will obviously help in more proper way of preventing petroleum product spillage, as the great destructive effect of petroleum product spillage on soil and water will be seen after the research.

1.3 Significance of Study

Since this study seek to assess the effect of petroleum products spillage on soil and water, it is therefore significant to assess the content of a petroleum product spilled affected soil and water, so that it can be distinguish from the unaffected soil and water, so that the soil and water not affected can be used for irrigation farming in Eluku/Ojutaiye farms and other farms around that had been affected by petroleum product spillage.

This will go a long way in increasing yield as soil affected by petroleum product spillage will be seen to have a devastating effect on the crops, thereby reducing yield.

1.4 Scope of Work

The effect of petroleum products spillage on Agricultural soil and water as its affect. Plants growth and yield, the constituent of the water and soil

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affected by the spillage in Eluku/Ojutaye will be studied by collecting 2 different samples of soil and water affected by the spillage from 2 different farms in Eluku/Ojutaye village.

Underground water will also be collected to serve as control, while soil which is not affected by the petroleum products spillage will also be taken, after which different analysis will be done on the various samples to ascertain their constituent.

1.4. Delimitation

This research will only cover the physical and chemical effects the oil spillage has on soil and water as reflected by the plants found in the area, the research will not concern itself with the nutrient analysis.

1.5 Limitation

The non-availability of finance, materials and time really affects the work, as wide geographical area could not be covered.

CHAPTER II

2.0 LITERATURE REVIEW

2.1 Oil How Do We Get It

In the United States in the 19th Century, a new source of artificial light was needed to replace the inconveniences of flickering light produced by fats, whale oil, and other substance. What was the solution? Oil where could it be found?

In 1859, Edwin L.Drake, a retired railroad conductor, using an old stream engine, drilled a well 70feet (22meters) deep to the first crude oil discovered near Titusville, Pennsylvania, U.S.A. That marked the beginning of the oil era. As oil was discovered in many parts of the world, it caused great economic and political repercussions. It proved to be the high quality source of artificial light that the world eagerly awaited.

Soon, frantic buying of land and drilling of wells was a major activity in the oil regions of the United States.(awake,2005).

In 1870, John D. Rockefeller and a few associates incorporated the standard oil company. This company dominated the kerosene market until competitors appeased, especially in the Russian Oil Industry. One rival was Marcus Samuel, a founder of the Royal Dutch/shell group. In addition, as a result of ingenuity of Nobel brother a powerful oil enterprise was established in Russia with the oil extracted from fields in Baku. (Awake, 2005)

2.2 How much Oil, and Where Is It

In terms of production, the important factor is, not the number of fields discovered, but their size. How big are they?

Oil fields that contain at least 5Billion barrels of recoverable oil- called super-giant-are the largest in classification, while the second largest (from five hundred million to five billion barrels) are called world class giants. Although some seventy countries are listed in the "U.S geological survey world petroleum assessment 2000" as having some oil reserves, only a few of them have giant oil field (Awake, 2003). The largest number of super-giant oil field are group in the Arabian-Iranian sedimentary basin, which comprises the area in an around the Persian Gulf.

The search for new oil sources has not stopped. Instead it has been reinforced by state-of-the- art technology. Currently the Caspian Sea region, made up of the nations of Azerbaijan, Iran, Kazakhstan, Russia, Turkmenistan and Uzbekistan, has caught the attention of oil producers. This region has huge potential for the exploitation of oil and natural gas. (U.S Energy Information Administration 2005).

2.3 How The Petroleum (CRUDE OIL) Form

Crude oil is an important fossil fuel. Fossil fuel was formed millions of years ago, when much earth was covered by water containing billions of tiny plants and animals. After these organisms dies the accumulated on ocean floors, where, over time, sand and mud are drifted down to cover them. As these layers piled up over millions of year, the weight created pressure and heat that change the decaying organic material into oil and gas (Ababio 1990).

2.4 How is Oil Extracted

Geologist and Surveyors search for places where crude oil could be trapped underground. After performing some specific measurement and taking samples, a drill to confirm that there is actually oil. In the early days,

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successful hitting an oil field might have meant being showered by a guster of mud and oil, with the consequent loss of initial outpouring and the risk of explosion.

However by means of measuring instrument and special valves, today drilling rigs prevent these from happening. As explained by the American Petroleum Institute, modern technology includes horizontal drilling, done virtually parallel to the earth's crust, which reduces the number of wells that must be bored. Off-shore extraction Which began in 1947 in the Gulf of Mexico, greatly increased oil production. (Awake, 2005).

2.5   Petroleum Product

Petroleum products are useful material derived from crude oil (petroleum) as it is processed in oil refinery. According to crude oil composition and demand, refineries can produce different shares of petroleum product. Largest share of oil product is used as energy carriers, various grades of fuel oil and gasoline.

Refineries also produce other chemicals, some which are used in chemical process to produce plastic and other useful materials. Since petroleum often contains a couple of percent sulphur, large quantities of sulphur are also often produced as petroleum product.

Hydrogen and Carbon in the form of petroleum coke may also be produced as petroleum products. The hydrogen produced is often used as an intermediate product for other oil refinery processes such as hydrogen catalytic cracking (Hydro-cracking) and hydride sulphurization.

Major Product of Oil Refinery

- Petrochemicals (plastic)

- Asphalt

- Diesel fuel

- Fuel oils

- Gasoline

  Kerosene

- Liquefied petroleum gas(LPG)

- Lubricating oils

- Paraffin wax

- Tar

2.5.1 Kerosene

Sometimes spelled kerosene in scientific and industrial usage is a combustible hydrocarbon liquid the name is derived from Greek word "Keros." The word kerosene was registered as a trade mark by Abraham Gesner in 1854 and for several years only the North American gaslight company and the downer company (to which Gesner had granted the right) were allowed to call their lamp oil, kerosene.

It eventually became generalized, it is commonly called paraffin (some times paraffin oil) in the U.K and South Africa (not to be confused with the waxy solid also called paraffin wax or just paraffin or the much more vicious paraffin oil used as a laxative). Kerosene is widely used to power jet engine aircraft, but is also commonly used as a heating fuel. The heat of combustion of kerosene is similar to that of diesel. It lower heating value is around 43.1Mj/kg and its higher heat value is 46.2Mj/kg.

Kerosene is a thin clear liquid formed from hydrocarbon, with density of 0.78-

0.8g/cm3. Kerosene is obtained from fractional distillation of petroleum between 150oc and 275oc, resulting in a mixture of carbon chains containing 12-15 carbon atoms.

2.5.2 Diesel

Petroleum diesel also called petrol diesel or fossil diesel is produce from petroleum and is a hydrocarbon mixture, obtained in the fractional distillation of crude oil between 200oc and 350oc at atmospheric pressure. The density of petroleum diesel is about 0.85kg/L where as petrol (gasoline) has density of about 0.72kg/L, about 15% less when burnt diesel typically releases about 38.6mj/L

where as gasoline releases 34.9mj/L 10% less by energy density, but 45.41mj/kg and 48.47mj/kg, 6.7% more by specific energy. Diesel is generally simpler to refine from petroleum than gasoline. Diesel is immiscible with water, petroleum derived diesel is composed of about 75% saturated hydrocarbon and 25% aromatic hydrocarbon. The average chemical formula for common diesel fuel is $C_{12}H_{24}$ ranging from $C_{10}H_{20}$-$C_{15}H_{28}$.

2.5.3 Liquified Natural Gas (LPG)

Also called LPG, GPL, LP gas or auto gas is a mixture of hydrocarbon gases used as fuel in heating appliances and vehicles and increasingly replacing chloro-

fluorocarbon as an aerosol propellant and refrigerant to reduce damage to the ozone layer.

