PETROLEUM HYDROCARBONS POLLUTION OF NIGERIAN WATERS AND SEDIMENTS AROUND LAGOS AND NIGER DELTA AREA OF NIGERIA

By

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ABSTRACT

There is a paucity of scientific data on the levels and pattern of distribution of petroleum hydrocarbons in the Nigerian aquatic environment. The levels of total hydrocarbons in 241 water and 222 sediment samples in the major river systems draining into Nigerian coastal environment around Lagos and the Niger Delta area have been used to monitor the pattern of distribution of hydrocarbons within these areas over different weather regimes during 1984-85. The Utorogu pipeline oil spillage incident in Bendel State of Nigeria in 1984 was used as a case study for assessment of environmental impact of oil spillage in aquatic ecosystem in Nigeria. Samples were also collected and analyzed for total hydrocarbons from Kaduna (Northern Nigeria) and Ibadan (Western Nigeria) for comparative information and controls respectively.

Water samples were analyzed for petroleum hydrocarbon by infrared (IR) and gas chromatographic (GC) techniques whereas sediment samples were analyzed by gravimetry and gas chromatography (GC).

The infrared (IR) results for 1984 (wet season) showed that Lagos and Lekki lagoons had hydrocarbon level (presented as range followed by mean value in bracket), 1.64-11.40 (5.60) mg/l; Niger Delta, ND (not detectable)-70.70 (6.18)mg/l; Utorogu 0.17-10.50 (2.22)mg/l; Kaduna 4.30-9.90 (6.98)mg/l, while Ibadan water samples (serving as control area) showed no detectable levels of hydrocarbon.

In 1985 (dry season) there was a decrease in the hydrocarbon levels found in the water samples. Lagos and Lekki lagoons recorded 0.10-0.41 (0.25)mg/l; Niger Delta 0.10-1.80 (0.52)mg/l and Utorogu 0.17-4.67 (2.14)mg/l.

The gas chromatographic values for hydrocarbon concentration in water were much lower than the infrared values. All the samples except Upomani discharge point (3.36 mg/l) had values below 1 mg/l by GC. Nonetheless, the IR values correlated well with the GC values.

The corresponding hydrocarbon levels (on dry weight basis) in sediment samples in 1984 were: Lagos and Lekki lagoons ND-95.54 (30.33) µg/g;

Niger Delta ND-74.05 (9.09) µg/g; Utorogu 14.04-267.48 (98.88) µg/g and Kaduna 0.62-21.52 (12.36) µg/g.

In 1985 the values of hydrocarbon levels recorded in the sediment samples were as follows: Lagos and Lekki lagoons 0.20-10.30 (4.20) µg/g; Niger Delta 0.05-44.06 (6.64) µg/g; Utorogu (Jan-Feb.) ND-9.41 (2.98)µg/g; Utorogu (June-July) 0.03-68.06 (21.66)µg/g; Kaduna 2.91-5.00 (3.96)µg/g and Ibadan 8.09-27.79 (17.94)µg/g. The Lagos lagoon sediment samples monitored from January to December 1985 gave ND-2766.27 (11.13)µg/g.

The results of this work showed that Lagos lagoon was more polluted than the Niger Delta in terms of petroleum hydrocarbons. Highest values of petroleum hydrocarbons were recorded close to oil activity points such as Ogharife field effluent canal, Chanomi creek at Egwa field, Orughene creek, in the Niger Delta area; or near human settlements such as Obotebe and Bakana or in an industrial area like Lever Brother's discharge point and Berger/National Oil/Ijora in Lagos.

The results of Utorogu oil spillage gave a picture of the impact of oil in the aquatic environment. During the first sampling trip which took place within four months after the oil incident, aquatic lives (plants and animals) were seriously affected in the Utorogu swamp, but before the end of the study period (June 1985) the swamp had recovered and was bubbling with life again.

Oil pollution indicator parameters such as the Carbon Preference Index (CPI), Pristane:Phytane ratio (Pr/Ph); Presence of Phytane, and Unresolved Complex Mixture (UCM) and the Marine Oil Pollution Index (MOPI) indicated that some of the stations were polluted by oil while most of the points studied in both Lagos and the Niger Delta were contaminated with petroleum hydrocarbons which may be from crude oil, refined oil or both.

Moreover, all the contaminated and polluted samples showed petroleum hydrocarbon at different stages of weathering as reflected in their carbon range, the Pristane: $n\text{-}C_{17}$; Phytane:$n\text{-}C_{18}$ and UCM: n-alkane ratios.

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My sincere thanks go to my supervisor, Dr. O. Osibanjo, for his guidance, criticisms, suggestions, encouragement and supervision to make this work a success. He was a constant inspiration to me throughout the programme and I also learnt some useful lessons from him.

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hopeless. I doff my hat in great salute to my Jewel of inestimable value. I also thank my children, Toyin, Tosin, Tope Diipo (Jnr.) and Tomilola for their love, understanding and patience during the course of this work.

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Finally, I am very grateful to my Heavenly Father and to Him I give all thanks, honour and glory for His kindness and mercy over me and my family.

DEDICATION

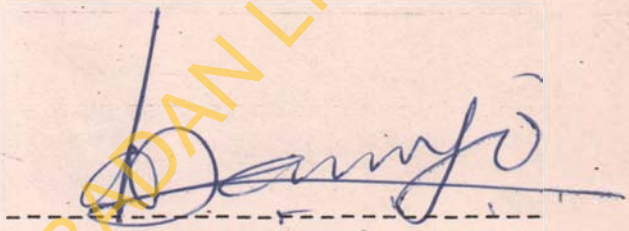
This work is dedicated to the GLORY OF GOD for HE has been so wonderful and gracious to me and my family through CHRIST JESUS.

"Give thanks in all circumstances,
for this is God's will
for you in Christ Jesus."

I Thes. 5:18.

CERTIFICATION

I certify that this work was carried out by Oladipo Ebenezer ADEKANMBI in the Department of Chemistry, University of Ibadan.



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1. INTRODUCTION

1.1 THE ORIGIN OF PETROLEUM

Crude oil has its origin in the organic debris of plants, algae, bacteria, fungi, and a multitude of micro-organisms that have been deposited into aquatic sediments for a long time. The type of organic matter is dependent on the environment of deposition. Generally, marine, continental and paralic (transitional between marine and continental) environments are colonised by different flora and fauna. Hence the corresponding sediments may contain grossly different types of organic matter. While marine biota are dominated by primitive plants and animals like planktons, algae, and diatoms, higher plants are preponderant in the continental shelf. Petroleum generated from different sources sometimes show gross dissimilarities in their content of certain classes of organic compounds due to the variation in composition of proteins, carbohydrates, lignin, lipid, etc. of the living organisms from which they are formed. For instance, petroleum from marine source

rocks are generally more aliphatic than their terrigenous counterparts[1]. This mainly reflects the difference in the lower (<C20) n-alkanes contents of marine and non-marine lipids.

On the other hand, substantial evidence show that high wax crude oils were generated in sediments with significant contributions of terrigenous organic matter[1]. Petroleum wax (n-C20-n-C30 alkanes) might have originated from higher (>C20) fatty acids, alcohols and alkanes which are characteristic of higher plant lipids. Hence, high wax crudes are generally restricted to rocks deposited in continental and paralic or near shore-marine paleoenvironments rather than marine areas where higher plant influence is minimal[2].

In most aquatic systems, the rate of accumulation of organics in sediments is quite small compared to the primary productive rate in the surface water where most of the organic carbon produced is ultimately respired. In the presence of oxygen, bacteria degradation of organic debris takes place by the reaction[3]:

$$(CH_2O)_n + O_2 \longrightarrow nCO_2 + nH_2O.$$

While in the absence of oxygen, anaerobic oxidation of organic material proceeds because certain bacteria utilize sulphate as a source of oxygen, according to the general reaction:

$$CH_2O + SO_4^{2-} \longrightarrow CO_2 + H_2O + H_2S.$$

Further bacteria action continues with the reduction of carbon dioxide by hydrogen or attack by bacteria on such substrates as low molecular weight organic acids and methanol to produce methane. In oxygenated water, organic debris is oxidized relatively rapidly and extensively, so that little is preserved. In water lacking oxygen, on the other hand, organic debris is more likely to be preserved.

The debris deposited in sediments also is subject to microbial attack, leading to further degradation. Further breakdown of organic material likewise is enhanced in oxic environments by bioturbation which facilitates the diffusion of oxidants through the sediment, and by the presence of animal scavengers on or within the sediment. If sedimentation rates are identical in oxic and anoxic environments, the

bioturbation that occurs under oxic water prolongs by hundreds of years the exposure of organic matter by oxidation, which strongly reduces its preservation and accumulation.

However, in highly productive systems, or in systems with estuarine type circulation patterns or stagnant bottom water, anoxic conditions may develop in bottom waters and hence prevent or retard the oxidation of detrital carbon. Such anoxic systems probably play an important role in the formation of oil. The widespread nature of oil deposits has suggested that significant amounts of oil may have been formed from organics that accumulated at the bottom of normally oxidizing systems during sedimentation[4]. Such organics would necessarily have been rather refractory in nature. Since oxygen level in sediment generally drops to zero below a depth of no more than a few centimetres, any organics that are preserved sufficiently long to be buried below a few centimetres of sediment would be efficiently removed from the possibility of aerobic oxidation. Thus, the first step in the formation of oil presumably requires one or more

of the following conditions[5].

(a) The existence of anoxic bottom waters.

(b) The production of refractory carbon compounds.

(c) Rapid sedimentation.

1.1.1 METAMORPHOSIS

The organic carbon buried in the sediment is ultimately incorporated into sedimentary rocks such as shales, sandstones, and carbonate rocks. The organic carbon content of recently formed sedimentary rocks is on the order of no more than 0.1-10% of the rock[4]. The trapped organic carbon in these rocks is apparently the source of the world's petroleum reserves. There is a slow transformation of the carbon under conditions of elevated temperature (probably 100-150°C) and pressure found deep underground and perhaps through the mediation of catalysts such as aluminosilicate minerals. It has been suggested by Disalvo et.al.[4] that Humic acids, which are among the principal forms of organic carbon in sedimentary rocks, are probably the principal source of carbon for petroleum.

However, the presence of nitrogen and sulphur in virtually all crude oils indicates that other types of organic substances are also involved. The sequence of transformation that convert sedimentary organic detritus into petroleum is a continuous process and undoubtedly highly complex. By correlation of the composition of crude oil with the age, it is possible to get some idea of the sequence of transformations that organic compounds undergo while buried in sedimentary rocks. In general there is a tendency for the higher molecular weight compounds to be broken down with time, leading to the formation of paraffins and ultimately to the production of methane and perhaps graphite as end products of the transformation. Thus, oil can be viewed as an intermediate stage in the breakdown of organic detritus under reducing (anaerobic) conditions and under the influence of physical and chemical conditions (e.g. temperature, pressure, presence of catalysts) peculiar to deeply buried sedimentary rocks..

In the geosphere, all deposited biomass undergo transformation in the first few hundred metres of

burial leading the conversion of the unstable bio-polymers to nitrogeneous and Humic complexes which constitute the insoluble Kerogen (Kerogen is the organic matter of rocks that is insoluble in organic solvents, non-oxidising mineral acids and bases, which also yields one or more hydrocarbons on heating). A small amount of soluble organic matter, bitumen, which might be compositionally similar to crude oil, and sometimes referred to as protopetroleum is also formed.

Organic matter (Kerogen) in sediments occurs in many different forms, but can be classified into four main types(6).

Liptinite Kerogen: have high hydrogen but low oxygen content due to the presence of aliphatic carbon chains. They are considered to have been derived mainly from algae material (often bacterially degraded). They have high potential for petroleum.

Exinite Kerogen: contain a high hydrogen content (but lower than liptinites), with aliphatic chains and some saturated naphthene and aromatic rings and oxygen containing functional groups. This organic

matter is derived from membraneous plant materials such as spores, pollen, cuticle and other structured portion of plants. Exinites have a good potential for oil, can generate condensate and have a good potential for gas at higher maturation levels.

Vitrinite Kerogen: have a low hydrogen content, high oxygen content and consist mainly of aromatic structure with short aliphatic chains connected by oxygen containing functional groups. They are mostly derived from structured woody (ligno cellulose) materials and have a limited potential for oil, but a high potential for gas.

Inertinites Kerogen: are the black opaque debris (high carbon, low hydrogen) that are derived from highly altered woody precursors. They have no potential for oil or gas.

The main factors for recognition of a hydrocarbon source rock are its content of Kerogen, its type of organic matter and stage of organic maturation. Good source rocks ideally require about 2-4 per cent organic matter content of a suitable type to generate and release their hydrocarbons. Under

favourable geochemical conditions, oil can be generated from sediments containing liptinite and exinite organic matter. Gas is usually generated from vitrinite-rich source rocks or by thermal cracking of previously generated oil.

1.1.2 MIGRATION

The oil is formed over a much larger area and ultimately migrated to a localized deposit. The liquid petroleum once formed, could move upward through porous crustal materials until trapped by an impervious overlying substratum. Oil deposits are often overlaid by a pocket of gas (less dense than the oil) and invariably underlain by a reservoir of water (more dense than the oil). The existence of these two fluid in association with an oil deposit simply reflects the tendency of fluid substances to migrate upward through porous rocks until an impervious substratum is encountered. The migration and pooling of oil has been essential for its storage over millions of years and hence for its abundance today.

The most important characteristic of oil is the energy that can be derived from burning (oxidizing) it. This energy was of course originally fixed via photosynthesis millions of years ago and has been stored in the chemical bonds of the organic substances of which oil is composed. The anaerobic transformations that lead to the formation of oil release some of the original stored energy, but a sufficient amount remains in the chemical bonds of petroleum to provide a highly useful energy source.

The different reactions involved in the conversion of organic materials into fossil fuels have been discussed by R. Paul Philip[3] (Fig. 1). At temperatures below 50°C, many of the reactions are chemical (such as condensation) or biochemical and are referred to as "diagenesis". As depth of burial increases and temperatures rise into the 50 to 200°C range, thermal alteration (maturation reactions) known as "Catagenesis" occurs. Ultimately, at temperatures above 200°C "metagenesis" of the organic matter takes place, converting any residual organic material, liquid or solid, into methane and graphite.

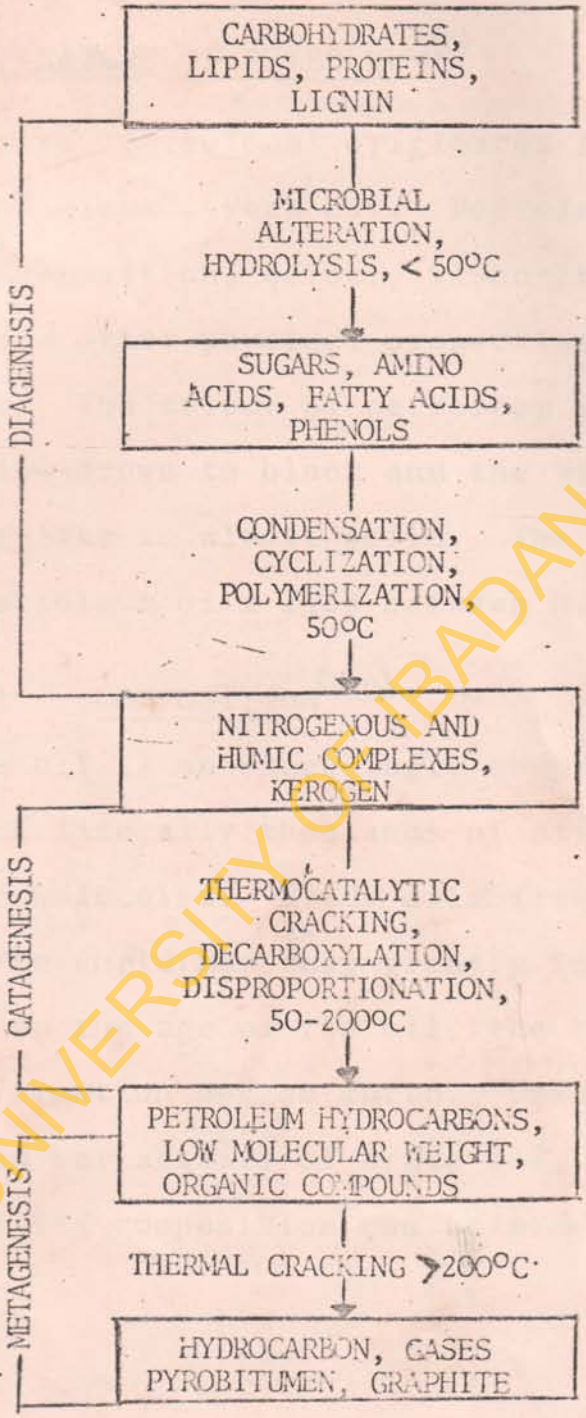


Fig. I: Scheme Showing Transformation of Organic Material to Fossil Fuels by Reactions at Varying Temperatures[5]

1.2 THE NATURE OF PETROLEUM[6]

The word 'petroleum' originates from the Latin word "petra oleum", rock oil. Petroleum varies in chemical composition, colour, viscosity, specific gravity, and other physical properties depending on the source. The colour of petroleum varies from light yellow-brown to black and the viscosity varies from water-like to almost solid. The specific gravity of most petroleum oils lies between 0.735 and 0.950.

1.2.1 COMPOSITION[7-9]

Crude oil is an exceedingly complex mixture, composed of literally thousands of different kinds of organic molecules. Crude oils from different parts of the world may vary greatly in composition, depending on the age of the oil, the conditions of its transformation and so forth. Despite the complexing and variability of crude oil, some generalisation about its composition can be made.

1.2.1.1 HYDROCARBONS

Crude oil consists primarily of hydrocarbons. Some crude oils contain as much as 98% hydrocarbon by composition[10]. In addition to hydrocarbons, the organic substances in crude oil include compounds containing sulphur, nitrogen and/or oxygen, with sulphur being more abundant than nitrogen and nitrogen greater than oxygen. In addition, there are small concentrations of metals such as nickel, vanadium, iron, aluminium, sodium, copper and uranium[11-12].

Crude oils can be roughly characterized according to the relative amounts of the major kinds of hydrocarbons they contain. The main classes of hydrocarbons found in crude oil are the straight-chain alkanes, the branched alkanes, the cycloalkanes, and the aromatics. Alkenes do not occur in crude oil. Combinations of straight or branched alkanes with either cycloalkanes or aromatic and of cycloalkanes and aromatics are numerous. Figure 2 shows the basic hydrocarbon structures found in petroleum. For a given carbon number the straight-chain alkane or n-paraffin is the most

abundant species found. Branched alkanes or iso-paraffins occur in decreasing quantities as the number of branches increases and as the branch point becomes further removed from the terminal end. The cycloparaffins or naphthenes usually contain a cyclo-pentane or cyclohexane ring. Bicyclic and polycyclic naphthenes are also found. The aromatic portion of petroleum is usually less than the paraffinic portion as shown by Koons[13] for an "average" crude oil (Table 1). Aromatics occurs as single or multiple ring compounds with various alkyl substituents. Aromatics also occur in compounds such as tetralin where one ring is aromatic and the other ring is a cycloparaffin.

The aliphatic hydrocarbons consist of the fully saturated normal and iso (or branched) alkanes of the general molecular formula (C_nH_{2n+2}) with n ranging from 1 to usually around 40 although compounds with $n > 60$ carbons have been reported by Posthuma[12]. Above C_{13} the most important group of isoalkanes are the isoprenoid hydrocarbons (Pristane, Fig. 2) consisting of isoprene building blocks. Pristane (C_{19})

TABLE 1: THE "AVERAGE" COMPOSITION OF CRUDE OIL[13]

	Average Crude (%)
By Molecular Size	
Gasoline (C_5-C_{10})	30
Kerosene (C_{10}-C_{12})	10
Light distillate oil (C_{12}-C_{20})	15
Heavy distillate oil (C_{20}-C_{40})	25
Extremely heavy residuum oil	20
By Molecular Type	
Saturated hydrocarbons (normal and branched alkanes)	30
Naphthene hydrocarbons (cycloalkanes)	50
Aromatic hydrocarbons	15
Polar (NSO) compounds	5

and phytane (C_{20}) are usually the most abundant isoprenoids, while the C_{10} to C_{20} isoprenoids are often major petroleum constituents, extended series of isoprenoids (C_{20}-C_{40}) have been reported [14].

The saturated hydrocarbon class includes the aliphatic saturated hydrocarbons and the alicyclic alkanes consisting of compounds in which all or some of the carbon atoms are arranged in a ring. The vast majority of saturated ring structures, also called cycloalkanes or naphthenes, consist of important minor constituents which like the isoprenoids have specific animal or plant precursors [12] (e.g. steranes, diterpanes, and triterpanes (Fig. 2) and which serve as important molecular markers in post oil spill and geochemical studies [15,16].

Aromatic hydrocarbons are usually less abundant than the saturated hydrocarbons, contain one or more aromatic (benzene) rings connected as fused rings (e.g. naphthalene) or linked rings (e.g. biphenyl). Petroleum contains many homologous series of aromatic

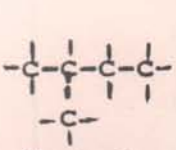
hydrocarbons consisting of unsubstituted or parent aromatic structures (e.g. Phenanthrene) and like structures with saturated side chains, which replace a hydrogen atom in the ring with up to 10 or more carbon atoms in methyl-type substituents. This higher degree of alkylation is most prevalent in two and three ringed aromatics although the higher polynuclear aromatic families (3 rings) do contain alkylated (1-3 carbons) side groups. The polycyclic aromatics with more than three rings consist mainly of pyrene, chrysene, benzanthracene, benzypyrene, benzofluorene, benzofluoranthene, and perylene structures. The naphthenoaromatic compounds consist of mixed structures of aromatic and saturated cyclic rings. This series increases in importance in the higher boiling fractions along with the saturated naphthenic series. The naphthenoaromatics appear related to resins, kerogen and sterols. The structures of some of the compounds described above are given in Figure 2 and Table 2.

n - ALKANES

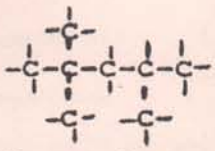
CH_4 $CH_3—CH_3$ $CH_3-(cH_2)_n-CH_3$

methane ethane n-alkane

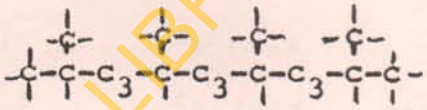
ISOALKANES (Hydrogen omitted)



Isobutane



Iso octane

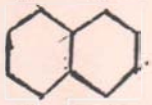


PRISTANE (ISOPRENOID)

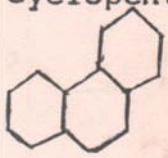
CYCLOALKANES (NAPHTHENES, side chains and hydrogen omitted)

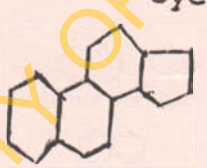
Cyclopentane

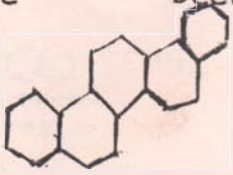
Cyclohexane



Decaline



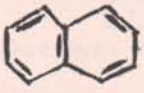




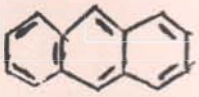
TRI, TETRA AND PENTACYCLIC NAPHTHENES

AROMATICS (including napththenoaromatics, hydrogen omitted)

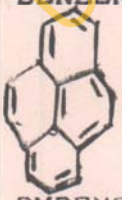
BENZENE



NAPHTHALENE



ANTHRACENE



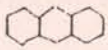
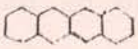
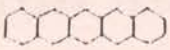
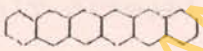
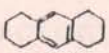
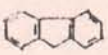
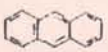
PYRENE

INDANE

FLUORENE

FIG. 2 : TYPES OF HYDROCARBONS FOUND IN PETROLEUM

Table · 2 : Hydrocarbon compound types[17]

Compound types	Typical structure	General formula
Paraffins	$CH_3 - R - CH_3$	C_nH_{2n+2}
Monocycloparaffins		C_nH_{2n}
Dicycloparaffins		C_nH_{2n-2}
Tricycloparaffins		C_nH_{2n-4}
Tetracycloparaffins		C_nH_{2n-6}
Pentacycloparaffins		C_nH_{2n-8}
Hexacycloparaffins		C_nH_{2n-10}
Naphthalenes	 tetrahydroacenaphthenes  dinaphthenebenzenes.  naphthalenes	C_nH_{2n-12}
Acenaphthenes	 acenaphthenes  tetrahydrophenathrenes	C_nH_{2n-14}
Fluorenes	  hexahydropyrenes	C_nH_{2n-16}
Phenanthrenes	  anthracenes	C_nH_{2n-18}

1.2.1.2 POLYNUCLEAR AROMATIC HYDROCARBONS (PAHS)

Polynuclear aromatic hydrocarbons (PAHS) can be defined as organic compounds containing two or more benzenic ring structures which may or may not have substituted groups attached to one or more rings. They have chemical properties intermediate between those of benzene, a highly aromatic compound and olefinic hydrocarbons.

They are formed during the high temperature pyrolysis of hydrocarbons but more recently strong evidence has indicated that polynuclear aromatic hydrocarbons may be produced by bacteria and green plants[18]. Polynuclear aromatic hydrocarbons (PAHS) formed during combustion processes are transported seaward via direct deposition on the seas surface or rainout over land followed by storm-water runoff. PAH compounds are, therefore, ubiquitous chemical components of marine systems throughout the world

Aromatic hydrocarbons from combustion sources are characterised by a lesser degree of alkylation than aromatic from petroleum. The degree of alkylation within a homologous series of aromatics (e.g. Phenanthrenes) in a given PAH assemblage is dependent on the temperature of formation of the PAH, high temperature processes (in complete combustion or pyrolysis) favour less alkylation; relatively low temperature processes (Petroleum maturation) favour higher degrees of alkylation.

Some polynuclear aromatic hydrocarbons commonly found in the marine environment are listed in Table 3 below.

TABLE 3

SOME POLYNUCLEAR AROMATIC HYDROCARBONS FOUND IN THE MARINE ENVIRONMENT

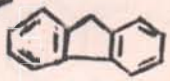
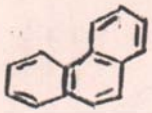
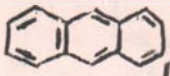
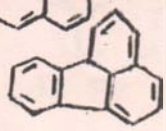
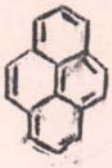
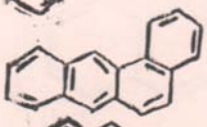
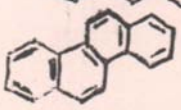
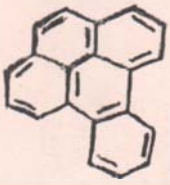
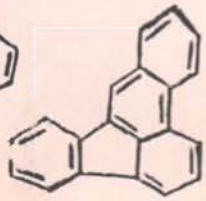
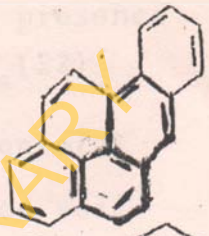
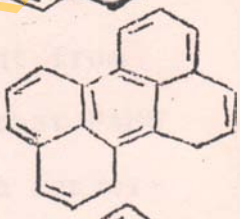
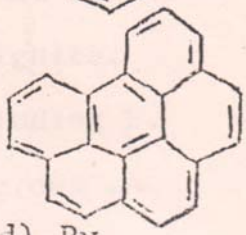
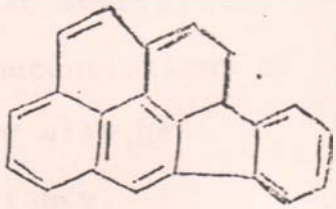
COMPOUND	ABBREVIATION	STRUCTURE
Naphthalene	Nph	
Acenaphthene	Ace	
Fluorene	Fl	
Phenanthrene	Phe	
Anthracene	An	
Fluoranthene	Ft	
Pyrene	Py	
Benz (a) Anthracene	B (a) A	
Chrysene	Chy	
Benzo (e) Pyrene	B (e) Py	
Benzo (b) Fluoranthene	B (b) Ft	

TABLE 3 (Contd.)

COMPOUND	ABBREVIATION	STRUCTURE
Benzo (a) Pyrene	B (a) Py	
Perylene	Per	
Benzo (ghi) Perylene	B (ghi) Per	
Indeno (1, 2, 3-cd) Pyrene	I (1, 2, 3-cd) Py	

Sources and Occurrence

Analysis of soil samples has shown the presence of several polynuclear aromatic hydrocarbons[22]. Blumer[24] had found concentrations of Benzo(a) Pyrene of between 40 and 1300 μgkg^{-1} in dried soil samples taken from forests and fields distant from major highways and industry. He suggested that PAHS might be formed by soil organisms, or in the conversion of soil organic matter to peat and lignite.

It has been shown that bacteria including E. coli synthesize benzo(a) pyrene when grown on solid culture media freed from PAH by prior benzene extraction and that algae can synthesize several polynuclear aromatic hydrocarbons[25]. Concentrations of individual PAH of about 100 μgkg^{-1} have also been found in dried plankton from Lake Constance.

Vegetables used for human consumption have been found to contain levels of Benzo(a) Pyrene of 10-20 μgkg^{-1} dry weight of sample[26] and concentrations of individual PAH of 5-100 μgkg^{-1} of dry material have been found in other plants, with strong evidence to suggest that such compounds were

the products of biochemical synthesis by the plants[18]. Graf and Diehl[26] showed that PAH were synthesized during germination and growth of rye, wheat and lentils. Later experiments showed that the rate of growth of a number of plants could be increased by feeding carcinogenic PAH and that the grain output of rye could be increased as much as threefold.

Groundwater samples have shown levels of 0.045-0.51 $\mu g l^{-1}$ for total PAH with the carcinogenic PAH accounting for between 0.001 and 0.081 ug/l[27]. Treated river water has been found to contain PAH from 0.025-0.234 $\mu g l^{-1}$, the carcinogenic compounds accounting for 0.007-0.054 $ug l^{-1}$ of the the total PAH[27] untreated river water may contain ten times higher levels of PAH than ground water and treated river water.

Mallet et.al.[28] have also investigated levels of Benzo(a) Pyrene in marine organisms and sediments. Some marine organisms are able to synthesize or concentrate polynuclear aromatic hydrocarbons[24-33].

Suess[34] has suggested that other sources of PAH in the marine environment include contamination of estuaries and coastal waters by shipping and harbour oil, industrial and municipal effluent, atmospheric fallout, precipitation and run-off.

Raw sewage from domestic sources can contain very significant levels of PAH but in general the longer the industrial contribution to the sewage, the higher the PAH concentrations of the polyaromatic hydrocarbons[35]. During a heavy storm, levels of PAH in a sewage works input may increase more than hundred-fold over a dry weather period (from 0.846 to 87.6 $\mu g l^{-1}$) and Borneff and Kunte[35] concluded that run-off from roadways may contribute substantially to levels of PAHs in sewage. Analysis of run-off from a motorway after a period of dry weather has also indicated levels of PAH comparable with those in domestic sewage.

Polynuclear aromatic hydrocarbons in road run-off can arise in a number of ways. Bituminous road surfaces and car tyre wear have been known to contribute polynuclear aromatic hydrocarbons to run-off[36].

In addition, polynuclear aromatic hydrocarbons emitted in vehicle exhausts are deposited upon the roads and nearby soil[37-38]. It is thus apparent that elevated levels of these hydrocarbons in the water cycle may result from road run-offs[35]. Other sources of PAH in domestic sewage include, washing of clothing, infiltration from soil and washing-out from the atmosphere, as well as road run-off.

It is well established that PAHs are formed in high temperature pyrolysis systems[39]. It has been shown that carcinogenic tars, containing polynuclear aromatic hydrocarbons are formed as pyrolysis of aliphatic and aromatic hydrocarbons, cholesterol and yeast[40]. Effluents from such industrial plants as oil refineries, where catalytic cracking and reforming of crude oil take place, may contribute PAH to rivers and sewage systems. Industries involving plastic and dyestuffs manufacturing which use petroleum products, as well as those which use high temperature furnaces may also produce PAHs.

1.2.1.3 NON-HYDROCARBONS

The non-hydrocarbon petroleum constituents (Fig. 3) can be grouped into six classes according to Posthuma[12]:

(a) Sulphur compounds
(b) Nitrogen compounds
(c) Porphyrins
(d) Oxygen compounds
(e) Asphaltenes, and
(f) Trace metals.

Sulphur compounds comprise the most important group of non-hydrocarbon constituents. Most sulphur present is organically bound (e.g. heterocyclic) although elemental sulphur may be present in concentrations as high as 1%. The organosulphur compounds consist of thiols, disulphides, sulphides, and cyclic sulphide (e.g. thiacyclohexanes) and thiophenes. The benzothiophenes and dibenzothiophenes are important constituents of the higher molecular weight aromatic fractions of environmental samples with the tetramethyl dibenzothiophenes the highest molecular weight sulphur heterocyclics[41]

Nitrogen is present in all crude oils in two categories, basic and non-basic. The basic compounds consist of compounds such as pyridine, quinolines, benzoquinolines, and acridines while the acidic compounds are made up of pyrroles, indoles, carbazoles and benzcarbozoles.[42] The porphyrins are nitrogen containing compounds derived from chlorophyll and consisting of four linked pyrrole rings. Porphyrins occur as organo-metallic complexes of vanadium and nickel.

The oxygen content of crude oils (0-2%) is found primarily in distillation fractions above 400°C. The oxygen compounds consist of phenols, carboxylic acids, ketones, esters, lactones, and ethers.

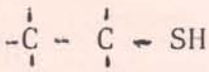
Petroleum contains a significant fraction (0-20%) of higher molecular weight material (1,000-10,000) consisting of both hydrocarbon and NSO compounds called asphaltenes. Those compounds consisting of 10-20 fused rings with aliphatic and naphthenic side chains contribute significantly to the properties of petroleum in geochemical formations and in spill situations as well (e.g. related to emulsification

behaviour).

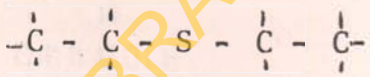
Vanadium and nickel are the most abundant metallic constituents of crude petroleum sometimes reaching thousands of parts per million but most often lower. They are present in porphyrin complexes and as free metals as well[42].

Table 4 below shows the elemental analysis of crude oil.

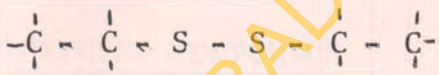
SULPHUR COMPOUNDS



Ethanethiol



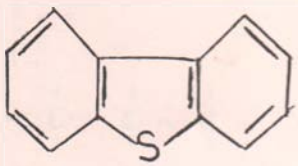
3-Thiapentane



3, 4 - Dithiahexane

Thiocyclohexane

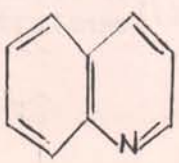
Thiophene



Dibenzothiophene

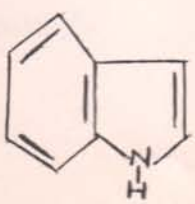
NITROGEN COMPOUNDS

Pyridine



Quinoline

Pyrrole

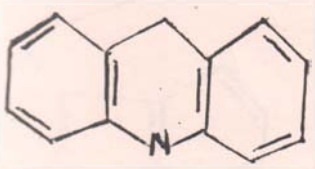


Indole

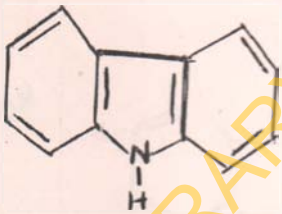
BASIC

NON-BASIC

FIG. 3: Some Basic Structures Of S,N,O Compounds In Petroleum.(12)

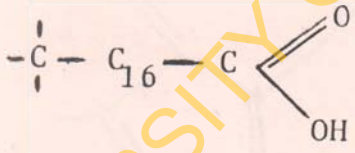


ACRIDINE

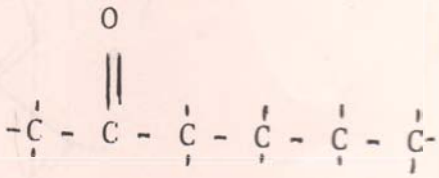


CARBAZOLE

OXYGEN COMPOUNDS

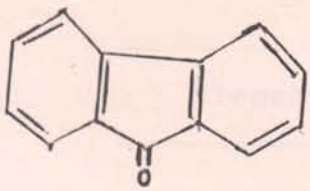


STEARIC ACID

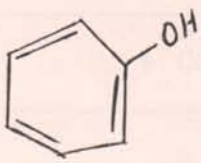


METHYL-n-BUTYL KETONE

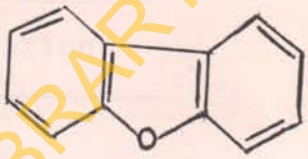
FIG. 3: Some Basic Structures Of S, N, O Compounds In Petroleum (12)



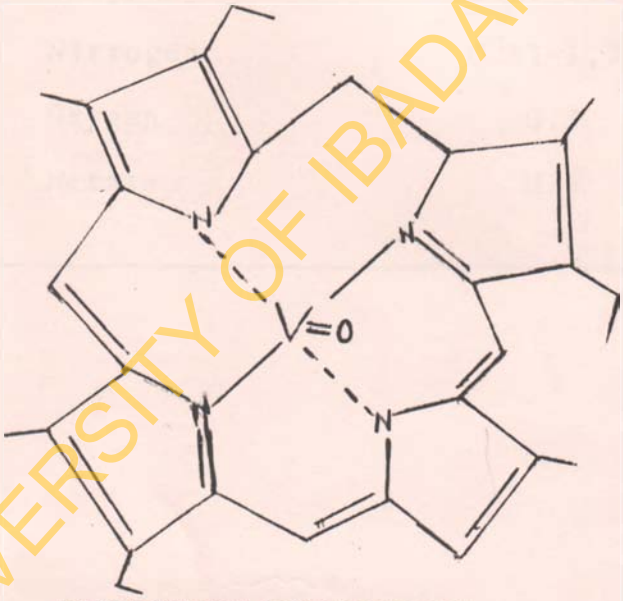
FLUORENONE



PHENOL



DIBENZOFURAN



ISOPRENOID HYDROCARBON

+ VANADYL PORPHYRIN (Biological Marker).

FIG. 3: Some Basic Structures Of S, N, O Compounds In Petroleum (12)

TABLE 4: ELEMENTAL ANALYSIS OF CRUDE OILS[9,43]

Elements	% Composition
Carbon	83.9-87.0
Hydrogen	11.4-14.0
Sulphur	0.06-8.0
Nitrogen	0.11-1.7
Oxygen	0.5
Metals	0.3

1.3 DISTINGUISHING FEATURES BETWEEN BIOGENIC AND ANTHROPOGENIC HYDROCARBONS

The geochemical processes responsible for the formation of crude oil lead to the production of an immense number of individual hydrocarbons, including isomers and members of different homologous series of hydrocarbons[44]. Also, a single molecule may contain straight or branched chain sub-units or saturated and aromatic rings. Each petroleum is an individual product whose composition reflects the chemistry of its source materials. In addition, it carries the indelible imprint of the geochemical subsurface processes that have led to its formation.

Marked compositional differences exist between hydrocarbons from living organisms on one hand and hydrocarbons derived from anthropogenic source on the other. Sometimes, hydrocarbons from one source can be detected in the presence of those from other sources[45]. The composition of hydrocarbons recovered from the sea is influenced by all the physical, chemical and biological processes to which the oil has been exposed during formation, production,

refining and weathering.

Hydrocarbons of biological origin may derive from terrestrial plants or marine flora and fauna. In higher plants, hydrocarbon generally occur as component of leaf-waxes and although their distribution is not the same in all higher plants, there is well-established and easily recognized finger print with the following characteristics[46-49]:

(a) The biogenic hydrocarbons are, in general, composed almost exclusively of straight chains with between 25 and 35 carbon atoms (branched chain or cyclic compound are usually present as minor components only).

(b) The odd-numbered hydrocarbons predominate over the even-numbered hydrocarbons defined mathematically by the carbon preference index (CPI)[50,51]. The CPI for n-alkanes may be defined briefly as

$$CPI = \frac{\sum \text{Odd numbered n-alkanes}}{\sum \text{Even numbered n-alkanes}}$$

over the same carbon-number range.

Example:

$$CPI\ C_{16-33} = \frac{1}{2}\left[\frac{\sum C_{17}^{31}}{\sum C_{16}^{30}} + \frac{\sum C_{17}^{31}}{\sum C_{18}^{32}}\right]$$

There is generally a decrease in the CPI as the age of the sediment increases.

(c) When higher plant alkanes are analysed by gas chromatography, there is often very little else showing above the baseline other than the n-alkanes.

Algae present a different hydrocarbon distribution from higher plants. Generally (but not always) macro-algae (benthic algae or seaweeds) contain principally the n-C_{15} or n-C_{17} alkanes and a wider range (n-C_{15}-n-C_{21}) of less-abundant mono- and poly-olefins. Blue/green algae contain isomeric methylheptadecanes and some n-C_{15}-n-C_{17} mono- and dienes whereas micro-algae (phytoplankton) often contain large amounts of the polyolefin, heneicosahexaene [52-54],

Another important distribution of the paraffinic hydrocarbons appears to be that found in Sphagnum mosses in which the predominant hydrocarbons are n-C_{21} and n-C_{23} alkanes. Zooplankton can apparently convert part of the chlorophyll molecule, phytol, to the saturated C_{19} isoprenoid hydrocarbon, which has frequently been found to occur in the marine environment.

In contrast to the simple distribution of hydrocarbons in biological systems noted above, those in petroleums are generally much more complex. Some of these differences are:

(a) Petroleum contains a much more complex mixture of hydrocarbons over wider boiling ranges than biogenic input.

(b) Crude oil contains no olefins.

(c) The ratio of odd to even carbon number alkanes in various boiling ranges expressed as either the odd-even preference (OEP)[55] or carbon preference index (CPI)[56] is near unity.

C_{16} n-alkane is rarely found in biolipids[57].

(d) Petroleum contains several homologous series of compounds - normal alkanes, branched alkanes, cycloalkanes, isoprenoid alkanes, including branched cyclohexanes, steranes, and triterpanes.

(e) Petroleum contains homologous series of alkylated aromatics (e.g. mono-, di-, tri-, tetramethyl benzenes; naphthalenes; fluorenes; dibenzothiophenes, phenanthrenes).

(f) Petroleum contains numerous naphthenic and naphtheno aromatic compounds.

(g) Petroleum contains numerous heterocyclic compounds containing S, N and O.

(h) Hydrocarbons of a petroleum origin should have little ^{14}C activity.

(i) Stable carbon isotope ratio are isotopically heavier than biogenic inputs.

(j) Recent study has confirmed the presence of both α- and β-hopanes. The 17(α) H -hopanes are characteristics of petroleum or recent diagenesis,

while the less stable 17(β) H -hopanes are biogenic in origin. The polyhydroxyhopane precursors shown in Fig. 4a have a 17(β) H 21(β) H stereochemistry[58].

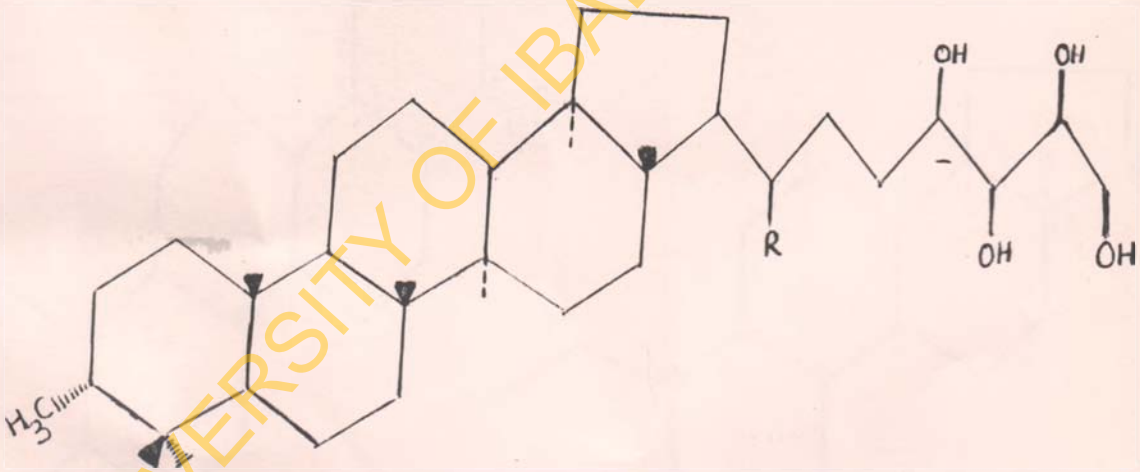


Fig. 4A: Polyhydroxyhopane.

and saturated hydrocarbons deriving from such precursors by low temperature diagenesis (as might occur in immature and unpolluted recent sediment) have also 17(β) H, 21(β) H or 17(α) H, 21(β) H stereochemistry, Figs. 4B and 4C, but have only one C_{22} isomer.

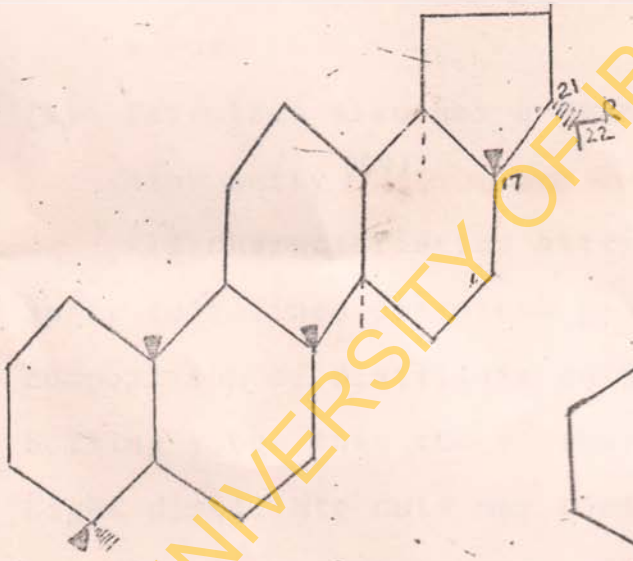


Fig. 4B: 17(β) H, 21(β) H

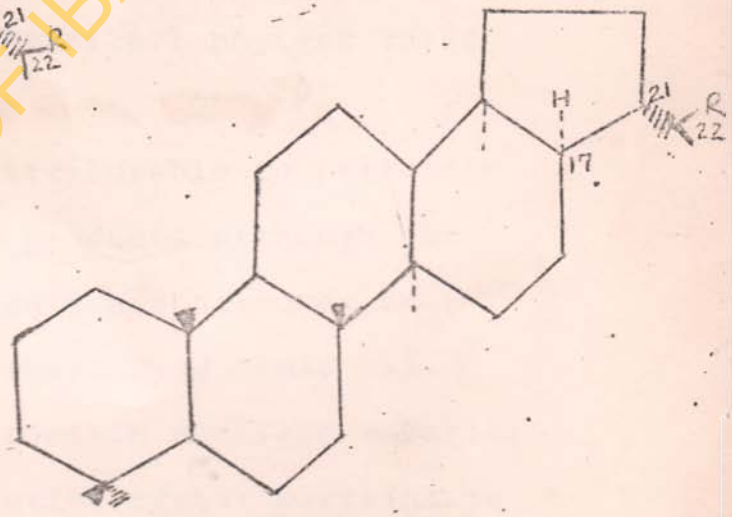


Fig. 4C: 17(α) H, 21(β) H

This would give only one gas chromatographic peak for each hopane homologue above C_{31}. In contrast, in oils, the hopanes from C_{31} to C_{35} show two gas chromatographic peaks. That is in members of the latter (mature) series with more than 30 carbon atoms, isomerisation has taken place at C_{22} to give a mixture of 22R and 22S isomers which appears as a recognisable fingerprint of doublets. However, in the former 17(β) H, 21(β) H series, only one stereoisomer occurs at position 22 so that doublets do not occur.

(k) Petroleum also has a Pristane: phytane ratio near unity (59).

All characteristics attributable to petroleum apply to refined petroleum products although the composition of distillate cuts are narrower in boiling range than the corresponding crude oil. Light distillate cuts may contain olefinic material.

One important interpretive caveat pertains to item C. Smooth distributions of alkanes (CPI or OEP = 1) within the crude oil non-volatile boiling

range have been reported for marine bacteria by Han and Calvin[60] and have been detected in marine fish by Boehm[61]. Thus paraffinic tar and biogenic alkanes may be very similar in the C_{20}-C_{30} range. Furthermore, smooth n-alkane distributions have been noted in urban air by Hanser and Pattison[62] and in laboratory dust samples by Gelpi et al.[63]. Thus, n-alkane distributions alone in environmental samples and especially in marine fish cannot be attributable to oil pollution without corroboration by other petroleum compositional features.

1.4 CONCEPT OF POLLUTION

Marine pollution has been defined by a group of experts on the Scientific Aspect of Marine Pollution (GESAMP) as "the introduction by man directly or indirectly, of substances or energy into the marine environment (including estuaries) resulting in such deleterious effects as harm to living resources, hazards to human health, hinderance to marine

activities including fishing, impairment of quality for use of sea water and reduction of amenities"[64].

It is not uncommon for all chemical wastes discharged to the water bodies to be regarded as pollutants. This, however, is a misconception since by international convention marine pollution is defined as stated above. If chemical wastes are discharged in such a manner that they do not give rise to any of these deleterious effects, they cannot be regarded as pollutants.

It must be recognised that any substance discharged to the marine environment will have at least some small effect but whether the effect is significant and deleterious is a matter of judgement which may depend on the use made of the receiving waters. In theory, it should be possible to use ecological techniques to assess the significance of any effects on marine life but in practice it is no simple matter to say whether they are deleterious since changes in the diversity and numbers of animals due to natural

causes are usually of much greater magnitude than those resulting from man's activities.

By comparison with ecological techniques, it is a comparatively simple matter to measure the concentration of constituents of effluents in water, sediments and marine organisms using chemical methods and quite often when constituents are detected they are automatically regarded as pollutants although there may be no evidence whatsoever of determining effects. It is only prudent to assume that these substances are pollutants, if, for example, similar levels have clearly been shown to be harmful during laboratory experiments[65].

The pollution results from physical, chemical and biological factors. Domestic sewage, complex solutions of organic chemicals, organic materials entering natural waters from terrestrial ecosystem constitute the pollutants and are influenced by physical factors e.g. currents, vertical mixing and temperature stratification. Chemical properties include biological nutrients and poisons, soluble chemicals, and insoluble precipitate while the

biological vectors are - oxygen used in metabolism and trophic concentration. These factors combine together to alter the marine environment and destabilize the marine ecology.

1.4.1 MARINE POLLUTION[66]

As human populations multiply and industrialization increases and diversifies, the problem of the pollution of the environment becomes more critical. Pollution problems mount as population move to the coasts seeking the amenities, and recreational opportunities of the sea shore, as well as the convenience and advantages to be found there for certain kinds of industry. With the growing use of sea lanes for commerce, the ever-increasing size and variety of cargo ships and tankers and the use of the bed for mineral extraction, the threat of pollution to the marine environment from deliberate or accidental release of noxious materials from ships and cargoes becomes more acute everyday. The sea is also polluted by fall-out from the atmosphere and large amounts of pollutants and wastes reach the oceans through the rivers and run-off from the land.

Water is the usual recipient of human pollution in our environment. It is commonly the vehicle of pollution, and all too often the hydrosphere is the final repository or sink of pollution. There are some good reasons why this is so. To put a pollutant into the atmosphere usually requires a great deal of energy viz: gasification, combustion, vaporization, or of very fine pulverization. However, to put a pollutant into the hydrosphere or lithosphere requires very little energy. A pollutant is toxic or at least inimical to the producer, thus pollution must be transported away from its point of origin. Pollutants are highly mobile in the atmosphere yet immobile in the lithosphere. Pollutants, such as solid wastes, deposited in the lithosphere, tend not to disperse and to accumulate eventually exhausting space in which to put them. However, pollutants dumped into the hydrosphere are also mobile and are readily transported away from the point of origin if they are soluble or dispersable, often to create a problem elsewhere. There is a pollution disposal dilemma in the process. We want to get rid of the

pollutant to mobilize it, to disperse it. Yet the greater the mobility, the greater the dispersal, the greater the area contaminated[67]. Now it appears that we may have entered into a new grim period in which global pollution of the hydrosphere of the world's oceans, has become a real threat. Lithospheric pollution alone tends to be local and contained, although leaching by ground waters, stream flooding, and so on, lithospheric pollution all too often can become hydrospheric pollution. Generally, the natural processes that remove pollutants from the hydrosphere, unlike the atmosphere are much slower than the rates of input, especially cultural stress. Thus, in addition to being the major vehicle for the transport of pollutants in our environment, the hydrosphere, notably the oceans, tends to become the sink or final repository where pollution accumulates.

1.4.2 THE FATE OF POLLUTANTS

Preston et.al.[68] and Widmark[69] have tried to compile a list and classify some of the more important pollutants that man dumps or leaks into

the oceans while Ketchum[70] has tried to represent diagramatically the major processes that determine the distribution and fate of pollutants in the marine environment.

Some of the organic pollutants both of natural and synthetic origins from Widmark et.al.[69] are shown in Tables 5(a) and 5(b). A sound knowledge of what becomes of the different pollutants being introduced into the aquatic environment is highly desirable for the understanding of their distribution and prediction of future pattern. For each pollutant, there are many possible patterns and interactions with the living and non-living components of the marine environment.

Ketchum[70] summarized the various processes that will affect the ultimate distribution of a pollutant as illustrated in Fig. 5. The favourable conditions for the disposal of waste, in the marine environment, are reflected through the dilution and dispersion of pollutants by turbulent mixing and ocean currents. Due to insufficient mixing, proper dilution of the waste fails to occur.

Pollutants may be concentrated by biological, chemical and physical processes. The concentration by biological processes may ultimately lead back to man as he uses the food resources of the sea. Bio-accumulation of chemical species occur with the marine organisms whereby they accumulate chemical species in amount far above their concentration in the sea water. It has been shown that the organisms are highly selective in this respect[71]. Some species of tunicates (species of fish) have been found to accumulate the trace element Vanadium and Niobium from sea water. Other species of tunicates concentrate neither element. Some species of oysters are enriched in zinc some sea weeds in ruthenium. 2,2-bis(P-chlorophenyl)-1,1,1-trichloroethane (DDT) is concentrated from sea water by the higher gilled organisms. The processes involved in this accumulation and specificity in the species are not well understood.

TABLE 5(A): ORGANIC POLLUTANTS OF NATURAL ORIGIN PARTLY CHANGED BY PROCESSING (TENTATIVE)[69]

Pollutants	Comments
Tannins	Waste from dye industry.
Lignin	Waste from paper and pulp mill industry.
Carbohydrates	Waste from paper and pulp mill industry, breweries, whisky industry and from sugar production. Oxygen consumption of local importance.
Proteins, included Peptides, Amino Acids, Amines, Fatty Acids, Lipids	Waste from slaughteries, dairies, and fish industry. Oxygen consumption of local importance.
Hydroxy Fatty Acids Humic Acids	Waste from the bark chipping of pine.
Pyrenthrines	Insecticides.
Terpenes	Floatation of ore.
Polycyclic Aromatic Hydrocarbons (PAH)	Found in marine organisms and sediments, and in areas with volcanic activity.

TABLE 5(B): ORGANIC POLLUTANTS OF SYNTHETIC ORIGIN (TENTATIVE)[69]

Pollutants	Comments
Alkylbenzen Sulphonates (ABS)	Detergent of the "hard" type, toxicity to marine organisms increasing with increasing branching. Not readily biodegradable.
Linear Alkyl Sulphonates (LAS)	Detergent of the "soft" type, less toxic to marine organisms than the former and more rapidly degraded by biological organisms.
Phenols	In waste from industry, coke and gas works, also found in natural sea water (1.3 µg/liter).
Polycyclic Aromatic Hydrocarbons	From oil refineries, heating, and so on.
Aniline and Related Compounds	From dye industries.

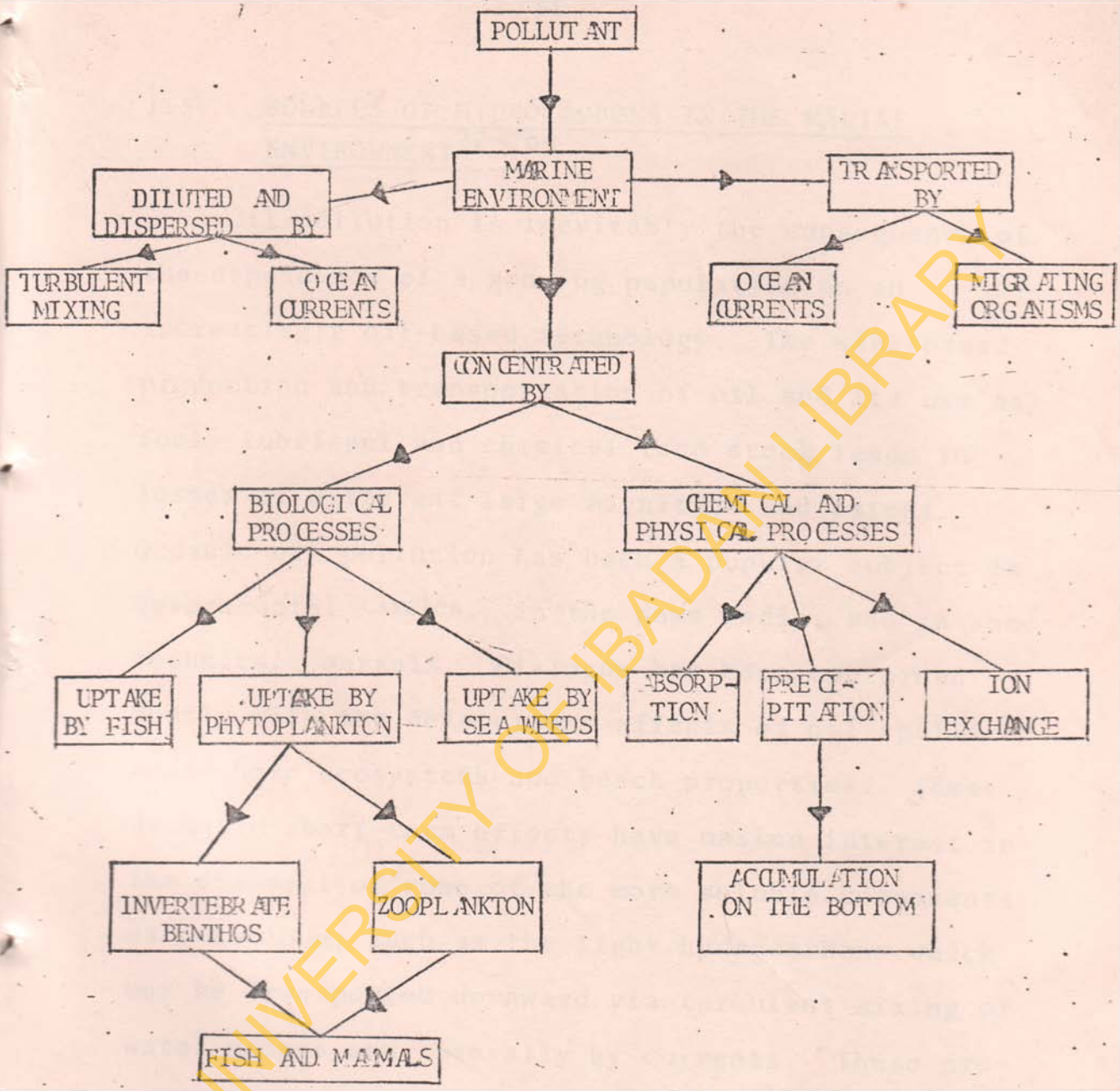


FIG. 5: The Various Processes Which Determine The Fate And Distribution Of A Pollutant Added To The Marine Environment (12)

1.5 SOURCES OF HYDROCARBONS IN THE MARINE ENVIRONMENT[72-76]

Oil pollution is inevitably the consequence of the dependence of a growing population on an increasingly oil-based technology. The widespread production and transportation of oil and its use as fuel, lubricant and chemical feed stock leads to losses of different large magnitude and extent. Oceanic oil pollution has been a popular subject in governmental circles,, in the news media, and in some technical journals. Dialogue has been concerned mostly with the deleterious effects of oil spills on near-shore ecosystems and beach properties. These dramatic short-term effects have masked interest in the disposal of some of the more soluble components of petroleum, such as the light hydrocarbons which may be transported downward via turbulent mixing of water masses and laterally by currents. These processes lead to unnaturally high light hydrocarbon concentrations over areas much larger than the visible extent of the spills.

Introduction of oil into the world's ocean through

major spills accounts for several million tons of hydrocarbons released annually. Sources of oil into the coastal waters include, tanker accidents, deballasting operations and tank washing as well as natural seepages and losses from off-shores production. Tank washing and accidents also release fuel oil and other refined products to the marine environment . Generally, hydrocarbon sources into the coastal and marine environment can be grouped under three main headings, namely;

(a) Biosynthesis;

(b) Geochemical and

(c) Anthropogenic inputs.

1.5.1 BIOSYNTHESIS

Petroleum is formed from biogenic matter deposited in ancient seas, lakes and lagoons from natural precursors in organic-rich sediments. Although it is clear that most of the actual compounds found in petroleum result from diagenetic activities within the source rocks, it is clear that living organisms are capable of biosynthesising a restricted range of

'natural' hydrocarbons, some of which are found in petroleum and some are characteristic of recent organic matter.

Both aquatic and terrestrial organisms synthesise hydrocarbons either de novo or by conversion from other compounds (such as phytol to pristane). Phytoplankton produces normal alkanes in the range n-$C_{15,17,19}$ and $_{21}$ with n-C_{17} usually dominant[77]. In the large brown algae (e.g. Laminaria) a single n-alkane, pentadecane (n-C_{15}) predominates to the virtual exclusion of all other n-alkanes. Land plants contribute a vast input of hydrocarbon matter to inshore waters. In such terrestrial plants the odd-numbered n-alkanes n-$C_{27,29,31,33}$ predominate, mainly in leaf waxes[46].

Apart from these odd carbon n-alkanes there are few other hydrocarbons produced in living organisms which are also found in petroleum. However, there are several hydrocarbons found only in such organisms, notably the unsaturated alkenes.

These hydrocarbons may be released during metabolism or upon the death and decomposition of the

organisms. Estimates of the rate of biosynthesis of hydrocarbons by marine primary productivity are generally given as 1-10 million metric tonnes per year

Recent studies also suggest the recent biogenic origin of certain cyclic alkanes. It appears that pentacyclic triterpanes of the hopane type such as the 17β (H)-hopanes are biogenic in origin and represent less stable forms of the 17α (H)-hopanes characteristic of petrogenic sources (from early diagenesis).

1.5.2 GEOCHEMICAL PROCESS

The geochemical processes responsible for the formation of crude oil lead to the production of an immense number of individual hydrocarbons, including many isomers and members of different homologous series. Each petroleum is an individual product whose composition reflects the chemistry of its source materials. In addition, it carries the indelible imprint of the geochemical subsurface processes that have led to its formation. For certain classes of

compounds, the compositional variability between crude oils is well known. Examples are the relative predominance of odd carbon number paraffins and of the C_{19}-isoprenoid pristane in young ('immature') but not in older oils and the progressive changes in the complexity of the multi-ring saturated and aromatic hydrocarbons with increasing thermal stress of the oil. Many structures formed by living organisms (four and five ring naphthenes, porphyrins, etc.) survive in crude oil. Their composition is strongly affected by the intensity of the chemical processes responsible for the formation of petroleum. Thus, the very small number of tetrapyrrole pigments may be coverted by geochemical processes into thousands of different fossil porphyrins whose structures are a unique reflection of the subsurface conditions.

Submarine and coastal land-seeps release petroleum hydrocarbons to the marine environment. The annual input rate is variously estimated at between less than 0.1 million metric tons[79] and 10 million metric tons[80]. A recent

review of this subject has arrived at an annual input rate of 0.6 million metric tonnes per year[11].

Weathering of soils and sediments; including the mobility of some of the hydrocarbons in these sediments to the marine environment also contribute to the oil input. However, the petroleum hydrocarbon contribution from weathering is small relative to other sources because of slow degradation of the hydrocarbons during the weathering process. No estimates of the annual rate of input from these sources are available.

There are chemical synthesis processes which are sources of hydrocarbons. Forest fires inject an estimated 6 million metric tonnes of hydrocarbons per year[11] into the atmosphere. An unknown portion is eventually delivered to marine environment. There are also chemical reactions occurring during the diagenesis of organic matter in sediments which yield hydrocarbons. Diagenetic hydrocarbon constituents include:

(a) Aliphatic hydrocarbons

(b) Cycloalkanes

(c) Sterenes

(d) Polycyclic aromatic hydrocarbons (PAH), and

(e) Pentacyclic triterpanes.

One of the most significant sets of diagenetic products are the PAH compounds including some compounds which are also found in petroleum and other hydrocarbon sources as well[81]. These diagenetic compounds may constitute important components of recent sediment hydrocarbon assemblages. Perylene and Retene are among those compounds formed in reducing sediment from higher plant precursors and which constitute major components of reducing sediment[82,83].

These hydrocarbons finally get to the marine environment either by submarine exposure of sediments or by diffusion out of the sediments.

1.5.3 ANTHROPOGENIC INPUT

The largest source of oil entering the ocean is from the land, either directly from effluent pipelines

from refineries or petrochemical plants or from other discharges into rivers. These may be waste oil put accidentially or deliberately into the water course or the discharge of oily effluent from factories of all types. Automobiles use in total a great deal of oil. Some are burnt but some are discharged as oil mist and some drip from the vehicle onto the road or car park. A great deal of used sump oil is also poured into drains or onto the ground by car owners doing their own maintenance. Oil from any of these sources is likely to arrive eventually in the sea. Even gaseous discharges can be washed from the air by rain onto the ground and finally join the general run-off into the sea. The amount from this source is highly speculative. A more generally accepted figure for the run-off from land is 1.4 million tonnes per annum.

Discharges directly into the sea from tankers and other ships can be divided into four main groups:

1. Operational discharges from tankers during tank washing;
2. Bilge discharges;

3. Spills caused by marine accidents, collisions, groundings, etc.
4. Spills during loading, discharging or bunkering.

Tank washing used to be the major cause of marine pollution from ships. If all the residual oil left in the tanks after normal discharge is washed out, about 0.3 per cent of the cargo will be so discharged. Improved methods of tank washing (load-on-top and crude oil washing) have been introduced, which have greatly reduced the total amount of oil discharged in this way. The increase in the price of crude oil has given an added incentive to reduce the loss of oil from tank washing.

All ships take in small amount of water which collect in the lower parts of the vessel or bilge. Oil fuel, used for firing boilers and oil used for lubricating can leak or be spilt and enter the engine room bilges which are periodically pumped out. Oil-water separators are now being used in most vessels to reduce the amount of oil escaping into the sea through this route.

Several authors like Porricelli and Keith[85] have reviewed the available statistics concerning losses due to tanker accidents, covering various periods and different ranges of ship size, and found the results to range from 0.05 to 0.25 million tonnes per annum. There are major variations in total spillage from year to year depending on the occurrence of major accidents. The most recent and complete study strongly suggests that the rate of spillage is at the upper end of the range.

The data on non-tanker accidents are scanty. There are about nine times as many non-tankers as tankers, but their average size is much smaller; also, the only oil normally carried in them in bulk is bunker fuel. Reported estimates for the annual rate of loss range from 0.02 million tonnes per annum to 0.25 million tonnes per annum (mta).

Figure 6 and Table 6 depict the amount of oil introduced into the marine environment from different sources. River run-off constitutes the major pathway

followed by tankers and bilges bunkering. Industrial wastes, municipal wastes and urban run-off contribute equally to petroleum hydrocarbon source into the marine environment. Fig. 7 depicts the pathways of petroleum hydrocarbons in the municipal environment.

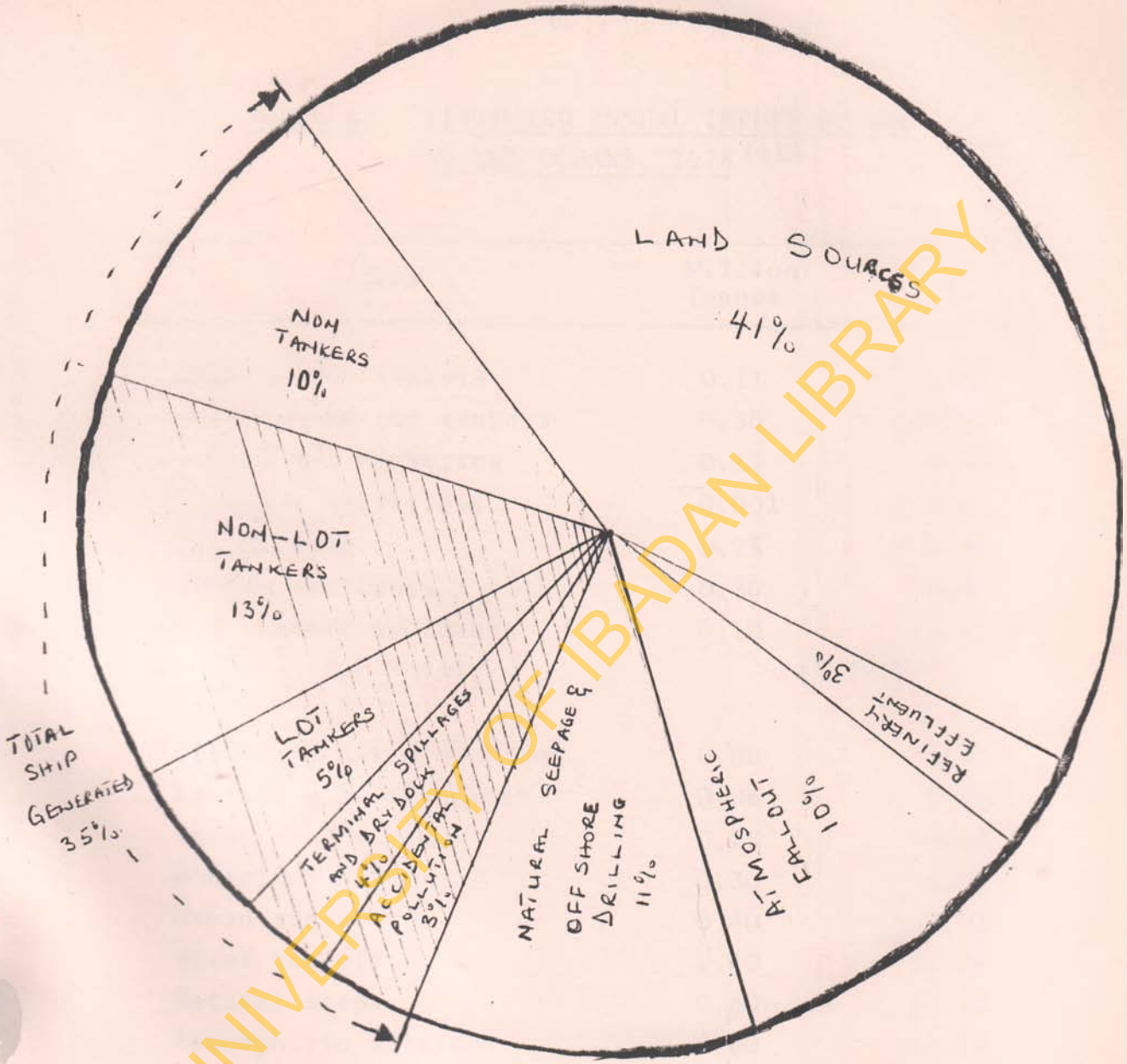


Fig. 6: Petroleum Hydrocarbons Introduced Into The Oceans.(31)

TABLE 6: ESTIMATED ANNUAL INPUTS OF OIL TO THE OCEANS, 1978 (11)

Source	Million Tonnes	%
Load-on-top tankers	0.11	2.22
Non-load-on-top tankers	0.50	10.10
Bilges and bunkering	0.12	2.42
Terminal operations	0.001	0.02
Dry docking	0.25	5.05
Tanker accidents	0.30	6.06
Non-tankers accidents	0.10	2.02
Sub-Total	(1.381)	
Off-shore oil production	0.06	1.21
Coastal oil refineries	0.06	1.21
Industrial waste	0.15	3.03
Municipal waste	0.30	6.06
Urban run-off	0.40	8.08
River run-off	1.40	28.28
Natural seeps	0.60	12.12
Atmospheric rain-out	0.60	12.12
Sub-Total	(3.57)	
Overall Total	4.951	

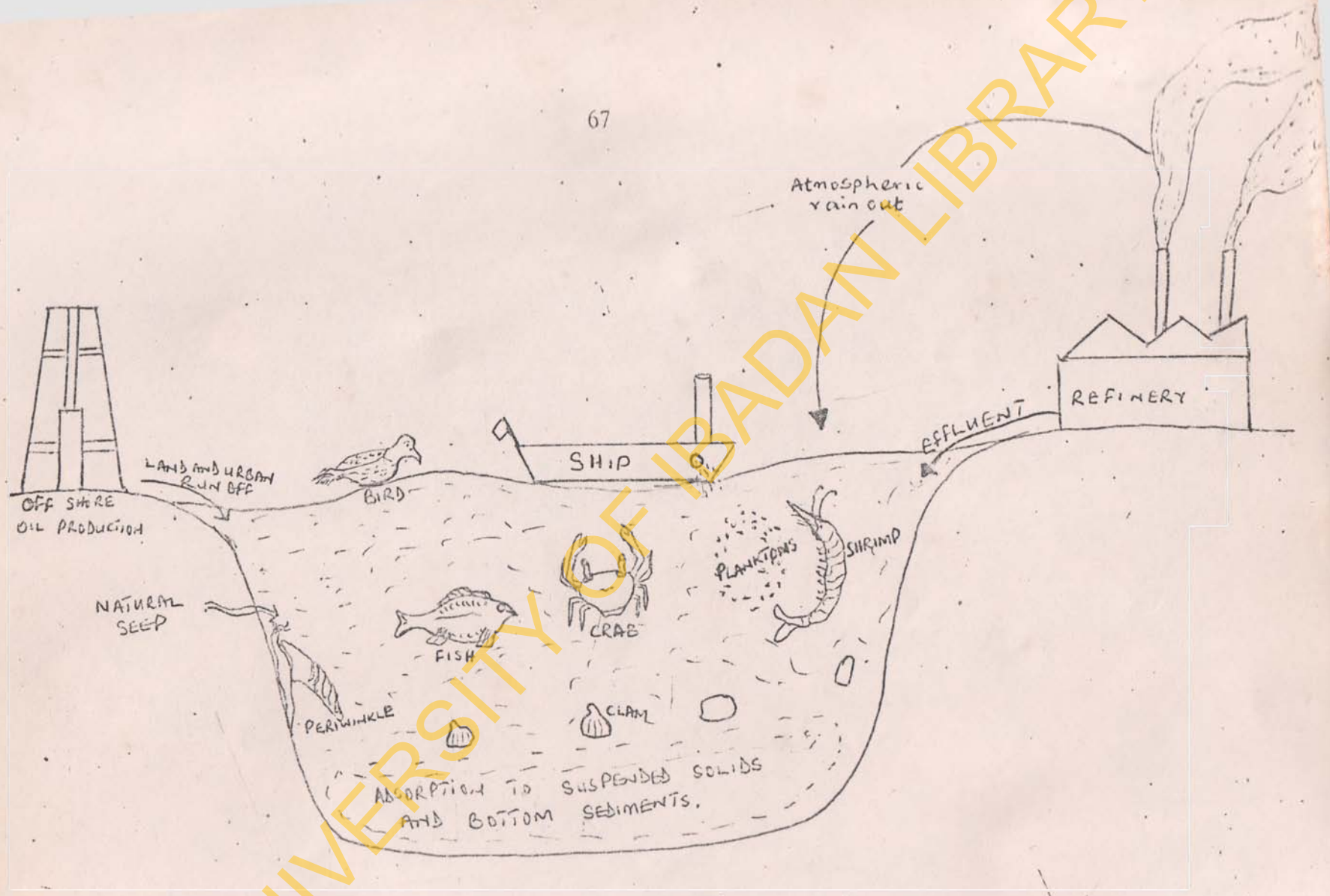


Fig. 7 : Pathways Of Petroleum Hydrocarbons In The Marine Environment.

1.6 AIR POLLUTION FROM THE USE OF PETROLEUM

1.6.1 INTRODUCTION

Air pollution can be defined as the additions to our atmosphere of any material(s) having a deleterious effect on life. Typical air pollutants include things such as carbon monoxide (CO), nitrous oxides (NOx), sulphur oxides (SOx), and various hydrocarbons and particulates. They can be one of two types:

1. A primary pollutant, or one lethal as it originates from the source; or
2. A secondary pollutant, one formed through the reaction of primary pollutants (this reaction can occur at the emission point, or at far removed localities).

Air pollution is generated by six major types of sources: (Table 7)

1. Transportation
2. Domestic heating
3. Electric power generating
4. Refuse burning
5. Forest and agricultural fires
6. Industrial fuel burning and process emissions.

TABLE 7: INDUSTRIAL SOURCES OF AIR POLLUTANT EMISSIONS[86]

	Type of Industry	Type of Emissions
1.	Petroleum refining	Particulates, sulphur oxides, hydrocarbons, CO.
2.	Smelters for Al, Cu, Pb, Zn	Particulates, sulphur oxides.
3.	Iron foundries	Particulates, CO.
4.	Kraft pulp and paper mills	Particulates, CO, sulphur oxides.
5.	Coal cleaning and refuse	Particulates, CO, sulphur oxides
6.	Coke (for steel manufacturing)	Particulates, CO, sulphur oxides.
7.	Iron and steel mills	Particulates, CO.
8.	Grain mills and grain handling	Particulates
9.	Cement manufacturing	Particulates.
10.	Phosphate fertilizer plants	Particulates, fluorides.

It is necessary to also examine the effects of these air pollutants on animals (including man), on plants, and or materials, as well as the meteorological effects.

1.6.2 EFFECTS ON MAN

Health Effects

Many of the common air pollutants can have very serious effects on human health. For example, CO is known to contribute to heart disease. Considering all sources of pollution, especially transportation, it is one of the major, if not the major, pollutants, and is also one of the most difficult to eliminate. It is formed during the combustion of carbon-containing compounds whenever there is a lack of oxygen (O_2):

$$2C + O_2 \longrightarrow 2CO \text{ (in limited } O_2\text{)}.$$

$$C + O_2 \longrightarrow CO_2 \text{ (in excess } O_2\text{)}.$$

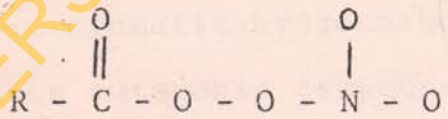
This substance affects the central nervous system even in very low concentrations, by forming carboxy-haemoglobin in the bloodstream, which interferes with the normal transport of oxygen to the body

cells[86]. Two per cent carboxyhaemoglobin is enough to generate observable effects, and can be formed by an 8-hour exposure to only 10 ppm CO. Oxygen transport is clearly affected at 5% carboxyhaemoglobin, generated at CO levels of 30 ppm or greater. Heavy automobile traffic can generate 50-140 ppm CO, and the smoking of cigarettes can create up to 15% carboxyhaemoglobin. In addition to the immediate effects of poor oxygen transport, high carboxyhaemoglobin levels tend to make a person retain cholesterol in the aorta. The sulphur oxides SO_2 and SO_3 are generated primarily in the combustion of high sulphur fuels. The sulphur oxides are toxic to the human body, especially disease such as emphysema. They can also accentuate viral pneumonia. The sulphur oxides usually can be detected by their odor, but prolonged exposure may desensitize a person to these compounds.

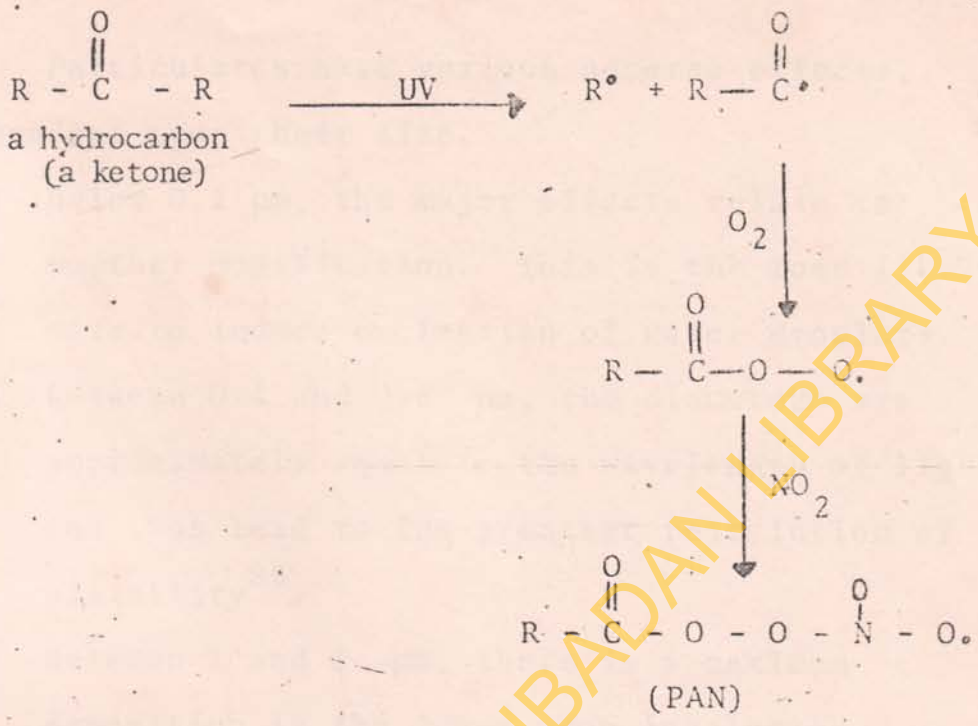
The oxides of nitrogen NO and NO_2 are usually found in much lower concentrations. They are generated only in high-temperature combustion situations, and hence have been referred to as an elitist pollutant,

only present in technologically advanced societies. Their ultimate effect on humans is not clearly understood, but they do act as irritants to breathing, and create discomfort to the eyes. NO_2 can also destroy the celia in the respiratory system and suppress alverolae macrophage activity, the lung's final defence against foreign matter.

Recent studies of various nitrogeneous air pollutants have indicated that these compounds may be more serious health hazard than one thought. In particular the peroxy nitrates are quite stable at lower air temperatures, and may be more important pollutants than Ozone. Peroxyacetylnitrate (PAN) is created by photochemical reactions involving hydrocarbons. PAN has a general structure of



where R stands for hydrocarbon chain of varying lengths (CH_3-CH_2-CH_2- ...). A typical formation mechanism would be as follows:



Some PAN are generated naturally, for coniferous vegetation is a major source of hydrocarbons and NO_2 is prevalent everywhere. NO can also react with some polycyclic aromatic hydrocarbons in laboratory tests to produce mutagenic compounds[87].

