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<tr>
<th>Author</th>
<th>NNADOZIE, Scholastica Oluchi</th>
</tr>
</thead>
<tbody>
<tr>
<td>PG/M.Sc/03/34028</td>
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</tr>
<tr>
<td>Title</td>
<td>Determination of Total Petroleum Hydrocarbon in Sediment from Qua Iboe River Estuary</td>
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<tr>
<td>Department</td>
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<td>September, 2006</td>
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DN: CN = Ojionuka Arinze, C = US, O = University of Nigerian, OU = University Library
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Location: Enugu State
Date: 2010.05.24 13:21:08 -07'00'
DETERMINATION OF TOTAL PETROLEUM HYDROCARBON IN SEDIMENT FROM QUA IBOE RIVER ESTUARY

BY

NNADOZIE SCHOLASTICA OLUCHI
PG/M.Sc/03/34028

PURE AND INDUSTRIAL CHEMISTRY
UNIVERSITY OF NIGERIA
NSUKKA

SEPTEMBER 2006
DEPARTMENT OF PURE AND INDUSTRIAL CHEMISTRY FACULTY OF PHYSICAL SCIENCES UNIVERSITY OF NIGERIA, NSUKKA.

RESEARCH PROJECT (CHEM 561)
DETERMINATION OF TOTAL PETROLEUM HYDROCARBON IN SEDIMENT FROM QUA IBOE RIVER ESTUARY.

A RESEARCH PROJECT SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF MASTER OF SCIENCES, DEGREE IN PETROLEUM CHEMISTRY

BY

NNADOZIE SCHOLASTICA OLUCHI
(REG. NO. PG/MSC/03/34028)

HEAD OF DEPARTMENT PROJECT SUPERVISOR
DR. C.O.B OKOYE PROF. C.A. NWADINIGWE
DEDICATION

This work is dedicated to the memory of my late mother, Maria Ceiline Nnadozie.
ACKNOWLEDGEMENTS

It is necessary to record my deep appreciation to a number of people. First of all I wish to express my sincere gratitude to my project supervisor, Prof. C.A. Nwadinigwe, for his continuous encouragement and constructive criticism of the work.

I also wish to express my deep appreciation to Dr. Vincent Osabor and Godwin Udor for reading through the manuscripts.

I must also appreciate my husband Mr. Iwebi Victor and my baby Iwebi Joel Chideraa for all their support and understanding throughout the period of this work. My entire family deserves distinguished recognition here for their more support and continuous intercessory prayers.

Above all, may the Almighty God receive all the glory.

Nnadozie S.O.

Sept. 2006
ABSTRACT

The petroleum hydrocarbon composition of sediments from Qua Iboe River Estuary, Ibeno, South-Eastern Nigeria, was studied to determine the levels of these hydrocarbons in the marine environment. Ten sediment sites were sampled using a van veen Grab sampler. Chemical parameter, such as total organic carbon (TOC), was assessed using Blackey-walkey titration method. Soluble organic matter (SOM) was assessed using soxlet extraction method and total petroleum hydrocarbon (TPH) was assessed using liquid column chromatography to fractionate the hydrocarbons.

The results obtained show that the TOC contents range from 1.02% to 2.03% while the SOM contents of the sediments range from $0.2 \times 10^4$ to $1.3 \times 10^4$ ppm. This shows that the sediments are very rich in organic matter. The TPH contents ranged from $7.9 \times 10^4$ ppm to $74.1 \times 10^4$ ppm. The values are all above the permissible limit for hydrocarbon pollution in sediment. Deduction from this study reveals heavy pollution of Qua Iboe River with petroleum hydrocarbon.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Title page</td>
<td>i</td>
</tr>
<tr>
<td>Dedication</td>
<td>ii</td>
</tr>
<tr>
<td>Acknowledgment</td>
<td>iii</td>
</tr>
<tr>
<td>Abstract</td>
<td>iv</td>
</tr>
<tr>
<td>Table of Content</td>
<td>v</td>
</tr>
<tr>
<td><strong>CHAPTER ONE</strong></td>
<td></td>
</tr>
<tr>
<td>1.0 Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Sources of water pollution</td>
<td>4</td>
</tr>
<tr>
<td>1.1.1 Pollution of estuaries</td>
<td>5</td>
</tr>
<tr>
<td>1.2 Historical background of the study area</td>
<td>7</td>
</tr>
<tr>
<td>1.2.1 Climate / Meteorology</td>
<td>9</td>
</tr>
<tr>
<td>1.2.1.1 Winds</td>
<td>10</td>
</tr>
<tr>
<td>1.2.1.2 Thunderstorms and squalls</td>
<td>11</td>
</tr>
<tr>
<td>1.2.1.3 Rainfall</td>
<td>12</td>
</tr>
<tr>
<td>1.2.1.4 Visibility</td>
<td>13</td>
</tr>
<tr>
<td>1.2.1.5 Relative humidity/ Atmospheric pressure</td>
<td>14</td>
</tr>
<tr>
<td>1.2.1.6 Temperature</td>
<td>15</td>
</tr>
<tr>
<td>1.2.1.7 Sunshine</td>
<td>16</td>
</tr>
</tbody>
</table>


1.3 Aims and objectives of this study

CHAPTER TWO

2.0 Literature review
2.1 Origin of crude oil
2.2 Definition of crude oil
2.3 Composition of petroleum
2.4 Classification and characterization of crude oil
2.5 Some physical properties of crude oil and petroleum products
2.6 Total petroleum hydrocarbons
2.6.1 Aliphatic hydrocarbons
2.6.2 Aromatic hydrocarbons
2.6.2.1 Polycyclic aromatic hydrocarbons
2.7 Fate of spilled oil
2.8 Processes that affect the impact of oil released
2.8.1 Weathering
2.8.1.1 Evaporation
2.8.1.2 Emulsification
2.8.1.3 Dissolution
2.8.1.4 Oxidation

<table>
<thead>
<tr>
<th>Section</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0 Literature review</td>
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<tr>
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<td>2.6.2 Aromatic hydrocarbons</td>
</tr>
<tr>
<td>2.6.2.1 Polycyclic aromatic hydrocarbons</td>
</tr>
<tr>
<td>2.7 Fate of spilled oil</td>
</tr>
<tr>
<td>2.8 Processes that affect the impact of oil released</td>
</tr>
<tr>
<td>2.8.1 Weathering</td>
</tr>
<tr>
<td>2.8.1.1 Evaporation</td>
</tr>
<tr>
<td>2.8.1.2 Emulsification</td>
</tr>
<tr>
<td>2.8.1.3 Dissolution</td>
</tr>
<tr>
<td>2.8.1.4 Oxidation</td>
</tr>
</tbody>
</table>
2.9 Petroleum hydrocarbon pollution and its possible effects

2.9.1 Transport

2.9.1.1 Horizontal transport

2.9.1.2 Spreading

2.9.1.3 Advection

2.9.1.4 Langmuir circulation

2.9.1.5 Horizontal dispersion

2.8.1.6 Vertical dispersion and entrainment

2.9.2 Sinking and sedimentation

2.9.3 Shoreline stranding and tarball formation

2.9.4 Seeps

2.10 Review of works done on Qua Iboe sediments

2.11 Identity and analysis of total petroleum hydrocarbons

2.12 Chemical and physical information

2.12.1 Automotive gasoline

2.12.2 Jet fuel

2.12.3 Fuel oil

2.13 Analytical methods

CHAPTER THREE

3.0 Results and discussion
CHAPTER ONE

1.0 INTRODUCTION

While the amount of annual oil spills in the marine environment is significant, the coastal marshes and estuaries are constantly at risk from oil pollution from accidents, leakage or rupture of oil pipelines, oil and gas explorations and even natural seeps. The adverse environmental impact of oil contamination in these marine ecosystems cannot be over emphasized. As a result, increasing attention is being focused on understanding the fate of the oil spills in the environment and the weathering mechanism. Oceans and other salt water bodies are referred to as marine environments, while lakes, rivers and other in-land bodies are called fresh water environments. The term aquatic environment refers to both marine and fresh water environments.

The unique features of these coastal marshes such as organic-rich sediment and anoxic conditions favour the accumulation and penetration of oil in the soil. Oil penetration through soil reduces aeration and upsets indigenous microbial communities, which directly affects the fate of the oil trapped in the sediments. The severity of the impact of an oil spill depends on a variety of factors including characteristics of the oil itself. Natural conditions such as water temperature and weather also influence the behaviour of oil in aquatic environment.
Petroleum hydrocarbon extraction, transportation, refining and consumption by industry and the public account for a high percentage of the foreign exchange earning of the Nigeria economy. Oil is the dominant fuel in the Nigerian economy, providing 90% percent of the nation’s energy and almost 100% percent of its transportation fuel. Such widespread use, however of this substance will inevitably lead to accidental and intentional releases. Liquid petroleum, whether crude oil or refined product such as tar, lubricating oil, gasoline or kerosene, possesses many properties and contains many individual toxic compounds that can make such releases harmful to the environment. Because of increased consumption of petroleum, there will be significant increase in land-based run-off of petroleum hydrocarbon.

The release of petroleum to the marine environment can take place in a wide variety of ways, and the size and impact of releases varies dramatically as each release involves a unique combination of physical, chemical and biological parameters. An estimate of the total load of petroleum entering the marine environment worldwide in and of itself is not particularly meaningful, given the huge volume of water that comprises the global ocean. Petroleum entering the marine environment through spills or choice releases such as urban run-off, is eventually broken down or removed from the environment by natural processes or is diluted to levels well below even conservative concentration of concern. However from the
time the material enters the environment until it is removed or sufficiently diluted to levels, it does pose some threat to the environment. The magnitude of that threat varies dramatically depending on the size, composition, location, and timing of the release, the interactions of the introduced petroleum with various processes that affect the material after its introduction, and the sensitivity of the organisms exposed. Sources of frequent large release have been recognized as an area where greater effort to reduce petroleum pollution should be concentrated.

Currently, there is a great deal of concern regarding contaminated sediments and water and their impacts on ecosystem health. The concern associated with the oil-related contaminants sorbed to the sediments is that commercial species and food chain organisms spend a major portion of their life cycle in or on aquatic sediments. This provides a pathway for these oil-related contaminants to be consumed by higher aquatic life and humans. Direct transfer of contaminants from sediments to the organisms is now considered to be a major route of exposure for many species.

However, because contaminants are not necessarily fixed permanently in the sediment, they could be remobilized when physicochemical conditions change. If concentrations in water phase are low, sediment-bound contaminants may have greater impact on aquatic organism than dissolved concentrations. The basic premise has been to restrict contaminants from occurring in water at concentrations above the known
chronic or toxic levels. This approach should also apply to sediments but it has to include the long-term behavior of contaminants, which is determined by the physico-chemical reactions in the system.

1.1 Sources of water pollution

There are many sources of water pollution but two general categories exist: point source and non point source. Point source pollution is when the sources of pollution comes to the river at one point, while non point source pollution is when sources of pollution have resulted in the disturbance of the earth or contamination of the surrounding land. Point source accounts for over 60% of the water pollution today.

Although point source discharges still produces some pollution, currently, less visible non point sources of pollution are more wide spread and introduce vast quantities of pollution into surface and ground water bodies in a dispersed manner rather than from discrete pipe or other conveyance. Non-point sources include atmospheric deposition, contaminated sediments, and many land activities that generate polluted runoff, such as agriculture, logging and on site disposal.

In contrast, point sources discharge waste into water bodies from a discrete point that is easily identified. The most common point sources are industrial facilities, municipal treatment plants and combined servers. Other sources cited include atmospheric deposition, in-place contaminants, and
Atmospheric deposition refers to contaminants entering waters from polluted air, in-place contaminants were natural sources. Atmospheric deposition refers to contaminants entering waters from polluted air, in-place contaminants were generated by past activities, such as discontinued industrial discharges, logging or one-time spills. In-place contaminants often reside in sediments but continue to release pollutants back into the water column. Natural sources refer to an assortment of water quality problems:

- Natural deposits of salt, gypsum, nutrients and metals in soils that leach into surface and ground water.
- Warm weather and dry conditions that raise water temperature, depress dissolved oxygen concentrations and dry up shallow water bodies.
- Low-flow conditions and tannic acids from decaying leaves that lower PH and dissolved oxygen concentrations in swamps draining into streams.