Varieties of LPG bought and sold include mixes that are primarily propane, mixes that are primarily butane, and the more common mixes including both propane (60%) and butane (40%) depending on the season- in winter more propane, in summer more butane. Propylene and butylenes are usually present in small concentrations; a powerful odourant ethenethiol is added so that leaks can be detected easily.

LPG is usually derived from fossil fuel sources been manufactured during the refining of crude oil, or extracted from oil or gas stream as they emerged from the ground. At normal temperature and pressure LPG will evaporate, because of this, LPG is supplied in pressurized steel bottles. The pressure at which LPG becomes liquid, called its vapour pressure varies depending on composition and temperature, it is approximately 220Kilo Pascal (2.2 bar) for butane at $20^\circ c$ (68f) and approximately 2.2mega Pascal (22bar) for pure propane at 55^0c (131f) LPG is heavier than air and then will flow along floors and tend to settle in low spots such as basement.

LPG is the lowest carbon emitting hydrocarbon fuel available in rural areas, emitting 19% less CO_2 per Kw/h than oil, 30% less than coal and more than 50% less than coal generated electricity distributed via the grid. LPG burns cleanly with no soot and very few sulphur emulsions, posing no grand or water pollution hazards.

Large amount of LPG can be stored in bulk tanks and can be buried underground if required. Alternatively gas cylinders can be used LPG has a

typical caloric value of 46.1Mj/Kg compared to 42.5Mj/Kg for diesel and 43.5Mj/Kg for premium grade petrol (Gasoline).

2.5.3.1   Use of LPG In Vehicles

When LPG is used to fuel internal combustion engine it is often referred to as auto gas. In some countries it has been used since the 1940s as an alternative fuel for spark ignition engine. More recently, it has a...o be used in diesel engines. Its advantage is that it is non toxic non corrosive and free of tetra-ethyl lead or any additives and has a high octane rating (108RON). IT burn more clearly than petrol or diesel.

LPG as a vehicle fuel has 2 main disadvantages firstly:

It has a lower energy density than either petrol or diesel, so the equivalent fuel consumption is higher. Secondly, some designs of internal combustion engine

require the lubrication of petrol or diesel with lead or lead substitute, and LPG's unleaded fuel, equipped with hardened valve seat, are usually suitable for use with LPG without added upper cylinder lubrication.

2.5.4 Asphalt

This is a black and highly viscous liquid or semi-solid that is present in most crude petroleum and in some natural deposits sometimes termed asphaltum.It is most commonly modeled as a colloid, with asphaltenes as the dispersed phase and maltenes as the continuous phase.

In the U.S. terminology, asphalt is the carefully refined residue from the distillation process of selected crude oils. Outside North America the product is called bitumen. The primary use of asphalt is in road construction, where it is used as the glue or binder for the aggregate particles.

Asphalt can be separated from other components in crude oil(such as naphtha, gasoline and diesel) by the process of fractional distillation, usually under vacuum conditions. A better separation can be achieved by further processing of the heavy fractions of the crude oil in a de-asphalting unit, which uses either propane or butane

in a super critical phase to dissolve the lighter molecules which are then separated.

Natural deposit of asphalt includes lake asphalt (primarily from the pitch lake in Trinidad and Tobago and Bermudez Lake in Venezuela).

Asphalt was mined at Ritchie county, West Virginia in the United States from 1852-1873. Asphalt is typically stored and transported at temperature around 300 degrees Fahrenheit (150c).sometimes diesel oil or kerosene are mixed in before shipping to retain liquidity.

2.5.5 Petrol (GASOLINE)

Petrol is another product from petroleum, which is a mixture of many organic substances it has properties that can give rise to fire, explosion, health and environmental hazard. The actual properties of petrol can vary widely depending on its source, has boiling range 25-220°c, vapour pressure at

37.8°c of 350-900kPa, water solubility of 30-100mg/L, auto-ignition

temperature greater than 250°c, density at 15°c is 0.72-0.79g/ml.

By far the most common used of petrol is as fuel from motor vehicles

especially cars, light-vans and motorcycles. In addition to its role as fuel for

motor vehicles is also commonly used as solvent or raw material in the

chemical and other manufacturing industries.

2.5.5.1   Behaviour of Petrol In Soil

Petrol adsorbed into the soil will because of its known toxicity have a detrimental or

fatal effect on the flora and fauna within the contaminated area, its subsequent dispersion

will depend on air movement causing evaporation, the water solubility of hydrocarbons,

water movement, bio degradation and soil absorption.

The extent and duration of the pollution will also depend on the quantity

and duration of the petrol release and any subsequent action. Small releases

may disperse on their own according to the above processes but large or

persistent releases may require expensive soil surveys and remedial action.

2.5.5.2   Behaviour of Petrol To Ground Water

Many of the components of petrol have significant solubility in water

and once dissolved their rate of biodegradation is much reduced. Component

levels are then only significantly reduced by dilution and dispersion.

As far as been toxic to aquatic life, petrol will cause health problems to

humans if ingested and because of these any contamination will have to be

removed from portable water by the relevant water supply companies or from

irrigation water by the Engineers. Vapour releases from petrol as a result of

spill or leaks and more significantly during transfer operations lead to the

formation of damaging ozone in

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the lower atmosphere. A build up of ozone in the atmosphere adversely affects human and animal health, interferes with plant growth and damages building materials.

2.5.5.3   Environmental Hazard of Petrol

This can arise if petrol is mis-used off site and for this reason it is important that petrol is only dispensed into proper designed and labeled container. Petrol is a complex mixture of up to 240 individual hydrocarbon most of which have varying degrees of toxicity towards living organisms and plants. If released at a filling station by spillage or leaks from tanks and pipes it may, in the absence of adequate controls either soak, into the ground directly or flow into drains or culverts. Its subsequent dispersion and movement will be difficult to predict and will depend on the geology of the area and physio-chemical properties of the soil and rocks. In most cases some of the following type of petrol adsorbed unto soil particles or held in the soil pores:-

- Free petrol floating on the ground water;

- Petrol constituent dissolved in the ground water;

- Free petrol at impervious grand layers such as clay;

- Petrol floating on surface water (i.e. Rivers and lakes)

- Petrol constituent dissolved in surface water

- Free petrol in drains (In use or redundant) or underground voids;

- Petrol vapour released from the above sources into the atmosphere or underground voids etc.

Vapour released from petrol as a result of spill or leaks and more significantly during transfer operations will lead to the formation of damaging ozone in the lower atmosphere. A build up of ozone in the

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lower atmosphere adversely affect human and animal health, interferes with plant growth and damages building materials.

2.5.6 Transporting of Refined Petroleum Products

2. 5.6.1 Pipelines and Tankers

Most pipelines above the ground, below the ground and under the sea transport one form of liquid or the other oil. Other method of transport includes tankers, barges, and rail cars. In 1863 in Pennsylvania, small diameter wooden pipelines were built for transporting oil, as they were cheaper and less cumbersome to use than 42galon (159L) barrels moved on horse-carts.

Today, pipeline systems have evolved and multiplied, according to the association of oil pipelines, the United state alone has a network of 200,000miles (300,000km) of petroleum pipeline (Awake 2005). Such pipeline system mainly

made of metal transport not only crude oil to the refineries but also final product to distributors.

Modern pipeline technology allows for automated systems that monitor flow and pressure. So called intelligent-pigs (devices use to inspect 100 of miles of pipeline). Magnetic flux leakage inspection, and ultrasonic inline inspection have also been developed (Awake, 2005), yet all that the ordinary user of the final product will probably see is a sign indicating that petroleum pipeline lies underground and warning that no digging should be done at the site.