There are hundreds of hydrocarbons which form air pollutants. Many of them are possibly carcinogenic and might be at least partially responsible for the current increase in lung cancer.

Particulates have various adverse effects, dependent upon their size.

(1) Below 0.1 μm, the major effects relate to weather modification. This is the most likely size to induce nucleation of water droplets.

(2) Between 0.4 and 0.8 μm, the diameters are approximately equal to the wavelength of light, and thus lead to the greatest restriction of visibility[88].

(3) Between 1 and 5 μm, there is a maximum deposition in the lungs upon inhalation.

(4) Between 3 and 15 μm, the particulates are deposited in the upper respiratory system.

(5) Between 10 and 100 μm, the particulates create dust and dirt.

Those particulates which are inhaled are damaging to respiratory systems. In addition, they may be toxic. For example, mercury and other heavy metals lead to direct biochemical reactions. The particulates may end up deposited in the lungs, causing a build-up on the lung lining. This could result in a disease called silicosis. This build-up on the lungs reduces

the ability of the lungs to transfer oxygen into the blood. The normally elastic and spongy lung tissues harden, reducing the lung's breathing efficiency. In order to pump an adequate oxygen supply, the heart must then work harder. This leads to shortness of breath, possibly to an enlarged heart, and eventually to premature death.

In addition, particulates can sometimes cause excessive mucus secretion as a protective reflex. This excess mucus can restrict the bronchiole tubes and lead to bronchitis.

The worst condition for human health is from the combination of particulates with a high SO_2 concentration. A large percentage of the SO_2 in the atmosphere is due directly or indirectly to natural sources (volcanoes, decay vegetation, sea spray, etc.). The SO_2 generated naturally is, however, so dispersed over the world that it never builds up to dangerous levels. Man's SO_2 contribution - the "anthropogenic" SO_2 - tends to be concentrated in industrial and urban areas, and hence can rise to dangerous levels. The SO_2 in the air, often with particulates acting as

a catalyst, can be converted to SO_3:

$$2SO_2 + O_2 \xrightarrow{\text{Particulates}} 2SO_3 .$$

The particulate surfaces can provide a reaction site for the formation of SO_3 to occur. The SO_3 can readily react with water vapour to produce sulphuric acid (H_2SO_4). This acid can easily damage lung tissues.

In the atmosphere, some of the sulphuric acid droplets can react with ammonia (NH_3) to generate solid ammonium sulphate, $(NH_4)_2SO_4$. In 1948, Donora, Pennsylvania experienced large deaths because the concentration of acid sulphate salts (zinc ammonium sulphate and zinc sulphate) was high in the atmosphere around the area.

The H_2SO_4 in the air gets washed down whenever it rains, generating "acid rain". Acid rain has been linked not only to damaged trees and other plants, increased weathering and corrosion of materials and buildings, and water pollution problems, but also is possibly an added threat to human health[89]. Acid rain is also formed from NO emission, which can react

to form nitric acid (HNO_3) in the atmosphere. Recently, acid rain was declared as possibly "the most severe environmental problem of the century.

1.6.3 EFFECTS ON ANIMALS

The health effects of the various pollutants on animals are much the same as their effects on humans. In addition, insecticides may also be a major problem to animals. Frequently, their food sources become contaminated by one form or another of air pollutant. Many pesticides can be carried right through the food chain. For example, if a pesticide is sprayed over a large area, much of it ends in a lake or stream for consumption by fish. The fish can be eaten by certain types of birds, which can then be affected. Chlorine containing pesticides have, for instance, been related to thinner than normal eggshells in fish-consuming predatory birds. The thin eggshells lead to breakage before the eggs hatch, and hence to a loss of those offspring.

1.6.4 EFFECTS ON PLANTS

The major pollutants which affect plant life are the primary pollutants SO_2 and hydrogen fluoride (HF), and the secondary pollutants O_3 and PAN.

SO_2 can have either chronic or acute effects on plant life. An initial bleaching of plant cells and a stunting growth often leads to death.

PAN is very reactive toward the nitrogen in plant materials, probably disrupting the bond in protein molecule.

Particulates usually lead to photo-toxicity inhibition of respiration and/or photosynthesis.

1.6.5 METEOROLOGICAL EFFECTS

Air pollution can have a major effect on the climate, both regionally and globally. Regionally, rainfall can be drastically altered by the presence of air pollution.

The formation of rain in the air involves collection of moisture in the tiny droplets, using a particulate as the nucleus. These tiny droplets

initially collect and form clouds. If a sufficient concentration of moisture is present, the droplets can attract more water vapour to themselves and grow in size and eventually form rain. The presence of the particulate thus catalyzes the initial moisture condensation and droplet formation.

Because of this behaviour, air pollution can also have the opposite influence on precipitation. Too many particulates can encourage the formation of too many small, nuclear particles compared to the available moisture. Each particle cannot attract enough water vapour to itself, so, it cannot grow enough to form rain droplets. The net effect is a decrease in precipitation.

1.7 THE PHYSICAL, CHEMICAL AND BIOLOGICAL FATE OF OIL IN THE MARINE ENVIRONMENT

There have been several extensive reviews of the fate of oil in the marine environment. The major processes which act on crude oil or oil products spilled on water are essentially four different modes of degradation[90-92].

(1) Evaporation

(2) Dissolution

(3) Microbial degradation and

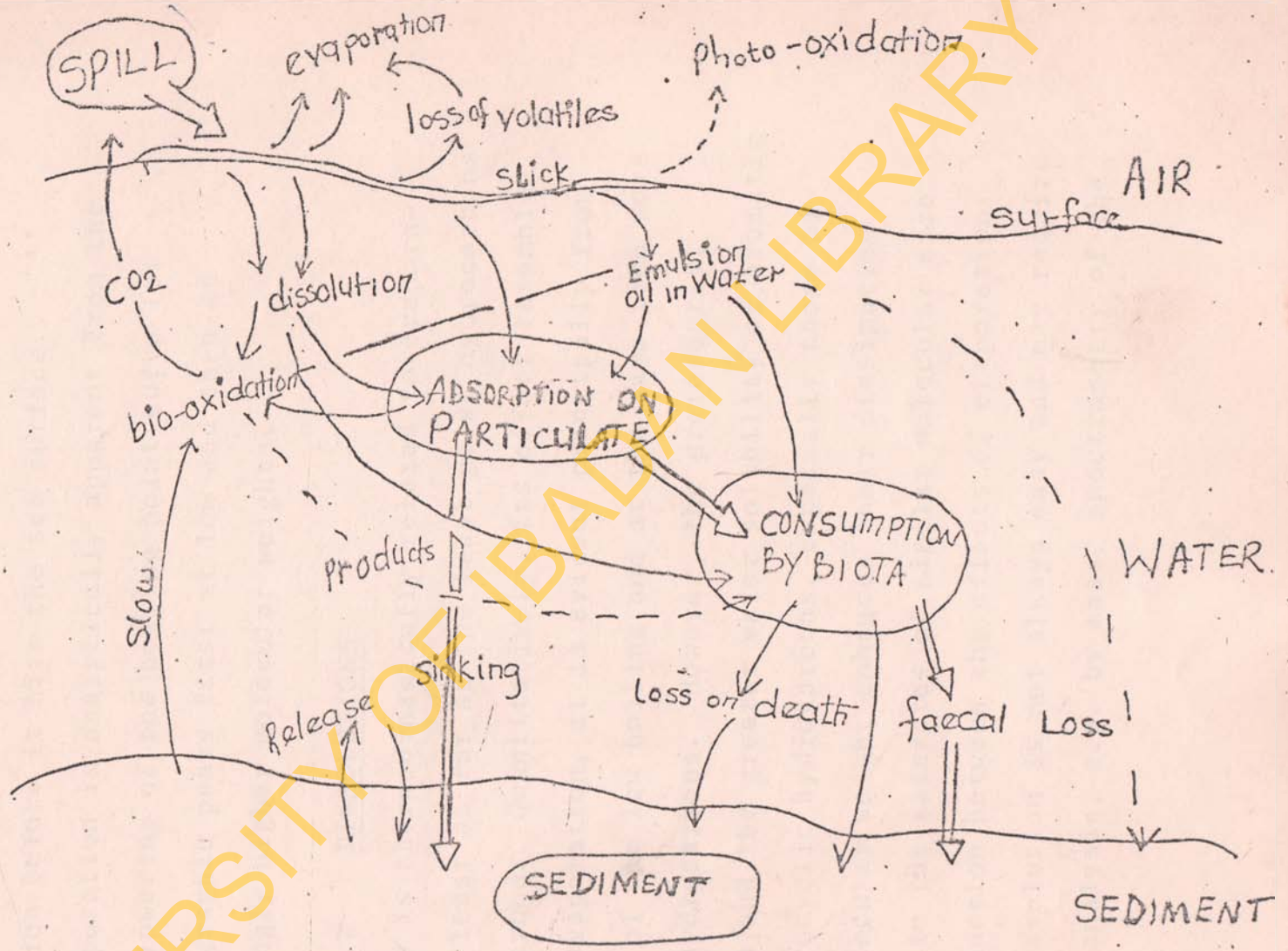
(4) Chemical degradation.

When petroleum spills on the ocean, it immediately begins to disperse. The rate of dispersal depends on a variety of environmental factors such as the speed of the wind, size of the waves, temperature, salinity, water depth, and currents and on the nature of the oil, its specific gravity, degree of refinement, and the quantity involved[93]. Theoretically, the oil will spread until it is a mono-molecular layer, but this tendency is counteracted by viscosity and other forces. According to Blokker[94], the thickness of a uniform oil slick decreases exponentially with time. The viscosity, density, chemical composition, pour point of the oil, the wind speed and current will influence the rate of spread. Emulsification reduces the tendency of the oil to spread[95].

1.7.1 EVAPORATION

When oil is released on to the ocean surface (e.g. as a slick) it spreads quickly. There is a selective depletion of the lower boiling components of an oil, but this leads to little or no fractionation among hydrocarbons of the same volatility that belong to different structural series. Most unweathered crude oils have a smooth boiling point distribution over a rather wide range, due to the non-selective, random nature of the geochemical processes that are involved in petroleum formation. There is a logarithmic dependence of the boiling point on the molecular volume. Evaporative losses decrease rapidly for higher members of homologous series[8].

Evaporation removes the most volatile materials first, and then progressively the higher-boiling compounds. Low-molecular-weight compounds such as monoaromatics are lost. Since those volatile compounds include the more toxic hydrocarbons, the longer the dispersion period, the lower the residual toxicity of the oil (Fig. 8).



G. 8: FATE OF OIL IN THE MARINE ENVIRONMENT

OURCE:- JOHNSTON C.S[76]

In the case of a blow-out, the oil is hot and much often than 30-50% is lost by immediate evaporation before it hits the sea surface.

Evaporation is analytically apparent from the gradual lowering of the boiling point curve (or chromatographic peaks first at low and then at increasingly higher molecular weights.

1.7.2 DISSOLUTIONS

This is thermodynamically related to evaporation, at least as far as the least polar hydrocarbons are concerned. Quantitatively, its effect resembles that of evaporation, it is evident principally from the loss of the low boiling and at the same time more soluble hydrocarbons. However, the preferential solvation and the greater water solubility of aromatic and heterocyclic hydrocarbons, especially those of lower molecular weight enhances their dissipation relative to the saturates of similar molecular size. The distinction between the effects of evaporation and of dissolution is not always easy and may require detailed analysis, e.g. by mass spectrometry of the

aromatic fraction.

Again, it is the lower-molecular-weight hydrocarbons which are the most soluble in water. Also, degradation products of the larger molecules can be more polar and thence have greater solubility. Thus again, the more toxic compounds tend to be dispersed preferentially, which means that in an area of good dispersion, there is a rapid decrease in risk to marine life.

Rates of dissolution for the various components of a petroleum slick depend on rather complex interactions between properties inherent to the oil (that is, molecular structure of compounds and relative abundance of these components) and the physio-chemical properties of the immediate environment (that is, salinity, temperature, etc.). Not only does this complex interaction of compositional and environmental factors exist for rates of evaporation, the overall rate of slick disappearance depends on interactions between evaporation and dissolution processes(96).

Many studies have provided data to define

solubility as a function of molecular structure, principal determinants of solubility for any particular petroleum hydrocarbon include the molecular volume (expressed as cm^3/mole) and the presence of "active" groups (e.g. aromatic rings or olefinic bonds). Solubility is generally inversely proportional to molar volume, which is a linear function of carbon number. Roughly, the solubility decreases by a factor of three per carbon number, but linearity of this relation falls off for n-alkanes above $n\text{-}C_{10}$[97-100].

Branched alkanes demonstrate greater solubilities for a given carbon number than their straight-chain counterparts, and this seems to be due to increased vapour pressure relative to corresponding compounds, as opposed to a structural function.

Ring formation also enhances solubility for a given carbon number or molar volume. The degree of saturation is inversely proportional to solubility for both chain and ring structures. The addition of a second or third double bond increases solubility proportionately, and it has been shown that the

presence of a triple bond increases solubility to a greater proportion than presence of two double bonds. Therefore, the most water-soluble petroleum hydrocarbons will be those with the lowest molar volume and greatest aromatic/olefinic character.

An inverse relationship exists between salinity and hydrocarbon solubilities for both aliphatic and aromatic components, with an approximate decrease of 30% for n-paraffins between fresh and seawater[101]. Table 8 lists the solubilities for some aliphatic and aromatic petroleum hydrocarbons in distilled water and sea water ($35^{o}/_{oo} \pm 0.5$) at $25^{o}C$. For the paraffins, the magnitude of this "salting-out" effect is directly proportional to the molar volumes in accordance with the McDevit-Long theory[102], which attributes "salting in" or "salting out" to the effect of electrolytes upon water structure.

Dissolved organic matter in the marine environment enhances solubility, due to its surface-active nature[103]. One study, utilizing natural marine water and NaCl solutions, examined the effect on various hydrocarbon solubilities due to removal of the

TABLE 8: SOLUBILITIES OF ALIPHATIC AND AROMATIC PETROLEUM HYDROCARBONS IN SEAWATER AND DISTILLED WATER AT 25 °C(102)

Compound	Solubility in Distilled Water	Solubility in Sea Water
Dodecane (C_{12})	3.7 ppb	2.9 ppb
Tetradecane (C_{14})	2.2 ppb	1.7 ppb
Hexadecane (C_{16})	0.9 ppb	0.4 ppb
Octadecane (C_{18})	2.1 ppb	0.8 ppb
Eiocosane (c_{20})	1.9 ppb	0.8 ppb
Hexacosane (C_{26})	1.7 ppb	0.1 ppb
Toluene	534.8±4.9 (ppm)	379.3±2.8 (ppm)
Ethylbenzene	161.2±0.9 ppm	111.0±1.3 ppm
O-xylene	170.5±2.5 ppm	129.6±1.8 ppm
M-xylene	146.0±1.6 ppm	106.0±0.6 ppm
P-xylene	156.0±1.6 ppm	110.9±0.9 ppm
Isopropylbenzene	65.3±0.8 ppm	42.5±0.2 ppm
1,2.4-Trimethyl-benzene	59.0±0.8 ppm	39.6±0.5 ppm
1,2,3-Trimethyl-benzene	75.2±0.6 ppm	48.6±0.5 ppm
1,3,5-Trimethyl-benzene	48.2±0.3 ppm	31.3±0.2 ppm
n-Butylbenzene	11.8±0.1 ppm	7.09±0.0 ppm
s-Butylbenzene	17.6±0.2 ppm	11.9±0.2 ppm
t-Butylbenzene	29.5±0.3 ppm	21.2±0.3 ppm

dissolved organic matter. A 50 to 99% decrease in the amounts solubilized was observed for n-alkanes and isoprenoids, with the decreases being directly proportional to the amount of dissolved organic matter removed (e.g. by activated charcoal and UV oxidation). However, the aromatics examined (anthracene, phananthrene, and dibutylphthalate) were unaffected by this process.

1.7.3 MICROBIAL (BIOCHEMICAL) DEGRADATION

Microbial degradation of crude oil appears to be the natural process by which the bulk of the polluting oil is eliminated[104]. Under anaerobic conditions, oil is preserved, whereas in the presence of oxygen, microbial degradation takes place. The first step of microbial degradation is to convert the hydrocarbon molecule to a fatty acid. This results in the so-called chocolate mousse (Fig. 9) and a colloidal effect that acts to further the rate of microbial degradation and disperse the oil in the sea. In areas that are well aerated and where the microbial population is adapted to oil influx, the rate of oil

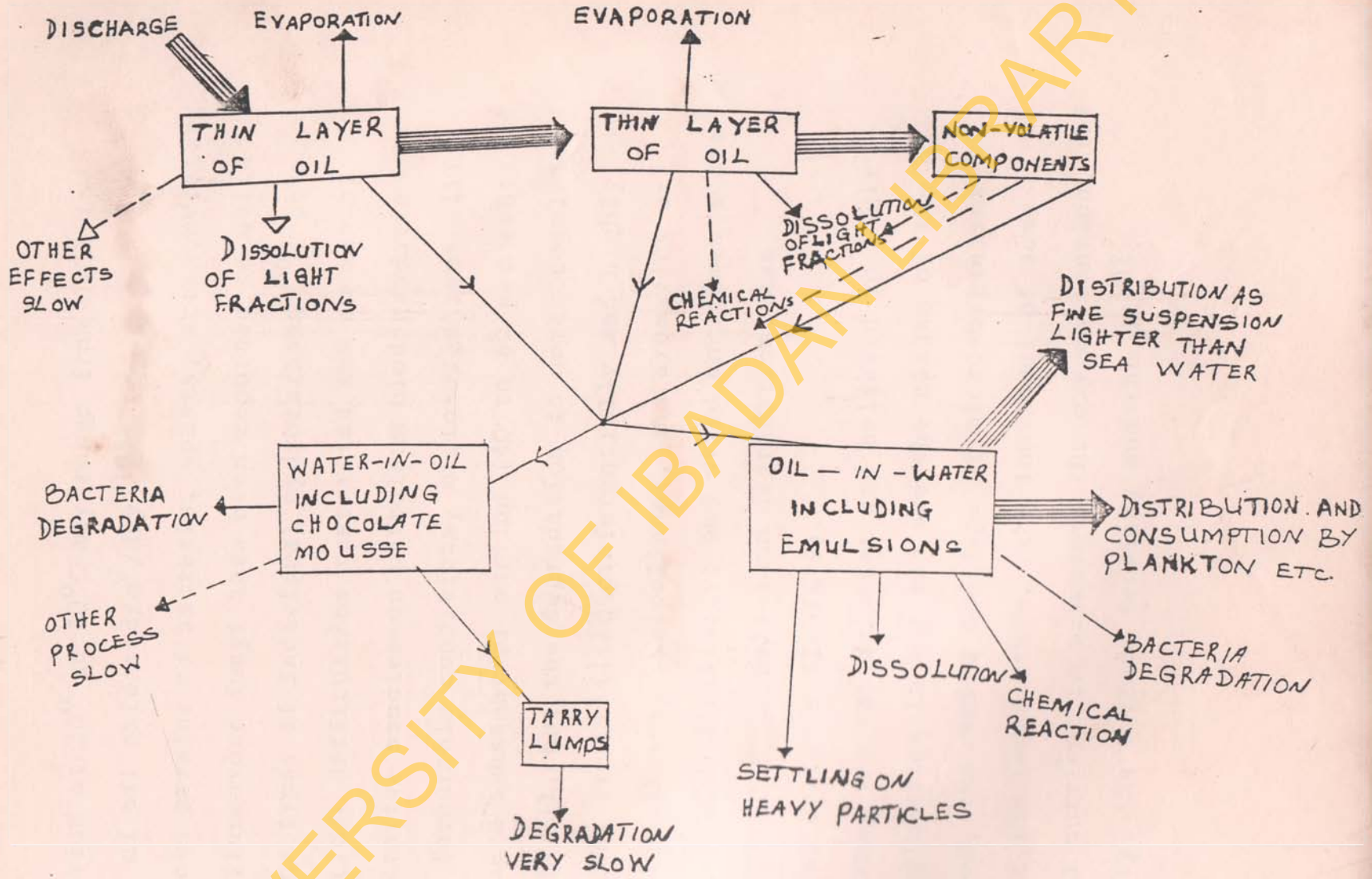


FIG.9: THE POSSIBLE CHANGES THAT CAN OCCUR WHEN CRUDE OIL IS INTRODUCED INTO THE MARINE ENVIRONMENT(82)

oxidation at 20° to 30°C may range from 0.02 to 02.0g of oil oxidized/m^2/day[105].

Numerous strains of bacteria, yeasts, actinomycetes, and filamentous fungi have been reported to utilize various types of individual hydrocarbons[106], but analytical difficulties restricted the number of quantitative studies on petroleum biodegradation. Given favourable conditions, micro-organisms will degrade a substantial portion (40 to 80 per cent) of a crude oil, but the degradation is never complete; n-alkanes are utilized preferentially and highly branched alkanes, cycloalkanes, and aromatics are utilized with difficulty; and mixed enrichments are more effective in petroleum degradation than isolated cultures (Table 9).

Among the factors that are believed to limit oil degradation in the sea are the nature of the oil involved, the number and type of micro-organisms present, the temperature, the low level of some mineral nutrient in seawater, the oxygen tension, the salinity, the surface tension, and the pH[107].

Nitrogen and phosphorous (available as NO_2^-, NO_3^-, NH_4^+ and PO_4^{3-}) have been shown to be limiting factors to both rates and extents of petroleum compound degradation, as well as having a stimulating effect by addition of nutrient supplements (e.g. $(NH_4)_2 SO_4$ and K_2HPO_4) to the immediate experimental environment[108]. Iron is now known to become limiting when precipitated out of the environment as ferric hydroxide, under alkaline conditions. However, both the natural abundance of iron in the lithosphere and marine pH ranges would probably prevent this limitation from occurring.

The environmental temperature can affect degradation rates by acting upon the microbial populations in several ways. Ambient temperature will select for microbial species tolerant to the temperature range present, such as psychrophilic bacteria with optimal growth rates from 15°-$20^{\circ}C$. Thus, qualitative shifts may occur within the microbial population (and in the inherent petroleum degradative capacity), as reflected by the relative presence of hydrocarbonoclastic microbes. Low temperatures generally suppress

degradation rates by suppressing growth rates and metabolic rates of the microbes involved and/or by actually inhibiting growth due to increased retention of toxic components in the petroleum. Inhibition due to toxic volatile compounds that evaporate more slowly at low temperatures, or to the increased solubilities of potentially toxic petroleum compounds at higher temperatures may occur[109-113].

Microbial degradation attack compounds over a much wider molecular weight range than evaporation and dissolution. In general, hydrocarbons within the same homologous series are attacked at roughly the same rate. This is in sharp contrast to the logarithmic dependence of evaporation and dissolution on the molecular volume of the hydrocarbons. The ease of bacterial degradation decreases in the order n-alkanes, iso-alkanes, cyclo-alkanes, aromatics[114]. Analytically, microbial degradation is most readily apparent from the decrease in normal alkane concentration, relative to more resistant components of similar boiling point and solubility.

TABLE 9: MICRO-ORGANISMS CAPABLE OF OXIDIZING/CO- OXIDIZING PETROLEUM HYDROCARBONS AND/OR THEIR DERIVATIVES

Organism Type	Species Name	Source Environment(s)[a]
Bacterium	Achromobacter sp.	T.M.
	A. Cycloclastes	(T,M)[b]
	Acinetobacter sp.	T,F,M,MS
	Aeromonas sp	M,MS
	Alcaligenes sp	
	A. eutrophus	
	Bacillus naphthlinicum	
	Beijerinekia sp	
	Brevibacterium sp	T,M
	B healii	(T,M)
	Cellulomonas galba	
	Cornybacterium sp	T,M
	Flavobacterium sp	FS,M

TABLE 9 (contd.)

Organism Type	Species Name	Source Environment(s)[a]
Bacterium	Micrococcus Cerificans	
	Mycobacterium sp	,MS
	M. rhodochrous	
	Nocardia sp	M,MS
	N. Coeliaca	(M,MS)
	N. coralina	(M,MS)
	N. minima	(M,MS)
	N. opaca	(M,MS)
	N. salmonicolor	(M,MS)
	Pseudomonas sp	T,F,M,MS
	P. aeruginosa	T,F,M,MS
	P. desmolytica	FS(T,F,M,MS)
	P. desmolyticum	(T,F,M,MS)
	P.fluorescens	(T,F,M,MS)
	P. LIgustri	(T,F,M,MS)
	P. methanica	(T,F,M,MS)

TABLE 9 (contd.)

Organism Type	Species Name	Source Environment(s)[a]
Bacterium	P. oleovorans	(T,F,M,MS)
	P. orvilla	(T,F,M,MS)
	P. pseudomaleii	(T,F,M,MS)
	P. putida	FS(T,F,M,MS)
	P. testosterni	(T,F,M,MS)
	Serratia marinoruba	
	Streptonyces sp	
	Vibrio sp	T,M,MS
Yeast	Candida petrophilium	(F,M)
	C. trophicalis	M,F
	Endomycopsis lipolytical	M,F
Fungi filamentous	Aspergillus versi color	
	Cephalosporium	
	Acremonium	

TABLE 9 (contd.)

Organism Type	Species Name	Source Environment(s)[a]
Fungi, filamentous	Cladosporium resinae	T,F,M
	Cunningham elegans	
	Penicillum zonatum	
	P. ochro-chlorens	
Algae	Prothotheca zophi	M

SOURCE: OIL SPILLS.

a. T = terrestrial sediment; M = Marine water column
F = Freshwater MS = marine bottom sediment;
FS = freshwater bottom sediment.

b. Key letters in parentheses designate the genus being indigenous to the specified environment.

1.7.4 CHEMICAL DEGRADATION[115-116]

When oil is subjected to autoxidation or photo-oxidation, there is chemical transformation of its components. Sunlight initiates free-radical reactions that convert hydrocarbons into hydroperoxides. These hydroperoxides are then further transformed to alcohols, acids and other oxygenated compounds. The free-radical reactions also lead to the polymerization of the partially oxidized hydrocarbons. The resulting 'tar' is denser, more polar, and more viscous than the parent hydrocarbons[117].

Photosensitizing compounds, such as Xanthone, 1-naphthol and other naphthalene derivatives have been shown to increase photo-oxidation rates for petroleum hydrocarbons. Compounds suitable as sensitizers must have strong absorption properties in the visible (or near UV) region, which results in a formation of a singlet or triplet state with a sufficient lifetime and energy to initiate free-radical chain reactions capable of proceeding at low temperatures. Obviously, this compound must also be

lipophilic and stable to oxidative processes within the oil-water system[118].

Xanthone has been determined to be most effective sensitizing compound in n-hexadecane photo-oxidation. A Type I photosensitized oxidation mechanism has been suggested, (Fig. 10). Light induces formation of triplet state xanthone via intersystem crossing from the excited singlet, which then extracts a hydrogen atom from n-hexadecane (forming a free-radical alkane). The xanthone-hydrogen complex interacts with molecular oxygen to reform the photosensitizer, accompanied by formation of a hydroperoxide radical. This radical then can interact further with other alkanes, which can then combine with molecular oxygen to form peroxides which can decompose to oxygenated radicals. These radicals may then interact with other alkanes to form alcohols.

Inhibition of photo-induced oxidation occurs via chain terminating reactions. Organo-sulphur compounds present in the petroleum are oxygenated to sulphoxide products by way of terminating the free radical chain reactions, and thus they inhibit complete oxidation

to carboxylic acids. Thus, preliminary evidence that the toxicity of Nigerian crude oil is not greatly affected by exposure to light could be ascribed to high levels of sulphur in the crude as compared with refined product [119].

The initial reaction rates may be influenced by the presence of dissolved metal ions of variable valence which act as catalysts, vanadium, for example is a common trace metal in petroleum and strongly catalyzes oxidations in the aqueous phase [95].

1.7.5 EMULSIFICATION

Within the water, emulsification remains the predominant dispersion process. It takes two main forms. Oil-in-water emulsion is formed on the surface and then dispersed by currents and waves; water-in-oil emulsion contains compounds of high molecular weight and is commonly called "mousse". It can contain up to 80% water, depending on the type of oil .

TYPE I PHOTOSENSITIZED OXIDATION MECHANISM FOR PETROLEUM

HYDROCARBONS:

$$X + h\nu \longrightarrow X^* \xrightarrow{ISC} X^{**}$$

$$X^{**} + RH \longrightarrow XH^{o} + R^{o}$$

$$XH^{o} + O_2 \longrightarrow X + HO_2{}^{o}$$

$$R^{o} + O_2 \longrightarrow RO_2{}^{o}$$

$$RO_2{}^{o} + RH \longrightarrow RO_2H + R^{o}$$

$$RO_2{}^{o} + XH^{o} \longrightarrow RO_2H + X$$

$$RO_2H \longrightarrow RO^{o} + {}^{o}OH$$

$$RO^{o} + RH \longrightarrow ROH + R^{o}$$

$$RO_2H + R^{o} \longrightarrow RO^{o} + ROH$$

X = Xanthone.

X* = Xanthone Singlet.

X** = Xanthone triplet.

RH = n-hexadecane.

ISC = Inter-system crossing.

FIG. 10: Hypothetical mechanism for sensitizer-induced free-radical oxidation in petroleum hydrocarbons, Gesser et al.(118)

Natural or added surface-active substances induce one or the other type of emulsion. Furthermore, a not negligible fraction of crude oil (containing atoms of N, S, O, P) having surface-active properties may play an important part in the dispersion of oil products. The suspended particles in the sea (oxides, hydroxides, carbonates, clays) also play a role in the dispersion by stabilizing or disrupting the emulsion[120].

The use of chemical surface-active agents to break up oil slicks so that marine, land and air species do not become impregnated with oil has been highly contested. The surface-active agents increase the probability that droplets of hydrocarbons will meet particles suspended in the water, and volatile hydrocarbons which might otherwise have been eliminated from the marine environment by evaporation or dissolution will thus be deposited on the sea floor. The dispersants used on the coast, in particular for clearing up mobile substrata, can act as vehicles for the oil and allow it to infiltrate deeply, which compromises biodegradation and

contaminates burrowing species, years afterwards, old and totally inert hydrocarbons can be found on beaches.

1.7.6 FORMATION OF TAR LUMPS

Stretching over a very long period, hydrocarbons which have not been degraded in the first two phases (microbial and chemical degradation) are found in different parts of the marine environment in the form of virtually stabilized agglomerates (tar lumps), accumulates in living organisms or in the mobile substrata. Tar lumps consist of very heavy hydrocarbons (up to C_{40}), oxygen, nitrogen or sulphur compounds and mineral compounds (35%), especially iron oxide[91].

1.8 PATHWAYS AND TOXICOLOGICAL EFFECTS OF PETROLEUM POLLUTION

Petroleum and its compounds which have been released into the environment are eventually degraded into simple compounds of their constituent elements by physio -chemical or biological agencies, with or without human assistance. They become innocuous; but

in the process, may cause serious damage to plants and animals or their physical surroundings and thus impede human exploitation of natural resources. The effects of oil pollution also vary widely according to the history of the spillage, the nature of the locality and the state of its biota. An oil pollution incident may interfere directly with industry or commerce, spoil the enjoyment of amenity pursuits or affect natural processes seemingly unconnected with human affairs. It should be remembered that every influence which, however, remotely diminishes the richness and variety of our environment ultimately diminishes the fullness and perhaps even the span of our lives.

1.8.1 EFFECTS OF OIL POLLUTION ON LAND

The nature of terrestrial oil pollution ranges from a massive single spillage resulting, for example, from a split or overflowing storage tank, overturned transport vehicle or fractured pipeline - through the small, but perhaps repetitive, losses which often arise from careless handling at small

factories and similar installations, or the surreptitious dumping of their waste oils, to such continuous but usually small-scale sources as an undetected leak or an oil-contaminated flow of waste water. Storm water carries from vehicle-parks and heavily-used roads a quantity of lubricating and other oils which is usually ignored, but which can be a significant source of local pollution. Although the site of any given incident cannot normally be predicted, most pollution is nevertheless restricted to the immediate vicinity of areas where petroleum is produced, processed, transported or used, since spilled oil rarely spread far in the terrestrial environment.

The first noticeable effect of oil spilled across the surface of the land in any quantity is likely to be upon vegetation. Plants exchange the gases involved in respiration and photosynthesis through small pores, mostly on the underside of their leaves. Some specialist plants of waterlogged, anaerobic soils also transport air from these pores to their roots, improving the soil condition locally[121]. The

pores may readily be penetrated by thin oils, a process which is usually demonstrated by a darkening of the leaf as its air-spaces become filled with the oil; heavier fractions may block them up, while a coating of dark oil excludes or filters the sunlight necessary to the functioning of all green plants. Once it has received a significant covering of an active oil, an individual leaf invariably dies. Oil percolating into the soil around the roots may interfere with their uptake of water or cause the release of substances toxic to the plant.

The damage which might be caused by a widespread spill of the more toxic or penetrating oils is indicated by the fact that selected blends have been used as herbicide sprays in their own right in addition to their frequent use as a medium for specific herbicidal substances[122,123]. On the other hand, some light fractions have little toxic effect and have been used against plant fungal diseases or as solvents for insecticide sprays with little or no damage to crops or livestock.

1.8.2 EFFECTS OF OIL POLLUTION ON AQUATIC ORGANISMS[124,125]

The effects of oil pollution can be grouped under two categories:

(a) The effects associated with coating or smothering of an organism with oil; such effects are associated primarily with the higher molecular weight, water insoluble hydrocarbons, the various tarry substance that coat the feathers of birds and cover intertidal organisms such as clams, oysters, and barnacles. Tube worms are surprisingly little affected by such coating,[124] although the effect on organisms such as aquatic birds may be devastating.

(b) Disruption of an organism's metabolism due to the ingestion of oil and the incorporation of hydrocarbons into lipid or other tissue in sufficient concentration to upset the normal functioning of the organism. With respect to this second effect, it is generally agreed that aromatic hydrocarbons are the most toxic, followed by cycloalkanes, the olefins, and

lastly alkanes. There is also a definite tendency for the toxicity per unit molecular weight to decrease as the molecular size of the hydrocarbon increases[124].

The toxicity with respect to the second category closely parallels their solubility in water. Thus, the most toxic components and also the most soluble in water are the low molecular weight aromatics such as benzene and toluene. Whereas the least toxic and least soluble are high molecular weight alkanes, aromatics and other toxic hydrocarbons apparently exert their effects in part by becoming incorporated into the fatty layer that makes up the interior of cell membranes[124]. As a result, the membrane is disrupted, and ceases to properly regulate the exchange of substances between the interior and exterior of the cell.

In extreme cases the cell membrane may lyse, allowing the contents of the cell to spill out and obviously destroying the cell. Although the low molecular weight alkanes and cycloalkanes were once

considered to be harmless to aquatic life, it is now known that these compounds can cause narcosis and anesthesia in a variety of lower animals[126]. Such effects are probably due in part to disruption of cell membranes[124].

Hydrocarbons also interact with proteins in a variety of animals. Both enzymes and structural proteins appear to be affected. Once again, aromatics seem to be more toxic than other hydrocarbon classes with respect to this effect.

The relative toxicity of various types of oil can be deduced from the above information. Refined petroleum products such as gasoline or kerosene contain virtually no high molecular weight hydrocarbons, and hence exert very little in the way of a smothering or coating effect. However, because refined products do contain a higher percentage of low molecular weight hydrocarbons than crude oil, these products exert greater second-category type toxic effect than does a comparable amount of crude oil. In this respect, it is noteworthy that two of the most ecologically damaging oil spills, the grounding of the

tanker Tampico Maru off Baja, California in 1957, and the grounding of the tanker Florida in Buzzard Bay, Massachussetts in 1969, involved spillage of refined petroleum, namely diesel oil and No. 2 fuel oil respectively[127].

Crude oil on the other hand contains a significant fraction of high molecular weight hydrocarbons, which give it a viscous, sticky character. As a result, the greater damage from crude oil discharges may be the first category sort, that is the coating of plants and animals with high molecular weight hydrocarbons. Undoubtedly the organisms most affected by oil coating or "oiling" are certain kinds of aquatic birds, namely awks (murres, guillemots, razor bills, puffins, etc.) penguins and diving sea ducks. These birds are particularly susceptible to oiling for the following reasons:

(1) They spend most of their lives on the surface of the sea.

(2) They are poor fliers or are flightless.

(3) They dive rather than fly in response to a disturbance.

When oil is adsorbed to the feathers and down of these birds, their plumage becomes matted, and the air spaces which normally provide buoyancy and insulation become filled with water and oil. They get drowned due to their inability to maintain a proper body temperature without adequate insulation from their plumage. Invariably oiled birds attempt to clean themselves by preening their feathers, but in the process, they may ingest as much as 50% of the oil in their plumage [124] and die from toxic effects of the ingested oil.

A list of various sublethal effects on the physiology, histology, and behaviour of organisms and on their populations are described in Table 10. The sublethal modifications may affect the characteristics of the populations of each species, changing the rates of birth, death, and dispersal, as well as the age structure and spatial pattern. Also, changes in the ecological communities may occur in the affected area.

Potentially carcinogenic hydrocarbon components of crude oil occur in the marine environment, and are accumulated or retained in marine animals, and then by

man. The belief that oil can induce cancer in marine organisms is based on the fact that polycyclic aromatic hydrocarbons have been identified as carcinogenic agents. They are widely distributed over the ocean and are found in crude oil; and they concentrate in animal tissues. Cancer has been found in clams from oil spill sites. However, there has been no conclusive evidence to date implicating oil as the direct cause of the observed neoplasms. It has been observed that not all aromatic hydrocarbons but only particular configurations (e.g. Phenanthrene, Chrysene and Benzo(a) Pyrene) have carcinogenic potency and that many animals (e.g. Macoma inquinata, a detritus feeding clam and Abarenicola pacifica, a burrowing polychaore) can transform these to less harmful forms (Phenanthrene could be conjugated into highly polar metabolites). Mixed function oxidases (MFO) such as aryl hydrocarbon hydroxylases (AHH) capable of coverting benzo(a) pyrene into polar metabolites, have been found in several polychaetes, e.g. Nereis sp. and Capitella capitata (128)

Ingested hydrocarbons tend to become fixed in tissues containing fat reserves, such as the liver, the pancrease in invertebrates, or the gall bladder; but also in the lipoproteins in plasma and all cutaneous and nervous tissues. By affecting cellular mechanisms they may cause cutaneous changes such as necroses or tumors. According to Halstead, 12% of a sample of 16,000 sole from San Francisco Bay presented an average of 33 tumors per fish in the vicinity of petrochemical waste disposal sites. Parry and Yevich in 1973, demonstrated frequent neoplasma in shell-fish (Menidia menidia and Mya arenaria) contaminated by insoluble and soluble fractions of oil from Texas and Louisiana and gonadal and nematoporetis neoplasms in 29% of animals collected on the coasts of the State of Maine which are permanently polluted by hydrocarbons. Polycyclic aromatic compounds are also formed naturally by micro-organisms and are not necessarily associated with oil from spills. Concentrations of benzopyrene in marine organisms may nevertheless reach 400 ppb along highly industrialized coasts. The risk of

TABLE 10: EVALUATION OF EXPERIMENTS AND OBSERVATIONS OF THE SUBLETHAL EFFECTS ON ORGANISMS BOTH OF POLLUTION AND OF OTHER ASSOCIATED ACTIVITIES OF THE PETROLEUM INDUSTRY

Group	Species	Reference	Type of Petroleum Product	Concentration	Effects and Evaluation
A Reproduction Fecundity Crustacea	Pollicipes Polymerus	Straughan, 1971	Crude oil, Santa Barbara blowout field study		Inverse relationship between the fraction of adults brooding and the amount of oil on the adults (p.0.5); heavily and moderately oiled areas had no recruitment whereas settlement was recorded from all unoiled samples.
Mollusca	Mytilus edulis	Blumer et al, 1971	No. 2 fuel oil, West Falmouth spill field observations		Gonads of mussels failed to develop in affected areas
Fish	Godus morrhua	Kuhnhold, 1970	Iranian crude extracts (paraffin based)	Aqueous extracts from 10^4, 10^3, 10^2 ppm total oil (author estimates 10^4 yields 10 ppm soluble hydrocarbons, 1 ppm may be more likely.	Eggs: "Some cases" were sublethal but embryos and larvae did not survive, apparently, 10^2 ppm does not differ from control. Larvae: "Showed typical behavior symptoms in oil extracts: increased activity was followed by a reduction of swimming activity, which finally stopped... which slowly deepened until the 'critical point' when no responses of the larvae were obtained even by touching or prodding": time to "critical point" varies with age of larvae and amount of oil: 10^3 ppm not different from control (14-5.5 days for 1-10 day old larvae); 10^2 ppm (8.4-4.5; 10^4 ppm (4.2-0.5); "herring larvae were less, and plaice larvae more resistant than cod"; "chemoteceptors seemed to be blocked very quickly at the first contact with oil"; insufficient quantification; no measure of uncertainty; no chemical analysis
Lobster	Homarus americanus	Wells, 1972	Venezuelan crude	0.1,1,6,10, and 100 (emulsions)	100 ppm lethal to all larval stages; 10 ppm; stage 1-3 more sensitive than stage 4. Long- term experiments with newly hatched larvae. 10 ppm 9-day mean survival time; 6ppm longer time to 4th longer than at lower concentrations; concentration at which development was prolonged are too high to be important in the field

TABLE 10 (contd.)

Group	Species	Reference	Type of Petroleum Product	Concentrations	Effects and Evaluation
B Growth Phytoplankton	Chorella vulgaris	Kauss et al., 1973	Aqueous extracts of several crude oils and outboard motor oil; 90% solutions of aqueous extracts used	1 part oil to 20 parts water	Inhibition of growth varied from 5 to 41% after 2 days of exposure; after 10 days, cell yields were close to controls, suggesting inhibiting substance was eventually lost. After 2 days of cell growth, cell numbers were significantly lower in 25,50, and 90% oil extracts than in control: concentrations of water-soluble hydrocarbons and comparison of oils unknown
C Metabolism Photosynthesis Phytoplankton	Mixed natural samples	Gordon and Prouse, 1973	Venezuelan crude No. 2 and No. 6 fuel oil	10-200 g/(ppb)	Concentrations below 10-30 µg/l were found to stimulate photosynthesis, while at concentrations between 60 and 200 µg/l, were somewhat suppressed below controls for all but No. 2 fuel oil which depressed photosynthesis to approximately 60% of controls at concentration between 100 and 200µg/l environment in Bedford Basin: 0.5-60 g/l; highest content (under slick): 800 µg/l
2 Respiration Fish	Cyprimodon variegatus lagodon Micropogon undulatus	Steel and Copeland, 1967	Petrochemical wastes	0.2-2.0 ppm in addition 0.4-4.0 phenol	Clams respiratory inhibition at low concentration then stimulation approaching TL48 as general pattern; only 1 of the 3 species fit this pattern; insufficient acclimation; too high concentrations
Fish	Juvenile Onchorhynchus tshanysha (salmon) and Morone saxatilis (striped bass)	Brocksen and Bailey, 1973	Benzene	5 and 10 ppm changed every 48 h	Respiratory rate was increased during the early (24-48-h) period of exposure to both 5 and 10 p.p.m. of benzene; after longer periods, respiration decreases back to near-control levels: when tested at daily intervals after exposure, found both fish species returned to control levels
D Behavior Fish	Ictalurus natalis	Todd, 1972			Feeding unaffected; social behavior altered after 1-3 days and returned to normal in about 1 week second additions after return to normal again disrupted social behavior

TABLE 10 (contd.)

Group	Species	Reference	Type of Petroleum Product	Concentrations	Effects and Evaluation
Crustacea	Homarus americanus	Atema and Stein, 1972	La Rosa crude and extracts thereof		Chane in feeding times (doubling of waiting time) and behavior caused by addition of 1:100,000 parts crude oil to water: soluble fractions giving same oil/water ratio had no effect; light and electron microscopy showed no change in morphology of odor receptors; response similar over 5-day period, although hydrocarbons' characteristics did change by "weathering"; experimentally good as possible, but long-term effects and recovery not considered: very difficult problem
E Histological Changes Fish	Menidia menidia	Gardner, 1972	Texas-Louisiana crude oil	1lw/40 l seawater, then separate fractions (soluble and insoluble); exposed for 168 h	Various types of histological abnormalities exhibited after exposure to both the soluble and insoluble fractions: largely chemoreceptor structures studies but also ventricular myocardium; no analyses of concentratons seen by fish; technique seems good, but tissue and water content of hydrocarbons needed
D Behavior (continued) Fish	Gulf of Mexico species	Bechtel and Copeland, 1970	Petrochemical wastes	Different % Houston Ship Channel water	Claims that percent polluted water is a good predictor of species diversity; unfounded because confounded with salinity; to convincingly demonstrate that oil pollution responsible for decreased diversity, compare with samples covering a similar range of salinites in an unpolluted control bay

increasing contamination in the products of the sea is thus real.

1.9 OIL SPILLS: A GLOBAL PICTURE

Oil spills, particularly on the sea and Navigable Waters, have excited more public interest and concern than any other waste or spilled materials, even if the latter are potentially or actually far more hazardous. These accidental spills constitute a small fraction (3 to 4 per cent) of the annual rate of addition of petroleum into the marine environment. Some of these spills occur within confined marine areas, such as bays or estuaries where the concentration may remain high for extended period causing the biological impacts to be greater than if the oil were released where rapid dispersion could take place. Such releases are generally large compared with chronic low-level additions and, furthermore, they commonly occur in coastal waters where man makes maximum use of marine resources. A list of some of the more important oil spills is given in Table 11.

TABLE 11: MAJOR OIL SPILLS (1957-83)[129]

Date of Spill	Source & Location	Type and Amount of Oil (Barrels)	Nature of Incident
March 1957	"Tampico Maru" Baja California, Mexico	55,220 No. 2 fuel oil	Grounding
July 1962	"Argea Prima" Guayanilla Harbor, Puerto Rico.	70,000 Crude oil	Grounding
January 1967	"Chryssi P." Goulandris, Milfold Haven, England	⩾1,800 crude oil	
March 1967	"Torrey Canyon" Cornwall S.W. England	821,000 Kuwait oil	Grounding
September 1967	"R.C.Stoner." Wake Island	126,000 Aviation gas J-P4 Jet fuel A-1 turbine oil and Bunker C oil	Grounding
March 1968	"Ocean Eagle" San Juan, Harbor, Puerto Rico	83,000 Crude oil	Grounding

TABLE 11 (contd.)

Date of Spill	Source & Location	Type and Amount of Oil (Barrels)	Nature of Incident
April 1968	"Esso Essen" S. Africa	20,000-28,000 Crude oil	
December 1968	"Witwater" Galeta Island, Canal Zone	20,000 Diesel and Bunker C oil	
January 1969	Well A-21 Santa Barbara Channel, USA	33,000 Crude oil	Blowout
January 1969	Santa Barbara oil rig offshore Santa Barbara California, USA	70,000 - 700,000 Asphaltic Crude	Blowout
September 1969	"Florida" barge West Falmouth, Buzzard Bay Massachussets, USA	6,000 NO.8 diesel fuel	
February 1970	"Arrow" Chedabucto Bay, USA	108,000 Bunker C	Grounding
February 1970	Chevron oil Rig Offshore Gulf of Mexico	30,000 Gulf crude	Blowout
December 1970	Shell oil rig off Louisiana Coast near Grande Isle, La, USA	53,000 Gulf crude	Blowout

TABLE 11 (contd.)

Date of Spill	Source & Location	Type and Amount of Oil (Barrels)	Nature of Incident
January 1971	San Francisco Bay, Below Golden Bale Bridge, USA	27,100 Bunker C oil	Tanker Collision
January 1971	Arizona Standard and Oregon standard san francisco bay USA	20,000 Bunker C oil	
February 1971	"Wafra" Cape Aulhas S. Africa	445,000 Crude oil	
April 1971	March point dock facility, Anacortes, Washington USA	5,000 No. 2 Fuel oil	
October 1971	Amoco oil rig offshore Louisiana coast, USA	400 Gulf Crude	Blowout
January 1972	General M.C. Meigs, Wreck Cove Washington Coast, USA	3,000 Navy Special Oil	Collision
1976	Urguiola La Coruna in Spain	60,000 Crude oil	Struck an Underwater obstruction

TABLE 11: (contd.)

Date of Spill	Source & Location	Type and Amount of Oil (Barrels)	Nature of Incident
1976 (contd)	Jakob Maersk Oporto in Portugal	80,000 Crude oil	
	Metula Straits of Magellan in Chile	50,000 Bunker C oil	
December 1977	Ven oil and ven pet port Elizabeth, S. Africa	30,000	Collision
December 1977	Ekofisk North Sea Norway	80,000 Crude oil	Grounding
March 1978	Amoco Cadiz Portsall Brittany Coast France	220,000 Light Arabian oil	Grounding
1979	Ixtoci compuche Bay Mexico	2,700,000 Crude oil	Collision
1983	Sivand East Coast of Humber, Britain	104,000 Nigeria Crude oil	Collision

The ecological effects of these spills depend largely on the type of oil involved, the quantity, the physical, chemical and biological states of the impacted area. These effects include the possibility of:

(1) Human hazard through eating contaminated sea food.

(2) Decrease of fisheries resources or damage to wildlife such as sea birds and marine mammals.

(3) Decrease of aesthetic values due to unsightly slicks or oiled beaches.

(4) Modification of the marine ecosystem by elimination of species with an initial decrease in diversity and productivity.

(5) Modification of habitats, delaying or preventing recolonization.

Apart from the global incidents shown in Table 11, a record of some accidents in West and Central Africa is also available as can be seen in Table 12 below.

TABLE 12: OIL SPILL INCIDENTS IN WEST AND CENTRAL AFRICA, 1975-1980 INVOLVING SHIPPING 129

Date of Spill	Source & Location	Type and Amount of Oil (Barrels)	Nature of Incident
12/17/75	Mobile Refiner Douala, Cameroon	45 tons bunker fuel	Collision
4/16/77	Universe Defiance off senegal	Unknown quality bunker fuel	Explosion in engine room
10/26/77	Uniluck (not tanker) 4 miles from Fouche Island, Nigeria	Unknown Quality Fuel oil	Grounding
11/01/77	Arzen cotonou (Dahomey)	50-5,000 Product	Fire while discarging
6/21/79	Petro Bouscat 20 miles south of Douala Cameroon	Fuel oil quantity	Grounding
8/16/79	Loannis Angeli Louanda, Angola (6o 16'S 11° 33'E	Ship discharge Crude unknown quantity	Grounding
1/16/80	Salem off senegal (12° 32'N 18° 34'W	"Theoretically loaded with 200,000 tons of kuwait crude	Explosion and Sinking

TABLE 12 (contd.)

Date of Spill	Source & Location	Type and Amount of Oil (Barrels)	Nature of Incident
3/11/80	Off Mauritania (20° 32'N 18° 13'W	Ship in ballast unknown quantity	Explosion and sinking
4/04/80	Mycene off the Ivory coast	Ship in ballast unknown quantity	

The ecological damage caused by refined products is always more devastating than when the spill involves crude oil. Observational data based primarily on fish catches and repopulation of sub-tidal and intertidal benthic communities in the area of the two most widely publicized major oil spills ("Torrey Canyon" and Santa Barbara) indicated slight acute damage to marine life with the exception of waterfowl. In both areas, recolonization of benthic organisms which had been killed occurred within a year following each accident. Contrastingly, the barge "Flordia" accident which released 162,000 gal. of No. 2 fuel oil in Buzzard Bay, Massachusetts, was reported to cause a massive mortality of fish and benthic communities in the immediate area of the spill. Gas chromatographic (GC) analyses of hydro-carbons extracted from sediment samples revealed the presence of the fuel oil two years after the spill. GC analyses also showed that the oil was taken up and retained by oysters and scallops in the area of the spill (130).

1.10 OIL POLLUTION PROBLEMS IN NIGERIA

Nigeria is one of the major oil producing nations of the world. The development of oil industry in Nigeria has contributed significantly to the economic growth of the country, and the well-being of Nigerians. Over 90 per cent of the annual revenue comes from the oil sector. Apart from the billions of petro-dollars realised annually from oil, however, there are other attendant negative ecological impacts on the environment. The effects are mostly felt by people living in the oil activity areas where there is environmental degradation associated with oil industry.

Most of the oil produced in Nigeria comes from the Niger Delta (Fig. 11) and it is here that most dramatic and impactive oil-well blow-outs have occurred. This area has also borne the brunt of crude oil storage tank failures and effluents from production and refinery operations. In 1970, the Shell-BP, Bomu-11 well blew out while the Satrap (now ELF) Obasi-21 oil well blew out in 1972. Their effects, according to studies carried out by experts

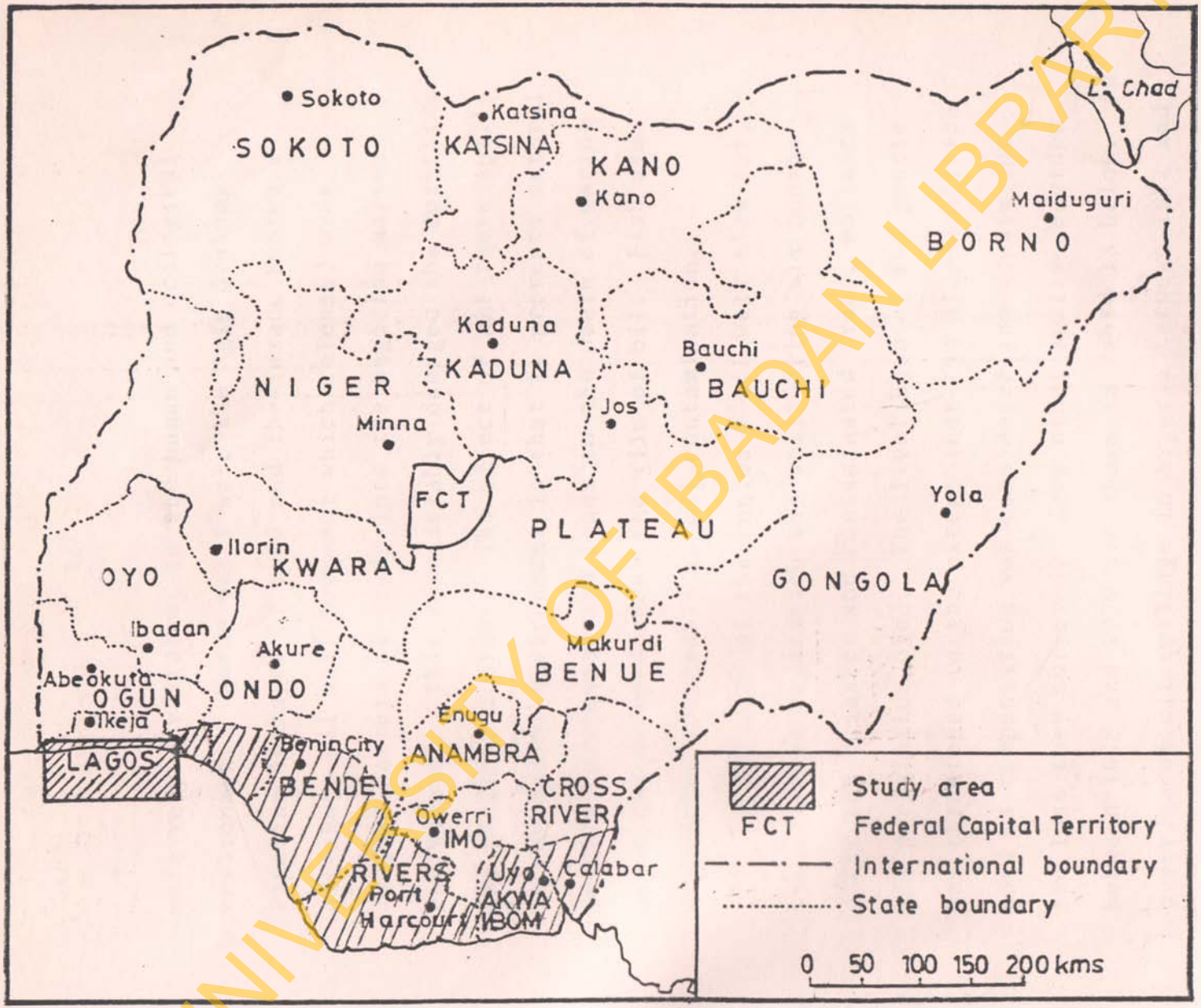


Fig. 11: MAP OF NIGERIA SHOWING THE STUDY AREA.

were very devastating to the human and ecological environment. Worse still were the Agip Oyakama Pipeline leakages of 1980 and the Texaco Funiwa V off-shore oil well blow-out which released over 400,000 barrels of crude into the Nigerian marine environment. This considerably damaged the coastline and mangrove ecology. The effect of all these spills on the marine environment is that it prevents natural aeration processes and leads to the death of marine organisms trapped under the film of oil. Fish are especially vulnerable to oil contamination.

In the case of the Funiwa V oil well blow-out, the mangrove vegetation was still dying six months after the disaster and contaminated crabs, molluscs and periwinkles died. The livelihood of the people was threatened to the extent that the ₦12.00 million paid as compensation was considered inadequate for the loss they suffered. Some other spills recorded between 1978 and 1979 are shown in Table 13 below. An overview of oil spillage in Nigeria between 1972 and 1979 is given in Table 14. While Table 15 shows the yearly distribution of oil spills between 1970 and

1982. The areas mostly affected and under constant threat of oil spillage are Rivers, Cross River and Bendel States where the oil companies operating in Nigeria have most of the oil wells, pipelines and storage tanks. Occasionally, oil spillage also occur at the oil depots or along the interstate pipelines, e.g. the Abudu pipeline oil spillage (1982). Also oil spillage and seepage incidents have been reported at Warri, Port Harcourt and Kaduna refineries.

TABLE 13: THE MAJOR OIL SPILLS IN NIGERIA 1978/79 (131)

Date of Spill	Location	Barrels Spilled	Barrels Recovered
13 May, 1978	Qua Iboe Terminal	3,170	1,600
3 July, 1978	TNP near Idu Ekpanya Billage	2,000	Not Definite
16 Sept., 1978	Elelebu Flow Station	2,000	1,000
20 Oct., 1978	SBM-1 Bonny off-shore	66,000	Nil
22 Nov., 1978	TNP near Akinima	6,000	Nil
24 Nov., 1978	Isimiri flow station	700	200
27 Dec., 1978	Opobo manfold	6,000	Nil
16 Mar., 1979	TNP near Rumueke Junction	60,000	30,000
14 April 1979	Okan	900	Nil
5 May 1979	Bomu flow station	7,000	Not Definite
6 June 1979	SBM-2 Bonny off-shore	1,973	Nil
12 June 1979	TNP at Ihuowo	600	Nil
20 June 1979	SBM-2 Bonny off-shore	706	Nil
24 June 1979	SBM-2 Bonny off-shore	7,820	Nil
6 July 1979	Forcados Terminal Tank 6	570,000	20,000

TNP- Trans Niger Pipeline. SBM - Single Bonny Mooring

TABLE 14: AN OVERVIEW OF OIL SPILLAGE IN NIGERIA, 1972-79 (131)

Year	Crude Oil Production	Recorded Number of Spills	Approximate Quantity of Unrecovered Spilled Oil (BBL)
1972	665,293,292	5	39,000
1973	719,376,760	7	2,619
1974	823,317,843	24	23,368
1975	660,146,040	16	3,544
1976	758,055,728	26	3,133
1977	766,052,636	61	4,374
1978	597,719,214	143	101,211
1979	513,193,653	71	638,235

TABLE 15: YEARLY DISTRIBUTION OF OIL SPILLS 1970-1982 (132)

No.	Year	No. of Spills	Net Volume (BBLS)
1	1970	1	150.00
2	1971	14	15,111.00
3	1972	41	51,390.00
4	1973	59	95,580.00
5	1974	105	65,714.00
6	1975	128	56,854.82
7	1976	128	20,023.00
8	1977	104	31,144.00
9	1978	154	97,250.00
10	1979	157	630,405.00
11	1980	241	558,053.00
12	1981	233	22,840.00
13	1982	216	34,474.60
TOTAL	13 YEARS	1,581	1,678,989.40

1.11 AIM OF STUDY

Nigeria is one of the world's major producers and exporters of petroleum. Our economy is very much dependent on the revenue earnings from oil which amount to billions of dollars annually. The activities of the oil companies are causing a lot of ecological problems for the inhabitants of the Delta area where the "black gold" is being exploited. Oil spill from maritime activities at Lagos port and industrial effluents also impact the environment.

The ecological damage caused by oil has been reported in many parts of the world, these include formation of tar balls on beaches, thereby destroying the aesthetics of beaches as well as constituting severe public health hazard and in open sea; damage to fishing gear, tainting of fish with a reduction in the economic value and consumption in many places.

The largest source of oil entering the ocean is from the land, either directly from effluent pipelines from refineries or petrochemical plants or from other industrial discharges into rivers. These may be waste oil or the discharge of oily effluent from factories of

all types. A great deal of used sump oil is also poured into drains or canals by petrol service stations or vehicle repair garages.

It is clear from studies of the effect and fate of oil discharged to the marine environment that the availability of adequate information on the existing state of affairs before a spill or discharge occurred is essential to the full interpretation of the fate and effect of the discharge. Since there is no area that is oil-free, it therefore become very necessary to have baseline data - i.e. existing concentrations and composition of hydrocarbons in an area such as the Niger Delta and Lagos if the impact of oil exploration, production and transportation is to be effectively monitored and evaluated.

There is a paucity of data on the relative levels of petroleum contamination in our coastal waters which makes it difficult to compare the pollution level with other countries.

In order to bridge the data gap and also assess the impact of the current level of petroleum industry operations on the coastal and marine environment of the

country. The basic objectives of this study among others include:

(a) Determination of the levels and present distribution of the petroleum hydrocarbons in water and sediments in coastal and marine environment of Nigeria, thus providing baseline data which could be useful input for future legislation.

(b) To assess river input into petroleum hydrocarbon budgets of Nigerian coastal waters.

(c) To assess seasonal variation and establish a system of petroleum hydrocarbons monitoring to reflect changes in input of petroleum into the aquatic environment.

CHAPTER TWO

2. DETERMINATION OF PETROLEUM HYDROCARBONS IN ENVIRONMENTAL SAMPLES

2.1 INTRODUCTION

The major portion of the oil that is present in our environment originates from major disasters, according to the data supplied by Blumer[126] since only about 0.1% of all the oil, which is presently shipped by sea, is accidentally lost during transit. But the bulk of the oil is from the countless day-to-day incidents that occur during the transportation, transferral and consumption of oil.

If this trend is allowed to continue, the problem of oil pollution of the environment will become more acute as the amount being introduced to the environment continues to be on the increase. In order to keep this environmental risk in check, some safety valves must be applied. This therefore calls for efficient and unambiguous analytical methods for the monitoring and characterization of these spillages from the standpoint of the enforcement of the pollution control, designed

to protect the public health and the environment.

The prevention and control of oil spills and less spectacular losses of fossil fuels to the aquatic environment require methods for identifying unknown oil samples. Oil identification is not simply "nailing polluters" but is a capability required in managing oil resources and preventing minor, inevitable losses from becoming major discharges. Oil producing, transporting, refining, distributing, consuming and disposal processes all require monitoring to minimize loss. Many analytical methods have been developed some of which will be discussed in this chapter. However, from the variety of analytical methods, apparently no standard method of analysis has been selected for particular types of environmental samples (water, sediment and biota). Therefore, earlier attempts of oil characterization have been performed by a multimethod approach, the particular combination of analytical techniques depends on the facilities and the experience existing in a laboratory and the expenditure which is justified to identify any known source.

Representative example of these overall approaches are reported in figures 12 and 13 below. The basic analytical procedures for the isolation and identification of petroleum hydrocarbons in marine samples may be separated into four steps[133] .

(i) Sample collection without contamination.

(ii) Extraction of lipid by use of solvents such as tetrachloromethane (CCl_4), methanol or benzene.

(iii) Separation of petroleum hydrocarbons from other lipids by chromatography (Thin Layer Chromatography (TLC), Column Chromatography, High Performance Liquid Chromatography, (HPLC)).

(iv) Identification and interpretation of the data obtained by some methods such as Infrared, Ultraviolet and fluorescence spectrometry, Gas chromatography or Gas chromatography-Mass spectrometry.

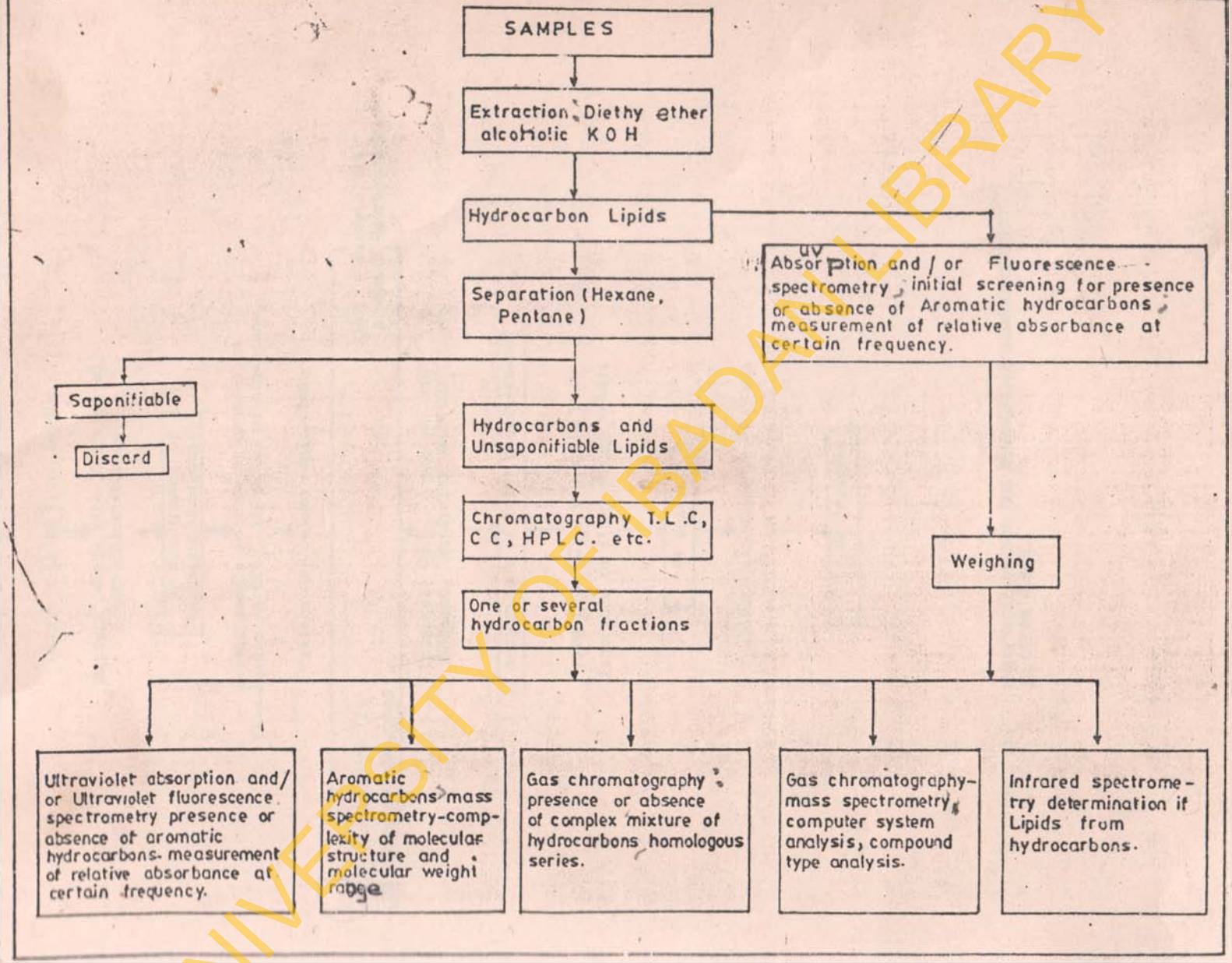


FIG. 12: FLOW DIAGRAM FOR ANALYTICAL TECHNIQUES TO DETECT AND ESTIMATE PETROLEUM CONTAMINATION.

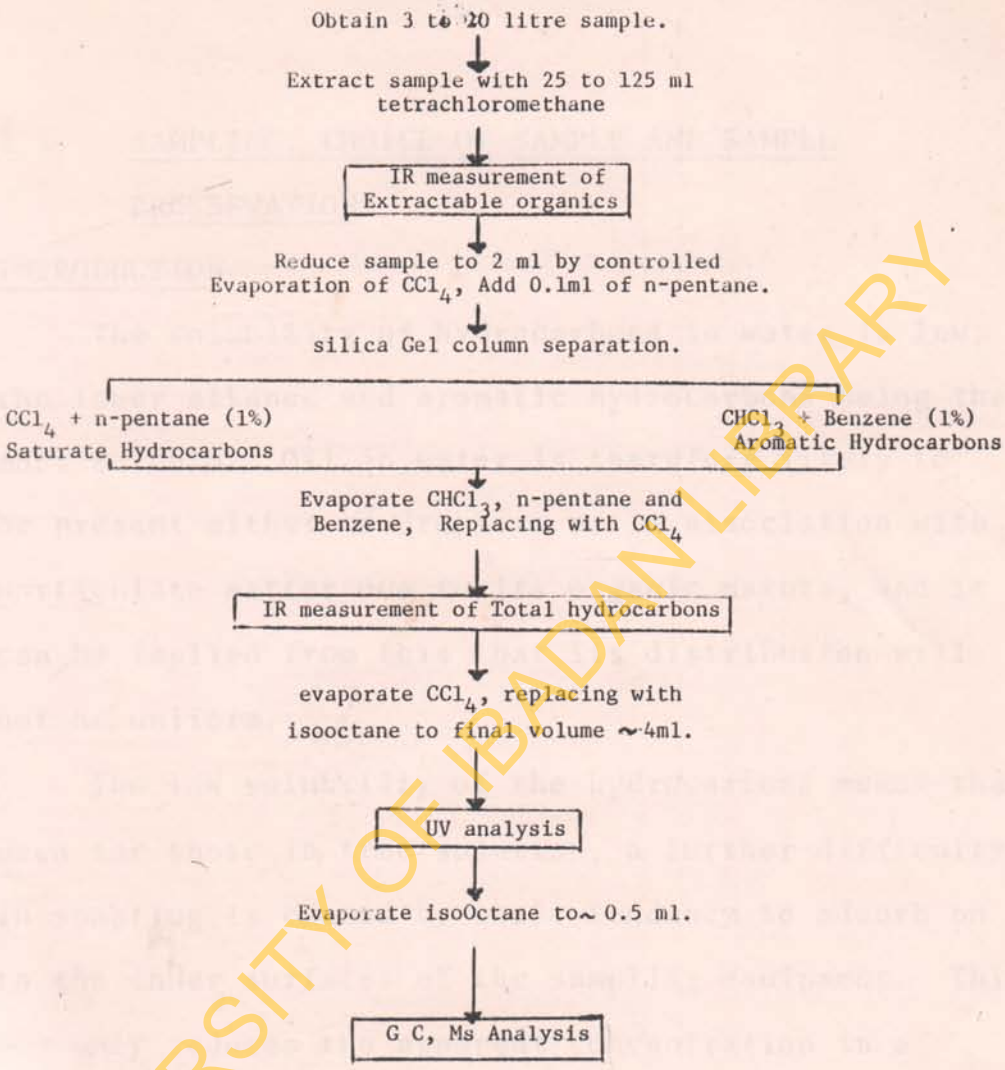


FIG. 13: ANALYTICAL METHOD FOR NONVOLATILE HYDROCARBONS[109] IN OCEAN WATER.

2.2 SAMPLING, CHOICE OF SAMPLE AND SAMPLE PRESERVATION

INTRODUCTION

The solubility of hydrocarbons in water is low; the lower alkanes and aromatic hydrocarbons being the most soluble. Oil in water is therefore likely to be present either as droplets or in association with particulate matter due to its organic nature, and it can be implied from this that its distribution will not be uniform.

The low solubility of the hydrocarbons means that, even for those in true solution, a further difficulty in sampling is caused by their tendency to adsorb on to the inner surfaces of the sampling equipment. This not only reduces the apparent concentration in a sample, but if not removed from the sampler, the hydrocarbons will remain to be desorbed into a future sample of lower concentration.

Sample collection for baseline studies in the sub-part per billion to part per million concentration range from pristine environments, requires that every possible precaution be taken to minimize contamination

and sample handling errors. At these ultra-low concentrations it is imperative that a creditable sampling programme be designed in order to obtain meaningful results.

The quantity of sample required depends on the analysis to be undertaken. A representative sample should be drawn for oil determination and the size of sample will depend on the anticipated oil content.

2.2.1 WATER

Water is an important medium in the dispersion of oil. Solubility of crude and refined petroleum products in water varies for type of crude and products, the heavier fractions having less soluble components than the lighter fractions. Mckee et al[135] stated that the solubility of modern petrol in water is in the range of 20 to 80 mg/1 (with mean value of 50 mg l^{-1}). However, soluble hydrocarbons in water give rise to objectionable tastes and odour at concentration as low as 0.001 mg l^{-1}.[136]

The aromatic fraction which is a toxic component of petroleum is soluble in water to an extent that can

be detected with a reasonable accuracy. In order to evaluate the danger to which the aquatic plants and animals are being exposed, the level of hydrocarbons in water is very important and must be determined. This will help in our bid to protect the quality of our environment.

2.2.2 SEDIMENT

Crude oil on landing on water spreads over wide areas with very limited mixing with the water. When it spreads in this manner, volatile substance escape rapidly while water soluble materials disperse and the material remaining is subjected to bacterial degradation. Certain portion combine with silt and sink to the bottom, where they are incorporated into the sediment. Occasional mixing allows the re-entrying of the hydrocarbon into the water and for the bottom feeders to feed on the contaminated particles.

Marine and freshwater sediments can provide a wealth of information relating to the ecological impact of industrial and domestic development. In contrast to samples of water and biota, the sediments can

be considered to be reflective of local environmental conditions over a finite period of time. Aquatic sediments are the main final accumulation site of water-borne constituents derived from natural (living organisms and their detritus in-situ and surroundings) and artificial (domestic, urban-industrial and agricultural wastes) sources. The aquatic sediments can provide not only a historic record of sedimentary environments, but also reserve the features of average sedimentary environmental conditions. Besides they are vice versa, also possible sources of chemical constituents in waters[137].

2.3 SAMPLE COLLECTION AND FREQUENCY OF SAMPLING

The purpose of sampling is to obtain reliable results through a carefully obtained representative sample. A good analysis takes its root from a truly representative sample.

Sampling may be discrete or continuous when dealing with water samples. It is discrete sampling when a known amount of sample is withdrawn at a time but it is continuous when water sample is pumped

continuously through pre-combusted filters. This normally involves a large quantity of water of about 200 litres.

There has been some advantages advanced for grab (discrete) samples. These include the fact that spot results can be obtained quickly, trends can be followed and multiple samples can be taken readily for different analyses. Composite samples obtained by bulking grab samples are prone to gross errors due to excessive handling of the samples. A composite result can only be obtained by taking an average of the grab sample results.

The frequency of sampling may be daily or weekly or can even be monthly, depending on the time available, transport facilities, site requirements and nature of the samples.

After sample collection, the sample information tag should contain the information such as the time and place of sampling. The depth of sampling must also be chosen with care. In order to avoid change of concentration and the pH which may change during sunny days, it is preferable to sample in the first

half of the morning[138].

However, sampling and sample pre-treatment depends on the nature of sample, type of parameter required and the purpose of analysis. Sampling stations on rivers should be located along the axis of flow of the rivers.

2.3.1 SAMPLE CONTAINERS

Contamination of the sample may come from the container, therefore a great care needs to be taken when preparing the container for sample collection. For oil in water analyses, glass bottles are preferred with glass stoppers. Plastic caps are to be avoided because of contamination of the samples by plastic. Cap liner should be avoided, and cork stoppers should not be used (to prevent adsorption of oil).

The cleaning procedure often employed[139] involves washing of the glass container with soap and water, followed by acid washing with concentrated H_2SO_4 for 5 minutes. The bottles can then be properly rinsed with distilled water and

hydrocarbon-free water (obtained by redistilling distilled water over $KMnO_4$-KOH and pumped through a 9¼ cm by 2.5 cm preparative scale chromatographic column packed with XAD-2 resin). This is finally rinsed with singly distilled methanol and doubly distilled n-pentane

The aluminium bottle cap liners to be used must be properly cleaned with acetone. In the case of sea water, degreased tin foil is used in place of aluminium foil to avoid sea water corrosion of the aluminium foil.

Sediment samples can be taken in clean aluminium can or clean glass bottles or wrapped in aluminium foil.

2.4 SAMPLING AND SAMPLE PRESERVATION

2.4.1 SAMPLING

Water samplers of different shapes, sizes and materials for collecting samples for hydrocarbon analysis have been reported in literature. Levy[140] used a Niskin Sampler for collecting seawater

samples in the determination of conjugated polyalkanes and aromatic hydrocarbons by UV fluorescence spectrometry. These samplers were developed by Niskin and consists of a series of ten or more bottles arranged around a central axle. The lids of these bottles are closed by means of a rubber string or teflon coated metal spring inside the sampler. Niskin samplers are available up to 30 dm^3, but samplers with volumes more than 1.7 dm^3 have restricted openings with respect to their diameter, and are therefore not encouraged.

A simple and reliable equipment for collecting surface water samples for hydrocarbon analysis was designed by Zsolnay[141]. This device consists of a weighted frame which accomodates Merck reagent bottles of any shape or volume.

Nansen also designed some tube liquid samplers made of brass and painted with nickel, tin or silver. Modern types are coated inside and out with an epoxy resin or other suitable polymer, since the continued use of metals has been known to cause changes in the chemical composition of water. The use of metals was

also discouraged since the lids have to be greased from time to time and this is a source of gross contamination. Nansen bottles are now manufactured with plastic linings, mainly teflon or its homologues.

Some common water samplers are now available . They are made of special carboy glass. Usually, they consist of a support or holder for holding the collector (carboy glass). The holder may be in the form of a metal cage provided with a line which may be a polypropylene rope or narrow metal rod. The rope or line is used for lowering the sampler to the desired depth. There is also a mechanical system for shutting the lid at depth after the water has been collected. Figures 14 and 15 below show a simple device of this nature.

Other methods of collecting surface film samples and water samples at depths not too far into the water column include the use of 1 litre sampling bottles. The water samples are collected by attaching the bottle to a polypropylene line and immersing in water to the desire depth with the cover carefully placed to prevent surface water from entering. At the depth the cover is displaced for the bottle to be filled. After retrieving the bottle, part of the water is discarded to allow for expansion. The bottle was then tightly sealed with the glass cover.