1.1.1 Pollution of estuaries.

Estuaries are coastal areas where fresh water from rivers and streams mixes with salt water from the ocean. Many bays, bounds and river mouths along the coast are estuaries. They are characterized by varying degrees of salinity; complex water movement affected by ocean tides and river currents, and high turbidity levels. They are also highly productive
ecosystems with a range of habitats for many different species of plants, shellfish, fish and animals.

Many species permanently inhabit the estuarine ecosystem; others, such as shrimp use the nutrient rich estuarine waters as nurseries before traveling to the sea. Estuaries are stressed by the particularly wide range of activities located within their watersheds. They receive pollutants carried by rivers from agricultural land and cities, they often support marine harbours and commercial fishing floats and their surrounding lands are highly prized for development. The stresses pose a continual threat to the survival of these bountiful waters.

Municipal sewage treatment plants, urban runoff / storm sewers, and agriculture are the leading sources of pollution in the estuarine waters. Other leading sources include industrial point sources, resource extraction. Point sources continue to have a significant impact on estuarine water quality because concentrated population centers and industrial operations are located adjacent to major estuarine systems.

The Federal Government, industrial and environmental groups have been attempting to understand the problems of estuarine contamination with petroleum hydrocarbons. Potential estuarine contaminant of concern include total petroleum hydrocarbon and related polynuclear aromatic hydrocarbons (PAH), used oil – related metals and volatile organic compound (VOC). Contaminants are carried to the seabed by sedimentary
The river originating from Umuahia hills transverses mainly sedimentary terrain of cretaceous to recent ages and develops into extensive meanders before emptying into the Atlantic Ocean. Creeks and channels islands are common throughout the length of the estuary; white sandbars occur at the mouth as a result of interplay between the long shore drift which runs approximately in a West – East direction (parallel to the shoreline) and the river current.¹²

Like other estuaries in the area, the Qua Iboe River estuary experiences great fluctuation in salinity between the wet (May – September) and the dry (October - April) seasons as well as the normal gradient extending upstream from the mouth of the river.

Ecological habitat therefore varies from purely marine to those of brackish and fresh water. Tidal currents, which are strong at the mouth of the estuary but weak along the upper reaches and the creeks, play an important role in the sediment size distribution in the environment. Water clarity is diminished by sediments suspension, which is enhanced by constant water agitation, associated with tidal flushing, wave and increased negation necessitated by petroleum exploitation in the area.¹²

Qua Iboe River estuary is relatively faced with several possible threats to the water quality. Potential contaminant sources include the Mobil Oil Producing Nigeria Unlimited, runoff from agricultural activities and several active and in-active landfills. Studies on sediments from
different sources have provided adequate information on increased contaminant mobilization into the environments.

1.2.1 Climate/ Meteorology

Two season regimes (dry and wet seasons) influenced by two dominant wind currents prevail in the study area. The winds are the South West “rain bearing” wind, which reaches the Guinea Coast as a warm, moist wind stream; and the Northeast Harmattan wind, blowing from the Sahara as a hot, dry and often dusty wind stream. For most of the year it is the warm, moist rain-bearing wind that prevails in the study area, and it is strongest and most persistent during the period from May to September, the rainier part of the year. The dry season in the study area is thus short, not more than 3 months; from December through February when rain-bearing winds are sometimes replaced by the Harmattan wind.

The weather is hot and humid throughout the year. It is usually very sunny in the short dry season although even in the rainy season many days have bright sunshine. Heavy and sometimes prolonged periods of rain combined with high humidity make the 9-month rainy season in Nigeria’s coastal area uncomfortable. Winds are fairly consistent and typically mild, except during squalls associated with thunderstorms. It is these thunderstorms and the local “tornadoes” (high winds creating conditions similar to small tornadoes) accompanying them are the most impressive
features of weather in the study area. They occur throughout the year, even during the dry season, producing wind gusts of up to 15 m/s. They may also cause water sports over the sea, and present some aviation and marine transport hazard

1.2.1.1 Winds

The Northeast Trade Winds blow almost continuously north of 20° N, although from August onwards they push towards the South, normally reaching latitudes similar to that of the Gulf of Guinea by December and January. In the following six months they retreat Northwards. Once South of 20° N, these winds can bring hot, dry, dusty air from the interior of the African continent. These winds, known as the harmattan, are more prevalent in January and sometimes create navigation problems because of the extensive dust they carry from the Sahara. In lower latitudes this dust storm extends well out to sea.

In the study area, surface winds from the Southwest dominate during both the wet and dry seasons. The secondary wind direction is from the northeast, with northeasterly winds occurring more frequently during the dry season than the wet season. The strongest winds (mean monthly speeds of about 5 m/s) occur during the wet season. The weakest winds (mean monthly speeds of about 2.5 m/s) occur during the dry season.
Although the diurnal variation in the surface wind is small, there is a tendency for the wind speed to be at a maximum during the night, as a result of radiation cooling leading to instability in the surface layer. The diurnal variation will be most marked during periods of reduced trade wind activity and clear skies.

1.2.1.2 Thunderstorms and squalls

Thunderstorms are regular features of Equatorial West Africa and their high frequency may severely disrupt weather-sensitive operations. The greatest frequency of thunderstorms occurs around the equator, from Cameroon to the Congo, with around 100 to 150 thunderstorms a year. Storms are rarer in the study area occurring mainly during the rainy period.

‘Squalls’ are sudden increases in wind speed that last for several minutes and are associated with the leading edge of multi-cell thunderstorms. Squalls could result from unstable atmosphere (relatively cold air overlying relatively warm, more buoyant air); moist air, and a trigger mechanism (converging air at low levels e.g. at the inter-tropical convergence zone or terrestrial heating).

The thunderstorms associated with the inter-tropical convergence zone (ITCZ) typically develop from Cameroon to Gabon; these storms are steered westward at about 12.5M/S towards the coast to Nigeria offshore operating areas by upper winds. They are often seen as a line of
thunderstorms commonly refers to as “line squalls”. As they travel across the lower plains, the warm ground provides a source of heat causing updrafts. Passage across open water enables them to pick up significant volumes of water vapour.

In the study area, squalls generally travel in the east-west direction. Squalls are possible anytime of the year, but in the months, March to November of the rainy season, the normal wind regime is interrupted by these brief but intense wind events more frequently. They present a serious hazard to aviation and may impede shipping and other offshore activities.

1.2.1.3 Rainfall

The hydrological cycle depends fundamentally on the inter-relationship between the circulation of the ocean and the atmosphere by the process of evaporation, which is dependent on factors such as air/sea temperature, wind strength and humidity.

Rainfall in the study area as monitored from MPN’S Qua Iboe terminal (QIT) over a period of eleven years (1992-2002) is in two regimes. The wet season exhibits heavier rains in the period May-October with less intense rainfall occurring in November, March and April. The wettest month in the area is August with an average of 722.1mm, followed by July.
(678.0mm). The dry season runs from December through February (mean is
56.3mm). The annual rainfall ranges between 3,668mm and 5,287mm.

### Table 1.1 Monthly Rainfall Data in the study area (1992 – 2002)

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Source: Mon’s Qua Iboe Terminal Meteorological Data record

#### 1.2.1.4 Visibility

Visibility over the sea adjoining the Niger Delta is generally 32km or
more. Mist or fog occurs very rarely off shore. Fog is typically confined to
the immediate nearshore waters within a few kilometers of the shore.

Visibility around the shoreline and over the sea is affected by the harmattan
in the dry season, December to February. At such times the visibility may fall to 500m for a few hours and may be reduced to about 2km for periods of 2 to 3 days. This reduced visibility can be experienced almost everyday in January.

During the rainy season, principally in June, July, August, and September, heavy rain frequently reduces visibility in the project area to about 1km, and occasionally to 100m, for periods of up to one hour. In severe "tornadoes" over the sea, visibility may be reduced to a few yards. Morning fog or mist occurs occasionally in this season, usually clearing soon after dawn. Dust and haze during the dry season or heavy rainfall during the wet season can cause navigational problems in the Gulf of Guinea, over the shoreline approaches and within the Niger Delta estuaries.

1.2.1.5 Relative humidity / Atmosphere pressure

Relative humidity within the project area is high. The lowest mean humidity value (81%) in the area is in January/February while the highest in July to October is 91%. During nighttime, the dew point (100% humidity) is often reached, limiting the drop in overnight temperature. During the drier months (December through February), humidity can fall sharply when the harmattan wind blows in from the north, leading to greater daily
humidity variations than in other months of the year. However, this is not a common occurrence in the offshore area.

The atmospheric pressure varies on a diurnal basis and ranges between 1010MB in the dry season and 1014MB in the wet season. These are subject to rapid changes during the passage of thunderstorms.

1.2.1.6 Temperature

There is little monthly variation in mean air temperature in the study area; this is corroborated by records of the maximum air temperature data in the study area, as monitored at the QIT from 1992 to 2002. The annual mean of daily maximum air temperature in the area ranged from 28.8°C to 30.2°C during this period. The hottest months are November to April (with means of maximum daily temperature by month ranging from 27.0°C - 27.5°C). Air temperature, like relative humidity and atmospheric pressure, is subject to rapid changes during the passage of thunderstorms.
Table: 1.2 Average maximum temperatures in the study area by month (1992-2002)

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Mean: MPN's Qua Iboe Terminal Meteorological Data Record.

1.2.1.7 Sunshine

The average of daily hours of bright sunshine by month in the project area is between 6.40 and 10.1 hours per day. The lowest values of bright sunshine are recorded between July and September with about 6.40 to 8.40 hours of sunshine per day due to greater propensity for cloud cover during this period. Also, January (6.40 hours per day) and, February (8.50 hours per day) experience relatively low values of bright sunshine. April, May
and October have the highest average values (9.70 to 10.1 hours per day) of bright sunshine per day.

Table 1.3 Mean Daily Hours of Bright sunshine in the study area by month (1992 – 2002)

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Source: MPN’s QUA Iboe Terminal Meteorological Data Record.

1.3 Aims and objectives of this study.

This work focuses on sediment contamination with petroleum hydrocarbon. It highlights the fact that sediments are important resources since sediments are both carriers and potential sources of contaminants in an aquatic system.
Studies on sediments of aliphatic hydrocarbons, aromatic hydrocarbons and total petroleum hydrocarbon in Qua Iboe River sediments could provide useful information on the processes going on within the river.

Therefore this work is carried out to trace the various sources of petroleum or oil contaminants into a segment of Qua Iboe River, and quantify their levels in the sediments. It also provides a brief overview on the impact of oil spill on microbial activity and functions and the influence of selected environmental and physical factors on the biodegradation of petroleum hydrocarbons in marine sediments.
CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Origin of crude oil

It is generally accepted that petroleum has been derived from the remains of plants and animal deposited together with fine-grained minerals at the bottom of the sea.

The greater similarity between the chemical structure of compounds present in petroleum and those of compounds in living organisms strongly support the idea that petroleum is of biogenic origin. Development of modern techniques such as gas chromatography and mass spectrometry has permitted the isolation and identification of many of these compounds. From the analysis of the extracts of recent and ancient sediments and of petroleum, it follows that petroleum is a product of the partial conversion of the original organic matter.

The evidence that part of the organic matter which has been buried in mud under high pressure and temperature has been converted into hydrocarbon can be obtained from investigation of shallow and deep rock extracts. Petroleum represents merely an accumulation of the hydrocarbon synthesized by living organisms. In recent sediments, high molecular weight n-alkane of odd carbon number predominated over those with even carbon number.
Transformation of organic matter into petroleum can take place by the cracking hypothesis which is a low temperature cracking reactions which generates hydrocarbon. The transformation reactions may proceed at the catalytic sites provided by the adjacent rock surfaces in the presence of water, hydrogen sulphide, sulphur and their inorganic materials. During these processes, petroleum, which is diffusely scattered, accumulates by migrating in reservoirs. The process of petroleum formation is divided into three stages, which are: the origin of petroleum constituents, the migration of this petroleum and its final accumulation in the reservoir. Different lipids and non–lipids produce different types of hydrocarbon. The type of organic matter is dependent on the depositional environment since different environments are colonized by different living organisms with variable amounts of proteins, carbohydrates and lipids.

Lipids and peptides (amino acids) contain gasoline range of hydrocarbon. Fatty acids and terpenes have low molecular weight paraffins; Steranes and terpenes, related naphthalenes, chlorophyll pigments and waxes have iso–paraffins; Non–lipids like cellulose, humates, and lignins are mainly methane gas (Biogenic).