As useful as it is, though a pipeline system is not practical for the transportation of large quantities of oil overseas. But early oil entrepreneur found a solution for those too-immense oil tankers.

These are specially designed ships as much as a quarter of a mile long (400meters long). Tankers are the largest ship to sail the oceans and are able to carry up to a million or more barrels of oil.

Unfortunately as mighty as they look, tankers have a vulnerability that has not been surmounted. Barges and railcars are also common means of bulk oil transportation.

2.6 How Do Spill Happen

Oil spills into rivers, bays and ocean are caused by accidents involving tankers,

barges pipelines, refineries and storage facilities.

Spill happens usually while the oil is been transported to us its users. During oil spill many things are affected,   One of the major things being animals and birds in the sea. Fish, shrimp, and crab and of course plants, as its affects soil permeability, porosity e.t.c.

Spills can be caused by

- People making mistakes or being careless
- Equipment breaking down
- Natural disasters such as hurricanes
- Deliberate acts by terrorists, countries at war, vandals, or illegal dumpers.

2.6.1 Spilled Oil

An oil spill is the release of a liquid petroleum hydrocarbon into the environment as a result of human activity which can be intentional or unintentional.

Oil can refer to many different materials, including crude oil, refined petroleum products (such as gasoline or diesel fuel or by-products, ships' bunkers, oily refuse or oil mixed in waste. Spills take months or even years to clean up (Wikipedia 2008).

Most man-made oil pollution comes from land based activity, but public attention and subsequent regulations has tended to focus most sharply on sea-going
oil tankers. (Wikipedia, the free encyclopedia).

Since petroleum is often extracted in places that are far away from areas where it is refined and eventually used, it must be transported in large quantities by ocean tankers, in land-water barges, or overland pipelines.

Accidental oil spills can occur at anytime during the loading, transportation, and unloading of oil. Some oil spills have been spectacular in magnitude and have caused untold environmental damage. The amount of oil lost at sea in 1983 by spillage, fire, or container sinking, rose dramatically- 930% over 1982. The oil spill intelligence Report 2000 pinpoints the loss at 241.8 million gallons. The largest single loss-80million gallons-occurred in the Persian Gulf, where attacks in the Iraqi-Iranian conflict caused oil-well blowouts and prevented repairs.

Accidental oil spills from tankers and offshore rigs are estimated at about 950million litres per year. In 1967, off the coast of Southern England, the

Torrey Canyon ran aground, spilling about 120million litres of crude oil. In 1978, the Amoco Cadiz went aground in the English Channel, spilling over 240million litres of crude oil. In 1979, offshore exploration rig IXTOC-1 had an uncontrollable blowout that spilled more than 52million litres of crude oil into the Gulf of Mexico. (Wikipedia .2008).

The most damaging oil spill ever to occur in North American waters was the Exxon Valdez accident of 1989. The 42million litres of spilled oil affected about 1900kilometres of shoreline of Prince William sound and its surrounding in Alaska.

Large quantities of crude oil have also been spilled during warfare. The largest-ever spill of petroleum into a body of water occurred during the Persian Gulf 1991-1992. Iraqi forces deliberately released an estimated 1,900 million litres of petroleum into the Persian Gulf from several tankers and an offshore taker-loading facility.

Iraqi forces also sabotage and set fire to over 500 oil wells in Kuwait. Before the fires were extinguished and the wells capped, an estimated 35 to115billion litres of crude oil had

been spilled. Much of the oil burned, releasing toxic petroleum vapours into the atmosphere.

A potential ecological disaster arose in January 2001 when a tanker carrying 885,690litres of diesel and bunker (a heavy mixed fuel used by tourist boats) spilled the bulk of its load after it ran aground near the Galapagos Islands (Wikipedia 2008).

Serious shipping accidents continue to happen, with massive oil spillage and the tragic aftermath of beach and sea life pollution. Frequent near-misses are often averted only by the skill and vigilance of ship officers. (Awake 2005). Put table of largest oil spill here

2.6.2 Oil Spill In Nigeria

About five decades after the discovery of oil in commercial quantity, Nigeria has woken up to the reality of the danger of oil spill on the host communities and the nation at large.

Recently the federal government set up the national oil spillage detection and response Agency, (NOSDRA). The agency as the name implies, has the clear mandate of monitory the coastal areas of the Niger Delta to ascertain the possibility of oil spill, degree of the spillage when it happens and consequently initiate remediation activities for the purpose of restoring and recovering impacted sites.

Though the agency is being set up belatedly, it is also instructive that it is coming at this time when the nation has been having Herculean task try to manage the aftermath of oil spill.

Nigeria is a key member of the organization of petroleum exporting countries (OPEC), the fifth largest supplier of crude oil to the United States, the largest producer in Africa and the eight largest exporters of same in the world. Currently she enjoys a daily quota of 2.4billion barrels per day (bpd).

This has also placed enormous pressure on the oil producing communities due to increased seismic and sundry oil-prospecting activities in the area.

Not only are the people put under pressure, the facilities particularly the pipelines

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are subjected to continual usage. The net effect is a spate of burst pipelines occasioning oil spills. But by far the major cause of oil spill is vandalization, more commonly described as "act of sabotage" by the oil firms. For instance, in 2003 alone shell recorded 221 incidents of oil spills, but which two thirds were allegedly caused by saboteurs.

Nigeria has had the misfortune of one spill to many due largely to negligence on the part of the oil companies when they fail to adhere to basic international standards in facilities installation and clear acts of sabotage of oil bunkerers and miscreant. Add to that is oil waste dumping and indiscriminate gas flaring.

All these coalesce to destroy the biodiversity of the affected areas leading to loss of wildlife, aquatic life, and soil and health degradation. In the main the nation loses economically and socially. Sometimes, when there is a spill, it creeps and spreads to the shoreline, thus threatening both coastal and terrestrial life.

The Niger-Delta region, the prime targets of the oil spills, has experienced all these and the effects are made manifest in the brackish waters of the region and the disappearance of fishes from the sea bed.

Oil spill is not a novelty. It has been since the history of oil, and it is not peculiar to Nigeria. The only difference however, is that in other climes, response by both governments and the oil companies are usually swift. The nuisance of oil spill has become so worrisome to the extent that it has produced ancillary companies specializing in the manufacture of oil spill containment facilities.

Such products include oil skimmers used to recover and eliminate oil spill, oil spill containment devices, emergency spill kits, crude oil sludge control systems, stem jet refrigeration, bio-remediation product, chemical clearing solutions, among others.

On the Nigeria Coastal environment, large sareas of the mangrove ecosystem have been destroyed. Oil spill has also destroyed farmlands, polluted ground and drinkable water and caused drawbacks in fishing off the coastal waters. There have been continuous regional crises in the Niger Delta area as a result of the oil spill pollution of the coastal ecosystem, e.g the Idoho oil spill of 1998 polluted coastal waters from Akwa Ibom state in the East to Lagos state in the West. Mobil producing unlimited commissioned a verification exercise to determine the extent and impacts of this oil spill.

During the verification exercise, it was observed that the spill destroyed fish nets, boats and fishing ponds.

2.6.3   Management of Oil Spills In Nigeria

A number of laws already exist in the Nigerian oil industry. Most of these laws provide the framework for oil exploration and exploitation. However, only some of these laws provide guidelines on the issues of pollution (Salu 1999).

According to the Federal environmental protection Agency Lagos Nigeria, the following relevant National laws and international agreement are in effect namely:

1. Endangered species Decree cap 108 LFN 1990.

2. Federal Environmental protection Agency Act caps 131 LFN 1990.

3. Harmful waste cap 165 LFN 1990

4. Petroleum (Drilling and production) Regulations,1969

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5. Mineral oil (Safety) Regulations. 1963

6. International convention on the Establishment of an international fund for compensation for oil pollution Damage 1971

7. Convention on the prevention of Marine Pollution Damage 1972

8. African Convention on the conservation of Nature and Natural Resources, 1968.

9. International convention on the Establishment of an international fund for the compensation for oil Pollution Damage 1971.