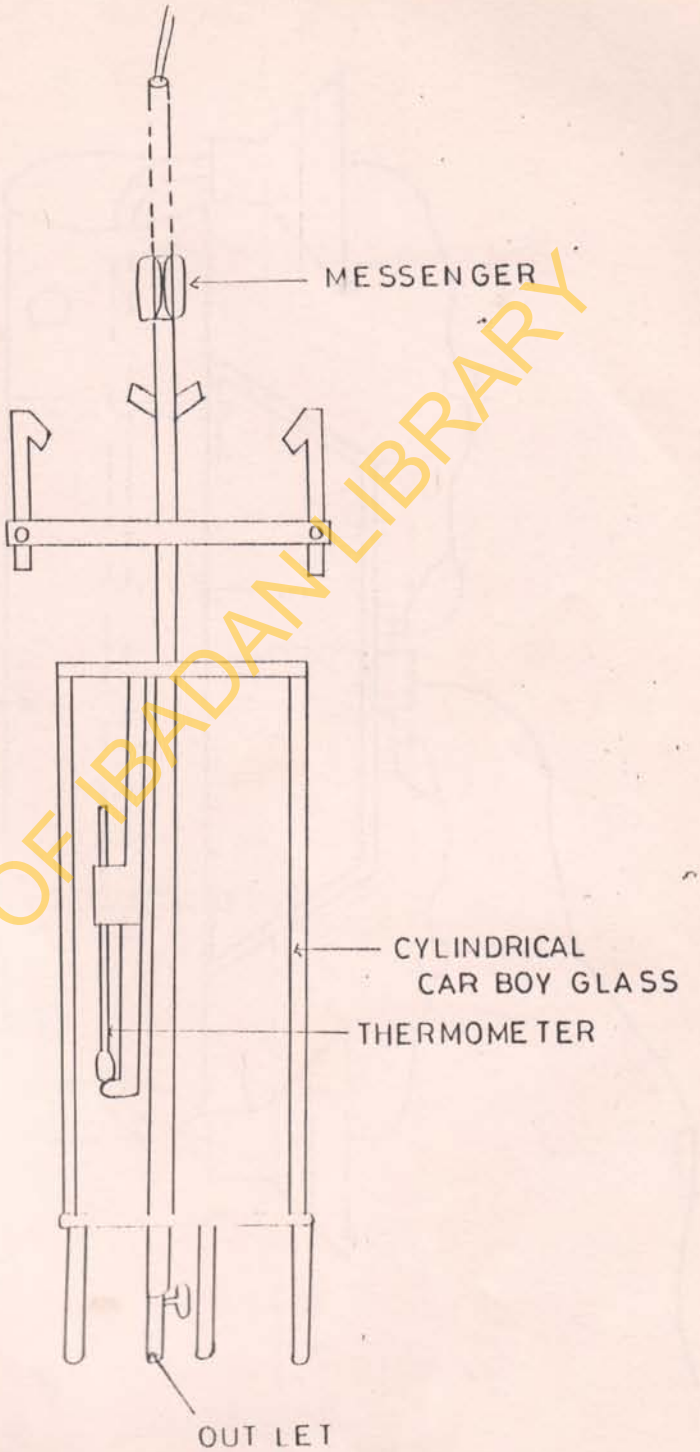


FIG-14 VERTICAL WATER SAMPLER

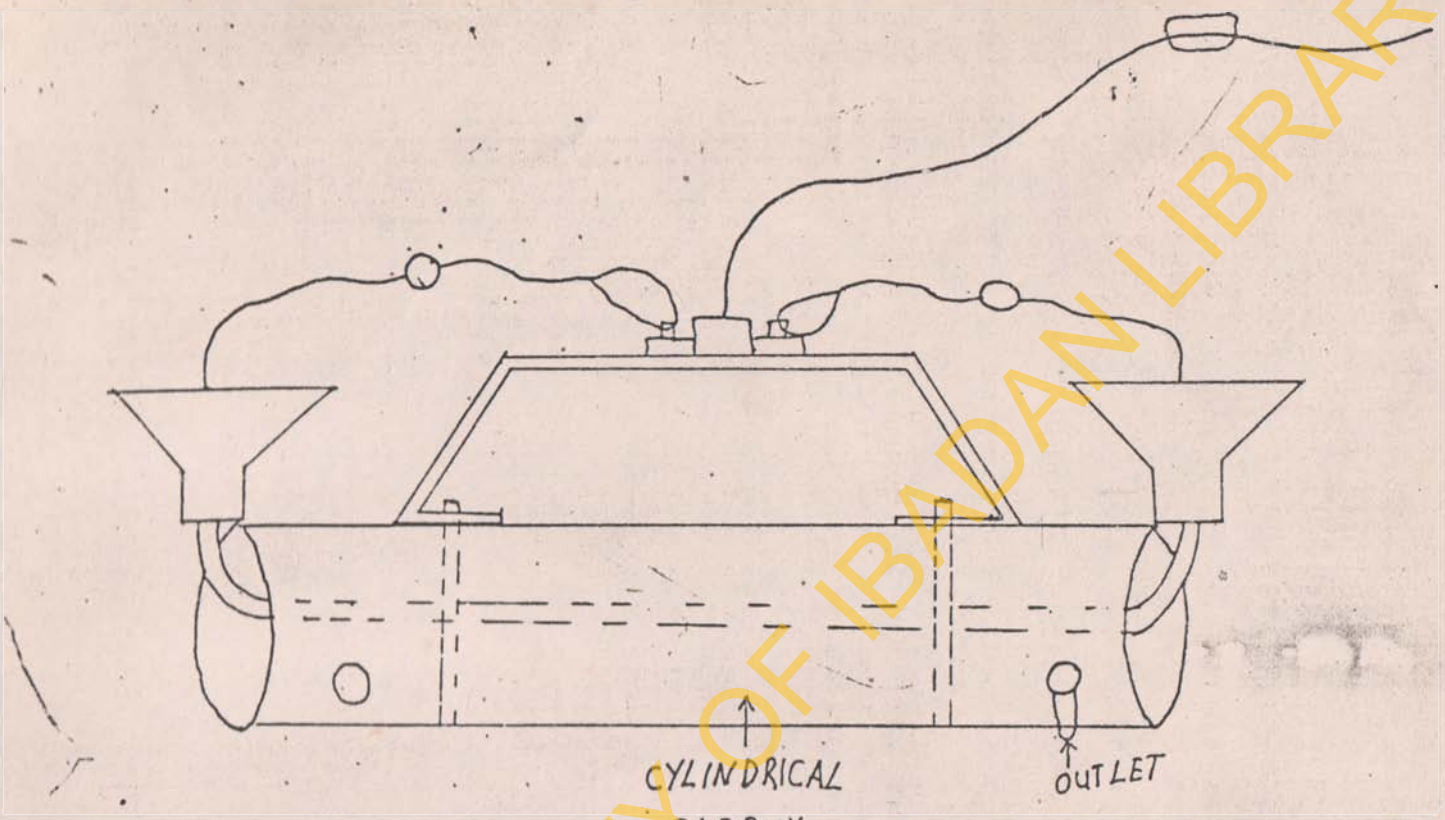


FIG. 15: HORIZONTAL WATER SAMPLER

2.4.2 IN-SITU SAMPLING SYSTEMS FOR WATER

In this system, hydrocarbons are extracted from water at depth by adsorption on a suitable material (e.g. polyurethane foam)[142]. This system gives greater flexibility in the volume of water sampled since the volume of water extracted is not limited to the sampler capacity as is the case with the ordinary devices mentioned earlier, rather, the volume of water extracted is a function of the rate at which water is pumped through the column of adsorbent material.

In-situ sampling also makes it possible to collect large volumes desirable for detailed chemical characterization, particularly of open ocean water with only trace levels of hydrocarbons.

The equipments required for in-situ sampling are also smaller than conventional large volume samplers since water is extracted at depth rather than collected. This limited size eliminates the need for special ship preparations and makes the equipment easier to handle.

In-situ sampling system also offers a high degree of contamination control. All immediate sources of

contamination, including collection vessels, storage vessels, and solvents have been eliminated.

However, the efficiency of this technique is limited by the affinity of the adsorbent material for individual hydrocarbon fraction.

2.4.3 PROBLEMS OF SAMPLING FOR WATER

The inhomogenous nature of the oil-water suspension makes it difficult to obtain representative samples. It is also difficult to obtain a sample that is truly representative of the conditions that exist at any given depth because oil particles are not uniformly distributed with respect to either their size or population density throughout the water column.

There is also the problem of determining the depths from which water samples should be obtained. However, most samples collected have been taken either from the surface, i.e. surface film samples or at 1 m depth[143]. Deeper samples may be collected depending on the type of sampling equipment available.

2.4.4 SAMPLING FOR SEDIMENT

Samples may be taken from shallow water areas by divers. The top sediment layer is scrapped into glass jars which are then closed under water to avoid contamination while retrieving.

Samples may be collected from boats or ships with dredge type instruments or grab samplers. Dredges are simple devices or apparatus for bringing up mud (sediment) oysters, specimens etc. from the bed of the sea, while grab samplers are mechanical devices for holding up or obtaining materials or objects. These are often used for obtaining surface samples and when deeper samples are required, dredges may be used.

Sediment corers are more sophisticated mechanical devices which allow sampling for horizontal layers of sediment.

Grab samplers include the Van Veen grab[144,145] (fig. 16). This consists of a pair of jaws of galvanised iron plates fitted with a metal band to ensure that the jaws fit correctly. The plates are attached by means of a strong chain to a mechanical device which permits opening and closing of the jaws.

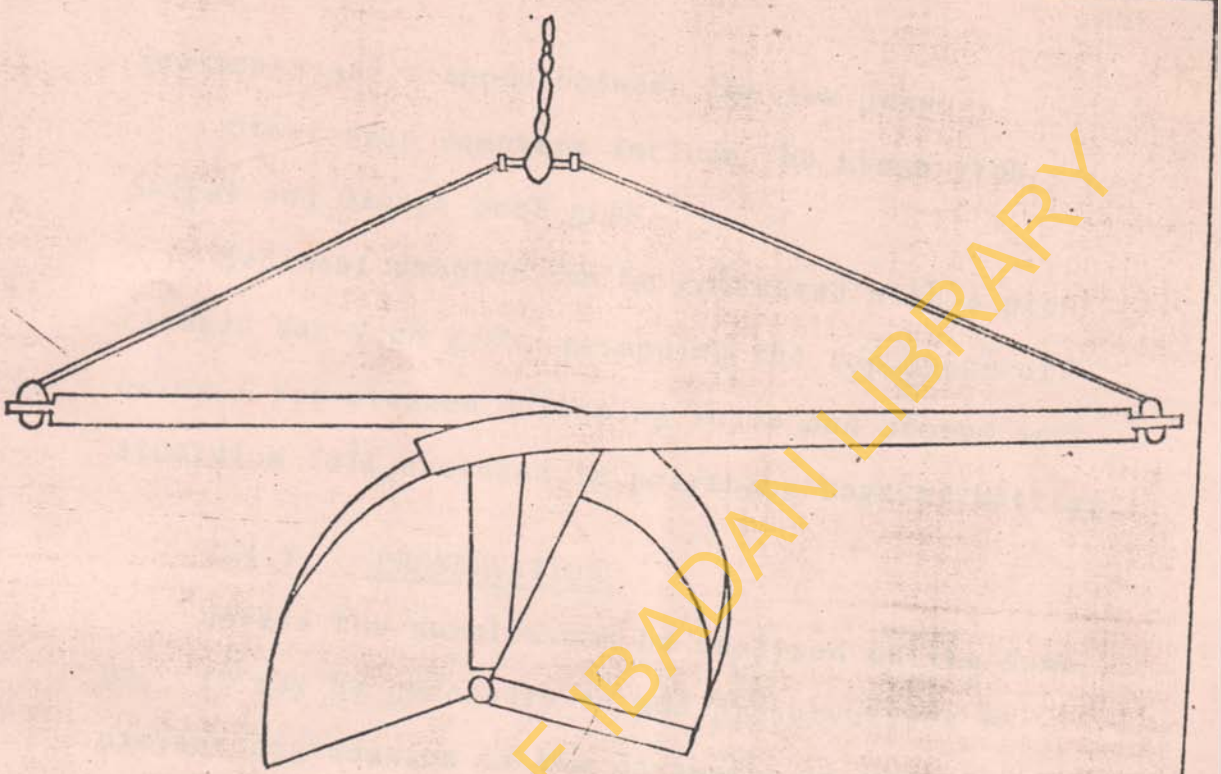


Fig. 16 : Van veen grab for sediment sampling (119)

Sediments are trapped between the two jaws.

Other grap samplers include the Ekman grab, Shipek and Orange peel grab.

Sediment samples can be collected with a pre-cleaned Van Veen grab, scrapping the top 3-5cm off using a pre-cleaned scrapping knife and stored in aluminium foil enclosed in polythene bags or bottles.

2.4.5 PRESERVATION

Unless the samples can be analysed on the same day, it may be necessary to add preservatives to prevent degradation of the parameter to be measured. The preservative used will depend on storage time and the particular parameter of interest, but for oil in water samples, acidification to prevent biodegradation is recommended. Acids commonly used include H_2SO_4 and HCl [146]. About 5ml of the acid to a litre of water sample to bring the pH to 2 is recommended [147,148]. Chloroform and tetrachloromethane can as well be used. These two solvents (5 ml per litre of sample), can concentrate the oil and prevent microbial degradation.

Mercuric chloride[149] (1.5mg saturated solution per litre) has also been used and if possible the sample may be stored at 4°C prior to analysis in the laboratory.

Sediment samples can be preserved in a deep freezer (-20°C) or in dry ice during field trips and transportation. Long term storage is usually carried out in a deep freezer maintained between -70°C and -80°C (150). This very low temperature is used to eliminate changes due to biological processes which can occur at "household" freezer storage temperatures. Sediment samples can also be preserved by freeze-drying whereby the water content is eliminated.

2.5 EXTRACTION OF SAMPLES

After collecting the samples, a suitable analytical method must be chosen for the analysis of the samples for the different hydrocarbon components present. Most techniques require the prior extraction of the hydrocarbons from the samples into an organic solvent. Extraction of hydrocarbons from all marine

samples has involved the same basic procedure.

2.5.1 EXTRACTION OF WATER SAMPLES

In water, sample may be extracted for total oil (i.e. both dissolved and adsorbed oil) or the sample may be filtered and analysis carried out on both the dissolved oil in water and the adsorbed oil on particulate matter separately.

Extraction of hydrocarbon materials from aqueous system usually involves the use of liquid-liquid extraction method, since it is the simplest and most direct method. It also has the advantage that blanks can easily be prepared. Single or mixed solvents are used as extractants.

Different organic solvents are used for the extraction of hydrocarbons. Each of them has its own merit and demerit, and also with different levels of efficiency. While some are safe to handle e.g. methanol, hexane, methylene chloride and freon 113 (trichloro trifluoro ethane (TCF). Others are toxic e.g. tetrachloromethane, chloroform and benzene

Some of the organic solvents that are commonly used include hexane, tetrachloromethane, methylene chloride, freon 113, chloroform, diethylether methanol, benzene and toluene[151,152].

2.5.2 DETERMINATION OF VOLATILE HYDROCARBONS IN WATER

The methods for determining volatile hydrocarbons in water differ from those used for analysing the high molecular weight fractions, mainly in the extraction technique.

In headspace sampling, dissolved hydrocarbons are stripped from solution by purging with a suitable carrier material. Inert gases and purified air are suitable materials for the stripping procedure. Purified hydrogen may also be used. The type of stripping material used and the carrier gas flow rate chosen for a particular assay have to be optimised. Stripping of hydrocarbons from water can be carried out at room temperatures or at elevated temperatures say 70°C and above, but usually between 70°-90°C.

May et.al.[153] used purified nitrogen gas as stripping material at 150 ml/min. for two hours, followed by another period of two hours at 70°C, using the same flow rate. The first stripping was done at room temperature. The stripping time used depends on the volume of liquid sample and the carrier gas flow rate. It is also a function of the hydrocarbon boiling range to be extracted.

Swinnerton and Linnenbon[154] used purified Helium gas at 50 ml/min. to extract C_1-C_4 hydrocarbons. The stripping procedure was carried out for only 15-20 minutes, because of the narrow hydrocarbon range extracted.

After the stripping procedure, the hydrocarbon rich gas is passed through an adsorbent material on which the hydrocarbons are trapped. Activated carbon is the most widely used adsorbent and has a number of advantages over most materials. It is chemically stable and does not release substances that would result in contamination. Activated carbon is also thermally stable, thereby permitting desorption of adsorbed materials by heat. However, heat

desorption is not encouraged as it may lead to loss of volatile fractions.

Generally, adsorbent materials should have good pure characteristics such as a high surface area. They should be chemically stable and should not release materials which could lead to contamination. Their affinity for hydrocarbons should not be so high that desorption becomes only partially completed.

2.5.3 COUPLED COLUMN LIQUID CHROMATOGRAPHY

This is a method developed for the determination of both the low molecular weight (volatile) and the high molecular weight (non-volatile) hydrocarbons in water samples with minimum loss of the volatile fraction. It is possible to analyse a given water sample for both volatile and non-volatile hydrocarbons by dynamic headspace sampling followed by coupled column liquid chromatography.

After headspace sampling of the liquid sample, the volatile hydorcarbons are trapped on an adsorbent material while the sampled liquid is extracted by pumping through a chromatographic pre-column. A

stainless steel column (6.5 x 0.6 cm) packed with a 37-50 unipellicular (superficially porous) support with bonded C_{18} stationary phase was used by May et.al.[153] (fig. 17).

The pre-column is attached to a liquid chromatograph capable of gradient elution, so that the effluents from the pre-column passes to the analytical column. The liquid chromatographic column used here is made of stainless steel (30 x 0.6 cm) and packed with a 10 μm micro-particulate (totally porous) support; also with a bonded C_{18} stationary phase (μ Bondapak C_{18})[155].

Elution of adsorbed hydrocarbons from the analytical volume is carried out with 30:70 (v/v) methanol-water mixture at 3 ml/min. with the gradient programmed to increase the percentage of methanol in the mobile phase to 100% in 40 minutes. The effluent from the analytical column is then analysed as appropriate (e.g. by UV, fluorescence, or MS).

The main advantage this technique has is that liquid-liquid extraction of hydrocarbons from the sampled liquid is avoided. This minimises the

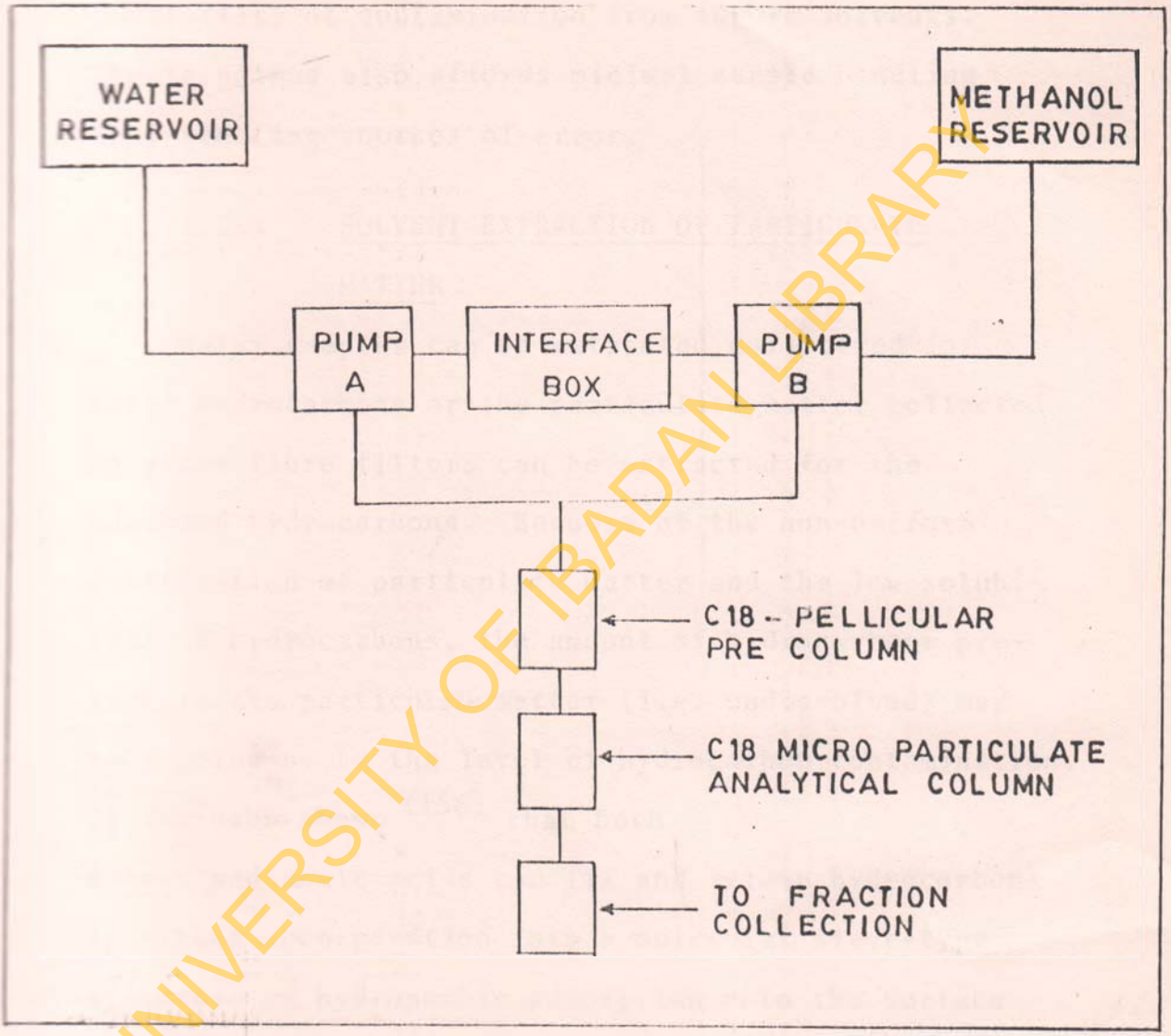


Fig. 17: Flow diagram for coupled liquid column chromatographic analysis (130)

possibility of contamination from impure solvents. The technique also affords minimal sample handling thus reducing sources of error.

2.5.4 SOLVENT EXTRACTION OF PARTICULATE MATTER

Water samples can be extracted unfiltered for total hydrocarbons or the particulate matter collected on glass fibre filters can be extracted for the adsorbed hydrocarbons. Because of the non-uniform distribution of particulate matter and the low solubility of hydrocarbons, the amount of hydrocarbons present in the particulate matter (i.e. undissolved) may be a guide as to the level of hydrocarbon contamination. It has been shown [156] that both fulvic and humic acids can fix and retain hydrocarbons by either incorporation into a molecular sieve-type structure or hydrophobic adsorption onto the surface of these humic materials. It has also been reported reported[157] that up to 50% of the organic material in sewage effluents may play a major role in the transport and deposition of hydrocarbons

introduced by waste water effluents into estuaries and coastal waters.

For these reasons, particulate matter are collected on pre-combusted Gelman type A/E glass fibre filters held in millipore stainless steel filter holders and stored at -20°C in pre-cleaned mason jars with teflon linen caps and dried before extraction[158,159].

The filter can be extracted in soxhlet extractor with hexane for 4 hours and then with chloroform for 4 hours more. The extracts are combined and the solvent removed[160]. Blanks can also be evaluated by extracting unused filters and subjecting them to the same analytical scheme.

For total hydrocarbons, sample volume of between 500ml and 1 litre are usually collected. The sample may be extracted immediately after collection (i.e. on board) or about 10 ml of hexane may be added to the sample in the bottle (the organic components will be concentrated in the hexane layer) and stored on board at -5°C.

2.5.5 SOLVENT EXTRACTION OF WATER

Different solvents have been used individually or in admixture for extraction of petroleum hydrocarbons in water. The commonly used solvents are pentane, hexane, benzene, tetrachloromethane, trichlorotrifluoroethane and methylene chloride.

Extraction of oil from water with hexane was carried out by Burns and Villeneuve [161] using a sample-solvent ratio of about 50:1. Two or three extractions were carried out on each sample (500 ml). It was reported that about 80% recovery can be obtained for total hydrocarbon with hexane as extractant.

At the end of the extraction exercise the combined hexane extract can be freed from the residual water by running the extract through a funnel containing anhydrous sodium sulphate on glass wool. What is collected here is then evaporated at 50°C with nitrogen gas, on a thermostically controlled water bath.

Gearing, J. [162] extracted water and sediment samples with hexane and concluded that fresh

hydrocarbons may be extracted much more efficiently by hexane while not efficiently extracting weathered or indigenous hydrocarbons. This discrimination could be of practical importance when the interest is mainly on recently added hydrocarbons.

Extraction of water sample with tetrachloromethane (CCl_4) can be performed in two ways, namely, liquid-liquid extraction of water sample with CCl_4 and polyurethane foam adsorption followed by soxhlet extraction with CCl_4. Both methods are oil preconcentration techniques.

In the liquid-liquid extraction technique about one litre of water sample is required for the extraction. The extraction is carried out in a two-litre separatory funnel with 30 ml CCl_4 added for each extraction[163,164]. The separatory funnel with its contents is subjected to 30 seconds agitation and 3 minutes settling period, the non-aqueous phase is then drained through a funnel containing about 30g of anhydrous sodium sulphate over a glass wool plug and collected in a 100 ml volumetric flask. The extraction step is

then repeated twice more. The sodium sulphate is rinsed with 5 ml of CCl_4 and added to the extracts.

The polyurethane foam adsorption method required polyurethane discs for the collection of samples[165]. About 1-5 litres of water is passed through the foam in a stainless steel holder and then the retained oil is extracted in a soxhlet apparatus with CCl_4. There is need for new foam disc to be cleaned before use by Soxhlet extraction with CCl_4 for 4-6 hours in order to reduce blank values to acceptable levels. It has been shown that recoveries of oil were greater than 85% for those concentration above 5 mg per litre.

Gruenfeld[166] has worked on dispersed oil in water using trichlorotrifluoroethane (TCF) as an extraction solvent. This solvent is particularly recommended for extracting dispersed oils from water, because it is virtually as efficient for these extractions and as usable for the Infrared (IR) determinations of oil as CCl_4. It is especially preferable to CCl_4 in situations where adequate

ventilation may be lacking, such as in some mobile laboratory and field use.

The recommended procedure for extracting dispersed oil from water is the addition of 5 ml of 50% H_2SO_4 and 5g of NaCl to 1 litre samples. Extraction is carried out with four 25 ml portion of TCF in 2-litre separatory funnels. The acidity is checked ($pH < 3$) prior to solvent extraction and completeness of extraction should be evaluated. Sea-water can be analysed without addition of NaCl.

The TCF layer from the separatory funnel is drained through a funnel containing solvent-moistened filter paper into a clean tared distilling flask. If a clear solvent layer cannot be obtained, 1g of Na_2SO_4 is added to the filter paper cone and slowly drain the emulsified solvent onto the crystals. The extraction procedure is repeated twice more, and the combined extracts is transferred to the tared distilling flask and the filter washed with an additional 10 to 20 ml TCF. The TCF is evaporated under nitrogen. The residue is cooled in a desiccator for exactly 30 minutes and weighed. This can then be

cleaned up for the hydrocarbon determination.

Kennicutt and Jeffrey[167] used chloroform to extract water sample initially sterilized by the addition of chloroform (5 ml per litre of sample and 3-5 ml of concentrated HCl to maintain pH at 2). A sample to solvent ratio of 70:1 was used for each extraction.

Direct extraction of water with dichloromethane for total hydrocarbons was carried out by Farrington et. al.[168]. Table 16 below compares the concentrations of filterable (particulates) and filter-passing oil and unfiltered samples.

Concentrations of filterable and filter-passing oil compared to concentrations obtained if water is unfiltered. All concentrations (µg/100ml) were obtained by fluorescence spectroscopy. The difference of the means was not significant at 95% level when estimated with a t-test.

The summary of some analytical methods for determining petroleum hydrocarbons in water is set out in Table 17 below.

TABLE 16: RELATIVE CONCENTRATIONS OF OIL IN FILTERABLE, FILTER-PASSING AND UNFILTERED SAMPLES (BY FLUORESCENCE SPECTROMETRY)(160µg/100 ml.

Sample	Filterable (Particulates) (A)	Filter Passing (B)	A+B	Unfiltered
1	22.2	4.8	27.0	23.9
2	14.8	4.7	19.5	24.2
3	19.2	5.2	24.4	23.2
4	15.8	4.5	20.3	22.8
5	16.4	4.2	20.6	22.5
6	11.8	3.6	15.4	18.0
7	11.8	3.3	15.1	18.3
8	11.8	4.1	15.9	18.0
9	13.8	4.5	18.3	14.1
10	12.2	3.7	15.9	17.3
Mean			19.2	20.2

TABLE 17. ANALYTICAL TECHNIQUES FOR THE DETERMINATION OF HYDROCARBONS IN WATER (11)

Technique	Component Determined	Sample Size (g)	Advantages	Disadvantages	Equipment (Approximate Cost in Dollars)	Analysis Time Operator (Elapsed)	References
C_1-C_{10} Hydrocarbons							
Gas equilibration	Individual hydrocarbons and hydrocarbon type	50-250ml	Parts per trillion sensitivity, separates hydrocarbons from nonhydrocarbons. No sample preparation	Analysis time relatively long	Gas chromatographs (15,000)	10-30 min (0.5-2 h)	Mc Aulifie, 1969, 19
Gas stripping	Individual hydrocarbons and hydrocarbon type	1-2 liters	Measure background levels of C_1, C_2, C_2, C_3, C_3, i-, n-C_4 in open ocean waters	Nonhydrocarbons can interfere. Analysis time relatively long	Gas chromatograph (15,000)	10-30 min (0.5-1 h)	Swinnerton and Linnerbom, 1967
Vacuum degassing	Individual hydrocarbons and hydrocarbon type	4-20 liters	As above, can be used to continuously measure hydrocarbons in water	Normally used to measure C_1-C_4 in sea-water. Equipment expensive	Complete system-pumps, gas chromagraph (300,000; 2.500 per day rental)	3-30 min (3-30 min)	Schink et al., 1971 Fort et al., 1973
C_{11} plus Hydrocarbons							
Gravimetric	Nonvolatile extractables	1-4 liters	Simple minimum equipment	Nondiagnostic, conc. between 0.3-1,000 mg/liter	Glassware, balance (1,000)	20 min (40 min)	Environmental Protection Agency, 19
UV absorption spectrometry	Conjugated polyalkenes, aromatics	1 liter	Useful for conc. 10 g/litef	Not very diagnostic, less sensitive than fluorescence spectrometry. No information on saturated HCs	UV absorption spectrometer (3,000-5,000)	20 min (20 min)	Levy, 1971
UV fluorescence spectrometry	Unsaturated compounds, aromatic	1 liter	Useful for conc. 10 g/liter; measure HCs in open ocean waters	Not very diagnostic. No information on saturated HCs. Fluorescence may be quenched.	Fluorescence spectrometer (10,000)	20 min (20 min)	Levy, 1971; Thur- Knight, 19 Zitko and Carso-1970
Infrared spectrometry	Methyl, methylene, carbonyl, aromatic Total hydrocarbons	1-4 liters	Information on functional groups. Identify contaminants such as silicones, plasticizers	Concentrations 3 g/liter, 0.1 mg. Not very diagnostic	Low or high resolution infrared spectrometers (3,500-35,000)	5-10 min (20-40 min after separation from water)	Brown et al. 19 Kawahara, 196 Simard et al.
Gas chromatography (low resolution)	Hydrocarbon profiles and boiling range of sample, C_{11}-C_{50}	1-20 liters	Quick examination, reasonably diagnostic	Little information from highly weathered of biodegraded oils	Gas chromatography (10,000-15,000)	10 min (2 h)	Adlard et al. 19 Brown et al,. Duckworth,1 Ehrhardt and 1972
Gas chromatography (high resolution), special detectors	More detailed hydrocarbon profiles. Sulfur profiles, individual hydrocarbon ratios, C_{11}-C_{40}	1-20 liters	Better diagnostic power. Sulfur compounds assist in identification	Little information from highly weathered or biodegraded oils	Gas chromatograph (15,000-20,000)	10 min (2 h)	Kreider, 1971; 1973; Ramsd Wilkinson, 19 Zafiriou et al
Mass spectrometry	Hydrocarbon types	1-10 liters	Provides complete HC type information	Complex and expensive equipment. Requires computer interface	Low resolution, mass spectrometer (60,000). High resolution, (80,000-150,000)	10 min (2 h)	Aczel et al. 19 Hastings et al Hood and O 1959; Robin 1971
Gas chromatograph, mass spectrometer	Specific hydrocarbon, C_4-C_{30}	1-10 liters	Identify and measure individual hydrocarbons	Very comples and expensive equipment	Add gas chromatograph cost to above	2-4 h (2-4 h)	

(11) Hydrocarbons are extracted from water and then separated from nonhydrocarbons by column or thin layer chromatography.

2.5.6 COMMENTS ON THE SOLVENT EXTRACTION OF WATER SAMPLES

As earlier stated, extraction step is a major factor in obtaining a reliable result. The pollutant to be determined must be isolated from other materials which can serve as contaminants.

In the choice of solvents for extraction process tetrachloromethane (CCl_4) is very efficient but toxic[170]. Methylene chloride or trichlorotrifluoroethane can be used to provide the same level of effitiency. In the choice of methylene chloride as a substitute for CCl_4, the factors in its favour are its lower toxicity and lower boiling point (40.1°C compared to 76.8°C). A comparison of the two solvents indicates that using CCl_4 causes about half the fluorescencing material in seawater (both raw and spiked with fresh crude oil) to be lost, most probably during the evaporation step (Table 18).

In the case of trichlorotrifluoroethane, it is also safer than CCl_4. They have been found to be about equally effective for extracting the dispersed oils from water. Virtually the same number of extractions

TABLE 18

COMPARISON OF METHYLENE CHLORIDE (CH_2Cl_2) AND TETRACHLOROMETHANE (CCl_4) AS SOLVENTS FOR EXTRACTING PETROLEUM RESIDUES FROM SEA WATER COLLECTED ALONG THE HALIFAX-BERMUDA SECTION. USING T-TEST FOR PAIRED VARIABLES-THE DIFFERENCE WAS SIGNIFICANT AT THE 95% LEVEL.

EQUIVALENT mg OIL/LITER

CH_2Cl_2 EXTRACT	CCl_4 EXTRACT
8.0	0.6
2.3	0.5
0.3	3.4
1.9	0.2
3.6	1.3
1.8	0.0
6.1	0.2
0.9	0.6
1.5	1.1
1.3	0.2
4.3	1.7
1.4	0.5
2.0	0.7
0.7	0.8
1.5	0.6
2.5	0.1
0.0	0.4
0.0	0.0
$\bar{x}$ = 2.56	0.72

with each solvent effected removal of the oils. In addition TCF has the following advantages over other solvents.

(1) It is non-polar and is not a hydrocarbon.

(2) It is heavier than water, which enables it to be removed simply with a pipette from the bottom of the extracting vessels.

(3) It boils at 47.6^{o}C enabling it to be concentrated quite readily.

(4) It is transparent to UV light at 254 nm.

It has also been found out that while non-chlorinated solvents such as hexane and pentane are excellent for extracting petroleum hydrocarbons from water, having a specific gravity of less than one, they are difficult to recover from large volumes of seawater (2 litres) under difficult field conditions.

2.5.7 EXTRACTION OF SEDIMENT

In the techniques applied to sediments, the extraction step varied from a simple elution with petroleum ether of a column containing the dry sample to the long Soxhlet

extraction with methanol[172,173]. Digestion method with methanolic potassium hydroxide has also been used. Sediments can be extracted wet or dry.

Extraction of hydrocarbons from sediments usually requires more vigorous techniques than water sample because the hydrocarbons are incorporated into the sediment matrix. In the analysis carried out by Oudot et.al.[174], frozen samples which were thawed and dried at 60°C for 48 hours were used. The extraction step involved chloroform as solvent, and the sample was extracted for 10 hours in a Soxhlet apparatus. In some samples, internal standards (1μg g^{-1} dry weight n-eicosene and 1 μg g^{-1} dry weight phenanthrene) were added prior to extraction extraction[175]. The total lipid extract obtained was dehydrated and purified by percolating through Na_2SO_4 over florisil (magnesium trisilicate, 60-100 mesh) column.

Lake et. al.[176] had worked on sediment for the determination of petroleum hydrocarbon level. The sediment sample analysis involved

drying the sample at 105°C in an oven and grinding the sample in a mortar. The organic matter content was determined in a sample aliquot as ash free dry weight at 550°C and is expressed as a percentage of dry weight. The 'oil and grease' content was determined by extracting dried (105°C) pulverized sediment with petroleum ether (b.p. 40°C) in a Soxhlet apparatus for 2 hours. After drying the extract at 105°C, then it is cooled and weighed to a constant weight. This is called the extractable amount, considering that pigments and other natural organic compounds are also included.

Giger and Blumer (138) Blaylock, Bean and Wildding 173 extracted partially thawed sediment sub-sample in pre-combusted glass Soxhlet thimbles for 18 hours with 250 ml of methanol/benzene (2:3 v/v). After cooling, the extract was washed with 1N HCl saturated with NaCl and the benzene layer was separated. The aqueous layer was separated twice with 75 ml of pentane and the combined benzene and pentane extracts were washed again with the acidic saturated salt solution. The organic layer was separated and dried

over anhydrous Na_2SO_4 overnight. Activated copper was used to remove sulphur.

Some of the other methods tried by different chemists are displayed in Table 19 and the comparative results of the extraction efficiency with internal standard were found to vary from about 30% (Shaw method) to almost 100% (Blaylock method).

However, from the variety of analytical methods, apparently no standard method of analysis has been selected for particular types of marine sediment sample. Instead, interlaboratory calibration studies have been reported. Results of such studies indicated that the analysis of marine sediments poses many difficulties. Concetnration values for a given sediment sample may vary by a factor of 30 for "polluted" samples and by a factor as great as 135 for trace levels (ug kg^{-1}) of hydrocarbon in sediments. The difficulty of preparing homogeneous sediment samples is often stated as one of the reasons

TABLE 19

ANALYTICAL TECHNIQUES FOR THE DETERMINATION OF HYDROCARBONS IN SEDIMENT

	APPLICATION	SAMPLE NATURE	EXTRACTION TECHNIQUE		PURIFICATION TECHNIQUE		COMPONENT DETERMINED	AUTHOR
			EQUIPMENT USED	SOLVENT SYSTEM	COLUMN FORM	ELUTION		
a	SEDIMENTS	Dry at 80 °C	1 x 10 cm column	Petroleum ether	-	-	Total Hydrocarbons (THC)	171
b	SEDIMENTS	Wet	Soxhlet	MEOH, n-pentane	SiO_2/Al_2O_3 3/2 (v/v)	4 bed volume of n-Pentane	Total Hydrocarbon (THC)	53
c	SEDIMENTS	Wet	Soxhlet	MEOH, n-hexane	-	-	Petroleum like fraction in the lipids	172
d	SEDIMENTS	Freeze-dried	Soxhlet	MEOH,, benzene n-pentane	1 x 30cm, 10g SiO_2/ 10g Al_2O_3	70ml n-pentane, 100ml benzene	HC in two fractions: saturate and aromatic	173
e	SEDIMENTS	Wet	Grinding with ashed $MgSO_4$ and ashed grinding sand	n-hexane	3 x 15 cm SiO_2	1.5 bed volume of n-hexane	THC	179
f	SEDIMENTS	Wet	waring blender	$CHCl_3$,MEOH, n-pentane.	1x35 cm 15g SiO_2	100ml n-pentane 50 ml 25% benzene in pentane	HC in two fractions: aliphatic and aromatic	180
g	SEDIMENTS	Wet	Shaker	n-pentane	SiO_2/Al_2O_3 3/2 (v/v)	4 bed volume of n-pentane	THC	182

for poor agreement of results between participating laboratories, but this was shown in the study carried out by Wong and Williams[188] as unlikely to be the prime cause of such large variations.

In the work of Wong and Williams[188], three extraction procedures were studied namely (Table 20):

(1) Digestion by methanolic KOH and further extraction with methanol

(2) Soxhlet extraction with chloroform[132] and and

(3) Soxhlet extraction with tetrachloromethane[189,190].

The results obtained were also given in Table 20 below.

The sediment sample used was thoroughly mixed in order to get a homogeneous sample, which was divided into two portions. One portion, designated wet sediment, was stored in a freezer at a temperature maintained at $0^{o}C$. The other portion, designated the dried sediment, was transferred to aluminium foil and dried in an oven at $45^{o}C$ for two days. The dried

TABLE 20: COMPARISON OF EXTRACTION METHODS FOR HYDROCARBONS IN MARINE SEDIMENTS

Procedure	Sample Nature	Extraction Technique	Purification Technique: Column Form	Purification Technique: Elution	Results $\mu g g^{-1}$
1. Methanolic-KOH digestion and extraction.	Wet	Digestion of sediment sample with 50ml methanolic 1N KOH for 24 hours. Followed by soxhlet extraction with methanol for 24 hours. The combine extract was extracted 4 times with a total of 200ml of 5% (V/V) benzene in pentane after the addition of 5ml of distilled water.	1.5x20cm 1cm Al_2O_3 (120 mesh)	10ml of 20% (V/V) benzene in pentane 30ml of pentane.	1. For wet sediment sample; mean value obtained for total organic extract (TOE) i.e. pre-column purification = 7714±342 ugg^{-1} dry weight, value obtained for post column purification = 6349±508.
		The organic extract was dried with sodium sulphate overnight and then evaporated to 1ml in rotary evaporator at 30°C. The solution was finally evaporated to dryness in a vial under pure nitrogen gas. The residues redissolved in 2ml of n-pentane. One ml of the solution was transferred to a column for purification. The other portion was used to determine the total organic extract before column purification.	10cm SiO_2 (100mesh) 5% deactivation.		
	Dry	5ml of distilled water was added to the methanolic-KOH solution to prevent transesterification. All other steps were as given above.			2. Dried sediment: TOE=6271+265; post column purification = 5330+183.

Procedure	Sample Nature	Extraction Technique	Purification Technique: Column Form	Purification Technique: Elution		Extract 1: Pre-column	Extract 1: Post-column	Extract 2: Pre-column	Extract 2: Post-column
2. Soxhlet Extraction with Chloroform	Both wet and dry	Extraction with 150ml of chloroform in soxhlet extractor. After 24 hours, 75ml of the $CHCl_3$ was withdrawn and replaced with 75ml fresh solvent. The operation was repeated after another 24 hours extraction. Total extraction time was 72 hours with a total of 300ml solvent = Extract 1.	As above	As above	Wet sediment.	6154± 2971	3739± 1470	1856± 1339	992± 1011
		The sample was extracted for further 72 hours with 300ml of fresh solvent following the same procedure as described above = Extract II.			Dried	8226± 381	4904± 303	205	86
3. Soxhlet extraction with tetrachloro methane.	Wet and dry	As above in procedure 2 with CCl_4 as solvent.	As above	As above	Wet sediment.	4604± 1462	2188± 869	2316± 1175	1041± 628
					Dried sediment.	6358± 201	4438± 282	82	39

sediment was ground to fine powder in a glass mortar, kept in a small reagent bot le and stored in a desiccator.

Prior to analysis, the wet sediment was thawed at room temperature for several hours, and the required amount of sediment taken out and weighed. About 8-10g of wet sediment or 3-4g of dried sediment were used for each determination. The water content of the wet sediment was taken as the loss in weight on drying at 105°C for 24h. The extraction techniques and analyses were given in Table 20.

The results of the 3 extraction procedures for dried sediment were comparable and with reasonable precision, although the hydrocarbon values (i.e. post-column values) obtained from procedure 2 and 3 were slightly lower than that from procedure 1. A closer look at the results revealed that drying at 45°C resulted in the loss of the more volatile organic components of the sediment sample. Thus, the total hydrocarbon value of a dried sample is about 16% less than that of a wet sample, based on results from procedure 1.

For wet sediment, the precision of procedure 1 is fairly good. However, procedures 2 and 3 gave values that were much lower than that of procedure 1. Furthermore, replicate determinations gave greater variability. Reasons advanced for this are sample inhomogeneity and the effect of water in the sediments with the latter being the major factor.

Explanation: When fresh, the water in the sediment was probably well mixed and bound to the sediment sample matrix, and was not readily absorbed by the extraction thimble. As a consequence, "wetting" of the sediment by the solvent is inhibited, thus reducing the contact of the solvent with the sediment. After storage of $0^{o}C$ for several weeks and subsequent thawing, some of the water present was reported to have separated from the sample, presumably due to a freeze-drying effect, followed by crystallization on the walls of the container during storage. That the physical state of the water present did affect the extraction efficiency was borne out by comparing concentration figures of Extract I and Extract II for procedures 2 and 3 (Table 20). The extraction efficiency

was lowest for fresh samples for both solvents, chloroform and tetrachloromethane

Chloroform came out to be more efficient in extracting hydrocarbons than tetrachloromethane for wet sediment samples. In the case of dried samples, both gave values of hydrocarbons close to those found using procedure 1. Chloroform, being more polar than tetrachloromethane extracted more lipid material from both the wet and dried sediment samples.

Good recoveries were obtained for the three hydrocarbon compounds used. The results are given in Table 21. However, the good recovery merely showed that losses during operations for the three extraction procedures were minimal. It did not reflect the extraction efficiency of the procedures studied.

An earlier attempt has been made by the National Bureau of Standard to compare results for individual hydrocarbons. Collaborating laboratories (8) were asked to report identities and concentrations of the three most abundant aliphatic and

TABLE 21 PERCENT. RECOVERY OF HYDROCARBONS ADDED TO SEDIMENT

Method	No. of run	C_{13}	C_{22}	Phenanthrene
Extraction Procedure 1				
(CH_3OH-KOH digestion and extraction)	2	94±6	95±4	91±8
Extraction Procedure 2				
(Soxhlet $CHCl_3$ extraction)	2	92±5	91±3	96±3
Extraction Procedure 3		83±12	92±2	94±1
(Soxhlet CCl_4 extraction)				

aromatic hydrocarbons, respectively. The intercalibration material consisted of two intertidal sediment samples from the Prince William Sound and North eastern Gulf of Alaska, U.S.A. The sampling sites were Hinchinbrook Island; this site is at the ocean entrance to the Prince William Sound and is constantly being washed with water from the Gulf of Alaska.

Katalla River; this site is downstream from a known oil seep and provides samples with hydrocarbons known to be of petroleum origin.

The analytical methods employed by each of the participating laboratories are summarized briefly in Table 22.

The results of homogeneity studies by National Bureau of Standards (NBS) utilizing the dynamic headspace sampling technique showed that the precision was better for the Katalla sediment than for the Hinchinbrook sediment. (Katalla 910 mg/kg $\pm$ 25% n = 9 and Hinchinbrook 420 g/kg $\pm$ 30% n = 12). The average recovery of phenanthrene internal standard used for the two sediments was 83% for Katalla and 41% for Hinchinbrook. These results (recovery) were used to

TABLE 22: METHODS OF SEDIMENT ANALYSIS IN INTERLABORATORY CALIBRATION[187]

Lab NBS	Extraction	Separation	Gas Chromatography	
			Column	Standard
	(a) Dynamic headspace extraction of 100 g sediment in 500 mL pure H_2O. Volatiles trapped on Tenax GC adsorbent.		100 m SE-30 SCOT 80°C for 4 min - 275° at 4°/min.	Aliphatic and aromatic internal standard added prior to sample work-up at start of analysis.
	(b) Diethyl ether and methylene chloride Soxhlet extraction of 100 g wet sediment.	Liquid chromatography on µBondapak NH_2 to remove polar biogenic compounds	Same as above	Squalene internal standard added at start of analysis.
2	Diethyl ether extraction of 100 g wet, acidified sediment on ball-mill tumbler for 18 h.	Column chromatography on activated silica gel. Aliphatics eluted with petroleum ether. Aromatics eluted with methylene chloride in petroleum ether.	20-30 m SE-30 SCOT 60°C for 10 min - 250° at either 2 or 4°/min.	Hexamethylbenzene standard added prior to GC analysis
3	300 g wet sediment dried by washing with methanol. Reflux extraction with benezene-methanol (3:2) for 14 h. Saponification with 0.5 N KOH in methanol; extraction into benzene and taken to dryness. Residue taken up in hexane.	Column chromatography on alumina:silica gel (1:3). Aliphatics eluted with hexane. Aromatics eluted with benzene. Polar fraction eluted with methanol.	6 ft 4% FFAP on Gas Chrom Z. 80°C - 225° at 4°/min. or 6 ft 3% SP 2100 on Supelcoport 100°C - 225° at 4°/min.	External standard containing several aliphatic, aromatic, and olefinic hydrocarbons
4	250 g wet sediment extracted with methanol and benzene; methanol azeotrope. Reduced volume and extracted with hexane and methylene chloride. Reduced volume.	Organic extract partitioned in nitromethane:cyclohexane to give polycyclic fraction. Column chromatography on silica gel; eluted with hexane.	3% OV-17. 70°C - 300° at 8°/min.	External standard containing polynuclear Aromatic hydrocarbon.

TABLE 22 (contd.)

Lab NBS	Extraction	Separation	Gas Chromatography	
			Column	Standard
5	150 g dried sediment extracted with heptane on ball-mill tumbler for 4 h.	Column chromatography on alumina:silica gel (1:1) aliphatics eluted with heptane; aromatics eluted with benzene.	20 ft 5% eutectic ($LiNO_3$, $NaNO_3$, KNO_3) on Chromosorb G 150°C - 280°C at 20°/min.	Spiked blanks: C_{18}, C_{20}, phytane, anthracene, pyrene.
6	Freeze-dried sediment reflux extracted with toluene:methanol (3:7) for 14 h; sediment reextracted with hexane. Combined extracts saponified with KOH in methanol and toluene. Extracted nonsaponifiables into hexane.	Column chromatography on alumina:silica gel (1:2) aliphatics eluted with hexane; aromatics eluted with benzene.	5% FFAP on Gas Chrom Q 70°C - 270°C at 6°/min.	External standard C_{16}, C_{18}, C_{21}, C_{24}, C_{26}, C_{32}, pristane, phytane.
7	80 g wet sediment saponified in KOH: methanol under reflux for 24 h. Extracted into hexane.	Column chromatography on alumina:silica gel (1:1) aliphatics eluted with hexane; aromatics eluted with benzene.	OV-101 80°C for 2 min - 280° at 8°/min.	Spiked blank and n-alkane external standard.
8	100 g freeze-dried sediment reflux extracted with toluene:methanol (3:7). Extract saponified in 6N KOH:methanol:water; extraction into hexane.	Column chromatography on alumina:silica gel aliphatics eluted with heptane; aromatics eluted with benzene.	152 m stainless steel capillary coated with 10% Apiezon L. 155°C for 8 min - 280° at 2°/min.	External standard

explain the effect of the sediments' affinity for hydrocarbons - the Hinchinbrook sediments have greater affinity for hydrocarbons than the Katalla sediments. This may be due to the nature and level of organic matter present in the sediments.

The results of measurement of hydrocarbons in the gas chromatographic range vary widely among the eight laboratories, the agreement was better for the Katalla sediments than for the Hinchinbrook sediments. The procedure for gas chromatographic quantification was sited as one of the sources for variability of data. This may be due to the difficulty in quantifying low levels of hydrocarbons in samples.

The interlaboratory comparison carried out by Macleod et. al.[191] was an improvement over the previous one reported by Hilpert et.al.[187] in that the reported results for individual hydrocarbons were better (i.e. comparable). The methods used include Soxhlet, shaker/tumbler, reflux and sonication. The solvents were benzene, chloroform, dichloromethane, hexane, methanol and toluene. The

combination of soxhlet with hexane/methanol, reflux with methanol, soxhlet with benzene/methanol gave relatively higher results of individual hydrocarbons than others.

A summary of interlaboratory intercalibration exercises 1976-81 is given in Table 23.

TABLE 23: SUMMARY OF INTERLABORATORY INTERCALIBRATION EXERCISES 1976-1981

Name of Study	Sponsoring Organization	Sample Type	Analytical Basis of Data	No. of participating laboratories	Reference	Results
Santa Barbara Sediment	BLM	Sediment spiked with South Louisiana Crude oil	1. Saturated (f_1) and aromatic (f_2) hydrocarbons by gravimetric and GC analyses 2. Individual n-alkane concentrations 3. Individual 2-ring aromatics	12	Farrington (1978)	- Individual component concentrations vary by factors of 1-40 (generally 5-10) - Much less variability in gravimetric values for total fraction weights (1-4)
NBS Sediment	NBS/EPA/ BLM	Alaskan intertidal sediments	1. Total f_1 and f_2 by GC 2. Most abundant aliphatic (f_1) and aromatic (f_2) components 3. Identity and amount of PAH 4 rings and larger	8	Hilpert et al. (1978)	Large variability in all parameters reported ($1^\circ = \circ 25\%$)
NBS Mussel	NBS/BLM	Santa Barbara and Alaskan mussel	1. Total f_1 and f_2 by GC 2. Most abundant aliphatic (f_1) and aromatic (f_2) components 3. Identity and amount of PAH 4 rings and larger	8	Wise et al. (1980)	- Large variability in parameters ($\bar{x} = 40\%$) especially individual aromatic and saturated compounds

TABLE 23 (contd.)

Name of Study	Sponsoring Organization	Sample Type	Analytical Basis of Data	No. of participating laboratories	Reference	Results
Duwamish I	BLM/NOAA	Estuarine sediment	1. Individual aliphatic and aromatic components by GC (specified lists of components); statistical analysis	11	Brown et al. (1980); MacLeod et al. (1981a)	- Major improvements in consistency of parameters reported - Most values within a factor of two
Duwamish II	BLM/NOAA	Estuarine sediment (finer-grained)	1. Individual aliphatic and aromatic components by GC (specified lists of components); statistical analysis	9	MacLeod et al. (1981a)	- Comparable results achieved in spite of use of different extraction procedures
ICES	ICES	Crude oil Dried sediment Mussel homogenate	1. Analytical and reporting requirements not specified for advance; GC, IR, and UV used 2. Fluorescence data specified using IOC/WHO methods	25	Law and Portman (1981)	- Good comparisons of sediment fluorescence data due to pre-prescribed quantification method - Good comparisons of methodology differences - Poor results for tissues
IKU	IKU/ Norway	Homogenized seawater sediments and biota from experimental spill	1. GC quantifications of alkanes and aromatic groupings	3	Haegh et al. (undated)	- Data on sediments and organisms not comparable due to quantification method differences; data on seawater not reported on a consistent basis

TABLE 23 (contd.)

Name of Study	Sponsoring Organization	Sample Type	Analytical Basis of Data	No. of participating laboratories	Reference	Results
EPA-megamussel	EPA	Mussel homogenate	1. Individual alkane and aromatic components by GC	4+	No data	- Preliminary limited data shows good alkane and aromatic agreements (factor of <2)
IDOE-1,3,5	NSF	- 1,3: cod liver oil spiked with fuel and crude oil - 5: cod liver lipid extract spiked with distillate oil - tuna meal	1. Total petroleum by GC 2. Individual component, pristane	3	Farrington et al. (1976b)	- Good agreement on "total hydrocarbon" parameter (± 12%) - Mixed results on quantification of individual components

2.5.8 COMMENTS ON THE SOLVENT EXTRACTION OF SEDIMENT SAMPLES

Different results have been reported for various analytical methods of sediment analysis and because of the complexity of the composition of hydrocarbons in environmental samples, analysts have had to choose methods of extraction suitable to the particular range of compounds of interest in their research programmes.

Although no method has been declared as the best method or as the standard method over the others, some of these methods reviewed above have some advantages which can be utilized for more reliable results.

Most lipid extracts obtained with the methods used contain esters of fatty acids (e.g. waxes and glycerides). The esters often interfere with the isolation of alkanes and aromatic hydrocarbons. Saponification with potassium hydroxide breaks the esters in fatty acid salts and alcohols which are easily removed. This method also helps in removing the interference from sulphur which may be present in

the sediment samples. The method can be used alone without going through the activated copper procedure for removing sulphur from extracts.

The main problem with saponification method is that of transesterification of the existing esters to methyl or ethyl esters. Farrington (193) had noted that saponification in the presence of 25% water will reduce transesterification considerably. Complete saponification is confirmed by the absence of the carbonyl (C = O) absorption band for esters in the IR spectra of the material remaining after saponification.

On the other hand, if the work involves extraction of a wide range of samples, by a single procedure, then a Soxhlet extraction provides a suitable method for all types of environmental samples.

2.6. A RAPID FIELD METHOD FOR DETECTING OIL IN SEDIMENTS

There are a number of occasions where a rapid method of determining the relative concentration of oil in sediments under field conditions would be a valuable

operational tool. Conventional laboratory methods of detecting oil are not well suited to field use since they are time-consuming and require sophisticated equipment and skilled technicians. In the advent of an oil spill in coastal waters, it would be highly desirable to be able to trace the migration of the oil into the sediments in the field rather than have to wait for the result of laboratory analyses (194).

Procedure

A 5ml graduated beaker was carefully filled with sediments, and with spatula, the sediment sample was transferred to a 30ml beaker. An optional step involved the addition of 1g of Na_2SO_4 to the sediment sample with mixing. 2ml of hexane was pipetted into the 5ml sample-measuring beaker; stirred and poured into the 30 ml beaker. Sediment and hexane were thoroughly mixed for 1 minute. The hexane was then poured into a 5ml vial and the volume reduced to approximately 0.5ml under a stream of pure nitrogen gas.

A micro-sampling pipette was used to place 25 µl of the concentrated hexane extract on the active side

of the TLC, type SA chromatographic paper strip, approximately 1.5cm above the bottom of the paper. The spot was allowed to dry thoroughly. The development of the paper strip was carried out in a jar containing the developing solvent (35% petroleum ether - 65% benzene) for 45-60s. The strip was removed and allowed to dry and viewed under ultraviolet light. A reference sample of oil solution in hexane was carried through the same TLC procedure.

The presence of a blue fluorescent spot on the developed chromatogram is indicative of the presence of oil. The greater the intensity of the fluorescence, the greater the quantity of oil.

This method has been used on a variety of different crude oils, including empire mix, Saudi Arabian, Iranian, Nigerian and Venezuelan mixed with sediments of different composition. The TLC method has demonstrated the presence of oil in the samples [illegible]. The results of this technique has also been confirmed by a newly developed liquid chromatographic (LC) technique. [illegible] The new technique involves using chloroform as the solvent and

measuring fluorescence at approximately 418nm after excitation at 403nm.

2.7 CLEAN-UP OF SAMPLE EXTRACTS

A variety of techniques has been used to separate hydrocarbons from the lipids co-extracted by the procedures discussed earlier. When substances in a mixture are to be separated, partition of the compounds between two immiscible liquids may often be used. However, when the chemical properties of the compounds differ very slightly, such simple methods are not sufficiently efficient. Chromatographic methods are then very useful tools that can easily be modified for individual separation problems.

Three main purposes exist for these techniques. Firstly, to isolate compounds which are to be studied. This is usually called a clean-up procedure. Secondly, to separate compounds which are all to be studied, from one another; and thirdly to characterize compounds e.g. retention times in gas chromatography, R_f values in thin layer chromatography, etc.. This is helpful in the identification of a substance.

Some of the methods used for carrying out the separation of the hydrocarbons from the lipids are: column chromatography (CC); thin layer chromatography (TLC); and paper chromatography. High pressure liquid chromatography has also been used.

2.7.1 COLUMN CHROMATOGRAPHY (CC)

This involves mounting of a glass tube (column) vertically and filled with the stationary phase, either dry or as a suspension. The substance, normally dissolved in a solvent with a low elution ability, are placed on the top of the column. Finally, a solvent reservoir is connected to the top. With a proper choice of conditions, the substances will separate during the passage through the column and can be collected in different fractions.

In the application of liquid-solid (column) chromatography, it is necessary to choose the proper adsorbent or combination of adsorbents with the most advantageous activity and mesh size for the length and diameter of the column. Additional decisions must be made as to loading (adsorbent/ sample v/w), solvent systems and fraction volumes.

Column chromatography commonly uses silical gel for separating hydrocarbons from non-hydrocarbons or alumina for separating high molecular weight polar compound from non-polar compounds [195]. A dual column of alumina packed above silica gel successfully takes advantage of both adsorbents. Deactivation of the adsorbents with water (up to 5%) prevents formation of hydrocarbon artifacts from biogenic hydrocarbons [196]. Non-polar solvents (usually pentane or hexane depending on degree of volatality desired) can be used to elute the saturated hydrocarbon from the column and the application of more polar solvents (benzene, tetrachloromethane, methanol, acetone) allows the removal of the more polar hydrocarbon from non-hydrocarbon compounds.

Standard compounds are normally used to determine the efficiency of the packed column [197].

2.7.2 THIN LAYER CHROMATOGRAPHY (TLC)

In this technique the stationary phase is a solid (e.g. silica gel) applied as a thin layer -0.25mm on a glass plate . The sample is applied as drops of a more or less concentrated solution. This addition is made as a spot, a few centimetres from one edge of the plates, together with the sample, but as a separate spot. A standard is also applied.

When the spots have dried the plate is placed in a development chamber. This chamber is a glass container with a tightly fitting lid. The sides of the chamber are lined with a sheet of filter paper. Fifty millilitres of a suitable solvent is added to the chamber. The filter paper becomes saturated with the solvent thus ensuring a uniform atmosphere in the entire volume of the chamber.

The glass plate is introduced into the chamber and placed so that the edge with the samples is immersed into the solvent. The surface of the solvent should not reach up to the spots.

The solvent will now ascend along the stationary phase, carrying the samples. However, the components

of the samples will not move with the same speed as that of the solvent. The speed is determined by the strength with which the components are adsorbed to the stationary phase.

The distance travelled by each substance is a characteristic and reproduceable quantity for the substance if the governing factors are carefully controlled. Thus, the measured distance serves as a means of identification. The plate can be visualized under UV light. If the substances absorb long wave UV-light (about 360nm) or short wave UV-light (about 254nm), such as aromatic substances in general , they can easily be visualized by looking at the plates in suitable UV-light. However, fluorescence indicator are usually incorporated in the thin layer. The substances will then appear as dark blue spots on a light green background.

Spraying reagents e.g. 50% H_2SO_4 in methanol or specific reagents for a special compound or a class of compounds which after heating will carbonize the compound. The substances appear as grey or black spots.

The separated compounds can then be scrapped or eluted from the plate for further analysis. The different fractions can be collected separately.

2.8 INSTRUMENTAL ANALYSIS OF PETROLEUM HYDROCARBONS

Because of the wide range of composition of oils, no single technique is available which can determine all the components of an oil unambiguously, and yield an entirely accurate quantification of that oil. When oils are added to water, the composition of the dissolved hydrocarbon content does not accurately reflect the composition of the fresh oil, as the higher solubility of aromatics (particularly the lower ones) and of low alkanes increases their concentration relative to less soluble compounds. This is reflected in the estimate of the total oil concentration derived from the various analytical methods which may consequently be either "under-" or "over- estimated".

Again, a variety of techniques have been tried for identifying and quantifying petroleum residues in biological samples and sediment. Gravimetric methods for quantitatively determining petroleum

pollution are useful only with relatively high concentrations (10^{-4}g) of a total fraction weight

Spectrophotometric methods - IR[198], UV fluorescence usually provide rapid estimates of the total absorbance or fluorescence respectively of all materials at a specific wavelength, but they give little indication of the complexity or molecular weight range of a sample. These approaches, however, provide limited discrimination between biogenic hydrocarbons and those contributed from petroleum pollution. If a known pollutant with a reproducible absorbance or fluorescence characteristic is present (from an oil spill or bioassay experiment), then spectrophotometric methods are often used as quick, simple and sensitive monitoring tools.

Gas chromatography provides both a separation and a quantitative estimate of specific compounds based on their boiling points and polarity with respect to the column liquid phase and to the type and resolution capability (Packed, capillary, surface-support coated, etc.). The gas chromatograph can provide, in its simplest form, a "fingerprint" of the components in

the sample; more detailed data, requiring additional expenditure of time, can provide substantial information on individual hydrocarbons which can indicate the origin of the materials. Any detailed study into petroleum uptake in marine organisms and in sediments should consider the incorporation of spectrometric identifications, especially in the use of computerized gas chromatograph/mass spectrometer systems. However, this tool should be used to complement existing methods which allow for more rapid and less expensive analyses of large numbers of samples.

2.8.1 GRAVIMETRY

Farrington et.al. (152) and Mallevialle (191) applied this method to determine total oil content by weight in water samples. This method involves extraction of water samples with n-hexane, petroleum ether, tetrachloromethane, or trichlorotrifluoroethane, then the solvents are evaporated off and the residue weighed. The evaporation of sample to dryness should not be allowed to continue for any length of time following the completion of solvent removal because the evaporation

may cause the loss of aliphatic hydrocarbons up to n-undecane (C_{11})-[redacted] (199) and of aromatics up to naphthalene . The method is therefore unsuitable for determining concentrations of light oils, although it can be reasonably accurate for the heavier oils. By use of a microbalance, the limit of detection of the method can be as low as about 4 µg/litre, but at these levels the errors are usually high. Any non-hydrocarbon material soluble in the extracting solvent will also be included in the final weight, thereby giving erroneous result.

2.8.2 SPECTROPHOTOMETRIC METHODS

These generally involve the measurement of a specific function of a class of compounds present in an oil. The magnitude of this measurement is compared with that of a known weight of the oil in solution to obtain a quantification. The methods considered under this heading are infrared, ultraviolet and fluorescence spectrophotometry.

2.8.2.1 INFRARED SPECTROMETRY

This method involves the measurement of light absorption by the sample at one or more wavelengths within the 2800-3100 cm^{-1} region, corresponding to the C-H stretch of CH, CH_2 or CH_3 groups within molecules. The most commonly used wavelength is 2930 cm^{-1} ($-CH_2$ groups). Carlberg & Skarstedt[200]; Brown et al.[201]; Mallevialle[198]; and Carlberg.[185]

The extracting solvent used must not absorb light in this region, otherwise absorption by the sample would be masked. For this reason, tetrachloromethane which has only C-Cl bonds, has been commonly used. Because of fears about its toxicity, however, other solvents such as freon 113 (TCF) used by Gruenfeld are now more usually used.

Most of the CH, CH_2 and CH_3 groups will be present in aliphatic compounds. These predominate in oil and so the standardisation of the content of oil in a water, fish or sediment sample against the original is not usually subject to major errors.

Simard et al.[203] stated that aliphatic

hydrocarbons are also produced biogenically (e.g. pristane, n-pentadecane and n-heptadecane), and this may introduce some errors at low levels. The sensitivity of the IR method is around 0.05mg/litre and its usefulness for environmental samples is therefore limited, although in effluent analysis and in monitoring of oily water discharges this level of detection is quite adequate.

Brown et.al.[201] used this method for the identification of oils. The method involves the measurement of absorptivities at 21 wavelengths within the fingerprint region of the spectrum (800-1400 cm^{-1}), the calculation of absorptivity ratio between these wavelengths, and their comparison with those of suspected source oils.

Both of the methods mentioned so far determine hydrocarbons regardless of whether they are of petrogenic origin or not. Thus any natural vegetable or animal oils or greases present will enhance the quantity of oil measured. To some extent this interference can be eliminated by including a saponification stage which removes the vegetable and animal oil.

However, as with the gravimetric technique, the necessary evaporation stages are also liable to remove the lower alkanes and other compounds with low boiling points.

It is of interest to note the usefulness of infra-red absorption spectroscopy as a method for quantitative and qualitative analysis of oil-contaminated waters. The C-H stretching frequencies in the 2850-3100 cm^{-1} region of the infrared spectrum are relatively strong and are also indicative of the structural nature of the hydrocarbons that give rise to them. For instance, it is possible to differentiate between aliphatic $-CH_3$ and $-CH_2$ groups and also to observe aromatic and unsaturated aliphatic carbon-hydrogen groupings. In the case of an oil-contaminated water, the hydrocarbon contaminant is extracted into a relatively small volume of either tetrachloromethane or trichlorotrifluoroethane and the infrared spectrum of this extract is run using 10mm quartz cells. Quantification of the oil content is obtained either by measurement of the peak absorption value at 2930 cm^{-1} or alternatively by measuring the area under the total

complex infrared absorption band, between about 2850 and 3100 cm^{-1}. This technique permits measurement of oil in water at levels down to about 50 ppb. A 10mm length glass-stoppered rectangular silica cell can also be used.

After extraction of samples with CCl_4 or freon 113 and the removal of traces of water from the extract by addition of anhydrous Na_2SO_4, the volume of the extract can be made up to 100ml with CCl_4 or freon 113. The infrared spectra can then be taken in a 10mm cell with NaCl windows. Solution should be transferred via a pasteaur pipette, washing the cell twice with the solution to be observed before filling. Spectra are then scanned from 3400 cm^{-1} to 2500 cm^{-1} using 5 to 10 times expansion of the percentage transmission scale. The C-H stretching band at 2930 cm^{-1} is used for analysis.

The absorptivity at this wavelength as calibrated with a motor oil (SAE 30 weight) and a typical procedural blank corresponded to an oil concentration of less than 0.010 mg/l in water samples.

The total aliphatics and aromatics can also be

quantified by infrared spectrophotometry, using a PYE Unicam SP4000, 1mm sodium chloride cells and the analyte being diluted with tetrachloromethane Quantitation is carried out using hexadecane, benzene, and isooctane (37.5:25:37.5) as standards employing the C-H stretching frequencies in the 2900 cm^{-1} region and the C-H stretch at 3030 cm^{-1}. Correction for amino acids can be made according to the procedure of Mark et.al.[204] by subtracting the absorbance at 1650 cm^{-1} (contribution of the biological materials) multiplied by 1.3 (arbitrary average of all $-CH_2-$/-NH-) from the total 2925 cm^{-1} absorbance.

2.8.2.2 ULTRAVIOLET ABSORPTION SPECTRO-PHOTOMETRY

Oils absorb strongly in the ultraviolet region and their spectra may exhibit maxima or shoulder at 225-235nm, 250-270nm and 315-325nm respectively[205] Hydrocarbon content is calculated by measuring the absorption of light at a wavelength within this range and comparing it with that of a known weight of a standard oil in solution. The

accuracy of this method is dependent upon the standard used, as the calibration may vary by as much as an order of magnitude for different oils[206]. Only aromatic compounds are determined by this technique.

The particulate oil, which was retained after filtering water samples through 0.45 µm Millipore filters can be dissolved after drying in approximately 4ml of spectro-analysed n-hexane. The resulting extract is then made up to 5ml in a volumetric flask and its ultraviolet absorbance at 256nm is measured with a Beckman Model DU Spectrophotometer. The concentration of oils in the extract is estimated by reference to a series of n-hexane dilutions of a standard solution of crude oil suspected to be present (or collected at the area of spill). This procedure constituted a convenient and rapid shipboard method for the estimation of oil in sea water and provided adequate data where the concentration of the oil is 10 ppb or greater[207]. This method is particularly useful when the data are required immediately after samples have been collected.

UV method can be used to provide only qualitative information about the approximate level of dicyclic and higher aromatic hydrocarbons. Zero UV absorption is a reliable indication for absence of aromatics.

Teal et.al.[208]; Mackie et.al.[209]; and Grald-Nielson et.al.[210] have studied environmental biodegradation and found that aromatic hydrocarbons are the most resistant to biodegradation. Since aromatic substances are rare in the marine environment, their detection is a good criterion of oil pollution in the environmental samples.

UV-absorption spectra reflects the composition of the aromatic compounds in a crude oil sample. Although the aromatic fractions account for 1.22-30%[210] by mass of crude oil, they play a more important role (toxic) in the pollution of marine animals than their amount in the polluting oil implies.

In the identification of petroleum products, subsamples of each sample can be treated with spectro-analyzed n-hexane and the insoluble material is removed

by filtration through a Whatman No. 42 filter paper. The filtrates are then diluted to 100ml and their absorbances at 256nm are measured.

For the standards, stock solutions of several types of lubricating, distillate and residual fuel oils, including Bunker C oil are prepared by dissolving approximately 10mg of each of the oils in spectro-analyzed n-hexane [211] insoluble materials are removed by passing these extracts through Whatman No. 42 filter papers and the filtrates are diluted to 100ml (100mg/l) [212] [213]. Three series of standard solutions containing 20,30,40, 50 and 75mg l^{-1} are prepared from the Bunker C oils (or any other crude) by appropriately diluting the stock solution. Standards containing 30 mg l^{-1} of each of the other oils are used.

The ultra-violet absorption spectra of these solutions are obtained relative to n-hexane by scanning the region from 350 to 210 nm with a Beckman ACTAV recording spectrophotometer. In addition, the absorbances of these solutions at 256nm and on the crest of the peak which is centred at approximately 228nm are

measured with this instrument in the double beam mode of operation.

The concentrations of the extracts from the samples are then adjusted so that their absorbances are in the range of 0.4-0.8 corresponding to the absorbances of the Bunker C standards which contained 30 mg l^{-1} of the oil.

The absorption spectra of these solutions are then scanned over the range of 350nm to 210nm and their absorbances at 256nm and at 228nm are measured as outlined for the standards.

Ultra-violet absorption spectra provide a convenient method for the identification of the source of petroleum products present in the marine environment. The absorbance at 228nm relative to that at 256nm has been shown to be a sensitive and reliable criterion for distinguishing between different members of similar types of oils and is not subject to many of the uncertainties of other methods of identification.

Ultraviolet method is particularly very useful where naphthalene and alkylnaphthalenes are to be determined because of their strong absorbance in the far

UV region. This method can be used to monitor contamination of marine animals because naphthalene and alkylnaphthalenes have high toxicity to marine organisms [214] and their persistence relative to other petroleum hydrocarbons in the tissues of oil contaminated marine animals. As little as 0.1 ppm of naphthalene and alkylnaphthalenes can be detected in tissue without difficulty. The detection limits in seawater are in the range of 0.01 to 0.05 ppm.

The UV method yielded average recoveries of 104± 9.5% and 98.8±1.8% for naphthalene and 2-methylnaphthalene respectively for seawater extracted with n-hexane [215] In Table 24, UV spectra of the hexane extracts of water-soluble fractions prepared from three test oils - the No. 2 fuel oil, Bunker C residual oil and South Louisiana crude oil, gave similar spectra for both No. 2 fuel oil and Bunker C, both have a sharp absorbance maximum at 221nm with a prominent shoulder at 224nm. On the other hand, the hexane extract of the water-soluble fraction (WSF) of South Louisianan crude oil

has a strong absorbance below 211nm with only a shoulder evident at 221nm. The concentrations of naphthalene, methylnaphthalenes and dimethylnaphthalenes in the three water-soluble fractions were determined by gas chromatography (216) and UV spectrophotometry. The two analytical techniques gave roughly comparable results for the WSFs of No. 2 fuel oil and Bunker C residual oil, the UV technique giving slightly higher values in both cases. However, concentrations of naphthalene, methylnaphthalenes and dimethylnaphthalenes in the WSF of South Louisiana crude oil as determined by the UV technique were about 2 times higher than value obtained by gas chromatography because some are lost at the evaporation stage for gc analysis.

TABLE 24

CONCENTRATIONS (IN PPM) OF NAPHTHALENE (N), METHYLNAPHTHALENES (MN) AND DIMETHYLNAPHTHALENES (DMN) IN WATER SOLUBLE FRACTIONS OF 3 OILS AS DETERMINED BY GAS CHROMATOGRAPHY (GC) AND ULTRAVIOLET SPECTROPHOTOMETRY (UV) (214)

Analytical method	South Louisiana Crude			Bunker C Residual Oil			No. 2 Fuel Oil		
	N	MN	DMN	N	MN	DMN	N	MN	DMN
GC	0.12	0.11	0.06	0.21	0.39	0.20	0.84	0.82	0.24
UV	0.26	0.22	0.19	0.30	0.48	0.31	0.92	0.94	0.52

This method also permits a quantitative analysis in polluted sediment samples many months after oil spill. The ultraviolet spectra of samples of an oil pollutant and crude oil at various concentrations were examined. Strong absorption maxima appear at

approximately 228nm and 256nm. These are the salient features of the UV spectra of the aromatic fraction of crude oil. Levy [211] showed that the ratio of the peak heights at 228nm and 256nm (R-value) is constant for a particular oil but varies with different oils (Table 25). This ratio is independent of the concentration of oil over the range 8 to 75 mg l^{-1}. The peak height at either 228nm or 256nm can be used for quantitative analysis. The relationship between concentration of oil and peak height in the concentration range 8 to 78 mg l^{-1} is linear. Levy [211] also found the R-value for crude and residual fuel oil to range from 1.23 to 2.11.

Outside this range (i.e. concentration 75 mg l^{-1}) deviation from Beer's law at 228nm will set-in resulting in lowering the absorbance ratio. The absorbance ratio is a reliable criterion for identifying oils only within concentration ranges at which Beer's law is valid at both wavelengths (Table 26).

TABLE 25

ULTRAVIOLET ABSORBANCE CHARACTERISTICS OF THE OIL AT DIFFERENT CONCENTRATIONS FROM POLLUTED VICTORIA BAY (194)

Concentrations mg l^{-1}	Absorbance 228nm	256nm	Ratio A_{228}/A_{256}
8.7	0.105	0.071	1.47
17.3	0.218	0.151	1.44
25.9	0.347	0.239	1.45
34.6	0.443	0.306	1.44
43.3	0.541	0.373	1.45

The R-value mean = 1.45; standard deviation = 0.01

and coefficient of variance (S.D/M x 100) = 0.85% with n = 5

TABLE 26

ULTRAVIOLET ABSORBANCE CHARACTERISTICS OF A CRUDE OIL AT DIFFERENT CONCENTRATIONS.(211)

Concentrations mg l^{-1}	Absorbance 228nm	Absorbance 256nm	Ratio A_{228}/A_{256}
7.8	0.095	0.058	1.64
15.5	0.155	0.095	1.63
31.1	0.310	0.190	1.63
38.8	0.400	0.240	1.67
62.1	0.620	0.380	1.63
77.7	0.760	0.470	1.62

The R-value mean = 1.64; std dev. = 0.02 and coeff: of variance (S.D/M x 100) = 1.07 with n = 6.

2.8.2.3 FLUORESCENCE SPECTROMETRY

Fluorescence is different from both the IR and UV absorption in that it does not involve merely the absorption of light. When a compound fluoresces it absorbs light at a particular wavelength and then immediately emits light at a longer wavelength. Fluorescence is not a property shared by all hydrocarbons, but only occurs with aromatic compounds. The aromatic content of oil is very variable, both in terms of its total content and composition, and this means that the accuracy of quantification is very dependent on the standard used. The solvent also may affect the degree of fluorescence, by promoting or quenching, and so must be chosen carefully. Some natural products present in samples may also fluoresce. Although subject to these limitations, this method is very sensitive and is capable of measuring concentrations down to around 1 μg/litre. The wavelength of both excitation and measurement can be varied but the most commonly used procedure involves excitation of the sample at 310nm and measurement of the intensity of fluorescence emission at 360nm.

This method was first applied to the analysis of petroleum in organisms by Zitko and Carson [205] soon after Levy [140] applied the method to the detection of low concentrations of petroleum residues in seawater. Levy [140] ; Gordon and Michalik ; Levy [211] , and Levy and Walton [218] used Arrow Bunker C fuel oil as standard. This was justified when monitoring the presence of Bunker C in Chedabucto Bay after the Arrow disaster in February, 1970.

A means of using fluorescence as a qualitative technique has also been developed, namely that of synchronous scanning of excitation and emission. The emission spectrum of an oil is recorded from 260nm to 460nm, and at the same time the excitation wavelength 25nm lower down is scanned. The position of the fluorescence bands corresponds to the number of fused rings in the compounds causing fluorescence.

For fluorescence analysis, the n-hexane, tetrachloromethane or methylene chloride extracts are evaporated to dryness on a rotary evaporator at 30°C

and reduced pressure. The residue is taken up in 10ml spectrophotometric grade n-hexane for fluorescence analysis. Part of the extract is placed in a 1cm quartz cell and analysed in a double beam monochromator spectrofluorometer equipped with a xenon lamp. Intensities are measured using the following settings of the excitation and emission monochromators:
230/340nm, 270/360nm, 310/400nm
(219). A standard solution of reference oil is run at intervals between the samples.

Quantification is carried out by comparing intensities at the different wavelength combinations with the corresponding intensities of a standard solution of the reference oil. Corrections are made for concentrations found in the solvent used for extraction.

2.8.3 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

Although basically a separation technique, high performance liquid chromatography is used in combination with mass-spectrometer and other sophisticated instrumental techniques to give a measure of individual oil compounds.

HPLC is an extremely valuable technique for the analysis of labile or non-volatile compounds. Examination of the oil-seep in sediment by HPLC (with selective UV absorption and fluorescence emission detection) yielded qualitative information about the polynuclear aromatic hydrocarbons (PAH s) in the sample [186] . The PAH s in the sediment are chromatographically separated according to the number of condensed rings using reversed-phase HPLC to separate out the alkyl-substituted homologs within each fraction. The HPLC effluent is monitored simultaneously with UV absorption and fluorescence emission detectors. The fluorescence emission spectra obtained for each chromatographic peak are utilized for compound identification. The column is packed with μBondapak C_{18}. Mobile phase is 50-100% acetonitrile - H_2O linear gradient in 30 minutes [220]

In order to determine the hydrocarbon concentration in small water samples rapidly and fairly simply, two separate but related methods were developed. Both are based upon the use of high performance liquid chromatography. They are more sensitive than the IR

methods, which tend to have a maximum sensitivity of 0.05mg [200], and they are probably more specific than UV or fluorescence methods used without column chromatography [140]. Their main advantage over Gas Liquid Chromatography (GLC) lies in the fact that they are simpler and more rapid for obtaining quantitative results.

In a system to separate non-hydrocarbons from the hydrocarbons, a column with internal diameter of 1.8mm and 5cm long packed with 10% deactivated silica gel is used. n-nonadecane is used as the standard. The saturated hydrocarbons were all found to have a response between 76 to 110% of n-nonadecane. Unsaturation decreased the response per unit weight. This decrease was minor among the mono-unsaturated compounds, but quite strong among the poly-unsaturated alkenes such as carotene and squalene.

Aromatic hydrocarbons will also be underestimated. Naphthalene, for example, has a response that is only 29% of that of nonadecane [221][222].

For the determination of the aromatic hydrocarbons, the same extracting and concentrating procedure is used as above. The apparatus is somewhat different in that a UV detector, which measures absorbance at 254nm, replaces the flow calorimeter. A longer column (10cm) with more active (2% deactivated) silica gel is also used, since aromatic hydrocarbons are somewhat polar and more care must be taken to ensure their separation from other weakly polar compounds.

The chief disadvantage in the use of a UV detector lies in the fact that the response per unit weight varies enormously from compound to compound. As a result all values can only be given relative to a standard and will vary greatly depending upon the standard selected.

HPLC analysis has also been performed on a water associates ALC/GPC-502 liquid chromatograph with an FS-770 Schoeffel fluorometer.[223]. A 30cm x 6mm OD, 10μ porasil column, with a chloroform solvent flow rate of 1.0ml/min. The data are analyzed with the help of a Hewlett-Packard 3380A integrator. The number of counts (area) of the oil peak in an

unknown sample is compared to a graph prepared from injection of known amounts of oil. In all cases, a graph has to be prepared for each kind of oil.

A series of tests was performed in which the Liquid Chromatography (LC) system and the fluorescence excitation and emission wavelengths were varied. An LC solvent system of chloroform and an excitation wavelength of 403nm with a kV 418 emission filter (418nm range) provided complete selectivity between petroleum hydrocarbons and biogenic hydrocarbons. From the outcome of the work performed to determine the effect of sample preparation on the results, it was discovered that the benzene eluate provided results that were more reproducible. The data obtained from biological samples also indicated that the benzene eluate gave the most reliable results.

2.8.4 GAS LIQUID CHROMATOGRAPHY (GLC)[224-225]

Gas liquid chromatography is a technique of separation of mixtures in microgram quantities by passage of the vaporised sample in a gas stream through a column containing a stationary liquid on a stationary solid

support. Components migrate at different rates due to difference in boiling points, solubilities or adsorption. In gas-liquid chromatography (GLC), the column contains a support material which is coated with a liquid stationary phase. This phase is so chosen that the components of the sample are soluble in the phase as well as in the carrier gas. Every component has a characteristic solubility in the liquid and in the gas. Thus, a partition of each component takes place between the two media. As the carrier gas passes through the column during the entire analysis, the components are transported and eluted from the column by the gas. The components which are most soluble in the gas will be eluted first and those which are more soluble in the liquid will come later.

On leaving the column, the components enter the detector (e.g. flame ionization detector, FID). The detector gives an electrical response for the components. The electrical output is amplified and fed to a strip chart recorder which delivers a continuous plot of detector response versus time. When all governing conditions are kept constant, the time from

sample injection to the appearance of a component peak - the retention time - is constant too. Thus, the retention time is used as a means of identification of the components. The area under the peak is proportional to the amount of the eluted compound. By comparing the retention time and peak area of a compound in the sample with that of an injected standard of known concentration the level present in the sample can be estimated. Often peak heights instead of peak areas are used.

Gas-liquid chromatograph with a flame ionisation detector is generally used as a quantitative method for investigating the major component composition of oils and for observing the presence of biogenic hydrocarbons in environmental samples. Column oven temperature programming enables samples to be analysed over a wide boiling range. Quantitative use has been made of this technique by measuring the concentrations of n-alkanes (226) or by integrating the total area of chromatograms.

The method is not, however, readily applicable to specific aromatic compounds as these tend

to be lost, even when using capillary columns in the unresolved envelope or "hump" under the alkane peak baseline[199].

Of all the techniques used for oil spill identification, gas chromatography has been the most widely exploited. A low-resolution packed column will give the boiling range of the spill and sometimes a tentative identification. A high-resolution column is capable of giving a large amount of information, which can be handled as a simple fingerprint or can be quantified by measuring the ratios of isoprenoid hydrocarbons (in particular pristane and phytane). Extra diagnostic power can be achieved by the use of selective detectors.

In chromatographic analysis different column materials, packing and conditions are used in solving the problems posed by the wide range of petroleum hydrocarbons present in the marine environment - water, organisms and sediment.