The hydrocarbon potential of a source rock is defined as the total hydrocarbon that is potentially recoverable, regardless of the size, accessibility or economics of the postulated field involved. Type of kerogen is a controlling factor leading to different hydrocarbon products.
while the nature of hydrocarbon generated is linked with the nature of organic matter present in the source rock, a basic factor should be made as relative abundance of marine and terrestrial plant remains. The convertibility of organic matter of sedimentary rock to petroleum depends on the types of organic matter and hence on the kerogen composition of the rocks. The burial of sediments at depth results in a temperature and pressure increase that includes a progressive transformation of kerogen. Since living organisms vary in their composition of protein and carbohydrates, lipids, lignin and others, therefore petroleum generated from different source phase sometime show gross dissimilarities in their content of organic compound.

It is generally accepted that hydrocarbon accumulation comes from organic matter indigenous to contiguousous source rock. The nature of the organic matter and its depositional environment play important roles in determination of the volume and character of generated hydrocarbon.

2.2 Definition of crude oil

Oil is a general term that describes a wide variety of natural substances of plant, animal, or mineral origin, as well as a range of synthetic compounds. Crude oil is naturally occurring oil generated by geological and geochemical processes. A variety of petroleum products are then derived from this natural resource. Because their compositions vary,
each type of crude oil or petroleum product has a unique characteristics or properties. These properties influence how petroleum will behave when it is released and determine its effect on biota and habitats.

Crude oil and derived products collectively referred to here as petroleum are made up of dozens of major hydrocarbon compounds and thousands of minor ones. Hydrocarbons occur naturally in great abundance and in a variety of forms. Although petroleum is overwhelmingly composed of hydrocarbon compounds, not all hydrocarbon compounds come from petroleum. Hydrocarbon compounds containing less than five carbon atoms e.g. methane, ethane and other gases are abundant and widespread and their behaviour differs so greatly from liquid petroleum. Furthermore, non-petroleum oils e.g. vegetable oils, animal fats etc have spills that are not trivial but present unique fate and effect problems.

Crude oil, the naturally occurring liquid form of petroleum, is an important part of the current energy mix of fossil fuels, as this fossil fuel is extracted, refined, transported, distributed or consumed, spills and other releases occur. In addition, natural processes can result in seepage of crude oil from geologic formations below the sea floor to the overlying water column. Understanding the nature and distribution of sources and their inputs, as well as the behaviour of petroleum in the environment is the key for understanding the potential effect on the marine environment.
2.3 Composition of petroleum

Petroleum is composed principally of hydrocarbons (compound containing only hydrogen and carbon). Thus the term petroleum and hydrocarbons are often used interchangeably. In fact, the elements hydrogen and carbon together (occurring as hydrocarbons or related compounds) constitute about 97 percent of most petroleum, while the minor elements Nitrogen, sulphur, and oxygen make up the remaining 3 percent. Therefore petroleum is a complex mixture of hydrocarbons, varying widely in both physical and chemical properties depending on the sources.

Crude oil sometimes contains mineral salts, as well as trace metals such as nickels, vanadium and chromium. The hydrocarbon compounds found in crude oil are characterized by their structure. These compounds include the saturates, Olefins, aromatics, and polar compounds. Understanding these different compounds and their structures is important for understanding the fate and effect of releases of crude oil or products derived from it.

The Saturate group of compounds in various crude oils consists primarily of alkanes which are composed of hydrogen and carbon with the maximum number of hydrogen atoms around each carbon. This term “saturate” is used because the carbons are saturated with hydrogen. Saturates include straight or branched chain n-alkanes and the cycloalkanes.
with one or more saturated rings. Higher - molecular - weight saturate compounds are often referred to as "waxes".

Olefins or unsaturated compounds are those that contain fewer hydrogen atoms than the maximum possible Olefins have at least one carbon - to - carbon double bond, which displace two hydrogen atoms. Significant amounts of olefins are found only in refined products.

Aromatic compounds include compounds with one or more fused aromatic rings each of which may be attached to saturated side chains (alkyl substituent). Benzene rings are very stable and therefore persistent in the environment, can have toxic effects on organisms. The more volatile monoaromatic (Single - single) compounds found in crude oil are often referred to as BTEX, or benzene toluene, ethyl benzene, and xylene.

Polar compounds are those that have significant molecular charge as a result of bonding with elements such as sulphur, nitrogen, or oxygen. The polarity of the molecules results in behaviour that differs from that of unpolarized compounds under some circumstance. In the petroleum industry, the smallest polar compounds are known as resins, which are soluble in n - heptane principally containing heterocyclic compounds, acids and sulphoxides. The larger polar compounds are called asphaltenes and often make up the greatest percentage of the asphalt commonly used for road construction. Asphaltenes consist of high molecular - weight compounds that are not soluble in a solvent such as n - heptane.
2.4 Classification and characterization of crude oil.

Crude oils are complex mixtures, which vary widely in composition. However, they can be divided into three broad groups of compounds which help the responder assess the initial impacts and fate of oil. These groups are very simple:

1. Light-weight Components
2. Medium-weight Components
3. Heavy-weight components.

Compositional data on crude oils are used to characterize them as to the amounts of each group present in the oil, and thus predict the behaviors of the oil and the risks it poses to natural resources of concern.

Light-weight components are characterized by hydrocarbon compounds containing up to ten carbon atoms; a boiling range up to 150°C; rapid and complete evaporation usually within a day; High acute toxicity because they contain the monoaromatic hydrocarbons; High water solubility; usually contributes > 9% of water - soluble fraction; No potential for bioaccumulation (they evaporate instead); Mostly composed of alkenes and cycloalkanes which have low solubility (and thus low acute toxicity potential).

These light ends evaporate so quickly that they do not persist in the environment. Even though individual aromatic compounds have solubility of over 1,000 mg/l they are rapidly removed from solution by evaporation.
One important exception to this general rule is when the dissolved fraction is rapidly mixed into the water column under cold conditions.

Medium-weight components are characterized by hydrocarbon compounds containing between 10 and 22 carbon atoms; a boiling range from about 150 to 400°C; evaporation rates of up to several days, although there will be some residue which does not evaporate at ambient temperatures; low water-soluble fraction (at most a few mg/l); moderate acute toxicity because they contain diaromatic hydrocarbons (naphthalenes) which are toxic in spite of their low solubilities; moderate potential for bioaccumulation and chronic toxicities associated with the diaromatic hydrocarbons, alkanes which are readily degraded.

These medium-weight components pose the greatest environmental risks to organisms because the compounds are more persistent, they are biologically available, and polycyclic aromatic hydrocarbons have high toxicities. The alkanes (aliphatic hydrocarbons) are readily biodegraded under right conditions.

The heavy-weight components are characterized by hydrocarbon compounds containing more than 20 carbon atoms; almost no loss by evaporation; almost no water-soluble fractions; potential for bioaccumulation, via sorption onto sediments otherwise not highly bioavailable; potential for chronic toxicity, because they contain polynuclear aromatic hydrocarbons (phenanthrene, anthracene etc); most of
the components are waxes, asphaltenes, and polar compounds which do not have any significant bioavailabilities or toxicities; Long-term persistence in sediments, as tar balls or asphalt pavements.

These heavier components pose little acute toxicity risks, except that due to smothering, because of very low solubilities of the individual compounds. Animals have to be exposed via sediment pathway or through the food chain. However these are the most persistent components of oil and degradation rates will be very slow.

2.5 Some physical properties of crude oil and petroleum products.

The properties of liquid petroleum including crude oil or refined products, which are most important in understanding the behaviours and fate of spills or other releases and the ability of the oil to spread, include viscosity, density, solubility and surface tension.

Viscosity is the measure of a liquid's resistance to flow. The lower the viscosity the more readily the liquid flows and vice versa. The viscosity of oil or petroleum products is determined largely by the proportion of lighter and heavier fractions that it contains. The greater the percentage of light components such as saturates and the lesser the amount of asphaltenes, the lower is the viscosity. Highly viscous oil tends to weather more slowly because they do not spread into thin slicks. Instead they form tar balls,
which can be transported long distances and accumulate in thick deposits on shorelines that can persist for decades.

Density is the mass of a given volume of oil or petroleum product and is typically expressed in gram per cubic centimeter. It is the property used by the petroleum industry to define light or heavy crude oils. Density is also important because it indicates whether a particular oil will float or sink in water. The density of pure water is 1.0 g/cm³ (at 15°C) and the density of most oils ranges from 0.7 to 0.99 g/cm³ (at 15°C), thus most is will float on water since the density of seawater is 1.03 g/cm³ (at 15°C), thus even heavier oils will usually float on it. Density is often used as a surrogate for predicting the relative rate of natural weathering when crude oil or other petroleum products are released to the environment. Light oils contain petroleum hydrocarbons that are readily lost via evaporation and microbial degradation. Heavy oils contain a greater percentage of the higher molecular-weight petroleum hydrocarbons that are more resistant to weathering and they sink and form tar balls or may interact with rocks or sediments on the bottom the water body.

Solubility in water is the measure of the amount of an oil or petroleum product that will dissolve in the water column on a molecular basis. Because the amount of dissolved oil is always small, this is not as significant a loss mechanism as evaporation. In fact, the solubility of oil in water is generally less than 100 parts per million (PPM). However,
solubility is an important process because the water soluble fractions of the oil are sometimes toxic to aquatic life. Thus although solubilization represents a minor loss process, the concentration of toxic compounds dissolved in water from oil may be sufficient to have impacts on marine organisms.

2.6 Total Petroleum Hydrocarbon

The term “Total Petroleum Hydrocarbon” (TPH) is generally used to describe the measurable amount of petroleum-based hydrocarbons in the environment, and thus the TPH information obtained depends on the analytical method used. Petroleum hydrocarbons (PHCs) are common site contaminants, but they are not generally regulated as hazardous wastes. As gross measures of petroleum contaminants, TPH results simply show that petroleum hydrocarbons are present in the sampled media. Measured TPH values suggest relative potential for human exposure and, the relative potential for human health effects. Leaking underground storage tanks (LUST) are the most frequent causes of Federal Government involvement in petroleum hydrocarbon problems. Therefore there is a need to reduce potential petroleum hydrocarbon contaminant to a manageable size. Specific contaminants that are components of TPH are the aliphatic and the aromatic hydrocarbons.
2.6.1 Aliphatic hydrocarbons

Aliphatic hydrocarbons (alkanes) are generally considered to be non-toxic. They are valuable for tracing the spilled oil, useful for studying the fate of spilled oil, and can provide information on the degree of weathering of the sample. According to some Authors, the predominance of odd-numbered carbon compounds indicates hydrocarbons of recent biological origin. Petroleum hydrocarbons are supposed to have approximately equal amounts of even and odd-numbered carbon compounds. Some Authors have used the pristane / n - C17 and phytane / n - C19 ratios to indicate exposure to petroleum pollutants. Many genera microbes are able to completely oxidize alkanes, and straight chain aliphatic hydrocarbons are easier to be degraded than branched chain aliphatic hydrocarbons.

2.6.2 Aromatic hydrocarbon

Aromatic hydrocarbons may account for about 1 to 20 percent of the total hydrocarbon in crude oil. Benzene and alkyl benzenes with one or two methyl or ethyl groups (toluene, xylene, ethylbenzene) the BTEX compounds, may be present at a concentration of several percent in light crude oil, but more typically present at concentration of 1,000 to 10,000 mg/kg. Usually, toluene is the most abundant of the BTEX compounds, followed by benzene or one of the three xylene isomers. More highly alkylated benzenes usually are present at low concentration in crude oils.
The abundance of aromatic hydrocarbon in petroleum usually decreases with increasing molecular weight. In most cases one ring (Benzene) through three-ring (phenanthrene) aromatic hydrocarbon and related heterotypic aromatic hydrocarbons, such as dibenzothiophene, account for at least 90 percent of the aromatic hydrocarbons that can be resolved in crude petroleum. Four through six-ring PAH (pyrene) Flouranthene through Coronene, some of which are known mammalian carcinogens, usually are present at low or trace concentrations in crude oil.

2.6.2.1 Polycyclic aromatic hydrocarbons (PAH)

Polycyclic aromatic hydrocarbons (PAH) also consist of at least two rings. A typical crude oil may contain 0.2 percent to more than 7 percent total PAH. PAH includes those compounds that have the most serious environmental effects of the compounds in crude oil. PAH in the environment are derived largely from combustion of oil and coal, but are also produced by burning of wood, forest fires, and a variety of other combustion sources.