Due to increasing awareness in preventing and controlling spills in Nigeria, the clean Nigeria associates (C.N.A) was formed in November 1981. The C.N.A. is a consortium of eleven oil companies operating in Nigeria, including N.N.P.C. The primary purpose of establishing the C.N.A. is to maintain a capability to combat spills of liquid hydrocarbons or pollutants in general. The environmental Impact Assessment (EIA) decree No 86 of 1992 was promulgated to protect and sustain our ecosystem. The law makes EIA compulsory for any major project that may have adverse effects on the environment (Ntukekpo, 1996) (Olagoke 1996)

The decree was to control activities that have environmental impact on the host communities, facilitates the promotion and implementation of the policy, encourage information exchange, it sought to assess the likely or potential environmental impacts of proposed activities, including their direct or indirect, cumulative short term and long term effects and to identify the measures available to mitigate adverse environmental impact of proposed activities, and assessment of those measures.

The guideline made provisions for offshore operations, safety measures, liability and compensation (Ozekhome, 2001).

2.7   Behaviour of Oil at River

Most of the weathering processes, such as evaporation, dispersion, dissolution and sedimentation, lead to disappearance of oil from the surface of the river, whereas others, particularly the formation of water-in-oil emulsions (MOUSSE) and the accompanying increase in viscousity; promote its persistence. The speed and relative importance of the processes depend on factors such as the quantity and type of oil; prevailing weather and river conditions; whether the oil remain at river or is wash ashore, ultimately, the river environment assimilates

spilled oil through the long term process of bio-degradation.

2.7.1   Spreading

As soon as oil is spilled, its start to spread over the river surface, initially as a single slick. The speed at which this takes place depends to a great extent upon the viscosity of the oil. Fluid with low viscosity, moves more quickly than those with a high viscosity.

Nevertheless, slicks quickly spread to cover extensive areas of the river surface. Spreading is rarely uniform and large variations in the thickness of the oil are typical.

After a few hours the slick will begin to break up and, because of winds and wave action, and water turbulence will then form narrow bands or windrows parallel to the wind direction. The rate at which the oil spreads is also determined by the prevailing conditions such as temperature, water currents, tidal streams and wind speed. The more severe the conditions, the more rapid the spreading and breaking up of the oil. (ITOPF, 2008)

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2.7.2 Evaporation

Lighter components of the oil will evaporate to the atmosphere. The amount of evaporation and the speed at which it occurs depend upon the volatility of the oil.

Oil with a large percentage of light and volatile compounds will evaporate more than one with a larger amount of heavier compounds. For example petrol, kerosene and diesel oils, all light products tends to evaporate almost completely in a few days; while little evaporation will occur from a heavy fuel oil. (ITOPF, 2008)

In general, under temperate conditions, those components of the oil with a boiling point under 200°c tend to evaporate within the first 24hours.Evaporation can increase as the oil spreads, due to the increased surface area of the slick. Rougher rivers, high wind speed and higher temperatures also tend to increase the rate of evaporation and the proportion of an oil loss by this process. (ITOPF, 2008).

2.7.3   Dispersion

Waves and turbulence at the river surface can cause all or part of a slick to break up into fragments and drop of varying sizes. These become mixed into the upper levels of the water column. Some of the smaller droplets will remain suspended in the water while the larger ones will tend to rise back to the surface, where they may either coalesce with other droplet to reform a slick or spread out to form a very thin film.(ITOPF.2008)

The oil that remains suspended in the water have a greater surface area than before dispersion occurs. This encourages other natural processes such as

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dissolution, bio-degradation and sedimentation to occur. The speed at which

an oil disperses is largely depended upon the nature of the oil and the state of

the river, and occur most quickly if the oil is light and if low viscosity and if

the river is very rough. These factors led to the complete dispersion of the oil

spilled from the BRAER (SHETLAND ISLAND, UNITED KINGDOM,

1993).The addition of chemical dispersants can accelerate this process of

natural dispersion.

2.7.4 Emulsification

An emulsion is formed when two liquids combine, with one ending up

suspended in the other. Emulsification of crude oil refers to the process

whereby river water droplet becomes suspended in the oil. This occurs by

physical mixing promoted by turbulence at the river surface. The emulsion

thus form is usually very viscous and more persistent than the original oil and

is often referred to as chocolate mousse because of its appearance. (ITOPF,

2008).

The formation of this emulsion causes the volume of pollutant to

increase between three and four times. This slows and delays other processes

which would allow the oil to dissipate oils with asphaltene content greater than

0.5% tend to form stable emulsions

which may persist for many months after the initial spill has occurred.

That oil containing a lower percentage of asphaltene is less likely to form

emulsions and is more likely to disperse. Emulsions may separate into oil and

water again if heated by sunlight under calm conditions or when stranded on

shorelines. (ITOPF, 2008)

2.7.5 Dissolution

Water soluble compounds in oil may dissolve into the surrounding water. This depends on the composition and state of the oil, and occurs most quickly when the oil is finely dispersed in water column. Components that are most soluble in sea water are the light aromatic hydrocarbons compounds such as benzene $ toluene (ITOPF, 2008).

However, these compounds are also those first to be lost through evaporation, a process which is 10-100times faster than dissolution. Oil contains only small amounts of these compounds making dissolution one of the less important processes.

2.7.6 Oxidation

Oil react chemically with oxygen either breaking down into soluble products or forming persistent compounds called tars. This process is promoted by sunlight and the extent to which it occurs depends on the type of oil and the form in which it is exposed to sunlight.
However, this process is very slow and even in strong sunlight, thin films of oil breakdown at no more than 0.10% per day. (ITOPF, 2008)

The formation of tars is caused by the oxidation of thick layers of high viscosity oils or emulsions. This process forms an outer protective coating of heavy compounds that result in the increased persistence of the oil as a whole. Tar balls, which are often found on shorelines and have a solid outer crust surrounding a softer, less weathered interior, are typical example of this process. (ITOPFS, 2008)

2.7.7 Sedimentation/Sinking

Some heavy refined products have densities greater than one and so will

sink in fresh or brackish water. However sea water has a density of approximately 1.025 and very few crude are dense enough or weather, sufficiently, so that their residues will sink in the marine environment. Sinking usually occur due to the adhesion of particles of sediment or organic matter to the soil. Shallow waters are often laden with suspended solids providing favourable conditions for sedimentation. (ITOPF, 2008).

Oil stranded on sandy shorelines often becomes mixed with sand and other sediments. If this mixture is subsequently washed off the beach back into the sea it may then sink. In addition, if the oil catches fire after it has been spilled, the residue that is sometimes formed can be sufficiently dense to sink. (ITOPF, 2008)

2.7.8 Biodegradation

Sea water contains a range of micro-organisms or microbes that can partially or completely degrade oil to water soluble compounds and eventually to carbon dioxide and water. Many types of microbe exist and each tends to degrade a particular group of compounds in crude oil. However some compounds in oil are very resistant to attack and may not degrade (Maki A.W. 1991).

The main factors affecting the efficiency of biodegradation, are the levels of nutrients (nitrogen & phosphorous) in the water, the temperature and the level of oxygen present. As biodegradation requires oxygen, this process can only take place at the oil-water, interface since no oxygen is available within the oil itself. The creation of oil droplets,

either by natural or chemical dispersion, increases the surface area of the oil or

increases the area available for biodegradation to take place (Hoff R.1993).