Column materials commonly used are stainless steel and glass of varying dimensions. The length depends on whether it is to be used as packed column

(1.5m long) or open tubular. The latter is always longer, and can be wall coated (WCOT) or support coated (SCOT). The major points to be considered under gas chromatography relating to pollution are: sample introduction, column selection and sample recovery.

2.8.4.1 SAMPLE INTRODUCTION

Samples may be introduced conventionally in solution, by a column injection or by vaporization in a heated injection block. Carbon disulphide is a suitable solvent. Some special introduction techniques are applicable to the pollution field. The British Institute of Petroleum Standardization (IPS) committee has described a modified inlet system that accepts a solvent free oil sample in a glass tube (212). The tube is inserted via two ball valves into the heated injector. A similar but simpler technique involves the rapid insertion into the injector of the oil contained inside a short piece of glass tubing. The injector is immediately closed by septum and nut. The tube is left in the injector at a temperature and

for a time that assures evaporation of hydrocarbons but minimizes thermal decomposition of the residue. The front end of the column is cooled with air or dry ice. Later, the glass tube containing the residue is withdrawn and the temperature programme is started. In this way the injection port remains clean. The technique is highly tolerant of the presence of high boiling materials e.g. asphaltenes, lipids.

2.8.4.2 THE SUPPORT

The support plays a critical role in several ways in the performance of the column. First, it governs the efficiency of the column (narrowness of peaks). The structure of the support, and the manner in which it is coated also contributes to the column efficiency. Secondly, the support can interact with the sample to cause the chromatographic peaks to "tail" i.e. they can be highly asymmetrical and consequently difficult or impossible to measure. Ideally, the support should not interact with the sample but, in practice, this does occur. By careful Selection of the support and conditions one can minimize this problem.

The "tailing" phenomenon is caused by active sites on the surface of the support. These sites are ones that can form a hydrogen bond. Consequently, samples that form a strong hydrogen bond tail badly. In practice, compounds such as water, glycols, alcohols, acids, and amines tail severely while carbonyl compounds such as esters, ketones, and aldehydes tail to a lesser degree. Hydrocarbons that do not form hydrogen bond such as the alkanes are not bothered by tailing.

To eliminate or reduce the tailing problem, one modifies the support surface by[227]:

(1) removing the active sites by acid and/or base washing;

(2) modifying the surface by silanization, or

(3) covering the active sites with the stationary phase having polar functional groups in it.

Acid washing is effective in removing mineral impurities from the support surface as well as miscellaneous extraneous material. Base washing does not impart any special advantage to the support that is not obtained with a well acid washed support. Acid washing by

itself is not effective in reducing tailing but it is recommended where a polar phase is used such as the polyesters and polyglycols.

Silanization, particularly with dimethyldichlorosilane (DMCS) is very effective in reducing tailing. Combined with acid washing and DMCS treatment, the resulting support is recommended for most columns. Silane treatment is a very difficult process to control. When silicone stationary phases are used, it becomes mandatory that an acid washed and DMCS treated support be used. The silicone stationary phases, particularly when used in the 1-5% level, are not effective in deactivating the support and require a silane treated support.

The third procedure for deactivation, using a polar stationary phase, requires that the phase contain functional groups such as an ester, an ether, a hydroxyl, and an amine group. These functional groups have strong hydrogen bonding characteristics and tie up the active sites on the support surface. These phases do not require a silanized support although, when they are used at a level of 5% or less,

silanization can be useful. When analyzing acids it is necessary that the stationary phase contain an acid to deactivate the support.

When working with basic compounds such as amines, the stationary phase must contain a base to deactivate the support otherwise severe tailing will result. KOH is frequently used at a 1-2% level for the purpose. A basic stationary phase such as polyethyleneimines also may be used.

Most of the GC supports in current use are made from diatomaceous earth, also called diatomite. The diatomite is processed in several ways producing two basic types of supports. These are conveniently recognized by their colour.

The particle size of supports are generally expressed in terms of screen openings since screens are normally used to prepare them. The particle sizes normally used in GC are as follows:

60/80 mesh; 250-177 microns

80/100 mesh; 177-149 microns

100/120 mesh; 149-125 microns.

The designation 60/80 mesh means that the particles

have passed through a 60 mesh screen (-60) and will not pass through the 80 mesh screen (+80). It then means that the particles are between 250-177 microns in size. The column efficiency improves with decreasing particle size. At present the 80/100 mesh is the most popular size, but 100/120 mesh is used with increasing frequency when more efficient columns are desired.

2.8.4.3 COLUMN TUBING

The choice of the tube used for the column should be carefully made. Both the materials of construction and its dimension must be considered. Glass, stainless steel, aluminium, and copper are the materials commonly used for columns. While glass is the most inert of the tubing, stainless steel is the most widely used.

Glass is used in situations where the sample might interact with the walls of the tube. It is standard operating procedure to use glass columns when working with pesticides and biochemicals such as steroids and hormones. Glass is more inert than the

metals and rarely causes tailing or decomposition of the sample. Glass columns are also used generally in situations where it is desirable that the sample be injected directly into the column. Glass column also affords visual observation of how well a column has been packed.

Metal columns are used where glass is not required. Stainless steel is generally considered more inert than aluminium or copper. The hardness of the materials appears to be important in transmitting the "shock" when the column is vibrated or tapped.

Most instruments are designed to handle 1/8" outer diameter (OD) metal columns. When glass columns are to be used, the instruments are usually equipped to handle 1/4" OD columns. The glass can be made with a heavy glass wall cutting down considerably on the problem of breakage. A reasonable flow rate recommended for 4 mm (id) columns is 80ml/min., while for 2mm (id) columns a good rate is 20 ml/min.

2.8.4.4 UPPER TEMPERATURE LIMIT

Each stationary phase has an upper temperature limit above which the column should not be operated. Most stationary phases are polymers that consist of materials having a range of molecular weights. As the column temperature is increased, the more volatile portion of the polymer is swept out of the column by the carrier gas. The volatile products could also be formed by thermal degradation of the stationary phase while the column is being used. This is called "bleed" and is seen on the recorder as a rise in the baseline or as noise. Above the maximum upper limit, the bleed rate is very high and the column will have a relatively short life. In some cases, the bleed rate may be so high that it will not be possible to move the recorder pen off of full scale.

The different stationary phases and conditions that have been used in chromatographic analysis of hydrocarbons are given in Table 27.

TABLE 27: SUMMARY OF ANALYTICAL METHOD (GC) FOR PETROLEUM HYDROCARBONS IN ENVIRONMENTAL SAMPLES

	Column Type	Column Materials	Compound Determined	Conditions	Detector	Reference
1.	Packed Column					
	Stainless Steel 2m x 2.2mm i.d	12% FFAP on Chrom W 80/100 mesh	Aromatics	Temp. Prog. 125°C-270°C at 4°/min. held at 270°C until n-C_{28} eluted carrier gas: He 12.3ml/min.	FID	183
2.	Stainless Steel 1.8m x 3.2mm 0.d	3% Apiezon L on Chrom W 80/100	Aliphatic	80-290°C at 6°/min held at 290°C until n-C_{28} eluted. Injection Port 200-210°C carrier gas: N_2 12.9ml/min or He	FID	183
3.	Stainless Steel 2' x 0.125"	3% SE 30 gas Chrom Q 80/100	Aliphatic	Oven temp. 120°-280°C at 8°/min. Carrier gas: He	FID	178
4.	Glass Column 10' x 2.0mm i.d	Dual column 10% SE-30 3% OV-17 or 3% OV-1 on 100/120 mesh chrom Q	Aliphatic	Injection - 250°C Detector - 350°C Col. 60°300°C at 8°/min. maintained at 300°C for 20 min. Carrier gas: He	FID	216

TABLE 27 (contd.)

	Column Type	Column Materials	Compound Determined	Conditions	Detector	Reference
5.	Stainless Steel (Varian 1200gc) 3m x 2.5mm 0.d	3% W/W SE-30 on gas Chrom Q 100/120 mesh	Aliphatic	Inj - 300°C det 320°C, Oven - 80°-270°C at 6°/min carrier gas: N_2 30ml/min	FID	213
6.	Varian Aerograph Model 1200, 1.9m x 0.32cm 0.d (Stainless Steel)	1.5% RTV.502 Silicone rubber on Chrom GHP 80/100 mesh recorder 1mV atten. 8X on range 1(8×10^{-12} amp)	Aliphatic	Inj-300°C det-360°C Col.-60°-332°C Carrier gas: N_2 29ml/min H_2-28ml/min Air-240ml/min		197
7.	Glass Column 10' x 2.0mm i.d	1% SE-30 on Chrom WHP 100/120	Aliphatic	50°C for 4 min. then programmed to 350°C at 8°/min. Carrier gas: He 30ml/min	FID	220
8.	Varian Aerograph 10' x 1/8"	2.5% Dexsil 300 GC on 760/80 mesh Chrom. P	Aliphatic	Inj-325°C det-325°C Prog.-100°-300°C at 10°/min. Carrier gas: He 15ml/min	FID	172

TABLE 27 (contd.)

	Column Type	Column Materials	Compound Determined	Conditions	Detector	Reference
9.	OPEN TUBULAR					
	SCOT 25m x 0.5	SE-30	Aliphatic	Temp. prog. 80/120°C 290/310°C at 3°C/min Carrier gas: He 4ml/min	FID	174
10.	SCOT 100m x 0.65mm i.d glass	SE-30	Aliphatic	80°C for 4min then prog. to 270°C at 8°/min. Carrier gas: He 6ml/min	FID	20
11.	SCOT 200m x 0.03mm i.d (Stainless Steel)	SE-30	Aliphatic	50°C for 4min. then prog. to 270°C at 8°/min. Carrier gas: He 6ml/min	FID	53
12	WCOT 30mm x 0.25mm i.d	SP2100 (OKIOL)	Aliphatic	det.-290°C inj.-270°C 35°C for 5min.-260°C at 3°/min held for 20min. Carrier gas: He	FID	216
13	Perkin-Elmer Model 900GC WCOT 150'x 0.01" i.d (Stainless Steel)	Apiezon L or butanediol succinate (BDS) polyester	Aliphatic	60°-220°C, 5°/min 120°-170°C at 5min. Carrier gas: He	FID	220
14.	20cm x 0.3mm i.d Capillary	SE-52	Polynuclear Aromatic Hydrocarbons	Temp. prog. 70°-250°C at 2°/min. Carrier gas: H_2 1.0 atm.	FID	216

2.8.4.5 SAMPLE RECOVERY

Various instruments and techniques have been described for preparative gas chromatography effluents. Large preparative gas chromatographs often suffer from inadequate plate efficiency, poor recovery of small samples, thermal decomposition of small samples, especially of olefins, on the necessarily large columns is common. Sufficient sample for further analysis can be recovered from efficient analytical columns. Thus, many studies on natural hydrocarbons in organisms have used the efficient trapping of samples from a modified flame tip in a melting point capillary, whose interior has been roughed with carborundum powder in order to provide a larger surface area

Microgram samples can be recovered with high yields. Thus, sufficient sample for further spectral, chemical and chromatographic analysis can be recovered.

Typical chromatograms consist of a large unresolved "hump" that extends over a wide time scale and on which are superimposed a number of sharp peaks due primarily to n-alkanes and isopranes. The

unresolved hump contains the aromatic, cycloaliphatic and branched aliphatic hydrocarbons[228,229]. The total structure of the chromatogram can go a long way towards identifying the original source of a crude oil.

2.8.4.6 DETECTOR

A flame ionization detector is sensitive to organic compounds, mainly hydrocarbons, and is often used as a carbon counter. It does not respond to heteroatoms and is not affected by moisture. This makes it particularly suitable for aqueous and environmental samples.

The diagnostic powers of gas chromatography for petroleum hydrocarbon analysis can be further improved by using a flame photometric detector with sulphur selective filters. This detector responds to organo-sulphur compounds. Adlard[230] used a capillary column for high resolution of chromatographic peaks with a sulphur selective flame photometric detector in parallel with a flame ionization detector. With this method, he was able to obtain simultaneously, two

different 'fingerprints', one for organo-sulphur compounds and the other for hydrocarbons.

The available detectors and their applications are shown in Table[28].

2.8.4.7 PACKED GC COLUMNS FOR SEPARATING HYDROCARBONS

A wide variety of gas chromatographic column types is available for separating hydrocarbon mixtures. The type of packed column chosen depends on the nature of the hydrocarbon mixture to be separated. There are several basic categories of packing including

(a) adsorbents
(b) modified adsorbents
(c) conventional GLC columns (stationary phase coated on a support); and
(d) conventional GLC columns with stationary phase plus complexing agent on a support.

TABLE 28

GAS CHROMATOGRAPHIC DETECTORS AND THEIR APPLICATION

DETECTOR	APPLICATION	REFERENCE
Flame lonization (FID)	Widely used for all hydrocarbon compounds	160
Flame photometric (FPD)	Used for determination of Sulphur and phosphorus contanning compounds	230
Nitrogen Phosphorus (NPD or thermionic)	Determination of nitrogen heterocy clics	176
Hall electrolytic Conductivity	Determination of nitrogen and Sulphur Containing compound	192
Ultraviolet	Determination of PAH	216
Electron Capture (ECD)	PAH with Oxygen doping halogenated compounds	223

2.8.4.7.1 ADSORBENTS [231]

Inorganic adsorbents used in GC include silica gel, alumina, molecular sieves and carbons. Silica gel and alumina can be used to separate hydrocarbons in the C_1 to C_4 range. Molecular sieves are generally limited to separating methane and permanent gases such as H_2, O_2, N_2 and CO. Carbon (Carbosieves S-II and G) can be used to separate hydrocarbons in the C_1 to C_3 range, along with permanent gases such as H_2, O_2, N_2, CO and CO_2. Organic adsorbents (the so-called porous polymers) are large surface area resins made from such materials as styrene and divinyl benzene. It is the surface of the adsorbent which causes the separation to occur. The porous polymers have been used to separate light hydrocarbons.

2.8.4.7.2 MODIFIED ADSORBENT

The usefulness of a number of adsorbents may be substantially extended by modifying their surfaces. This is done in some cases by bonding the stationary phase to the surface of the adsorbent, or in other cases by merely coating the surface. Halasz[232]

modified the surface of a special silica gel, Porasil C, by bonding to its surface a series of stationary phases. These are now commercially available as the Durapak series manufactured by Waters. Guillemin et.al.[233] have extended this work, using Spherosil, and have developed a series of bonded spherosils.

Brunner, Di Corcia, Liberti and co-workers have studied the graphitized carbons sold by sulpelco under the trade names carbopack B and C, after modifying their surfaces with a stationary phase. The carbopacks are useful for separating the C4 unsaturates as well as various C4 and C5 hydrocarbons. Earlier, Eggertsen et.al.[234] had reported that a carbon black (Pelletex) modified with 1.5% Squalane could be used to separate the C5 and C6 saturates according to their boiling points.

2.8.4.7.3 CONVENTIONAL PACKED COLUMNS

A conventional packed column consists of a stationary phase coated on a support. The choice of the type and amount of phase, as well as the type and

particle size of the support are governed by the type of sample to be separated. The boiling point range of the sample and the amount of stationary phase are considered first. A very volatile sample is quickly eluted from a column while a high boiling one is only slowly eluted at the same temperature. Secondly, the amount of stationary phase in the column is important in the elution of the sample; the greater the amount of stationary phase, the greater will be the elution time. In order to separate very low boiling compounds, it is necessary to use a relatively high concentration (20-30%) of a specific stationary phase; a medium boiling sample requires a 10% loading, and a high boiling sample requires a 3% loading of a general purpose stationary phase. A methyl silicone stationary phase is well suited for both medium and high boiling samples. For very high boiling mixtures such as microcrystalline waxes, a short (18") column filled with 1% Dexsil 300 is capable of giving rapid separation.

The pink or chromosorb P type supports have twice the density and twice the capacity of the white or chromosorb W type supports. As a consequence, the pink

supports are favoured for those packings which require high (20-30%) loading. In the case of the medium boiling range samples, either the chromosorb P or W type will suffice. For the high boiling samples, the chromosorb W type supports are favoured because the samples are more rapidly eluted.

The particle size of the support used is an important factor in the efficiency of the column, the smaller the particle size, the more efficient the column. The most commonly used particle sizes are 60/80, 80/100, and 100/120 mesh. The 100/120 mesh size will give the most efficient column. It has been known also that as the particle size of the support is reduced, the column back pressure will increase.

2.8.5 COMPARISON OF CAPILLARY COLUMN AND PACKED COLUMN GC FOR HYDROCARBONS ANALYSIS

Glass capillary gas chromatography $(GC)^2$ or High Resolution Gas Chromatography (HRGC) now routinely used by many laboratories, was first described more than 20 years ago. Many commercially

available GC instruments are available for use with glass capillary columns, instruments which combine automated sample injection with specially designed injection (sample inlet systems) and rapid and sensitive electrometer/integration systems to accurately record areas of sharp peaks. Characterization of oils by high resolution GC[2] has been discussed by Rasmussen (1976)[235], Crowley et.al.(1980)[236], and Cram and Yang (1980)[237].

The features and applications of packed column GC have been discussed in section 2.8.4.7.3. The packed column and the glass capillary can then be compared on the following basis:

(1) Nature of the column. This includes column material, length, internal diameter and packing
(2) Sample capacity
(3) Separation efficiency and resolution.

2.8.5.1 NATURE OF THE COLUMNS

Capillary columns are usually very long, narrow bore tubes of approximately 25m x 0.25mm; the insides of which are coated with a uniform thin film of

stationary phase. The inner wall may be coated directly with the liquid stationary phase (wall coated open tubular column) or it may be coated with a layer of adsorbent material e.g. calcite and the liquid phase adsorbed onto calcite. With WCOT columns, the liquid stationary phase was found to adhere to the sides of the inner tube, thereby decreasing the amount of liquid phase in contact with the mixture in the carrier gas stream.

Packed columns are short tubes with larger internal diameters of approximately 1.5m x 3mm. The liquid stationary phase is coated around an inert support material, which is then carefully packed in the column.

2.8.5.1.1 COLUMN MATERIAL

For capillary columns, glass is an effective material. Glass has advantage over other materials (mainly metals; stainless steel, Cu, Al, etc.) in that it is smooth and inert. It is possible to obtain a thin and uniform coating on glass because of the smoothness of the surface. However, in some earlier work done in this field, stainless steel capillary

columns were used with Apezon L. Fused silica capillary columns now represent the state-of-the art in GC. They are inherently straight without surface activity as well as being extremely flexible and virtually unbreakable in normal use.

Both glass and stainless steel are used as materials for packed columns since there is no requirement for uniform coating.

2.8.5.2 SAMPLE CAPACITY

The main disadvantage of capillary columns which may limit their usage in GC analysis of mixtures is the very small sample capacity, usually in the microlitre range. On the other hand, packed columns are able to analyse a larger quantity of sample. The requirement of peak symmetry may not be fully achieved because of the low sample capacity of capillary columns for mixtures which contain both trace level and major levels of components. When a very small quantity of the extract is injected into the capillary column, those components that are present at major levels will be separated effectively and in some cases

may saturate the column; thereby making it almost impossible to separate the trace components. These are then eluted unresolved, causing tailing of the chromatographic peaks.

Capillary columns are better for analysing complex mixtures on GC. They give better separations, though the small sample capacity that can be handled by such columns is a draw-back of the column.

2.8.5.3 SEPARATION EFFICIENCY AND RESOLUTION

The separation efficiency of any column is viewed in terms of complete elution of each component with corresponding peaks which are narrow, symmetrical and well defined. The total peak area or height should also represent 100% of that component.

Maximum separation efficiency is obtained in terms of the number of theoretical plates obtainable in a given column. Usually, the longer a column is, the larger the number of theoretical plates. Capillary columns have a relatively higher number of theoretical plates (150,000 plates) than do packed columns (5,000 plates).

The theoretical plate concept in GC is based on the plate theory of chromatography which visualizes the column as consisting of a series of equilibration steps or plates at which partitioning of substances between the carrier gas stream and the liquid stationary phase occurs. A very detailed theoretical concept of column efficiency based on the Van Deemter equation explains the main factors which determine the efficiency of a column[238].

The low flow resistance per plate of open tubular columns recommended them over packed columns, as this asset can be flexibly apportional among characteristics such as resolution, shortened analysis time, and lowered operating temperatures. Such flexibility facilitate optimizing systems with severe requirements. Furthermore, oils and environmental samples have been analyzed with superior resolution on such column. Same oil "fingerprint" cannot be obtained on nominally identical packed columns, the problem has been traced to the difficulty of making columns with simultaneously identical plate counts and flow resistances; efficiency-resistance relationships are expected to be

more uniform for open tubular columns.

Comparability and reproducibility required minimizing irreversible changes in the columns themselves. High operating temperatures and excessive inputs of semi-volatile material to the column were considered to be the principal causes of avoidable column ageing. High loading (more stationary phase e.g. SCOT) increases elution temperature, but also durability, relative to wall-coated column.

A typical separation example of the 2 columns are shown below (Fig. 18), with the conditions given in Table 29.

2.8.6 GAS CHROMATOGRAPHY-MASS SPECTROMETRY

This is at present the most powerful technique for the analysis of hydrocarbons. It is not normally used for the quantification of total hydrocarbons, although this is possible by integration of the total area of chromatograms. Its major use is in the unequivocal identification of specific hydrocarbons, and their quantification, even in the presence of much larger quantities of other compounds. This is achieved

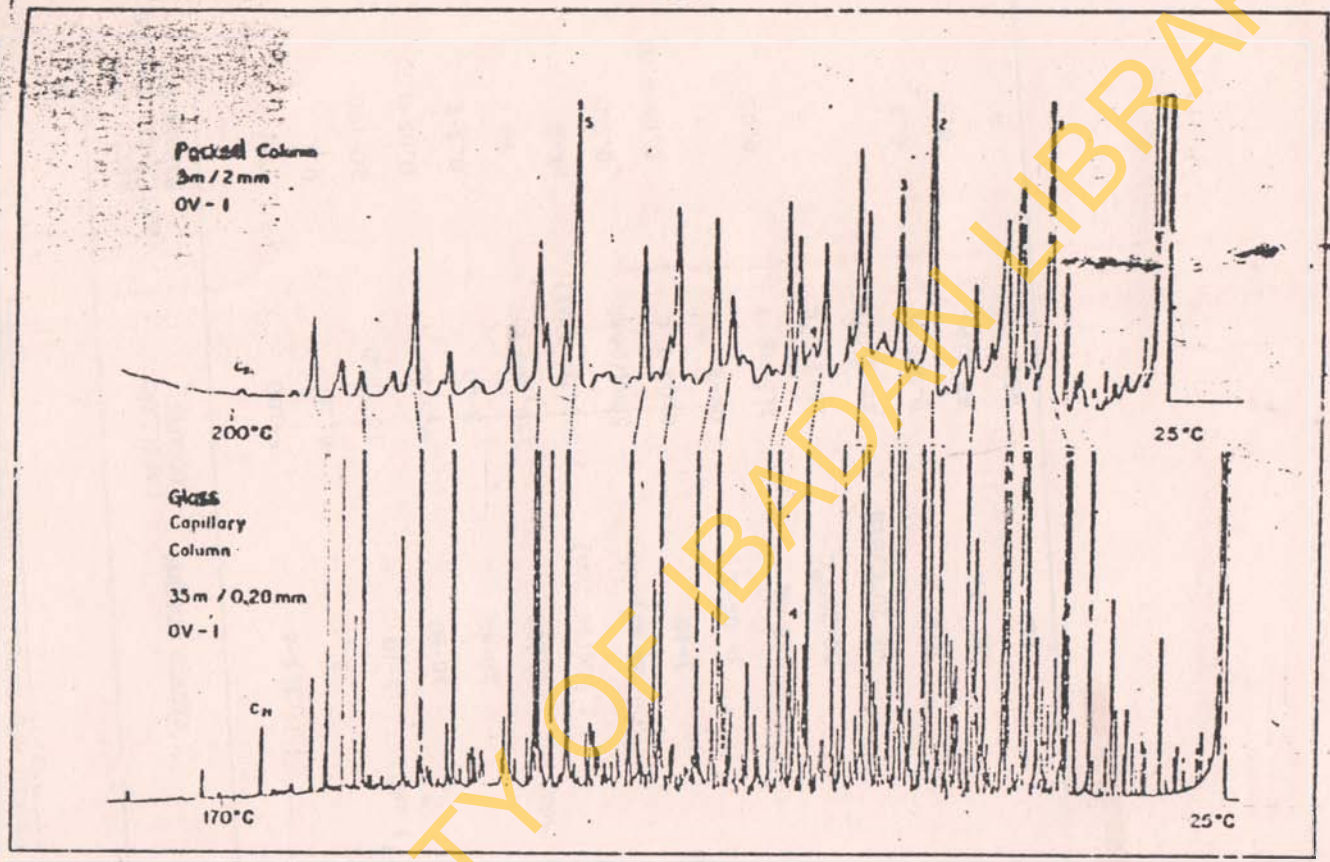


Figure 18: Comparison of typical separation from packed and capillary columns. Sample (extract from river water) and liquid phase identical. Dotted lines indicate corresponding sample components. (from Grob and Grob, 1976).

TABLE 29

COMPARISON OF PACKED AND CAPILLARY COLUMNS AND METHODS.

	PACKED COLUMN	CAPILLARY COLUMN	RATIO OF CAPILLARY: PACKED PARAMETER
Length, metres	1.5-6	5-100	3-17
Inside diameter, millimeters	2	0.28	0.1
Specific Permeability, (10^{-7}) cm^2	1-10	10-1000	10-100
Flow, ml/min	10-60	0.5-15	0.05-0.25
Pressure Drop, psi	10-40	3-40	0.3-1
Total Effective plates (2m, 50m)	5,000	150,000	30
Effective Plates per Metre	2,500(id 2mm)	3,000(id 0.25)	1.2
Capacity	10 g/peak	50ng/peak	0.005
Liquid Film Thickness, rim	1-10	0.05-1.0	0.05-0.01
Stationary Phase	3% OV-1	OV-1	-
Stationary phase load	120 mg	1.5 mg	0.01
Temperature	50-200°C	25-170°C	-
Progran	at 20°C/min	at 3.5/min	
Sample size	0.15 1	0.024 1	0.2
Analysis time	90 min	45 min.	0.5
Number of peaks	118	450	4

by the technique of mass fragmentography, which has been used to assess the petroleum hydrocarbon content of water by analysing for each specific component of oil at concentrations down to 1ng/litre[240].

Quantification of components of a given sample is by comparison of peak areas with those of an internal standard following establishment of relative response factors for the compounds to be quantified. The lower limit of detection by GLC-MS is 0.5ng for aromatic hydrocarbon and 0.1ng for aliphatic hydrocarbons.

Periodically throughout the analyses different concentrations of the external standards are analysed (5 trials each). The overall accuracy (±11.1% R.E.) are calculated as the combined deviations from actual and average values, respectively, for the hydrocarbon standards. Full mass range (M/Z 50-500) scanning GC/ms is used to verify the identification of the peak quantified.

CHAPTER THREE

EXPERIMENTAL

3.1 DESCRIPTION OF THE SAMPLING AREA

This study is focused on the Petroleum hydrocarbon distribution and levels in Lagos and Lekki Lagoons; and the major river systems in the Niger Delta area of Nigeria. Some sampling points were also located around Kaduna refinery and Ibadan City where there are no known petroleum related industrial activity, for comparison.

Lagos is a well known commercial and industrial centre, a position she enjoys by virtue of her location as a coastal city and major port; and the seat of the Federal government. Her closeness to the sea coupled with well developed ports and other utilities have contributed in no small measure to her rapid industrialisation. Most of the early industries in Lagos were located very close to the lagoon in order to take full advantage of the Apapa port for entry of imported raw materials and the large body of water of Lagos Lagoon

was regarded as a bottomless sink for industrial wastes. Some of the big industrial houses such as Lever Brothers, National Oil and Chemicals Marketing Company, Chemical and Allied Products, 7-up Bottling Company are located in Apapa and Iganmu areas of Lagos, while the oil companies such as African Petroleum, Mobil, Total and Texaco all have their depots in Apapa. Petrol filling and service stations are scattered all over the city.

The Lagos Lagoon apart from serving as the final sink or clearing house for all the waste generated from these industrial houses also serves as routes for ferries and provides berthing spaces for maritime ships and vessels. Some of the vessels introduce their waste waters and de-ballast water into the Lagoon. This practice has been going on for a very long period such that the once productive Lagos Lagoon in terms of fish-catch and other sea foods has experienced diminished resources.

The Lagos and Lekki Lagoons system was selected for the following reasons:-

(a) The Lagoon in the Lagos area is heavily stressed.

(b) An NNPC oil facility is located near the entrance of the Lagoon.

(c) A number of industries discharge their effluents in the lagoon either directly or after some treatments.

(d) A papermill - Iwopin paper mill-is located on the shore of Lekki Lagoon.

(e) Lekki Lagoon is at present a relatively unpolluted, major freshwater fishing area.

The Niger Delta bordering the Atlantic Ocean occurs at the southern end of Nigeria and extends from about longitude 3° - 9°E and latitude 4°30' - 5°20'N (Fig 20). The River Niger empties its waters into the Gulf of Guinea through a large number of tributaries forming the Niger Delta.. Brass, Bonny, Escravos, Forcados, Qualboe, Benin and Pennington rivers are only some of the important tributaries, with estuaries large enough to permit navigation to inland ports.

The Niger Delta produces all of Nigeria oil and gas resources. The exploration, prospecting, mining, refining and oil transportation activities in the area has made the Delta region important in any consideration of environmental impact of the oil industry in Nigeria. The area which was previously poorly developed economically is now the

scene of intense industrial activity of various kinds
Kakulu (1985)[240] had earlier studied the impact of the petroleum industry on baseline levels of heavy metals in the Niger Delta.

The sampling points located in the Delta were chosen because of the following reasons:

(a) A large number of oil fields lie within the area.
(b) A number of pipelines cross the river systems.
(c) Oil terminals are located at the entrance of some of the river systems.
(d) Existence of old oil spill sites.
(e) Location of two refineries (Port Harcourt and Warri).
(f) Existence of oil terminals and ports with heavy ship traffic.
(g) Recent spill sites.
(h) Others are for baseline data in areas without petroleum activities.

The description of the sampling stations with the corresponding station codes are given in Table 30. The stations as identified by code numbers are shown in figures 19 and 20 for Lagos and Lekki Lagoons and the

Niger Delta river systems respectively, as part of NNPC/RPI baseline study. The codes were selected by NNPC/RPI.

The selection of sampling sites was dictated by

(a) A Petroleum refinery

(b) Oil wells and flow stations

(c) Oil Jetties

(d) Large settlements

(e) Control Stations (far from human activities)

The study area, concerned with petroleum - related activities, falls mainly within the Niger Delta. Here, stations were identified close to various petroleum operations. Control stations were also established far from human activities. Two other areas of interest were identified for this study, the first includes the Lagos and Lekki Lagoon and the other around the Kaduna refinery and Ibadan as control.

Sampling stations were chosen in the Lagos and Lekki Lagoons and in the following rivers in the Niger Delta:

(i) Benin

(ii) Escravos

(iii) Forcados/Warri

(iv) Ramos

(v) Nun/Ekole/Brass

(vi) Orashi

(vii) Bonny/New Calabar

(viii) Imo

(ix) Cross River/Calabar

(x) Kaduna.

Samples were also taken in Ogunpa river at Agodi garden and on Asejire river all in Ibadan.

In July 1984 an oil spillage incident was reported at Utorogu in Bendel State from one of Shell's flow stations. The Utorogu swamp which opens into Okpari river was affected. Sampling stations were established within the Utorogu swamp and on Okpari river, for the purpose of monitoring the impact of petroleum on the aquatic environment. Table 31 contains the station codes with the locations while figure 21 shows the sampling locations. This particularly presents a case study.

The peculiar nature of lagos Lagoon as a river system under stress from human developmental activities

but with a restricted circulation led to a decision for a close monitor of the Lagos Lagoon sediments during the 1985 season (i.e January to December). The sampling points and time table are given in table 32 with figure 22 showing the various sampling points.

TABLE 3.0

DESCRIPTION OF SAMPLING STATIONS FOR WATER AND SEDIMENTS AROUND LAGOS AND NIGER DELTA AREAS OF NIGERIA 1984-85

S.N	STATION No.	STATION LOCATION	DATE COLLECTED	RIVER SYSTEM
	1	LAGOS-LEKKI LAGOON		
1	086	LAGOS HARBOUR OFF FEDERAL PALACE HOTEL	16-10-84	LAGOS LAGOON
2	087	LAGOS HARBOUR NORTH OF NNPC FACILITY	16-10-84	"
3	845	LAGOS HARBOUR AT LEVER BROTHERS' DISCHARGE	16-10-84	"
4	847	LAGOS HARBOUR AT OKOBABA SAWMILL FACILITIES	16-10-84	"
5	848	LAGOS HARBOUR AT ADENIJI ADELE NEAR 3RD M. BRIDGE	16-10-84	"
6	849	LAGOS LAGOON OFF UNIVERSITY OF LAGOS	17-10-84	"
7	850	LAGOS LAGOON JUST EAST OF AGBOYI CREEK	17-10-84	"
8	851	LAGOS LAGOON AT IBESE	17-10-84	"
9	852	UNNAMED CREEK MOUTH TO NORTH OF OGUN RIVER	17-10-84	"
0	855	LAGOS LAGOON AT EPE	18-10-84	"
	856	LEKKI LAGOON OFF PAPERMILL NORTH OF IWOPIN	18-10-84	"

TABLE 30 (contd.)

	2.	BENIN		
12	134	ASAGBA (ETHIOPE RIVER)	04-08-84	BENIN
13	311	BENIN CITY (IKPOBA RIVER)	04-08-84	"
14	804	OKUABODE (MANYAHA CREEK)	04-08-84	"
15	835	OLAJI CREEK	06-10-84	"
16	836	UROJU CREEK DOWNSTREAM	06-10-84	"
17	837	GWATO CREEK AT DUDU TOWN	06-10-84	"
18	838	OLAGUA CREEK/BENIN RIVER CONFLUENCE	06-10-84	"
19	347	KOKO (ETHIOPE RIVER)	06-10-84	"
20	057	BENIN RIVER AT ROBBINS CREEK	06-10-84	"
21	877	OSSIOMO RIVER WEST OF ROAD AT PIPELINE CROSSING	02-11-84	"
22	878	OSSIOMO RIVER EAST OF ROAD AT PIPELINE CROSSING	02-11-84	"
23	884	BENIN RIVER MOUTH SOUTH SIDE	15-11-84	"
24	O-1	OCHARIFE FIELD DISCHARGE POND	2-11-84	"
25	O-2	OCHARIFE FIELD EFFLUENT CANAL	01-11-84	"

TABLE 30 (contd.)

	3	ESCRAVOS		
26	054	ESCRAVOS TERMINAL	09-1o-84	ESCRAVOS
27	055	AGHIGHO	04-1o-84	"
28	098	ESCRAVOS RIVER MOUTH SOUTH SIDE	15-11-84	"
29	360	JONES CREEK AT JONES CREEK FIELD	09-10-84	"
30	362	NANA CREEK OPPOSITE BAKOKODIA	07-10-84	"
31	831	BENIN CREEK	04-10-84	"
32	832	ESCRAVOS RIVER	04-10-84	"
33	833	ESCRAVOS RIVER AT CHANOMI CREEK	04-10-84	"
34	834	ESCRAVOS RIVER AT NANA CREEK	04-10-84	"
35	839	UNNAMED CREEK OFF JONES CREEK EAST OF JONES CREEK FIELD	07-10-84	"
36	840	JONES CREEK FIELD OPPOSITE FLOW STATION WKDY-2	07-10-84	"

TABLE 3.0 (contd.)

	4	FORCADOS/WARRI		
37	040	PATANI	03-08-84	FORCADOS
38	049	FORCADOS RIVER AT UPSTREAM TIP OF PENFOLD ISLAND	25-10-84	"
39	050	WARRI RIVER SOUTH EAST OF ODIDI FIELD	24-10-84	"
40	051	UGHELLI (OLD BRIDGE)	03-08-84	"
41	052	AGBARHO	04-08-84	"
42	053	WARRI RIVER AT WARRI RIVER FIELD	24-10-84	"
43	351	CHANOMI CREEK BELOW MOUTH OF OYEYE CREEK	23-10-84	"
44	352	CHANOMI CREEK AT CONFLUENCE OF UNNAMED CREEK DRAINING ODIDI FIELD	23-10-84	"
45	353	CHANOMI CREEK AT CONFLUENCE OF TWO OTHER UNNAMED CREEKS	23-10-84	"
46	372	UNENUCHI (OKPARI CREEK)	03-08-84	"
47	858	CHANOMI CREEK AT CONFLUENCE OF UNNAMED CREEK DRAINING EGWA FIELD	23-10-84	FORCADOS/ ESCRAVOS
48	859	UNNAMED CREEK DRAINING ODIDI FIELD	23-10-84	"
49	860	FORCADOS ESTUARY EAST OF TERMINAL	23-10-84	"
50	861	WARRI RIVER UPSTREAM OF REFINERY JETTY AT OGUNO CHANNEL	24-10-84	"
51	862	UNNAMED CREEK OPPOSITE AJUJU FIELD	24-10-84	"

TABLE 30 (contd.)

52	863	WARRI RIVER ABOVE KEREMO	24-10-84	FORCADOS
53	864	FORCADOS RIVER ABOVE AYAKOROMO	25-10-84	"
54	865	FORCADOS RIVER ABOVE OBOTEBE	25-10-84	"
55	866	FORCADOS RIVER ABOVE BURUTU	25-10-84	"
56	867	FORCADOS RIVER BELOW BURUTU	25-10-84	"
	5	RAMOS RIVER SYSTEM		
57	038	RAMOS ESTUARY NORTH EAST OF AGHORO	26-10-84	RAMOS
58	382	RAMOS ESTUARY NORTH EAST OF AGGE	26-10-84	"
59	869	NIKOROGBA CREEK AT UPSTREAM TIP OF IDIWINI ISLAND	26-10-84	"
60	870	ORUGHENE CREEK NEAR UPSTREAM JUNCTION WITH AKASSA CREEK	26-10-84	"
61	871	MURI CREEK	26-10-84	FORCADOS/ RAMOS
	6	NUN/EKOLE/BRASS		
62	023	AGIP SLOT	17-08-84	BRASS
63	024	NORTH END OF ISLAND NORTH OF WALTERKIRI	17-08-84	BRASS

TABLE 30 (contd.)

64	030	SOUTH OF KAIAMA	17-08-84	NUN
65	036	TAYLOR CREEK/ZARAMA	01-08-84	TAYLOR CREEK
66	043	DIEBU CREEK OFF NUN RIVER	31-10-84	NUN
67	094A	BRASS RIVER MOUTH EAST SIDE	14-11-84	BRASS
68	095B	BRASS RIVER MOUTH WEST SIDE	14-11-84	BRASS
69	260	OKOSO/SANDY FLOODPLAIN	01-08-84	NUN
70	281	ELPE CREEK OFF EKOLE CREEK ABOVE YENAGOA	17-08-84	NUN/BRASS
71	803	KAIAMA/PATANI FLOODPLAIN	03-08-84	NUN
72	825	EKOLE CREEK, NW OF SANGAKUBU	17-08-84	BRASS
73	872	NUN RIVER BELOW PEREMABIRI	31-10-84	NUN
74	873	NUN RIVER ABOVE DIEBU CREEK FIELD OPPOSITE EKJAMBIRI	31-10-84	NUN
75	874	DIEBU CREEK FIELD AT WELL ~~11~~8	31-10-84	NUN
76	875	DIEBU CREEK FIELD BETWEEN WELLS 4 AND 13	31-10-84	NUN
	7	ORASHI		
77	012	DOWNSTREAM OF OBAGI FIELD	15-08-84	ORASHI
78	013	ONOSI RIVER (NEAR EBOCHA)	02-08-84	"
79	014	OGUTA PONTOON CROSSING	02-08-84	"
80	016	LAKE OGUTA (SOUTH SHORE)	02-08-84	"

TABLE 30 (contd.)

81	021	OPPOSITE DEGEMA	14-08-84	SOMBREIRO
82	022	AHOADA	01-08-84	"
83	035	ENWHE FLOW STATION AND FIELD	14-08-84	ORASHI
84	250	MBIAMA	15-08-84	"
85	251	ORASHI RIVER ABOVE NDONI CREEK (OBRIKOM)	15-08-84	"
86	252	OKOGBE WEST	01-08-84	"
87	262	NDONI CREEK (DOWN)	15-08-84	"
88	801	OKOGBE EAST	01-08-84	"
89	802	OBAGI EVAP. PIT/SWAMP	02-08-84	"
90	819	LOWER ORASHI RIVER	14-08-84	"
91	820	ORASHI RIVER AT EGORIBIRI CREEK (EGBEMA)	14-08-84	"
92	821	OKARKI	14-08-84	"
93	824	ORASHI RIVER ABOVE OMOKU CREEK	15-08-84	"
94	881	SOMBREIRO RIVER MOUTH EAST SIDE	14-11-84	SOMBREIRO
95	882	SOMBREIRO RIVER MOUTH WEST SIDE	14-11-84	"
	8	BONNY/NEW CALABAR		
96	018	OKRIKA REFINERY JETTY (OPPOSITE)	06-08-84	BONNY
97	020	UMUOCHI (ALUU)	07-08-84	NEW/CALABAR

TABLE 30 (contd.)

98	093	BONNY/NEW CALABAR RIVER MOUTH EAST SIDE	14-11-84	BONNY/NEW CALABAR
99	121	BONNY RIVER AT BODO CREEK	06-08-84	BONNY
100	233a	PORT HARCOURT HARBOR	06-08-84	"
101	236	ELELE ALIMINI	01-08-84	NEW CALABAR
102	807	BAKANA (UP)	06-08-84	BONNY
103	808	OPPOSITE IWOFE	07-08-84	NEW CALABAR
104	809	BELOW CHOBA SERVICE CENT.	07-08-84	"
105	810	NORTH OF ALAOCHA	07-08-84	"
	9	IMO		
106	078	NEW BRIDGE	12-08-84	IMO
107	128	ABOVE KONO WATERSIDE	12-08-84	"
108	806	ALIMINI RIVER AT ABA	06-08-84	"
109	813	IMO RIVER AT AZUMINI RIVER (ABA)	12-08-84	"
110	816	ISIMIRI FLOW STATION AND FIELD	12-08-84	"
111	817	OTAMIRI	12-08-84	"
112	818	IMO RIVER NEAR OTAMIRI RIVER	12-08-84	"

TABLE 3.0 (contd.)

113	880	IMO RIVER MOUTH EAST SIDE	13-11-84	IMO
	10	CROSS RIVER -CALABAR		
114	070	CALABAR RIVER	10-08-84	CALABAR
115	071	CALABAR HARBOUR ABOVE NAVY BASE	09-08-84	"
116	072	CALABAR BETWEEN MARKER 31 & 32	10-08-84	"
117	079	CROSS RIVER EAST SHORE	10-08-84	CROSS
118	210	IKOT EKPENE RIVER	10-08-84	KWA IBOE
119	805	CROSS RIVER FLOODPLAIN	10-08-84	CROSS
120	811	PARROT ISLAND	09-08-84	"
121	812	CALABAR RIVER AT URIYAMA RIVER	09-08-84	CALABAR
122	826	CALABAR TRIBUTARY	10-08-84	"
123	827	NEW CALABAR PORT COMPLEX	09-08-84	"
	11	KADUNA		
124	141A	RIVER ROMI TRIBUTARY DOWNSTREAM OF REFINERY EFFLUENT CANAL	11-10-84	KADUNA
125	141B	RIVER ROMI TRIBUTARY UPSTREAM OF REFINERY EFFLUENT CANAL	12-10-84	"
126	843	KADUNA RIVER AT DOKA PARK (KADUNA)	12-10-84	"
127	844	KADUNA RIVER FLOODPLAIN NORTH OF KADUNA AT MALALI	12-10-84	"

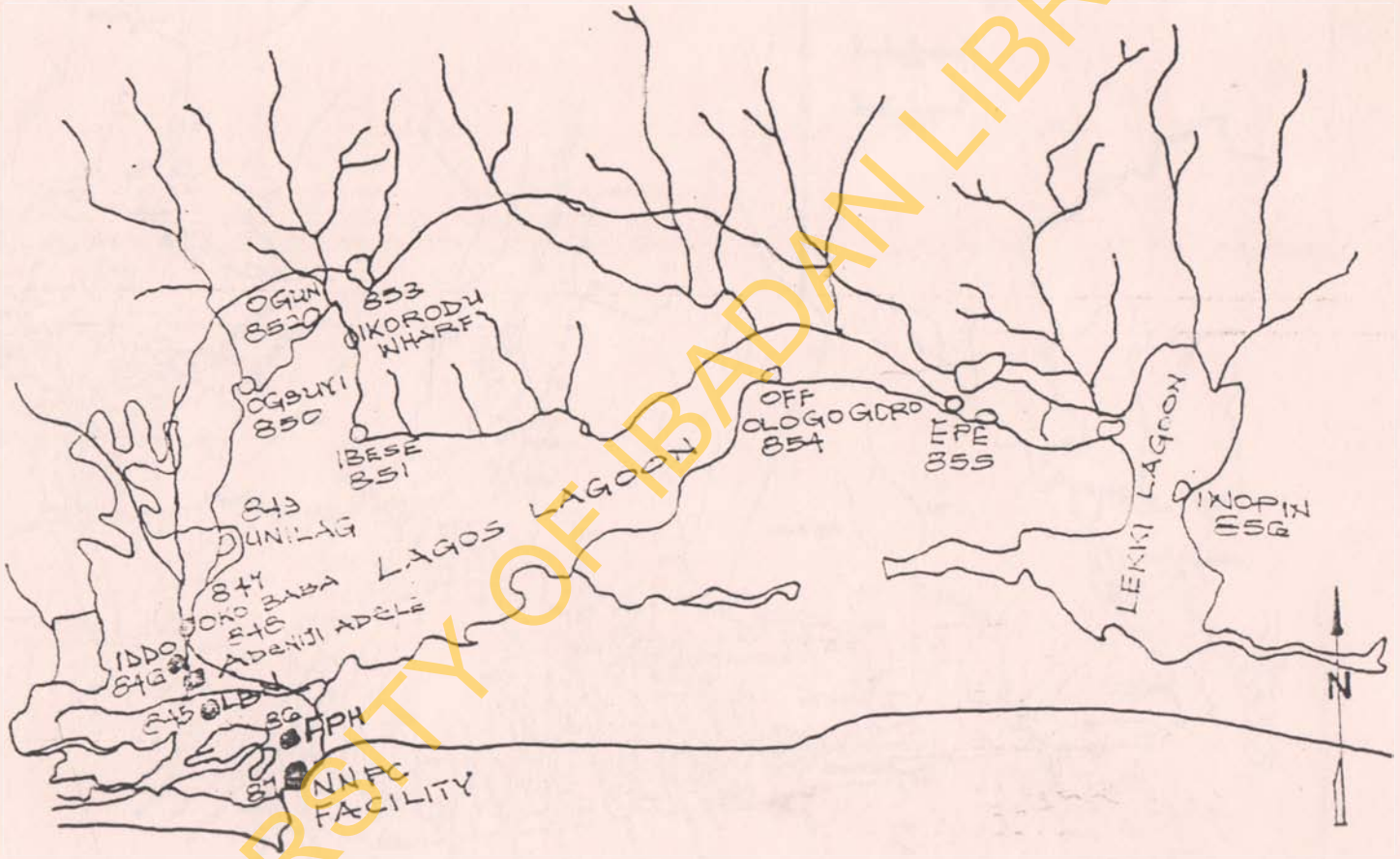


FIG 19 : LAGOS AND LEKKI LAGOONS STATIONS SAMPLED IN 1984 – 85

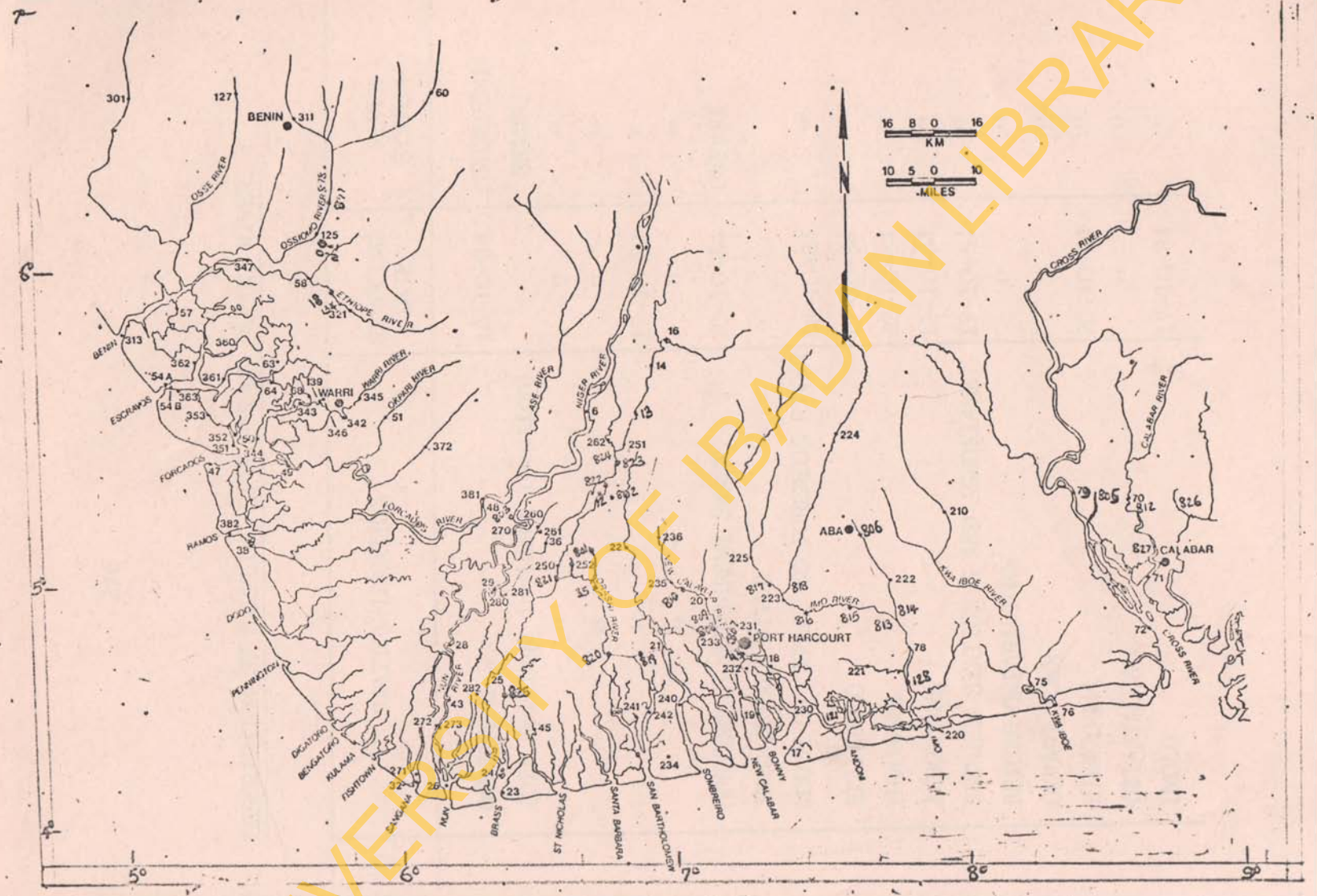


FIGURE 20: NIGER DELTA STATION LOCATIONS SAMPLED IN 1984-85.

TABLE 31: DESCRIPTION OF SAMPLING STATIONS ON OKPARI RIVER.

STATION NO	STATION LOCATION	SAMPLING DATE	RIVER SYSTEM
A	OTUJEREMI (Oil Spillage incident location)	16-10-84	OTUJEREMI SWAMP.
B	"	"	"
C	"	"	"
D	"	17-10-84	
E	"	"	"
G	OPENING OF OTUJEREMI SWAMP INTO OKPARI RIVER	20-10-84	OKPARI
J	MOUTH OF OKPARI TO FORCADOS RIVER	18-10-84	"
K	EKAIGBODO	17-10-84	"
M	EHRUWARE	20-10-84	"
N	AGBOKIAMA	19-10-84	"
O	BETWEEN STATION G AND AGBOKIAMA	19-10-84	"
P	BEFORE OKPARI TOWN	"	"
R	OKPARI TOWN	"	"
T	BIKOROGHA	20-10-84	"
U	OBI-AYAGHA	"	"
V	UMOLO	17-10-84	"

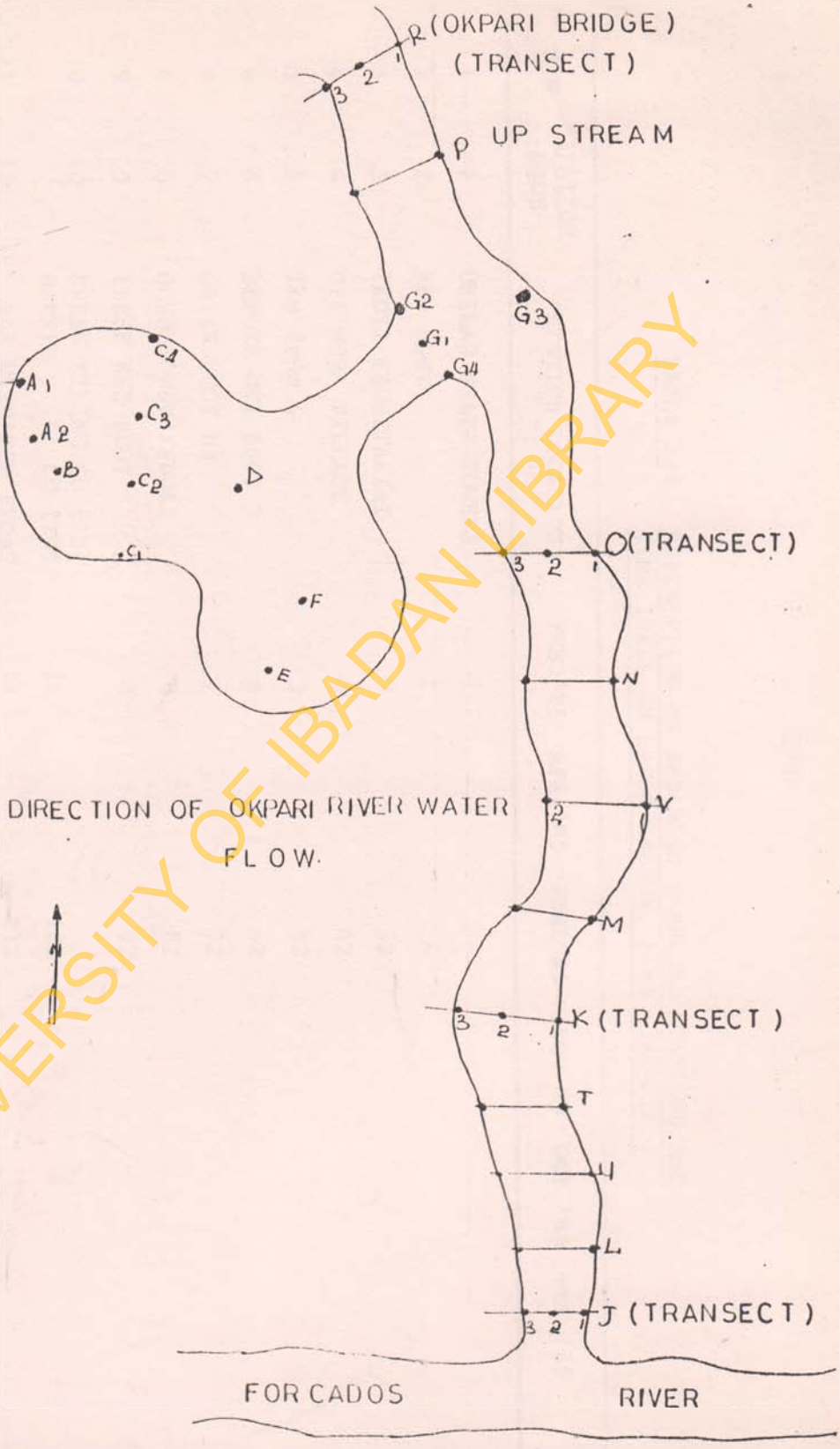


FIG. 21: OKPARI RIVER STATIONS SAMPLED IN 1984-85

TABLE 32: DESCRIPTION OF SEDIMENT SAMPLING STATIONS AND TIME TABLE ON LAGOS LAGOON, 1985 (JAN-DEC.)

S.N	STATION CODE	STATION LOCATION	FEB.'85	APR.'85	JUNE'85	AUG. 85	OCT.'85	DEC. 85
1	1	UNILAG STAFF TOWERS	1		-			
2	2	RED BUOY	2		-			
3	3	IKOYI SECRETARIAT	3		32			
4	4	OFF MOBA VILLAGE	4		42			
5	5	IKm from 4	5		52			
6	6	BEFORE OYI BUOY 3	6		62			
7	7	GREEN BUOY N3	7		72			
8	8	OGUDU/OWORONSHOKI	8		82			
9	9	IBESE RED BUOY	9		92			
10	10	GREEN PILING GO (15) MARKED CC (10)	10		102			
11	11	BAR WITH RED FLOAT HANGING	11		112			
12	12	BAR (NO FLOAT)	12		-			
13	13	MOUTH OF R. OGUN	13		132			
14	14	IKORODU (NEAR FISHING (TERMINAL)	14		142			

TABLE 32 (Contd.)

S.N	STATION CODE	STATION LOCATION	FEB.'85	APR.'85	JUNE'85	AUG.'85	OCT.'85	DEC.'85
15	15	3 LOG OF WOOD	15		-			
16	16	BUOY 21	16		-			
17	17	PALAVER ST	17	-	-	173	-	175
18	18	TARKWA BAY	18	-	-	-	184	185
19	19	TIN CAN ISLAND/OFF SHIP WRECK	19	191	192	-	-	195
20	20	BERGER/NATIONAL OIL/ IJORA	20	201	202	203	-	205
21	21	IDDO/ENGINE HOUSE	21	-	-	-	-	-
22	22	3RD BRIDGE ISLAND	22	-	222	-	-	225
23	23	OKOBABA (PYLON 134)	23	-	232	-	234	-
24	24	POWER ST, IJEDE	24	-	242	-	-	245
25	25	ISLANDS OFF PALAVER ST	25		252			
26	26	ITOOMU CREEK	26		262			

SAMPLE CODES:

FEBRUARY SAMPLE # with (-)
APRIL SAMPLE # with (1)
JUNE SAMPLE # with (2)
AUGUST SAMPLE # with (3)
OCTOBER SAMPLE # with (4)
DECEMBER SAMPLE # with (5)

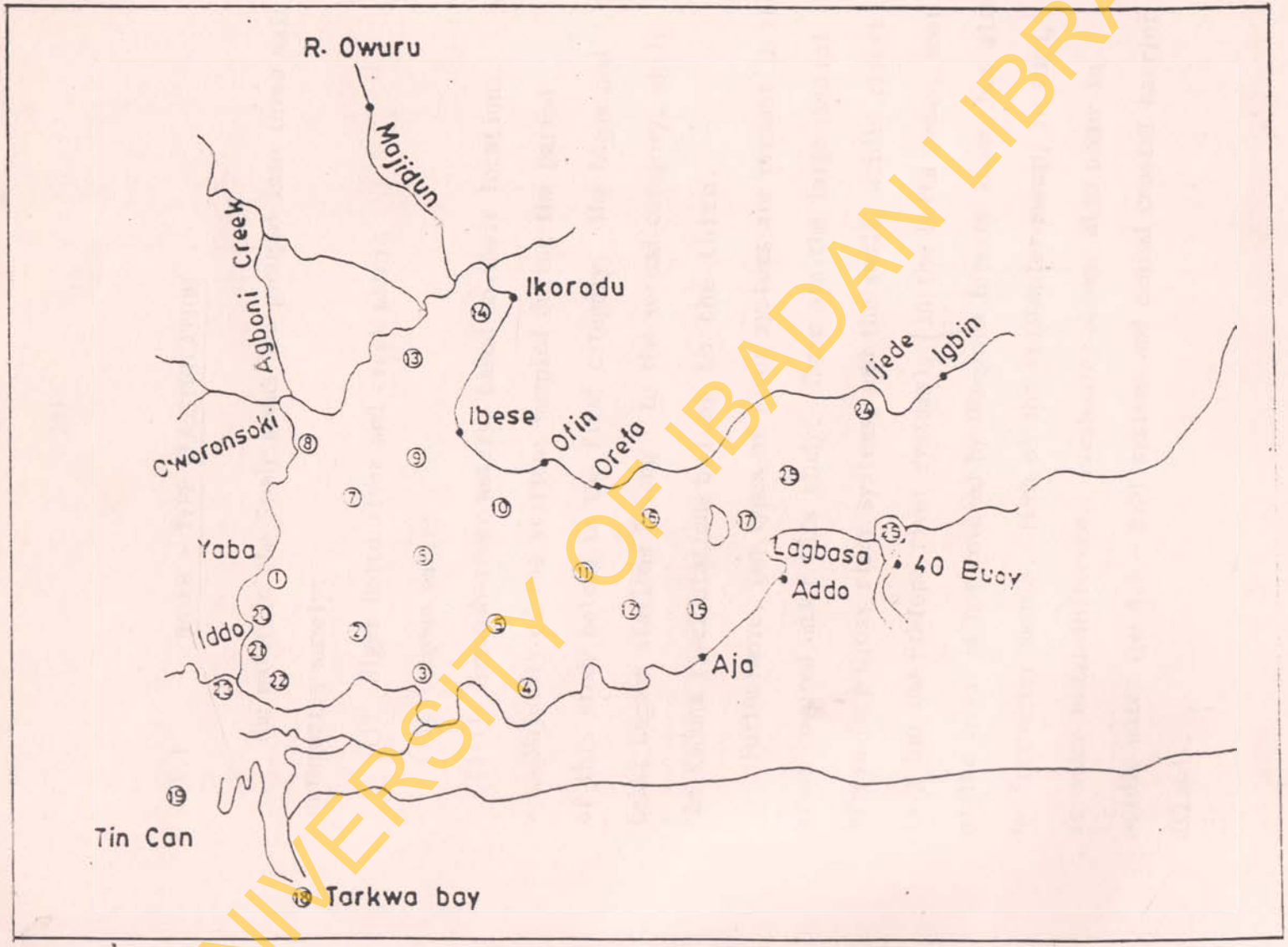


Fig. 22: Lagos Lagoon station where sediments were sampled in Jan.– Dec. 1985.

3.1.1 WATER - TYPE CLASSIFICATION

The water in the Study areas are grouped into three main categories namely:

(i) Niger Delta river and creek waters

(ii) Lagoon waters

(iii) Savanah-river waters, based on their locations.

Majority of the stations sampled during the period of this study belong to the first category. The Lagos and Lekki Lagoon stations belong to the second category, while the Kaduna river stations belong to the third.

Furthermore, two types of river systems are present in the areas covered under this study. These are the large neutral rivers (e.g Cross river systems) and the small, acidic rivers (e.g Imo and Ethiope river systems). In the Delta areas, most of the area is not covered by Mangrove forests alone, but also by freshwater swamps. Much of the freshwater swamp, in turn, is under tidal influence. Freshwater swamps also occur in acidic water (pH 4.5 - 6.0) systems and behind coastal barrier islands.

As shown in figure 23, the major aquatic zones of the oil-producing area of Nigeria include (Powell and Onwuteaka, 1980)[242]

(1) Non-tidal, freshwater swamps-

(2) Tidal freshwater-

(3) Mangrove (Saline) swamps.

Further classification of the waters into 'white', 'black' and 'clear' was based on Sioli's method in his description of the Amazon River basin water (Sioli, 1975). The use of Sioli's Amazon framework is appropriate to the Niger Delta because of the many similarities between the two river basins. Sioli's classifications were based on both chemical (e.g conductivity, total alkalinity, pH) and physical (e.g tidal influence) properties of the Amazon River water and explained by the sedimentology, and weathering history of watersheds. 'White water' was derived from watersheds where the weathering products produced clays and where erosion was occuring because of soil disturbance. 'Black water' rivers, drained watersheds with leached, sandy substrates and heavy vegetation cover. As a result, these waters had low dissolved or suspended solids, and the degradation of the organic matter, produced organic acids which lowered the pH and coloured the water brown.

The "White" (or "mes-ionic") waters are characterized

by marked turbidity, normal freshwater conductivity range, with 30 - 100 μmho/cm, nearly neutral pH values, and strongly seasonal flood regimes. All features are due to rivers draining large, inland, savanah areas with strongly seasonal rainfall resulting in exposure (weathering) in the soil and basement complex rocks. 'White waters' in the Niger Delta are associated with Niger and Cross river systems.

The "Clear" and "Black" waters are generally acidic, mineral-deficient rivers that can be termed "Oligo-ionic" referring to the low level of electrolytes. Under natural conditions, these water systems drain lowland forest areas with heavily leached, nutrient-deficient soil. These rivers have virtually no suspended matter, extremely low levels of dissolved salts (conductivity values well below 30 μmho/cm) and low pH (4.0-6.5). They show little or moderate seasonality in discharge, resulting in low banks with well defined, permanent marginal vegetation of aquatic macrophyte.

Mangrove swamps are synonymous with saline water in Nigeria. Thus, the mangrove swamp delineates the saline zones. Large isolated patches of freshwater swamps within the saline zone occur behind the high coastal beach ridges.

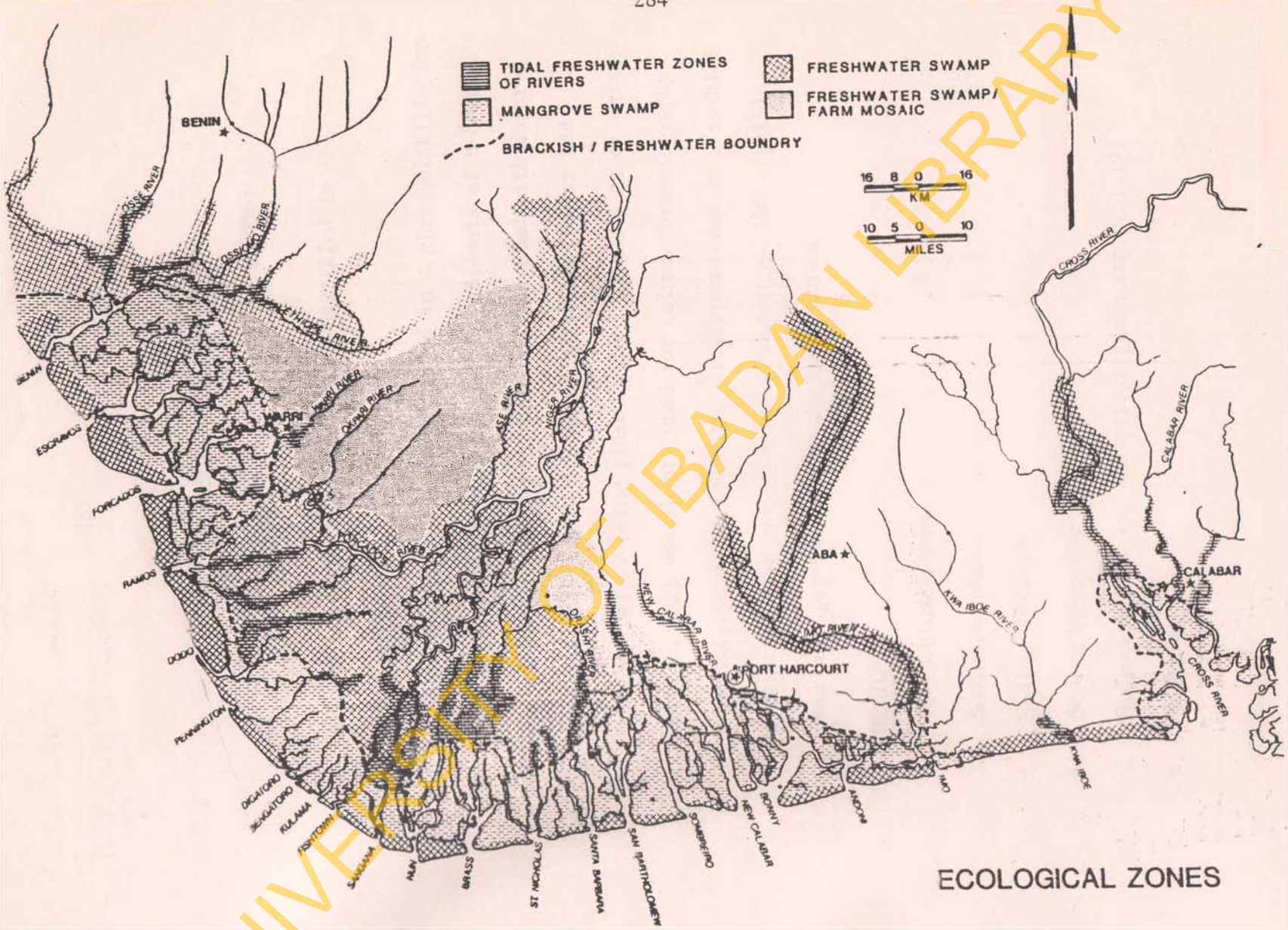


FIGURE **23** Ecological zones of the Niger Delta.

3.2 SOLVENTS AND CHEMICALS

3.2.1 PRECAUTIONARY MEASURES:

(a) All the solvents used were doubly distilled in all glass apparatus.

(b) Distilled water used was distilled in a glass-distillation apparatus and partitioned against 3 aliquots of n-hexane.

(c) All glassware used were thoroughly cleaned with detergent and rinsed with tap water, distilled water and methanol before being rinsed with 3 aliquots of di chloromethane. All absorbents used for column chromatography were solvent extracted with dichloromethane in a soxhlet apparatus. The anti-bumping granules and KOH crystals used were pre-cleaned in dichloromethane.

3.2.2 CHEMICALS

1. Tetrachloromethane
2. Sodium Sulphate
3. Sodium chloride
4. Sodium hydroxide
5. Hydrochloric acid, analytical grade (sp.gr.1.19)
6. Methanol

7. Potassium hydroxide
8. Chromic acid containing 4g potassium dichromate in 1 litre of concentrated sulphuric acid.
9. Hexane
10. Dichloromethane
11. Distilled water
12. Boiling stones
13. Ultra pure Nitrogen gas
14. Silica gel (Kieselgel 60) particle size 100 - 120 mesh.
15. Aluminium oxide (Neutral), activity grade one for chromatography. Particle size 80-100 mesh.

Silica gel and Alumina were purified by soxhlet extraction for 8 hrs using hexane. Both salts were then activated at 130^{o}C for 24 hours and deactivated with 5% (W/W) distilled water. Equilibration was done for 24 hours before use.

3.2.3 REFERENCE OIL: (for Infrared analysis)

For the purpose of IR calibration, synthetic reference oil was prepared from:-

(1) n - Hexadecane (analytical grade)

(2) iso - Octane (analytical grade)

(3) Benzene (analytical grade).

The synthetic reference oil mixture composition was

15.0ml n-Hexadecane (37.5% by volume)

15.0ml iso-Octane (37.5% " ")

10.0ml Benzene (25.0% " ")

Accurately weighed amount of the reference oil was dissolved in terrachloromethane and diluted with the same solvent to prepare a stock solution of known concentration. Working standards were prepared from the stock solution by serial dilution of the stock.

3.2.4 INTERNAL STANDARDS

A compound similar in physical and chemical properpeties to the analyte in the sample can be added to the sample prior to analysis. Internal standard responses are incorporated into quantitative analysis calculations thus serving to normalize all data to a known amount of a common reference. An internal standard will correct for the biases associated with determinative steps in an analytical procedure.

The following standards were used as internal standards during the analysis of the samples.

n - Tetradecane ($n\text{-}C_{14}$)
n - Hexatricontane ($n\text{-}C_{36}$) } Aliphatic Internal Standards

Anthracene, and
Phenanthrene } Aromatic Internal Standards

3.2.4.1 PREPARATION OF INTERNAL STANDARDS.

STOCK SOLUTIONS.

n - Tetradecane - 53.50mg/50ml = 1070 $\mu g\ ml^{-1}$

n - Hexatricontane - 49.00 mg/50ml = 980 $\mu g\ ml^{-1}$

Anthracene - 50.40 mg/50ml = 1008 $\mu g\ ml^{-1}$

Phenanthrene - 49.90 mg/50ml = 998 $\mu g\ ml^{-1}$

5ml of each standard was diluted to 50ml in a volumetric flask. 1ml of the diluted standards were used to spike the samples.

3.2.4.2 EXTERNAL STANDARDS

External standards are a mixture of compounds of interest (analytes to be determined) prepared in a suitable organic solvent and diluted to approximate environmental residue concentrations. It is used for calibrating and checking detector response prior to instrumental analysis. External standard establish response and retention factors necessary for quantitative analysis when internal standard method is not used. Nonetheless external and internal standards can also be used simultaneously.

A mixture of some n-alkane hydrocarbons over the range

C_{10} - C_{36} and 2 isoprenoid hydrocarbons (pristane and phytane) was prepared and used as external standards for identification and quantification of the different aliphatic components present in extracts of the samples analysed for this work.

The compounds were weighed and quantitatively transferred into volumetric flasks and made up to the mark with analytical grade iso-octane. 1ml of each standard was then taken with graduated pipette and transferred into a 50ml volumetric flask. The final volume was adjusted by adding iso-octane. See table 33 for concentration of each standard in mixture of standards.

Table 34 is for the composition of the mixed aromatic standards used as external standards for the identification and quantification of the aromatic fractions.

TABLE 33: COMPOSITION OF MIXED ALIPHATIC HYDROCARBON STANDARDS FOR GC ANALYSIS

COMPOUND	CONCENTRATION IN $ng\mu l^{-1}$ OF MIXED STANDARD	DETECTION LIMIT $mg\,l^{-1}$
$n\text{-}C_{10}$	58.59	2.3×10^{-6}
$n\text{-}C_{12}$	58.82	2.4×10^{-6}
$n\text{-}C_{14}$	62.94	2.5×10^{-6}
$n\text{-}C_{16}$	58.82	2.4×10^{-6}
$n\text{-}C_{17}$	67.41	2.7×10^{-6}
$n\text{-}C_{18}$	59.88	2.4×10^{-6}
$n\text{-}C_{20}$	46.71	1.9×10^{-6}
$n\text{-}C_{22}$	59.88	2.4×10^{-6}
$n\text{-}C_{23}$	69.06	2.8×10^{-6}
$n\text{-}C_{24}$	56.35	2.3×10^{-6}
$n\text{-}C_{26}$	58.82	2.4×10^{-6}
$n\text{-}C_{28}$	59.53	2.4×10^{-6}
$n\text{-}C_{30}$	62.82	2.5×10^{-6}
$n\text{-}C_{32}$	64.71	2.6×10^{-6}
$n\text{-}C_{34}$	58.00	2.3×10^{-6}
$n\text{-}C_{36}$	57.65	2.3×10^{-6}
Pr	58.82	2.4×10^{-6}
Ph	32.47	1.3×10^{-6}

TABLE 34: COMPOSITION OF MIXED AROMATIC HYDROCARBON STANDARDS FOR GC ANALYSIS

COMPOUND	CONCENTRATION IN $ng\mu l^{-1}$ OF MIXED STANDARD	DETECTION LIMIT mgl^{-1}
Naphthalene	71.85	2.9×10^{-6}
DimethylNaphthalene	72.45	2.9×10^{-6}
Acenaphthene	70.70	2.8×10^{-6}
Phenanthrene	71.30	2.9×10^{-6}
Anthracene	72.00	2.9×10^{-6}
Fluoranthrene	70.85	2.8×10^{-6}
Pyrene	70.85	2.8×10^{-6}
1,2-Benzanthracene	217.60	8.7×10^{-6}
7,12-Dimelthy l Benz (a) anthracene	144.40	5.8×10^{-6}
3-Methyl Cholanthracene	68.80	2.8×10^{-6}
1,2,3,4-Dibenzanthracene	46.65	1.9×10^{-6}
1,2,5,6-Dibenzanthracene	96.80	3.9×10^{-6}

3.3 APPARATUS AND EQUIPMENT

1. 1 litre glass separatory funnels with teflon stopcocks.
2. 250ml glass separatory funnels with teflon stopcocks.
3. 100ml standard flasks
4. 50ml standard flasks
5. 25ml standard flasks
6. 250ml round bottomed flasks, Quick fit.
7. 1ml, 5ml, and 10ml calibrated pipettes
8. 5ml, 10ml, 25ml, 100ml, 250ml and 1000ml measuring cylinders.
9. Pasteur pipettes
10. Reflux condensers
11. 60ml glass reagent bottles
12. 10ml sample bottles
13. Analytical mettler balance type H15
14. Aluminium foil
15. Concord Refridgerator for storage of water samples
16. Scanfrost Deep freezer for storage of sediment samples
17. Isomantle Gerhardt Bonn
18. Buchi Rotavapor

19. Buchi Rotavapor
20. 1µl, 10µl Hamilton syringes for injection of samples.
21. Gallenkamp Drying Oven. (30^{o} - 200^{o}C)
22. Gas chromatograph - Varian 3700 model.
23. Chart recorder, Varian 9176 model
24. Varian Chart recorder paper
25. Infrared Spectrophotometer, Pye Unicam SP 2000 model.
26. Infrared Spectrophotometre, Perkin Elmer 457 model.

3.4 APPROACHES TO THE PETROLEUM HYDROCARBON DETERMINATION.

In the detection and determination of low levels of hydrocarbon pollution, two approaches used in this study are:

(1) Measuring the specific properties of the oil extract and comparing the results with those of standards.

This approach involves the use of IR spectrometry and UV absorption/fluorescence spectrometry[205,218]. This approach assumes that the components of the standard used are identical to those of the sample, an assumption that may not be true. More importantly, these techniques can neither differentiate between biogenic and petrogenic hydrocarbons nor indicate the complexity or molecular weight range of the sample.

These latter disadvantages have limited the use of these techniques for detailed characterisation of petroleum pollutants. But IR can be

used as a good screening technique to detect "hot spot" areas.

(2) The second approach involves quoting the individual contents of the sample while attempting to distinguish between the biogenic and petrogenic component using the type distribution of its classes[244]. This approach involves the use of more diagnostic analytical tools like gas chromatography(Gc), mass spectrometry and computerized gas chromatography mass spectrometry(Gc-ms) after prior separation, usually by liquid chromatography.

In this work both approaches are involved in the analyses and the techniques chosen are the IR and GLC. Gravimetric method was also used for the determination of both the total aliphatic and total aromatic components in the sediment samples. For the IR analysis of water Samples a Pye Unican SP2000, and a Perkin Elmer 457 Grating IR spectrophotometer were used while Varian Model 3700 Gas Chromatograph was used for the gas chromatographic analysis of the water and sediment samples.

3.5 CLEANING OF APPARATUS AND REAGENTS.

Glass bottles (1 litre) were used in the collection and storage of water samples prior to the determination of petroleum hydrocarbon. Glass stoppers were preferred in order to prevent adsorption of oil on cap liners or cork stoppers. The bottles and stoppers were cleaned by the method of Bruce[139] . . They were detergent washed followed by distilled water rinse, then acid washed with concentrated H_2SO_4 for 5minutes, and properly rinsed with distilled water. Finally rinsing with double distilled methanol and doubly distilled n-hexane were also carried out. The bottles were oven-dried at 350°C overnight.

The wide-mouth glass bottles and aluminium foil for collecting sediment samples were treated with acetone and n-hexane in like manner.

All glasswares used in the laboratory were thoroughly cleaned as described in section 3.2.1 above.

The tetrachloro methane used was double distilled over calcium hydride while the alumina, silica gel,

sodium chloride and sodium sulphate were soxhlet extracted with n-hexane for eight hours each.

3.6 WATER SAMPLE COLLECTION AND PRESERVATION

Water is a medium through which oil is moved from the point of introduction to areas quite removed from the pollution source. Because of the nature of oil, its concentration along the water body or down the water column is not uniform. For reliable results, samples were taken at different depth, in order to bring out the true picture of the distribution levels of oil in the area under study.

Rivers and lagoon waters were sampled with pre-cleaned water sampler (Fig. 14 & 15) made of carboy glass with string attached to it, along which a steel messenger can travel down to close the sampler under water at the desired depth, in order to prevent contamination of sample with surface water. The bottom and mid-water samples were taken by lowering the opened (solvent-cleaned) sampler with the aid of the attached string. At the appropriate depth, the messenger was released to close the sampler. The sampler was then retrieved and the water sample transferred into solvent-cleaned bottles bearing labels

to indicate, the date, time, and location of the samples. The standard bottles used for sample collection were the 1 litre pyrex glass bottles with glass stoppers.

In order to preserve the integrity of the samples, preservative was added in form of 5ml 1:1 v/v hydrochloric acid (U.S. EPA method 413.2 storet no 4550)[245] per litre of water and kept in ice in the field to arrest microbial activity.

Water samples from the surface were taken with solvent-cleaned stainless steel bucket. All samples were taken from the windward side of the boat to prevent contamination by the oil from the boat's engine. For shallow rivers, water samples were collected by lowering a 1 litre pyrex glass bottle with a strong cotton rope tied to its neck.

The temperature and pH values were taken on board the sampling boat.

3.7 SEDIMENTS

All the sediment samples were collected using a pre-cleaned Van veen grab sediment sampler (Fig. 16). The top 3-5cm in each case was scraped with a pre-cleaned scrapping knife and stored in a solvent-

cleaned bottle or solvent-washed aluminium foil, carefully wrapped and kept in labelled cellophane bags before being frozen on board the boat or in a cooler containing iceblocks when necessary.

3.8 DETERMINATION OF PETROLEUM HYDROCARBONS:

Petroleum hydrocarbons in coastal and marine environment have been extracted, separated, isolated, identified and quantified by a number of methods. Since no single technique provides a complete analysis of Petroleum residues in water, sediment, and other biological samples, some considerations for selecting methods and for understanding potential problem areas are necessary.

In order to decide what combination of analytical procedures will be most useful, there is the need to determine the level of sensitivity and selectivity necessary to meet the requirements of our scientific goal. The various analytical techniques have their advantages and disadvantages. Their usefulness therefore depends on the precision, accuracy, speed and sensitivity. It is on this premise, that a comparison of some of the methods is necessary before a final choice is made.

3.8.1 RECOVERY STUDIES BY IR

The analytical methods of Simard et al.,[203] Lindgren[246] American Petroleum Institute (API, 735-58[247]; Storet no 45501 (method 418.1) scholl and Fuchs; Carlberg and Skarstedt[200]; U.S. EPA method 413.2 and FAO Fisheries technical paper N137 on the determination of small amounts of 'non-polar' hydrocarbons (mineral oil) in natural waters which all have same procedure were combined and used.