The PAH in petroleum often contain one or more methyl, ethyl or occasionally higher alkyl constituents on one or more aromatic carbons. These allocated PAH are more abundant than the parent compounds in petroleum. Most of the PAH compounds in petroleum are not as toxic.
as those produced by certain combustion processes. PAH are responsible for many of the biological affects of petroleum due to their persistence, high affinity for biological lipids and direct or long-term harmful effects. PAHs may be of natural origin, and most environmental samples contain PAHs from a combination of sources. PAHs may also undergo transformation prior to and after deposition, which can convolute results. Land run-off is estimated to contribute up to 10-20% of PAH contamination in receiving streams.

In aquatic systems, PAHs tend to become adsorbed to sediments, though during disturbance e.g. (during dredging) can be resuspended in water. Lower PAHs are mostly released from sediments into this dissolved form. The burden of PAH in the environment is rising, as degradation of PAHs in sediments is gradual.

A number of PAH concentration ratios exist, which can be used as an instrument to determine probable sources of PAH contamination. Two commonly used ratios are the phenanthrene/anthracene (P/A) and chrysene/benz[a]anthracene (C/BaA) ratios. Phenanthrene and anthracene are structural isomers, but anthracene degrades more rapidly in oil-related contamination compared to combustion-sourced contamination. Therefore lower P/A ratio indicates pyrolytic pollution source while higher P/A ratio (>10) indicates petrogenic pollution. A C/BaA ratio <1 indicates
combustion sources and values of 1 gives mixed sources, values >1 is petrogenic source.

2.7 Fate of spilled oil

Natural actions are always at work in aquatic environments. These can reduce the severity of an oil spill and accelerate the recovery of an affected area. There are many physical, chemical and biological mechanisms that process hydrocarbon loadings once they enter the ocean. Models combine the inherent properties of petroleum components (e.g., solubility, volatility, reactivity) with the interacting water to predict petroleum hydrocarbon concentrations. Minimum information required to translate loads into concentrations, therefore includes knowledge of the chemical composition of the loadings and the hydrodynamics of the interacting water.

A full understanding of the impact of petroleum loadings into the ocean requires an accurate assessment of the magnitude, spatial extent, and duration of exposure. The “fate” (where it goes) and “persistence” (how long of remains in the system) of petroleum in the seawater are controlled by processes that vary considerably in space and time. The processes that control petroleum transport (movement) in surface waters are reasonably well understood in a specific area for periods of time (less than one week).
There exist interrelationships among the physical, chemical, and biological processes that crude oil undergoes when introduced into the marine environment before it, subsequently weathers, and is then transported away from the source. Processes involved in the weathering of crude oil include evaporation, emulsification, and dissolution; whereas chemical processes focus on oxidation, particularly photo oxidations. The principal biological process that affects crude oil in the marine environment is microbial oxidation. As crude oil weathers, it may also undergo various transport processes including advection and spreading, dispersion and entrainment, sinking and sedimentation, partitioning and bioavailability, and stranding which leads in some cases to tar ball formation.

2.8. Processes that affect the impact of oil released

2.8.1 Weathering

Following an oil spill or any other event that releases crude oil or crude oil products into the marine environment, weathering processes begin immediately to transform the material into substances with physical and chemical characteristics that differ from the original source material.

2.8.1.1 Evaporation.

In many oil spills, evaporation is the most important process in terms of mass balance. Within a few days following a spill, light crude oils can
lose up to 75 percent of their initial volume and medium crude up to 40 percent. In contrast, heavy or residual oils will lose no more than 10 percent of their volume in the first few days following an oil spill. Most oil spill behaviour models include evaporation as a process and as a factor in the output of the model.

Despite the importance of the process relatively little work has been conducted on the basic physics and chemistry of oil spill evaporation\textsuperscript{3}. The particular difficulty with oil evaporation is that oil is a mixture of hundreds of compound, and this mixture varies from source to source and overtime. Much of the work described in the literature focuses on “calibrating” equations development for water evaporation\textsuperscript{36}. Initial prediction of oil evaporation was carried out using water evaporation equations.

Later works were applied to describe the evaporation of crude oil through the use of mass transfer coefficients as a function of wind speed and spill area. Stiver and Mackay (1984) further developed relationships between evaporative molar flux, mass transfer coefficient at vapour pressure of the bulk liquid, gas constant, and temperature.

In all this previous work, boundary layer regulations were assumed to be the primary mechanism for petroleum evaporation. Subsequently, Fingers (1995) showed that boundary regulation is slight for petroleum evaporation in the thin layers typically found on surface oil slicks and a simple equation can be used to model evaporation.
Percentage evaporation = \( C (T) \ln (t) \), where \( C \) is a constant that can be empirically determined or predicted on the basis of distillation data, \( T \) is temperature, and \( t \) is time. Empirical equation for many oils have been determined, and the equation parameters found experimentally for the evaporation of oils can be related to commonly available distillation data for the oil.

2.8.1.2 Emulsification.

Emulsification is the process of formation of various states of water in oil; often called “chocolate mousse” or “mousse” among oil spill workers. These emulsions significantly change the properties and characteristics of spilled oil. Stable emulsions contain between 60 and 85 percent water thus expanding the volume by three to five times the original volumes of spilled material. The density of the resulting emulsion can be as great as 1.03/ml compared to as low as 0.80g/ml. Most significantly, the viscosity of the oil typically changes from a few hundred to seconds, a typical increase of three orders of magnitude. This increase in viscosity can change a liquid petroleum product into a heavy, semi-solid materials.

Emulsification, if it occurs, has a great effect on the behaviour of oil spills at sea. As a result of emulsification, evaporation slows spreading by orders of magnitude, and the oil rides lower in water column, showing different drag with respect to the wind. Oils will generally take up water once spilled.
at sea, but emulsions may not always form. Water can be simply
"entrained" by the oil due to various forces, without forming a more stable
emulsion. This emulsification also has significant effects on the choice of
oil spill recovery models.

In the late 1960s, they measured several physical properties and
described the emulsions as forming because of the presence of asphaltenes
and resins. Several studies have shown that water is stabilized in oil by two
forces: Viscous and elastic forces resulting from the interfacial action of
resins and asphaltenes. This stabilization was noted as early as 1970s when
formation of emulsion correlated with the oil. In the 1990s, studies showed
the effect of composition and proposed clear reasons for water-in-oil-
emulsions. A significant factor in defining mechanisms and other
characteristics of emulsion has been the development of analysis technique
for them.

Mclean et al (1998) studied water-in-crude emulsion and found that
there were two stabilizing factors, viscosity and surface-active agents.
Systems were studied using model emulsions with the addition of resins and
asphaltenes accumulate at the oil-water interface to form a barrier to re-
coalescence. Asphaltenes form more stable emulsions than those stabilized
by resins alone. The state of asphaltene solubilization influences the
stability of the emulsion. If aromatic solvents are in abundance, the
emulsions are not as readily formed. The amounts of asphaltenes and resins were very important as are the ratios between these compound mixtures.

Stability is an important characteristic of water-in-oil emulsion. Characterization of emulsion as stable or unstable is required before other properties can be considered, because properties change significantly for each type of emulsion.

Emulsion stability are four-in-oil states: stable emulsions, meso-stable emulsions, unstable emulsions (or simply water or oil) and entrained water. These four states are distinguished by perseverance through time, visual appearance, and theological measurements. Meso-stable emulsions, which can be red to black in appearance, have properties between stable and unstable emulsions. Meso-stable emulsion, lack sufficient asphaltenes to render them completely stable, although the viscosity of the oil may be high enough to stabilize some water droplets for a period of time. Meso-stable emulsions may degrade to form layers of oil and stable emulsions. Unstable emulsions are those that largely decompose to water and oil after mixing, generally within a few hours. Some water, usually less than about 10 percent, may be retained by the oil, especially if the oil is viscous. This entrained state has a short life span, but residual water, typically about 10 percent, may persist for a long time.

All stable emulsions are usually reddish colour, but unstable emulsions are always the colour of the starting oil. Water content is not an
indicator of stability because excess water may be present. Stable emulsions often have water contents greater than about 60 percent, whereas unstable emulsions or entrained water in oil generally have water contents less than 50 percent.

2.8.1.3 Dissolution

Dissolution is the chemical stabilization of oil components in water. Dissolution accounts for only a small portion of oil loss, but it is still considered an important behaviour parameter because the solution components of oil, particularly the smaller aromatic compounds are more toxic to aquatic species than the aliphatic components. Modeling interest in dissolution is directed at predicting the concentrations of dissolved components in the water column. Most models in existence do not separate the dissolution components. The entrainment model is sometimes used but fails to distinguish between dispersing and dissolution.

Brookman et al (1985) reviewed the solubility of oil and oil components in water. Most solubility data were obtained for distilled water at 25°C, using various schemes. The solubility of oil components, in water varies widely depending on composition. Table below shows the solubility of very common aromatic hydrocarbons typically found in crude oils. Solubility decreases very rapidly with increasing size and increasing substitution. In contrast, the solubility of the aliphatic oil components is
very low relative to that of aromatic hydrocarbons and is considered to be negligible. The solubility of crude oil and petroleum products was investigated by using several methods in two different laboratories and under a variety of conditions.

In oil spill models, dissolution is often assumed to occur immediately. Some models have incorporated the effect of oil droplet size in the water column and used this parameter to create a kinetic behaviour models. In ground water, kinetics of dissolution are models based on the rate of water flow.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solubility (MG/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>1700</td>
</tr>
<tr>
<td>Toluene</td>
<td>539</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>170</td>
</tr>
<tr>
<td>P-xylene</td>
<td>150</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>30</td>
</tr>
<tr>
<td>1-methylnaphthalene</td>
<td>28</td>
</tr>
<tr>
<td>1,3-Dimethylnaphthalene</td>
<td>8</td>
</tr>
<tr>
<td>1,3,6-Trimethylnaphthalene</td>
<td>2</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>1</td>
</tr>
<tr>
<td>Flourene</td>
<td>2</td>
</tr>
<tr>
<td>Dibenzothiophene</td>
<td>1.1</td>
</tr>
<tr>
<td>Chrysene</td>
<td>0.002</td>
</tr>
</tbody>
</table>

Table 2.1 solubility of some aromatic oil components
2.8.1.4 Oxidation

Crude oil is a complex mixture of organic compounds, mostly hydrocarbons. Oxidation alters these mixtures by creating new compounds and by rearranging the distribution of residual compounds, based on their susceptibility to the oxidative process. The ultimate oxidation fate of all of the organic compounds, given an unrestricted supply of oxygen and time is conversion to carbon dioxide and water, as expressed in the following equation.

\[ CH_2O + O_2 \rightarrow CO_2 + H_2O \]

Where \( CH_2O \) is a symbol for all organic compounds. Not only is this the basic reaction for oxidation (to the right), it is the reaction known as "respiration in animals and "combustion" when high temperatures are involved, and the reverse reaction (to the left) is the basic equation for photosynthesis. Hence this reaction is fundamental to life on earth.

In the oxidation of crude oil, hydrocarbons are oxidized to alcohols, ketones, and organic acids. Oxidized products are more water-soluble than the hydrocarbon compounds from which they are derived. The order in which hydrocarbons are oxidized depends on a variety of factors, but in general, small molecules up to \( C_{20} \) (molecules with 20 carbon atoms or less) are oxidized before larger ones. Within the same molecular weight range, the order is the aliphatic \( n \)-paraffins (\( n \)-alkanes) first followed by branched and cyclic alkanes (naphthalenes) and then the aliphatic and aromatic
hydrocarbons. Thus, the degree of oxidation can be ascertained on the residue based on the type and distribution of the residual compounds. In addition, preferential oxidation of low molecular weight compounds increases the density of the unoxidized residue.

Oxidation of crude oil is mediated by two processes: photooxidation and microbial oxidation that provide the energy to drive the oxidative reactions. Where crude oil is exposed to sunlight and oxygen in the environment, both photooxidation and aerobic microbial oxidation take place. Where oxygen and sunlight are excluded in anoxic environments, anaerobic microbial oxidation takes place.