2.7.9 Combined Processes

The processes of spreading, evaporation, dispersion emulsification and dissolution

are most important during the early stages of a spill whilst oxidation sedimentation and

Biodegradation are more important later on and determine the ultimate fat of

the oil. To understand how different oils change over time whilst at sea, one

needs to know how these weathering process interact.

To predict this, some simple models have been developed based on the oil

type. Oils have been classified into groups roughly according to their density;

generally oils with a lower density will be less persistent. (Atlas R.M. et al

1992)

However, some apparently light oils can at like the heavy ones due to

the presence of waxes. Although simple models cannot predict the changes oil

undergoes very precisely, they can provide clues about whether oil is likely to

dissipate naturally or whether it will reach the shoreline. This information can

be used by spill responders to decide upon the most effective spill response

techniques and whether such techniques can be initiated quickly enough.

(Atlas R.M. et al 1992).

2.8 Environmental Impact

The exact nature and duration of any impacts from an oil spill depend

on a number of factors. These include the type and amount of oil and its

behaviour once spilled, the physical characteristics of the affected area.

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weather conditions and season, the type and effectiveness of the clean-up response, the biological and economic characteristics of the area and their sensitivity to oil pollution. (Atlas, R.M. 1981)

Typical effects on marine organisms range across a spectrum from toxicity (especially for light oils and products) to smothering (heavier oils and weathered

residues). The presence of toxic components does not always cause mortality, but may induce temporary effects like narcosis and fainting of tissues, which usually subside over time.

Oil floats on salt water (the ocean) and usually floats on fresh water (river and lakes). Very heavy oils can sometimes sink in fresh water, but this happens very rarely.

Oil usually spreads out rapidly across the water surface to form a thin layer of oil stick. As the spreading process continues, the layer becomes thinner and thinner, finally becoming a very thin layer called a sheen, which often looks like a rainbow.(Nyman, et al. 1999).

2.8.1 Environmental Impact Asssement

- Assessment of environment damage at Aznal collar- Sevilla, Spain.

Analysis performed on some spilled tailing immediately after the accident demonstrated that the sediments contain a large amount of several heavy metals like Zn, Pb, Cu, As, Cd and Hg, associated with the pyrite minerals extracted in the mine. In other to evaluate the future effects of the accident on the agriculture of impacted region, a green house study was conducted using affected soils that had been reclaimed by clean-up and restoration efforts, and

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six agricultural plants (corn, sun flower, sugar, beets, rapeseed, wheat and barley) typically grown on the

impacted area.

Heavy metal analysis and rist evaluation, soil, water and plant tissue analysis, expert counseling for remediation work, and control laboratory services for the local authorities and other particles responsible for dealing with the damages (Battelle 1998-99).

Analysis carried out on underground soil and the aquifer of an oil company site was found to be polluted by hydrocarbons. Battelle Memorial Institute, Geneva Research Centre, performed extensive finger printing analysis on samples coming from an area where in the past there were industrial activities with use and storage of chemical products, the analysis included PAH, total hydrocarbons, Pb, and VoCs surface and deep soil, and ground water samples(Carballeira, A. et al 2000).

CHAPTER III

3.0 METHOD AND PROCEDURE

3.1 SAMPLE AREA

Soil and water samples were from farms in Eluku/Ojutaye Oke-oyi area Ilorin East Local Government Ilorin, Kwara state.

The village is situated very close to the Nigerian National Petroleum Corporation, Ilorin depot in Kwara state while lies approximately between latitude $7^{0.}15^1$ and 11^0North and longitude $2^0 30^1$ and $6^0 45^1$East.

3.1.1 MATERIALS AND EQUIPMENT

- PH meter.

- Platinum electrode

- Saturated Calomel electrode

- Buffer solutions, PH 4 and 7

- Magnetic stirrer and stirring bar

- Ion chromatography equipped with conductivity detector, and integrator or chart recorder.

- Anion separator column

- Syringe and microfolters

- Stock solutions of Cl^- and SO_4^{2-}

- Mobile phase

- Atomic Absorption Spectrometer

- Aluminium Nitrate solution.

- Calcium Solution

- Hydrogen Peroxide

- Potassium Chloride

- Stock Solution of each metal to be analyzed

- Nitric acid

- Hot plate or steam bath.

- Lanthanum Solution

- Standard $AgNo_3$ Solution, 0.0141M

- Primary STANDARD Nacl 0.0141

- Potassium Chromate Solution, K_2crO_4, 5%

- Sodium Hydroxide, 0.1M

- PH Meter& electrodes (SO_4)

- Magnetic Stirrer & bar

- Stop watch

- Barium Chloride Crystalline

- Glycerol-ethnol Solution

- Standard Sulphate Solution

- Nacl-hydrochloric acid reagent

3.2   SOURCE OF RAW MATERIALS

The soil and water samples were taken from farms in Eluku/Ojutaye village in Ilorin east local government area of Kwara state in May 2008. The soil map unit is composed of about 60% Lithic Ustorthents 35% rock outcrops and 5% soils of minor extent.

The Lithic Ustorthents are soils that occur dominantly on upper hill slopes and summits.   They are very shallow or shallow and excessively drained. Typically the surface layer is dark cobbly, loamy-sand about 15cm

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thick the sub-surface layer is very dark brown very cobbly loamy-sand that is
under-lain by un-weathered quartz-schist at a depth of about 30cm. A
permeability of the Lithic Usthorthents is moderately rapid. The effective
rooting depth is limited by un-weathered bed rock at the depth of about 15-
50cm. The available water capacity is very low. The inherent facility is low.

3.3 METHOD OF DIGESTION

After shaking the bottle thoroughly, 50-100mL of the sample was placed
in a beaker and 5mL concentrated HNO_3 was added. This was boiled slowly
on hot plate, then evaporated down to about 20mL. A further 5mL
concentrated HNO_3 was

added. It was then covered with a watch glass and heated.

Concentrated HNO_3 and heat was been continually added until the
solution appears light coloured and clear indicating the completion of
digestion.

3.4   MINERAL ANALYSIS (HEAVY METALS)

A mixed calibration standard containing every metal was prepared, by
pippeting aliquots of 1000mg /L standard solution into a series of volumetric
flask (50-100mL). 1mL of concentrated nitric acid was added to each flask
and was diluted to the mark.

The Atomic absorption Spectro-photometer (AAS) was switched on and
the appropriate hollow cathode lamp was selected and the lamb current
adjusted to the value recommended in the instrument manual. The
monochrometor and slit settings were set to the recommended value. The
wavelength setting was fine-tuned and the beam was alighed.

The gain setting was then optimized, and the fume hood turned on, switching on the flame according to the recommended procedure. The sample was aspirated, standard and blanked into flame of Atomic absorption Spectophotometer(AAS) equipped with the appropriate hollow cathode lamp and operated at the wavelength recommended.

3.5 DETERMINATION OF MAJOR ANIONS

3.5.1 STANDARDIZATION OF AgNO₃

This was done by titrating with primary standard 0.0141M Nacl solution. 20mL aliquots of the standard Nacl solution in 100mL conical flask was pippeted, and the pH adjusted between 7and 10. 1mL of the chromate indicator solution was added and titrated with AgNO₃ to the first appearance of the red Silver chromate.

The result of the first titration was discarded and the titration repeated three more times on separate aliquots of Nacl solution. A blank titration was carried out by adding 1mL of chromate indicator solution to 20mL of laboratory water and titrated with AgNO₃.

The volume of the titrant required for the blank titration was subtracted from the volume of titrant required for the titration of Nacl solution and molarity of the standard AgNO₃ solution was calculated.