Samples used in the recovery study were produced by adding different known weights of Reference oil (2.3.3) to 1 litre sample bottles which were then filled about one-fourth ($\frac{1}{4}$) full with distilled water and shaken. Hydrochloric acid (5ml 1:1 v/v) was added, the bottles were each filled with 1 litre distilled water and properly shaken for uniform distribution of the reference oil.

The samples (750ml) were poured into 2litre separatory funnels and 15ml of tetrachloromethane was used to wash each of the bottles from which the samples were removed. This same tetrachloromethane

was then used to extract the water samples. 1.0g of sodium chloride was added to each sample. The samples were extracted by shaking vigorously for 5 minutes. The layers were allowed to separate. The layer of tetrachloromethane was then drawn off into a 50ml volumetric flask through a funnel containing solvent moistened filter paper and anhydrous sodium sulphate (binding traces of water). Another 15ml aliquot of tetrachloromethane was added to the water sample in the separatory funnel. The contents in the funnel were again shaken for another 5 minutes, allowed to settle for 10 minutes and the tetrachloromethane layer was drawn off. This was passed into the same volumetric flask through the same filter paper. The extraction procedure was carried out thrice for each sample. The combined extracts in the volumetric flask were made up to the mark with more tetrachloromethane added through the same filter paper used in the extraction. The total final volume was designated as V_E, while the volume of the aqueous solution from which the oil was extracted was designated as Vw. A blank sample was obtained by rinsing an empty sample bottle with

tetrachloromethane and carried through the procedure stated above in order to detect possible interferences from the glass container and the reagents used.

3.8.2 PRECISION STUDIES BY IR SPECTROPHOTOMETRIC METHOD.

The reproduce bility or precision of the Infrared spectrophotometric method for the quantification of oil in water was tested by ten replicate analysis of known concentration of the Reference oil in water.

The procedure was as outlined in section 3.8.1 above the only difference being the amount of Reference oil (2.3.3) added to the water samples. In precision studies, equal amount of the Reference oil was added to each of the ten water samples used. Ten equal volumes of sample (750ml) containing equal amount of Reference oil were extracted with tetrachloromethane (3 x 15ml). The concentrations of the final extracts were then determined by IR spectrophotometric method as would be discussed in 3.8.3 below.

3.8.3 CALIBRATION GRAPH FOR OIL IN WATER BY INFRARED SPECTROMETRY

Standard stock solutions of synthetic oil was prepared as outlined above (3.2.3). Working standards were then prepared by taking the appropriate volume of the stock and diluting to the chosen volume with tetrachloromethane.

Table 35 summarizes the concentrations of synthetic oil and the absorbance values at 2960cm^{-1}, 2925cm^{-1}, and 2850cm^{-1}. The mean of the 3 values is also given.

The infrared spectromotric (IR) spectra (2500-3400cm^{-1}) of the standards were taken on SP - 2000 IR double beam spectrophotometer using 1.0cm quartz cuvette. Reagent blank was used as reference. The instrument was calibrated with a polystyrene film. The pair of empty clean quartz cuvette were placed at the reference and sample compartments to see if they absorbed at the working region (2500-3400cm^{-1}). They were then rinsed and filled with blank solvent and placed in the compartments. The 'gain' knob was adjusted until the absorbance scale read

0.0 (or 100%T). With the absorbance of the blank set at 0.0 (or 100%T), the net absorbance due to the oily matter can be read directly from the absorbance scale. The sample cell was rinsed and filled with a standard oil in tetrachloromethane or the synthetic standards. The absorbances at 2960cm^{-1}, 2935cm^{-1} and 2850cm^{-1} for the CH_3-, CH_2- and CH- hydrocarbon peaks were calculated. The mean value of the three was used as absorbance A (Table 35). The spectra of the standards were shown in Figure 24.

The calibration curve is shown in Figure 25. It gave a straightline, through the origin. The absorptivity, K, was calculated to be 1.10×10^{-2} $ppm^{-1}cm^{-1}$ for the synthetic oil. It has been demonstrated that the standard mixture is in good agreement with most kinds of mineral oil

The sample cell was then filled with the sample extract. The absorbance was calculated and substituted in the equation below for the corresponding concentration of oil in the water sample.

$$Cw = \frac{A.\ V_E.\ F}{K.\ Vw}$$

Where Cw = concentration of oil in water sample (mg/l)

A = Absorbance of the oil extract.

V_E = Total Volume of the extract (ml)

F = Dilution factor

K = Absorptivity constant from the calibration graph ($ppm^{-1}\ cm^{-1}$)

Vw = Volume of the water sample from which the oil was extracted (ml).

A Pye Unicam SP2000 double beam IR spectrophotometer was used for this work. The spectrophotometer has a wavenumber accuracy of $3cm^{-1}$ in the range 1500-$4000cm^{-1}$ and a wavenumber repeatability (precision) of $3cm^{-1}$ in the same range. The photometric accuracy of the instrument was +1% transmittance.

TABLE 35

CONCENTRATIONS AND ABSORBANCE DATA OF SYNTHETIC STANDARD FOR THE CALIBRATION GRAPH OF OIL IN WATER BY INFRARED SPECTROPHOTOMETRIC METHOD

CONCENTRATION OF STANDARD mg/1	ABSORBANCE $A_1 = 2960cm^{-1}$	$A_2 = 2925\ cm^{-1}$	$A_3 = 2850cm^{-1}$	$\bar{X}_n = \frac{A_1 + A_2 + A_3}{3}$
2	0.01	0.03	0.02	0.02 ± 0.01
5	0.04	0.08	0.05	0.06 ± 0.01
10	0.07	0.16	0.10	0.11 ± 0.03
15	0.11	0.23	0.14	0.16 ± 0.04
20	0.14	0.30	0.18	0.21 ± 0.05
25	0.18	0.38	0.23	0.26 ± 0.07
30	0.22	0.45	0.27	0.31 ± 0.08
40	0.30	0.61	0.37	0.43 ± 0.10
50	0.37	0.74	0.46	0.52 ± 0.12

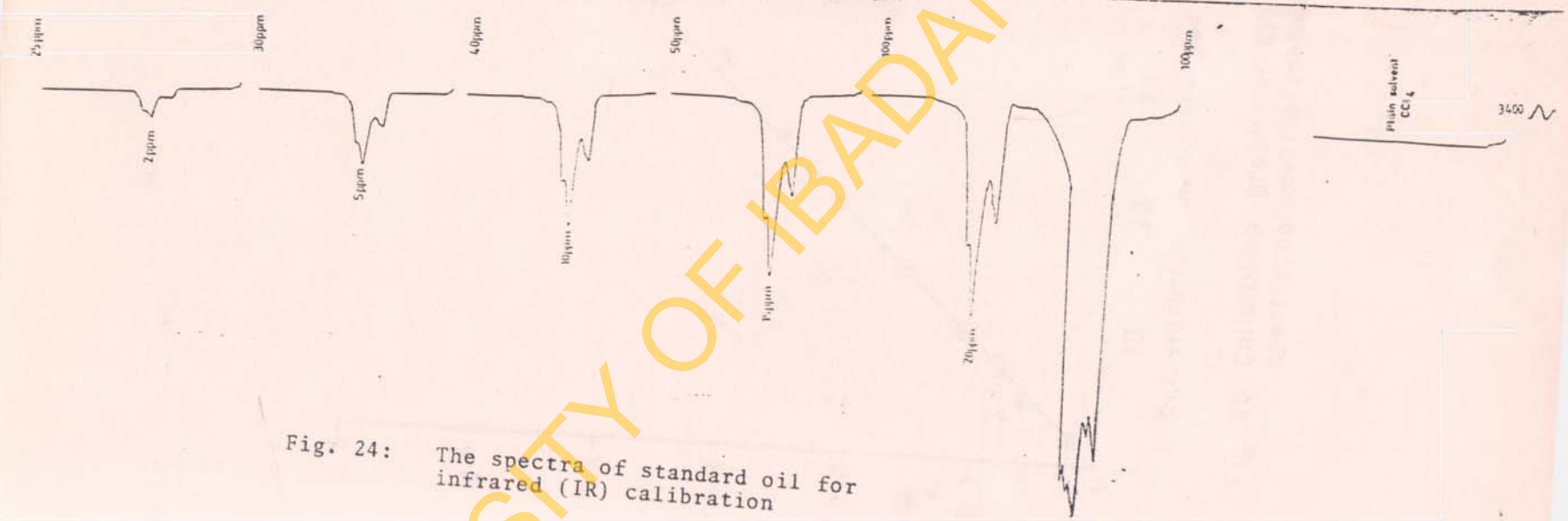


Fig. 24: The spectra of standard oil for infrared (IR) calibration

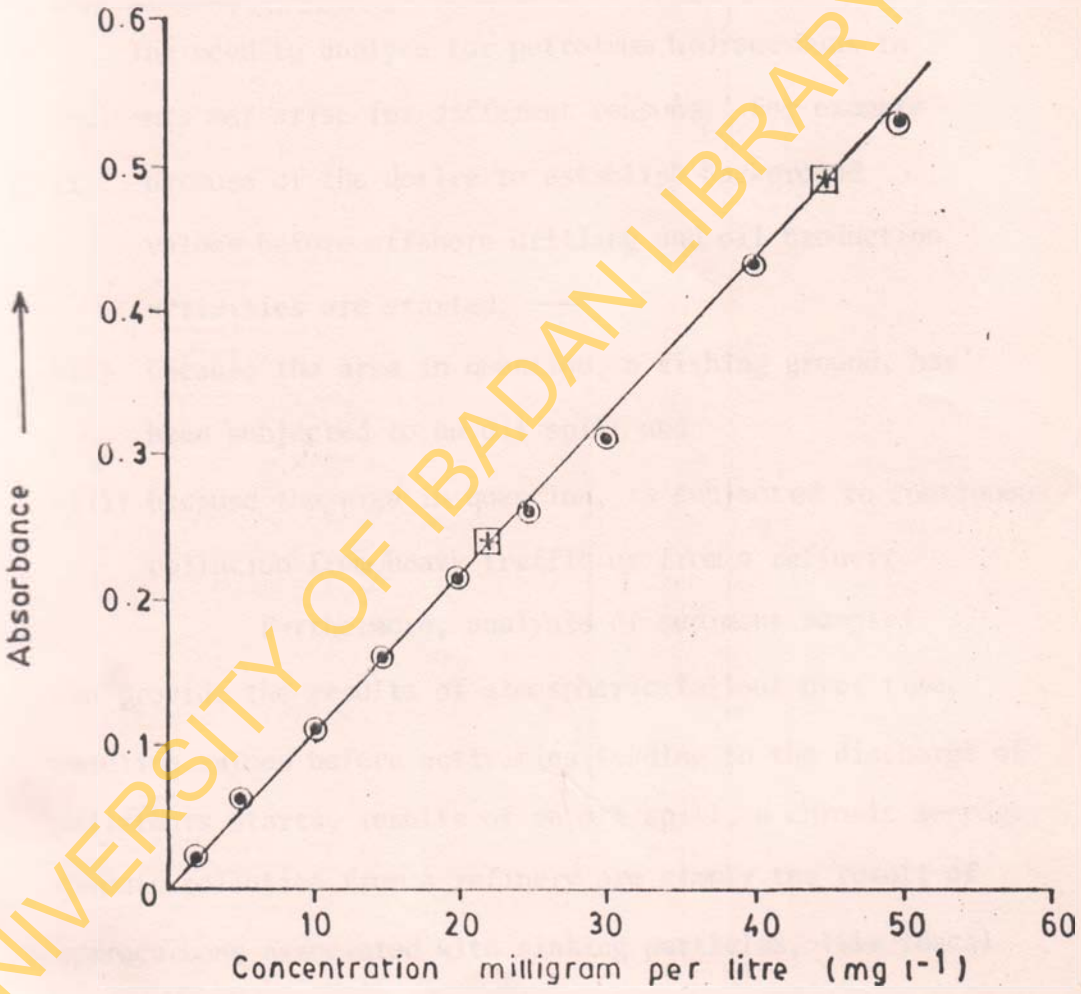


Fig. 25 : Calibration graph for oil in water by IR spectrophotometric method.

3.9 DETERMINATION OF PETROLEUM HYDROCARBONS IN SEDIMENTS.

3.9.1 INTRODUCTION

The need to analyze for petroleum hydrocarbons in sediments may arise for different reasons. For example

(i) because of the desire to establish background values before offshore drilling and oil production activities are started,

(ii) because the area in question, a fishing ground, has been subjected to an oil spill and

(iii) because the area in question, is subjected to continuous pollution from heavy traffic or from a refinery.

Furthermore, analysis of sediment samples can provide the results of atmospheric fallout over time, baseline values before activities leading to the discharge of pollutants starts, results of an oil spill, a chronic seepage, chronic pollution from a refinery are simply the result of hydrocarbons associated with sinking particles, like feacal pellets[248] dead or living organisms, clay minerals, and silicates. These particles are usually responsible for the removal of hydrocarbon from the water

Additionally, the dissolved petroleum hydrocarbon may be absorbed directly by the sediment according to

their content of indigenous matter as for example, humic acids. Sediments therefore, act as the final sink for petroleum hydrocarbons introduced into the aquatic environment.

3.9.2 EXTRACTION TECHNIQUES

Details of the twoextraction techniques tested are given below.

3.9.2.1 REFLUX METHOD (144)

PRINCIPLE: After collecting the sediment samples the petroleum hydrocarbons are isolated from the sediment samples by saponification with methanolic KOH for 1.5 hours followed by extraction with hexane. A subsample is used for the determination of the dry weight. The extract is purified on a silica gel column and separated into alkane fraction and aromatic fraction on an alumina column. Quantitative analysis was carried out on a packed column gas chromatograph.

3.9.2.1.1 SAMPLE PREPARATION

An empty, round-bottomed, clean and dry flask with the ground stopper removed was weighed. About 100g of partly thawed sediment was weighed into the flask

and the wet weight of the sample was obtained by difference.

3.9.2.1.2 DETERMINATION OF DRY WEIGHT OF SEDIMENT SAMPLE

A clean weighing bottle with the ground stopper removed, was put into the drying oven (105°C, 2 hours), using a pair of clean crucible tongs. This was to prevent leaving fingerprints and particles of dirt on the weighing bottle. The stopper and bottle were put into a desiccator to cool.

The empty bottle and stopper were then carefully weighed on an analytical balance. About 30gm of wet sediment material was placed in the weighing bottle and carefully determined.

The bottle was placed in an oven (105°C) with the stopper removed and left in the oven for 24 hours. After 24 hours the stopper was replaced in the bottle, both were removed from the oven and placed in a desiccator to cool. The bottle with the stopper was re-weighed. The drying cycle was repeated until the difference between subsequent weighings was less than 5% of the total weight.

This was then used in the calculation of the wet weight: dry weight ratio.

3.9.2.1.3 DIGESTION OF SEDIMENT SAMPLE

200ml of redistilled methanol, 6g KOH and pre-extracted boiling stones were added to 100g of wet sediment sample in a round bottomed flask. 1ml of a mixture of n-alkane standards and 1ml of polycyclic aromatic hydrocarbons standards dissolved in hexane were added. (Tables 33 and 34).

Another set was prepared but without the standards added. A spiked blank was also included in the set. Five replicates of spiked and unspiked samples were set up. The flasks with their contents were set up and refluxed for 1 hour 30 minutes.

3.9.2.1.4 EXTRACTION OF PETROLEUM HYDROCARBONS

The methanol extracts from the above experiment were cooled to room temperature, and transferred into 250ml separatory funnels by filtration through pre-extracted filter papers. The filtrate in each separatory funnel was extracted twice with 25ml redistilled hexane. The methanol phase was then

separated from the hexane phase. The hexane extract was passed through anhydrous sodium sulphate (Na_2SO_4) in a funnel into a sample bottle. The hexane extract was then reduced with a rotavapor to about 1ml. This was quantitatively transferred into a weighed glass vial using hexane. The final evaporation was carried out under a stream of pure nitrogen gas.

The vial and content were then weighed. The difference in weight gave total organic extract (TOE), that is (petroleum hydrocarbons, lipids and other materials sobluble in hexane).

The results are given in Chapter four.

3.9.2.1.5 CLEAN UP OF EXTRACTS USING SILICA GEL COLUMNS.

A Pasteur pipette fitted with a solvent-cleaned glass wool plug was filled with 0.5g deactivated silica gel (5% w/w water) The column was rinsed thrice with hexane, the sample extract was then placed on top of the column. The petroleum components were totally eluted with 12ml of hexane in all. The extract was evaporated to

dryness under pure itrogen. The weight by difference gave the weight of the total hydrocarbons. A reagent blank run was also carried out.

3.9.2.1.6 SEPARATION OF ALKANES AND AROMATICS USING ALUMINA COLUMN.

A pasteur pipette fitted with a solvent - washed glass wool plug was filled to about 5 cm (with 1.15g) with deactivated neutral aluminium oxide (5% w/w water) The column was rinsed 3 times with 2 ml hexane, and the sample extract was added to the top of the column. The elution was performed as shown in the Table 36, below. The different eluates were reduced to dryness using a stream of pure nitrogen gas. For the gas chromatographic analysis, the residues were dissolved in a known amount of hexane (between 40µl and 1ml depending on the concentration of hydrocarbons in the sample).

TABLE 36: THE ELUTION OF THE DIFFERENT FRACTIONS IN THE SEPARATION OF ALKANES AND AROMATICS FROM A SEDIMENT EXTRACT

Eluate Number	Volume of Eluate (ml)	Elution Solvent	Solvent Ratio	Resulting Fractions
1	4	Hexane		Alkanes
2	4	Hexane		Solvent only
3	4	Hexane:Dichloromethane	7:3	Light aromatics
4	4	Dichloromethane		Higher aromatics

METHOD 2

Modified Interantional Laboratory of Marine Radioactive Method (ILMR MONACO, 1984)

3.9.2.2 SOXHLET EXTRACTION METHOD

3.9.2.2.1 EXTRACTION

This method involves the extraction of the sediment sample in a soxhlet extractor with methanol followed by saponification with 0.7M KOH.

About 100g of partially thawed sediment sample was weighed and transferred into a pre-cleaned extraction thimble which was then placed in the inner tube of the soxhlet apparatus. The apparatus was then fitted to a round-bottomed flask of appropriate size containing the methanol to which mixtures of alkanes and aromatic standards had been added (Tables 33 and 34), and boiling chips, and to a reflux condenser. Another set was prepared but without the standards added. A spiked blank was also included in the set. Five replicates of spiked and unspiked samples were set up. The sediment samples were

extracted for 8 hours and cooled.

20 ml of 0.7M KOH and 30 ml of pre-extracted water (with hexane) were added to the solvent flasks. The extractions were continued for another two hours. This saponifies the lipids. The flasks were cooled and the solutions were tested to be sure they were basic (with litmus paper).

The non-saponifiable lipids (containing the petroleum hydrocarbons) were partitioned with hexane in glass separatory funnels. The methanol extracts were transferred into the separators. 40 ml hexane was used to rinse each of the extraction flask and then 50ml hexane adding each rinse to the separator. The content of the separator was vigorously shaken for several minutes. The separator was allowed to stand for phase separation. Emulsion problem was solved with the addition of pre-extracted water and small amount of saturated sodium chloride solution.

The hexane phase was filtered through glass wool and sodium sulphate to dry the extracts. The extraction was repeated with two more 50ml aliquots of hexane. All the hexane extracts were combined in a

round bottomed flask. The volume was reduced on a Rotary Evaporator with water bath maintained at 30°C. The reduced extract was transferred into a tarred bottle and the flask was rinsed with small quantity of hexane which was combined into the bottle. The final evaporation of the extract was carried out under nitrogen gas.

The total extractable organic matter (TOE) was determined by evaporating a known amount of the extract (0.1ml) and weighing the residue. The extractable organic matter is given as follows:

$$\text{E.O.M. (mg/g)} = \frac{\text{wt. of residue (µg) x vol. of extract (ml)}}{\text{amount evaporated (µl) x quantity of sample extracted (g)}}$$

3.9.2.2.2 COLUMN CHROMATOGRAPHY

The silica gel and alumina columns for cleaning and separation respectively were prepared with precleaned adsorbents. Each was activated in an oven at 200°C for 4 hours and then 5% (w/w) pre-cleaned water was added to deactivate the adsorbents. They were well mixed with the water and equilibrated overnight in air-tight containers.

Columns were prepared by plugging a glass burette with glass wool and filling the column with hexane. The supports were layered into the column and encouraged to settle evenly by gentle tapping of the glass. For the 1 cm diameter column, 10 ml of silica gel was first added and layered with 10 ml of alumina gel. Finally, one gram of Na_2SO_4 was layered on top. The hexane was drained to the top of the adsorbent bed and further hexane added to rinse the column.

1 ml of the extract was placed on the top of the column and allowed to drain into the adsorbent bed. The column was carefully eluted by adding hexane in small aliquots at a time. Saturated hydrocarbons were eluted with 20 ml (1 column volume) of hexane. Unsaturated hydrocarbons were eluted with 20 ml of 30% methylene chloride in hexane followed by 20 ml methylene chloride. The fractions were reduced with nitrogen gas. They were evaporated to dryness in tarred bottles and the extract with the bottles were weighed to obtain the weight of each fraction. They were later analysed on a GC with a flame ionization detector.

3.9.3 PRECISION STUDIES

Five replicate analyses of sediment samples by the two methods discussed above were carried through the procedures with n-C_{36} and phananthrene used to spike the samples.

The reflux method was used for all the samples analyzed for this study.

3.10 QUALITATIVE AND QUANTITATIVE DETERMINATION OF PETROLEUM HYDROCARBONS IN SEDIMENTS

The isolated hydrocarbon fractions obtained from the alumina column were analyzed on a Varian Model 3700 Gas Chromatograph (GC) equipped with flame ionization detector (FID). 2 m stainless steel (1/8" i.d.) packed column of 10% OV-101 on chromosorb W (HP) 80-100 mesh was used for the aliphatic fractions. A glass packed column of 3% SE-52 on chromosorb W.AW/ DMCS 100-200 mesh was also used in this study for both the aliphatic and aromatic fractions.

The temperature programme 80°-290°C at 8°C per minute was used, holding at the final temperature for 25 minutes. The instrumental conditions are listed in

Table 37. Compounds were identified by comparing retention indices of peaks in the samples to retention indices of known compounds in a standard mixture that was analyzed daily.

Hydrocarbons eluting between n-C_{10} and n-C_{36} were routinely quantified.

TABLE 37

PACKED COLUMN GAS CHROMATOGRAPHY/FLAME IONIZATION DETECTION ANALYTICAL CONDITIONS USED IN THE PRESENT STUDY

INSTRUMENT:	Varian 3700 gas chromatograph
DETECTOR:	Flame ionization
COLUMN:	
f_1:	1/8" I.D. x 2m 10% OV-101 on chrom W(HP) 80-100 mesh.
f_2:	1/8" I.D x 2m 3% SE-52 on chrom W.AW/DMCS 100-120 mesh.
GASES:	
Carrier	Pure nitrogen 10 ml/min
Detector	Air 300 ml/min. Hydrogen 30 ml/min
TEMPERATURE:	
INJECTION PORT:	270°C
DETECTOR:	370°C
COLUMN OVEN:	80° - 290°C at 8°C/Min.
RECORDER:	Varian 9176 model.
CHART SPEED:	1 cm/min.
DAILY CALIBRATION:	ALKANE/AROMATIC MIXTURE

3.10.1 CALIBRATION

One of the major advantages of gas chromatography is that quantitative detectors can be employed, which produce signals which can be fed to a recorder. Thus not only can a component be identified from the time taken to emerge from the column (retention time), but also its concentration may be determined.

For quantitative analysis, it is most often necessary to calibrate the detector. This is usually done by injecting standard solutions of known components. The calculated areas are then plotted against the concentrations. For a particular detector closely related members of a homologous series, for example n-alkanes show a linear relationship (Fig. 26).

3.10.2 IDENTIFICATION

The compounds present in the chromatograms were determined by comparison of their retention times with authentic standards on columns of OV-101 and SE-52.

Authentic standards of n-alkanes (n-C_{10} - n-C_{36}) and 2 isoprenoids (pristane and phytane) in a mixture as given in Table 33 were injected under the same

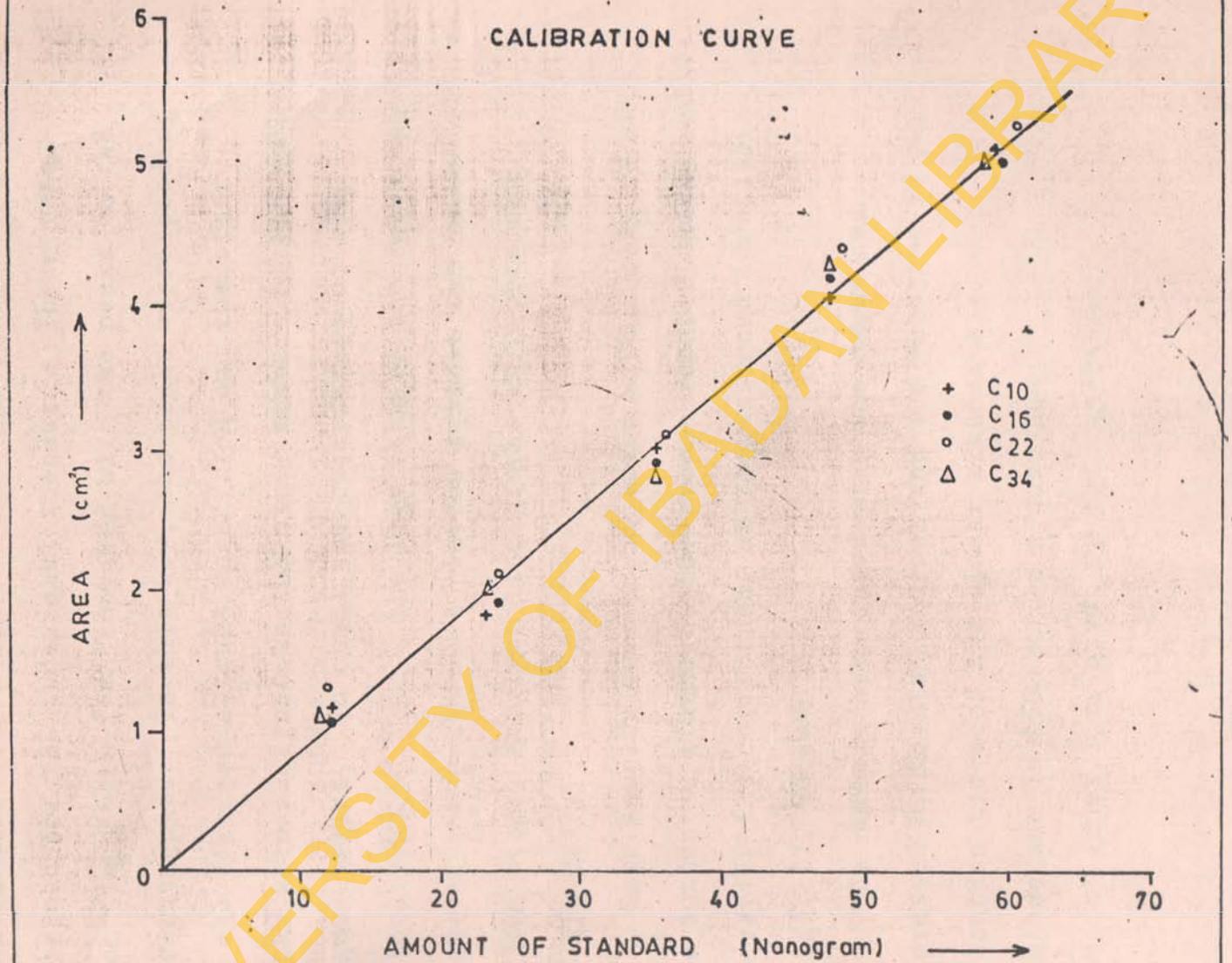


Fig. 26.: FID detector response for n - Alkane at different concentrations

conditions as the samples and their retention times obtained for the individual standard. These retention times were then compared with the peaks on the chromatograms. In this way, the peaks corresponding to the standard alkanes were fixed and the other peaks were assigned to the other members of the homologous series. To check the correctness of the allocations, the logarithms of the retention times of the peaks were plotted against the number of carbon atoms. Straight line graphs were obtained in all cases.

Some samples were co-injected with a mixture of the authentic standards for proper identification and to verify the correctness of the assigned identities (Figs. 27, 28 and 29).

The numbers associated with the peaks are expressed by Kovats' indices and are relative to the retention times of the linear alkanes e.g. n-pentadecane is 1500 while n-docosane is 2200. The Kovats' index, I, is given by the expression:

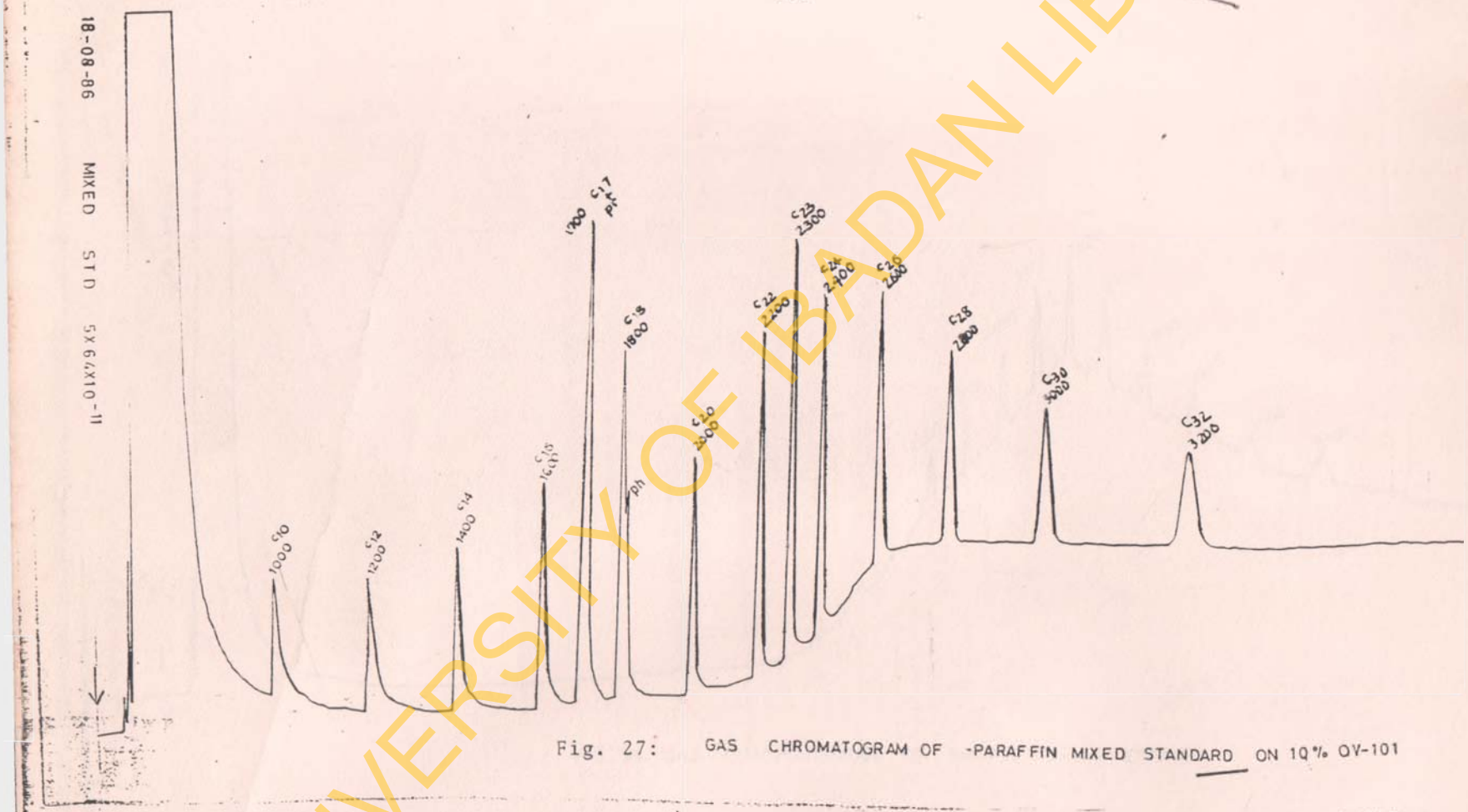


Fig. 27: GAS CHROMATOGRAM OF -PARAFFIN MIXED STANDARD ON 10% OV-101

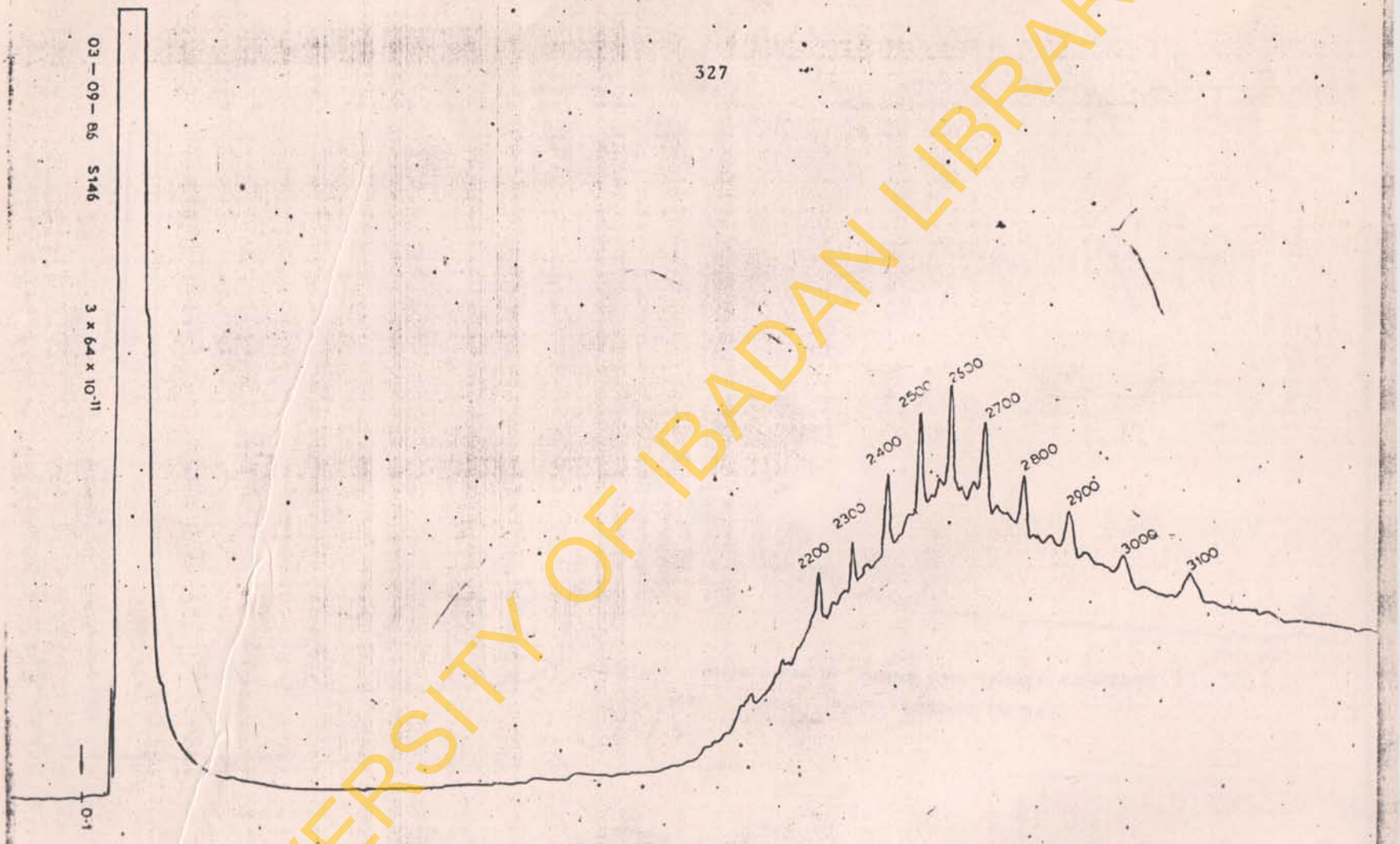


FIG 28: GAS CHROMATOGRAM OF SAMPLE S-146 EXTRACT.

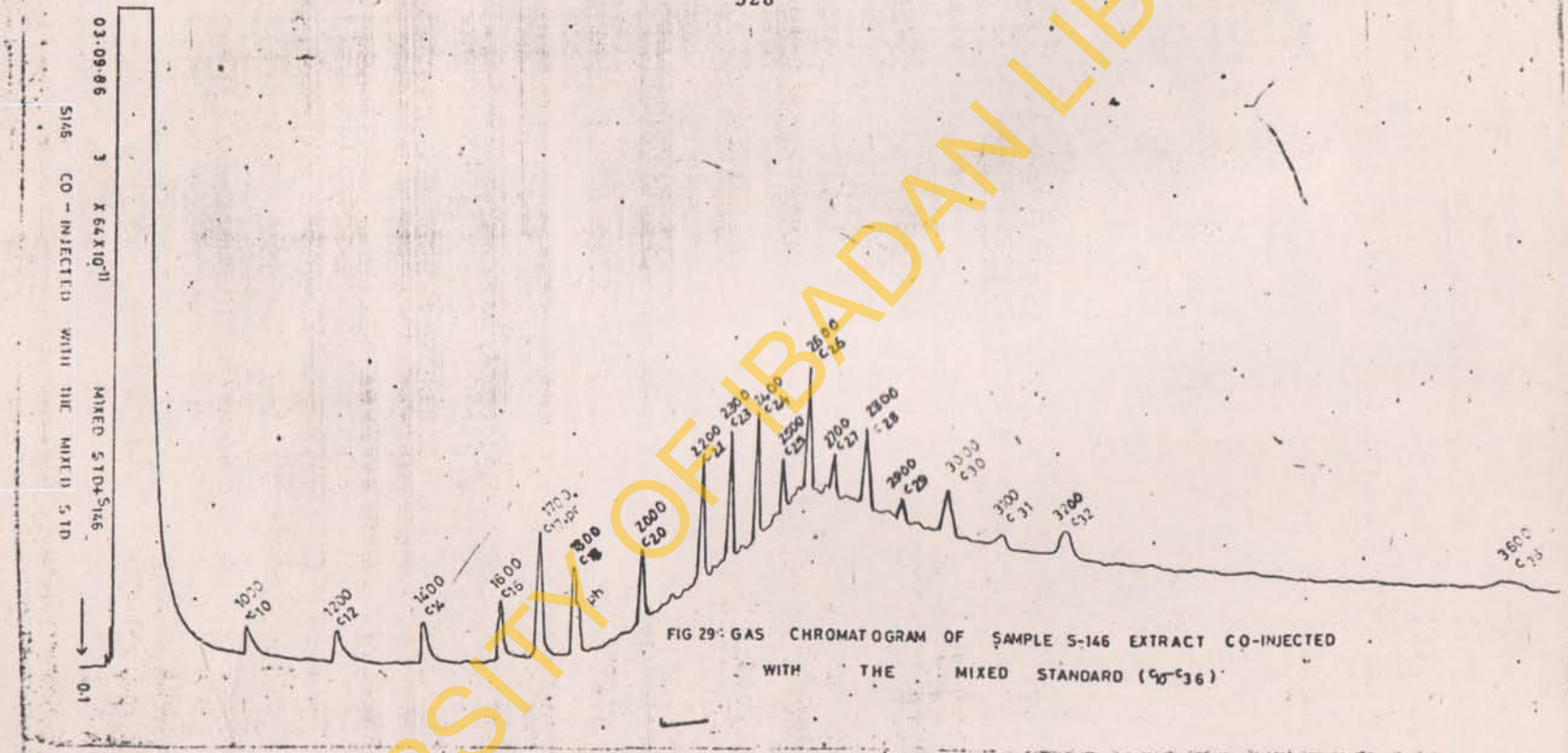


FIG 29: GAS CHROMATOGRAM OF SAMPLE S-146 EXTRACT CO-INJECTED WITH THE MIXED STANDARD (C_{10}-C_{36})

$$I = \frac{100 \log V_N \text{ (subst.)} - \log V_N(n\text{-}C_Z)}{\log V_N(n\text{-}C_{Z+1}) - \log V_N(n\text{-}C_Z)} + 100Z$$

$V_N(n\text{-}C_Z) \leq V_N(\text{subst.}) \leq V_N(n\text{-}C_{Z+1})$

V_N = the net retention time

(Subst) = substance whose identity is to be determined

$n\text{-}C_Z$ = n-paraffin with Z n-carbon atoms

$n\text{-}C_{Z+1}$ = n-paraffin with Z+1 carbon atoms

Z = carbon atoms.

3.10.3 QUANTIFICATION

In gas chromatography it has been established that the integrated area of a peak is directly proportional to the amount of solute eluted. There are various methods of area measurement that have been used in chromatogram calculations. These include:

(a) Geometric method (triangulation)

(b) Planimetry.

(c) Cutting-out and weighing

(d) Automatic integration.

3.10.3.1 PEAKS

In calculating the peak areas of the chromatograms, the geometric method of triangulation was used. As normal peaks have a Gaussian profile, which approximates to an isosceles triangle, their area can be estimated by multiplying the height by the width at half height.

Chromatogram peak area = peak height x width at $\frac{1}{2}$ height

This can then be substituted in the formula for calculating the concentration of hydrocarbon in a given weight of sediment sample.

$$\text{Concentration of hydrocarbon} = \frac{\text{mass of hydrocarbon}}{\text{sample weight}} \times \frac{1}{\text{dilution factor}} \times \frac{1}{\% \text{ recovery}}$$

Mass of peak = response factor, R_f x peak area (detector)

The R_f is obtained from the standard run

$$R_f \text{ (standard)} = \frac{\text{mass of standard injected}}{\text{area of standard}}$$

$$= \frac{V_{std} \times C_{std}}{A_{std}} = \frac{\text{Amount of standard}}{\text{Area of standard}}$$

V_{std} = Volume of standard injected (µl)

C_{std} = Concentration of standard (ng/µl)

A_{std} = Area of standard (cm^2)

Concentration of sample, C_s (µg/g)

$$= \frac{RF_{std} \times A_s}{\text{Sample weight}, W_s} \times \frac{\text{Pre-injection volume}, V_{extract}}{\text{Volume of sample injected}, V_{inj}}$$

$$\times \frac{1}{\% \text{ Recovery}}$$

$$\left(\text{i.e. } C_s = \frac{RF_{std} \times A_s}{W_s} \times \frac{V_{extract}}{V_s \text{ inj.}} \times \frac{1}{\% R}\right)$$

The units of concentration are derived below:

$$\mu g/g = \frac{ng \times \mu l \times cm^2}{\mu l \times cm^2 \times g} \times \frac{1000\ \mu l(ml)}{\mu l} \times \frac{1}{\% R(\text{no unit})}$$

$$= \frac{ng \times 1000}{g}$$

$$= \mu g/g \text{ (unit)}$$

$$\frac{RF_{std}}{RFs} = \frac{C_{std}}{A_{std}} \cdot \frac{A_s}{C_s}$$

3.10.3.2 UNRESOLVED COMPLEX MIXTURE (UCM)

The unresolved complex mixture (UCM) comprising $n\text{-}C_{14}$ - $n\text{-}C_{34}$ range was traced on chart paper and carefully cut out and weighed.

$$RF_{UCM} = \frac{\text{Mass of UCM in ng}}{\text{Area of UCM in mm}^2}$$

$$RF_{std} = \frac{\text{Mass of stds in ng}}{\text{Area of stds in mm}^2}$$

$$\frac{\text{Mass of UCM in ng}}{\text{Area of UCM in mm}^2} = RF_{std}$$

Let weight of 1 cm^2 paper = x mg

i.e. 100 mm^2 paper weighs = x mg = y

$\therefore$ Let weight of UCM = X mg = z

$$\therefore \frac{y}{100\ mm^2} = \frac{z}{\text{Area of UCM}}$$

$$\therefore \text{Area of UCM} = \frac{100}{y} \times z\ mm^2$$

$$\frac{\text{Mass of UCM}}{\text{Area of UCM}} = RF_{std}$$

$$\text{Mass of UCM} = \frac{100}{y} \times z \times RF_{std}$$

i.e. $C_{UCM} \times V_{UCM} = \frac{100}{y} \times z \times RF_{std}$

$$C_{UCM} = \frac{100}{y} \times z \times \frac{RF_{std}}{V_{UCM}} \times \frac{V_{extract}}{\text{Mass of sample}}$$

$$= \frac{100\ mm^2 \times mg}{mg} \times \frac{ng \times \mu l}{100 \times \mu l \times mm^2 \times \mu l} \times \frac{1000\ \mu l}{g}$$

$$= \frac{1000\ ng}{g}$$

Conc. of UCM = $\mu g/g$

Total hydrocarbon (aliphatic or aromatic) in the boiling range used ($n\text{-}C_{10}$ - $n\text{-}C_{34}$)

= Total Resolved Peaks + UCM.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 ANALYTICAL DATA QUALITY ASSURANCE

The determination of hydrocarbons in environmental samples involves steps such as organic solvent extraction, column chromatographic cleaning and separation. The final results will depend on how the samples are carefully taken through all these steps with minimum loss, because part of the samples are lost at different stages due to volatilization etc. It therefore becomes very important to report the efficiency of the extraction process in order to be able to express the accuracy of the final results after the instrumental analysis. The reliability of the final results can therefore be checked with the results of replicate analysis of samples spiked with authentic hydrocarbon standards.

4.1.1 THE RECOVERY STUDY OF OIL IN WATER

The results of the recovery study of oil in water to determine the performance of the tetrachloromethane

extraction method are shown in Table 38, while the results of the precision study are shown in Table 39.

The recovery was calculated from the formula

$$\frac{Cs_2 - Cs_1}{Cs} \times \frac{100}{1}$$ where

Cs_1 :- concentration of petroleum hydrocarbon in sample

Cs_2 :- concentration of petroleum hydrocarbon in spiked sample

Cs :- concentration of added petroleum hydrocarbon.

The range of concentrations of oil used to spike the water samples (1 - 30mg/l) was chosen to reflect the levels that are likely to be encountered in areas covered by this study.

The average recovery was 89.8% and the average error is 6.8%. The method may be judged to be reliable, since the quantity of oil in the sample can be determined with good relative standard error. The results are comparable to what have been reported in the literature for similar work. Schatzberg and Jackson[165] reported that the recoveries of oil concentrations above 5mg/l were greater than 85%.

TABLE 38- RECOVERY DATA OF OIL IN WATER BY INFRARED SPECTROPHOTOMETRIC METHOD

Amount of Oil Added mg/l	Amount of Oil Recovered mg/l	% Recovery
2.00	1.50	75.0
	1.69	84.5
3.00	2.70	90.0
	2.55	85.0
5.00	4.58	91.6
	4.72	94.4
20.00	18.20	91.0
	19.33	96.7
30.00	26.78	89.3
	28.60	95.3

$\bar{X}$ = 89.75%

SD = ±6.2

RSD = 6.8%

TABLE 39: PRECISION DATA OF OIL IN WATER BY TETRACHLOROMETHANE EXTRACTION WITH INFRARED SPECTROPHOTOMETRIC METHOD

Amount of Oil Added mg/l	Amount of Oil Recovered mg/l
5.00	4.58
5.00	4.72
5.00	5.28
5.00	4.18
5.00	4.32
5.00	3.80
5.00	5.07
5.00	4.62
5.00	4.75
5.00	4.56

$\bar{X} = 4.59$

SD = ±0.42

RSD = 9.23%

The precision can be said to be equally good because the results reflect a good reproducebility with the level of relative standard deviation of 9.23%.

The high mean percentage recovery coupled with the good precision further confirmed why tetrachloromethane has been the choice for hydrocarbon extraction from water. Its high extraction efficiency for both fresh and weathered oil makes it a suitable extraction solvent except for its toxicity.

4.1.2 THE RECOVERY STUDIES OF PETROLEUM HYDROCARBONS IN SEDIMENTS

The results of the recovery studies of the alkanes and aromatics are shown in Tables 40 and 41 respectively. The two methods compared are the reflux and soxhlet as earlier discussed in sections 3.9.2.1 and 3.9.3.

The results of the percentage recovery in Table 40 for the alkanes showed that both methods gave comparable results but the reflux (the method used for this work) seems a little superior to the soxhlet method, especially in the higher hydrocarbon ($> C_{20}$) region.

TABLE 40: PERCENTAGE RECOVERY OF ALKANES FROM SPIKED SEDIMENT SAMPLES BY TWO DIFFERENT EXTRACTION METHODS.

ALKANE	REFLUX R1	R2	R3	R4	R5	$R\bar{x}$	ALKANE	SOXHLET S1	S2	S3	S4	S5	$S\bar{x}$	+
C16	45.3	53.0	42.0	49.0	58.1	49.6±6.3	C16	61.8	49.6	62.5	58.7	54.8	57.5	±5.4
C17	69.2	75.3	67.2	63.0	69.4	68.8±4.4	C17	75.0	70.3	71.3	66.1	70.2	70.6	±3.2
Pristane	85.1	88.4	83.5	80.7	86.2	84.8±2.9	Pristane	81.2	78.4	78.7	72.1	76.4	77.4	± 3.4
C18	65.9	78.6	85.2	63.8	69.6	72.6±9.0	C18	69.1	64.9	79.0	70.0	72.1	71.1	± 5.2
Phytane	76.3	80.0	82.0	75.7	78.3	78.5±2.6	Phytane	72.5	75.2	81.3	69.5	73.4	74.4	± 4.4
C20	78.0	76.8	90.8	77.6	82.2	81.1±5.8	C20	76.3	74.6	86.2	72.5	81.7	78.3	± 5.6
C22	85.8	88.5	91.3	82.5	85.1	86.6±5.1	C22	73.3	78.2	75.8	70.9	71.9	74.0	± 2.7
C23	98.5	102.7	106.1	95.3	97.4	100. ±4.3	C23	77.4	89.3	84.1	81.4	82.5	82.9	± 4.3
C24	92.8	96.4	102.7	94.7	95.2	96.4±3.8	C24	88.7	72.0	63.7	66.8	64.9	71.2	± 10.3
C26	86.7	89.3	92.4	78.4	88.3	86.6±5.2	C26	83.0	83.5	82.6	78.5	79.5	81.4	± 2.3
C28	80.2	85.5	88.9	79.0	80.4	82.8±4.2	C28	70.4	79.7	76.3	75.8	67.7	74.0	± 4.8
C30	78.4	73.0	75.4	70.5	71.2	73.7±3.2	C30	65.8	74.6	61.3	65.9	68.5	67.2	± 4.9
C32	76.2	70.4	74.0	69.4	68.5	71.7±3.3	C32	75.5	70.6	75.9	72.2	70.6	73.0	± 2.6
		-	-	-	-		C34	64.4	62.1	57.3	62.2	64.9	62.2	± 3.0

TABLE 41: PERCENTAGE RECOVERY OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) FROM SPIKED SEDIMENTS BY TWO DIFFERENT METHODS.

PAHS	REFLUX						SOXHLET					
	R_1	R_2	R_3	R_4	R	$R_{\bar{x}}$	S_1	S_2	S_3	S_4	S_r	$S_{\bar{x}}$
Phenanthrene & Anthracene	74.5	53.1	43.1	82.7	76.7	66.0± 17.0	78.1	83.2	64.8	63.6	63.8	70.7±09.3
Fluoranthrene	56.2	72.4	54.3	75.4	68.4	65.3± 09.6	67.0	86.9	59.4	75.1	68.3	71.3±10.3
Pyrene	62.3	70.6	60.7	78.9	70.2	68.5± 07.3	61.4	84.7	56.7	79.7	62.3	67.8±11.3
1,2-Benzan-thracene	67.1	72.3	63.7	75.2	73.1	70.3± 04.7	73.5	81.4	52.2	77.9	75.4	72.1±11.5
7,12-Dimethy-Benzanthracene	63.5	75.2	61.3	80.3	74.2	70.9± 08.1	62.7	73.5	54.6	68.2	60.2	77.8±07.3
3-Methy-Cholanthracene	24.2	13.6	16.8	14.8	18.3	17.5± 04.1	32.5	38.5	24.3	37.3	35.4	33.6±05.3

In both methods, lower hydrocarbons ($< C_{15}$) were either lost completely or with very poor recovery. The loss might be due to evaporation because the hexane extract in each case was evaporated to dryness prior to both the gravimetric and gas chromatographic analysis. However, most of the samples showed chromatograms of heavily weathered oil with the lower hydrocarbons already lost.

The percentage recoveries for the aromatics shown in Table 41 gave the soxhlet a slight edge over the reflux but with a higher level of errors. Naphthalene, dimethynaphthalene and acenaphthene were lost in both methods. This may be due to the same reason given above for the lower alkanes.

Both methods also gave poor recoveries for 3-methycholanthracene.

The precision data for both the reflux and soxhlet method are given in Table 42. Reflux method recorded a higher concentration of hydrocarbons than the soxhlet method but the soxhlet method has a superior reproducibility than the reflux method. The two results can be

TABLE 42 : PRECISION DATA OF HYDROCARBONS IN SEDIMENTS BY REFLUX AND SOXHLET EXTRACTION METHODS

	Reflux µg/g		Soxhlet µg/g
R_1	1.170	S_1	0.990
R_2	1.079	S_2	0.786
R_3	0.864	S_3	0.691
R_4	0.902	S_4	0.650
R_5	1.014	S_5	0.721
R_6	0.815	S_6	1.123
R_7	0.855	S_7	0.905
R_8	1.404	S_8	1.001
R_9	0.766	S_9	0.884
R_{10}	0.749	S_{10}	0.777
$\bar{X}$	0.962	$\bar{Y}$	0.853
SD	0.21	SD	0.15
RSD	21.5%	RSD	17.9%

tested for their comparability by applying both the F-test and t-test to see if there is any significant difference between the two means. The objective of the tests is to show whether the difference observed in the two means is as a result of indeterminate error or that the two means are essentially different.

4.1.3 STATISTICAL ANALYSIS[249]

$$\text{Mean } (\bar{X}) = \frac{\sum X}{N} \quad \ldots\ldots\ldots (1)$$

where X-represent individual experimental result obtained

N-Total number of results in the set.

$$\text{Standard deviation } (s) = \sqrt{\frac{\sum_{i=1}^{i=N} (X_i - X)^2}{N - 1}} \quad \ldots (2)$$

In comparing two experimental means a pooled standard deviation is used in place of the expression given in (2) above.

$$\text{pooled } s = \sqrt{\frac{(N_1 - 1)S_1^2 + (N_2 - 1)S_2^2}{M - K}} \quad \ldots\ldots\ldots (3)$$

K – sets of data

$M = N_1 + N_2$

F-test is used to establish if the two sets have similar precisions.

This test uses the ratio of the variances of the two sets

$$F = \frac{S_1^2}{S_2^2} \quad \ldots\ldots\ldots\ldots \quad (4)$$

where $S_1 > S_2$

If the standard deviations of the two sets of data agree at a reasonable confidence level, then the mean results can be compared, using the t-test.

$$t = \frac{(\bar{X} - \bar{Y})}{s} \sqrt{\frac{N_1 N_2}{N_1 + N_2}} \quad \ldots\ldots\ldots \quad (5)$$

where $\bar{X}$ is the mean of N_1 determinations (reflux)

$\bar{Y}$ the mean of N_2 determinations (soxhlet)

s the pooled standard deviation.

$\bar{X}$ = 0.962 (Table 76)

$\bar{Y}$ = 0.853 (Table 76)

using equation (2) above

s for reflux replicate analysis (S_1)=0.21

s for soxhlet replicate analysis (S_2)=0.15

F-test (equation (4))

(F_e=F expected) $F_{exp.} = \frac{S_1^2}{S_2^2}$

$$= \frac{(0.21)^2}{(0.15)^2} = 1.96$$

F_{crit} at the 95% confidence level is $\geq$ 3.14.

Since the value calculated is less than the tabulated value (1.96 < 3.14), it means that the standard deviations have no significant difference, so it is possible to proceed to use the t-test.

$$\text{pooled } s = \sqrt{\frac{(10-1)(0.21)^2 + (10-1)(0.15)^2}{10 + 10 - 2}} = 0.18$$

$$t = \frac{0.962 - 0.853}{0.18} \sqrt{\frac{100}{20}} = 1.36$$

$t_{18,\ 95\%}$ = 2.09 (i.e. t at 18 degree of freedom and 95% confidence level from table = 2.09).

Since t-value calculated, 1.36 is less than t - from statistical table 2.06; it means that there is no significant difference between the two means. This implies that the two methods of extraction gave comparable results.

The two methods were applied in the analysis of a reference sample (00039/IAEA Monaco) and the results are presented below in Table 43. The chromatograms of the reference sample for the reflux and soxhlet methods are shown in Figures 30 & 31.

4.2 CONFIRMATION OF THE HYDROCARBON COMPOUNDS

Two different columns were used to establish the correct allocation of peaks to the various hydrocarbon compounds in the samples analyzed. The columns were 10%Ov - 101 on chromosorb WHP 80/100 mesh and 3% SE-52 on chromosorb W.AW/Dmcs 100-120 mesh. The chromatograms from both columns have the same hydrocarbon arrangement

TABLE 43: RESULT OF REFERENCE SAMPLE (00039TAEA/MONACO) EXTRACTED BY BOTH REFLUX AND SOXHLET METHODS

	Reflux		Soxhlet	
	1	2	1	2
n-Alkanes	2.28	2.49	1.83	1.91
UCM	84.04	92.07	67.67	70.12
Total Aliphatic Hydrocarbons	86.33	94.56	69.50	72.03
$\bar{X}$	90.44		70.76	
SD	± 5.83		± 1.79	
RSD	6.4%		2.53	

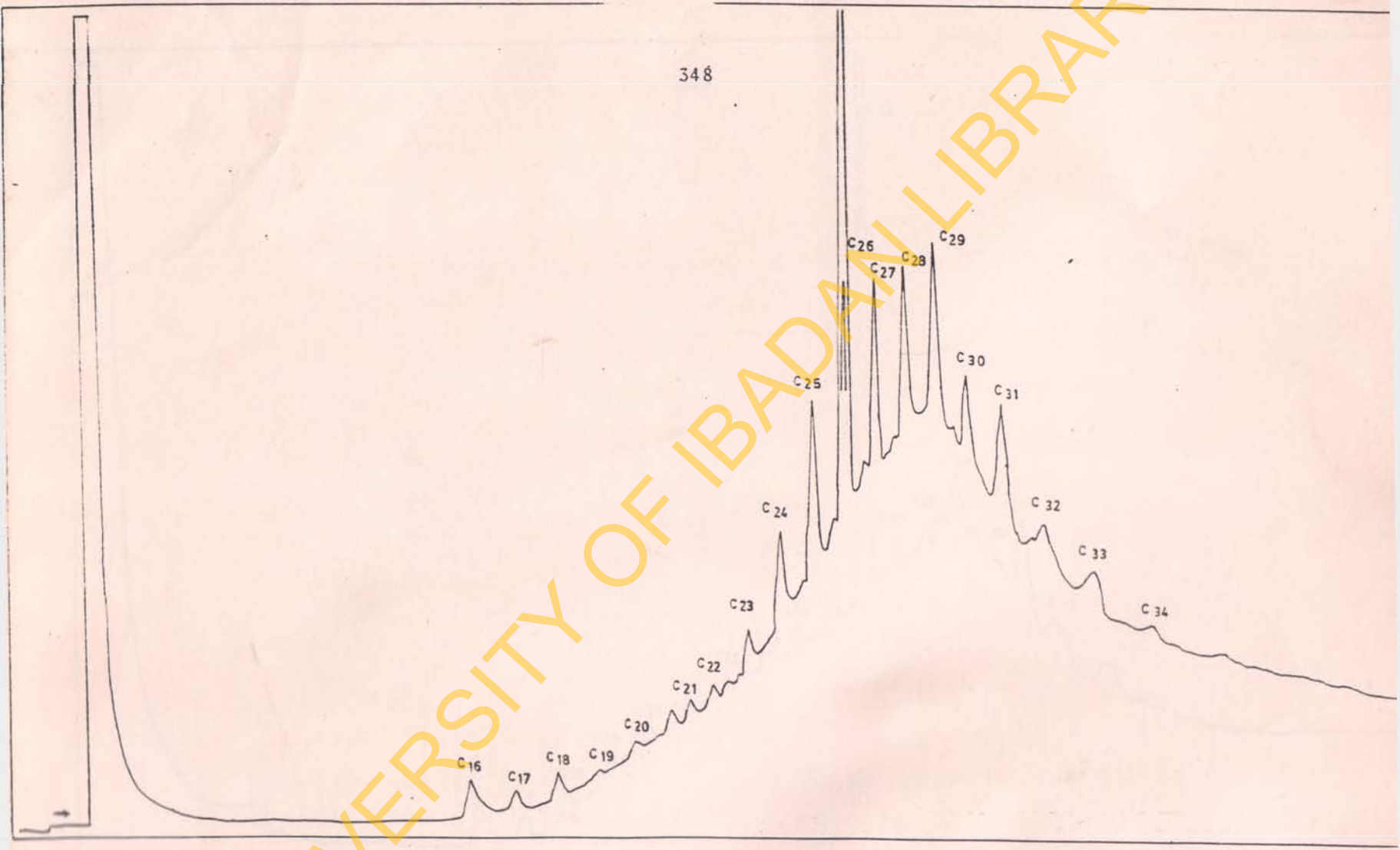


Fig. 30: Chromatogram of a reference sample extracted by reflux method.

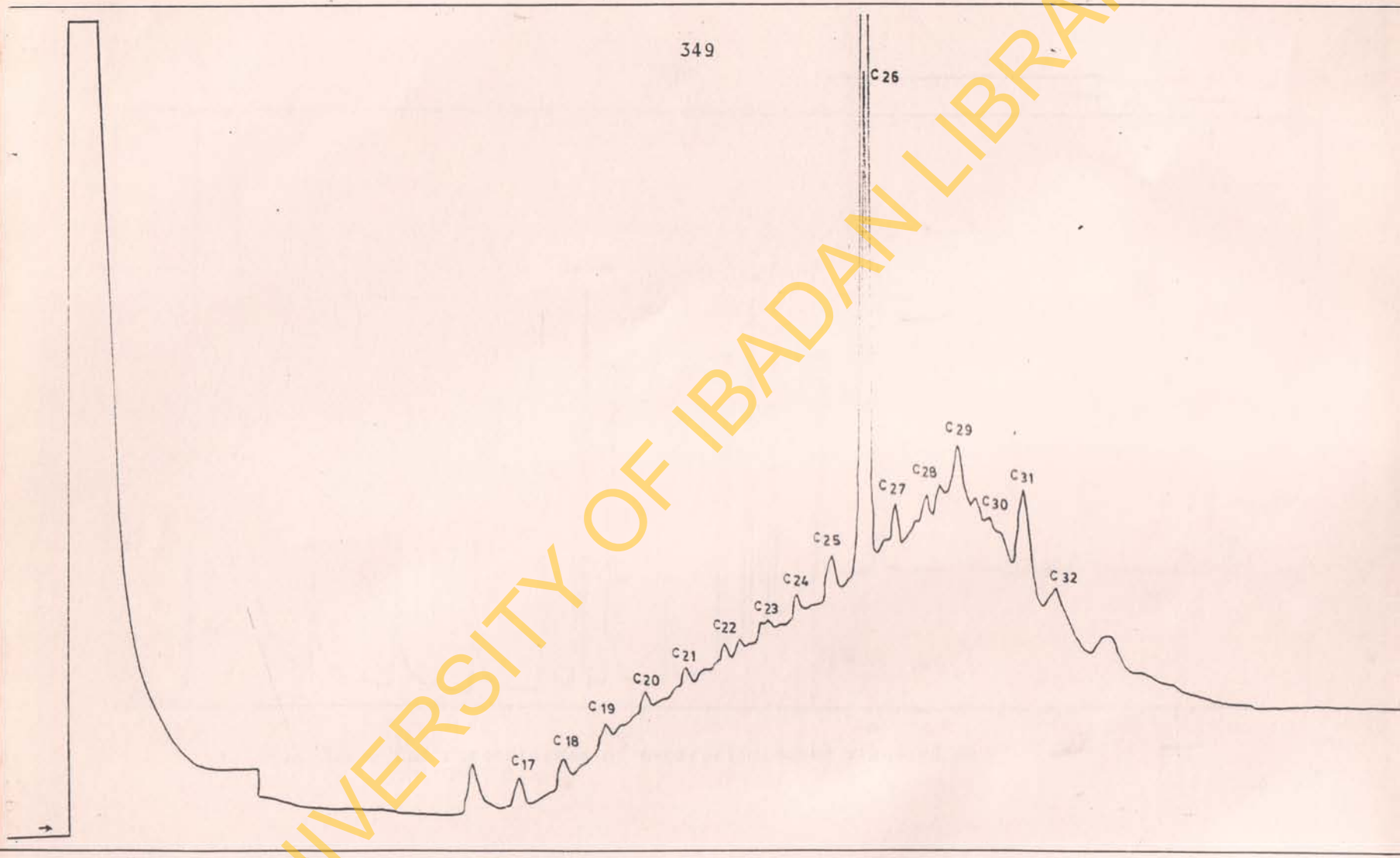


Fig. 31: Chromatogram of a reference sample extracted by soxhlet method.

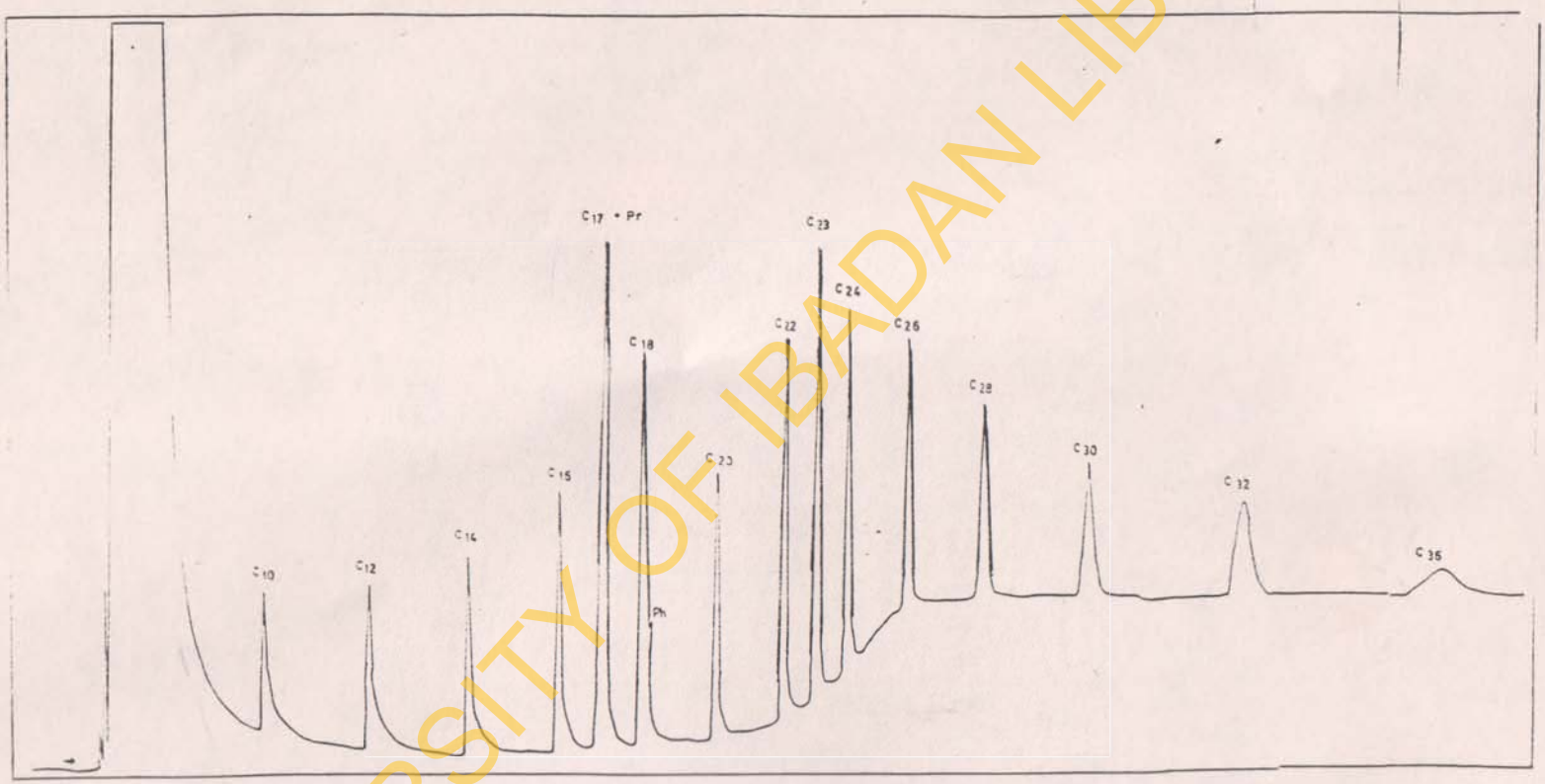


Fig. 32: Gas chromatogram of n-paraffin mixed standard on 10% OV-101.

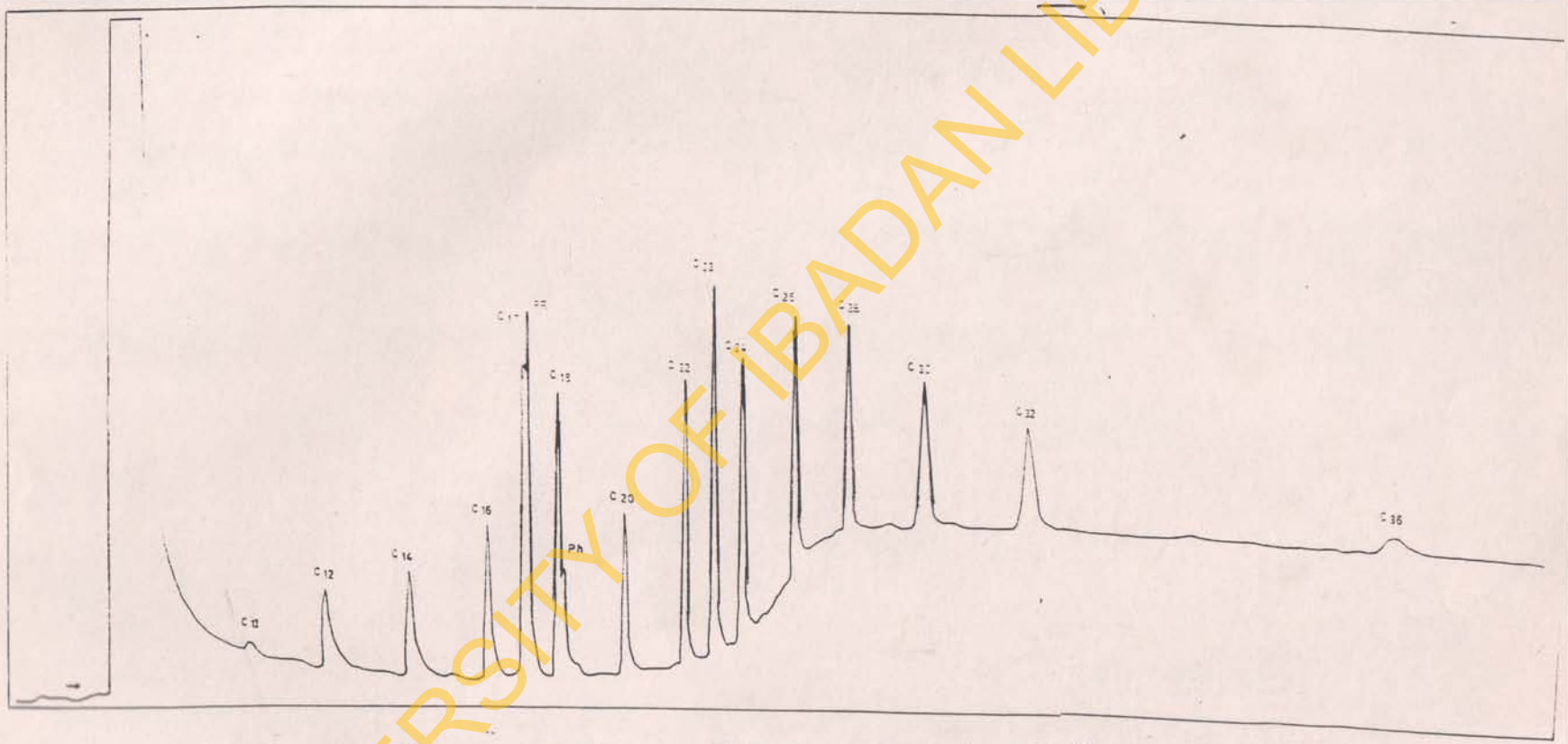


Fig. 33: Gas chromatogram of n-paraffin mixed standard on 3% SE-52.

(i.e. C_{10} - C_{36}) as can be seen in the two chromatograms given below (Figs. 32 and 33).

3% SE-52 column yielded quantitative separation of the n-C_{17} and pristane, and the n - C_{18} and phytane, while the 10% OV-101 was able to separate n - C_{18} and phytane but with n - C_{17} and pristane coming out as a single peak.

SE-52 was also used for the aromatics. n - C_{36} alkane standard was used as an internal standard for the aliphatic fraction while phenanthrene was used for the aromatics.

4.3 RESULTS

4.3.1 SURFACE WATER RESULTS

The hydrocarbon content of water samples from the major river systems around Lagos and the Niger Delta area of Nigeria was determined by infrared spectrophotometric (IR) method and for more detailed information some of the samples were also analyzed for the aliphatic hydrocarbons by gas chromatographic (GC) method. The results of the analyses of the samples are set out in

Tables 44.1 - 44.12. The samples are grouped under the different river systems studied.

Tables 44(1-12) show the results of the IR and the GC for samples from 12 river systems with the range (R) and the arithmetic mean ($\bar{X}$) for each system given below it. The tables show the hydrocarbon levels for both the 1984 (wet) and 1985 (dry) seasons of some of the stations where relevant.

4.3.1.1 LAGOS AND LEKKI LAGOONS

On the Lagos and Lekki Lagoons, the hydrocarbon levels as determined by the IR method for the wet season ranged from 1.64mg/l (Epe - 855) to 11.40mg/l (Lever Brothers' Discharge - 845) with an average of 5.60mg/l. The GC values ranged from 0.01mg/l to 0.27mg/l with an average of 0.16mg/l. This river system had consistently high values for both methods, with stations 086 (off Federal Palace Hotel), 087 (North of NNPC facility on Lagos Harbour), 847 (Okobaba Sawmill), 854 (off Ologogoro) and 856 (off Iwopin) having above 3.00mg/l by IR and 0.10mg/l by GC.

The values of hydrocarbon (by IR) found during the 1985 (dry) season for all the stations were below 0.50mg/1 with the highest being 0.41mg/1 (East of Ogboyi Creek). The mean value recorded for the 1985 dry season samples was 0.25mg/1, which is relatively low compared with 5.60mg/1 recorded for the 1984 (wet) season. Within the Lagos and Lekki Lagoons, the observed trend is that most of the high values recorded were from points located near oil activity area (087 - NNPC facility) along boat or ship traffic routes or near effluent discharge points from the industrial houses bordering the Lagos Lagoon (Federal Palace Hotel, Lever Brothers' discharge point and a point off the University of Lagos - 849).

4.3.1.2 BENIN RIVER SYSTEM

The hydrocarbon levels recorded during the 1984 (wet season) varied from a level not detectable by both the IR and the GC (878 - Ossiomo river) to 30.10 mg/1 (134 - Asagba on Ethiope river), the average value of 7.07mg/1 (IR) was recorded. Other points where high values were recorded are Dudu Town (837), Olagua Creek at Benin river confluence (838), Robbin

Creek (057), and Ogharife field effluent canal (O-2). These points were located next to towns (837) and oil field (O - 2).

The values for the points sampled in the 1985 (dry season) were low with range 0.15 - 0.32mg/1 and mean value of 0.23mg/1 (IR).

4.3.1.3 ESCRAVOS RIVER SYSTEM

Points on the Escravos river system recorded a range of values from 3.80mg/1 to 17.50mg/1.with a mean value of 9.17mg/1. The highest values were at Upomani oil discharge station (831), Jones creek at Jones creek field (360), Chanomi creek (833), Aghigho (055) and an unnamed creek east of Jones creek (839). There was an appreciable decrease in the levels recorded during the 1985 dry season, with the Escravos Terminal recording the highest for the period (0.71mg/1).

All the points where high values were recorded were well situated within the oil activity areas, or along the water traffic routes, which may therefore account for the observed high levels of hydrocarbon recorded.

4.3.1.4 FORCADOS - WARRI RIVER SYSTEM

The hydrocarbon levels obtained during 1984 (wet season) ranged between 0.60mg/l (Warri river upstream of refinery Jetty at Oguno Channel - 861) and 7.70mg/l (Keremo on Warri river - 863). High values were also recorded at Unenuchi (Okpari creek - 372), Forcados river above Burutu (866), Ughelli (051), Warri river field (053), unnamed creek draining Odidi field (859), and Forcados river above Obotebe (865).

All the stations sampled in 1985 dry season had values between 0.11mg/l (unnamed creek opposite Ajuju field - 862) and 1.40mg/l (Forcados river below Burutu - 867). Most of the stations were located close to oil installations or on boat traffic route and close to towns (e.g. Burutu stations).

4.3.1.5 RAMOS RIVER SYSTEM

The 5 samples analyzed gave values which ranged from 1.10mg/l (Nikorogba creek - 869) to 2.20mg/l (Ramos estuary northeast of Aghoro - 038). No sample was collected during the 1985 dry season sampling trip.

4.3.1.6 NUN - EKOLE - BRASS

The average value obtained for the 1984 wet period samples was 3.39mg/1, with a range of values from a non-detectable value at a point below Peremabiri (872) to 17.60mg/1 - Kaima/Patani floodplain. High values were also recorded at Agip slot (023), Taylor creek (036), Diebu creek (043), Brass river mouth west side (094B) and Ekole creek (825). Agip slot, Taylor creek and Okoso/sandy floodplain (260) recorded high hydrocarbon levels for both wet and dry seasons.

4.3.1.7 ORASHI RIVER SYSTEM

On the Orashi river system the levels of hydrocarbon recorded ranged from 0.20mg/1 - Sombreiro river mouth west side (881) to 38.90mg/1 - Ahoada (022) in 1984 wet season. The average was 6.52mg/1. Stations where high values were recorded for both wet and dry seasons included Onosi near Ebocha (013), Oguta Pontoon crossing (014), Lake Oguta (016), Enwhe flow station (035), Okogbe west (252), Okogbe East (801), and Okarki (821).

Dry season (1985) values ranged between 0.10mg/l and 1.80mg/l with a mean of 0.60mg/l.

4.3.1.8 BONNY - NEW CALABAR RIVER SYSTEM

The range of hydrocarbon values was from 0.30mg/l, Bodo creek (121) to 70.70mg/l Elele Alimini (236). High values were recorded for Elele Alimini in both the 1984 and 1985 samples. Other points where appreciable levels of hydrocarbon were recorded are Okrika refinery Jetty (018), Umuochi (020), Port Harcourt Harbour (233a), Bakana (807), Iwofe (808) and a point north of Alaocha (810). Apart from Elele Alimini, all these other points had values below 0.70mg/l for the 1985 dry season.

4.3.1.9 IMO RIVER SYSTEM

The highest level of hydrocarbon was recorded at Azumini near Aba (806) - 10.10mg/l and the lowest was at the new bridge on Imo river (078) - 0.80mg/l. Other stations of note were Kono waterside (128), Isimiri flow station (816), Otamiri (818) and Imo river mouth east side (880). Only Azumini was sampled in 1985. The level of hydrocarbon was down to 2.00mg/l.

4.3.1.10 CROSS RIVER - CALABAR RIVER SYSTEM

High levels of hydrocarbon were recorded during 1984 wet season on Calabar river (070) - 4.87mg/1, Calabar between marker 31 and 32 (072) - 4.20mg/1, Cross river floodplain (805) - 6.90mg/1, Calabar tributary (826) - 3.40 and the new Calabar Port Complex (827) - 2.30mg/1. Only stations 805 and 826 were sampled for the 1985 dry season. The values recorded were 0.30 and 0.50mg/1 respectively.

4.3.1.11 KADUNA RIVER SYSTEM

The two points sampled in 1984 on the Kaduna refinery effluent channel gave 9.90 and 6.50mg/1 for the points down stream and upstream respectively. The other two points located on river Kaduna gave 7.20mg/1 - Doka park (843) and 4.30mg/1 for the River Kaduna floodplain at Malali (844).

4.3.1.12 IBADAN

Samples taken from Agodi garden on Ogunpa river and Asejire river (Ife-Ibadan Road) did not show any detectable level for both the 1984 and 1985 seasons.