**Photooxidation in sea water.**

Photooxidation is a family of light-catalyzed reactions that oxidize the reduced carbon in petroleum hydrocarbon. These reactions include both direct photoreactions, where the reactant absorbs light energy, to form less stable intermediate and indirect photoreactions, where other chemical species in solution absorb light energy. The necessary ingredients for photooxidation are radiation and light-absorbing molecules (chromophore) because few petroleum hydrocarbons absorb sunlight efficiently, most photooxidation occurs via indirect photoreactions. Heterogeneous photooxidation, in which reactions occur at the liquid-solid and liquid-liquid interfaces, may also be important. Photooxidation plays an important
role in the removal of dissolved petroleum hydrocarbons. Aliphatic and aromatic fractions of petroleum are oxidized photochemically in sunlight to more polar ketones, aldehydes, carboxylic acids and esters. Because these products are more soluble in seawater, photooxidation enhances the overall solubilization of intact petroleum. These dissolved products can undergo further oxidative processes by either direct or indirect photolysis. In contrast photooxidation may also result in higher-molecular weight products through the condensation of peroxide intermediates, ultimately leading to tar and gum residues.\textsuperscript{45,46,47}

The aromatic and unsaturated fractions of dissolved petroleum hydrocarbons undergo both direct and indirect photolysis in seawater. Polycyclic aromatic hydrocarbons (PAH) degrade to relatively stable quinines via reactions initiated by electron transfer from singlet state PAH to molecular oxygen.\textsuperscript{47}

The extent of photooxidation depends upon:

1. The spectrum and intensity of incident light.
2. The optical properties of the surface water as modified by the petroleum hydrocarbon and other dissolved and particulate constituents.
3. The optical properties of the hydrocarbon themselves.
4. The presence of photo-quenchers and activator compounds.
Petroleum photooxidation occurs faster under short-wave-length light (<300nm) than in broad-spectrum natural sunlight.

**Microbial Oxidation.**

Biodegradation of hydrocarbons has been considered one of the principal removal mechanisms in the aquatic environment. Since 1990, biodegradation of hydrocarbons has become a premiere research area as noted by at least five reviews on the topic. Complete microbial oxidation of oil produces CO₂ and H₂O often from the breakdown of smaller alkanes and cyclic hydrocarbons. More complex hydrocarbons such as branched alkanes and multicyclic compounds (polycyclic aromatic and aliphatic hydrocarbons), require multiple metabolic pathways for degradation and likely involve a consortium of bacterial strains.

Anaerobic degradation of hydrocarbons by sulfate and iron-reducing bacteria has recently been measured in marine environments. Because energy yield is relatively low, anaerobic degradation of hydrocarbons in marine environment is limited to low oxygen area where heterotrophic bacteria can not out compete the anaerobic for carbon substrate.

Rates of biodegradation are dependent on the ability of microbes to contact hydrocarbons as well as on the bacteria metabolic process operating...
within the cell. Rate of biodegradation in a natural experiment range; from 50 to 100 g/m³ per day. In the environment, rate of degradation have been reported to be between 0.001 and 60 g/m³ per day. In marine environments subject to oil spills (e.g. harbors) prior exposure to hydrocarbons decreases the response times for biodegradation to occur but does not increase the rate. In more pristine environments, there is a longer time lag between the oil spill and biodegradation because the natural population must adapt to a new carbon substrate and produce the necessary enzymes.

There is a general hierarchy for rates of biodegradation of hydrocarbons: Saturated alkanes are more quickly degraded by microorganisms than aromatic compounds; alkanes and smaller sized aromatics are degraded before branched alkanes, multi-ring and substituted aromatics and cyclic compounds. Polar petroleum compounds such as sulphur and nitrogen-containing species are the most resistant to microbial degradation. There are several reasons for this, including water solubility and surface area that affect their availability for bacterial adhesion and metabolism. Emulsification (formation of small droplets) provides greater surface area for microorganisms to attach. This implies that only a certain percentage of an oil can be readily biodegraded.

Environmental factors such as oxygen concentrations, nutrients, temperature, salinity and pressure, as well as the physical properties of oil (including surface-to-volume ratios, and the energy level of the
environment, can greatly influence biodegradation rates. In addition, energy levels in marine systems such as the physical mixing of water as well as wind and wave action, can impede biodegradation by aiding in the formation of large oil globules that have a low surface area-to-volume ratio and impede microbial cell attachment and composition processes. In marine systems, microorganism growth is controlled by oxygen activity, nutrient concentrations, light, temperature, salinity, and pressure.

Temperature can influence biodegradation. In low-temperature environments, oil viscosity increases and water solubility decreases, therefore limiting microbial attachment. In addition, volatilization of toxic, short-chained hydrocarbons is decreased and may be detrimental to microorganisms.

2.9 Petroleum hydrocarbon pollution and its possible effects.

Three activities – extraction, transportation and consumption are the main sources of anthropogenic petroleum hydrocarbon pollution in the sea.

The acute toxicity of petroleum hydrocarbons to marine organisms is dependent on the persistence and bioavailability of specific hydrocarbon, the ability of organisms to accumulate and metabolise various hydrocarbons, the fate of metabolised products, the interference of specific hydrocarbons with normal metabolic processes that may alter an organism's chances for survival and reproduction in the environment. Weathering
processes may alter oil composition and thus its toxicity. With weathering, there is a subsequent loss of monoaromatic compounds and the polycyclic aromatic hydrocarbons become more important contributors to the toxicity of weathered oils. Other factors that may contribute alterations in toxicity include photodegradation and photoactivation.

Data gathered from several spills that occurred in the 1970s and 1980s demonstrated that the higher molecular weight aromatic compounds, such as the alkylated phenanthrenes and alkylated dibenzothiophenes are among the most persistent compound in both animal tissues and sediments. Impairment of feeding mechanism, growth rates, development rates and increased susceptibility to disease and other histopathological disorders are some examples of the types of subtle effects that may occur with exposure to petroleum hydrocarbons. Early developmental stages can be especially vulnerable to hydrocarbon exposure, and recruitment failure in chronically contaminated habitats may be related to direct toxic effects of hydrocarbon-contaminated sediments.

Marine birds and mammals may be especially vulnerable to oil spills if their habitats or prey become contaminated. In addition to acute effects such as high mortality, chronic low-level exposure to hydrocarbons may affect survival and reproductive sublethal effects of oil on seabirds include reduced reproductive success and physiological impairment, including increased vulnerability to stress. Oil can also indirectly affect the survival
or reproductive success of marine birds and mammals by affecting the distribution, abundance, or availability of prey.

Oil inputs from consumption activities vary widely in composition, persistence, loading rates by area and season and effects. Chronic contamination by petroleum hydrocarbons from sources other than oil spills may be found in many coastal urban areas as a result of non point source petroleum spillage, the burning of fossil fuels and municipal waste water discharges. The persistence of some compounds such as PAH in sediments, especially in urban area with multiple sources of petroleum inputs, is an example of chronic persistence and toxicity beyond the observations made following oil spills. Transfer of contaminants to marine biota and the human consumer and toxicological effects on the ecosystem are dependent on the availability and persistence on these contaminants within benthic environment. The incidence of tumors in bottom dwelling fish and shellfish from contaminated coastal areas is a possible link to chronic hydrocarbon exposure and uptake. It is clear that the ecological effects of oil inputs is a function of many factors including oil type, release rates, fate processes, and distribution of biological resources. Regional data may be of benefit to shallow waters, areas of restricted flow and dispersion, water with a high concentration of suspended particulates, and fine-grained anaerobic sediments. There are clear effects of produced water discharges on estuarine water sediments and wing resources in inshore production where the
receiving environment is not conducive to the dispersion of the effluent plume.

2.9.1 Transport

2.9.1.1 Horizontal transport

Horizontal transport and horizontal dispersion are separate processes that stand apart from, but may enhance, spreading and Langmuir circulation. Horizontal transport means displacement along a horizontal axis; whereas, horizontal dispersion or diffusion is movement about a defined point and does not necessarily involve net movement.

2.9.1.2 Spreading

The most used model for spreading are based on some works suggesting that spreading is best described in three phases – inertial, viscous, and surface tension. The inertial phase is dominated by gravity forces, the viscous phase by gravity and viscosity forces, and the surface tension phase by surface tension spreading. This observation may be explained in part as a consequence of horizontal diffusion resulting from shear diffusion of waves.

2.9.1.3 Advection

Few studies have been conducted on the subsurface advection of oil. The potential for mixing petroleum with water due to evaporation and
cooling of surface waters seems limited, as the buoyant forces working on
the droplets tend to overcome these mechanisms. Limited observations
suggest that the dissolved and particulate oil move as the bulk water moves
in concert with mass circulation including the influence of tide and
currents. Additional influences in the subsurface movement include
vertical mixing by Langmuir circulation. Empirical studies in the 1960s
established that oil slicks on a sea surface are transported with the surface
current (top centimeter of water at 2.5 to 4 percent of wind speed.

2.9.1.4 Langmuir circulation

Langmuir cells (LC), often expressed as windings, is a common
feature in the sea and is generated by a wind driven shear instability in
combination with the mean Lagrangian motion from surface water.

LC can potentially have many effects on surface oil. First, it enhances
movement of the slick. Second, LC can create convergence and divergence
zones on the surface that affect oil thickness, which in turn can affect biota,
weathering rates and clean up strategies. Finally, LC enhances vertical
dispersion of oil droplets. By pushing the droplets down into the water
column, LC can indirectly affect horizontal advection and dispersion, and
increase the amount of hydrocarbon that dissolves into the water column.

McWilliams and Sullivan (2001) compared the LC enhancement of
vertical and horizontal dispersion and argued persuasively that vertical
dispersion is the most important. Rye (2001) shows aircraft observations from numerous spills that indicate Le horizontal dispersion, but the effects are relatively small scale.

Lehr and Simecek – Beatty (2000) point out that Le may well be as important at enhancing vertical dispersion.

2.9.1.5 Horizontal Dispersion

Dispersion is a mixing process caused by the turbulence field in the ocean. It is the process that would cause a liter of instantaneously released dyed water to expand over time and eventually dissipate in the ocean. Without dispersion, advection would move that liter downstream, but the volume of dyed water will not change over time. Dispersion occurs in both the horizontal and the vertical directions, but because the hydrodynamic processes in the vertical and horizontal are often quite different, a distinction is usually made.

In oil spill modeling, horizontal dispersion is often combined with "spreading" but they are fundamentally different length and time scales. Although spreading and horizontal dispersion start to work immediately after a spill occurs, spreading is nearly complete within a day while dispersion continues to increase. For most offshore spills, dispersion will move more oil around than will spreading. Dispersion originates from
ocean eddies of various scales, Langmuir circulation, boundary layer, shear and other seemingly random turbulent.

2.9.1.6 Vertical Dispersion and Entrainment.

Vertical dispersion and entrainment are the movements of oil droplets of sizes less than about 100 µm in the water column. Typically droplets that display a residence time of minutes have droplet sizes less than about 25 µm. Larger droplets will rise quickly to the surface.

2.9.2 Sinking and sedimentation.

Sinking is the mechanism by which oil masses that are denser than the receiving water are transported to the bottom. The oil itself may have incorporated enough sediment to become denser than water. Sedimentation is the sorption of oil to suspended sediments that eventually settle out of the water column and accumulate on the seafloor. There is a significant difference in the relative amount of oil incorporated by the two processes.

Sinking oil may contain few percent sediment, whereas contaminated sediments accumulating on the seafloor will contain at most few percent oil. Sedimentation requires mechanism for oil to become attached to sediments. One mechanism is ingestion of small oil droplets dispersed in
the water column by zooplankton and excretion of oil in fecal pellets that sink to the seafloor.

Some factors determine whether spilled oil will sink. Because most non-floating oils are only slightly denser than water, the presence of currents can keep the oil in suspension and prevent its accumulation as a coherent mass on the bottom. For example, little or no oil accumulation on the bottom was reported after heavy-oil spills in the Mississippi River. In very few spills of oil that was heavier than water, the oil sank directly to the bottom, and these kinds of spills occurred only in sheltered settings. In contrast, a buoyant oil can pick up enough sediment either after stranding onshore or mixing action, to become an oil-sediment mixture that is denser than sea water. If the sediment separates from the oil mass, the still-buoyant oil can then refloat.
Oil – to – water density ratio

Currents

Sediment Interaction

<1.0

Majority floats initially

Oil floats, but
* quickly form tarballs
* overwashing shows weathering
* Tarballs reconcentrate
  in convergence zones
  And on shorelines

> 1.0

Majority does
Not float
Initially

Oil suspended in water column

Oil sinks
* After stranding and mixing with sand
* After mixing with sand suspended by wave action
* Oil can refloat after separating from sand

After mixing with sand
Transport and mixing
Sand (unsure of effect by current and waves

Oil disperses
* Transport and mixing
  by current and waves

Fig. 2.3 Factor determining whether spilled oil will float or sink.21
Over washing

Over washing is the temporary submergence of oil below the water surface. The oil can be described as "floating" just below the water surface. The principal cause of over washing is the action of waves and near-surface turbulence. Two other factors are also very important: The density of the oil must be close to that of water and the oil must become viscous enough so that the slick breaks up into discrete masses such as tarballs.