3.5.2 ANION ANALYSIS (CL⁻)

This was done by pippeting 100Ml of water sample into 50mL conical flask and adjusted the pH to between 7 and 10.A pH paper was used instead of a pH meter as the electrode may contaminate the sample. The indicator was added and

titrated as above.

A blank titration was also repeated using 100mL of laboratory water and corrected the volume of titrant used. The titration was repeated with three aliquots of each sample and the average taken.

The concentration of the chloride in the sample was calculated from the concentration of standardized $AgNO_3$ solution. Also corrected volume of titrant used and the volume of the sample was calculated.

3.5.3 ANION ANALYSIS (SO_4^{2-})

100mL of sample was measured into a 250Ml conical flask and placed on a magnetic stirrer, 20mL of the Nacl-Hcl solution and 2omL of Glycerol-ethanol solution was added while stirring. Approximately 0.3g of barium chloride was added and then stirred for two minutes.

Some solutions were immediately poured into an absorption cell and the absorbance at 420nM after exactly 3 minutes was measured. A series of calibration standard was prepared by pippeting aliquots of standard sulphate solution corresponding to between 0.5 and 5mg SO_4^{2-} (i.e. 5-50mL) into a 100mL volumetric flask and made up to the mark with water.

Analyzed in the same way as the samples, some blanks were prepared by adding all the reagents except barium chloride to 100mL of sample and the absorbance measured. Blanked readings obtained were subtracted from each sample reading and by using the same sample to compensate for sample colour and turbidity.

A calibration graph of absorbance against mg SO_4^{2-} was prepared. The amount of sulphate in the samples was read off using the corrected absorbance reading and the concentration in the sample was calculated as follows:

$$Mg\ SO_4^{2-}/L = 1000 \times mg\ SO_4^{2-}/V$$

Where V = volume of sample (mL)

3.6 ELECTRICAL MEASUREMENT

3.6.1 pH DETERMINATION

The combination of pH electrode and meter was calibrated using a two-point calibration with buffer solutions of pH 7 and 4.Then the pH electrode was immersed in the water sample and a measurement taken, after the solution had come to rest.

3.6.2 CONDUCTIVITY DETERMINATION

The working Potassium chloride (kcl) standard solution was placed in a beaker, and the conductivity cell was suspended, holding it 1.5cm above the bottom of the beaker, making sure it was not in contact with any of the beaker walls. The conductivity reading was adjusted to 100umhocm1.

The cell was rinsed with pure water and the measurement was carried out on the sample

3.7 ANALYSIS ON THE SOIL SAMPLE

3.7.1 SOIL CONDUCTIVITY DETERMINATION

20g of soil sample was weighed, and then placed in a beaker. 40mL of laboratory water was added and stirred vigorously on a magnetic stirrer. It was allowed to stand for 30 minutes and the conductivity determined as for the water samples, making sure the electrode cell was in the supernatant above the settled particles.

3.7.2 SOIL pH DETERMINATION

20g of the soil sample was weighed and placed in a beaker.40ml. of laboratory water was added and stirred vigorously manually, it was then allowed to stand for 30 minutes and the pH determined as for the water samples.

3.7.3 DETERMINATION OF SOIL Cd, Zn, Ni, Hg, Fe, As, Cu, Mn, and Cr.

Some air dried and sieved (< 2mm) soil sample sediment was grinded. 1.0g of it was weighted and placed inside a 100mL tall-form beaker, 30mL of

1:1 HNO_3 (10mL)

conc HNO_3) was boiled gently on a hot plate till the volume was reduced approximately to 5mL.

While stirring, 10mL 1:1 HNO_3 was added and repeated. The extract was cooled and filtered through a what man no 541 filter paper.

The beaker was washed, with the filter paper with successive small portions of 0.25M HNO_3. The filtrate and washings were transfer to a 50mL volumetric flask and diluted to the mark with the water.

A series of calibration standard over the required range was prepared by diluting aliquots of the working metal solution with 0.25M HNO_3.

A calibrate graph of absorbance against metal concentration was constructed and read off the concentration in the solid sample as concentration in soil (Mg/kg) = C x V/M Where C is the concentration of metal in the extract (Ngm/L), V is the volume of extract (mL) and M is the weight of sample (g).

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3.7.4 DETERMINATION OF PARTICLE SIZE (CLAY, SILT, SAND CONTENT) OF THE SOIL SAMPLE.

<u>Materials</u>

- Sodium diphosphate ($Na_2P_2O_7$). Dissolve 100g in water and make up to 1L with water.

- Weighing bottles, glass

- Sieve set with pore sizes: 2, 0.63, 0.2 and 0.063mm.

Procedure: A sample of air-dried soil was accurately weighed, and passed through the 2mm sieve. Stones and roots larger than 2mm were separated out; the mass of

the material > 2mm was weighed.

Accurately 20g of the soil that has passes through the 2mm sieve was weighed and placed in a bottle together with 25mL of water and shaked. Then the suspension was passed through the sieve set arranged in order of decreasing pore size and placed directly above a 1L measuring cylinder.

A large funnel with a surface area greater than that of the sieves above the cylinder was clamped before sieving of suspension. Each sieve was washed in water until particles smaller than the nominal size of the sieve pores have passed through.

The sieves were dried in an oven at 105^0c. Each sieve was weighed before   and after sieving the suspension.

The cylinder containing the sieved suspension were made up to 1L with water, stopper and shaked for 1Min. It was left to stand and the time noted.

After 9.5Min, 10mL of the solution was removed from 20cm below the surface using a pipette and placed in a pre-weighed glass weigh:. bottle.

The pipette was rinsed with water and the rinsed water was added to the same weighing bottle. Particles < 20um were contained in this suspension.

After 18.5min, a further 10mL of solution was removed from the 10cm below the surface and transferred to a pre-weighed weighing bottle. The pipette was rinsed

into the bottle. This suspension contains particles < 10mm. After 3h and 5min, another 10mL aliquot was taking from 4cm below the bottle. The pipette was rinsed into the bottle.   This suspension contains clay particles smaller than 2um. Then weighing bottles were dried before and after adding the suspension, in an oven at 105°c to complete dryness. It was then cooled in desiccators and weighed.

The mass of each particle fraction in the weighing bottles were determined by difference. 25mg were subtracted from each measurement in order to correct for the presence of Sodium diphosphate reagent and multiply by 5 to give each fraction as

% of the original weight. The percentage of the total mass that is present in each size fraction was tabulated.

3.7.5 DETERMINATION OF SOIL SODIUM ADSORBTION RATIO

Two criteria are currently recognized in the scientific literature as indices of Salinity. These are Sodium adsorption ratio (SAR) with a reported threshold of 12 (Cmol/kg) 0.5, and exchangeable Sodium percentage (ESP) with a reported threshold of 15%.

SAR= Na { Ca^{2+} + Mg^{2+}) /2}0.5

Where SAR = Sodium Adsorption ratio (Cmol/kg) 0.5

Na^+, Ca^{2+}, Mg^{2+}, = measured exchangeable Na^{2+}, Ca^{2+}, and Mg^{2+}.