TABLE 44.1: TOTAL HYDROCARBON CONCENTRATIONS IN WATER SAMPLES FROM LAGOS AND LEKKI LAGOONS BY INFRARED SPECTROPHOTOMETRIC (IR) AND GAS CHROMATOGRAPHIC (GC) METHODS (mg/l)

SN	Station Code	Wet Season		Dry Season
		IR 1984	GC 1984	IR 1985
1.	086	5.60	0.14	NA
2.	087	7.60	0.27	0.30
3.	845	11.40	0.21	NA
4.	847	4.60	0.13	NA
5.	848	9.50	0.01	0.40
6.	849	3.50	0.10	0.21
7.	850	3.00	-	0.41
8.	851	4.00	-	0.10
9.	852	8.00	-	0.21
10.	854	5.04	0.20	NA
11.	855	1.64	0.03	NA
12.	856	4.50	0.16	0.11
13.	857	4.40	-	NA
	Mean, $\bar{X}$	5.60	0.16	0.25
	Range, R	1.64-11.40	0.01-0.27	0.10-0.41

TABLE 44.2: TOTAL HYDROCARBON CONCENTRATIONS IN WATER SAMPLES FROM BENIN RIVER SYSTEM (mg/l)

SN	Station Code	Wet Season		Dry Season
		IR 1984	GC 1984	IR 1985
1.	057	8.70	NA	NA
2.	134	30.10	0.90	0.32
3.	311	3.10	0.03	0.13
4.	347	5.30	0.04	NA
5.	804	0.90	NA	NA
6.	835	4.10	ND	NA
7.	836	2.20	NA	NA
8.	837	4.80	0.11	NA
9.	838	13.90	0.20	NA
10.	877	1.10	ND.	NA
11.	878	ND	ND	NA
12.	884	6.30	0.14	NA
13.	0-1	2.10	0.01	NA
14.	0-2	16.40	0.55	NA
	Mean, $\bar{X}$	7.62	0.25	0.23
	Range, R	ND-30.10	ND-0.90	0.13-0.32

TABLE 44.3 : TOTAL HYDROCARBON CONCENTRATIONS IN WATER SAMPLES FROM ESCRAVOS RIVER SYSTEM

SN	Station Code	Wet Season		Dry Season
		IR 1984	GC 1984	IR 1985
1.	054	3.80	0.04	0.71
2.	055	8.00	0.15	0.21
3.	098	9.50	NA	NA
4.	360	15.00	0.24	NA
5.	362	14.30	-	NA
6.	831	17.50	3.36	NA
7.	832	5.50	NA	0.20
8.	833	9.60	0.27	0.11
9.	834	5.00	0.01	0.43
10.	839	7.00	0.12	NA
11.	840	5.70	NA	NA
	Mean, $\bar{X}$	9.17	0.70	0.33
	Range, R	3.80-17.50	0.01-3.36	0.11-0.71

TABLE 44.4: TOTAL HYDROCARBON CONCENTRATIONS IN WATER SAMPLES FROM FORCADOS RIVER SYSTEM

SN	Station Code	Wet Season		Dry Season
		IR 1984	GC 1984	IR 1985
1.	040	0.90	NA	0.21
2.	050	1.00	NA	0.21
3.	051	1.80	0.03	0.11
4.	052	1.00	NA	0.32
5.	053	2.10	0.03	NA
6.	351	1.80	0.01	0.64
7.	352	2.80	NA	NA
8.	353	5.10	NA	0.61
9.	372	7.20	0.27	0.41
10.	858	6.40	NA	0.20
11.	859	0.80	0.03	NA
12.	860	2.00	0.01	0.11
13.	861	0.60	0.01	0.51
14.	862	6.70	NA	0.11
15.	863	7.70	0.01	0.12
16.	864	1.50	NA	0.20
17.	865	2.00	0.03	0.23
18.	866	4.70	0.12	0.40
19.	867	5.60	NA	1.40
	Mean, $\bar{X}$	3.25	0.07	0.36
	Range, R	0.60-7.70	0.01-0.27	0.11-1.40

TABLE 44.5: TOTAL HYDROCARBON CONCENTRATIONS IN WATER SAMPLES FROM RAMOS RIVER SYSTEM

SN	Station Code	Wet Season		Dry Season
		IR 1984	GC 1984	IR 1985
1.	038	2.20	0.04	NA
2.	382	1.10	0.01	NA
3.	869	1.10	NA	NA
4.	870	2.10	0.02	NA
5.	871	16.00	NA	NA
	Mean, $\bar{X}$	4.50	0.02	-
	Range, R.	1.10-16.00	0.01-0.04	-

TABLE 44.6: TOTAL HYDROCARBON CONCENTRATIONS IN WATER SAMPLES FROM NUN-EKOLE-BRASS RIVER SYSTEM

SN	Station Code	Wet Season		Dry Season
		IR 1984	GC 1984	IR 1985
1.	023	2.70	NA	0.97
2.	024	1.50	NA	NA
3.	030	1.60	NA	0.70
4.	036	6.50	0.08	1.40
5.	043	3.20	0.03	NA
6.	094A	6.10	NA	NA
7.	094B	0.60	0.05	NA
8.	260	1.60	NA	1.00
9.	281	1.80	NA	NA
10.	803	17.60	0.31	0.20
11.	825	1.50	0.07	NA
12.	872	ND	NA	NA
13.	873	2.80	0.01	NA
14.	874	1.80	NA	NA
15.	875	1.50	NA	NA
	Mean, $\bar{X}$	3.63	0.09	0.85
	Range, R.	ND-17.60	0.01-0.31	0.20-1.40

TABLE 44.7: TOTAL HYDROCARBON CONCENTRATIONS IN WATER SAMPLES FROM ORASHI RIVER SYSTEM

SN	Station Code	Wet Season		Dry Season
		IR 1984	GC 1984	IR 1985
1.	013	5.00	0.41	0.90
2.	014	2.50	0.11	0.51
3.	016	4.90	0.37	0.11
4.	021	3.20	NA	0.20
5.	022	38.90	NA	0.31
6.	035	3.60	0.06	NA
7.	250	8.20	NA	NA
8.	251	0.50	NA	NA
9.	252	4.00	0.07	1.80
10.	262	NA	NA	0.10
11.	801	4.10	0.32	0.30
12.	802	3.90	NA	NA
13.	819	20.00	0.01	0.20
14.	820	NA	NA	1.20
15.	821	3.10	0.22	1.00
16.	824	1.30	NA	NA
17.	881	0.20	NA	NA
18.	882	0.90	0.01	NA
	Mean, $\bar{X}$	6.52	0.18	0.60
	Range, R.	0.20-38.90	0.01-0.41	0.10-1.80

TABLE 44.8: TOTAL HYDROCARBON CONCENTRATIONS IN WATER SAMPLES FROM BONNY-NEW CALABAR RIVER SYSTEM

SN	Station Code	Wet Season		Dry Season
		IR 1984	GC 1984	IR 1985
1.	018	2.40	0.04	0.51
2.	020	1.70	0.02	0.50
3.	093	6.90	NA	NA
4.	121	0.30	0.01	0.61
5.	233a	39.70	0.01	0.20
6.	236	70.70	0.53	1.80
7.	807	42.20	0.22	0.40
8.	808	1.60	0.04	0.10
9.	809	1.60	0.01	NA
10.	810	2.00	0.05	0.40
	Mean, $\bar{X}$	16.91	0.13	0.57
	Range, R.	0.30-70.70	0.01-0.53	0.10-1.80

TABLE 44.9: TOTAL HYDROCARBON CONCENTRATIONS IN WATER SAMPLES FROM IMO RIVER SYSTEM

SN	Station Code	Wet Season		Dry Season
		IR 1984	GC 1984	IR 1985
1.	078	0.80	NA	NA
2.	128	3.20	0.04	NA
3.	806	10.10	0.14	2.00
4.	813	NA	NA	NA
5.	814	4.00	0.09	NA
6.	816	3.00	0.08	NA
7.	817	3.70	NA	NA
8.	818	2.60	0.06	NA
9.	880	1.60	0.02	NA
	Mean, $\bar{X}$	3.63	0.07	-
	Range, R.	0.80-10.10	0.02-0.14	-

TABLE 44.10: TOTAL HYDROCARBON CONCENTRATIONS IN WATER SAMPLES FROM CROSS RIVER-CALABAR RIVER SYSTEM

SN	Station Code	Wet Season		Dry Season
		IR 1984	GC 1984	IR 1985
1.	070	4.87	0.35	NA
2.	071	2.00	NA	NA
3.	072	4.20	0.82	NA
4.	079	1.10	0.03	NA
5.	210	3.00	NA	NA
6.	805	6.90	0.65	0.30
7.	811	1.70	NA	NA
8.	812	0.80	NA	NA
9.	826	3.40	0.06	0.50
10.	827	2.30	0.03	NA
	Mean, $\bar{X}$	3.03	0.32	0.40
	Range, R.	0.80-6.90	0.03-0.82	0.30-0.50

TABLE 44.11: TOTAL HYDROCARBON CONCENTRATIONS IN WATER SAMPLES FROM KADUNA RIVER SYSTEM

SN	Station Code	Wet Season		Dry Season
		IR 1984	GC 1984	IR 1985
1	141A	9.90	0.11	NA
2	141B	6.50	0.07	NA
3	843	7.20	NA	NA
4	844	4.30	NA	NA
Mean, $\bar{X}$		6.98	0.09	-
Range, R		4.30-9.90	0.07-0.11	-

TABLE 44.12: TOTAL HYDROCARBON CONCENTRATIONS IN WATER SAMPLES FROM IBADAN

SN	Station Code	Wet Season		Dry Season
		IR 1984	GC 1984	IR 1985
1	Ag-1	ND	ND	ND
2.	As-2	ND	ND	ND

ND = Not detected

NA = Not analyzed.

4.3.1.13 UTOROGU SWAMP AND OKPARI RIVER

The results of the IR analyses of the hydrocarbon levels at the various points sampled during the 1984 and 1985 sampling periods are displayed in Table 45. The area is divided into 3 parts - impacted swamp, upstream and downstream.

The values recorded for the swamp during the 1984 wet season range between 2.18 and 10.50mg/1 with a mean value of 4.82mg/1. The highest hydrocarbon levels recorded were for points C_3 (10.5mg/1), E (7.89mg/1), G_3 (6.70mg/1) and A (5.10mg/1). All the points within the swamp recorded appreciable levels of hydrocarbon because they were all impacted by the spilled crude oil.

Points P and R (transect) which were upstream points recorded hydrocarbon values between 0.49 and 0.78mg/1 with a mean 0.68mg/1. All the other points downstream from O (transect) to J (transect) gave values between 0.17 and 0.95mg/1 with a mean 0.49mg/1.

During the early 1985 sampling (dry season) most of the points within Utorogu swamp had dried up but samples were collected from 3 points which happened to be hidden by trees and shrubs from the direct impact of

TABLE 45' TOTAL HYDROCARBON CONCENTRATION IN WATER SAMPLES AT UTOROGU SWAMP AND OKPARI RIVER IN BENDEL STATE BY INFRARED SPECTROMETRIC (IR) METHOD (mg/l).

	STATION GODE	CONCENTRATION (mg/l) OCT-NOV 1984	JAN-FEB 1985
	IMPACTED SWAMP		
1	A	5.10	4.41
2	B	3.95	4.67
3	C_1	NA	NA
4	C_2	4.24	2.29
5	C_3	10.50	NA
6	C_4	4.30	NA
7	D	NA	NA
8	E	7.89	NA
9	F	2.49	NA
10	G_1	2.18	2.29
11	G_2	2.23	1.78
12	G_3	6.70	ND
13	G_4	3.41	ND
	$\bar{X}$	4.28	3.09
	R	2.18-10.50	1.78-467

TABLE 45 (contd.)

	STATION CODE	OCT-NOV 1984	JAN-FEB 1985
	UPSTREAM		
14	R_1	0.78	ND
15	R_2	0.78	ND
16	R_3	0.65	ND
17	P	0.49	ND
	$\bar{X}$	0.68	ND
	R	0.49-0.78	ND
	DOWNSTREAM		
18	O_1	0.56	4.29
19	O_2	0.79	0.43
20	N	0.51	0.79
21	V	0.50	ND
22	K_1	0.47	ND
23	K_2	0.19	0.23
24	K_3	0.46	ND
25	T	0.59	ND
26	U	0.36	ND
27	L	0.95	ND
28	J_1	0.30	ND
29	J_2	0.17	0.26
30	J_3	0.54	ND
	$\bar{X}$	0.49	1.20
	R	0.17-0.95	ND-4.29

the sun. The values recorded were 4.41mg/l (A), 4.67mg/l (B) and 2.29mg/l (C_2). Points G_1 and G_2 bordering the swamp on Okpari river had 2.29 and 1.78mg/l respectively.

Points P and R did not record any detectable level upstream. Downstream, point O_1 recorded 4.29 mg/l. Apart from points O_2 (0.43mg/l), Agbokiama-N (0.79mg/l), Ekaigbodo K_2 (0.23mg/l) and the mouth of Okpari to Forcados - J_2 (0.26mg/l), all the other points did not give any detectable level.

In June-July 1985 (wet season) sampling trip the swamp was flooded and Okpari river was also flooded. All the water samples analyzed had levels below the detection limit of the IR method (50 ppb) used.

4.4 DISCUSSION

THE INFRA RED RESULTS

The IR results recorded for most of the stations sampled during the 1984 wet season were quite high. Some of the values were more than 10mg/l (845, 134, 838, 0-2, 360, 362, 831, 803, 022, 819, 233a, 236 and

807), which is rather very high for water when compared with the values reported in the literature[251,252] which are from a few microgram per litre (ppb) to a few milligrams per litre (ppm) 6mg/1. Although most of the values reported were for oceans and seas where dilution is a major factor in preventing the accummulation of hydrocarbon in the water column. Most of these values reported were determined by gas chromatographic method (aliphatic, aromatic or total hydrocarbons) or fluorescence spectrometry (for aromatics). The values from these two techniques will always be lower than the IR values. The difference can also be seen when the IR values reported in Tables 44(1-12) are compared with the corresponding GC values for same sample. All the GC values except one - Upomani ((831) with 3.36mg/1) were below 1mg/1. Some of the reasons that may be given for the higher IR values above the GC values are that the IR spectra method detects many hydrocarbons, including fatty acids, which can be a large component of non-petroleum hydrocarbons.

In GC quantification only the hydrocarbons eluting from the column between n - C_{10} and n - C_{34} were quantified, because detector sensitivity is poor for the long-chain hydrocarbons. Thus, the values are a lower limit for the total hydrocarbons. There was little contribution added by hydrocarbons eluting before n - C_{10} and hydrocarbons eluted from the column past n - C_{34}. Because clean-up steps were used prior to GC the non-hydrocarbon components of the oil are not measured. IR also permits the measurement of many relatively volatile hydrocarbons, which may be lost during the evaporative stage for GC analysis.

In spite of all these handicaps, one interesting thing of note in the results presented in Tables 44 (1-12) is that those samples with high IR values also gave corresponding high GC values, which goes on to show that the non-diagnostic factor against the IR not withstanding, the results can still be used as good indicator in monitoring system of hydrocarbons in the environment. This point is clearly illustrated

by the following data:

		IR (mg/l)	GC (mg/l)
Lever Brothers' discharge			
Point on Lagos harbour	(845)	11.40	0.21
Asagba (Ethiope river)	(134)	30.10	0.90
Dudu town (Benin river)	(837)	4.80	0.11
Olagua Creek (Benin Confluence)	(838)	13.90	0.20
Ogharife field effluent canal	(0-2)	16.40	0.55
Upomani discharge	(831)	17.50	3.36
Unenuchi (Okpari Creek)	(372)	7.20	0.27
Kaima/Patani floodplain	(803)	17.60	0.31
Elele Alimini	(236)	70.70	0.53
Bakana (up)	(807)	42.20	0.22
Cross River floodplain	(805)	6.90	0.65
Kaduna refinery effluent channel downstream (Romi river)	(141A)	9.90	0.11

There is a significant positive correlation between the GC and IR values ($r = 0.668$).

The IR results for the 1984 and 1985 reported in Tables 44 (1-12) and 45 show that there was a sharp difference in levels of hydrocarbons present in the water

systems during the different seasons of the year. All samples that gave high values were collected during the 1984 wet season, that is:

Lever Brothers' Discharge (845)		-	11.40 mg/l
Lagos Harbour North or NNPC facility	(087)	-	7.60 "
Asagba (Ethiope river)	(134)	-	30.10 "
Olagua Creek/Benin river confluence	(838)	-	13.90 "
Ogharife field effluent canal	(0-2)	-	16.40 "
Upomani discharge	(831)	-	17.50 "
Unenuchi (Okapi creek)	(372)	-	7.20 "
Kaima/Patani floodplain	(803)	-	17.60 "
Elele Alimini	(236)	-	70.70 "
Bakana	(807)	-	42.20 "
Cross river floodplain	(805)	-	6.90 "

This may be due to the flushing of hydrocarbons accummulated on land through run off and storm water into the river systems during the wet season, which may completely be absent during the dry season. There may also be a re-suspension of petroleum hydrocarbons in the water column due to mixing.

The histogram of the mean hydrocarbon levels by IR in the different river systems is presented in Figure 34 below.

A closer study of the hydrocarbon levels for discernible trends brought out a picture of a distribution which is more of activity-related than water-type related. It is also difficult to use the water-type for explaining the observed hydrocarbon levels because the 'black-water' rivers (acidic with low conductivity, total alkalinity and high organic matter - RPI (1985) are all within the oil producing zone of the Niger Delta. In all the river systems sampled, high hydrocarbon levels were found in areas of known industrial activities such as Lever Brothers' discharge point (845) - 11.40mg/1, Lagos Harbour near the NNPC Oil facility (087) - 7.60mg/1. Areas of known oil pollution, such as the Upomani discharge (831) - 17.50 mg/1, Chanomi creek (833) - 9.60mg/1, Okpari creek - Utorogu swamp (points A - F, Table 43) - 3.95 - 10.50 mg/1. Other activity related points with high hydrocarbon levels were found close to oil fields and

refineries, these include Onosi near Ebocha (013) - 5.00mg/1, Enwhe flow station (035) - 3.60mg/1, Okrika refinery Jetty (018) - 2.40mg/1; Agip slot (023) - 2.70mg/1 and Kaduna refinery effluent channel (141 A and B) - 9.90 and 6.50mg/1.

Some points where high hydrocarbon levels were recorded have no oil installations located within their vicinity. Such points are

Elele Alimini	(236)	-	70.70mg/1
Ahoada	(022)	-	38.90 "
Bakana	(807)	-	42.20 "
Aba	(806)	-	10.10 ".

All these points were located near towns. The results clearly implicated human settlements as one of the main sources of hydrocarbon pollution of the aquatic environment. Possible sources of hydrocarbons in urban river waters include, disposal of crank case oil and lubricants, accidental or intentional discharge of fuel oils and sewage (152,179,254).

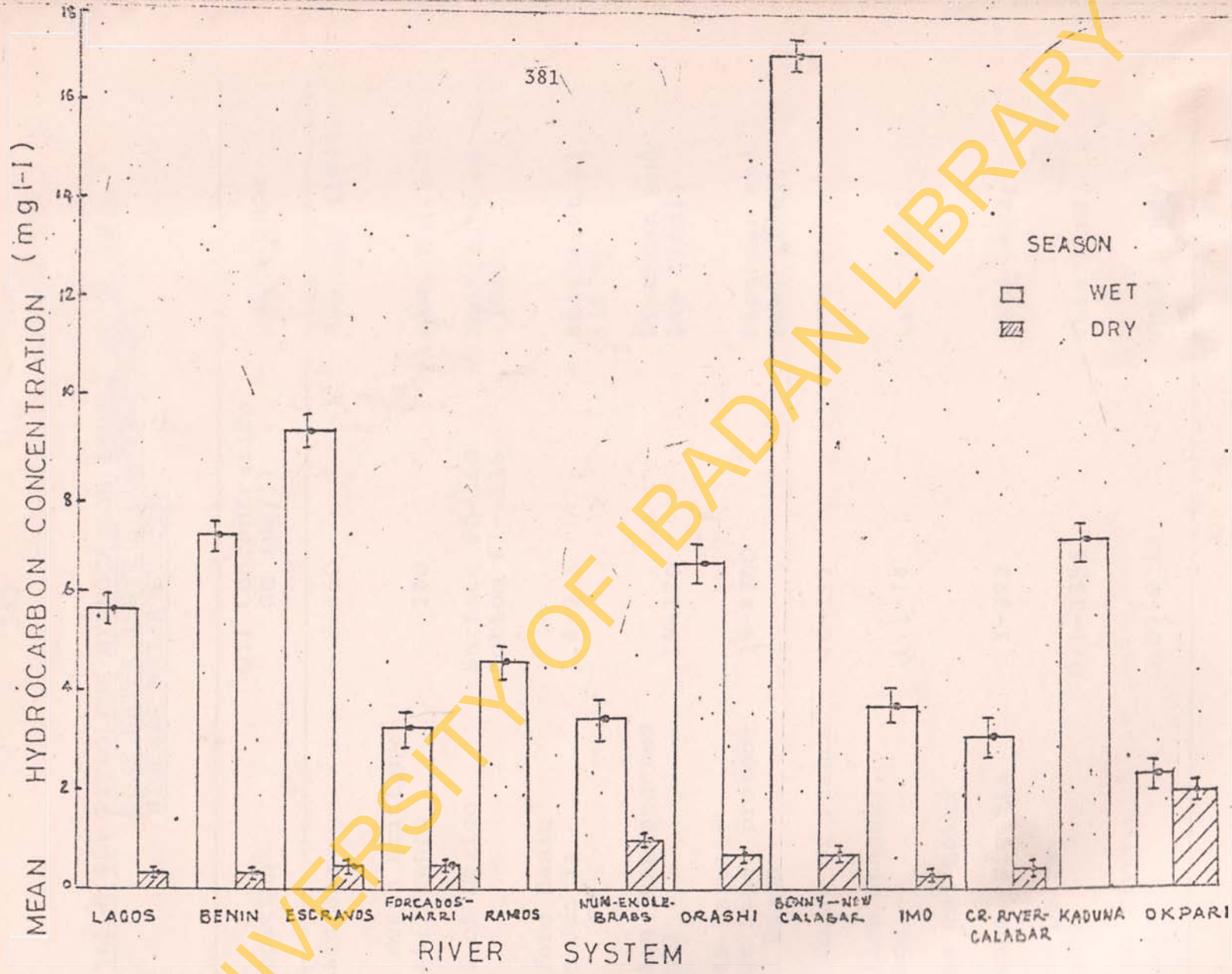


FIG 34: MEAN LEVEL OF PETROLEUM IN WATER OF LAGOS AND NIGER DELTA BY RIVER SYSTEM (mg/l).

TABLE 46: PETROLEUM HYDROCARBON LEVELS BY GC IN SOME WATER SYSTEMS COMPARED WITH NIGERIA WATER SYSTEM

Location	Oil Concentration GC (µg/l)	Reference
Baltic sea	8-150	Zsolany (1973)
The North Brittany Coast, France	240	Law, R.J.(1978a)
Gulf of Mexico	Surface 60-160 Bottom 61- 116	Kennicutt et al., (1981)
Bedford Basin Nova Scotia	1.6-9.3	Keizer et al., (1977)
Corton (unprotected Beach)	19-370	Blackman and Law (1981)
North Harbour Lower Stoft protected Beach	39-4700	Blackman and Law, (1981)
Off Coast of France	46-137	
English Channel, France	1.1-74	Law (1978)
Lagos and Lekki Lagoons, Nigeria	3-272	This Study
Niger Delta, Nigeria	0.1-3356	This Study
Kaduna river, Nigeria	0.07-0.11	This Study

Gas chromatographic values of petroleum hydrocarbon levels in water have been reported by many authors. The results of this work clearly point at one main fact, that most of the river systems in the Niger Delta and Lagos and Lekki Lagoons are either contaminated ($\leq$ 10µg/l) or polluted ($\geq$ 1mg/l)[235]. This fact is brought out clearly when the GC values for the samples in Tables 44.1-12 are compared with values in Table 46. The GC values for the hydrocarbon levels found in the river systems ranged between 1.00µg/l - Nana creek (834) - 0.1µg/l; Forcados estuary east of Terminal (860) - 0.2µg/l and Bodo creek (121) - 0.3µg/l and Upomani discharge (831) - 3,356µg/l with an overall average value of 179µg/l. These values are viewed alongside what have been reported from other parts of the world from inland waterways, coastal waters and the oil transport routes as shown in Table 46.

4.5 SEDIMENT

The results of sediments analysis for petroleum hydrocarbons by gravimetry for the Lagos and Niger

Delta area are shown in Tables 47 and 48. The parameters determined include the moisture content, the sample weight conversion ratio, total organic extract, aliphatic, aromatic and total hydrocarbon concentrations and the lithology of the samples.

4.5.1 LAGOS AND LEKKI LAGOONS .

Seven points were sampled around the Lagos-Lekki Lagoons in the 1984 wet season. The percentage moisture for the samples varied from 17.8% (North of NNPC loading facility - 087) which was a fine sand to 79.2% - Iwopin (856) a mud sample (Table 47). The total organic extract (TOE) gave a range of concentrations from 73.01μgg^{-1} (087) to 1153.70μgg^{-1} (Lagos Harbour at Lever Brothers' Discharge - 845) on dry weight basis with a mean value of 350.09μgg^{-1}. Other results for the aliphatic, aromatic and the total hydrocarbons (THC) are as follows with the mean given after the range in parenthesis, 27.99-316.64 (112.29), 7.75-243.57 (54.56), and 48.67-560.21 (166.85) μgg^{-1} dry weight respectively.

The highest concentration of total hydrocarbon (THC) was from Lever Brothers' discharge point (845) - 560.21μgg^{-1}, while a point north of NNPC loading facility (087) recorded the lowest THC level - 48.67 μgg^{-1}. Iwopin (856), which may be regarded as a pristine area in terms of petroleum activity on the Lekki Lagoon had 53.48μgg^{-1}.

4.5.2 BENIN RIVER SYSTEM

Nine samples were analyzed for petroleum hydrocarbons in 1984 wet season. The results of the moisture content, total organic extract, aliphatic, aromatic and total hydrocarbons were 17.5 - 61.6%, 43.17 - 317.08 (161.65), 8.49 - 183.69 (60.57), 2.58 - 75.36 (19.94) and 12.13 - 259.05 (80.52) μgg^{-1} dry weight respectively. Ogharife field effluent canal (O-2) had the highest level of THC - 259.05μgg^{-1} and Benin City (Ikpoba River) had the lowest THC - 12.13 μgg^{-1}. Asagba (134) - 110.29μgg^{-1}, Dudu Town (837) - 102.60μgg^{-1}, and Olagua creek (838) - 176.08μgg^{-1}.

4.5.3 ESCRAVOS RIVER SYSTEM

Six samples were analyzed in 1984 season with the results for moisture content, TOE, aliphatic, aromatic and THC as 26.2 - 75.0%, 28.34 - 919.10 (284.07), 10.80 - 117.37 (40.54), 2.70 - 60.71 (19.19) and 13.50 - 178.08 (59.73) μgg^{-1} respectively. Escravos terminal (054) recorded the highest value for THC and Upomani discharge (831) recorded the lowest - 13.50μgg^{-1}.

4.5.4 FORCADOS - WARRI RIVER SYSTEM

Sixteen samples were analyzed in 1984 wet season. The moisture content, TOE, Aliphatic, Aromatic and THC values are 20.4 - 68.9%, 47.66 - 589.32 (295.15); 10.49 - 237.83 (127.10), 2.41 - 176.7 (63.22) and 13.11 - 384.71 (190.32) μgg^{-1} respectively. The highest THC level was in Obotebe (865) on Forcados river and the lowest level was in Patani (040). All samples except 4 - Patani (040), upstream of Penfold Island (049), Agbarho (052) and Chanomi creek below mouth of Oyeye creek (351) recorded values above 100μgg^{-1} dry weight of THC.

4.5.5 RAMOS RIVER SYSTEM

Five points were sampled with the results for the moisture content, TOE, Aliphatic Aromatic and THC as follows 25.3 - 58.6%, 98.29 - 641.25 (409.48), 7.95 - 315.67 (171.55), 0.49 - 160.31 (119.03), 8.44 - 564.05 (302.58) μgg^{-1} dry weight. The highest THC value was recorded at Orughene creek (870) - 564.05μgg^{-1}, while Muri creek (871) recorded the lowest value of 8.44 μgg^{-1}.

4.5.6 NUN-EKOLE - BRASS RIVER SYSTEM

The range and mean values for the moisture content, TOE, Aliphatic, Aromatic and THC of the five samples analyzed are 20.7 - 54.5%, 62.73 - 332.79 (173.03), 6.17 - 159.89 (65.03), 0.15 - 81.80 (28.03) and 6.32 - 241.67 (93.06) μgg^{-1} dry weight. The highest THC level was recorded at Diebu creek (043) - 241.69μgg^{-1} and the lowest at Elpe creek (281) - 6.32 μgg^{-1}.

4.5.7 ORASHI RIVER SYSTEM

The fourteen samples analyzed gave the following results, moisture content - 17.4-58.0%, TOE - 11.91-771.40 (266.97) μgg^{-1}, Aliphatic - 1.60-135.69 (38.17)

μgg^{-1}, Aromatic - 0.54-91.90 (15.50) μgg^{-1} and THC 2.14 - 227.59 (53.67) μgg^{-1}. The highest value for THC was recorded for Degema (021) - 227.59μgg^{-1}, while Omoku creek (824) recorded the lowest THC level of 2.14μgg^{-1}. Oguta Pontoon crossing (014) and Lake Oguta (south shore) (016), recorded 107.72 and 103.68 μgg^{-1} THC respectively.

4.5.8 BONNY - NEW CALABAR RIVER SYSTEM

Seven samples were collected and the analysis gave the following results; moisture content - 18.2 53.3%, TOE - 78.86-1283.44 (369.69), Aliphatic 5.46-92.31 (36.86), Aromatic - 0.97-36.27 (17.45) and THC - 6.43-128.58 (54.31) μgg^{-1}. Bakana (upstream) (807) recorded the highest value - 128.58μgg^{-1} while the lowest was recorded at Alaocha (810) - 6.43 μgg^{-1}.

4.5.9 IMO RIVER SYSTEM

The results for the moisture content, TOE, Aliphatic, Aromatic and THC are 18.9-48.9%, 134.88-3894.34 (1430.72), 5.56-117.84 (51.62), 0.23-61.78 (23.60) and 5.79-179.62 (75.22) μgg^{-1} respectively.

The highest THC value was recorded at Kono waterside (128) - 179.62μgg^{-1}. Otamiri (817) recorded the lowest - 5.79μgg^{-1}.

4.5.10 CROSS RIVER - CALABAR RIVER SYSTEM

The moisture content, TOE, Aliphatic, Aromatic and THC results for the four samples analyzed are, 27.3-57.6%, 54.91-154.00 (105.59), 8.21-37.80 (18.76), 1.75-4.61 (3.68), and 9.97-42.00 (22.44) μgg^{-1} respectively. Calabar new port complext (827) recorded the highest THC, with Parrot Island (811) recording the lowest value for THC.

4.5.11 KADUNA RIVER SYSTEM

The results of the 3 samples from Kaduna for the moisture content, TOE, Aliphatic, Aromatic and THC are 21.2-34.1%, 14.86-232.90 (106.79), 7.43-112.65 (52.13), 1.49-58.86 (25.13) and 8.92-171.51 (77.26) μgg^{-1} respectively. The highest THC value was recorded at the Kaduna refinery effluent channel downstream, (141A) - 171.51 μgg^{-1}. Doka park in Kaduna on Kaduna river (843) recorded the lowest THC level.

TABLE 47 : GRAVIMETRIC DATA OF SEDIMENT SAMPLES AROUND LAGOS AND NIGER DELTA AREA OF NIGERIA. WET SEASON (AUGUST-NOVEMBER 1984) ($\mu g\ g^{-1}$ DRY WEIGHT)

SN	Station Code	Lithology of Sample	% Moisture	Wet Wt. / Dry Wt.	Dry Wt. of Sample (g)	TOE $\mu g\ g^{-1}$	Aliphatic $\mu g\ g^{-1}$	Aromatic $\mu g\ g^{-1}$	THC $\mu g\ g^{-1}$
	1. LAGOS - LEKKI LAGOONS								
1	086	MUD	25.8	1.22	74.30	119.79	51.15	43.07	94.22
2	087	FINE SAND	17.8	1.35	82.18	73.01	27.99	20.69	48.67
3	845	MUD	58.9	2.44	41.06	1153.70	316.64	243.57	560.21
4	847	MUD	66.1	2.94	34.05	202.64	132.31	26.43	158.74
5	851	MUD	42.9	1.75	51.63	154.94	127.82	7.75	135.57
6	856	MUD	79.2	4.82	18.70	374.37	42.79	10.70	53.48
7	857	MUD	77.2	4.39	18.54	372.17	87.33	29.74	117.07
					$\bar{X}$	350.09	112.29	54.56	166.85
					SD	±154.38	±41.24	±33.69	±73.08
					R	73.01	27.99	7.75	48.67
						-1153.70	-316.64	-243.57	-560.21
	2. BENIN								
8	057	MUD	30.7	1.44	69.50	43.17	11.51	2.88	14.39
9	134	MUD	28.4	1.41	72.54	317.08	104.77	5.51	110.29
10	311	COARSE SAND	17.5	1.21	85.50	77.27	8.49	3.64	12.13
11	347	MUD	61.5	2.59	38.79	103.11	18.04	2.58	20.62
12	835	MUD	31.3	1.46	68.78	189.00	11.81	4.27	16.08
13	837	MUD	61.6	2.621	38.99	128.25	82.08	20.52	102.60

TABLE 47 (contd.)

SN	Station Code	Lithology of Sample	% Moisture	Wet Wt. / Dry Wt.	Dry Wt. of Sample (g)	TOE $\mu g\ g^{-1}$	Aliphatic $\mu g\ g^{-1}$	Aromatic $\mu g\ g^{-1}$	THC $\mu g\ g^{-1}$
14	838	MUD	50.6	2.02	49.39	252.64	114.05	62.03	176.08
15	0-1	COARSE SAND	25.6	1.34	74.66	60.91	10.72	2.68	13.40
16	0-2	FINE SAND	21.2	1.27	78.86	283.43	183.69	75.36	259.05
					$\bar{X}$	161.65	60.57	19.94	80.52
					SD	±30.43	±19.47	±8.09	±27.43
					R	43.17	8.49	2.58	12.13
						-317.08	-183.69	-75.36	-259.05
	3.	ESCRAVOS							
17	054	MUD	53.2	2.14	24.71	429.01	117.37	60.71	178.08
18	055	MUD	33.8	1.51	67.46	919.10	18.12	4.50	22.62
19	360	MUD	75.0	4.00	25.11	123.46	23.90	15.93	39.83
20	362	MUD	59.4	2.46	40.60	141.87	57.39	22.46	79.85
21	831	MUD	26.2	1.36	74.11	28.34	10.80	2.70	13.50
22	839	MUD	65.9	2.94	35.34	62.64	15.66	8.83	24.49
					$\bar{X}$	284.07	40.54	19.19	59.73
					SD	±148.46	±17.76	±9.67	±27.43
					R	28.34	10.80	2.70	13.50
						-919.10	-117.37	-60.71	-178.08

TABLE 47 (contd.)

SN	Station Code	Lithology of Sample	% Moisture	Wet Wt. / Dry Wt.	Dry Wt. of Sample (g)	TOE µg g^{-1}	Aliphatic µg g^{-1}	Aromatic µg g^{-1}	THC µg g^{-1}
	4.	FORCADOS - WARRI							
23	040	CLAY	25.4	1.34	76.26	65.56	10.49	2.62	13.11
24	049	CLAY	41.5	1.71	58.52	73.92	21.96	16.84	38.81
25	050	MUD	62.4	2.66	33.90	383.48	200.30	176.70	377.00
26	052	FINE SAND	20.4	1.26	80.55	86.90	17.31	2.41	19.72
27	053	MUD	36.6	1.58	63.46	236.37	211.16	11.03	222.19
28	351	MUD	58.0	2.38	41.96	47.66	33.36	14.30	47.66
29	352	MUD	68.9	3.22	31.07	428.76	182.19	122.53	304.72
30	353	MUD	42.5	1.74	57.59	451.47	69.46	52.09	121.55
31	372	FINE SAND	21.8	1.28	79.92	589.32	147.64	27.53	175.17
32	858	MUD	67.9	3.12	29.08	481.48	237.83	113.76	351.59
33	860	MUD	56.4	1.87	35.37	267.65	167.46	54.34	221.80
34	862	MUD	43.5	1.77	56.56	256.58	157.07	75.30	232.37
35	863	MUD	62.0	2.63	38.05	446.84	178.28	55.20	233.48
36	864	CLAY	34.2	1.59	66.07	290.82	112.51	80.52	193.03
37	865	CLAY	36.7	1.58	63.64	415.71	220.00	164.71	384.71
38	866	MUD	39.6	1.65	60.67	198.90	66.59	41.65	108.24
					$\bar{X}$	295.15	127.10	63.22	190.32
					SD	±169.33	±79.42	±55.58	±124.60
					R	47.60	10.49	2.41	13.11
						-589.32	-237.83	-176.7	-384.71

TABLE 47 (contd.)

SN	Station Code	Lithology of Sample	% Moisture	Wet Wt. / Dry Wt.	Dry Wt. of Sample (g)	TOE $\mu g\ g^{-1}$	Aliphatic $\mu g\ g^{-1}$	Aromatic $\mu g\ g^{-1}$	THC $\mu g\ g^{-1}$
	5. RAMOS								
39	038	CLAY	52.7	2.11	45.32	446.33	225.66	108.61	334.27
40	382	MUD	53.2	2.14	46.86	512.12	117.11	121.63	298.74
41	869	CLAY	25.3	1.34	74.86	349.42	191.37	116.03	307.40
42	870	MUD	58.6	2.41	41.45	641.25	315.67	248.38	564.05
43	871	MUD	57.5	2.35	42.68	98.29	7.95	0.49	8.44
					$\bar{X}$	409.48	171.55	119.03	302.58
					SD	±108.59	±61.54	±31.96	±111.12
					R	98.29	7.95	0.49	8.44
						-641.25	-315.67	-160.31	-564.05
	6. NUN-EKOLE-BRASS								
44	036	FINE SAND	20.7	1.26	79.27	62.73	6.55	2.52	9.07
45	043	CLAY	46.3	1.86	53.79	332.79	159.89	81.80	241.69
46	281	MUD	54.5	2.82	35.51	75.98	6.17	0.15	6.32
47	872	CLAY	36.4	1.57	63.93	172.08	86.04	6.26	92.30
48	873	CLAY	41.5	1.71	58.67	221.59	66.48	49.43	115.91
					$\bar{X}$	173.03	65.03	28.03	93.06
					SD	±54.01	±30.74	±16.33	±47.07
					R	62.73	6.17	0.15	6.32
						-332.79	-159.89	-18.80	-241.69

TABLE 47 (contd.)

SN	Station Code	Lithology of Sample	% Moisture	Wet Wt. / Dry Wt.	Dry Wt. of Sample (g)	TOE µg g^{-1}	Aliphatic µg g^{-1}	Aromatic µg g^{-1}	THC µg g^{-1}
	7.	ORASHI							
49	012	COARSE SAND	17.4	1.21	83.97	11.91	8.34	1.19	9.53
50	013	MUD	30.5	1.41	59.20	48.74	16.74	13.36	30.10
51	014	CLAY	25.4	1.34	75.20	200.81	95.75	11.97	107.72
52	016	FINE SAND	22.2	1.29	78.84	279.04	84.65	19.68	103.68
53	021	MUD	57.9	1.38	42.03	452.02	135.69	91.90	227.59
54	035	FINE SAND	30.6	1.44	72.811	218.37	12.36	1.37	13.23
55	250	COARSE SAND	21.9	1.28	78.25	293.94	10.22	2.56	12.78
56	251	COARSE SAND	18.2	1.22	83.84	250.48	18.35	10.58	28.78
57	252	MUD	58.0	2.38	42.11	451.24	42.50	19.87	62.37
58	262	COARSE SAND	19.2	1.24	81.80	365.53	31.79	17.12	48.91
59	801	CLAY	18.2	1.22	83.92	47.66	19.53	7.38	26.91
60	802	CLAY	24.9	1.33	75.45	83.02	44.58	16.63	61.21
61	821	MUD	43.0	1.75	57.04	771.40	12.27	3.51	15.78
62	824	FINE SAND	20.4	1.26	79.57	263.94	1.60	0.54	2.14
					$\bar{X}$	266.97	38.17	15.50	53.66
					SD	±54.25	±9.58	±6.53	±16.10
					R	11.91	1.60	0.54	2.14
						-771.40	-135.690	-91.90	-227.59

TABLE 47 (contd.)

SN	Station Code	Lithology of Sample	% Moisture	Wet Wt. / Dry Wt.	Dry Wt. of Sample (g)		TOE µg g^{-1}	Aliphatic µg g^{-1}	Aromatic µg g^{-1}	THC µg g^{-1}
	8.	BONNY - NEW CALABAR								
63	020	COARSE SAND	18.2	1.22	81.99		110.98	13.42	7.32	20.74
64	121	MUD	53.3	2.73	36.67		300.00	16.36	10.91	27.27
65	2339	MUD	44.5	1.80	55.39		235.98	55.77	35.03	90.80
66	807	MUD	46.7	1.88	55.32		1283.44	92.31	36.27	128.58
67	808	MUD	36.6	1.58	63.40		78.86	37.85	14.20	52.05
68	810	SAND/PEBBLES	19.7	1.25	81.39		208.88	5.46	0.97	6.43
						$\bar{X}$	369.69	36.86	17.45	54. 31
						SD	±200.76	±14.48	±5.88	±20.36
						R	78.86	5.46	0.97	6.43
							-1283.44	-92.31	-36.27	-128.58
	9.	IMO								
69	128	MUD	48.9	1.96	51.41		3894.34	117.84	61.78	179.62
70	813	COARSE SAND	20.4	1.26	79.87		262.94	31.47	8.78	40.25
71	817	FINE SAND	18.9	1.23	81.55		134.88	5.56	0.23	5.79
						$\bar{X}$	1430.72	51.62	23.60	75.22
						SD	±1253.15	±37.43	±20.52	±57.94
						R	134.88	5.56	0.23	5.79
							-3894.34	117.84	-61.78	-179.62

TABLE 47 (contd.)

SN	Station Code	Lithology of Sample	% Moisture	Wet Wt. / Dry Wt.	Dry Wt. of Sample (g)	TOE µg g^{-1}	Aliphatic µg g^{-1}	Aromatic µg g^{-1}	THC µg g^{-1}
	10. CROSS RIVER - CALABAR								
72	071	CLAY	27.3	1.38	72.84	54.91	20.70	4.61	25.31
73	811	MUD	57.6	2.36	42.54	70.53	8.21	1.75	9.97
74	812	MUD	37.5	1.60	62.97	142.93	8.33	4.14	12.47
75	827	MUD	54.6	2.20	45.45	154.00	37.80	4.20	42.00
					$\bar{X}$	105.59	18.78	3.68	22.44
					SD	±24.77	±7.40	±0.72	±8.01
					R	54.91	8.21	1.75	9.97
						-154.00	-37.80	-4.61	-42.00
	11. KADUNA								
76	141A	CLAY	21.2	1.27	79.03	232.90	112.65	58.86	171.51
77	843	MUD	34.1	1.52	67.32	14.86	7.43	1.49	8.92
78	844	MUD	21.4	1.27	97.38	72.60	36.30	15.04	51.34
					$\bar{X}$	106.79	52.13	25.13	77.26
					SD	±72.68	±35.07	±19.12	±54.20
					R	14.86	7.43	1.49	8.92
						-232.90	-112.65	-58.86	-171.51

In 1985 (dry season) sampling, the number of sampling points were reduced in all the river systems. The results of the gravimetric determinations are shown in Table 48.

4.6.1 LAGOS AND LEKKI LAGOONS

Only 3 points were sampled and the results for moisture content, TOE, Aliphatic, Aromatic and THC are 39.0-70.5%, 58.99-127.53 (91.49), 22.51-40.60 (29.78), 13.53-20.01 (17.19) and 42.51-54.13 (46.96) $\mu g g^{-1}$ dry weight respectively. All the points recorded lower levels of THC than the levels recorded during the 1984 wet season. However, the Lever Brothers' discharge point still maintains the highest level of total hydrocarbon.

4.6.2 BENIN RIVER SYSTEM

Only Benin City (Ikpoba river) was sampled in Benin river system. The level of THC increased slightly from 12.13$\mu g g^{-1}$ in 1984 to 17.96$\mu g g^{-1}$ in 1985.

4.6.3 ESCRAVOS RIVER SYSTEM

Four points were sampled, with the results for moisture content, TOE, Aliphatic, Aromatic and THC as 56.7-86.7%, 217.83-325.56 (264.98), 46.17-195.49 (83.84), 5.73-90.23 (39.96) and 51.91-285.72 (123.80) μgg^{-1} respectively. The values are higher than those obtained during the 1984 wet season.

4.6.4 FORCADOS - WARRI RIVER SYSTEM

Ten points were sampled with the following results: moisture content - 19.6-69.7%, TOE - 23.87-730.62 (168.64) μgg^{-1}, Aliphatic: 8.04-42.49 (20.71) μgg^{-1}, Aromatic: 4.42-13.73 (9.85) μgg^{-1} and THC: 13.50-52.73 (30.56) μgg^{-1}. When the values are compared with the 1984 values there is no discernible trend because some of the points recorded higher THC values over the 1984, examples are Patani (040), Penfold Island (upstream) (049), and Agharho (052) with THC levels of 13.11, 38.81 and 19.72 μgg^{-1} respectively for 1984. In 1985 the THC levels for these three points moved up to 16.19, 33.34 and 52.73 μgg^{-1} respectively. All the other points recorded lower THC levels for 1985.

4.6.5 ORAHSI RIVER SYSTEM

Six samples were collected and analyzed, with the results as follows: moisture content: 21.8-58.6%, TOE: 18.46-116.52 (42.72) μgg^{-1}, Aliphatic: 11.66-54.99 (20.80) μgg^{-1}, Aromatic: 0.64-22.26 (9.46) μgg^{-1} and THC: 12.30 - 77.25 (30.26) μgg^{-1}. The mean values for all the parameters are lower than those recorded for the 1984 samples.

4.6.6 BONNY - NEW CALABAR RIVER SYSTEM

The results of the five samples collected for the 1985 seasons are moisture content: 50.7-74.6%, TOE: 68.92-147.13 (110.45), Aliphatic: 15.59-125.35 (60.98), Aromatic: 8.11-38.51 (19.10) and THC: 24.94-139.28 (80.07) μgg^{-1}. Most of the values are higher than the 1984 values.

4.6.7 CROSS RIVER - CALABAR RIVER SYSTEM

Only two samples were analyzed in 1985. The results are 19.8-23.1% - moisture content, 49.81-181.91 (115.86) μgg^{-1} TOE, 6.50-18.68 (12.59) μgg^{-1} Aliphatic, 2.60-12.45 (7.53) μgg^{-1} Aromatic and 9.10-31.13 (20.12) μgg^{-1} THC.

TABLE 48: GRAVIMETRIC DATA OF SEDIMENT SAMPLES AROUND LAGOS AND NIGER DELTA AREAS OF NIGERIA (FEBRUARY 1985) (DRY WEIGHT BASIS)

SN	Station Code	Lithology of Sample	% Moisture	Wet Wt. / Dry Wt.	Dry Wt. of Sample (g)	TOE µg g^{-1}	Aliphatic µg g^{-1}	Aromatic µg g^{-1}	THC µg g^{-1}
	1.	LAGOS-LEKKI LAGOONS							
1	845	MUD	70.5	3.39	29.56	87.96	40.60	13.53	54.13
2	851	MUD	39.0	1.64	61.03	58.99	26.21	18.02	44.24
3	857	MUD	60.0	2.50	39.99	127.53	22.51	20.01	42.51
					$\bar{X}$	91.49	29.78	17.19	46.96
					SD	±22.85	13.61	±2.16	±3.87
					R	58.99	22.51	13.53	42.51
						127.53	-40.60	-20.01	-54.13
	2.	BENIN							
4	311	COARSE SAND	16.5	1.20	83.54	83.79	11.97	5.99	17.96
	3.	ESCRAVOS							
5	054	MUD	56.7	3.61	21.70	294.49	195.49	90.23	285.72
6	055	MUD	86.7	3.48	6.65	325.56	64.52	36.87	101.38
7	830	MUD	62.8	4.51	18.17	247.66	60.87	32.22	93.09
8	833	MUD	62.6	3.72	23.02	238.92	52.13	34.75	86.88
9	834	MUD	65.1	2.81	34.89	217.83	46.17	5.73	51.91
					$\bar{X}$	264.98	83.84	39.96	123.80
					SD	±21.55	±29.86	±16.90	±46.76
					R	217.83	46.17q	5.73	51.91
						-325.56	-195.49	-90.23	-285.72

TABLE 48: (contd.)

SN	Station Code	Lithology of Sample	% Moisture	Wet Wt. / Dry Wt.	Dry Wt. of Sample (g)	TOE µg g^{-1}	Aliphatic µg g^{-1}	Aromatic µg g^{-1}	THC µg g^{-1}
	4.	FORCADOS - WARRI							
10	040	FINE SAND	32.1	1.47	67.94	47.78	4.42	16.19	16.19
11	049	CLAY	32.7	1.49	67.48	28.16	22.23	11.11	33.34
12	050	MUD	50.7	2.71	29.69	114.52	26.74	13.37	40.10
13	052	FINE SAND	19.6	1.24	80.43	53.57	42.49	10.24	52.73
14	053	MUD	60.8	2.93	31.46	289.79	8.04	5.47	13.50
15	351	MUD	63.3	3.65	23.87	92.17	13.73	7.49	21.22
16	353	MUD	69.7	5.43	15.74	730.62	19.06	12.71	31.77
17	860	MUD	30.5	1.56	54.47	23.87	27.34	13.67	41.02
18	862	MUD	63.1	3.84	22.20	252.25	16.90	13.73	30.63
19	866	MUD	52.2	2.09	47.81	54.38	18.83	6.28	25.10
					$\bar{X}$	168.64	20.71	9.85	30.56
					SD	±70.68	±3.45	±0.93	±3.92
					R	23.87	8.04	42.49	13.50
						730.62	42.49	-13 .73	-52.73
	5.	ORASHI							
20	021	MUD	58.6	2.413	41.480	26.52	12.05	9.64	21.70
21	250	FINE SAND	21.8	1.274	78.310	33,20	14.05	8.94	22.99
22	252	CLAY	23.7	1.310	76.385	116.52	54.99	22.26	77.25
23	801	CLAY	22.0	1.282	78,045	18.46	11.66	0.64	12.30

TABLE 48 (contd.)

SN	Station Code	Lithology of Sample	% Moisture	Wet Wt. / Dry Wt.	Dry Wt. of Sample (g)	TOE µg g^{-1}	Aliphatic µg g^{-1}	Aromatic µg g^{-1}	THC µg g^{-1}
24	819	CLAY	44.2	1.791	55.878	24.25	14.00	6.24	20.24
25	820	FINE SAND	22.5	1.290	77.590	37.38	18.04	9.02	27.07
					$\bar{X}$	42.72	20.80	9.46	30.26
					SD	±16.34	±7.22	±3.60	±10.83
					R	18.46	11.66	0.64	12.30
						-116.52	-54.99	22.26	-77.25
	6. BONNY - NEW CALABAR								
26	081	MUD	64.8	2.842	35.172	136.48	79.61	25.59	105.20
27	020	MUD	74.6	3.930	25.460	147.13	125.93	13.93	139.28
28	121	MUD	50.7	2.028	49.332	68.92	20.14	8.11	28.25
29	807	MUD	68.3	3.129	32.079	84.17	15.19	9.35	24.94
30	808	MUD	68.9	3.211	31.161	115 .53	64.19	38.51	102.70
					$\bar{X}$	110.45	60.98	19.10	80.07
					SD	±15.64	±21.95	±6.08	±22.87
					R	68.92	15.59	8.11	24.94
						-147.13	-125.35	-38.51	-139.28
	7. CROSS RIVER - CALABAR								
31	079	COARSE SAND	19.8	1.247	80.302	49.81	18.68	12.45	31.13
32	210	CLAY	23.1	1.300	76.960	181.91	6.50	2.60	9.10
					$\bar{X}$	115.86	12.59	7.53	20.12
					SD	±16.05	±6.09	±4.93	±11.02
					R	49.81	6.50	2.60	9.10
						-181.91	-18.68	-12.45	-31.13

TABLE 48: (contd.)

SN	Station Code	Lithology of Sample	% Moisture	Wet Wt. / Dry Wt.	Dry Wt. of Sample (g)	TOE µg g^{-1}	Aliphatic µg g^{-1}	Aromatic µg g^{-1}	THC µg g^{-1}
	8. KADUNA								
33	141A	CLAY	18.4	1.225	81.662	67.35	19.59	14.70	34.29
34	141B	CLAY	23.9	1.314	76.190	173.25	53.81	6.56	60.38
					$\bar{X}$	120.30	36.70	10.63	47.34
					SD	±53.0	±17.11	±4.07	±13.05
					R	67.35	19.59	6.56	34.29
						-173.25	-53.81	-14.70	-60.38
35	Ag-1	FINE SAND	18.6	1.229	81.814	47.670	32.00	ND	32.00
36	As-2	MUD	41.4	1.706	58.745	297.900	17.02	6.81	23.83

4.6.8 KADUNA

Only the Kaduna refinery effluent channel was sampled. The downstream and upstream values for moisture content, TOE, Alipahtic, Aromatic and THC are 18.4-23.9%, 67.35-173.25 (120.30), 19.59-53.81 (36.70), 6.56-14.70 (10.63) and 34.29-60.38 (47.34) μgg^{-1} respectively.

4.6.9 IBADAN

The two samples collected at Ibadan in Agodi Garden (Ogunpa) and Asejire gave the following results for moisture content, TOE, Aliphatic, Aromatic and THC

Agodi - 18.6%, 47.67, 32.00, ND and 32.00 μgg^{-1}

Asejire - 41.4%, 297.90, 17.02, 6.81 and 23.83 μgg^{-1} respectively.

Agodi sediment was a fine sand while Asejire sediment was muddy.

4.6.10 UTOROGU SWAMP AND OKPARI RIVER

The Utorogu swamp and Okpari river were sampled thrice (Oct. - Nov. 1984, Jan.-Feb., 1985 and June-July 1985). The results of the gravimetric method for the

moisture content, Total organic extract (TOE, Aliphatic, Aromatic and Total hydrocarbon (THC) are given in Tables 49-51 for the three sampling periods. The range and the mean (in parethesis) for these parameters for the 1984 samples are 22.8-83.0%, 89.12-805.00 (277.94), 21.22-249.92 (105.98), 4.21-122.15 (32.44) and 29.72-344.09 (138.42) μgg^{-1} dry weight, respectively.

The highest THC values were recorded at points B, D (swamp), G (transect), R (transect), O (transect), K (transect) and T.

The dry season samples (Jan.-Feb. 1985) gave 18.1-74.7%, 17.391-491.02 (94:83), 2.98-96.98 (27.17), 1.25-31.62 (11.04) and 5.47-122.76 (38.22) μgg^{-1} respectively for same parameter stated above.

The last set of samples collected during the early wet season in 1985 (June-July) recorded the following values: 16.9-73.7%, 18.35-283.21 (91.46), 10.23-11.73 (32.46), 1.42-66.64 (10.77), and 13.37-177.37 (43.23) μgg^{-1} respectively.

The 1984 samples recorded the highest values for all the parameters listed above. The levels came down

TABLE 49: GRAVIMETRIC DATA OF SEDIMENT SAMPLES AT UTOROGU SWAMP AND OKPARI RIVER IN BENDEL STATE OF NIGERIA (OCTOBER 1984)

SN	Station Code	Lithology of Sample	% Moisture	Wet Wt. / Dry Wt.	Dry Wt. of Sample (g)	TOE µg g^{-1}	Aliphatic µg g^{-1}	Aromatic µg g^{-1}	THC µg g^{-1}
	IMPACTED SWAMP								
1	B	MUD	47.0	1.887	53.072	354.64	133.78	80.27	214.05
2	D	FINE SAND	28.9	1.405	48.924	419.02	122.64	30.66	153.30
3	E	MUD	42.1	1.727	57.970	106.95	43.13	30.85	73.98
4	G-1	MUD	50.4	2.018	49.722	187.04	57.12	15.83	72.95
5	G-2	MUD	49.4	1.976	50.771	171.36	50/28	11.49	61.77
6	G-3	MUD	63.2	2.718	36,881	197.61	81.34	23.08	104.42
7	G-4	FINE SAND	25.5	1.342	74.660	220.55	139.30	38.38	177.68
					$\bar{X}$	236.74	89.66	32.94	122.59
	UPSTREAM				R	106.95	43.13	11.83	61.77
8						-419.02	-139.30	-80.27	-214.05
	R-1	FINE SAND	28.6	1.399	71.633	117.26	103.30	9.35	112.65
9	R-2	MUD	23.4	1.305	76.773	274.54	157.61	4.21	161.82
10	R-3	MUD	64.5	2.821	35.553	228.13	101.26	5.67	106.93
					$\bar{X}$	206.64	120.72	6.41	127.13
	DOWNSTREAM				R	117.26	101.26	4.21	106.93
11	O-1	MUD	65.7	2.915	34.411	274.54 805.00	157.61 249.92	9.34 83.31	161.82 333.23
12	O-2	MUD	56.3	2.290	43.705	796.25	221.94	122.15	344.09
13	N	MUD	31.5	1.459	68.530	245.11	61.29	8.36	69.65

TABLE 49: (contd.)

SN	Station Code	Lithology of Sample	% Moisture	Wet Wt. / Dry Wt.	Dry Wt. of Sample (g)	TOE $\mu g\ g^{-1}$	Aliphatic $\mu g\ g^{-1}$	Aromatic $\mu g\ g^{-1}$	THC $\mu g\ g^{-1}$
14	V	MUD	47.4	1.902	52.827	141.97	37.86	15.17	53.03
15	K-1	MUD	76.5	4.252	23.565	89.12	21.22	8.50	29.72
16	K-3	MUD	83.0	5.871	13.750	323.73	167.27	50.81	218.08
17	T	FINE SAND	22.8	1.295	77.264	171.38	98.36	20.15	118.51
18	U	FINE SAND	26.8	1.365	73.299	153.21	60.03	25.73	85.76
					$\bar{X}$	340.72	114.74	41.77	156.51
					R	89.12	21.22	8.36	29.72
						805.00	249.92	122.15	344.09

TABLE 50: GRAVIMETRIC DATA OF SEDIMENT SAMPLES AT UTOROGU SWAMP AND OKPARI RIVER IN BENDEL STATE OF NIGERIA (JANUARY - FEBRUARY 1985)

SN	Station Code	Lithology of Sample	% Moisture	Wet Wt. / Dry Wt.	Dry Wt. of Sample (g)	TOE µg g^{-1}	Aliphatic µg g^{-1}	Aromatic µg g^{-1}	THC µg g^{-1}
	IMPACTED SWAMP								
1	B1	CLAY	39.0	1.642	60.746	151.45	23.05	1.65	24.69
2	B2	CLAY	19.0	1.237	80.065	138.64	8,74	1.25	9.99
3	C	CLAY	18.6	1.228	81,463	491.02	96.98	25.78	122.76
4	D	MUD	55.2	2.237	44.611	126.90	38.11	6.73	44.83
5	E	CLAY	30.1	1.430	69.963	57.17	24.30	17.17	41.45
6	E2	CLAY	23.5	1.31	75.655	51.55	26.44	21.15	47.59
7	F	MUD	74.7	3.953	25.298	101.15	59.29	31.63	90.92
					$\bar{X}$	159.70	39.56	15.05	54.60
					R	51.55	8.73	1.25	9.99
						-491.62	-96.98	31.62	-122.76
UPSTREAM									
8	R-1	MUD	68.9	3.274	30.300	52.81	13.20	3.30	16.50
9	R-2	FINE SAND	22.0	1.282	78.059	42.28	32.03	5.12	37.15
					$\bar{X}$	47.55	22.62	4.21	26.83
					R	42.28	13.20	3.30	16.50
						-52.81	-32.03	-5.12	-37.15

TABLE 50 (contd.)

SN	Station Code	Lithology of Sample	% Moisture	Wet Wt. / Dry Wt.	Dry Wt. of Sample (g)	TOE µg g^{-1}	Aliphatic µg g^{-1}	Aromatic µg g^{-1}	THC µg g^{-1}
DOWNSTREAM									
10	0-1	MUD	59.7	2.483	40.250	17.39	2.98	2.48	5.47
11	0-2	FINE SAND	18.1	1.221	81.961	29.28	15.86	6.34	22.20
12	0-3	FINE SAND	29.4	1.416	70.658	35.38	16.98	14.15	31.15
13	N	FINE SAND	20.4	1.256	79.605	48.59	16.33	12.56	28.89
14	K-2	FINE SAND	24.1	1.318	75.858	52.73	15.82	10.55	26.37
15	T	FINE SAND	22.1	1.429	51.461	75.79	17.49	5.83	23.32
					$\bar{X}$	43.19	14.24	8.65	22.90
					RANGE	17.39	2.98	2.48	5.47
						-75.79	-17.49	-14.15	-31.14

TABLE 51: GRAVIMETRIC DATA OF SEDIMENT SAMPLES AT UTOROGU SWAMP AND OKPARI RIVER IN BENDEL STATE OF NIGERIA (JUNE-JULY 1985)

SN	Station Code	Lithology of Sample	% Moisture	Wet Wt. / Dry Wt.	Dry Wt. of Sample (g)	TOE $\mu g\ g^{-1}$	Aliphatic $\mu g\ g^{-1}$	Aromatic $\mu g\ g^{-1}$	THC $\mu g\ g^{-1}$
IMPACTED SWAMP									
1	A-1	MUD	69.3	3.255	30.738	126.88	53.68	17.89	71.57
2	B	FINE SAND	65.3	2.873	34.869	237.28	110.73	66.64	177.37
3	C-2	MUD	73.7	3.805	26.278	26.64	33.42	5.39	38.81
4	C-3	FINE SANS	54.2	2.183	45.812	74.22	41.84	8.37	50.21
5	D	MUD	71.8	3.545	28.209	42.58	25.86	7.76	33.62
6	F	MUD	46.8	1.879	53.252	108.92	30.42	3.38	33.80
7	G-1	MUD	63.2	2.714	36.864	73.24	22.23	10.32	32.55
					$\bar{X}$	98.54	45.45	17.11	62.56
					R	26.64	22.23	3.38	32.55
						-237.28	-110.73	-66.64	-177.37
UPSTREAM									
8	R-1	MUD	56.4	2.294	43.601	18.35	11.13	2.75	13.88
9	R-2	FINE SAND	21.0	1.266	79.092	283.21	17.78	10.03	27.82
10	R-3	MUD	50.1	2.004	49.882	60.14	10.80	2.57	13.37
11	P	FINE SAND	16.9	1.203	83.115	31.28	11.55	2.89	14.44
					$\bar{X}$	98.25	12.82	4.56	17.38
					R	18.35	10.80	2.57	13.37
						-283.21	17.78	10.03	-27.82

TABLE 51 (contd.)

SN	Station Code	Lithology of Sample	% Moisture	Wet Wt. / Dry Wt.	Dry Wt. of Sample (g)	TOE µg g^{-1}	Aliphatic µg g^{-1}	Aromatic µg g^{-1}	THC µg g^{-1}
DOWNSTREAM									
12	O-1	MUD	57.3	2.339	42.783	53.76	10.23	6.14	16.36
13	O-2	FINE SAND	18.7	1.230	81.396	24.57	22.29	9.83	32.11
14	O-3	FINE SAND	20.0	1.250	80.096	113.61	36.87	6.83	43.70
15	N	FINE SAND	18.2	1.222	81.941	30.51	15.99	7.20	23.19
16	V	FINE SAND	24.4	1.322	75.662	118.95	58.58	12.56	71.14
17	K-2	MUD	36.5	2.139	32.056	168.46	26.52	4.68	31.20
18	T	FINE SAND	24.3	1.321	75.730	178.27	58.70	22.80	81.50
19	U	FINE SAND	21.5	1.274	78.587	50.90	28.45	5.09	33.54
20	J-1	MUD	36.0	1.562	64.093	68.65	14.18	1. 42	15.60
21	J-2	FINE SAND	24.7	1.327	75.504	37.08	18.64	3.00	21.64
22	J-3	MUD	45.1	1.820	54.986	84.55	54.19	19.46	73.65
					$\bar{X}$	84.48	31.33	9.00	40.33
					RANGE	24.57	10.23	1.42	15.60
						-178.27	-58.58	-22.80	-81.50

sharply in 1985 but the differences in the mean values for the Jan.-Feb. 1985 samples and the June-July 1985 samples were not very significant when compared to the sharp drop between the 1984 and 1985 samples.

4.6.11 LAGOS LAGOON (JAN.-DEC. 1985)

Twenty-six points were sampled for this study and the gravimetric results for percentage moisture, total organic extract (TOE), Aliphatic, Aromatic and Total hydrocarbon THC) are given in Table 52. The values recorded for the above parameters throughout 1985 (Jan.-Dec.) are 15.5-68.6%, 5.06-4373.46 (202.28), 1.25-3466.78 (137.67), ND - 87.73 (10.01) and 1.25-3554.51 (147.68) $\mu g g^{-1}$ dry weight respectively.

The highest values were recorded at Berger/National Oil/Ijora (LS_{20}), throughout the year. Green buoy # 3(LS_{7}), mouth of Ogun river(LS13), Tin Can Island (LS 19) and Okobaba (LS 23) also recorded hydrocarbon levels indicating that they were also contaminated.

TABLE 52: GRAVIMETRIC DATA OF SEDIMENT SAMPLES FROM LAGOS LAGOON (FEBRUARY-DECEMBER 1985) (DRY WEIGHT BASIS)

SN	Station Code	Lithology of Sample	% Moisture	Wet Wt. / Dry Wt.	Dry Wt. of Sample (g)	TOE µg g-1	Aliphatic µg g-1	Aromatic µg g-1	THC µg g-1
1	LS-1	SAND	24.0	1.3150	75.6152	47.51	26.61	7.84	34.45
2	LS-2	MUD	27.9	1.3865	66.0860	19.08	13.59	4.54	18.13
3	LS-3	MUD	28.9	1.4066	68.5779	11.61	4.37	ND	4.37
4	LS-32	MUD	34.7	1.5312	49.9195	118.19	44.04	20.03	64.07
5	LS-4	FINE SAND	19.2	1.2375	80.0396	32.48	1.25	ND	1.25
6	LS-42	FINE SAND	21.0	1.2660	80.2852	13.42	4.98	ND	4.98
7	LS-5	MUD	56.4	2.2917	36.5639	49.23	18.20	7.73	25.93
8	LS-52	FINE SAND	21.8	1.2791	75.9876	21.52	9.21	ND	9.21
9	LS-6	MUD	48.5	1.9425	45.4933	84.74	19.78	4.40	24.18
10	LS-62	MUD	58.8	2.4281	41.2294	60.64	2.43	ND	2.43
11	LS-7	MUD	54.9	2.2183	25.8431	264.48	165.78	50.32	216.10
12	LS-72	MUD	49.3	1.9715	10.5311	140.64	89.32	18.49	107.81
13	LS-82	MUD	37.3	1.5958	34.1970	76.03	35.09	14.62	49.71
14	LS-92	FINE SAND	21.4	1.2724	78.9539	5.06	4.87	ND	4.87
15	LS-10	MUD	55.5	2.2546	35.7765	19.21	13.98	ND	13.98
16	LS-102	MUD	56.8	2.3134	43.7331	14.57	6.86	ND	6.86
17	LS-11	CLAY	25.7	1.3457	74.2087	41.77	15.39	2.70	18.09
18	LS-112	CLAY	24.9	1.3315	77.4888	14.91	12.58	2.06	14.64

TABLE 52 (contd.)

SN	Station Code	Lithology of Sample	% Moisture	Wet Wt. / Dry Wt.	Dry Wt. of Sample (g)	TOE µg g^{-1}	Aliphatic µg g^{-1}	Aromatic µg g^{-1}	THC µg g^{-1}
19	LS-12	FINE SAND	21.5	1.2732	78.3624	12.76	3.83	ND	3.83
20	LS-132	MUD	46.9	1.8837	19.0543	441.76	278.72	60.99	339.71
21	LS-14	MUD	38.3	1.6209	53.9470	202.05	12.98	3.71	16.69
22	LS-142	FINE SAND	22.4	1.2891	77.4703	12.91	2.08	ND	2.08
23	LS-15	FINE SAND	22.6	1.2926	76.9983	58.44	5.64	ND	5.64
24	LS-16	MUD	53.3	2.1421	32.3929	60.27	34.26	5.79	40.05
25	LS-17	CLAY	24.1	1.3169	75.6944	67.38	36.61	33.36	39.97
26	LS-173	FINE SAND	19.1	1.2354	82.2343	60.80	6.08	3.65	9.73
27	LS-175	FINE SAND	20.2	1.2530	82.5230	36.35	3.02	ND	3.02
28	LS-18	FINE SAND	17.1	1.2063	83.1827	39.04	30.40	4.35	34.75
29	LS-184	FINE SAND	23.1	1.2996	77.6624	47.64	3.86	ND	3.86
30	LS-185	MUD	29.3	1.4138	73.5842	70.38	46.21	6.79	53.00
31	LS-19	MUD	39.2	1.6459	60.3451	75.77	56.34	1.66	58.00
32	LS-191	MUD	68.6	3.1857	31.2446	188.83	104.61	18.07	122.68
33	LS-192	MUD	47.0	1.8885	53.0310	44.51	28.48	5.08	33.56
34	LS-195	MUD	46.1	1.8556	53.9685	42.05	24.09	3.71	27.80
35	LS-20	MUD	58.9	2.4324	34.1364	784.28	668.39	26.86	695.25
36	LS-201	MUD	37.4	1.5986	64.3146	655.49	474.63	34.55	509.18
37	LS-202	MUD	44.3	1.7945	25.8833	4373.46	3466.78	87.73	3554.51

TABLE 52 (contd.)

SN	Station Code	Lithology of Sample	% Moisture	Wet Wt. / Dry Wt.	Dry Wt. of Sample (g)	TOE µg g^{-1}	Aliphatic µg g^{-1}	Aromatic µg g^{-1}	THC µg g^{-1}
38	LS-203	CLAY	26.2	1.3544	73.8283	86.69	35.22	2.35	37.57
39	LS-205	MUD	56.3	2.2862	26.1408	604.42	429.53	21.32	450.85
40	LS-21	MUD	42.9	1.7525	58.0720	50.78	32.72	6.89	39.61
41	LS-22	MUD	48.1	1.3319	71.5276	68.65	25.98	2.35	28.33
42	LS-222	COARSE SAND	15.5	1.1838	80.5031	47.20	22.42	1.06	23.48
43	LS-225	FINE SAND	20.0	1.2467	85.8841	79.18	3.49	1.16	4.65
44	LS-23	MUD	65.7	2.9151	33.7594	188.86	129.62	18.95	148.57
45	LS-232	MUD	65.8	2.9205	20.3078	364.39	258.20	23.85	282.05
46	LS-234	MUD	40.6	1.2823	60.3686	351.23	207.09	15.30	222.39
47	LS-24	CLAY	20.8	1.2619	78.6274	232.75	169.25	12.75	182.00
48	LS-242	CLAY	23.8	1.3116	75.9546	23.70	2.63	1.32	3.95
49	LS-245	CLAY	24.3	1.3205	76.4522	98.10	67.00	9.42	76.42
50	LS-25	MUD	38.6	1.5284	46.6775	52.14	39.56	4.28	43.84
51	LS-252	FINE SAND	22.2	1.2852	78.8033	8,88	5.09	ND	5.09
52	LS-26	MUD	38.0	1.6124	59.7530	55.23	8.37	ND	8.37
53	LS-262	MUD	65.7	2.9196	9.4351	107.49	84.79	10.60	95.39

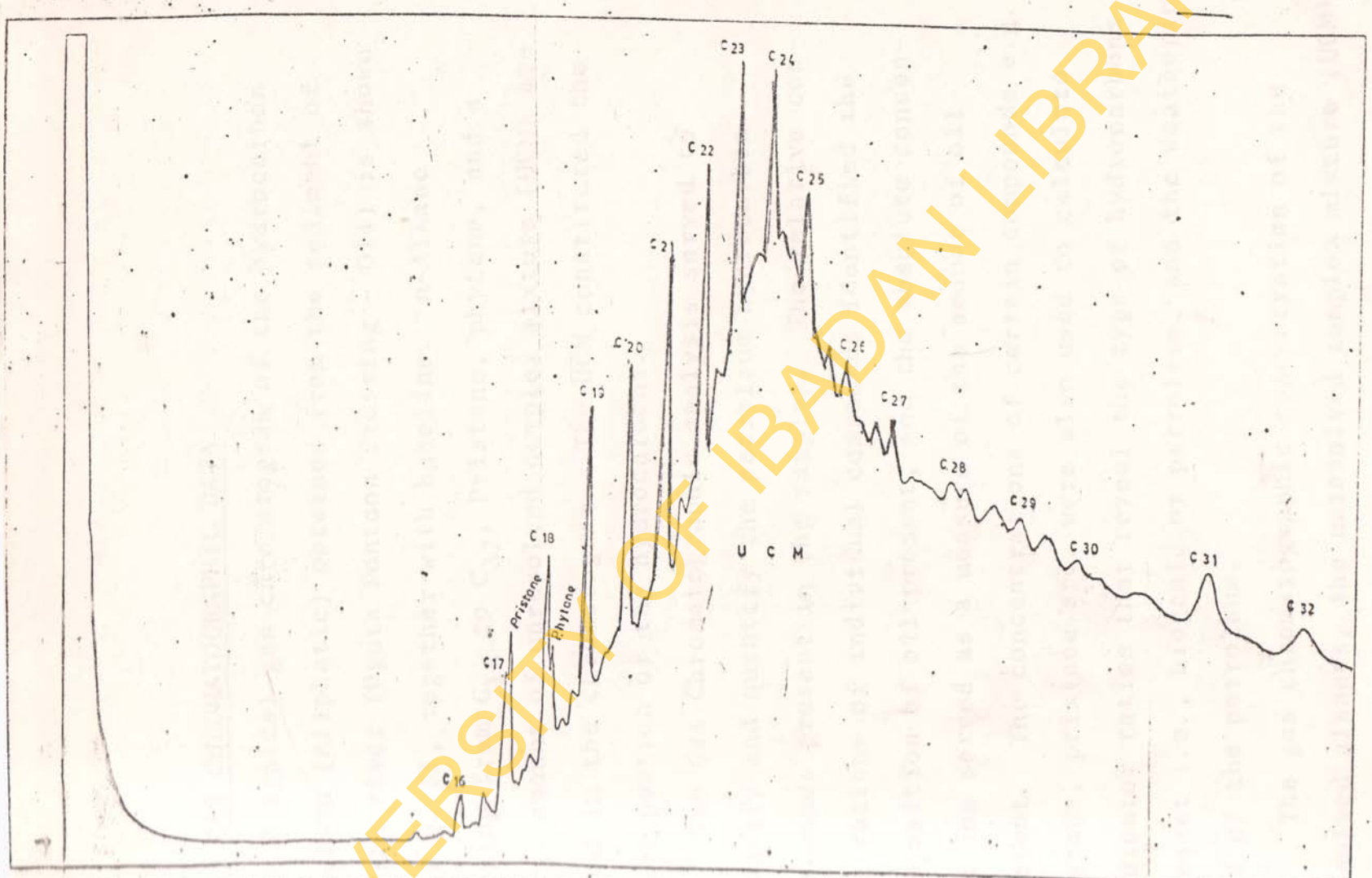


Fig. 35: Gas chromatogram of the hydrocarbon fraction obtained from the sediment sample collected from Oroshi River system (Ogura Pontoon Crossing)

4.7 GAS CHROMATOGRAPHIC DATA

A typical gas chromatogram of the hydrocarbon fraction (Aliphatic) obtained from the sediment of Orashi river (Oguta Pontoon Crossing - O14) is shown in Fig. 35, together with baseline. n-Alkane ranging from C_{16} to C_{32}, Pristane, phytane, and a large amount of unresolved complex mixture (UCM) are found in the chromatogram. The UCM constituted the major portion of the hydrocarbons.

The Gas Chromatographic analysis served to identify and quantify the petroleum hydrocarbon compounds present in the samples. The relative concentrations of individual compounds identified the composition of oil present, and the absolute concentration served as a measure of the amount of oil present. The concentrations of certain compounds e.g. phytane, pristane etc. were also used to calculate indicator ratios that reveal the type of hydrocarbons present i.e., biogenic or petroleum, and the weathering age of the petroleum.

The gas chromatographic concentration of the resolved alkanes, the unresolved complex mixture (UCM)

hydrocarbons, total aliphatic, total aromatic and the total hydrocarbons for all the sediment samples analyzed in 1984 and 1985 are reported in Tables 53 to 68, under the different river systems.

4.7.1 LAGOS AND LEKKI LAGOONS

The results of the 1984 samples are shown in Table 53. The concentrations of resolved alkanes, UCM, total aliphatic, total aromatic and total hydrocarbons for the sediment samples ranged from a non-detectable level (85) (ND) to 10.84μgg^{-1} (845) with an average of 1.88μgg^{-1}, ND - 80.23μgg^{-1} with an average of 25.01μgg^{-1}, ND to 91.07μgg^{-1} with an average of 26.85 μgg^{-1}, ND to 7.16 with an average of 3.48μgg^{-1} and from ND to 95.54 with an average of 30.33μgg^{-1} respectively. The carbon range found in the samples was C_{19} - C_{32}.

The highest concentration of total hydrocarbon was found in sample from Lever Brothers' discharge point (845) - 95.54μgg^{-1}, as earlier indicated by the gravimetric results. The sediment sample from Iwopin did not show any detectable level.

TABLE 53 THE HYDROCARBON CONTENT IN SEDIMENT AROUND LAGOS AND NIGER DELTA AREA OF NIGERIA IN PPM ON DRY WEIGHT BASIS (BY GC)

SN	Station Code	Carbon Range	Aliphatic			Aromatic Total Only	Total Hydrocarbon
			Resolved	UCM	Total Aliphatic		
1.	LAGOS-LEKKI LAGOON						
1	086	C_{19}-C_{32}	0.35	10.22	10.57	2.90	13.47
2	087	C_{20}-C_{33}	0.22	9.19	9.41	1.12	10.53
3	845	C_{16}-C_{33}	10.84	80.23	91.07	4.47	95.54
4	847	C_{19}-C_{26}	0.67	37.65	38.32	7.16	45.48
5	851	C_{20}-C_{32}	0.70	19.34	20.04	3.14	23.18
6	856	-	ND	ND	ND	ND	ND
7	857	C_{19}-C_{30}	0.39	18.15	18.54	5.55	24.09
	$\bar{X}$		1.88	25.01	26.85	3.48	30.33
	SD		±1.55	±11.46	±13.01	±1.02	±13.65
	R.		ND-10.84	ND-80.23	ND-91.07	ND-7.17	ND-95.54
2.	BENIN						
8	057	C_{16}-C_{31}	1.79	ND	1.79	1.21	3.00
9	134	C_{16}-C_{32}	1.11	3.21	4.32	1.57	5.89
10	311	C_{16}-C_{32}	0.16	1.83	1.99	0.68	2.67
11	347	C_{16}-C_{31}	0.06	1.08	1.14	0.91	2.05
12	835	C_{18}-C_{26}	0.04	ND	0.04	ND	0.04
13	837	C_{18}-C_{32}	0.99	3.01	4.00	2.26	6.26

TABLE 53. (contd.)

SN	Station Code	Carbon Range	Aliphatic			Aromatic Total Only	Total Hydrocarbon
			Resolved	UCM	Total Aliphatic		
14	838	$C_{19}-C_{32}$	0.28	7.32	7.51	1.63	9.14
15	0-1	$C_{19}-C_{28}$	0.08	ND	0.08	0.02	0.10
16	0-2	$C_{19}-C_{29}$	.4.32	36.90	41.22	1.63	42.85
	$\bar{X}$		0.98	5.92	6.90	1.10	8.00
	SD		±0.48	±4.10	±14.58	±0.25	±4.76
	R		0.04-4.32	ND-36.90	0.04-41.22	ND-2.26	0.04-42.85
3.	ESCRAVOS						
17	054	$C_{16}-C_{32}$	1.06	57.39	58.45	5.68	64.13
18	055	$C_{16}-C_{28}$	1.76	ND	1.76	0.54	2.30
19	360	$C_{16}-C_{33}$	1.20	2.46	3.66	0.604	4.26
20	362	$C_{16}-C_{31}$	0.56	8.16	8.72	1.76	10.48
21	831	$C_{18}-C_{32}$	0.87	NND	0.87	0.04	0.91
22	839	$C_{19}-C_{31}$	1.06	ND	1.06	0.43	1.49
	$\bar{x}$		1.09	11.34	12.42	1.51	13.93
	SD		±0.20	±9.57	±9.50	±0.94	±10.54
	R		0.56-1.76	ND-57.39	0.87-58.45	0.04-5.68	0.91-64.13

TABLE 53 (contd.)

SN	Station Code	Carbon Range	Aliphatic			Aromatic Total Only	Total Hydrocarbon
			Resolved	UCM	Total Aliphatic		
	4. FORCADOS						
23	040	$C_{16}-C_{31}$	0.08	0.20	0.28	0.03	0.31
24	049	$C_{24}-C_{27}$	0.14	0.97	1.11	0.23	1.34
25	050	$C_{19}-C_{27}$	15.84	ND	15.84	3.68	19.52
26	052	$C_{17}-C_{31}$	0.18	0.45	0.63	0.21	0.84
27	053	$C_{19}-C_{32}$	1.04	26.64	27.68	2.54	30.22
28	351	$C_{19}-C_{31}$	0.13	1.50	1.63	0.25	1.88
29	352	$C_{16}-C_{30}$	6.65	ND	6.65	0.52	7.17
30	353	$C_{20}-C_{31}$	0.15	2.30	2.45	0.15	2.60
31	372	$C_{16}-C_{32}$	1.22	2.95	4.17	0.24	4.41
32	858	$C_{16}-C_{28}$	16.19	53.33	69.52	4.53	74.05
33	860	$C_{20}-C_{31}$	0.26	4.64	4.90	1.77	6.67
34	862	$C_{16}-C_{29}$	0.56	3.76	4.32	0.56	4.88
35	863	$C_{16}-C_{30}$	5.52	ND	5.52	0.42	5.94
36	864	$C_{19}-C_{31}$	0.31	3.75	4.06	0.35	4.41
37	865	$C_{16}-C_{32}$	3.68	28.76	32.44	1.30	33.74
38	866	$C_{20}-C_{30}$	0.06	2.00	2.06	0.46	2.52

TABLE 53 (contd.)

SN	Station Code	Carbon Range	Aliphatic			Aromatic Total Only	Total Hydrocarbon
			Resolved	UCM	Total Aliphatic		
	$\bar{X}$		3.25	8.20	11.45	1.08	12.53
	SD		±1.01	±3.33	±4.33	±0.23	±4.61
	R		0.06-16.19	ND-53.33	0.28-69.52	0.03-3.68	0.31-74.05
5.	RAMOS						
39	038	$C_{16}-C_{27}$	8.06	27.04	35.10	2.22	37.32
40	382	$C_{16}-C_{32}$	5.81	ND	5.81	0.83	6.64
41	869	$C_{18}-C_{33}$	0.19	6.80	6.99	0.63	7.62
42	870	$C_{16}-C_{28}$	5.98	60.93	66.91	4.73	71.64
43	871	$C_{23}-C_{28}$	0.07	ND	0.07	0.05	0.12
	$\bar{X}$		4.02	18.95	22.98	1.69	24.67
	SD		±1.60	±12.19	±13.34	±0.94	±14.30
	R		0.07-8.06	ND-60.93	0.07-66.91	0.05-4.73	0.12-71.64
6.	NUN - EKOLE - BRASS						
44	036	$C_{19}-C_{31}$	ND	ND	ND	ND	ND
45	043	$C_{16}-C_{31}$	0.21	13.61	13.82	1.74	15.56
46	281	$C_{20}-C_{31}$	0.26	ND	0.26	0.06	0.32
47	871	$C_{20}-C_{31}$	0.12	3.79	3.91	0.63	4.54
48	873	$C_{22}-C_{32}$	0.16	3.24	3.40	0.31	3.71

TABLE 53 (contd.)