Over washing is particularly important because submerged oil is difficult to see visually or with remote sensors, making it difficult to detect the oil, track its path, and make accurate trajectory predictions. Submerged oil also weathers more slowly because there is almost always a thin water layer on top of the oil. Thus, relatively fresh oil can travel hundreds of kilometers from the release site. It is very difficult to recover submerged oil using standard skimming equipment.

There are three mechanisms by which submerged oil can resurface.

1. The density of the water increases as in an estuary where the oil moves from fresh water to salt water.
2. The turbulence of the water surface ceases, when the wind dies down or a river plume enters a bay.
3. The oil becomes stranded on a shoreline.
2.9.3 Shoreline stranding and tarball formation.

Persistent oil residues have two major fates: shoreline stranding for spills near to shore and tarball formation for releases in offshore waters. Oil loading on a shoreline can be highly variable and the amount of oil and the rate of natural removal drive the decision to conduct shoreline clean up.

As a result of the various physical and chemical processes that affect floating oil from seeps, spills, and operational discharges (e.g., discharges of blast water), oil can eventually result into residues called tarballs. While some tarballs may be as large as pancakes, most are con sized. Spills of heavy oils often quickly break into patches of tarballs, making them difficult to track. Tarballs are very persistent in the marine environment and can travel hundreds of miles, sometimes reconcentrating in convergence zones far from the original spill site. Tarballs are problematic because of their long-term persistence and ubiquitous nature along shipping routes.69,70,71

Biomarkers (organic compounds whose structure reflects the biological source) and isotope geochemistry (mainly 12C) have been widely applied to characterize tarballs and to differentiate anthropogenic from natural sources, as well as to discriminate among the many possible sub-sources of anthropogenic contamination.
2.9.4 Seeps

Crude oil released into the marine environment through natural seepage undergoes most of the same physical and chemical processes as crude oil released into the ocean at the seafloor. One main difference is in the rate of addition of oil to the environment. With natural oil seeps, the leakage rate is relatively low and chronic. On the other hand, oil spills result in a release that is sudden, one-time event. The same basic processes act to degrade and remove oil with time, although in the case of seeps, crude oil is replenished as long as the seeps remain active.

2.10 Review of works done on Qua Iboe sediments.

Essien, (2001) wrote on the levels and calculated fluxes of some metals (Pb, Fe, Cu, Cd and Zn) in sediments along a segment of Qua Iboe River. He reported that in areas with high anthropogenic activities, metal levels were observed to be high perhaps due to the discharge of municipal and industrial effluents particularly from the battery industry in the tributary of the river. He observed that the levels of the metals were much higher in downstream samples compared to upstream sample. Thus giving information on the role usually played by anthropogenic activities in environmental pollution. The study also reveals the fact that sediments do not only act as metal traps but are also capable of retaining these metals for years. 

72
Ekwere et al. (1992) analysed samples of recent sediments collected from Qua Iboe estuary and related creeks for organic matter, grain size and clay mineral types to determine their concentration in the sediments. They observed that coarse to medium grained sand occurs in the mouth of the estuary and that kaolinite constitutes the dominant clay mineral in the sediments. Zn and Cd values are higher than threshold values and so represent mild pollution.

Essien et al. (2000) studied the epipelic algae of Qua Iboe estuary in late summer, (between January and February) of 1999. He observed that unlike the epipsamic habitat, the epipelic habitat of the mangrove swamp of the estuary, harbour lower densities and fewer species of micro algae. Variation in species dominance and density show that the mangrove swamp epipelic algae structure is defined by few micro algae species. The pH and salinity levels observed to be high appear to be the most important determinants of species composition in the tidal mud flats. This study further confirms the adaptive potential of some freshwater phytoplankton to brackish water ecosystem.

Armin et al. (1994) described a method to assess the impact of toxicants on the actual anaerobic microbial degradation activity in sediments. He observed that under conditions closely related to insitu, the influence of isoproturon and three of its known metabolites on the actual carbon dioxide release rate and the actual methane production rate was
determined. He reported that for isoproturon only a slight inhibition (<10%) of the methane production rate was observed at concentrations up to 6.25mg/L.

Essiein et al (2003), wrote that based on spatial variations in tidal mud salinity, direct gradient analysis procedures were adopted to relate the productivity and distribution of epipellic microalgae along salinity gradients in mangrove swamp of the Qua Iboe estuary.

They observed that variation in mud salinities were due to distance from the coast, tidal incursions and fresh water inputs. The dilution effect of freshwater input from rainfall, urban runoff and associated freshwater creeks was most severe during the rainy season month of July, with much lower salinity values, recorded for same sampling locations during the drier month of December. However no microalgae species was found to occur on the highest values of mud salinity and there were overlapping range of occurrences and ecological optima for most species along the gradient²³.

Essiein et al (2003), in an effort to apply epipsammic microalgae indices as biological indicator of crude oil pollution and natural remediation in a tropical estuarine environment, the direct effort of a recent oil spill on the abundance of microalgae in the coastal shore of the Qua Iboe Estuary was investigated. A significant negative effect of contamination on the salinity, acidity and nutritive salts (CO$_3^{2-}$, Cl$^-$ and SO$_4^{2-}$) levels of the sandy beach soil was observed. There is increase in the density of microalgae with
distance from the boom. This implies that the effect of oil pollution was more severe on microalgal cells that are close to the boom. The overall effect was a distance-influenced reduction in the regeneration capabilities of the epipsammic microalgae. The absence of some diatom is recommended for use as an indicator of the short-term effect of oil pollution in coastal sandy beaches in a tropical estuarine environment.  

A report on the short term environmental impact assessment of 24 July Idoho - QIT pipeline rupture oil spill by Exomobil shows that the nearshore flow field largely determines the stranding and persistence of the spilled oil on the beach and in mangrove estuary ecosystems. Flow measurements in these environments around Qua Iboe River show a market ebb-dominance. This implies a high flushing potential of these ecosystems of any possible on-shore transported oil.

The general absence of oil (or low persistence if stranded) on the beach is a consequence of high self-cleansing potentials (where initially impacted) or high impedence of surf zone processes to oil transport towards the beach.

Heavy metal concentration on intertidal sandy beach sediments, especially nickel and vanadium depicted values 3 - 10 times lower than at apparently oiled muddy beach. This implies that fine-grained sediments in low-energy environments have a stronger hydrocarbon affinity than the coarser-grained counterparts.
2.11 Identity and analysis of total petroleum hydrocarbon.

Petroleum hydrocarbons (PHCs) are common site contaminants, but they are not generally regulated as hazardous wastes. The term “total petroleum hydrocarbon” (TPH) is generally used to describe the measurable amount of petroleum–based hydrocarbons in the environment. Due to the complexity little is known about their potential for health or environmental impacts. As gross measures of petroleum contamination, TPH results simply show that petroleum hydrocarbons are present in the sampled media. Measured TPH values suggest the relative potential for human exposure and, therefore, the relative potential for human health effects due to TPH exposure requires much more detailed information than what is provided by a single TPH value.

This chapter provides more detailed physical and chemical properties and analytical information on TPH and its components. The Federal government has left much of the specific regulations and oversight of crude oil production/refining to the States. Leaking underground storage tanks (LUST) are the most frequent causes of Federal and State government involvement in petroleum problems. Soil contamination has been a growing concern, because it can be a source of ground water (drinking water) contamination, contaminated soils can reduce the usability of land for development; and weathered petroleum residuals may stay bound to soils for years. Positive TPH test results may require action on the part of land
owners, local or state governments, and engineering firms called on to remove or reduce the TPH problem.

Specific contaminants that are components of TPH, such as BTEX (benzene, toluene, ethylbenzene, and xylenes), n-hexane, jet fuels, fuel oils, and mineral-based crank case oil have been studied and a number of toxicological profiles have been developed on individual constituents and petroleum products. Several approaches have been discussed for interpreting TPH and related analytical results. In all approaches there is a need to reduce a comprehensive list of potential petroleum hydrocarbons to a manageable size. Depending on how conservative the approach is, representative compounds for fractions of similar petroleum hydrocarbons have been selected. This fraction approach is the most demanding in information gathering and because of that would appear to be the most rigorous approach.

2.12 Chemical and physical information

Petroleum products are complex mixtures of hundreds of hydrocarbon compounds. The exact composition of petroleum products varies depending upon (1) the source of the crude oil (crude oil is derived from underground reservoirs, which vary greatly on their chemical composition) and (2) the refining practices used to produce the product.
During the refining process, crude oil is separated into fractions based on specific boiling ranges. These fractions are then modified by cracking, condensation, polymerization, and alkylation processes, and are formulated into commercial products, such as naphtha, gasoline, jet fuel, and fuel oils. The composition of any of these products can vary based on the refinery involved, time of year, variation in additives or modifiers, and other factors. The chemical composition of the product can be further affected by weathering and/or biological modification upon release to the environment.

2.12.1 Automotive gasoline

Automotive gasoline is a mixture of low boiling hydrocarbon compounds suitable for use in spark-ignited internal combustion engines and having an octane rating of at least 60. Additives that have been used in gasoline include alkyl butyl ethers (e.g. MTBE), ethanol, methanol, tetramethyl lead, tetraethyl lead, ethylene dichloride, and ethylene dibromide. Other categories of compounds that may be added to gasoline include anti-knock agents, antioxidants, metal deactivators, lead scavengers, anti-rust agents, anti-icing agents, upper cylinder lubricants, detergents, and dyes.

Automotive gasoline typically contains about 150 hydrocarbon compounds. The relative concentrations of the compounds vary.
considerably depending on the source of crude oil, refinery process, and product specifications. Typical hydrocarbon chain lengths range from C_4 through C_{12} with a general hydrocarbon distribution consisting of 4-8% alkanes, 2-5% alkenes, 25-40% iso alkanes, 3-7% cycloalkanes, 1-4% cycloalkenes, and 20-50% aromatics. However, these proportions vary greatly. Unleaded gasoline may have higher proportions of aromatic hydrocarbon than leaded gasoline.

2.12.2 Jet fuel

Jet fuels are light petroleum distillates that are available in several forms suitable for use in various types of jet engines. The exact compositions of jet fuels are established by the U.S. Air Force, using specifications that yield maximum performance by the aircraft. The major jet fuels used by the military are JP-4, JP-5, JP-6, JP-7, and JP-8. Briefly, JP-4 is a wide cut fuel developed for broad availability in times of need; JP-6 is a higher cut than JP-4 and is characterized by fewer impurities.

Typical hydrocarbon chain lengths characterizing JP-4 range from C_4 to C_{10}. Aviation fuels consist primarily of straight and branched alkanes and cycloalkanes. Aromatic hydrocarbons are limited to 20-25% of the total mixture because they produce smoke when burned. A maximum of 5% alkenes are allowed in JP-4. The approximate distribution by chemical
class is: 32% straight alkanes 31% branched alkanes, 16% cycloalkanes, and 21% aromatic hydrocarbons.

2.12.3 Fuel Oil

Fuel oil No 1 is a petroleum distillate that is one of the most widely used of the fuel oil types. It is used in atomizing burners that spray fuel into a combustion chamber where the tiny droplets burn while in suspension. It is also used as a carrier for pesticides, as a weed killer, as a mold release agent in the ceramic and pottery industry, and in the cleaning industry. It is found in asphalt coatings, enamels, paint thinners, and varnishes.

Fuel oil No. 2 is a petroleum distillate that may be referred to as domestic or industrial fuel oil. The domestic fuel oil No. 2 is usually lighter than straight-run refined. It is used primarily for home heating and to produce diesel fuel No. 2. Industrial distillate is the cracked type, or a blend of both. It is used in smelting furnaces, ceramics, kilns and packaged boilers.

Fuel oil No. 2 is characterized by hydrocarbon chain lengths in the C\textsubscript{11} - C\textsubscript{20} range, whereas diesel fuels predominantly contain a mixture of
C<sub>10</sub> – C<sub>19</sub> hydrocarbons. The composition consists of approximately 64% aliphatic hydrocarbons (straight chain alkanes and cycloalkanes), 1-2% unsaturated hydrocarbons (alkenes), and 35% aromatic hydrocarbons (including alkylbenzenes and 2-3 ring aromatics). Fuel oil No 2 contains less than 5% polycyclic aromatic hydrocarbons.