Respectively, (Mol/kg (Sumner, 1993)

CHAPTER IV

4.0 RESULT AND DISCUSSION OF RESULTS

4.1 RESULTS

TABLE 4.1

S/NO	PARAMETER	SAMPLES 1	2	3
1	PH	9.1	8.7	6.4
2	ECR/Km-1	17750	13900	2291
3	CL- (mgl)	474.8	272.6	201
4	SO42- (")	451	523	247
5	Lead (")	0.09	0.082	0.04
6	Manganese (")	0.314	0.300	0.12
7	Nickel (")	0.14	0.17	0.03
8	Cadmium (")	0.01	0.02	0.005
9	Cobalt (")	0.09	0.10	0.03
10	Copper(")	1.74	1.62	0.06
11	Boron (")	1.89	1.75	0.82
12	Arsenic(")	0.85	0.61	0.03
13	Mercury (")	NA	NA	NA
14	Silver	NA	0.03	NA
15	Barium (")	0.06	0.06	0.02
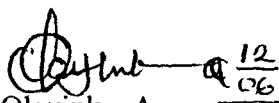
4.2 DISCUSSION OF RESULT

Table 4.1 shows, the level of pH, electrical conductivity, Cl⁻, SO₄, lead

manganese, nickel, cadmium, cobalt, copper, boron, arsenic, mercury, silver

and barium contest. The metals present in lower concentration a... barium

Cobalt lead, Cadmium, manganese. For none of which were there any

significant differences between the 2 source of samples, nor did the sources

differ with respect to barium content, but they did differ slightly with respect

to Boron, Nickel, Copper, and Arsenic.

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TABLE 4.2

S/NO	TEST	SAMPLE (SOIL)		
		1	2	3
1	Clay %	14.90	15.90	22.4
2	Sand %	78.50	80.00	68.50
3	Silt %	7.00	4.90	9.12
4	Soil pH	8.5	9.2	8.1
5	Soil Cadmium(mg/g)	0.012	0.014	0.003
6	Soil Zinc(mg/g)	27.4	29.5	2.1
7	Soil Nickel (mg/g)	0.015	0.032	0.003
8	Soil Mercury (mg/g)	5.75	2.0	NA
9	Soil Iron (mg/g)	6.12	4.32	1.04
10	Soil Arsenic (mg/g)	0.30	0.29	0.02
11	Soil Copper (mg/g)	0.117	0.122	0.005
12	Soil Manganese (mg/g)	0.360	0.344	0.160
13	SAR	0.234	0.197	0.052
14	EC $\Omega^{-1}km^{-1}$	577	539	134
15	Soil Chromium(mg/g)	0.006	0.021	NA

Lab. No.: 2008/IITA/ALC156-49

Olayinka, A.   12/06/08
(Lab. Technologist)

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TABLE 4.3   TYPICAL pH RANGES IN DIFFERENT RANGES

Water type	pH
Unpolluted surface water	6.5 - 8.5
Polluted surface water	3.0 - 12.0
Unpolluted rain water	4.6 - 6.1
Acidic rain water	2.0 - 4.5
Sea water	7.9 - 8.3
Swamp waters	5.5 - 6.0
Ground waters	$\leq 2.0 - 12.0$
Mine drainage waters	1.5 - 3.5
Industrial & municipal waste water	$\leq 1.0 - \geq 12.0$

TABLE 4.4   CONDUCTIVITIES OF SOME TYPE OF WATER

Water Type	Conductivity (u mho cm-1)
Freshly distilled water	0.5 - 2
Aged distilled water	2 4
Rain water	3 60
Drinking water	50 - 1500
Waste water	> 10,000

TABLE 4.5 PLANT RESPONSE TO SOIL CONDUCTIVITY

Soil conductivity (mmhocm-1)	Plant responses
> 1.00	Expected to cause damage to most plants.
0.71 - 1.00	May cause slight damage to most plants.
0,46 - 0.70	May cause slight to severe damage to salt-sensitive plants.
0.26 - 0.45	Suitable for most plants if recommended amounts of fertilizer are use
0 - 0.25	Suitable for most plants of recommended amounts of fertilizer are u:

TABLE 4.6 CONCENTRATIONS OF MAJOR IONS IN SEA WATER ($mgkg^{-1}$) SALT LAKES ($mgkgL^{-1}$) AND RIVER WATER (mgL^{-1})

Constituent	Sea water	Salt lake water	River water
HCO_3^-	140	180 - 17400	17.9 - 183
SO_4^{2-}	2649	264 - 13590	0.44 - 289
CL^-	18980	1960 - 112900	2.6 - 113
NO_3^-	2	1.2 - 1.6	0.3 - 1.9
Ca^{2+}	400	3.9 - 15800	5.4 - 94
Mg^{2+}	1272	23 - 41960	0.5 - 30
Na^+	10556	1630 - 67500	1.6 - 124
K^+	380	112 - 7560	0.0 - 11.8

TABLE 4.7 CONCENTRATIONS OF HEAVY METALS IN PLANTS & SOILS AND CRITICAL CONCENTRATIONS IN PLANTS AND SOILS

Normal range in plants (Mg kg-1)	Critical plant concentration A (Mg kg-1)	Critical plant concentration B (Mg kg-1)	Normal range in soils (Mg kg-1)	Critical soil concentration (Mg kg-1)
0.02-7	5 - 20	1 - 20	0.1 - 40	20 - 50
0.1 - 2.4	5 - 30	4 - 200	0.01 - 0.2	3 - 8
0.02 - 1	15- 50	4 - 40	0 5 - 65	25 - 50
0.03 -14	5 - 30	2 - 18	5 - 1500	75 - 100
5 - 20	20 - 100	5 - 64	2 - 250	60 - 125
0.005 - 0.17	1 - 3	1 - 8	0.01 - 0.5	0.3 - 5
20 - 1000	300 - 500	100 - 7000	20 - 10000	1500 - 300
0.03 -5	10 - 50	-	0.1 - 40	2 10
0.02 - 5	10 -100	8 - 220	2 - 750	100
0.2 - 20	30 - 300	-	2 - 300	100 - 400
0.00001 - 0.2	-	1 - 2	0.2 - 10	5 - 10
0.001 - 2	5 -30	3 - 40	0.1 - 5	5 - 10
0.2 - 6.8	60	63	1 - 200	50
0.001 - 1.5	5 - 10	5 - 13	3 500	50 - 100
1 - 400	100 - 400	100 - 900	1 - 900	70 - 400

apted from B.J. Alloway (1995)
concentration above which toxicity is likely, B: concentrations likely to cause a 10% uction in yield.

TABLE 4.8 DRINKING, SURFACE, AND IRRIGATION QUALITY CRITERIA (mgL⁻¹) FOR HEAVY METALS

Heavy metal	Drinking water Criteria	Surface water FWPCA b, d	Irrigation water continuous use b FWPCA any soil	NAS coarse-textural soil	Short term use[b] FWPCA Fine textural soil
Ag		0.05	-	0.1	-
As (iii)	0.19	0.05	1	0.75	0.0
B		1	0.75		2.0
Ba	2	1			-
Cd	0.005	0.01	0.005	0.01	0.05
Co		-	0.2	0.05	10.0
Cr (iv)	0.1	0.05	5.0		20.0
Cu	1.3	1	0.2	0.2	5.0
Pb	0.005	0.05	5.0	5.0	20.0
Mn		0.05	2.0	0.2	20.0
Mo			0.005	0.01	0.05
Ni		-	0.5	0.2	2.0
Se	0.05	0.01	0.05	0.02	0.05
Sb	0.05	-			-
Zn		5.0	5.0	2	10.0

After Adriano (1986); Bandman et al. (1989); and
EPA (1991.)
aUS EPA (1991)
b Adriano (1986)
c Bandman et al (1989)
d FWPCA, Federal Water Pollution Control
Association

Mercury and Silver content were not really available. The metal present in greatest concentration were Boron (1.75-1.89mg/L), and the highly toxic Copper (1.62-1.75mg/L), followed by Arsenic (0.61-0.85mg/L) Manganese (0.30-0.31mg/L) Nickel (0.14-0.17mg/L) and Cobalt and Lead (0.08-0.10mg/L).

Except for lead all these metals are released very slowly from fuel oil. (Roscup and Boroman, 1967).