SN	Station Code	Carbon Range	Aliphatic			Aromatic Total Only	Total Hydrocarbon
			Resolved	UCM	Total Aliphatic		
	$\bar{x}$		0.15	4.13	4.28	0.55	4.83
	sd		±0.05	±2.72	±2.76	±0.35	±3.11
	R		ND-0.26	ND-13.61	ND-13.82	ND-1.74	ND-15.56
	7. ORASHI						
49	012	$C_{16}-C_{31}$	0.17	ND	0.17	ND	0.17
50	0.3	$C_{16}-C_{31}$	0.20	1.05	1.25	0.62	1.87
51	014	$C_{16}-C_{31}$	1.23	2.85	4.08	2.10	6.18
52	016	$C_{16}-C_{32}$	0.47	3.41	3.88	1.21	5.09
53	021	$C_{19}-C_{32}$	0.20	4.83	5.03	1.15	6.18
54	035	$C_{16}-C_{31}$	0.58	ND	0.58	0.05	0.63
55	250	C16-C30	0.13	ND	0.14	ND	0.13
56	251	$C_{16}-C_{31}$	0.08	1.56	1.64	0.03	1.67
57	252	$C_{17}-C_{32}$	1.95	ND	1.95	ND	1.95
58	262	$C_{16}-C_{32}$	0.32	0.63	0.95	0.31	1.26
60	802	$C_{16}-C_{32}$	0.25	1.90	2.15	0.63	2.78
61	821	$C_{18}-C_{31}$	0.16	ND	0.02	ND	0.23
62	824	$C_{18}-C_{31}$	0.02	ND	0.02	ND	0.02

TABLE 53 (contd.)

SN	Station Code	Carbon Range	Aliphatic			Aromatic Total Only	Total Hydrocarbon
			Resolved	UCM	Total Aliphatic		
	$\bar{X}$		0.50	1.16	1.66	0.48	2.14
	SD		±0.13	±0.35	±0.36	±0.44	±0.44
	R		0.02-1.95	ND-4.83	0.02-5.03	ND-2.10	0.02-6.18
8.	BONNY - NEW CALABAR						
63	020	$C_{16}-C_{32}$	0.87	0.34	1.21	0.04	1.25
64	121	$C_{17}-C_{32}$	0.24	ND	0.24	0.02	0.26
65	233	$C_{16}-C_{32}$	0.55	6.76	7.31	1.20	8.51
66	807	$C_{16}-C_{31}$	3.69	13.55	17.24	4.20	21.44
67	808	$C_{16}-C_{31}$	0.59	1.41	2.00	0.15	2.91
68	810	$C_{18}-C_{32}$	0.88	ND	0.88	0.03	0.91
	$\bar{X}$		1.14	3.68	4.81	0.94	5.75
S	SD		±0.58	±2.26	±2.83	±0.70	±3.53
	R		0.24-3.69	ND-13.55	0.24-17.24	0.02-4.20	0.26-21.44
9.	IMO						
69	128	$C_{16}-C_{33}$	0.20	8.55	8.75	1.41	10.16
70	813	$C_{18}-C_{31}$	0.29	1.06	1.35	0.43	1.78
71	817	$C_{16}-C_{31}$	0.25	ND	0.25	0.05	0.30

TABLE 53 (contd.)

SN	Station Code	Carbon Range	Aliphatic			Aromatic Total Only	Total Hydrocarbon
			Resolved	UCM	Total Aliphatic		
	$\bar{x}$		0.25	3.20	3.45	0.63	4.06
	Sb		±1.03	±2.85	±2.83	±0.45	±3.29
	R		0.20-0.29	ND-8.55	0.25-8.75	0.05-1.41	0.30-10.16
10.	CROSS RIVER - CALABAR						
72	071	C_{16}-C_{29}	0.57	2.10	2.67	0.03	2.70
73	811	C_{16}-C_{31}	0.22	ND	0.22	0.04	0.26
74	812	C_{16}-C_{31}	0.46	ND	0.46	0.06	4.41
75	827	C_{16}-C_{33}	0.44	3.35	3.79	0.62	4.41
	$\bar{x}$		0.42	1.36	1.79	0.19	1.97
	Sb		±0.09	±0.84	±0.89	±0.15	±1.04
	R		0.22-0.57	ND-3.35	0.22-3.79	0.03-0.62	0.26-4.41
11.	KADUNA						
76	141 A	C_{16}-C_{32}	0.25	20.25	20.50	1.02	21.52
77	141 B	C_{16}-C_{32}	0.84	16.26	17.10	0.92	18.02
78	843	C_{16}-C_{32}	0.15	0.43	0.58	0.04	0.62
79	844	C_{16}-C_{32}	0.64	8.56	9.20	0.07	9.27
	$\bar{x}$		0.47	11.38	11.78	0.51	12.36
	Sb		±0.17	±4.96	±4.92	±0.25	±5.23
	R		0.15-0.84	0.43-20.25	0.58-20.50	0.04-1.02	0.62-21.52

4.7.2 NIGER DELTA

In the delta area the results showed wide variation in between samples from the same river system and also from one river system to the other. The highest concentration of total hydrocarbons were found in the following river systems: Forcardos - Warri 0.31-74.05 (12.53), Escravos - 0.91-64.15 (15.93) and Ramos - 0.12-71.64 (24.67) μgg^{-1}. The other river systems have mean values of total hydrocarbon below 10 μgg^{-1}. Benin - 0.4-42.85 (8.00), Nun - Ekole-Brass: ND - 15.56 (4.83), Orashi: 0.02-6.18 (2.14), Bonny - New Calabar: 0.26-21.44 (5.75), Imo: 0.30-10.16 (4.08) and Cross River - Calabar: 0.26-4.41 (1.97) μgg^{-1}.

The carbon range for the river systems are mainly C_{16} - C_{32} and C_{19} - C_{32}.

Only few points were selected for sampling in 1985 (dry season - Jan.-Feb.). The results of the total hydrocarbons reported for the 1985 samples, in respect of the Lagos and Lekki Lagoons and the Niger Delta river systems are shown in Table 54.

TABLE 54 THE HYDROCARBON CONTENT IN SEDIMENT AROUND LAGOS AND NIGER DELTA AREAS OF NIGERIA IN PPM ON DRY WEIGHT BASIS (FEBRUARY 1985) (BY GC)

SN	Station Code	Aliphatic	Aromatic	Total Hydrocarbons
1	LAGOS - LEKKI LAGOONS			
1	845	1.50	0.61	2.11
2	851	0.20	ND	0.20
3	857	9.00	1.30	10.30
	$\bar{X}$	3.57	0.64	4.20
	SD	±2.93	±0.43	±3.37
	RANGE	0.20-9.00	ND-1.30	0.20-10.30
2	BENIN			
4	311	1.00	0.02	1.02
3	ESCRAVOS			
5	054	41.00	3.06	44.06
6	055	6.70	1.10	7.80
7	830	1.40	0.08	1.48
8	833	1.40	0.05	1.45
9	834	0.20	ND	0.20
	$\bar{X}$	10.14	0.86	11.00
	SD	±8.16	±0.61	±8.77
	R	0.20-41.00	0.05-3.06	0.20-44.06
4	FORCADOS			
10	040	0.50	0.02	0.52
11	049	12.00	2.46	14.46
12	050	13.00	3.48	16.48
13	052	30.00	2.97	32.97

TABLE 54 (contd.)

SN	Station Code	Aliphatic	Aromatic	Total Hydrocarbons
14	053	0.30	0.06	0.36
15	351	0.10	ND	0.10
16	353	1.30	0.09	1.39
17	860	5.80	1.05	6.85
18	862	1.80	0.14	1.94
19	866	0.20	0.16	0.36
	$\bar{X}$	6.50	1.04	7.54
	SD	±2.99	±0.35	±3.29
	R	0.10-30.00	ND-3.48	0.10-32.97
	5 ORASHI			
20	021	1.50	0.08	1.58
21	250	0.10	0.02	0.12
22	252	23.00	2.10	25.10
23	801	0.60	0.43	1.03
24	819	1.30	0.32	1.62
25	820	0.30	0.06	0.36
26	821	0.60	0.17	0.77
	$\bar{X}$	3.91	0.45	4.37
	SD	±3.81	±0.35	±4.16
	R	0.10-23.00	0.02-2.10	0.12-25.10
	6 BONNY - NEW CALABAR			
27	018	7.40	1.02	8.42
28	020	10.00	2.52	12.52

TABLE 54 (contd.)

SN	Station Code	Aliphatic	Aromatic	Total Hydrocarbons	
29	121	2.00	0.81	2.81	
30	807	1.60	0.17	1.77	
31	808	0.20	0.04	0.24	
	$\bar{X}$	4.24	0.91	5.15	
	SD	±1.96	±0.50	±2.46	
	R	0.20-10.00	0.04-2.52	0.24-12.52	
7	CROSS RIVER - CALABAR				
32	079	9.20	2.14	11.34	
33	210	0.05	ND	0.05	
	$\bar{X}$	4.63	1.07	5.70	
	SD	±4.58	±1.07	±5.65	
	R	0.05-9.20	ND-2.14	0.05-11.34	
8	KADUNA				
34	141A	2.30	0.61	2.91	
35	141B	4.00	1.00	5.00	
	$\bar{X}$	3.15	0.81	3.96	
	SD	±0.85	±0.20	±1.05	
	R	2.30-4.00	0.61-1.00	2.91-5.00	
	IBADAN				
36	Ag-1	27.794	ND	27.794	$C_{15}-C_{33}$
37	As-2	6.849	1.241	8.090	$C_{16}-C_{35}$
	$\bar{X}$	17.32	0.62	17.94	
	SD	±14.81	±0.88	±13.93	
	R	6.85-27.79	ND-±.241	8.09-27.79	

According to the results, Lagos and Lekki Lagoons recorded between 0.20 and 10.30 μgg^{-1} dry weight for total hydrocarbons. All the other river systems in the Niger Delta area recorded between 0.05 and 44.06 μgg^{-1} total hydrocarbons. The highest was recorded at Escravos Terminal (054) - 44.06 μgg^{-1}, and the lowest concentration of total hydrocarbons was recorded at a point on Forcados river below the mouth of Oyeye creek (351) - 0.10 μgg^{-1}. For comparison, Kaduna samples gave 0.62-21.52 (12.36) μgg^{-1} total hydrocarbon. Agodi and Asejire recorded 27.79 and 8.84 μgg^{-1} THC respectively.

4.7.3 UTOROGU SWAMP AND OKPARI RIVER

The results of the 1984 samples for the hydrocarbons during the rainy season (Oct.-Nov. 1984) are shown in Table 55. The resolved alkanes - 0.74-46.26 (11.02) μgg^{-1}, UCM: 7.38-222.90 (79.30) μgg^{-1}, total aliphatic: 10.42-241.28 (91.76) μgg^{-1}, total aromatic: ND - 40.01 (9.90) μgg^{-1} and total hydrocarbons: 14.04-267.48 (101.66) μgg^{-1} dry weight of sediment.

TABLE 55: THE HYDROCARBON CONTENT IN SEDIMENT AT UTOROGU SWAMP AND OKPARI RIVER IN BENDEL STATE OF NIGERIA (PPM DRY WEIGHT BASIS) (BY GC)
(OCTOBER - NOVEMBER 1984)

SN	Station Code	Carbon Range	Aliphatic			Aromatic Total Only	Total Hydrocarbon
			Resolved	UCM	Total Aliphatic		
IMPACTED SWAMP							
1	B	$C_{22}-C_{28}$	28.78	85.27	114.05	40.01	154.06
2	D	$C_{20}-C_{29}$	2.27	103.63	105.90	20.90	126.80
3	E	$C_{-}-C_{32}$	3.18	23.19	26.37	5.50	31.97
4	G-1	$C_{20}-C_{31}$	4.81	37.38	42.62	3.55	46.17
5	G-2	$C_{18}-C_{32}$	4.81	35.53	40.4	2.37	42.71
6	G-3	$C_{20}-C_{28}$	12.55	39.32	51.87	3.72	55.59
7	G-4	$C_{20}-C_{28}$	21.53	102.56	124.09	9.96	134.05
	$\bar{X}$		11.19	60.98	72.18	12.30	84.48
	R		2.27-28.78	23.19-103.63	26.37-124.09	2.37-40.01	31.97-154.06
UPSTEAM							
8	R-1	$C_{18}-C_{32}$	3.27	86.42	94.73	3.11	97.84
9	R-2	$C_{19}-C_{32}$	3.27	148.46	151.73	ND	151.73
10	R-3	$C_{20}-C_{30}$	2.11	91.01	93.12	4.17	97.29
	$\bar{X}$		4.56	108.63	113.19	2.43	115.62
	R		2.11-8.31	86.42-148.46	93.12-151.73	ND-4.17	97.29-151.73
DOWNSTREAM							
11	O-1	$C_{17}-C_{31}$	18.38	222.90	241.28	26.20	267.48

TABLE 55 (contd.)

SN	Station Code	Carbon Range	Aliphatic			Aromatic Total Only	Total Hydrocarbon
			Resolved	UCM	Total Aliphatic		
12	O-2	C_{17}-C_{32}	26.14	150.66	202.93	13.90	216.83
13	N	C_{20}-C_{23}	0.74	44.00	44.74	7.50	52.24
14	V	C_{21}-C_{32}	3.89	11.06	14.95	4.60	19.55
15	K-3	C_{20}-C_{38}	3.04	7.38	10.42	3.62	14.04
16	K-3	C_{20}-C_{38}	46.26	99.76	146.02	25.70	171.72
17	T	C_{20}-C_{32}	6.54	83.38	89.92	2.10	92.02
18	U	C_{18}-C_{32}	1.23	55.45	56.68	1.15	57.83
	$\bar{X}$		13.28	84.32	100.87	10.60	111.46
	R		0.74-46.26	7.38-222.90	10.42-241.28	1.15-26.20	14.04-267.48

These levels came down drastically during the January-February period (dry season) in 1985 as the results in Table 56 revealed, resolved alkanes: ND - 1.014 (0.17) μgg^{-1}, UCM: ND - 7.336 (1.94) μgg^{-1}, total aliphatic: ND - 7.961 (2.106) μgg^{-1}, total aromatic: ND - 2.01 (0.387) μgg^{-1} and total hydrocarbons: ND - 9.414 (2.49) μgg^{-1}.

The levels of hydrocarbons recorded during the 1985 (wet season), for the Utorogu swamp and Okpari are reported in Table 57. The values were higher than those reported for the early (dry season) 1985 samples. The resolved alkanes range from 0.02 to 15.07 μgg^{-1} with an average of 2.76μgg^{-1}, other levels are UCM: ND - 62.77 (17.05) μgg^{-1}, aromatic: ND - 4.11 (0.814) μgg^{-1} and total hydrocarbons: 0.03-68.06 (20.62) μgg^{-1}.

For comparison, the Lagos Lagoon samples collected between January and December 1985 gave the results reported in Table 58. Resolved alkanes: ND - 179.23 (10.67), UCM: ND - 2524.15 (95.40), total aliphatic: ND - 2703.38 (104.11), total aromatic: ND - 62.89

TABLE 56: THE HYDROCARBON CONTENT IN SEDIMENT AT UTOROGU SWAMP AND OKPARI RIVER IN DENDEL STATE OF NIGERIA (PPM DRY WEIGHT BASIS) (BY GC)
(JANUARY – FEBRUARY 1985)

SN	Station Code	Carbon Range	Aliphatic			Aromatic Total Only	Total Hydrocarbon
			Resolved	UCM	Total Aliphatic		
IMPACTED SWAMP							
1	B1	$C_{20}-C_{26}$	0.07	7.34	7.40	2.01	9.41
2	B2	$C_{21}-C_{33}$	Q.08	2.14	2.22	1.62	3.84
3	C	C -C	0.04	1.17	1.21	ND	1.21
4	D	$C_{20}-C_{32}$	0.05	0.47	0.52	0.29	0.81
5	E1	$C_{20}-C_{33}$	0.33	2.37	2.70	0.40	3.10
6	E1	$C_{19}-C_{33}$	0.27	5.74	6.01	0.36	6.37
7	F		ND	ND	ND	ND	ND
	$\bar{X}$		0.12	2.75	2.87	0.67	3.58
	R		ND-0.33	ND-7.34	ND-7.40	ND-2.01	ND-9,41
UPSTREAM							
8	R-1		ND	ND	ND	ND	ND
9	R-2	$C_{22}-C_{28}$	0.26	0.56	0.83	0.11	0.94
	$\bar{X}$		0.13	0.28	0:42	0.06	0.47
	R		ND-0.26	ND-0.56	ND-0.83	ND-0.11	ND-0.94
DOWNSTREAM							
10	0-1	$C_{20}-C_{32}$	0.81	0.24	0.26	0.17	0.43
11	0-2	$C_{20}-C_{33}$	0.30	0.70	1.01	051	1.52
12	0-3	$C_{23}-C_{32}$	0.30	0.70	1.01	0.51	1.52
1	N	$C_{22}-C_{33}$	0.03	0.69	0.73	0.27	1.00
14	K-2	$C_{19}-C_{32}$	0.03	0.58	0.61	0.06	0.67
15	T	$C_{20}-C_{27}$	1.01	6.95	7.96	ND	7.96
	$\bar{X}$		0.23	1.55	1.79	0.20	1.95

TABLE 57: THE HYDROCARBON CONTENT IN SEDIMENT AT UTOROGU SWAMP AND OKPARI RIVER IN BENDEL STATE OF NIGERIA (PPM DRY WEIGHT BASIS) (BY GC) (JUNE - JULY 1985)

SN	Station Code	Carbon Range	Aliphatic			Aromatic Total Only	Total Hydrocarbon
			Resolved	UCM	Total Aliphatic		
IMPACTED SWAMP							
1	A-1	C_{19}-C_{32}	0.13	2.09	2.22	ND	2.22
2	B	C_{19}-C_{32}	1.19	62.77	63.95	4.11	68.06
3	C-2	C_{24}-C_{29}	0.12	2.83	2.95	0.58	3.53
4	C-3	C_{22}-C_{30}	0.28	2.88	3.15	0.54	3.69
5	D	C_{20}-C_{29}	4.07	15.02	19.08	4.68	23.76
6	F	C_{20}-C_{27}	3.88	14.47	18.35	1.91	20.26
7	G-1	C_{20}-C_{33}	1.18	14.17	15.35	0.13	15.48
	$\bar{X}$		1.55	16.32	17.86	1.11	19.57
	R		0.12-4.07	2.09-62.77	2.22-63.95	ND-4.68	2.22-68.06
	UPSTREAM						
8	R-1	C_{17}-C_{29}	0.02	ND	0.02	0.01	0.03
9	R-2	C_{19}-C_{31}	3.36	21.38	24.74	2.02	26.76
10	R-3	C_{19}-C_{27}	0.56	3.12	3.67	0.20	3.87
11	P	C_{19}-C_{28}	0.06	1.93	1.99	0.42	2.41
	$\bar{X}$		1.00	6.61	7.61	0.66	8.27
	R		0.02-3.36	ND-21.38	0.02-24.74	0.01-2.02	0.03-26.76

TABLE 57 (contd.)

SN	Station Code	Carbon Range	Aliphatic			Aromatic Total Only	Total Hydrocarbon
			Resolved	UCM	Total Aliphatic		
	DOWNSTREAM						
12	O-1	C_{22}-C_{32}	0.96	13.49	14.45	0.57	15.02
13	O-2	C_{19}-C_{28}	5.11	11.00	22.11	0.67	22.78
14	O-3	C_{19}-C_{33}	1.84	20.58	22.42	ND	22.42
15	N	C_{19}-C_{32}	0.84	21.80	22.64	ND	22.64
16	V	C_{19}-C_{29}	8.86	37.04	45.90	ND	45.90
17	M	C_{19}-C_{33}	3.48	11.21	14.68	ND	14.68
18	K-2	C_{20}-C_{32}	1.17	7.76	8.93	ND	8.93
19	J	C_{19}-C_{31}	4.82	47.75	52.58	0.39	52.96
20	U	C_{19}-C_{32}	3.36	23.33	26.69	ND	26.69
21	J-1	C_{19}-C_{32}	0.45	5.99	6.44	1.78	8.22
22	J-2	C_{19}-C_{32}	2.63	12.57	15.19	0.07	15.26
23	J-3	C_{19}-C_{32}	15.07	33.01	48.08	0.66	48.74
	$\bar{X}$		4.05	20.96	25.01	0.35	25.35
	RANGE		0.45-15.07	5.99-47.75	6.44-52.58	ND-1.78	8.22-52.96

TABLE 58: THE HYDROCARBON CONTENT IN SEDIMENTS AROUND LAGOS LAGOON (PPM DRY WEIGHT BASIS) (JANUARY - DECEMBER 1985) (BY GC)

SN	Station Code	Carbon Range	Aliphatic			Aromatic Total Only	Total Hydrocarbon
			Resolved	UCM	Total Aliphatic		
1	LS-1	$C_{17}-C_{27}$	1.93	21.88	23.81	4.34	28.15
2	LS-2	$C_{20}-C_{30}$	0.57	11.21	11.79	1.67	13.46
3	LS-3	$C_{22}-C_{27}$	0.31	ND	0.31	ND	0.31
4	LS-32	$C_{18}-C_{34}$	4.67	33.58	38.25	5.62	43.87
5	LS-4	$C_{16}-C_{29}$	1.15	ND	1.15	ND	1.15
6	LS-42	$C_{20}-C_{30}$	2.22	ND	2.22	ND	2.22
7	LS-5	$C_{17}-C_{30}$	1.32	15.83	17.16	3.11	20.271
8	LS-52	$C_{18}-C_{31}$	0.17	ND	0.17	ND	0.17
9	LS-6	$C_{19}-C_{29}$	1.54	15.07	16.61	2.04	18.65
10	LS-62	-	ND	ND	ND	ND	ND
11	LS-7	$C_{16}-C_{25}$	7.30	124.60	131.90	33.50	165.40
12	LS-72	$C_{20}-C_{24}$	25.12	ND	25.12	15.70	40.82
13	LS-82	$C_{18}-C_{29}$	1.63	ND	1.63	ND	1.63
14	LS-92	$C_{21}-C_{30}$	4.66	ND	4.66	ND	4.66
15	LS-10	$C_{20}-C_{25}$	5.19	ND	5.19	ND	5.19
16	LS-102	$C_{20}-C_{29}$	0.41	ND	0.41	ND	0.41
17	LS-11	$C_{17}-C_{32}$	1.20	11.30	12.50	2.40	14.90
18	LS-112	$C_{19}-C_{32}$	1.26	7.15	8.41	0.52	8.93
19	LS-12	$C_{20}-C_{30}$	0.48	ND	0.48	ND	0.48

TABLE 58 (contd.)

SN	Station Code	Carbon Range	Aliphatic			Aromatic Total Only	Total Hydrocarbon
			Resolved	UCM	Total Aliphatic		
20	LS-132	$C_{18}-C_{29}$	43.60	163.96	207.56	31.25	238.81
21	LS-14	$C_{25}CC_{32}$	1.48	ND	1.48	ND	1.48
22	LS-142	$C_{25}-C_{29}$	0.19	ND	0.19	ND	0.19
23	LS-15	$C_{18}-C_{31}$	3.88	ND	3.88	ND	3.88
24	LS-16	$C_{20}-C_{29}$	7.60	20.50	28.10	3.42	28.10
25	LS-17	$C_{18}-C_{25}$	0.79	28.42	29.22	1.05	30.26
26	LS-173	$C_{20}-C_{32}$	0.62	nd	0.62	ND	0.62
27	LS-175	$C_{20}-C_{31}$	0.25	ND		ND	00.25
28	LS-18	$C_{20}-C_{31}$	2.05	22.79	24.83	2.62	27.46
29	LS-184	C -C	ND	ND	ND	ND	ND
30	LS-185	$C_{19}-C_{26}$	8.30	ND	3.30	0.84	9.14
31	LS-191	$C_{23}-C_{29}$	18.56	ND	18.56	ND	18.56
32	LS-192	$C_{16}-C_{25}$	5.83	89.40	95.23	14.10	109.33
33	LS-192	$C_{18}-C_{26}$	0.72	22.73	23.45	3.91	27.36
34	LS-195	$C_{19}-C_{29}$	4.12	ND	4.12	ND	4.12
35	LS-20	$C_{16}-C_{27}$	29.87	488.72	518.59	20.70	539.29
36	LS-201	$C_{18}-C_{25}$	9.34	387.36	396.70	31.18	427.88
37	LS-202	$C_{14}-C_{25}$	179.23	2524.15	2703.88	62.89	2766.27

TABLE 58 (contd.)

SN	Station Code	Carbon Range	Aliphatic			Aromatic Total Only	Total Hydrocarbon
			Resolved	UCM	Total Aliphatic		
3838	LS-203	$C_{14}-C_{24}$	179.23	11.97	12.77	1.87	14.64
39	LS-205	$C_{14}-C_{34}$	11.88	381.53	393.40	16.42	409.82
40	LS-21	$C_{17}-C_{25}$	4.34	23.92	28.26	2.35	30.61
41	LS-22	$C_{17}-C_{31}$	1.57	20.76	22.34	1.79	24.13
42	LS-222	$C_{17}-C_{27}$	1.91	17.30	19.22	0.80	20.02
43	LS-225	$C_{28}-C_{31}$	0.47	ND	0.47	ND	0.47
44	LS-33	$C_{17}-C_{26}$	10.56	101.74	112.31	14.02	126.32
45	LS-232	$C_{17}-C_{34}$	41.11	174.01	215.12	18.67	233.79
46	LS-234	$C_{22}-C_{29}$	6.85	152.45	159.30	12.75	172.05
47	LS-24	$C_{17}-C_{32}$	17.49	120.39	137.88	10.20	148.09
48	LS-242	$C_{19}-C_{24}$	0.71	ND	0.71	ND	0.71
49	LS-245	$C_{17}-C_{32}$	5.52	44.47	49.99	5.42	55.41
50	LS-251	$C_{18}-C_{32}$	20.17	19.00	39.17	3.61	42.78
51	LS-252	$C_{22}-C_{28}$	1.34	ND	1.34	ND	134
52	LS-26	$C_{22}-C_{31}$	3.51	ND	3.51	ND	3.51
53	LS-262	$C_{20}-C_{29}$	59.75	ND	59.75	ND	59.75
		$\bar{X}$	10.67	95.40	104.107	6.088	110.131
		SD	±3.38	±47.63	±51.01	±1.19	±51.19
		R	ND-179.226	ND-2524.15	ND-2703.380	ND-62.885	ND-2766.265

(6.09) and total hydrocarbons: ND - 2766.27 (110.13) $\mu g g^{-1}$ dry weight of sediment.

4.8 DISCUSSION

Aquatic sediments are regarded as the main final accummulation site of water-borne constituents derived from natural and artificial sources. They are also possible sources of chemical constituents in waters. Several authors have demonstrated that in an aquatic system the underlying sediments can act as an indicator of processes in the water column[160,173,254]. Conover[255] has also concluded that zooplankton were responsible for the removal of oil droplets from the water column by ingestion and subsequent sedimentation in association with faecal material. The concentration of particulate organic matter has also been implicated as a vehicle for the transport of hydrocarbons from the water column to the sediment[256,257].

Two main factors interact to govern the fate of hydrocarbons in sediment: firstly, the penetration of oil which is decided by the permeability of sediment; secondly, the power of sediment to retain hydrocarbons, which is often known as Primary Oil Retention. These two parameters are directly controlled by the granulometry of the sediment, in particular by the mean grain size and stability [76]. In region of stable, fine grain sediment with a steady (or predictable) sedimentation (as in many mud-flats and sheltered subtidal sediments) the hydrocarbon levels may give rise not only to a reliable indication of recent contamination but a depth profile may give a good recent geochronological record of hydrocarbon input. HO, and Karim [253] had reported that very fine clay particles bind hydrocarbons so that they are held more firmly than hydrocarbons coating sand (quartz) particles. This binding ability was given as being 0.3-1.4 gm oil bound per gm of clay as against 0.03gm for quartz.

Other factors exist which affect the fate of hydrocarbons - Temperature has a considerable role to

play, and the amounts of water and organic material present in sediments exert an important effect.

The summary of the total organic extract and total hydrocarbon concentrations determined by gravimetric method and the total hydrocarbons determined by Gas Chromatographic method are given in Tables 59, 60 and 61 for all the samples analyzed in 1984 and 1985 respectively.

4.8.1 LAGOS AND LEKKI LAGOONS

The results of the 1984 samples show that sediment samples in this water system were contaminated to varying degrees. Lever Brothers' discharge point (845) on Lagos harbour recorded the highest level of total organic extract - 1153.21μgg^{-1} as well as total hydrocarbons - 560.21μgg^{-1} and 95.54μgg^{-1} gravimetry and GC respectively. The point had 58.9% moisture content, with fine mud particles. The level of its UCM was high with 80.23μgg^{-1} and representing. UCM has been used as one of the indicators of petroleum hydrocarbons.

Okobaba Sawmill (847) also on Lagos harbour recorded 202.64μgg^{-1} (TOE), with total hydrocarbons -

158.74 (Grav.) and 45.48 (GC). The moisture content and UCM were 66.1% and 37.65μgg^{-1} respectively. The sediment also had fine mud particles.

All the other points (except Iwopin 856) also recorded reasonably high levels of UCM, indicating that these points also must have been contaminated by petroleum hydrocarbons. Apart from Ibese (851), Iwopin (856) and Epe (857), all the other points are within an area heavily stressed because of input of industrial effluents and on the traffic routes of ship and boats. Epe (857) is also noted for fishing by boats which include engine boats, thus the level of hydrocarbon recorded at Epe with the presence of UCM - 18.15 μgg^{-1}.

The results of 1985 samples 0.20-10.30 (4.20) μgg^{-1} (range and mean respectively) compared with 1984 samples ND - 95.54 (30.33) μgg^{-1} (Table 53) did not indicate any serious contamination. They may be regarded as the background levels.

4.8.2 BENIN RIVER SYSTEM

The levels of total organic extracts recorded for the points under this river system (60.91-317.08

(161.65)μgg^{-1} did not indicate a highly contaminated river system. This was further supported by the low levels of total hydrocarbons with only Ogharife field effluent canal showing a highly contaminated (Table 53) sediment 42.85μgg^{-1}. The level of the UCM - 36.90 μgg^{-1} clearly indicated that the canal is contaminated by petroleum hydrocarbon.

All the other points can be said to have recorded the background levels of petroleum hydrocarbon. Points like Robin creek (057), Olaji creek (835); and Ogharife field discharge pond (o-1) did not show any sign of long term petroleum hydrocarbon contamination because they all contain n-alkanes without UCM (Table 53). Absence of UCM indicates presence of biogenic HC in the sediment.

4.8.3 ESCRAVOS RIVER SYSTEM

Escravos terminal was the only point in 1984 where appreciable levels of total organic extract - 429.01μgg^{-1}, total hydrocarbon - 178.08 (Grav.) and 64.13 (GC) μgg^{-1} were recorded. The point recorded 53.2% moisture and 57.39μgg^{-1} UCM, with mud as

sediment. Escravos terminal also recorded 294.93 μgg^{-1} (TOE), 285.72 and 44.06μgg^{-1} total hydrocarbon by Gravimetry and GC respectively in 1985.

Nana creek (362) recorded 59.4% moisture, 141.87 μgg^{-1} (TOE), 79.85μgg^{-1} (Grav.) and 10.48μgg^{-1} (GC), with UCM accounting for 8.16μgg^{-1}. Other points sampled did not show any serious contamination in the 1984 and 1985 samples as judged by the level of hydrocarbons and absence of UCM.

4.8.4 FORCADOS - WARRI RIVER SYSTEM

Some points recorded levels of TOE and hydrocarbons which indicated that they were contaminated. Such points are Warri river at South East of Odidi field (050): 383.48μgg^{-1} (TOE), 377.00μgg^{-1} (Grav.) and 19.52μgg^{-1} (GC) for 1984 sample and 114.52μgg^{-1} (TOE), 40.10μgg^{-1} (Grav.) and 16.48μgg^{-1} (GC) total hydrocarbon for 1985 sample, Warri river field (053): 236.37μgg^{-1} (TOE), 222.19μgg^{-1} (Grav.) and 30.20μgg^{-1} (GC) in 1984; Chanomi creek at confluence of unnamed creek draining Egwe field (858): 481.48μgg^{-1} (TOE), 351.59μgg^{-1} (Grav.) and 74.05 μgg^{-1} (GC). Forcados river above Obotobe (865): 415.71

μgg^{-1} (TOE), 384.71μgg^{-1} and 33.74μgg^{-1} total hydrocarbon by Gravimetry and GC respectively.

Apart from Odidi field (050), only Agbarho (052) recorded values that may be regarded as being above the background level. The values were 53.57μgg^{-1} (TOE), 52.73μgg^{-1} (Grav.) and 32.97μgg^{-1} (GC) total petroleum hydrocarbon respectively.

All the other points (except an unnamed creek draining Odidi field (352), and Warri river above Keremo (863) recorded low levels of petroleum hydrocarbon but they all showed the presence of UCM, which may be taken as an indication of petroleum hydrocarbon contamination.

4.8.5 RAMOS RIVER SYSTEM

This river system was only sampled in 1984. The results indicated that Orughene creek (870) with 58.6% moisture, 641.25μgg^{-1} (TOE), 564.05μgg^{-1} (Grav.) and 71.64μgg^{-1} (GC) total hydrocarbon had the highest level of contamination. The sediment was a fine mud. Ramos estuary north of Aghoro (038) came in next with 52.7%

moisture, 446.33μgg^{-1} (TOE), 334.27μgg^{-1} (Grav.) and 37.32μgg^{-1} (GC) total hydrocarbon. It has clay particles.

All the other three points sampled did not give any level to indicate serious contamination.

4.8.6 NUN - EKOLE - BRASS RIVER SYSTEM

Only 1984 samples were collected and analysed. They all gave levels (range ND - 15.56)(4.83) which may be classified as background levels. The only point with UCM level above 10μgg^{-1} was at Diebu creek off Nun river (043). The results showed 46.3% moisture, 332.79μgg^{-1} (TOE), 241.69μgg^{-1} (Grav.) and 15.56μgg^{-1} (GC) total hydrocarbon.

4.8.7 ORASHI RIVER SYSTEM

All the points sampled on Orashi river system in 1984 gave very low levels of hydrocarbon that cannot be anything but the background levels because all the points recorded hydrocarbon levels below 10μgg^{-1}, although they showed appreciable levels of total organic extracts, this can only be interpreted as being fairly high in organic loads that are not petroleum hydrocarbon.

In the 1985 samples, only Okogbe west (252) recorded values that showed contamination. It has 23% moisture, 116.52μgg^{-1} (TOE), 77.25μgg^{-1} (Grav.) and 25.0μgg^{-1} (GC) total hydrocarbon. All the other samples for 1985 were not quite different from those of 1984 in terms of hydrocarbon levels.

4.8.8 BONNY - NEW CALABAR RIVER SYSTEM

The only station where more than 10μgg^{-1} hydrocarbon was recorded was Bakana (upstream) (807). All other points had low level hydrocarbon, with nothing to indicate any serious level of contamination. The 1985 samples were not different because only Umuochi (Ahiu) (020) gave 12.52μgg^{-1} total hydrocarbon by GC.

4.8.9 IMO RIVER SYSTEM

The three points sampled in 1984 were Kono waterside (128), Azumini (Aba) (813) and Otamiri (817), which gave the following results for moisture content, total organic extract and total hydrocarbon: Kono waterside, 48.9% 3894.34μgg^{-1}, TOE 179.62μgg^{-1} (Grav.) and 10.16μgg^{-1} (GC). Azumiri (Aba) - 20.9%, 262.94

(TOE) 40.25μgg^{-1} (Grav.) and 1.78μgg^{-1} (GC) while Otamiri had 18.9%, 134.88μgg^{-1} TOE, 5.79μgg^{-1} (Grav.) and 0.30μgg^{-1} (GC). This river system was not sampled in 1985.

4.8.10 CROSS RIVER - CALABAR RIVER SYSTEM

For 1984 only four points were sampled and analyzed. These four samples did not show any unusual results. The levels were all below 5μgg^{-1}. But in 1985, only two samples were collected and analyzed. Cross river east shore (079) recorded a level that was higher than those recorded in 1984. The total hydrocarbon level was 11.34μgg^{-1} by GC analysis.

4.8.11 KADUNA RIVER SYSTEM

In 1984 four points were sampled, two on the Kaduna refinery effluent canal and two on Kaduna river. The difference was clear because while the two points on the effluent canal, upstream (141B) and downstream (141A) gave levels of hydrocarbon of 21.52 and 17.10 μgg^{-1} respectively. The other two points on Kaduna river (843) and Malali (844) gave 0.62 and 9.27μgg^{-1} respectively.

TABLE 59 SUMMARY OF THE TOTAL ORGANIC EXTRACT AND TOTAL HYDROCARBON CONCENTRATIONS OF LAGOS LAGOON AND NIGER DELTA SAMPLES (GRAVIMETRY AND GAS CHROMATOGRAPHY) $\mu g\ g^{-1}$ DRY WEIGHT

Code	August-September, 1984			January-February, 1985		
	TOE	GRAV. THC	GC THC	TOE	GRAV. THC	GC THC
1.	LAGOS-LEKKI LAGOON					
086	119.79	94.22	13.47			
087	73.01	48.67	10.53			
845	1153.70	560.21	95.54	87.96	54.13	2.11
847	202.64	158.74	45.48			
851	154.94	135.57	23.18	58.99	44.24	0.20
856	374.37	53.48	ND			
857	372.17	117.07	24.09	127.53	42.51	10.30
	$\bar{X}$ 350.09	166.85	30.33	91.49	46.96	4.20
	SD±154.38	±73.08	±13.65	±22.85	±3.87	±3.37
	R - 73.01-1153.70	48.67-560.21	ND - 95.54	58.99-127.53	42.51-54.13	0.20-10.30
2.	B E N I N					
057	43.17	14.39	3.00			
134	317.08	110.29	5.89			
311	77.27	12.13	2.67	83.79	17.96	1.02

TABLE 59 (contd)

Code	August-September, 1984 TOE	GRAV. THC	GC THC	January-February, 1985 TOE	GRAV. THC	GC THC
347	103.11	20.62	2.05			
835	189.00	16.08	0.04			
837	128.25	102.60	6.26			
838	252.64	176.08	9.14			
0-1	60.91	13.40	0.10			
0-2	283.43	259.05	42.85			
$\bar{X}$	161.65	80.52	8.00			
SD	28.46	27.44	4.76			
R	60.91	12.13	0.04			
	-317.08	-295.05	42.85			
3	ESCRAVOS					
054	429.01	178.08	64.13	294.93	285.72	44.06
055	919.10	22.62	2.30	325.56	101.38	7.80
360	123.46	39.83	4.26			
362	141.87	79.85	10.48			
830				247.66	93.09	1.48
831	28.34	13.50	0.91			
833				238.92	86.88	1.45
834				217.83	51.91	0.20

TABLE 59 (contd.)

Code	August-September, 1984			January-February, 1985		
	TOE	GRAV. THC	GC THC	TOE	GRAV. THC	GC THC
839	62.64	24.49	1.49	264.98	123.80	11.00
$\bar{X}$	248.07	59.73	13.93	264.98	123.80	11.00
SD	148.46	27.43	10.54	21.55	46.76	8.77
R	28.34	13.50	0.91	217.83	51.91	0.20
	919.10	-178.08	-64.13	-325.56	-258.72	-44.06
	FORCADOS - WARRI					
040	65.56	13.11	0.31	47.10	16.19	0.52
049	73.92	38.80	1.34	88.16	33.34	2.46
050	383.48	377.00	19.72	114.52	40.10	16.48
052	86.90	19.72	0.84	53.57	52.73	32.97
053	236.37	222.19	30.22	289.79	13.50	0.36
351	47.66	47.66	1.88	92.17	21.22	0.10
352	428.76	304.72	7.17			
353	451.47	121.55	2.60	730.62	31.77	1.39
372	589.32	175.17	4.41			
858	481.48	351.59	74.05			
860	268.65	221.80	6.67	123.87	41.02	6.85
862	256.58	232.37	4.88	252.25	30.63	1.94
863	446.84	233.48	5.94			
864	290.82	193.03	4.41			

TABLE 59 (contd.)

Code	August-September, 1984			January-February, 1985		
	TOE	GRAV. THC	GC THC	TOE	GRAV. THC	GC THC
865	415.71	384.71	33.74			
866	198.90	108.24	2.52	54.38	25.10	0.36
$\bar{X}$	295.15	190.32	12.53	184.64	30.56	6.34
SD	169.33	124.60	19.35	24.27	3.65	3.29
R	47.66	13.11	0.31	47.10	16.19	0.10
	-589.32	-384.71.	-74.05	-289.79	-52.73	-32.97
5	RAMOS					
038	446.33	334.27	37.32			
382	512.12	298.74	6.64			
869	349.42	307.40	7.62			
870	641.25	564.05	71.64			
871	98.29	8.44	0.12			
$\bar{X}$	409.48	302.58	24.67			
SD	108.59	111.12	14.30			
R	98.29	8.44	0.12			
	-641.25	-564.05	-71.64			
6	NUN - EKOLE - BRASS					
036	62.73	9.07	ND			
043	322.79	241.69	15.56			

TABLE 59 (contd.)

Code	August-September, 1984 TOE	GRAV. THC	GC THC	January-February, 1985 TOE	GRAV. THC	GC THC
281	75.98	6.32	0.32			
872	172.08	92.30	4.54			
873	221.59	115.91	3.71			
$\bar{X}$	173.03	93.06	4.83			
SD	54.01	47.07	3.11			
R	62.73	6.32	ND			
	-332.79	-241.69	-15.56			
7	ORASHI					
012	11.91	9.53	0.17			
013	48.23	30.10	1.87			
014	200.81	107.72	6.18			
016	279.04	103.68	5.09			
021	452.02	227.59	6.18	26.52	21.70	1.58
035	218.37	13.73	0.63			
250	293.94	12.78	0.13	33.20	22.99	0.12
251	250.48	28.93	1.67			
252	451.24	62.37	1.95	116.52	77.25	25.10
262	365.53	48.91	1.26			
801	47.66	26.91	1.77	18.46	12.30	1.03

TABLE 59 (contd.)

Code	August-September, 1984			January-February, 1985		
	TOE	GRAV. THC	GC THC	TOE	GRAV. THC	GC THC
802	83.02	61.21	2.78			
819				24.25	20.24	1.62
820				37.38	27.07	0.36
821	771.40	15.78	0.23	172.71	21.75	0.77
824	263.94	2.14	0.02			
$\bar{X}$	266.97	53.67	2.14	61.29	29.04	4.37
SD	202.88	61.14	2.17	22.04	9.28	3.57
R	47.66	2.14	0.02	18.46	12.30	0.12
	-452.02	-227.59	-6.18	-172.71	-77.25	-25.10
8	BONNY - NEW CALABAR					
018				136.48	105.20	8.42
020	110.98	20.74	1.25	47.13	39.28	12.52
121	300.00	27.27	0.26	68. 92	18.25	2.81
233	235.98	190.80	8.51			
807	1283.44	128.58	21.44	84.17	24.94	1.77
808	78.86	52.05	2.15	15.53	12.70	0.24

TABLE 59 (contd.)

Code	August-September, 1984			January-February, 1985		
	TOE	GRAV. THC	GC THC	TOE	GRAV. THC	GC THC
810	208.88	6.43	0.91			
$\bar{X}$	369.69	54.31	5.75	70.45	40.07	5.15
SD	200.76	20.36	3.53	24.19	18.50	2.46
R	78.86	6.43	0.26	15.53	12.70	0.24
	-1283.44	-128.58	21.44	-136.48	-105.20	-12.52
9	IMO					
128	3894.34	179.62	10.16			
813	262.94	40.25	1.78			
817	134.88	5.79	0.30			
$\bar{X}$	1430.72	75.22	4.08			
SD	1253.15	59.94	3.29			
R	134.88	5.79	0.30			
	-3894.34	-179.62	-10.16			
10	CROSS RIVER - CALABAR					
071	54.91	25.31	2.70			
079				49.81	31.13	11.34
210				181.91	9.10	0.05

TABLE 59 (contd.).

Code	August-September, 1984			January-February, 1985		
	TOE	GRAV. THC	GC THC	TOE	GRAV. THC	GC THC
811	70.53	9.97	0.26			
812	142.93	12.47	0.52			
827	154.00	42.00	4.41			
$\bar{X}$	105.77	22.44	1.97			
SD	24.27	8.01	1.04			
R	54.91	9.97	0.26			
	-154.0	-42.00	-4.41			
11	KADUNA					
141A	232.90	106.09	17.10	67.35	34.29	5.00
141B	534.79	171.51	21.52	173.25	60.38	2.91
843	14.86	8.92	0.62			
844	72.60	51.34	9.27			
$\bar{X}$	213.79	84.47	12.13			
SD	129.98	40.65	5.25			
R	14.86	8.92	0.62			
	-534.79	-171.51	-21.52			

In 1985 only the effluent canal points were sampled with stations 141A and 141B recording 5.00 and 2.91μgg^{-1} total hydrocarbon respectively.

4.8.12 IBADAN

The sample from Agodi garden was contaminated, the value of hydrocarbon was 27.79μgg^{-1}. Asejire sample recorded 6.849μgg^{-1} total hydrocarbons. Agodi pond is the recipient of refined petroleum products from domestic sources, mechanic garages, and the Nigerian bottling company.

4.8.13 UTOROGU - OKPARI RIVER

The samples were collected from three main areas - impacted swamp (A - G), upstream P and R, and downstream (O - J).

The results of the analysis for the three sampling periods are displayed in Table 60. All the points sampled in 1984 wet season had high levels of hydrocarbon with the impacted swamp recording the highest. The results for the total organic extract (TOE) and total hydrocarbon (THC - by both gravimetry and GC) are 106.95-419.02 (268.69), 73.98-214.05 (136.39) and

31.97-154.06 (95.62) μgg^{-1} respectively for the impacted swamp in 1984 (wet season).

Point R (upstream) had 206.64, 127.13 and 115.62 µg/g respectively for the same period. All the points downstream gave an average and mean values of 141.97-800.63 (286.46), 53.03-338.66 (131.59) and 19.55-242.16 (92.78) µg/g respectively.

The early 1985 (dry season) samples recorded levels far below what was recorded in 1984 (wet season). The impacted swamp still recorded the highest with an average and mean values of 54.36-491.02 (183.69) μgg^{-1} - TOE, 17.34-122.76 (64.07) µg/g - THC (Grav.) and ND - 6.62 (2.68) µg/g - THC (GC). The upstream point R gave TOE - 47.54µg/g, THC (Grav.) - 26.83µg/g and THC (GC) - 0.47µg/g. Downstream, the values were a bit higher (then the upstream values), the average and mean values for TOE and THC (Grav. and GC) are 27.35-75.79 (51.12), 19.60-28.89 (24.55) and 0.67-7.96 (2.58) µg/g respectively.

The last set of samples were collected in June-July 1985 (wet season). The values recorded showed an

upward trend over those obtained for the 1985 dry season (Jan.-Feb.). Both the impacted swamp and the points downstream had average results that were close while the reference (upstream) points had lower results. The results are as follows:

Imparted swamp - TOE, 42.58-237.28 (106.56) µg/g
THC (Grav.), 32.55-177.37 (65.57)µg/g
and THC (GC), 2.22-68.06 (22.24) µg/g

Upstream - TOE, 31.28-120.57 (75.93). µg/g
THC (Grav.), 14.44-18.36 (16.40)µg/g
THC (GC), 2.41-10.22 (6.32) µg/g

Downstream - TOE, 30.51-178.27 (94.78) µg/g
- THC (Grav.), 23.19-81.50 (42.14) µg/g
and - THC (GC), 8.93-52.96 (27.08) µg/g.

The increase in the levels of hydrocarbons recorded during the 1985 wet season over the early 1985 levels may be due to run off from land and mixing which allowed the levels of hydrocarbons in surface sediment to be increased.

TABLE 60: SUMMARY OF TOTAL ORGANIC EXTRACT AND TOTAL HYDROCARBON CONCENTRATION OF UTOROGU SWAMP AND OKPARI RIVER (GRAVIMETRY AND GAS CHROMATOGRAPHY) μgg^{-1} DRY WEIGHT

Sample Code	October 1984 Wet Season			January-Febrary 1985 Dry Season			June-July 1985 West Season		
	TOE	THC (GRAV.)	THC (GC)	TOE	THC (GRAV.)	THC(GC)	TOE	THC(GRAV.)	THC (GC)
IMPACTED SWAMP									
A							126.88	71.57	2.22
B	354.64	214.05	154.06	145.04	17.34	6.62	237.28	171.37	68.06
C				491.02	122.76	1.21	50.43	44.51	3.61
D	419.02	153.30	126.80	126.90	44.83	0.81	42.58	33.62	23.76
E	106.95	73.98	31.97	54.36	44.83	4.74			
F				101.15	90.92	ND	108.92	33.80	20.29
G	194.14	104.21	69.63				73.24	32.55	15.48
$\bar{X}$	268.69	136.39	95.62	183.69	64.07	2.68	106.56	65.57	22.24
R	106.95-419.02	73.98-214.05	31.97-154.06	54.36-491.02	17.34-122.76	ND-6.62	42.58-237.28	32.55-177.37	2.22-68.06
UPSTREAM									
R-1	206.64	127.13	115.62	47.54	26.83	0.47	120.57	18.36	10.22
							31.28	14.44	2.41
						$\bar{X}$	75.93	16.40	6.32
						R	31.28-120.57	14.44-18.36	2.41-10.22

TABLE 60 (contd.)

Sample Code	October 1984 Wet Season			January-Febrary 1985 Dry Season			June-July 1985 West Season		
	TOE	THC (GRAV.)	THC (GC)	TOE	THC (GRAV.)	THC(GC)	TOE	THC(GRAV.)	THC (GC)
	DOWN STREAM								
O	800.63	338.66	242.16	27.35	19.60	0.70	63.98	30.72	20.07
N	245.11	69.65	52.24	48.59	28.89	1.00	30.51	23.51	22.64
V	141.97	53.03	19.55				118.95	71.14	45.90
M							83.76	28.83	14.68
K	206	123.90	92.88	52.73	26.37	0.67	168.46	31.20	8.93
T	171.38	118.51	92.02	75.79	23.32	7.96	178.27	81.50	52.96
U	153.21	85.76	57.83				50.90	33.54	26.69
J							63.43	36.96	24.74
$\bar{X}$	286.46	131.59	92.78	51.12	24.55	2.58	94.78	42.14	27.08
R	141.97-	53.03-	19.55-	27.35-	29.60-	0.67-	30.52	23.19-	8.93-
	800.63	338.66	242.16	75.79	28.89	7.96	178.27	81.50	52.96

4.8.14 LAGOS LAGOON (1985 JAN.-DEC.)

The values calculated for the total organic extract (TOE), and total hydrocarbons (THC), the latter by gravimetric and chromatographic methods are given below in Table 61 for all the sampling periods.

The highest values were obtained in the early wet season (June), TOE ranged from 8.88μgg^{-1} to 4373.46 μgg^{-1} with an average of 327.18μgg^{-1} while the THC levels were 2.08-3554.51 (255.80) and ND - 2766.27 (191.72) μgg^{-1} dry weight for gravimetry and GC respectively. This was closely followed by the April samples with TOE: 188.83-655.49 (422.16) μgg^{-1}, THC: 122.68-509.18 (315.93) μgg^{-1} (Grav.) and 109.33-427.88 (268.61) μgg^{-1} (GC).

The results obtained during the February sampling were TOE: 11.61-786.28 (109.61) μgg^{-1}, THC: 1.25-695.25 (73.97) μgg^{-1} (Grav.) and 0.31-539.29 (56.19) μgg^{-1} (GC). December samples gave TOE: 36.35-604.42 (155.08) μgg^{-1}, THC: 3.02-450.85 (102.62) μgg^{-1} (Grav.) and 0.25-409.82 (79.87) μgg^{-1} GC.

October samples recorded TOE: 47.64-351.23 (199.44) μgg^{-1}, THC: 3.86-222.39 (113.13) μgg^{-1} Grav.) and ND - 172.05 (86.03) μgg^{-1} (GC). The lowest levels were recorded with the two samples collected in August, TOE: 60.80-86.69 (73.75) μgg^{-1}, THC: 9.73-37.57 (23.65) μgg^{-1} (Grav.) and 0.62-14.64 (7.63) μgg^{-1} (GC).

Berger/National Oil/Ijora (LS 20) came out as the most impacted site throughout the sampling period. The hydrocarbon levels recorded at this station (by GC) varied from 14.64 μgg^{-1} in August 1985 to 2766.27 μgg^{-1} in June 1985. Green buoy # 3 (LS 7), mouth of Ogun river (LS 13), Okobaba (LS 23), Power Station, Ijede (LS 24), Tin Can Island (LS 19), and Itu Omu (LS 26) recorded hydrocarbon levels between 50 and 441 μgg^{-1}. The highest values recorded were from fine, humus-rich sediments (Table 61).

There is a highly positive correlation between the gravimetry and Gas Chromatographic value shown in Tables 63 and 64 ($r = 0.797$).

TABLE 61: SUMMARY OF THE TOTAL ORGANIC EXTRACT AND TOTAL HYDROCARBON CONCENTRATIONS OF LAGOS LAGOON SEDIMENT SAMPLES (GRAVIMETRY AND GAS CHROMATOGRAPHY) (1985) ($\mu g\ g^{-1}$ DRY WEIGHT)

	February			April (1)			June (2)			August (3)			October (4)			December (5)		
	TOE	Grav. THC	GC THC	TOE	Grav. THC	GC THC	TOE	Grav. THC	GC THC	TOE	Grav. THC	GC THC	TOE	Grav. THC	GC THC	TOE	Grav. THC	GC THC
LS-1	47.61	34.45	28.15															
LS-2	19.08	18.13	13.48															
LS-3	11.61	4.37	0.31				118.19	64.07	43.87									
LS-4	32.48	1.25	1.15				13.42	4.98	2.22									
LS-5	49.23	25.93	20.27				21.52	9.21	0.17									
LS-6	74.74	24.18	18.65				60.64	2.43	ND									
LS-7	264.48	216.10	165.40				140.64	107.81	40.82									
LS-8							76.03	49.71	1.63									
LS-9							5.06	4.87	4.66									
LS-10	19.21	13.98	5.19				14.57	6.86	0.41									
LS-11	41.77	18.09	14.90				14.91	14.64	8.93									
LS-12	12.76	3.83	0.48															
LS-13							441.76	339.71	238.81									
LS-14	202.05	16.69	1.48				12.91	2.08	0.19									
LS-15	58.44	5.64	3.88															
LS-16	60.27	40.05	28.10															
LS-17	67.38	39.97	30.26							60.80	9.73	0.62				36.35	3.02	0.25
LS-18	39.04	34.75	27.46										47.64	3.86	ND	70.38	53.00	9.14
LS-19	75.77	58.00	18.56	188.83	122.68	109.33	44.51	33.56	27.36							42.05	27.80	4.12
LS-20	786.28	695.25	539.29	655.49	509.18	427.88	4373.46	3554.51	2766.27	86.69	37.57	14.64				604.42	450.85	409.82
LS-21	50.78	39.61	30.61															
LS-22	68.65	28.33	24.13				47.20	23.48	20.02							79.18	4.65	0.47
LS-23	188.86	148.57	126.32				364.39	282.05	233.79				351.23	222.39	172.05			
LS-24	232.75	182.00	148.09				23.70	3.95	0.71							98.10	76.42	55.41

TABLE 61 (Contd.)

	February			April (1)			June (2)			August (3)			October (4)			December (5)		
	TOE	Grav. THC	GC THC	TOE	Grav. THC	GC THC	TOE	Grav. THC	GC THC	TOE	Grav. THC	GC THC	TOE	Grav. THC	GC. THC	TOE	Grav. THC	GC THC
LS-25	52.14	43.84	42.78				8.88	5.09	1.34									
LS-26	55.23	8.37	3.51				107.49	95.39	59.75									
$\bar{X}$	109.16	73.97	56.19	422.16	315.93	268.61	327.18	255.8	191.72	73.75	23.65	7.63	199.44	113.13	86.03	155.08	102.62	79.87
R	11.61	01.25	0.31	188.83	122.68	109.33	8.88	2.08	ND -	60.80	9.73	0.62	47.64	3.86	ND	36.35	3.02	0.25
	-786.28	-695.25	-539.29	-655.49	-509.18	-427.88	-4373.46	-3554.51	2766.77	-26.69	-37.57	-14.64	-351.23	-222.39	-172.05	-604.42	-450.85	-409.82

4.9 OVERALL SUMMARY OF SEDIMENT RESULTS (1984-85)

The overall summary of results obtained from Lagos Lagoon and the Niger Delta area of Nigeria in 1984 and 1985, the Utorogu-Okpari (a case study), Kaduna (1984-85) and Ibadan (1985) are given in Table 62.

The mean concentrations of the total petroleum hydrocarbons against the different river systems are shown in a histogram (Figure 36). Looking through the data in Table 62 vis-a-vis the histogram in Fig. 36, there is really no definite trend as far as the petroleum hydrocarbon distribution in the samples with time (i.e. seasonal variation) is concerned. What appeared to be a higher wet season (1984) values over the dry season (1985) values in some of the river systems e.g. Lagos-Lekki Lagoons, Benin, Escravos and Forcado-Warri, may be due to changes in the lithology of the sample collected in 1985 rather than reflecting a clear-cut higher hydrocarbon levels in 1984 than in 1985 samples. The values recorded during the January to December monitoring of Lagos Lagoon clearly attest

to this fact as can be seen in the distribution graph (Fig. 37) below. Some points such as buoy # 3 (LS 7), 1km before Moba village (LS 5), Ijede Power Station (LS 24) and Island off Palaver St. (LS 25), recorded dry season figures that were significantly higher than those obtained for the wet periods. Same can be found at some points in the delta area too e.g. stations 052, 252, and 020.

However, certain generalizations can be made on the basis of the results presented in Table 62. Lagos Lagoon recorded the highest level of petroleum hydrocarbon at any given period of the study. The results of the 1985 January to December study brought to focus the extent to which the Lagoon has been polluted. The high levels recorded may be due to the restricted circulation system of the Lagoon coupled with the high rate of untreated effluent injected into the Lagoon system from urban run off and storm water from the industrial effluent channels. These factors were further complemented by the nature of the sediment particles found within the lagoonal system, which were

mainly fine clay and mud with efficient binding ability which may not allow for easy downward migration of the petroleum hydrocarbons and degradation process may also be very slow. All these would work together to promote the accummulation of hydrocarbons which are not easily dispersed because of the poor circulation system.

In the Niger Delta area, Escravos, Forcados-Warri, Ramos with Benin also recorded appreciable levels of petroleum hydrocarbons. Although the rivers flow through oil activity areas, the results of the analysis in most of the points sampled did not reflect any serious contamination. Within the delta the points of high petroleum hydrocarbon levels were spatially scattered but most of them were located very close to petroleum operation areas such as Ogharife (O-2), Escravos terminal (054), Warri river field (053), Chanomi creek at confluence of unnamed creek draining Egwa field (858), Forcados river above Obotebe (865), Aghoro (038), Orughene creek (870) and Bakana (807). Some were located close to towns and villages such as Umuochi (020) and Dudu town (837).

Alaocha (810), Ndoni creek (262) and Obagi field downstream (012) reflect the effect of particle size on the level of hydrocarbons retained by sediment. They were points located within oil activity area yet very low levels of petroleum hydrocarbons were recorded. This may be because they have coarse sand particles known for their poor adsorptive capacity of oil. They also contributed to the accelerated rate of degradation of any petroleum hydrocarbon incorporated into the sediment matrix. The tidal flush may also be a contributory factor.

The levels of petroleum hydrocarbons recorded for the Utorogu and Okpari samples clearly show that the area was polluted. The effects on the vegetation and the aquatic life was evident during the 1984 sampling trip, the aquatic life in Utorogu swamp was non-existent and the oil was carried downstream with the river flow. The quick recovery of the swamp and the river was quite astonishing. This may partly be explained by the result of Jenifer Baker (1981)[259] work on the influence of oil industry on tropical marine ecosystem. She came

out with a result that biodegradable or chemically unstable pollutants will degrade faster in warmer water of the tropics because of the shallowness and smaller tidal amplitude of the rivers. The different oxidative processes, especially microbial degradation also help to degrade the oil.

The Ibadan samples also reflected the effect of urban activities (e.g. washing of petroleum products into the water course) on the rivers flowing through the city. While Asejire (outside Ibadan) recorded a very low level of hydrocarbons, Agodi garden's sediment sample gave a result of a point contaminated with fresh petroleum hydrocarbons.

The Lagos Lagoon study in 1985 brought out a picture of a heavily stressed lagoon where there are localized accummulation of petroleum hydrocarbons at certain points on the lagoon. Such points are Green buoy #3 (LS 7), mouth of Ogun river (LS 13), Tin Can Island (off ship wreck) (LS 19), Berger/National Oil/ Ijora (LS 20), and Okobaba (Pylon 134) (LS 23).

On the whole the spatial distribution of points with high levels of petroleum hydrocarbon are activity

TABLE 62: SUMMARY OF THE DISTRIBUTION OF TOTAL ORGANIC EXTRACT (TOE), RESOLVED AND n-ALKANES, THE UNRESOLVED COMPLEX MIXTURE (UCM) TOTAL ALIPHATIC, AROMATIC, TOTAL HYDROCARBONS AND MOPI* IN SEDIMENTS OF ALL THE VARIOUS RIVER SYSTEMS STUDIED BETWEEN 1984-85 ($\mu g\ g^{-1}$ DRY WEIGHT BASIS)

River System	No. of Samples Analyzed	TOE		Resolved Alkane		n-Alkane		UCM		Total Aliphatic		Total Aromatic		Total Hydrocarbon		MOPI Range	Comment
		Range	$\bar{X}$	Range	$\bar{X}$	Range	$\bar{X}$	Range	$\bar{X}$	Range	$\bar{X}$	Range	$\bar{X}$	Range	$\bar{X}$		
Lagos-Lekki Lagoon (1984)	7	73.01-1153.70	350.09	±154.38 ND-10.84	1.88 ±1.55	ND-4.73	0.90 ±0.68	ND-80.23	25.01 ±11.46	ND-91.07	26.85 ±13.01	ND-7.16	3.48 ±1.02	ND-95.54	30.33 ±13.65	6.6-8.5 (7.8)	Moderately petrogenic
Benin (1984)	9	43.17 317.06	161.65	±43.90 ±30.43 0.04-4.32	0.98 ±0.48	0.04-4.24	0.87 ±0.47	ND-36.90	5.92 ±4.10	0.04-41.22	6.90 ±4.58	ND-2.26	1.10 ±0.25	0.04-42.85	8.00 ±4.76	-2.7-6.9 (2.5)	Biogenic to low trace petrogenic
Escravos (1984)	6	28.34-919.10	284.07	±148.46 0.56-1.76	1.09 ±0.29	0.33-1.08	0.61 ±0.13	ND-57.39	11.34 ±9.57	0.87-58.45	12.42 ±9.60	0.04-5.68	1.51 ±0.94	0.91-64.13	13.93 ±10.54	0.4-9.7 (3.8)	Biogenic to low trace Petrogenic
Forcados Warri (1984)	16	47.66-589.32	295.15	±169.33 0.06-16.19	3.25 ±5.39	0.06-12.07	2.10 ±3.70	ND-53.33	8.20 ±15.00	0.28-69.52	11.45 ±18.20	0.03-3.68	1.08 ±1.37	0.31-74.05	12.53 ±19.35	0.4-7.6 (4.7)	Low trace Petrogenic
Ramos (1984)	5	98.29-641.25	409.48	±108.59 0.07-8.06	4.02 ±1.61	0.06-2.52	1.33 ±0.49	ND-60.93	18.95 ±12.19	0.07-66.91	22.98 ±13.37	0.05-4.73	1.69 ±0.14	0.12-71.64	24.67 ±14.30	-1.8-9.0 (5.2)	Low trace to Moderately
Nun-Ekole-Brass (1984)	5	62.73-332.79	173.03	±54.01 ND-0.26	0.15 ±0.05	ND-0.20	0.12 ±0.04	ND-13.61	4.13 ±2.72	ND-13.82	4.28 ±2.76	ND-1.74	0.55 ±0.35	ND-15.56	4.83 ±3.11	-0.6-7.8 (4.6)	Low trace Petrogenic
Orashi (1984)	14	11.91-777.40	266.97	±202.97 0.02-1.95	0.50 ±0.57	0.02-1.95	0.43 ±0.50	ND-4.83	1.16 1.56	0.02-5.03	1.66 ±1.62	ND-2.10	0.48 ±0.63	0.02-6.18	2.14 ±2.17	-3.2-5.8 (1.5)	Biogenic
Bonny-New Calabar (1984)	6	78.86-1283.44	370.02	±260.76 0.24-3.69	1.4 ±0.62	0.24-0.95	0.59 ±0.12	ND-13.55	3.68 ±2.26	0.24-17.24	4.81 ±2.83	0.02-4.20	0.94 ±0.67	0.26-21.44	5.75 +3.53	-0.9-6.2 (2.5)	Biogenic to Low trace
Imo (1984)	3	262.94 3894.34	1430.72	±1210.47 0.20-0.29	0.25 ±0.10	0.18-0.27	0.23 ±0.03	ND-8.55	3.20 ±2.85	0.25-8.75	3.45 ±2.83	0.15-1.41	0.63 ±0.45	0.30-10.16	4.08 ±3.29	-0.3-6.8 (3.0)	Biogenic to low trace petrogenic
Cross River-Calabar (1984)	4	54.91-154.00	105.59	±24.77 0.22-0.47	0.42 ±0.14	0.22-0.47	0.40 ±0.06	ND-3.35	1.36 ±0.84	0.22-3.79	1.79 ±0.89	0.03-0.62	0.19 ±0.15	0.26-4.41	1.97 ±1.04	-0.6-4.3 (1.5)	Biogenic
Kaduna (1984)	3	14.86-232.90	106.79	±73.68 0.13-0.64	0.35 ±0.21	0.13-0.52	0.31 ±0.12	0.43-20.25	9.75 ±6.75	0.58-20.50	11.85 ±6.64	0.04-1.02	0.51 ±0.33	0.62-21.52	12.36 ±6.97	0.5-5.8 (2.6)	Biogenic to low trace petrogenic

TABLE 62 (contd.)

River System	No. of Samples Analzyed	TOE Range	TOE $\bar{X}$	Resolved Alkane Range	Resolved Alkane $\bar{X}$	n-Alkane Range	n-Alkane $\bar{X}$	UCM Range	UCM $\bar{X}$	Total Aliphatic Range	Total Aliphatic $\bar{X}$	Total Aromatic Range	Total Aromatic $\bar{X}$	Total Hydrocabon Range	Total Hydrocabon $\bar{X}$	MOPI Range	Comment
Okpari (1984)	18	89.12-805.00	277.94 ± 209.11	0.74-46.26	11.02 ±2.53	0.35-24.07	5.75 ±6.35	7.38-222.90	79.30 ±55.49	10.42-241.28	91.76 ±64.12	ND-40.01	9.90 ±11.12	14.04-267.48	101.66 ±70.73	5.6-10.2 (8.1)	Heavy Petrogenic
Lagos-Lekki Lagoons (1985)	3	58.999-127.53	91.49 ±22.85	-	-	-	-	-	-	0.20-9.00.	3.57 ±2.93	ND-1.30	0.64 ±0.43	0.20-10.30	4.20 ±3.37		
Benin (1985)	1	83.54	-	-	-	-	-	-	-		1.00		0.02		1.02		
Escravos (1985)	5	217.83-325.56	264.98 ±21.55							0.20-41.00	10.14 ±8.16	ND-3.06	0.86 ±0.61	0.20-44.06	11.00 ±8.77		
Forcados - Warri (1985)	10	23.87-730.62	166.64 ±70.68							0.10-30.00	6.50 ±2.99	ND-3.48	1.04 ±0.35	0.10-32.97	7.54 ±3.29		
Orashi (1985)	6	18.46-116.52	42.72 ±16.34							0.10-23.00	3.91 ±3.82	0.02-2.10	0.45 ±0.35	0.12-25.10	4.37 ±4.16		
Bonny-New Calabar (1985)	5	68.92-147.13	110.45 ±15.64							0.20-10.00	4.24 ±1.96	0.04-2.52	0.91 ±0.50	0.24-12.52	5.15 ±2.46		
Cross River-Calabar (1985)	2	49.81-181.91	115.86 ±66.05	-	-					0.05-9.20	4.63 ±4.58	ND-2.14	1.07 ±1.07	0.05-11.34	5.70 ±5.65		
Kaduna (1985)	2	67.35-173.25	124.30 ±52.95							2.30-4.00	3.15 ±0.85	0.61-1.00	0.81 ±0.20	2.91-5.00	3.96 ±1.05		
Okpari (1985-a) (Jan-Feb)	15	17.39-491.02	94.83 ±117.05	ND-1.01	0.18 ±0.29	ND-1.13	0.17 ±0.30	ND-7.34	1.94 ±2.57	ND-7.96	2.11 ±2.73	ND-2.01	0.39 ±0.61	ND-7.96	2.49 ±3.06	1.4-8.2 (3.9)	Low trace Petrogen
Okpari (1985 b)	22	18.35-283.31	91.46 ±71.13	0.02-15.07	2.76 ±3.45	0.02-9.52	1.85 ±2.15	ND-62.77	17.05 ±15.69	0.02-63.95	19.81 ±17.62	ND-4.11	0.81 ±1.29	0.03-68.06	20.62 ±18.08	2.8-3.8 (3.3)	Biogenic to low trace petrogen
Lagos Lagoon (1985 b)	33	5.06-4373.68	202.28 ±607.70	ND-179.23	9.20 ±22.13	ND-126.98	8.66 ±19.46	ND-2524.15	93.63 ±352.07	ND-2703.38	104.11 ±376.00	ND-62.89	6.09 ±11.61	ND-2766.27	110.13 ±385.58	-2.0-11.3 (4.4)	low trace petrogen
Ibadan	9	67.67-287.90	137.79 ±176.94	0.674-1.779	1.23 ±0.78	0.674-1.779	1.23 ±0.78	5.07-27.12	16.20 ±15.59	6.85-27.79	17.32 ±14.81	ND-1.24	0.62 ±0.88	8.09-27.79	17.94 ±13.93	3.7-7.8 (5.8).	Low trac to Moderate petrogen

MOPI = Marine Oil Pollution Index

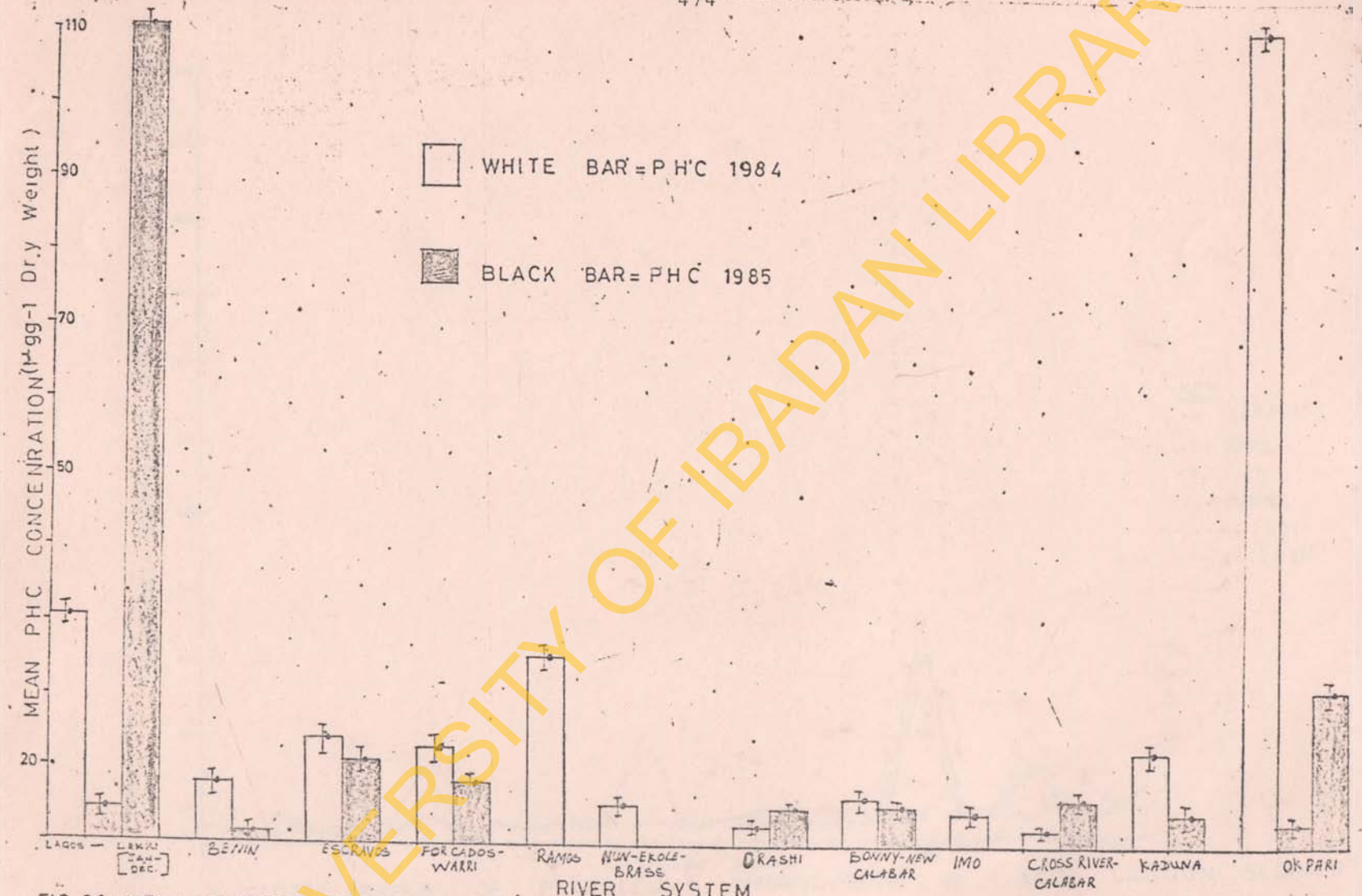


FIG. 36: MEAN LEVELS OF PETROLEUM HYDROCARBONS IN SEDIMENT OF LAGOS LAGOON, KADUNA AND THE NIGER DELTA AREA BY RIVER SYSTEM (in μgg-1 dry weight of sediment)

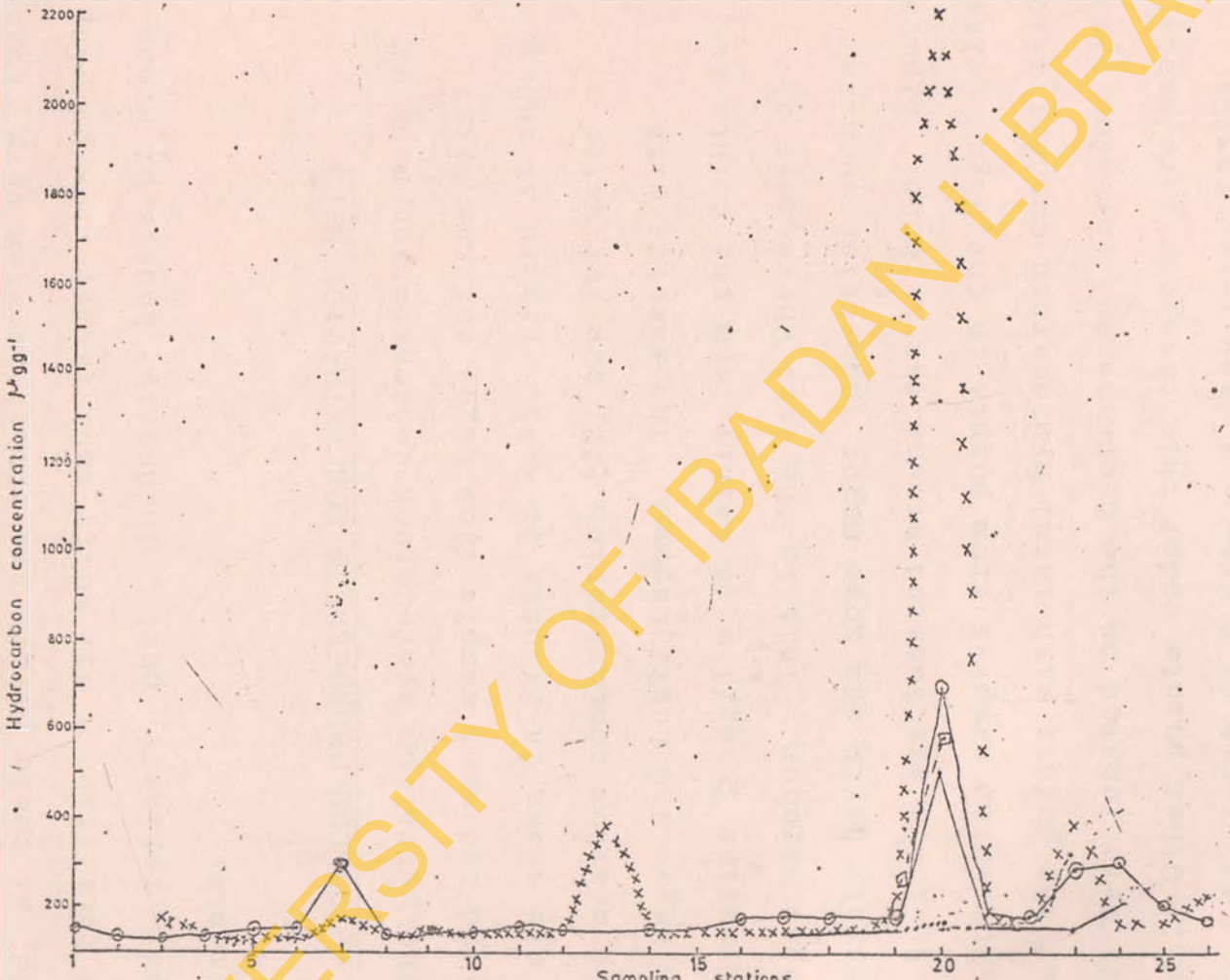


FIG 37: LEVELS OF PETROLEUM HYDROCARBONS IN LAGOS LAGOON SEDIMENTS (1985)

related, as these points are either located very close to oil facilities - oil well, tank farms, flow/pumping stations, refinery, ports, industrial houses or urban settlements.

4.10 PETROLEUM HYDROCARBON CONCENTRATION MAPS

The petroleum hydrocarbon concentration maps of water and sediment sample from Lagos and the Niger Delta are shown in Figures 38 - 45. Figure 38 shows the hydrocarbon concentration (IR) map for water around Lagos and Lekki Lagoons. The samples with concentration $>$ 5mg/l were mainly from the points on the Lagos Harbour. This is the area where most of the vessels berth and some major industries such as Lever Brothers are located around the harbour. Figure 39 is for water samples from points in the Niger Delta. Most of the points with total hydrocarbon concentration $>$ 5mg/l were located on the Escravos and Forcados river systems. Other points under this category were scattered in the delta, such as Okrika refinery jetty (233a), Elele Alimini (236), Ahoada (022) etc.

The maps for the sediment samples are shown in Figures 40 - 45. Figures 40, 41 and 42 are for the petroleum hydrocarbon concentrations in sediment around Lagos Lagoon for 1984 and 1985 (dry and wet seasons). All points with HC > 100µg /g were located around the Lagos' harbour except point 24 (Ijede Power Station). Most of the stations showed decrease in the levels of HC in 1985 wet season (June samples).

Finally, Figures 43, 44 and 45 showed levels of hydrocarbons in sediments from the Niger Delta area. The points had low levels of hydrocarbons for both the wet and dry seasons. They had what may be referred to as background levels (< 20µg/g).

The maps did not show any discernible trend downstream but the high concentrations were around the activity points.