Fuel oil No. 6 is also called Bunker C or residual. It is the residual from crude oil after the light oils, gasoline, naphtha; fuel oil No 1 and fuel oil No 2 have been fractionated off. Fuel oil No 6 can be blended directly to heavy fuel oil or made into asphalt. It is limited to commercial and industrial uses where sufficient heat is available to fluidize the oil for pumping and combustion.

Residual oils are generally more complex in composition and impurities than distillate fuels. Fuel oil No 6 includes about 25% aromatics, 15 % paraffins, 45% naphthenes, and 15% non-hydrocarbon compounds. Polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs and metals are important hazardous and persistent components of fuel oil No. 6.

Mineral oils, including mineral based crankcase oil, are often lubricating oils, but they also have medicinal and food uses. A major type of hydraulic fluid is the mineral oil class of hydraulic fluids. The mineral – based oils are produced from heavy – end crude oil distillates. Distillate streams may be treated in several ways, such as vacuum, solvent, acid or hydro-treated, to produce oils with commercial properties. Hydrocarbon
numbers ranging from \( \text{C}_{15} \) to \( \text{C}_{30} \) are found in the various types of mineral oils, with the heavier distillates having higher percentages of the higher carbon number compounds.

The mineral-based oils contain hundreds to thousands of hydrocarbon compounds, including a substantial fraction of nitrogen- and sulfur-containing compounds. The hydrocarbons are branches chain hydrocarbons (alkanes) cycloalkanes, and aromatic hydrocarbons. PAHs, alkyl PAHs and metals are important components of motor oils and crankcase oils, with the used oils typically having higher concentrations than the new unused oils. Typical carbon number chain lengths range from \( \text{C}_{15} \) to \( \text{C}_{30} \).

2.13 Analytical Methods

The purpose of this section is to describe well-established analytical methods that are available for detecting and/or measuring and/or monitoring TPH and its metabolites, as well as other biomarkers of exposure and effect of TPH.

Some conventional TPH methods have been used widely to investigate sites that may be contaminated with petroleum hydrocarbon products. The important disadvantages of these methods are:

1. The petroleum hydrocarbon composition varies among sources and over time, so results are not always comparable,
2. The more volatile compounds in gasoline and light fuel oil may be lost in the solvent concentration steps.
3. There are inherent inaccuracies in the methods and
4. The method provides virtually no information on the types of Hydrocarbons present.

Thus, these conventional TPH methods, although they provide adequate screening information on the extent of the contamination and product type will be replaced with n-hexane Extractable material (HEM) and silica Gel Treated n-Hexane Extractable Material (SGT-HEM) by extraction and gravimetry.

Gas chromatography (GC) methods do provide some information about the product type. Most methods involve a sample preparation procedure followed by analysis using GC techniques. An analytical method was developed for identifying and quantifying the presence of the groups or fraction with similar mobility in sediment. This technique called silica gel cleaning is used to fractionate the hydrocarbon into aliphatic and aromatic fractions.
CHAPTER THREE

3.0 Results and discussion

An analytical result of seafloor sediments gives a clearer view of the prevailing health status of the marine environment. This is because environmental contaminants have the tendency to accumulate in the particulates that are deposited on the seafloor over long periods. However, low level of anthropogenic sediment contamination is difficult to detect in some cases because natural background concentrations vary with grain size, carbon content and mineralogy.

Sediment samples were collected from ten stations within the study area. The summary results (in gram and ppm) for aliphatic, aromatic and soluble organic matter components are presented in tables 3.1, 3.2 and 3.3 respectively. Detailed results for sediment analysis are provided in table 3.4.

The levels and pattern of variation of the chemical parameters examined in the present investigation are presented in figs 3.1 to 3.5.

3.1 Total organic carbon (TOC)

Total organic carbon (TOC) gives an indication of the number of carbon containing compounds in a medium and provides a means for determining the degree of organic contamination. Also, the TOC content of
sediment gives an idea of the origin of the sediment materials. Organic carbon concentration less than 12% by weight of sediment samples imply that sediment materials is derived from mineral sources such as rocks while concentrations above 12% suggest that sediment materials has been derived from decayed organic sources. Organic carbon content may also be used as an indication of the abundance of benthic organisms and other microorganisms. High organic carbon content would result in an increase in the growth of micro-organisms, which in turn contribute to the depletion of oxygen supplies.

The % TOC content of the sediments are presented in table 3.4 TOC content of the sediments range from 1.02% at location Q6 to 2.03% of the Q4. Average TOC content of the Qua Iboe river sediments was found to be 1.41%. The seemingly light value of TOC at location Q4 may be attributed to high input of organic materials during periods of high rainfall by the transport of organic mater from terrestrial area. High value of TOC can also be seen at location Q7 of 1.93% which may be as a result of deposition of waste by man. The relatively low value of TOC of 1.02% at location Q6 may be due to tidal variations of the river which affect the deposition, accumulation and preservation of organic material.
3.2. Soluble organic Matter (SOM)

Soluble organic matter contents of the sediment are presented in table 3.2. They range between $0.2 \times 10^4$ ppm at location $Q_1$ and $1.3 \times 10^4$ ppm at location $Q_6$. The mean value is $0.6 \times 10^4$ ppm. The high value of SOM at locations $Q_6$ is attributed to the effects of industrial activities. Human activities such as waste disposal into the water increase the organic matter input into the water. Also, location $Q_{10}$ and $Q_9$ show high values of SOM, this could also be attributed to high input of materials both from terrestrial and aquatic areas. The SOM values are poorly correlated with $\%$ TOC (Fig 3.3.). This indicates different sources of organic matter input. The overall composition of the extract includes aromatic and aliphatic hydrocarbons.

3.3. Total petroleum hydrocarbon (TPH)

Hydrocarbons in the marine environment may be derived from a number of sources including natural sources (marine seeps and sediment erosion), offshore oil explorations and production, dry - docking and marine terminal operation (barges and fuel oils, tanker accidents and non-tanker accidents); other sources include municipal / industrial waste (municipal waste, non-refined industrial waste, urban run-off, river run-off and ocean dumping). Excessive amounts of hydrocarbons can interfere with aerobic and anaerobic biological processes.
Average TPH for the ten samples is $20.9 \times 10^4$ ppm. The TPH contents of the sediments are presented in table 3.4. The highest value was obtained in location Q₁ (74.1 $\times 10^4$ ppm). This was probably due to discharge of hydrocarbons from effluent discharge, crude oil transplantation, and natural seeps. This high value indicates that Qua Iboe River is heavily polluted with petroleum hydrocarbons.

As can be seen in table 3.4, the sample from control area has a very low level of total petroleum hydrocarbon of $4.9 \times 10^4$ ppm compared to the results of samples from study area. Chemicals meeting sediment quality standard (SQS) are not expected to cause adverse effects on biological resources and the environment. The results of samples from study area are above the sediment quality levels set by Federal Ministry of Environmental Protection Agency, which shows gross pollution of study area with petroleum hydrocarbon.

Accidental oil spill, discharge of oily substances offshore etc. during projects implementation has the potential to increase TH concentrations of the sediment in these areas.

### 3.4. Aliphatic hydrocarbons in sediments

Consistent with the TPH result concentrations of aliphatic hydrocarbons were high. The results of the Aliphatic hydrocarbon content are presented in tables 3.2. They range between $1.6 \times 10^4$ ppm at location Q₆.
and 55.6 x 10^4 ppm at location Q1 which shows high pollution. The control site result for aliphatic hydrocarbon is 2.0 x 10^4 ppm as shown in table 3.2 and results of Qua Iboe river samples were well higher than control site and sediment quality standards.

3.5. Aromatic hydrocarbon in sediments.

Consistent with the TPH results, concentrations of aromatic hydrocarbons were high with the lowest value of 3.7 x 10^4 ppm at location Q1 and highest value of 18.5 x 10^4 ppm at location Q1. The summary of sediment aromatic hydrocarbon results obtained from the study area is presented in table 3.3. The Control result for aromatic hydrocarbon is 0.3 x 10^4 ppm and as can be seen, in table 3.4, the results detected in Qua Iboe river sediment were at concentrations higher those in control area and sediment quality standards.

3.6. Variation of TOC with TPH

Plot of TOC against total petroleum of hydrocarbon (fig. 3.2) gives us an idea of hydrocarbon status of the sediment sample Q4 has the highest amount of TOC of 2.03 % and least value TPH was Q6 of 7.9 x 10^4 ppm sample Q6 has the low value of 1.026 for TOC while the highest value for 74.1 x 10^4 ppm.
The highest total petroleum hydrocarbon value of $74.1 \times 10^4$ ppm found here was attributed to discharges from crude oil. The TPH and TOC values suggest heavy pollution of the study area.

3.7. Calculation of averages

<table>
<thead>
<tr>
<th>Average</th>
<th>% TOC</th>
<th>Average SOM</th>
<th>Average TPH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.41%</td>
<td>65120</td>
<td>2092884.98</td>
</tr>
<tr>
<td></td>
<td>0.05</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.3 x $10^4$ppm</td>
<td>20.9 x $10^2$ppm</td>
</tr>
</tbody>
</table>

Conclusion

It is evident from the results that some of the sites are grossly polluted. The chemical and analytical techniques used in the assessment of sediments of Qua – Iboc river, South Eastern Nigerian have provided useful information on the evaluation of hydrocarbon pollution through organic matter richness and total petroleum hydrocarbon levels. Several sites exceeded standards laid out for sediment quality. Each site studied
demonstrated individual traits, based on local industry and other factors. No common strategy is apparent to combat the problems at all the sites.

There is petroleum hydrocarbon pollution in the sediment of Qua Iboe River, Ibeno south Eastern Nigeria and the major source of this pollution is anthropogenic.

Table 3.1
Soluble or extractable organic matter

<table>
<thead>
<tr>
<th>Sample No</th>
<th>Wt in (g)</th>
<th>wt in ppm x 10^4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Qo</td>
<td>0.108</td>
<td>0.2</td>
</tr>
<tr>
<td>Q1</td>
<td>0.241</td>
<td>0.5</td>
</tr>
<tr>
<td>Q2</td>
<td>0.268</td>
<td>0.5</td>
</tr>
<tr>
<td>Q3</td>
<td>0.276</td>
<td>0.6</td>
</tr>
<tr>
<td>Q4</td>
<td>0.286</td>
<td>0.6</td>
</tr>
<tr>
<td>Q5</td>
<td>0.634</td>
<td>1.3</td>
</tr>
<tr>
<td>Q6</td>
<td>0.243</td>
<td>0.5</td>
</tr>
<tr>
<td>Q7</td>
<td>0.250</td>
<td>0.5</td>
</tr>
<tr>
<td>Q8</td>
<td>0.337</td>
<td>0.7</td>
</tr>
<tr>
<td>Q9</td>
<td>0.513</td>
<td>1.0</td>
</tr>
<tr>
<td>Control</td>
<td>0.102</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Fractionation of Hydrocarbons

Table 3.2

<table>
<thead>
<tr>
<th>Sample No</th>
<th>wt in (g)</th>
<th>wt in ppm x 10^4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q1</td>
<td>0.06</td>
<td>55.6</td>
</tr>
<tr>
<td>Q2</td>
<td>0.06</td>
<td>24.8</td>
</tr>
<tr>
<td>Q3</td>
<td>0.02</td>
<td>7.5</td>
</tr>
<tr>
<td>Q4</td>
<td>0.02</td>
<td>7.2</td>
</tr>
<tr>
<td>Q5</td>
<td>0.06</td>
<td>20.9</td>
</tr>
<tr>
<td>Q6</td>
<td>0.01</td>
<td>1.6</td>
</tr>
<tr>
<td>Q7</td>
<td>0.01</td>
<td>4.1</td>
</tr>
<tr>
<td>Q8</td>
<td>0.04</td>
<td>16.0</td>
</tr>
<tr>
<td>Q9</td>
<td>0.01</td>
<td>3.0</td>
</tr>
<tr>
<td>Q10</td>
<td>0.01</td>
<td>1.9</td>
</tr>
<tr>
<td>Control</td>
<td>0.002</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Using

\[
\text{wt of residue (g) x } 10^4 = \frac{\text{wt of extract (g)}}{\text{Sample No}}
\]
<table>
<thead>
<tr>
<th>Sample No</th>
<th>wt of residue (g)</th>
<th>wt of Residue ppm x 10^7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q1</td>
<td>0.02</td>
<td>18.5</td>
</tr>
<tr>
<td>Q2</td>
<td>0.01</td>
<td>4.1</td>
</tr>
<tr>
<td>Q3</td>
<td>0.01</td>
<td>3.7</td>
</tr>
<tr>
<td>Q4</td>
<td>0.03</td>
<td>10.9</td>
</tr>
<tr>
<td>Q5</td>
<td>0.02</td>
<td>7.0</td>
</tr>
<tr>
<td>Q6</td>
<td>0.04</td>
<td>6.3</td>
</tr>
<tr>
<td>Q7</td>
<td>0.02</td>
<td>8.2</td>
</tr>
<tr>
<td>Q8</td>
<td>0.01</td>
<td>4.0</td>
</tr>
<tr>
<td>Q9</td>
<td>0.02</td>
<td>5.9</td>
</tr>
<tr>
<td>Q10</td>
<td>0.04</td>
<td>7.8</td>
</tr>
<tr>
<td>Control</td>
<td>0.003</td>
<td>2.9</td>
</tr>
</tbody>
</table>
Table 3.4 variation of % TOC, SOM, SHC, AHC, TPH in parts per million (ppm)