4.3 EFFECTS ON SOIL AND WATER

The soil, sample which is by far most affected is that of site (1) with total heavy metal (THM) content of 40.08mg/L. The affected soil at site (ii) had total heavy metal (THM) content 36.64mg/g. The heavy metal were virtually absent or rather not much in the control soil which had THM content of about 3.33mg/g.

The water samples were less affected, as the water from site one had THM content of 5.18mg/l and that from site two 4.74mg/l in THM content, it was also not much in the control water, which had a THM content of 1.15mg/l.

In the area of soil affected by the spill, oil had impregnated the roots of the plants constituting the predominant vegetation 'gluing soil particles to the root.

These areas exhibited a compact crust of very low porosity as discovered from the shallow rooting system of the vegetables present in the area.

Colour of the soil range from black at site one, where it was responsible for the high resistance to penetration of the affected soil, through a shade of gray at site two where the crust was thinner and offered lesser resistance to penetration, as discovered from the length of the rooting system.

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However, resistance to penetration was moderate in the control soil(site 3), as

vegetables in these areas had longer rooting system, than the vegetables in site 1 and 2 on the Eluku/Ojutaye farms.

The crust was composed of aggregates of fine material agglutinated which in by the oil, coating the final particles will have facilitated their entry and permanence in the larger pores and channels, gluing larger particles together and thus reducing porosity and permeability and increasing resistance to penetration, whereas under normal circumstances the particles of sandy soil reorganize during every cycle of wetting and drying and do not cohere, resulting in very low resistance to penetration (Andrade et al 2002).

The formation of this crust did alter gross particle size distribution, with the proportion of sand, silt, and clay slightly different in the two sites and even the control soil, all having sand, silt and clay content of 78.50,7.00,14.90 at site I, 80.00,4.90,15.90 at site ii and 68.50,9.12 and 22.4 in the control soil respectively.

Polluted soil differed from their unpolluted counterparts in permeability as well as in porosity, resistance to penetration. Polluted soils had significantly higher values than control soil with respect to total Cu, Cr, Fe, Pb. From table 4.3, we can see that the PH range for polluted surface water is between 3.0- 12.0, comparing with the values of pH from table 1, which shows that the PH of the water samples are high ranging between 8.7-9.1 at both site and 6.4 at control site.

This could be seen as an advantage as low pH causes the accumulation of Aluminum and manganese which may be toxic to plant roots, which also reduces the population of some useful soil organism, such as bacterial and earthworm, it also

cause disintegration of clay minerals which are leached from the soil. The electrical conductivity is between 13,900-17,750n/km in the water samples and between 539-577n/km in the soil sample. Table 4.5 shows the effect of different ranges of soil conductivity on plants.

The Cl⁻ ion which is a major ion in the surface water varies between 272.6-474.8mg/l in the water samples and is about 201mg/l in the control. SO_4^{2-}, also a major ion occurring in natural water was found to be between 451-523mg/l in water samples and 247mg/l in control water. Table 4.6 shows the level of both Cl⁻ and So42- in river water. In the case of the water samples the level of both Cl⁻ and SO_4^{2-} are very high. The level of SO_4^{2-} ion concentration in the water sample exceeds the maximum amount admissible for water for irrigational purposes, thus having a harmful effect on plant. (Mikua W.2001)

The sodium adsorption ratio of the soil sample varies between 0,197-0.234mol/kg and 0.052 in control soil.

The level of chloride in water supplies is limited to 250mgl-1, at higher concentration as in the case of the samples from the two sites, chlorides impacts a salty taste which make the water unpalatable for irrigational purposes . High chloride concentration are harmful to plants, some damages may occur at levels as low as 70-250mg/l. High chloride ion con: ..tration contribute synergistically to salt toxicity in plants. It also inhibits plant growth

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and electron flow through the photo system. However, the synergistic effect of sodium and chlorides shows that neither of these ions alone is responsible for salt stress induced damage.(Martin, P.K et al 2001) This also applies in the case of SO_4^{2-}.

In the case of electrical conductivity (EC), anything above, 0.45mmhocm/1, cases severe damage to plants. The value of SAR (sodium adsorption ratio) which ranges between (0.197-0.234) in the soil is very high. The application of this soil agricultural purposes may increase in soil salinity, as the alkali and the alkaline earth metal which are criteria in measuring sodium adsorption ratio in soil contributes greatly to the salt stress induced damage to plants.

Salinity becomes a problem when enough salt accumulate in the root zone to negatively affect plant growth. Excess salts in the root zone hinder plant roots from

withdrawing water from surrounding soil. This thus lowers the amount of water available to plant regardless of amount of water actually in the root zone (Sumner, 1993).

For irrigational purposes, the level of cu in the water samples (1.62-1.74) is somehow higher as the irrigation quality criteria for heavy metal (for cu) for water for

irrigational purposes is 0.2mg/l. (Adriano 1986; US EPA, 1991). Cu being very toxic affects seriously the growth of the plants.

For all the heavy metals present, there was deviation from the level of irrigation quality criteria for irrigation water, from the FWPCA standard, as shown in the table 4.4 below. The presence of the heavy metals in excess of

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the standard greatly affected the growth of the plants, by inducing temporary effects like narcosis and tainting of tissues, which usually subsid- over time. (Andrade, L et al 2004)

Also table 4.5 shows the concentration of heavy metals in plants and soils and critical concentration in plants and soils. At critical plant concentration A, (concentration above which toxicity is likely) and concentration B (concentration likely to cause a 10% reduction in yield(Alloway B. J 1995)

The level of heavy metal in the soil at the two sights is higher than the critical soil concentration reasons for the low yield and highly toxic soil at the two sites.

CHAPTER V

5.0 CONCLUSION

As expected, the degree to which the study area had been affected, as reflected by the THM contents of the polluted soils, differed widely. However, all the polluted soils exhibited, as the main microscopic effect of the pollution, a desk, compact crust with significantly lower porosity and greater resistance to penetration than those of unpolluted solids at the same sites.

Pollution also significantly lowered intrinsic permeability raised hydrophobicity, and increased greatly the concentrations of Cr, Cu, Fe, Pb and Ni.

5.1 RECOMMENDATION

Because mechanical clean up method are not as effective as bio-remediation, cleanup procedures should concentrate on enhancing the bio-degradation of the oil. The advantages of bio remediation must nevertheless be balanced against the prospect of its releasing high concentrations of toxic heavy metals into the ecosystem, and in considering costs and benefits it must also be kept in mind that release of heavy metals could also be induced by changes in soil acidity.

The Oil Industry in general should devote a considerable manpower and money towards the prevention of oil spills and abatement of accidental petroleum products spill on water and the land.

Effort should be made in developing new techniques and increase the inventory of clean up equipment as well as in the technology of control and clean up operations.

Establishment should be made of some co-operation like the Clean Seas Incorporated by major oil operations in the California area to protect the environment around their operating localities.

Sound environmental policy and effective research and development programs should be developed to solve the problem, like in the U.S.A. government which has provided safeguard and protection through the National Environmental Policy Act (NEPA) of 1970, water quality improvement act of 1970, Refuse act of 1971, the clean air amendments of 1970 and regulation concerning spills of oil and hazardous substances under the water quality improvement act of 1970.

Technologically speaking, there are basically two solutions to the problem of environmental pollution created by oil industries. The first short range solution consist of adding environmental control to the existing plants as an appendage. Such an alternative will only naturally increase the production cost which in turn will be passed on to the consumer.

The second, long range alternative constitute the ultimate solution to the problem through research and development such effort would result in totally new processes designed from the outset to eliminate or minimize the environmental problem. There are good possibilities that such innovative processes incorporating pollution controls, recycling provisions and by products recovery will be comparable in cost to the old processes without such controls.

I therefore recommended that the farmers in Eluku/Ojutaiye Village should move to the site least affected by the spill.

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