<table>
<thead>
<tr>
<th>SAMPLE NO</th>
<th>%TOC (ppm) x 10^4</th>
<th>SOM (ppm)</th>
<th>SAT H/C (ppm) x 10^4</th>
<th>AROMATIC H/C (ppm) x 10^4</th>
<th>TPH (ppm) x 10^4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q1</td>
<td>1.64</td>
<td>0.2</td>
<td>55.6</td>
<td>18.5</td>
<td>74.1</td>
</tr>
<tr>
<td>Q2</td>
<td>1.42</td>
<td>0.5</td>
<td>25.0</td>
<td>4.1</td>
<td>25.3</td>
</tr>
<tr>
<td>Q3</td>
<td>1.26</td>
<td>0.5</td>
<td>7.5</td>
<td>3.7</td>
<td>11.2</td>
</tr>
<tr>
<td>Q4</td>
<td>2.03</td>
<td>0.6</td>
<td>7.2</td>
<td>10.9</td>
<td>18.1</td>
</tr>
<tr>
<td>Q5</td>
<td>1.28</td>
<td>0.6</td>
<td>21.0</td>
<td>7.0</td>
<td>21.7</td>
</tr>
<tr>
<td>Q6</td>
<td>1.02</td>
<td>1.3</td>
<td>1.6</td>
<td>6.3</td>
<td>7.9</td>
</tr>
<tr>
<td>Q7</td>
<td>1.93</td>
<td>0.5</td>
<td>4.1</td>
<td>8.2</td>
<td>12.3</td>
</tr>
<tr>
<td>Q8</td>
<td>1.11</td>
<td>0.5</td>
<td>16.0</td>
<td>4.0</td>
<td>20.0</td>
</tr>
<tr>
<td>Q9</td>
<td>1.12</td>
<td>0.7</td>
<td>3.0</td>
<td>5.9</td>
<td>8.9</td>
</tr>
<tr>
<td>Q10</td>
<td>1.24</td>
<td>1.0</td>
<td>1.9</td>
<td>7.8</td>
<td>9.7</td>
</tr>
<tr>
<td>Control</td>
<td>0.88</td>
<td>0.2</td>
<td>2.0</td>
<td>2.9</td>
<td>4.9</td>
</tr>
</tbody>
</table>
CHAPTER FOUR

4.0 EXPERIMENTAL PROCEDURES

4.1 Sample collection and preservation.

The collection of sediments from sea floor requires to the special devices selected according to the character of the deposit and the depth of water.

Ten sediment samples were collected from the river using large van een grab sampler. Each site, has varying proportions of residential, commercial, industrial and highway run off. A control site with little or no anthropogenic inputs was sampled at Njaba River. Sub samples were taken from the centre of the grab to avoid contamination. The sediment samples were collected into sample bags with labeling made inside the bag as external labeling may be misplaced during transportation.

The wet samples were carefully oven dried at temperature of 105°C. since moisture is not needed to avoid difficulty in crushing the samples and to avoid the problem of separation of water from the sediment extract if the samples were crushed wet.

4.2 Sample preparation.

The samples were oven dried very well to enhance crushing. Crushing was effected in a hand percussion matter to 200 mesh size fine.
powder. Sieving was to ensure that the whole powder for analysis is below a certain grain size and also periodic sieving and removal of the finer fractions speeds up the crushing process by preventing matting and also minimized errors attendant upon excessive pulverization. A powder which passes through a 200 mesh screen was used to ensure efficient extraction.

Sufficient quantity was crushed while 50g of each of the samples was used for soxhlet extraction.

4.3. **Determination of total organic carbon (TOC)**

The following apparatus and regents were used.

**Apparatus**
- Burette
- Retort stand
- Conical flask (50mL)
- Beaker
- Measuring cylinder

**Reagents**
- Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$)
- Ferrous Ammonium Sulphate
- Sodium flouride (NaF)
- Distilled water
- Diphenyl ammine (indicators)
Concentrated tetraoxosulphate (vi) acid

Tetraoxophosphate (v) acid


The crushed sample of weight 0.5g was placed in a 500ml Erlenmeyer flat bottom flask. 10cm³ of 0.2M potassium heptaoxodichromate (vi) solution was added followed by the addition of 20cm³ of concentrated tetraoxosulphate (vi) acid with the acid of a burette to oxidize the organic material. The mixture was swirled for about a minute to ensure a stand for about 30 minutes.

After 30 minutes, the solution was diluted with 200 ml of distilled water and 10ml of 85% syrupy tetraoxosulphate (vi) acid was added to prevent the iron (ii) ions, which are formed in the course of titration of the iron (ii) salt from oxidizing the diphenylamine indicator prematurely. The iron (ii) ions are taken up as fast as they are formed or produced by oxidation into ion (iii) phosphate complex which is almost undissociated and the iron (ii) ions are thus prevented from oxidizing the diphenylamine.

Sodium Fluoride 0.2g, was immediately added to bind the refractory metals like calcium, magnesium etc; eight drops of diphenylamine indicator was added to the content of the flask.

The solution was back titrated with 0.25M ferrous ammonium tetraoxosulphate (vi) solution. On titration, the colour was observed to
change from greenish-brown to blue black and then bright green at the end point. A standard was first titrated and the result noted.

The percentage organic carbon was then calculated using this equation.

\[
\% \text{ TOC} = 10(1 - \frac{T}{S}) \times F^{-1}
\]

Where
- \( T \) = Sample Titration
- \( S \) = Standard or blank titration
- \( F \) = Factor derived as follows.

\[
F = \frac{1.0 \times 12}{4,000} \times \frac{1.72 \times 100}{0.5}
\]

\[
W = \text{Weight (in grams) of crushed sample used}
\]

If \( W = 0.5 \) g

Then

\[
F = \frac{1.0 \times 12}{4,000} \times \frac{1.72 \times 10}{0.5}
\]

\[
\% \text{ TOC} = 10(1 - \frac{T}{S}) 1.032
\]

Precaution

1. Freshly prepared \( \text{K}_2\text{Cr}_2\text{O}_7 \) and \( \text{Fe} (\text{NH})_2\text{SO}_4 \cdot 6\text{H}_2\text{O} \) were used.

2. Concentrated \( \text{H}_2\text{SO}_4 \) was added to the ferrous solution to avoid oxidation.
4.4 Extraction of soluble organic matter (SOM)

The following apparatus and reagents were used.

**Apparatus**

1. Soxhlet extractors (250 ml)
2. Round bottom flask (250 ml)
3. Condenser and rubber hosed water bath
4. Beakers
5. Glass spatula
6. Clamp and stand

**Reagents**

1. Acetone
2. Methanol
3. Water

**Method**

The method of extraction used was the Soxhlet extraction process. The crushed samples were weighed (50g each) and placed in the Soxhlet extraction thimble. A mixture of chloroform and methanol in the ratio of 3:1 v/v was used as the solvent for extraction and placed in a round bottom flask resting on a water bath and attached to the Soxhlet apparatus. Condensers were fitted on top of the extraction thimble. To ensure complete extraction, refluxing was carried out for about 12 hours after which the solvent in the extract were carefully
evaporated and the extracts were put in labeled sample beaker and covered with perforated filter paper to prevent the entry of unwanted material.

Precautions
1. All the solvents used were re-distilled to avoid contamination of extracts.
2. Continuous flow of water through the condensers was ensured to avoid loss of solvents.
3. The extracts were allowed to dry in the laboratory not in the oven to avoid loss of volatile components.
4. Anti bumping chips were used to prevent explosion.

4.5. Fractionation of soluble organic matter

The silica gel was activated at a temperature of 120°C for two hours before being developed in n-hexane. The silica gel was placed into the column, a little at a time to ensure uniform pacing and n-hexane allowed to run through the column each time. Aluminum oxide was packed on top.

The sample were first dissolved in a little quantity of dichloromethane (10ml) and introduced at the top of the column with the help of a syringe. Saturated hydrocarbons (SHC) was first eluted with 100% hexane, aromatic hydrocarbon (AHC) with 100% dichloromethane and nitrogen, sulphur and oxygen compounds (NSO) was eluted with 3:1 dichloromethane- methanol mixture.
Fig 4.1 Schematic Diagram of the analysis.
4.7 Summary

There is little argument that liquid petroleum crude oil and the products refined from it play a pervasive role in modern society. An examination of reports from a variety of sources, including industry, government, and academic sources, indicate that although the sources of petroleum input to the sea are diverse they can be categorized effectively into four major groups natural seeps, petroleum extraction, petroleum transportation, and petroleum consumption.

Sources of frequent, large releases are rightfully recognized as areas where greater effort to reduce petroleum pollution should be concentrated, despite the fact that not every spill of equal size leads to the same environmental impacts. This study attempts to develop a sense of what the major sources of petroleum entering the marine environment are.

The effect of a release of petroleum is a complex function of the rate of release, the nature of the released petroleum (and the proportions of toxic compounds it may contain) and the local physical and biological ecosystem exposed.

The environmental impact of contaminants in coastal marshes and estuaries is potentially serious. The microbial degradation of petroleum hydrocarbons in marine sediments is a rapidly growing research area with focus to develop a better understanding of the fate of spilled oil in marine
environment and devising remedial measures that fully utilize the indigenous microbial assimilative capacity.

A great deal of information available recognizes the significance of microbial degradation on the fate a trapped oil in marine sediments and acknowledges the influence of a variety of abiotic and biotic factors. However, the linkage of tidal flooding to overall microbial activity which in turn may influence the intrinsic biodegradation of spilled oil in coastal marsh sediments is not well established. On the other hand, there is an emerging question regarding the impact of oil spill recurrence on biodegradation potential of complex mixtures of petroleum hydrocarbons such as crude oil in marine sediments.

Spilled oil immediately begins to move and weather, breaking down and changing its physical and chemical properties. As these processes occur, the oil threatens surface resources and a wide range of subsurface aquatic habitats exist, with varied sensitivities to the harmful effects of oil contamination and different abilities to recuperate from oil spills. In some areas, habitats and populations can recover quickly. In other environments, however, recovery from persistent or stranded oil may take years. These detrimental effects are caused by both petroleum and non-petroleum oil.

From the analytical results of the study area, the high values of total organic carbon and total petroleum hydrocarbon shows that there is high
pollution of the study area which affects both the aquatic and terrestrial environments.

Finally, although there is no good evidence for the toxic effects of oil pollution, on individual organisms and on the species composition of communities, there is little information on the effects of either acute or chronic oil pollution on population or on the function of communities or ecosystems.

Recommendations.

For further understanding and better interpretation of results, it is recommended that further studies should be carried out in the following areas.

1. Sediment and biota analysis employed as a compliment to water analysis as a compliment to water of overall quality of urban catchments. This can identify key pressures and allows prioritization of actions to resolve problems in the future.

2. More petroleum hydrocarbon studies be monitored continuously through a specific period of time to assess the persistence of these hydrocarbons.

3. Other pollutants such as pesticides and PCBs may also have a significant impact in Urban areas, therefore additional monitoring may prove worth while.
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Fig 3.1 Plot of total organic carbon versus soluble organic matter.
Fig 3.2 Plot of total organic carbon versus aromatic Hydrocarbon
Fig 3.3 Plot of total organic carbon versus saturated hydrocarbon.
Fig. 3.4 Plot of total organic carbon versus total petroleum Hydrocarbon.