4.11 HYDROCARBONS SOURCE CHARACTERIZATION

A number of parameters generated from gas chromatographic analyses have been used to characterize the source(s) of hydrocarbons extracted from environmental

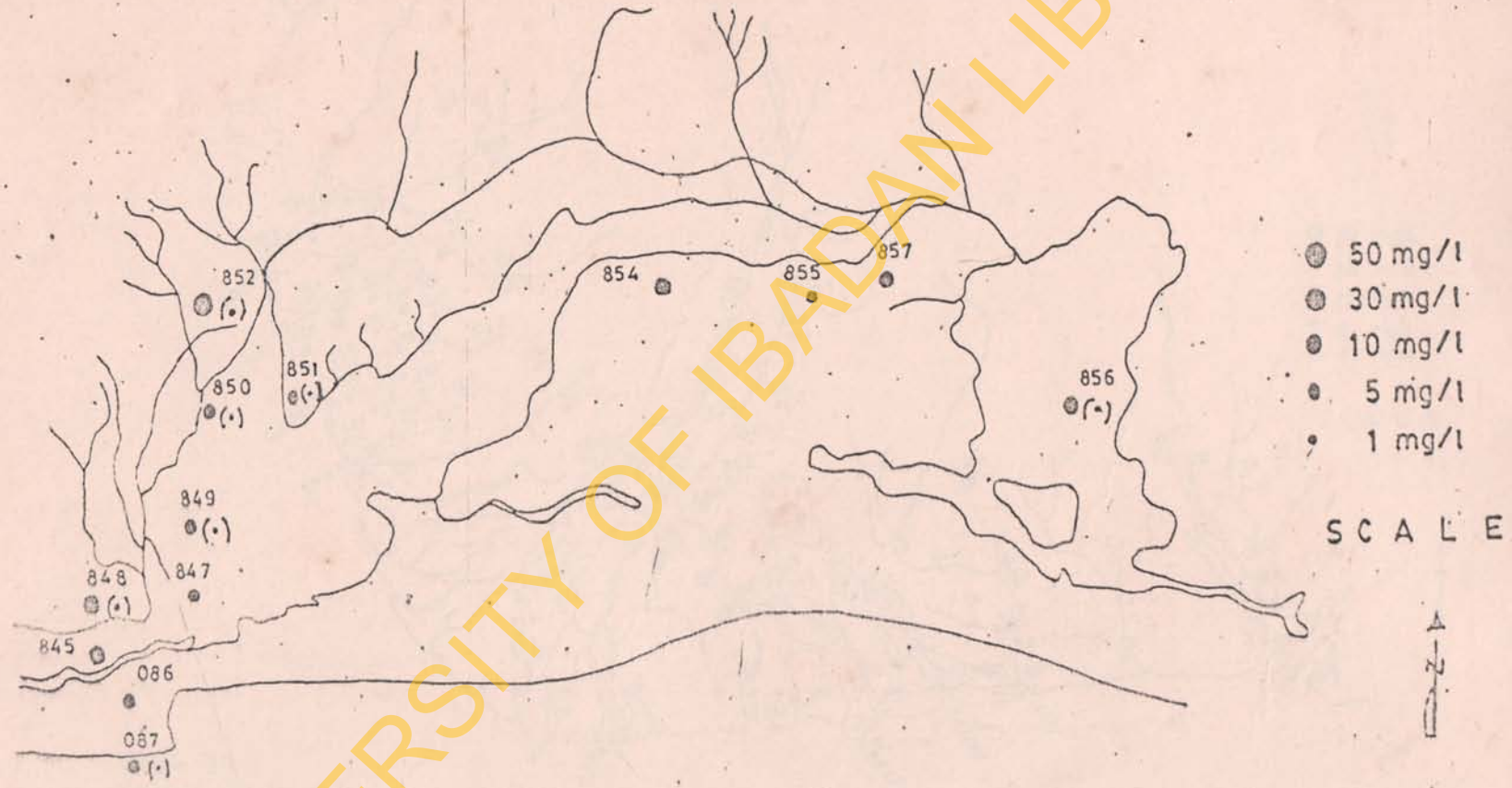


Fig. 38: Total hydrocarbon concentration (BY. IR) of water samples around Lagos and Lekki Lagoon (1984 - 1985) Location numbers are indicated with the concentration below [1985 concentration in bracket — (·)]

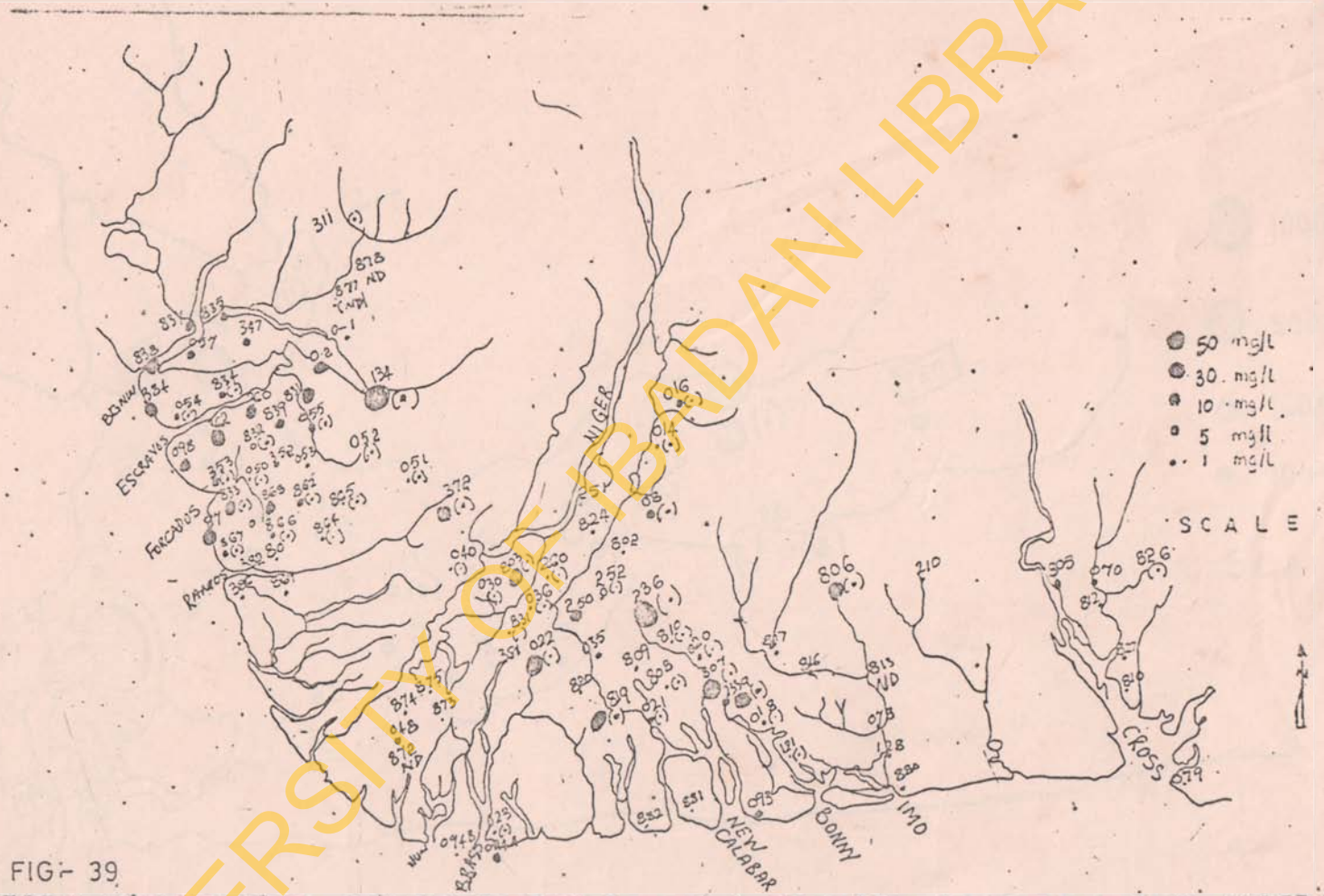


FIG- 39
TOTAL HYDROCARBON CONCENTRATION (BY IR) OF WATER SAMPLES IN THE NIGER DELTA (1984-85) LOCATION NUMBERS ARE INDICATED WITH THE CONCENTRATION BELOW (1985 CONCENTRATIONS IN BRACKET -(•)]

Fig. 40 : Aliphatic hydrocarbon (By GC) of sediment samples around Lagos Lagoon. Location numbers are indicated with the concentrations below (June 1985 Concentrations in bracket – (•)). 1984 Station – □.

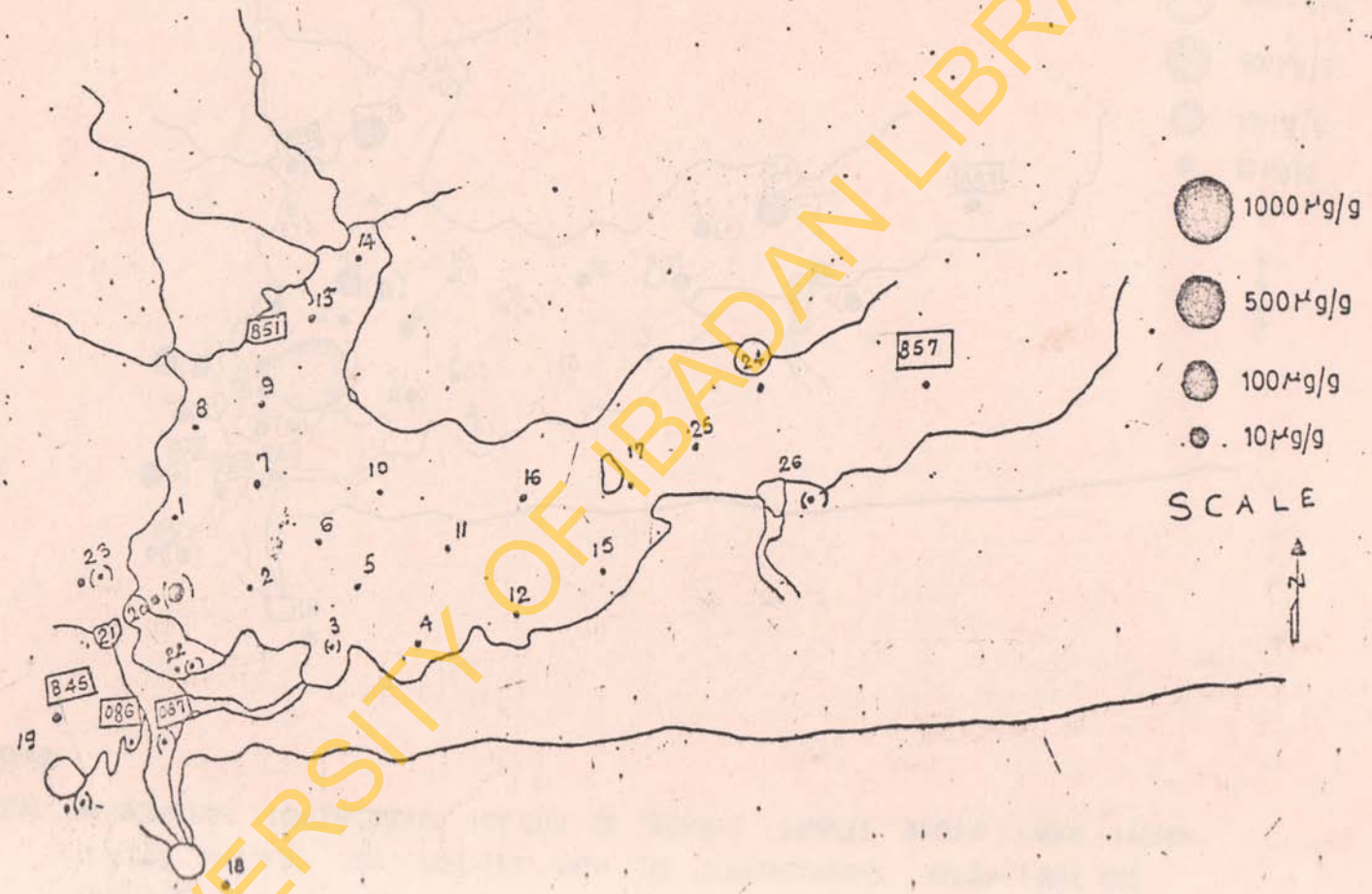


Fig 41 Aromatic hydrocarbon (By G C) of sediment samples around Lagos Lagoon. Location numbers are indicated with the concentrations below (June 1985 Concentrations in bracket — (•)) 1984 Stations — □

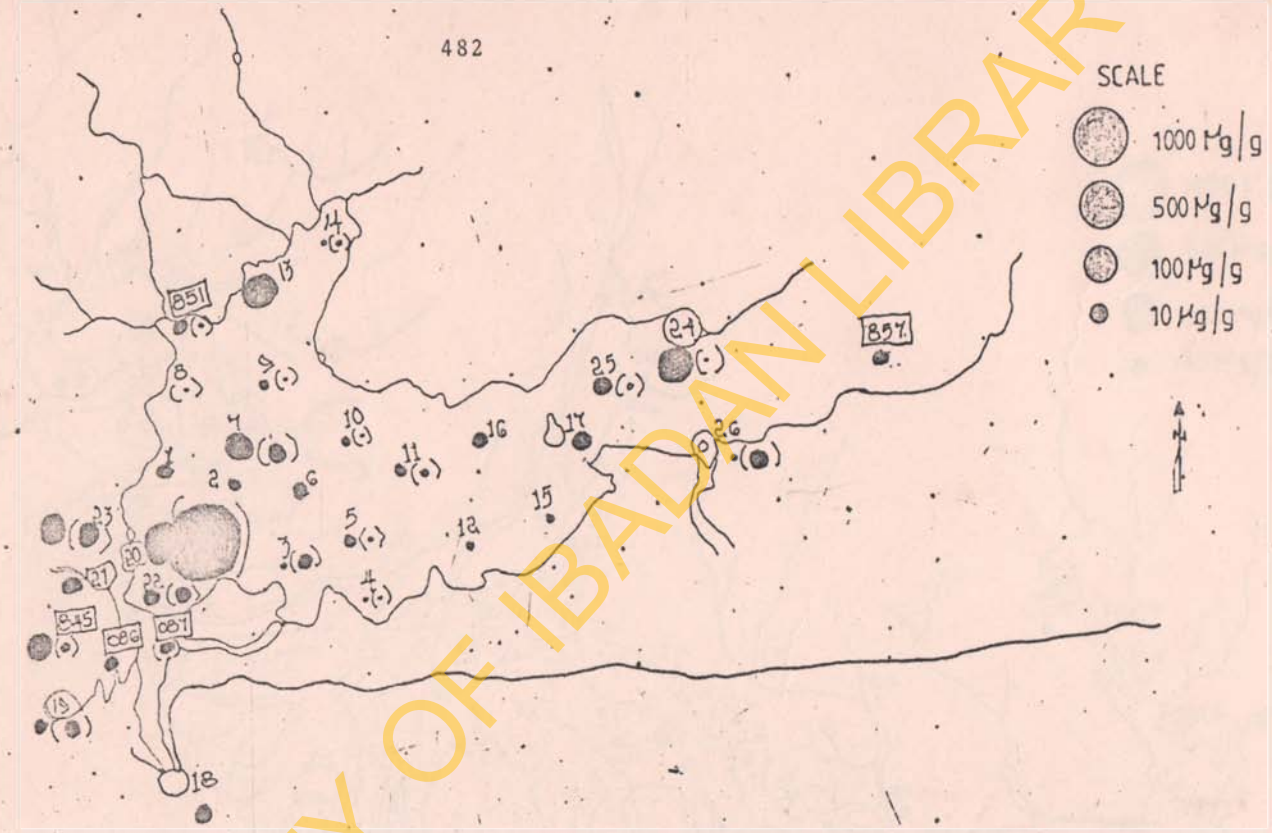


FIG 42:

TOTAL HYDROCARBON CONCENTRATION (BY G C) OF SEDIMENT SAMPLES AROUND LAGOS LAGOON. LOCATION NUMBERS ARE INDICATED WITH THE CONCENTRATIONS BELOW [JUNE 1985 CONCENTRATIONS IN BRACKET — (o)]. 1984 STATATIONS — □

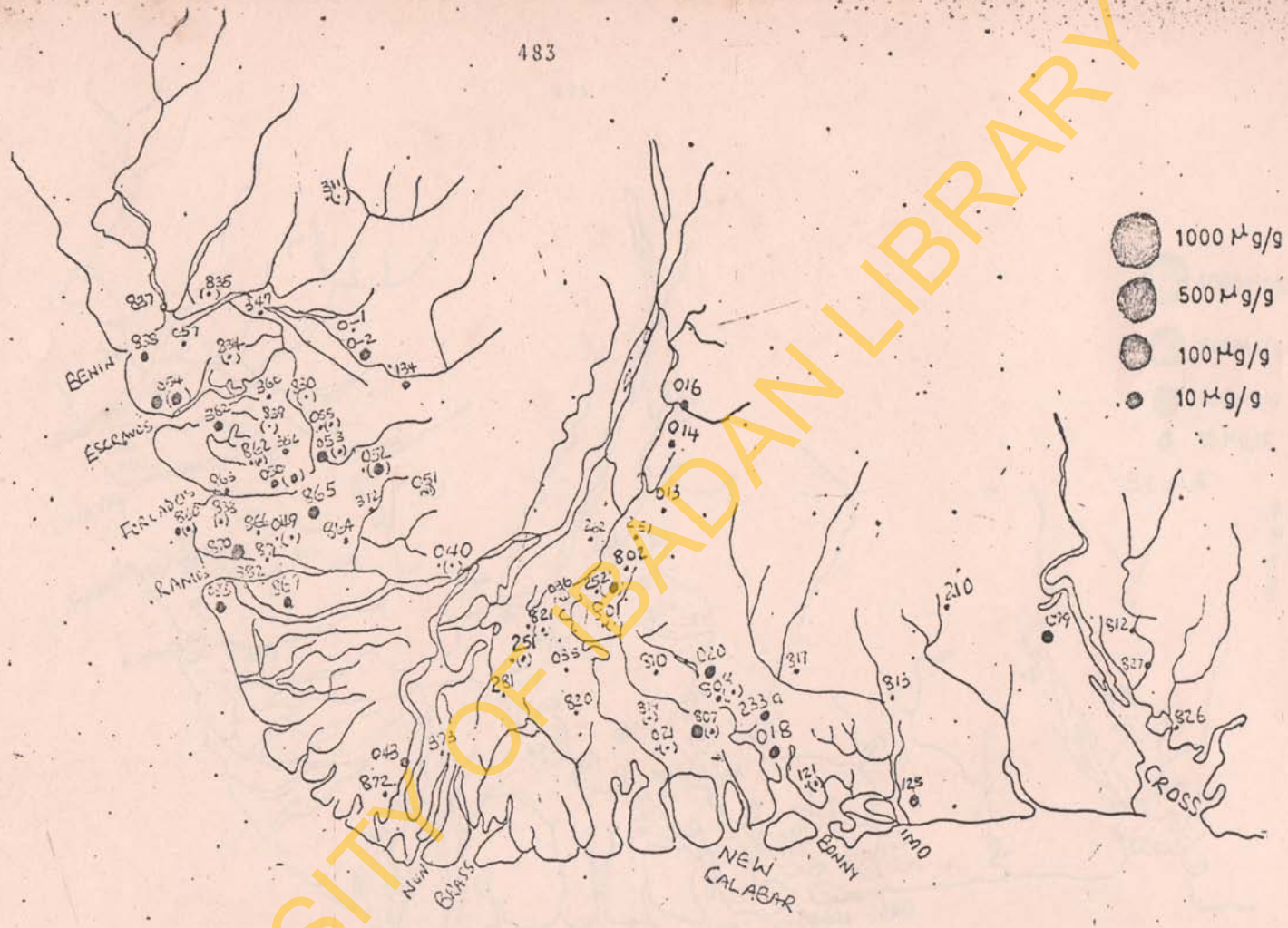


Fig. 43 : Aliphatic hydrocarbon concentration (By G C) of sediment samples in the Niger Delta. Location numbers are indicated with the concentrations below (1985 Concentrations in bracket — (•)).

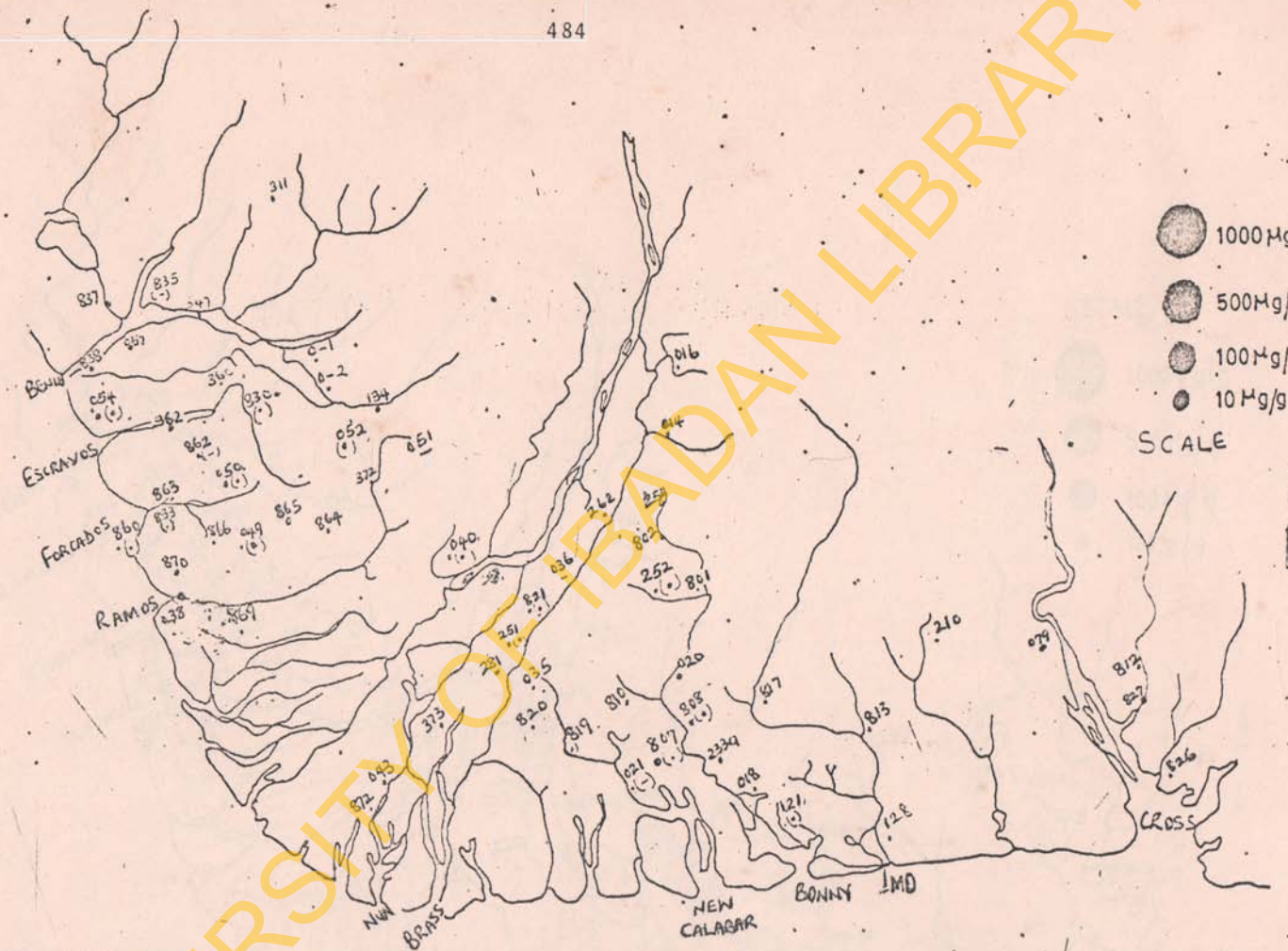


Fig. 44 :. Aromatic hydrocarbon concentration (By G C) of sediment samples in the Niger Delta. Location numbers are indicated with the concentrations below (1985 Concentrations in bracket – (·)).

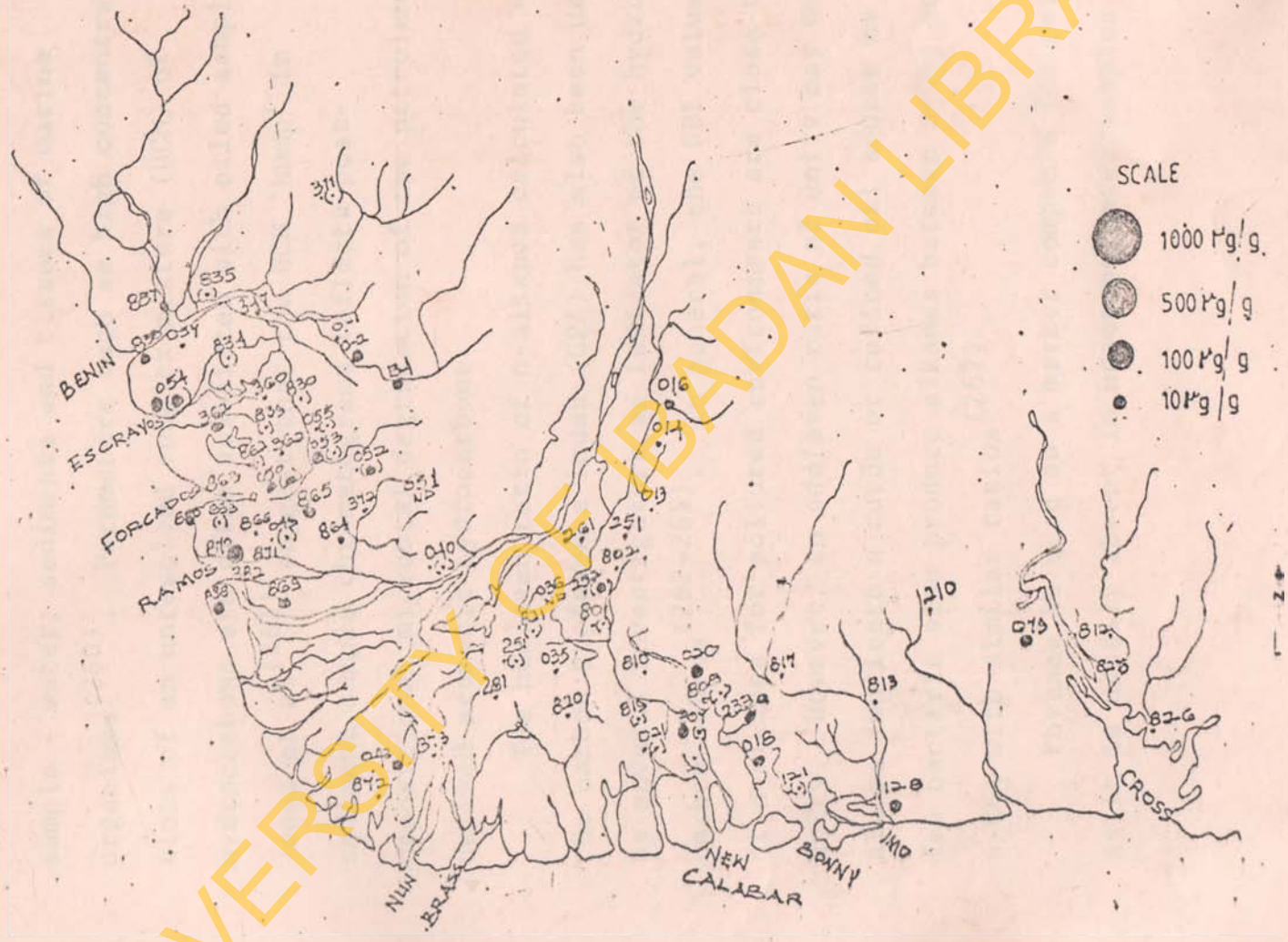


FIG. 45:

TOTAL HYDROCARBON CONCENTRATION [BY GC] OF SEDIMENT SAMPLES IN THE NIGER DELTA. LOCATION NUMBERS ARE INDICATED WITH THE CONCENTRATIONS BELOW [1985 CONCENTRATIONS IN BRACKET — (·)]

sample - water, sediments and tissues of marine organisms[260]. Parameters such as high concentrations of an unresolved complex mixture (UCM) of hydrocarbons are often associated with oiled samples. Jones et al[261] suggest that the UCM 'hump' in sediment sample chromatograms reflects post-depositional microbial degradation of the petroleum-derived aromatic hydrocarbons.

The odd/even ratio of n-alkanes calculated as the carbon preference index (CPI) has also been used by several investigators as indicator of the hydrocarbon source[262-265]. In general, the CPI values of n-alkanes for polluted environments are close to unity. However, an odd/even ratio of unity may not always implicate a curde or refined oil source as a few bacteria also produce alkanes between n-C_{25} and n-C_{33} with similar ratios[267].

Phytane is used as a marker compound for petroleum as it is usually absent in uncontaminated samples. The

pristane/phytane value is also indicator as a high value above unity indicate a greater contribution from the biogenic source.

The major constituents of the n-alkanes are also very useful as a source indicator.

Some of the parameters used in the source identification of the hydrocarbons in the sediment samples analysed are given in Tables 63-67.

In sediment samples from Lagos and Lekki Lagoons the CPI ($n\text{-}C_{14}$ - $n\text{-}C_{34}$) values calculated from the carbon chain length of C_{14} - C_{34}, ranged from 1.1 to 2.1. These values indicate the presence of petroleum in the environment. This point is strongly supported by the presence of phytane and low values of pr/ph in the samples. The level of deviation of these values from unity may be explained by the level of contribution from the C_{25} - C_{33} range, with odd-carbon numbered n-alkanes within this range contributing significantly to the CPI values.

The major constituents of hydrocarbons in the Lagos-Lekki Lagoons were mainly comprised of mixture of

odd- and even-carbon numbered compounds between n-alkanes in the major hydrocarbons for the sediment is 40%.

In the Delta area, the results also showed wide variations in the values of CPI calculated for the different points. There were some points that clearly indicated that contributions of n-alkanes were only from higher terrestrial plants (CPI > 3, Boehm 1982). Such points include Olagua creek/Benin river confluence (838), CPI - 6.6, unnamed creek off Jones creek (839) CPI 7.1, Bodo creek (121) CPI 3.2 and Uriyama river (812) CPI - 4.4. Phytane was totally absent in these samples and where present the concentrations were below 0.001 $\mu g g^{-1}$ and no UCM were observed.

Sediments from the Delta area also showed similar n-alkane distribution as was observed in Lagos samples, with the proportion of odd-carbon numbered n-alkanes in the major hydrocarbons as follows: Benin (60%), Escravos (60%), Forcados-Warri (56%), Ramos (40%), Nun-Ekole-Brass (65%), Orashi (61%), Bonny-New Calabar (63%), Imo (53%), Cross-River-Calabar (65%), Ibadan (50%).

The samples from Utorogu-Okpari river system and the Lagos Lagoon samples (1985) also exhibited wide variations in CPI values, phytane concentrations (where present) and the pr/ph values. The proportion of odd-carbon numbered n-alkanes in the major hydrocarbons of Okpari was 52%, Lagos Lagoon (1985) and Kaduna recorded 54% and 73% respectively.

All these data came out strongly to indicate that the n-alkanes were not purely from petroleum source alone but a mixture from both biogenic and petrogenic sources, that is, the complex assemblage of hydrocarbons in the Lagoon and river sediments indicates two sources, an input of terrestrial plant, ($n\text{-}C_{23}$ - C_{33} - alkanes from waxes of higher plants) which suggest a major sewage input, and input from fossil fuel (UCM). Urban storm-water and river run-off account for most of the input of petroleum hydrocarbons to the river systems.

More research work in the area of petroleum hydrocarbon pollution has also resulted in an index equation developed by Payne et al.,[268] and is known as Marine Oil Pollution Index (MOPI). This equation may be used to compare the relative magnitude of oil

contamination in a series of tissue or sediment samples. The equation has some component ratios put together, the component ratios are the UCM/resolved, even n-alkane/odd n-alkane, and branched hydrocarbon/n-alkane. These ratios can be used separately or in concert to characterize the hydrocarbon burdens in tissue or sediment samples. With each of the component ratios, higher numerical values typically correspond to greater petroleum hydrocarbon burdens. The equation is presented below with the index in Fig. 46.

$$MDPI = \ln\left[\left(\frac{UCM_H}{RES_H} + 1\right)\left(\frac{EVEN}{ODD} + 1\right)\left(\frac{\text{BRANCHED HYDROCARBONS}}{\text{n-ALKANES}} + 1\right)\left(RES_H + UCM_H + UCM_B\right)\right]$$

where

UCM_H = Unresolved complex mixture in the Hexane fraction in µg/g dry weight of sample.

RES_H = Total resolved hydrocarbons in the Hexane fraction in µg/g dry weight.

EVEN = Even numbered n-alkanes in µg/g dry weight

ODD = Odd numbered n-alkanes in µg/g dry weight

BRANCHED HC = Total resolved HC in the Hexane fraction minus total n-alkanes in Hexane fraction

UCM_B = Unresolved complex mixture in the hexane/dichloromethane fraction.

Interpretation: Subranges of MOPI values between -2 and 15 represent oil contamination levels corresponding to pristine (-2-1), biogenic (0-4), low-level petrogenic (2-6), moderately petrogenic (5-9), and heavily petrogenic (8-13) conditions respectively. Higher index values indicate progressively greater hydrocarbon contamination.

The MOPI values for individual samples are listed in Tables 63 - 67 while the range and mean values for the different river systems are listed in Table 62. The MOPI values can be used to further explain the trend indicated by other parameters earlier presented. The samples from Lagos-Lekki Lagoon showed high MOPI values from 6.6 to 8.6, this placed them in the moderately petrogenic zone on the MOP Index. The MOPI values for Lagos Lagoon are higher than the values obtained for the other river systems in the Niger Delta area. In ranking the other river systems in the Delta area, Ramos river system sediments MOPI values ranged from

-1.8 (Muri creek - 871) to 9.0 (Ramos estuary north east of Aghoro - 038), indicating low- or trace to moderately petrogenic contamination. Forcados-Warri and Nun-Ekole-Brass river systems MOPI values range between 0.4 - 7.6 and -0.6 - 7.8 respectively, placing them in the low- or trace-level petrogenic contamination. Benin, Escravos, Bonny-New Calabar and Imo river systems have MOPI values which place them in the Biogenic to low or trace-level petrogenic contamination zone, while Orashi and Cross River-Calabar river systems fall in the biogenic contamination zone. Cross River-Calabar river system was selected as the reference area in this study because of the absence of oil activity and low level of industrial activities in the area.

Kaduna samples recorded 0.5 - 5.8 MOPI values with a mean of 2.6 which place it in the biogenic to low- or trace-petrogenic contamination. Not surprisingly enough, the Agodi garden sample on Ogunpa in Ibadan recorded MOPI value of 7.8, input of oil from petrol garages, coca-cola factory, sewage etc., (moderately petrogenic). Asejire sample recorded 3.7 (biogenic to low- or trace-level petrogenic contamination.

On a point to point basis the heavily contaminated points are Berger/National Oil/Ijora (LS 20), Lever Brothers' discharge point (845), North of NNPC loading facility (847) all on Lagos Lagoon, Escravos Terminal (054), and Ramos estuary north east of Aghoro (038) showed values between 8.4 and 11.5 indicating heavily petrogenic contamination. Sediment samples from sampling sites near point sources of anthropogenic or near large settlements which were earlier identified as contaminated areas, also recorded higher values than sediment from more remote sites. As expected, sediment samples from Ogharife (O-2), Escravos Terminal (054), Warri river field (053), Chanomi creek at Egwa field (858), Forcados river above Obotebe (865), Orughene creek (870), and Bakana (807), all recorded MOPI values indicating moderately petrogenic contamination.

Stations like Muri creek (871), Mbiama (250), Bodo creek (121), Parrot Island (811) and Uriyama (812) showed values for pristine area. All the other stations recorded MOPI values which placed them under biogenic or low-trace petrogenic contamination.

TABLE 63: SOURCE CHARACTERIZATION OF HYDROCARBONS FOUND IN SEDIMENTS FROM LAGOS LAGOON, KADUNA AND DELTA AREA OF NIGERIA (concentration μg g-1)

SN	Station Code	n-alkane	% C_{25-33}	CPI_{14}^{34}	Pr	Ph	Pr/Ph	MOPI Value	Five Major Constituents %
		LAGOS - LEKKI LAGOONS							
1	086	0.28	81.2	1.4	0.001	0.001	0.67	6.6	C_{31}(18.6), C_{26}(13.5), C_{27}(12.4), C_{32}(11.8), C_{28}(09.8)
2	087	0.10	65.4	1.7	ND	0.001	-	7.5	C_{30}(14.7). C_{28}(13.6), C_{24}(12.5), C_{22}(10.3), C_{32}(10.0)
3	845	4.73	24.5	1.2	0.450	1.490	0.30	8.4	C_{20}(23.0), C_{19}(19.9 , C_{18}(12.6), C_{24}(06.8), C_{17}(04.6)
4	847	0.56	36.7	1.1	0.010	0.023	0.43	8.5	C_{22}(23.2), C_{19}(19.1), C_{26}(18.4), C_{25}(18.2), C_{21}(12.8)
5	851	0.45	66.0	1.6	0.002	0.007	0.29	7.3	C_{21}(22.8), C_{31}(14.3), C_{28}(13.3), C_{25}(10.7), C_{26}(08.7)
6	856	ND	ND	ND	ND	ND	ND	-	C (-), C (-), C ' (-), C (-), C (—)
7	857	0.16	37.0	2.1	0.001	0.002	0.50	8.6	C_{20}(27.5), C_{27}(11.5), C_{26}(10.9), C_{24}(08.4), C_{21}(08.1)
	$\bar{X}$	0.90	44.4	1.3	0:07	0.28	0.31	6.7	
	R	ND-	ND-	ND-	ND-	ND-	ND-	6.6	
		4.73	81.2	2.1	0.45		0.67	8.6	
2		BENIN RIVER SYSTEM							
8	057	1.20	20.5	1.1	0.043	0.059	0.73	1.6	C_{17}(27.9), C_{18}(25.3), C_{25}(08.5), C_{16}(07.7), C_{19}(05.7)
9	134	0.86	69.3	1.8	0.017	ND	-	3.6	C_{28}(15.1), C_{31}(14.1), C_{25}(12.7), C_{29}(08.8), C_{27}(08.2)
10	311	0.15	78.6	1.5	0.001	0.001	0.84	2.1	C_{31}(19.9), C_{27}(11.0), C_{25}(10.3), C_{29}(10.3), C_{26}(08.7)
11	347	0.06	77.8	1.8	0.001	0.001	0.68	3.6	C_{31}(21.3), C_{29}(14.9), C_{28}(11.3), C_{24}(10.1), C_{25}(09.6)
12	835	0.04	76.6	1.7	0.001	0.001	0.63	-2.7	C_{25}(58.8), C_{26}(17.8), C_{24}(07.1), C_{20}(05.6), C_{22}(05.3)
13	837	0.96	87.8	1.9	0.013	ND	-	3.0	C_{25}(70.5), C_{28}(04.6), C_{19}(04.3), C_{29}(03.2), C_{23}(02.4)
14	838	0.28	70.9	6.6	ND	ND	-	3.2	C_{26}(20.8), C_{28}(17.1), C_{31}(08.9), C_{27}(08.4), C_{21}(07.3)
15	0-1	0.28	26.1	1.4	0.001	0.001	2.03	-1.8	C_{20}(15.0), C_{23}(14.3), C_{22}(14.1), C_{21}(12.4), C_{24}(10.1)
16.	0-2	4.24	56.7	1.2	0.058	0.127	0.46	6.9	C_{24}(37.6), C_{27}(10.3), C_{20}(10.2), C_{19}(09.0), C_{21}(07.4)

TABLE 63: (contd.)

SN	Station Code	n-alkane	% C_{25-33}	CPI_{14}^{34}	Pr	Ph	Pr/Ph	MOPI Value	Five Major Constituents %
	3	ESCRAVOS RIVER SYSTEM							
17	054	0.47	62.4	1.0	0.003	0.002	1.50	9.7	C_{30}(16.1), C_{29}(13.6), C_{28}(12.9), C_{19}(08.5), C_{21}(07.6)
18	055	0.38	50.2	2.5	ND	ND	ND	2.7	C_{25}(30.4), C_{24}(24.6), C_{28}(13.2), C_{23}(10.1), C_{19}(07.8)
19	360	1.08	66.9	1.0	0.002	0.002	1.00	3.2	C_{26}(14.8), C_{27}(10.3), C_{24}(09.8), C_{28}(08.0), C_{31}(08.0)
20	362	0.33	71.1	1.2	0.003	0.008	0.38	6.1	C_{26}(18.3), C_{21}(13.5), C_{27}(13.0), C_{31}(09.4), C_{28}(09.4)
21	831	0.52	83.8	3.0	0.003	ND	-	0.7	C_{29}(24.0), C_{25}(22.2), C_{31}(11.8), C_{27}(08.3), C_{28}(06.6)
22	839	0.86	88.6	7.1	0.004	0.001	4.00	0.4	C_{25}(72.3), C_{26}(05.1), C_{24}(04.5), C_{31}(02.8), C_{27}(02.6)
	$\bar{X}$	0.61	70.5	2.6	0.01	0.01	1.15	3.8	
	R	0.32-1.08	50.2-88.6	1.0-7.1	ND-0.004	ND-0.01	ND-4.00	0.4-9.7	
	4	FORCADOS - WARRI RIVER SYSTEM							
23	040	0.08	75.7	2.1	0.001	0.001	0.63	0.4	C_{31}(18.0), C_{29}(15.1), C_{27}(13.5), C_{25}(12.0), C_{26}(06.8)
24	049	0.08	50.5	2.0	ND	ND	-	3.9	C_{24}(49.5), C_{25}(21.7), C_{26}(18.6), C_{27}(10.3), C (—)
25	050	10.03	39.8	1.8	ND	ND	-	6.2	C_{24}(53.8), C_{26}(20.2), C_{25}(11.5), C_{27}(08.1), C_{20}(02.7)
26	052	0.17	39.5	1.6	ND	ND	-	1.9	C_{23}(10.4), C_{24}(10.0), C_{22}(09.9), C_{25}(09.5), C_{19}(08.7)
27	053	0.73	74.7	1.5	0.002	0.004	0.50	7.6	C_{31}(21.4), C_{32}(20.4), C_{24}(13.8), C_{27}(10.4), C_{29}(10.0)
28	351	0.09	42.1	2.7	0.001	0.002	0.50	3.7	C_{21}(45.9), C_{26}(11.1), C_{29}(06.8), C_{25}(05.5), C_{27}(05.5)
29	352	2.62	29.3	1.1	0.491	0.668	0.74	3.5	C_{29}(17.3), C_{19}(16.2), C_{18}(12.8), C_{20}(12.1), C_{17}(11.7)
30	353	0.14	75.5	2.5	0.001	0.002	0.34	5.0	C_{26}(53.7), C_{21}(06.7), C_{27}(05.8), C_{24}(05.6), C_{25}(05.3)
31	372	1.15	65.2	2.2	0.001	0.001	0.63	3.1	C_{29}(26.5), C_{31}(12.8), C_{23}(09.2), C_{22}(08.7), C_{24}(08.3)
32	858	12.07	60.0	1.0	0.157	0.223	0.70	6.8	C_{24}(30.8), C_{25}(26.3), C_{26}(17.7), C_{27}(12.7), C_{19}(04.0)
33	860	0.21	64.4	1.0	0.001	0.001	0.67	5.7	C_{26}(39.5), C_{21}(11.1), C_{24}(11.0), C_{23}(07.2), C_{27}(06.2)
34	862	0.09	53.9	1.1	0.001	0,001	0.17	6.2	C_{26}(29.9), C_{24}(18.2), C_{25}(16.3), C_{21}(09.1), C_{23}(08.9)

TABLE 63: (contd.)

SN	Station Code	n-alkane	% C_{25-33}	CPI_{14}^{34}	Pr	Ph	Pr/Ph	MOPI Value	Five Major Constituents %
35	863	2.71	8.0	1.0	0.442	0.700	0.63	3.8	C_{16}(29.3), C_{17}(19.2), C_{19}(19.2), C_{20}(12.6), C_{18}(06.7)
36	864	0.25	83.9	1.0	0.001	0.001	0.67	5.2	C_{26}(47.2). C_{27}(09.6), C_{25}(08.6), C_{29}(07.1), C_{24}(05.5)
37	865	3.10	52.7	1.4	-	0.003	-	6.8	C_{24}(16.7), C_{22}(13.6), C_{32}(10.4), C_{26}(10.3), C_{27}(06.9)
38	866	0.06	47.0	2.0	0.001	0.001	0.33	5.3	C_{24}(31.8), C_{26}(20.7), C_{25}(17.1), C_{23}(11.6), C_{20}(05.1)
	$\bar{X}$	2.10	53.89	1.7	0.07	0.10	0.41	4.66	
	R	0.08	8.0	1.0	ND	ND	ND	0.4	
		-12.07	-83.9	-2.7	-0.49	-0.70	-0.74	-7.6	
5	RAMOS RIVER SYSTEM								
39	038	1.63	81.9	2.2	0.003	0.004	0.75	9.0	C_{26}(74.8), C_{27}(10.3), C_{25}(05.5), C_{20}(02.6), C_{22}(01.6)
40	382	2.52	21.9	1.2	0.067	0.108	0.62	3.5	C_{18}(27.2), C_{17} (14.7), C_{19}(13.6), C_{20}(09.0), C_{26}(08.3)
41	869	0.07	71.9	1.3	0.001	0.001	0.69	7.1	C_{29}(16.8), C_{28}(13.5), C_{27}(12.0), C_{26}(07.3), C_{30}(05.7)
42	870	2.35	12.4	1.0	0.372	0.835	0.45	8.3	C_{19}(19.4), C_{20}(18.6), C_{18}(13.6), C_{17}(13.5), C_{16}(08.6)
43	871	0.06	64.1	1.1	ND	ND	-	-1.8	C_{26}(32.4), C_{23}(24.0), C_{25}(22.9), C_{24}(11.9), C_{27}(04.6)
	$\bar{X}$	1.33	50.4	1.4	0.09	0.19	0.50	5.2	
	R	0.06	12.4	1.0	0.01	ND	ND	-1.8	
		-3.52	-81.9	-2.2	-0.37	-0.84	-0.25	-9.0	
6	NUN-EKOLE-BRASS RIVER SYSTEM								
44	036	-	-	-	-	-	-	-	C (—), C (—), C (—), C (—), C (—)
45	043	0.19	79.3	1.0	ND	ND	-	7.8	C_{28}(32.9), C_{25}(15.0), C_{20}(11.1), C_{31}(09.8), C_{29}(06.4)
46	281	0.20	49.1	1.8	0.017	0.021	0.81	-0.6	C_{17}(17.3), C_{28}(14.4), C_{31}(11.9), C_{20}(10.5), C_{29}(09.5)
47	872	0.07	76.4	1.0	ND	ND	-	6.2	C_{26}(21.5), C_{28}(14.3), C_{27}(13.9), C_{25}(09.0), C_{31}(08.3)
48	873	0.15	85.9	1.6	0.003	0.004	0.75	4.9	C_{27}(16.4), C_{29}(14.1), C_{31}(13.6), C_{28}(12.7), C_{25}(12.4)
	$\bar{X}$	0.15	58.1	1.1	0.01	0.01	0.31	3.7	

TABLE 63: (contd.)

SN	Station Code	n-alkane	% C_{25-33}	CPI_{14}^{34}	Pr	Ph	Pr/Ph	MOPI Value	Five Major Constituents %
	R	ND- 0.20	ND-85.9	ND -1.8	ND -0.02	ND-0.02	ND-0.81 -0.6	-7.8	
7	ORASHI RIVER SYSTEM								
49	012	0.16	30.0	1.0	0.002	-	-	-1.0	C_{23} (17.4), C_{22} (15.1), C_{24} (13.2), C_{21} (10.5), C_{25} (09.1)
50	013	0.20	75.1	1.7	0.001	0.001	0.62	2.5	C_{31} (13.6), C_{27} (13.2), C_{29} (12.9), C_{26} (12.4), C_{25} (12.3)
51	014	1.09	35.9	1.5	0.033	0.044	0.75	3.3	C_{31} (13.0), C_{21} (11.5), C_{19} (09.9), C_{22} (09.3), C_{20} (08.7)
52	016	0.42	46.9	1.3	0.012	0.001	12.00	4.2	C_{22} (12.2), C_{23} (11.4), C_{21} (10.1), C_{28} (09.3), C_{25} (08.7)
53	021	0.21	74.6	1.0	0.001	0.002	0.36	5.8	C_{26} (35.4), C_{24} (13.3), C_{31} (12.6), C_{27} (08.4), C_{29} (07.2)
54	035	0.56	73.0	1.9	0.001	0.001	0.63	-0.1	C_{29} (20.2), C_{25} (16.5), C_{28} (14.0), C_{31} (12.1), C_{20} (06.6)
55	250	0.13	56.3	1.0	0.001	0.001	0.63	-1.3	C_{28} (19.3), C_{25} (14.2), C_{19} (08.7), C_{27} (07.6), C_{24} (07.5)
56	251	0.07	63.0	1.3	0.001	0.001	0.63	4.2	C_{31} (13.4); C_{25} (13.4), C_{24} (09.6), C_{19} (09.0), C_{29} (09.0)
57	252	1.95	90.1	1.2	0.002	0.002	0.63	1.3	C_{28} (36.3), C_{29} (25.8), C_{31} (12.4), C_{27} (07.6), C_{25} (03.4)
58	262	0.32	39.2	1.2	0.001	0.001	0.64	1.7	C_{23} (16.3), C_{24} (14.6), C_{22} (14.5), C_{25} (13.0), C_{21} (08.3)
59	801	0.44	40.6	1.1	-	-	-	1.9	C_{24} (13.2), C_{23} (10.6), C_{22} (08.9), C_{19} (08.0), C_{26} (06.7)
60	802	0.25	58.3	1.8	0.005	0.007	0.71	3.4	C_{31} (21.5), C_{19} (11.1), C_{32} (09.5), C_{20} (08.4), C_{28} (06.3)
61	821	0.16	63.5	1.7	0.001	0.001	1.00	-1.4	C_{29} (17.9), C_{31} (17.4), C_{28} (15.1), C_{19} (07.0), C_{20} (06.1)
62	824	0.02	81.9	1.0	ND	ND	-	-3.2	C_{28} (21.3), C_{25} (16.9), C_{29} (14.1), C_{31} (11.3), C_{20} (10.7)
	$\bar{X}$	0.43	39.2	1.3	4.36	0.01	1.33	1.52	
	R	0.02	30.0	1.0	ND	ND	ND	-3.2	
		-1.95	-90.1	-1.9	-0.03	-0.04	-12.00	-5.8	
8	BONNY - NEW CALABAR RIVER SYSTEM								
63	020	0.48	69.2	1.6	ND	ND	-	1.6	C_{26} (16.4), C_{25} (14.2), C_{27} (12.5), C_{21} (08.5), C_{19} (06.8)
64	121	0.24	91.0	3.2	0.001	0.001	1.25	-0.9	C_{32} (25.9), C_{31} (20.9), C_{29} (17.2), C_{27} (11.0), C_{25} (07.3)
65	233a	0.55	71.2	2.3	0.004	0.003	1.33	5.0	C_{29} (19.5), C_{28} (18.6), C_{25} (11.2), C_{26} (06.8), C_{24} (06.4)
66	807	0.95	81.1	1.8	0.002	0.003	0.67	6.2	C_{27} (42.8), C_{28} (10.7), C_{25} (07.9), C_{26} (06.1), C_{24} (05.5)
67	808	0.45	67.0	1.1	0.002	0.002	1.00	2.8	C_{29} (21.1), C_{26} (19.8), C_{19} (09.2), C_{28} (08.3), C_{27} (07.2)

TABLE 63: (contd.)

SN	Station Code	n-alkane	% C_{25-33}	CPI_{14}^{34}	Pr	Ph	Pr/Ph	MOPI Value	Five Major Constituents %
68	810	0.87	69.8	1.8	-	-	-	0.4	C_{29} (18.5), C_{31} (11.4), C_{32} (11.0), C_{25} (10.4), C_{22} (07.6)
	$\bar{X}$	0.59	74.9	2.0	1.5	1.5	0.71	2.5	
		0.24	67.0	1.1	ND	ND	ND	-0.9	
	R	-0.95	-91.0	-3.2	-0.004	-0.003	-1.33	-6.2	
9	IMO ROVER SYSTEM								
69	128	0.18	56.6	1.0	0.001	0.001	1.20	6.8	C_{32} (12.4), C_{18} (11.8), C_{31} (11.5), C_{17} (08.4), C_{25} (07.1)
70	813	0.27	32.9	1.1	-	-	-	2.6	C_{23} (17.2), C_{22} (17.1), C_{24} (14.4), C_{21} (18.8), C_{25} (10.1)
71	817	0.24	39.2	1.2	0.001	0.001	0.64	-0.3	C_{23} (16.2), C_{22} (13.3), C_{24} (13.3), C_{25} (11.9), C_{26} (08.3)
	$\bar{X}$	0.23	42.9	1.1	0.001	0.001	0.61	3.03	
		0.18	32.9	1.0	ND	ND	ND	-0.3	
	R	-0.27	-56.6	-1.2	-0.001	-0.001	-1.20	-6.8	
10	CROSS RIVER - CALABAR RIVER SYSTEM								
72	071	0.47	26.5	1.3	0.038	0.045	0.84	3.3	C_{17} (20.4), C_{19} (13.6), C_{21} (11.0), C_{26} (10.5), C_{20} (09.7)
73	811	0.22	76.0	2.0	0.002	0.002	1.00	-1.1	C_{29} (18.4), C_{25} (17.2), C_{31} (11.5), C_{27} (10.3), C_{28} (18.7)
74	812	0.46	73.4	4.4	0.002	0.001	2.51	-0.6	C_{25} (49.1), C_{21} (16.4), C_{27} (08.2), C_{24} (05.6), C_{28} (04.5)
75	827	0.44	83.2	1.0	0.001	0.001	0.67	4.3	C_{26} (24.6), C_{29} (11.4), C_{31} (10.7), C_{27} (08.4), C_{32} (07.5)
	$\bar{X}$	0.40	64.8	2.2	0.01	0.01	1.26	1.5	
		0.22	26.5	1.0	0.01	10.01	0.67	-1.1	
	R	-0.47	-83.2	-4.4	-0.04	-0.045	-2.51	-4.3	
11	KADUNA RIVER SYSTEM								
76	141A	0.25	70.9	1.0	0.001	0.001	0.68	5.8	C_{26} (21.0), C_{31} (12.1), C_{27} (09.6), C_{25} (07.9), C_{28} (06.9)
77	843	0.15	68.3	1.2	0.001	0.001	0.62	1.4	C_{28} (17.5), C_{31} (13.9), C_{25} (12.7), C_{29} (11.5), C_{19} (06.9)
78	844	0.52	86.6	2.7	0.001	0.001	0.63	0.5	C_{31} (25.1), C_{29} (20.7), C_{27} (12.7), C_{28} (12.3), C_{25} (07.9)
	$\bar{X}$	0.31	75.3	1.6	0.001	0.001	0.64	2.6	

TABLE 63 (contd.)

SN	Station Code	n-alkane	% C_{25-33}	CPI_{14}^{34}	Pr	Ph	Pr/Ph	MOPI Value	Five Major Constituents %
	R	0.15 -0.52	68.3 -86.6	1.0 -2.7	0.001	0.001	0.62 -0.68	0.5 -5.8	
12	IBADAN								
	Ag-1	0.67	17.8	1.0	-	-	-	3.8	C_{20}(15.0), C_{19}(12.0), C_{17}(10.5), C_{18}(09.0), C_{22}(09.0)
	AS-2	1.78	69.7	1.6	-	-	-	2.8	C_{31}(12.6), C_{29}(11.4), C_{32}(10.8), C_{28}(09.6), C_{25}(07.8)
	$\bar{X}$	1.23	43.8	1.3	-	-	-	3.3	
	R	0.67 -1.78	17.8 -69.7	1.0 -1.6	- -	- -	- -	2.8 -3.8	

TABLE 64: SOURCE CHARACTERIZATION OF HYDROCARBONS FOUND IN SEDIMENTS FROM UTOROGU SWAMP AND OKPARI RIVER (OCTOBER 1984)

SN	Station Code	n-alkane	% C_{25-33}	CPI_{14}^{34}	Pr	Ph	Pr/Ph	MOPI Value	Five Major Constituents %				
1	B	24.07	76.9	1.0	-	-		7.2	C_{26}(25.9),	C_{25}(25.4),	C_{24}(22.4),	C_{27}(15.7),	C_{28}(09.9)
2	D	1.59	66.8	1.2	0.031	0.079	0.39	10.2	C_{26}(48.2),	C_{24}(13.6),	C_{22}(08.8),	C_{29}(07.0),	C_{27}(05.8)
3	E	2.96	96.4	1.6	-	-	-	7.2	C_{26}(72.2),	C_{25}(07.6),	C_{32}(05.3),	C_{27}(04.5),	C_{28}(02.6)
4	G-1	4.48	83.8	1.0	-	-	-	6.7	C_{26}(22.7),	C_{27}(13.4),	C_{28}(12.4),	C_{25}(11.2),	C_{29}(10.2)
5	G-2	4.42	75.7	1.4	0.008	0.002	4.00	6.8	C_{26}(30.1),	C_{27}(10.0),	C_{25}(09.4),	C_{28}(09.3),	C_{29}(07.1)
6	G-3	4.92	67.3	1.6	-	-	-	7.4	C_{26}(33.3),	C_{24}(31.5),	C_{25}(18.4),	C_{27}(15.0),	C_{20}(01.2)
7	G-4	9.21	68.7	1.4	-	-	-	8.4	C_{26}(28.9),	C_{24}(24.9),	C_{25}(20.7),	C_{27}(17.1),	C_{20}(04.9)
	$\bar{X}$	1.38	76.4	1.3	0.006	0.012	0.63	7.7					
	R	1.59	66.8	1.0	ND	ND	ND	6.7					
		-24.07	-96.4	-1.6	-0.031	-0.079	-0.63	-10.2					
8	R-1	3.02	87.9	4.5	0.060	0.028	2.14	8.2	C_{25}(46.1),	C_{31}(13.4),	C_{32}(10.9),	C_{27}(10.0),	C_{24}(06.4)
9	R-2	1.73	75.0	1.9	0.017	0.039	0.44	9.9	C_{31}(24.5),	C_{26}(12.0),	C_{21}(08.8),	C_{25}(08.8),	C_{29}(08.1)
10	R-3	0.97	74.2	1.6	-	-	-	9.6	C_{25}(34.9),	C_{26}(14.6),	C_{27}(12.5),	C_{28}(08.9),	C_{20}(07.9)
	$\bar{X}$	1.91	79.0	2.7	0.03	0.02	0.86	9.2					
	R	0.97	74.2	1.6	ND	ND	ND	8.2					
		-3.2	-87.9	-4.5	-0.06	-0.04	-2.14	-9.9					
11	O-1	11.97	83.0	1.4	0.079	0.057	1.39	8.7	C_{26}(35.5),	C_{27}(12.7),	C_{31}(10.5),	C_{29}(09.2),	C_{24}(08.7)
12	O-2	9.28	93.4	1.5	0.193	0.042	4.60	8.8	C_{26}(34.3),	C_{25}(26.1),	C_{27}(15.0),	C_{29}(13.0),	C_{24}(03.2)
13	N	0.33	50.5	1.7	0.015	0.006	2.50	9.2	C_{25}(19.4),	C_{23}(13.8),	C_{27}(13.5),	C_{26}(13.2),	C_{21}(11.7)
14	V	0.72	85.6	1.3	-	-	-	7.2	C_{26}(59.4),	C_{25}(08.6),	C_{24}(06.0),	C_{29}(06.0),	C_{22}(06.5)
15	K-1	1.32	69.6	1.4	-	-	-	5.6	C_{26}(39.6),	C_{24}(30.4),	C_{27}(15.1),	C_{25}(15.9),	C_{28}(01.1)
16	K-3	16.22	46.5	1.3	-	-	-	8.7	C_{24}(48.8),	C_{26}(23.1),	C_{25}(11.8),	C_{27}(09.1),	C_{28}(02.5)
17	T	4.89	86.1	1.4	-	-	-	8.5	C_{26}(43.7),	C_{25}(11.9),	C_{31}(10.9),	C_{27}(06.3),	C_{32}(06.1)
18	U	0.73	66.6	1.6	0.012	0.014	0.86	8.9	C_{27}(16.8),	C_{26}(12.1),	C_{25}(11.9),	C_{31}(09.8),	C_{20}(07.2)
	$\bar{X}$	5.68	72.7	1.5	0.04	0.01	1.17	8.2					
	R	0.33	46.5	1.3	ND	ND	ND	5.6					
		-16.22	-93.4	-1.7	-0.19	-0.057	-4.60	-9.2					

TABLE 65: SOURCE CHARACTERIZATION OF HYDROCARBONS FOUND IN SEDIMENT FROM UTOROGU SWAMP AND OKPARI RIVER (FEBRUARY 1985)

SN	Station Code	n-alkane	% C_{25-33}	CPI $^{34}_{14}$	Pr	Ph	Pr/Ph	MOPI Value	Five Major Constituents %
1	B_{1-1}	0.053	9.7	1.1	0.003	ND	_	8.2	C_{22} (61.9), C_{21} (22.8), C_{27} (05.5), C_{31} (04.2), C_{20} (02.3)
2	B_{2-1}	0.085	90.3	1.4	0.001	0.001	1.52	4.5	C_{33} (40.9), C_{32} (22.1), C_{27} (09.0), C_{31} (06.3), C_{30} (04.5)
3	C-1	ND	-	-	-	-	-	4.5	C (-), C (-), C (-), C (-), C (-)
4	D	0.055	87.7	1.0	0.001	0.001	3.50	4.8	C_{32} (39.5), C_{25} (12.4), C_{27} (08.0), C_{30} (08.0), C_{26} (07.9)
5	E_{1-1}	0.362	74.4	2.9	0.001	0.001	0.51	3.5	C_{25} (42.2), C_{27} (16.9), C_{23} (16.6), C_{33} (09.8), C_{21} (06.0)
6	E_{2-1}	0.255	62.8	1.5	0.001	0.001	1.35	5.3	C_{21} (19.2), C_{33} (14.0), C_{27} (10.1), C_{30} (07.5), C_{29} (07.1)
7	F	ND	-	-	-	-	-	-	
	$\bar{X}$	0.12	46.4	1.1	0.001	0.001	0.98	4.4	
	R	ND-0.036	ND-90.3	ND-2.9	ND-0.003	ND-0.001	ND-3.50	ND-8.2	
8	R-1	ND	-	-	-	-	-	-	
9	R-2	0.175	57.0	0.5	0.001	0.001	4.04	2.4	C_{24} (41.7), C_{25} (26.8), C_{26} (14.9), C (-), C_{28} (03.0)
10	0-1	0.011	91.1	1.0	0.001	0.001	1.35	2.6	C_{27} (29.6), C_{32} (16.7), C_{30} (14.4), C_{28} (11.1), C_{29} (06.2)
11	0-2	0.009	92.5	1.4	0.001	0.001	2.69	1.4	C_{29} (16.4), C_{27} (14.0), C_{31} (13.7), C_{26} (13.5), C_{28} (09.8)
12	0-3	0.378	04.1	3.3	-	-	-	2.7	C_{26} (56.8), C_{32} (18.1), C_{23} (15.7), C_{31} (05.5), C_{30} (03.0)
13	N	0.029	98.3	2.8	0.001	-	-	3.3	C_{25} (39.2), C_{32} (16.6), C_{28} (12.3), C_{27} (07.3), C_{24} (07.3)
14	K-2	0.034	67.1	1.2	0.001	0.001	4.00	3.1	C_{28} (10.3), C_{26} (10.2), C_{19} (10.2), C_{21} (10.0), C_{25} (10.0)
15	T	1.134	32.5	1.4	-	-	-	4.7	C_{21} (40.9), C_{22} (21.0), C_{26} (17.5), C_{25} (08.4), C_{27} (06.7)
	$\bar{X}$	0.27	77.6	1.85	0.001	0.001	1.34	3.0	
	R	0.01-1.13	32.5-98.3	1.0-3.3	ND-0.001	ND-0.001	ND-4.00	1.4-4.7	

TABLE 66: SOURCE CHARACTERIZATION HYDROCARBONS FOUND IN SEDIMENT FROM UTOROGU SWAMP AND OKPARI RIVER (1985 JUNE)

SN	Station Code	n-alkane	% C_{25-33}	CPI $^{34}_{14}$	Pr	Ph	Pr/Ph	MOPI Value	Five Major Constituents %				
		IMPACTED SWAMP											
1	A-1	0.13	85.0	1.0	ND	0.01	-	4.3	C_{26}(19.6),	C_{27}(13.1),	C_{29}(11.3),	C_{28}(11.3),	C_{25}(10.3)
2	B	1.01	70.8	1.2	0.01	0.01	1.0	9.1	C_{25}(12.1),	C_{26}(11.0),	C_{27}(10.3),	C_{30}(09.4),	C_{31}(09.3)
3	C-2	0.09	73.4	1.0	ND	ND	-	5.2	C_{25}(31.7),	C_{24}(26.6),	C_{26}(18.0),	C_{27}(12.7),	C_{29}(06.4)
4	C-3	0.24	47.4	0.6	ND	ND	-	5.2	C_{24}(45.6),	C_{25}(27.3),	C_{26}(07.7),	C_{23}(04.7),	C_{28}(04.0)
5	D	2.94	49.9	0.6	ND	ND	-	5.8	C_{24}(48.6),	C_{25}(28.0),	C_{26}(12.9),	C_{27}(07.7),	C_{20}(01.3)
6	F	2.40	46.9	0.4	ND	ND	-	6.2	C_{24}(50.2),	C_{25}(22.3),	C_{26}(17.4),	C_{27}(07.2),	C_{20}(02.9)
7	G-1	1.16	82.2	1.1	ND	ND	-	6.0	C_{27}(14.9),	C_{26}(14.4),	C_{28}(12.7),	C_{25}(11.3),	C_{29}(10.7)
		UP STREAM											
8	P	0.06	67.5	0.5	ND	ND	-	5.3	C_{26}(14.4),	C_{27}(12.7),	C_{25}(11.8),	C_{28}(11.5),	C_{24}(10.2)
9	R-1	0.02	89.0	1.5	ND	ND	-	3.0	C_{25}(37.5),	C_{24}(33.6),	C_{26}(11.9),	C_{27}(08.8),	C_{28}(01.8)
10	R-2	3.27	84.5	0.5	0.01	0.01	0.2	6.0	C_{24}(41.8),	C_{25}(31.5),	C_{26}(16.5),	C_{27}(05.5),	C_{20}(01.8)
11	R-3	0.25	44.0	0.9	ND	ND	-	4.8	C_{30}(25.4),	C_{32}(24.6),	C_{31}(17.4),	C_{26}(14.3),	C_{28}(07.3)

TABLE 66 (contd.)

SN	Station Code	n-alkane	% C_{25-33}	CPI_{14}^{34}	Pr	Ph	Pr/Ph	MOPI Value	Five Major Constituents %				
	DOWNSTREAM												
12	0-1	0.28	69.8	1.0	ND	ND	-	7.3	C_{27}(30.4),	C_{24}(19.9),	C_{25}(18.0),	C_{26}(11.3),	C_{30}(03.1)
13	0-2	2.45	70.5	1.8	ND	ND	-	5.7	C_{31}(12.5),	C_{27}(12.2),	C_{20}(10.6),	C_{29}(10.1),	C_{25}(09.2)
14	0-3	1.73	81.4	1.6	0.01	0.01	0.7	6.1	C_{24}(20.2),	C_{25}(19.2),	C_{29}(11.3),	C_{26}(09.1),	C_{27}(06.8)
15	N	0.55	68.9	1.2	0.01	0.01	0.4	7.5	C_{25}(52.5),	C_{24}(22.0),	C_{26}(09.0),	C_{27}(08.1),	C_{20}(03.2)
16	V	4.65	72.5	1.0	0.01	0.03	0.1	6.8	C_{29}(19.4),	C_{27}(14.2),	C_{26}(12.4),	C_{31}(09.9),	C_{25}(08.8)
17	M	1.39	70.2	1.4	0.01	0.01	0.2	5.5	C_{26}(42.9),	C_{25}(11.0),	C_{27}(09.6),	C_{24}(08.6),	C_{20}(05.9)
18	K-2	0.95	93.5	0.4	ND	ND	-	5.9	C_{25}(33.6),	C_{26}(29.0),	C_{27}(09.6),	C_{29}(09.6),	C_{28}(06.8)
19	T	3.29	73.4	1.9	0.04	0.14	0.3	7.2	C_{24}(38.2),	C_{25}(19.8),	C_{26}(16.6),	C_{19}(15.4),	C_{27}(07.7)
20	U	3.15	81.4	0.7	0.01	0.01	0.7	6.3	C_{25}(51.3),	C_{24}(19.3),	C_{26}(09.9),	C_{27}(06.9),	C_{19}(03.4)
21	J-1	0.45	75.3	1.0	ND	0.01	-	5.2	C_{25}(35.3),	C_{24}(25.1),	C_{26}(20.5),	C_{27}(12.0),	C_{28}(04.0)
22	J-2	2.14	63.5	1.0	0.01	0.02	0.1	5.4	C_{26}(29.3),	C_{27}(14.0),	C_{25}(13.6),	C_{29}(09.2),	C_{28}(08.1)
23	J-3	9.51	55.4	0.6	0.01	0.01	1.0	6.4	C_{26}(32.7),	C_{25}(11.8),	C_{27}(11.0),	C_{24}(08.0),	C_{28}(07.6)

TABLE 67: SOURCE CHARACTERIZATION OF HYDROCARBONS FOUND IN SEDIMENTS FROM LAGOS LAGOON (1985)

SN	Station Code	n-alkane	% C_{25-33}	CPI^{34}_{14}	Pr	Ph	Pr/Ph	MOPI Value	Five Major Constituents %				
1	LS-1	1.928	23.7	5.1	-	-	-	5.9	C_{23}(22.8),	C_{19}(22.4),	C_{25}(12.0),	C_{17}(11.6),	C_{27}(08.2)
2	LS-2	0.404	52.5	1.4	-	-	-	6.4	C_{21}(27.2),	C_{20}(12.4),	C_{27}(11.8),	C_{26}(10.4),	C_{30}(09.4)
3	LS-3	0.306	41.8	1.0	-	-	-	-0.4	C_{24}(29.4),	C_{23}(20.2),	C_{26}(15.6),	C_{25}(13.8),	C_{27}(12.4)
4	LS-32	4.590	67.1	0.8	0.036	0.040	0.90	6.6	C_{18}(11.0),	C_{30}(10.0),	C_{31}(10.0),	C_{28}(09.6),	C_{20}(09.4)
5	LS-4	0.912	20.8	7.1	-	-	-	0.5	C_{19}(31.6),	C_{23}(30.8),	C_{21}(10.8),	C_{25}(08.6),	C_{28}(05.8)
6	LS-42	1.722	74.8	1.2	-	-	-	0.2	C_{25}(28.4),	C_{20}(19.0),	C_{29}(15.0),	C_{28}(11.4),	C_{30}(11.2)
7	LS-5	1.034	63.1	1.2	-	0.008	-	6.3	C_{25}(20.0),	C_{28}(14.4),	C_{30}(11.2),	C_{23}(10.4),	C_{29}(09,8)
8	LS-52	0.162	80.2	-	-	-	-	-1.6	C_{31}(33.3),	C_{29}(25.9),	C_{27}(21.0),	C_{21}(12.3),	C_{18}(07.4)
9	LS-6	1.310	64.7	1.4	-	-	-	6.0	C_{29}(21.7),	C_{25}(20.6),	C_{20}(17.3),	C_{28}(13.0),	C_{26}(07.2)
10	LS-62	ND	ND	ND	ND	ND	ND	-	C (—),	C (—),	C (—),	C (—),	C (—)
11	LS-7	7.150	33.2	1.2	0.158	0.088	1.80	8.4	C_{25}(33.8),	C_{18} (20.6),	C_{20} (18.3),	C_{21}(12.0),	C_{19}(06.5)
12	LS-72	33.816	-	-	-	-	-	5.1	C_{24}(52.8),	C_{22}(16.8),	C_{20}(15.7),	C_{23}(08.2),	C_{21}(06.4)
13	LS-82	1.400	65.4	1.3	-	-	-	1.2	C_{29}(28.4),	C_{25}(10.7),	C_{28}(10.1),	C_{24}(10.4),	C_{26} (09.7)
14	LS-92	4.168	82.4	1.9	-	-	-	2.1	C_{25}(40.3),	C_{28}(14.7),	C_{21}(07.9),	C_{26}(07.9),	C_{27}(06.9)
15	LS-10	4.820	78.5	-	-	-	-	1.9	C_{25}(78.5),	C_{22}(07.9),	C_{23}(07.3),	C_{20}(06.4),	C (—)
16	LS-102	0.406	92.1	-	-	-	-	-0.7	C_{29}(74.4),	C_{26}(08.9),	C_{27}(08.9),	C_{20}(07.9),	C (—)
17	LS-11	0.818	54.3	1.6	0.002	0.036	0.06	5.9	C_{21}(26.9),	C_{25}(13.9),	C_{28}(11.5),	C_{32}(10.3),	C_{31}(09.0)

TABLE 67 (contd.)

SN	Station Code	n-alkane	% C_{25-33}	CPI^{34}_{14}	Pr	Ph	Pr/Ph	MOPI Value	Five Major Constituents %				
18	LS-112	1.076	43.1	1.3	-	-	-	4.8	C_{21} (22.1),	C_{28} (10.8),	C_{32} (08.4),	C_{29} (07.6),	C_{30} (07.4)
19	LS-12	0.438	53.9	0.9	-	-	-	0.1	C_{20} (15.1),	C_{25} (12.3),	C_{26} (11.9),	C_{21} (10.0),	C_{27} (10.0)
20	LS-132	40.222	91.6	6.7	-	-	-	7.1	C_{25} (42.8),	C_{29} (39.4),	C_{28} (05.4),	C_{26} (03.2),	C_{18} (00.9)
21	LS-14	1.446	100.0	1.0	-	-	-	1.2	C_{28} (20.7),	C_{29} (18.3),	C_{30} (14.8),	C_{27} (13.1),	C_{26} (10.1)
22	LS-142	0.186	100.0	-	-	-	-	-1.7	C_{29} ,	C_{25} ,			
23	LS-15	3.880	11.4	2.8	-	-	-	1.7	C_{19} 46.9),	C_{20} (13.9),	C_{23} (10.0),	C_{21} (06.9),	C_{18} (06.5)
24	LS-16	6.682	64.8	1.8	-	-	-	5.2	C_{25} (50.3),	C_{20} (23.7),	C_{29} (10.5),	C_{24} (09.7),	C_{28} (02.2)
25	LS-17	0.652	50.7	1.5	0.012	0.028	0.43	7.7	C_{25} (13.8),	C_{26} (13.5),	C_{19} (12.9),	C_{23} (12.0),	C_{27} (10.1)
26	LS-173	0.552	86.2	1.2	-	-	-	-2.0	C_{31} (18.8),	C_{29} (14.9),	C_{32} (13.8),	C_{30} (12.0),	C_{27} (09.1)
27	LS-175	0.254	73.2	1.2	-	-	-	-0.8	C_{29} (16.5),	C_{20} (13.4),	C_{27} (11.8),	C_{26} (11.0),	C_{30} (09.4)
28	LS-18	1.706	36.1	2.1	-	-	-	6.2	C_{21} (36.5),	C_{25} (12.7),	C_{24} (09.0),	C_{20} (08.2),	C_{23} (08.0)
29	LS-184	ND	ND	-	-	-	-	-					
30	LS-185	6.180	18.4	1.8	0.034	0.072	0.47	2.8	C_{21} (24.0),	C_{25} (18.0),	C_{18} (15.0),	C_{19} (12.0),	C_{22} (08.8)
31	LS-19	14.940	84.0	-	-	-	-	1.5	C_{25} (50.4),	C_{29} (33.5),	C_{23} (16.0)		
32	LS-191	5.152	10.2	-	0.288	0.490	0.59	8.1	C_{20} (25.7),	C_{18} (21.3),	C_{21} (14.1),	C_{19} (13.6),	C_{25} (11.0)
33	LS-192	0.722	28.0	1.2	-	-	-	7.3	C_{18} (31.6),	C_{19} (19.4),	C_{25} (17.7),	C_{21} (16.9),	C_{26} (10.2)
34	LS-195	4.094	74.1	-	-	-	-	-1.6	C_{25} (54.9),	C_{29} (19.2),	C_{22} (19.1),	C_{19} (06.8),	
35	LS-20	28.842	15.9	1.0	0.140	0.466	0.30	9.9	C_{20} (26.9),	C_{21} (21.2),	C_{19} (11.7),	C_{22} (07.7),	C_{26} (07.6)
36	LS-201	8.454	34.1	1.6	0.572	0.316	1.81	10.3	C_{25} (37.6),	C_{22} (20.4),	C_{21} (12.7),	C_{18} (07.7),	C_{20} (07.6)
37	LS-202	126.978	-	1.6	9.848	12.546	0.78	11.5	C_{19} (24.2),	C_{17} (16.4),	C_{15} (16.1),	C_{24} (09.5),	C_{20} (08.6)

TABLE 67 (contd.)

SN	Station Code	n-alkane	% C_{25-33}	CPI_{14}^{34}	Pr	Ph	Pr/Ph	MOPI Value	Five Major Constituents %				
38	LS-203	0.402	41.8	0.5	-	-	-	7.1	C_{18} (34.8),	C_{17} (13.9),	C_{16} (09.5),	C_{28} (07.0),	C_{29} (06.5)
39	LS-205	11.232	16.5	1.6	0.282	0.362	0.78	10.0	C_{25} (17.4),	C_{18} (16.2),	C_{21} (15.5),	C_{17} (14.1),	C_{22} (10.6)
40	LS-21	2.282	20.3	3.3	-	0.146	-	6.1	C_{19} (39.4),	C_{25} (17.4),	C_{21} (16.9),	C_{22} (07.8),	C_{20} (05.5)
41	LS-22	1:120	26.5	1.9	0.012	0.032	0.38	6.5	C_{21} (23.4),	C_{25} (14.1),	C_{19} (12.9),	C_{18} (11.1),	C_{20} (08.0)
42	LS-22	1.364	41.5	1.4	0.010	0.020	0:50	6.1	C_{31} (13.8),	C_{19} (11.6),	C_{20} (08.9),	C_{21} (08.5),	C_{22} (08.1)
43	LS-225	0.256	28.9	1.8	-	-	-	0.3	C_{31} (33.6),	C_{20} (28.9),	C_{25} (13.3),	C_{21} (08.6),	C_{27} (08.6)
44	LS-23	6.154	41.6	2.5	0.388	0.616	0.63	8.0	C_{25} (43.1),	C_{21} (14.2),	C_{18} (12.3),	C_{19} (08.2),	C_{26} (05.3)
45	LS-232	40.164	89.0	2.4	0.280	0.668	0.42	7.4	C_{25} (41.4),	C_{27} (07.2),	C_{26} (07.1),	C_{32} (05.8),	C_{31} (05.6)
46	LS-233	ND	-	ND	ND	ND	ND	-					
47	LS-234	6.854	89.3	14.1	-	-	-	8.3	C_{29} (53.9),	C_{25} (35.5),	C_{22} (05.1),	C_{23} (04.1),	C_{24} (01.3)
48	LS-24	16.270	31.4	2.4	0.070	0.154	0.45	7.5	C_{21} (40.5),	C_{19} (11.7),	C_{31} (07.6),	C_{20} (07.3),	C_{32} (07.1)
49	LS-242	0.170	-	0.7	-	-	-	2.0	C_{24} (37.6),	C_{19} (17.6),	C_{20} (17.6),	C_{21} (12.9),	C_{23} (09.4)
50	LS-245	4.394	56.3	1.8	0.008	0.026	0.31	6.8	C_{25} (23.9),	C_{21} (12.7),	C_{20} (07.9),	C_{24} (07.7),	C_{32} (07.3)
51	LS-251	20.170	47.8	1.0	-	-	-	5.0	C_{21} (41.6),	C_{26} (29.6),	C_{32} (06.6),	C_{22} (03.8),	C_{28} (03.2)
52	LS-252	0.756	33.5	0.9	-	-	-	1.6	C_{24} (27.2),	C_{23} (25.1),	C_{25} (18.0),	C_{22} (11.6),	C_{20} (10.8)
53	LS-26	2.378	68.9	1.6	-	-	-	1.2	C_{23} (25.3),	C_{27} (24.4),	C_{26} (23.6),	C_{30} (06.8),	C_{22} (05.8)
54	LS-262	36.116	72.2	5.9	-	-	-	4.7	C_{29} (48.3),	C_{25} (20.8),	C_{23} (13.4),	C_{20} (08.0),	C_{22} (04.9)

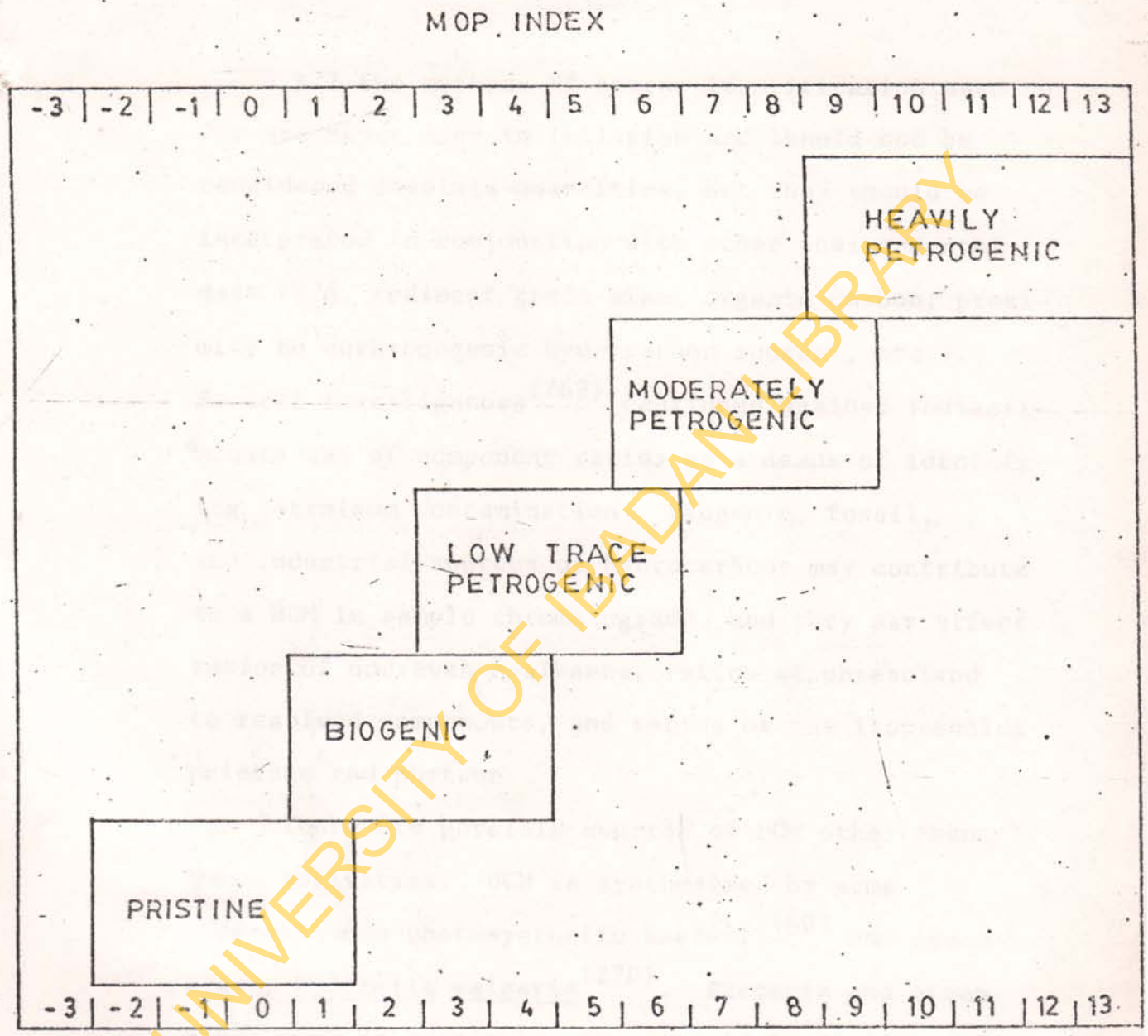


Fig. 46: Description of the Marine Oil Pollution Index (MOPI)

All the methods of source identification used so far are never used in isolation and should not be considered absolute quantities, but they should be interpreted in conjunction with other environmental data (e.g. sediment grain size, organic carbon, proximity to anthropogenic hydrocarbon sources, etc.). Several investigators[269] cautioned against indiscriminate use of component ratios as a means of identifying petroleum contamination. Biogenic, fossil, and industrial sources of hydrocarbons may contribute to a UCM in sample chromatograms, and they may affect ratios of odd:even n-alkanes, ratios of unresolved to resolved components, and ratios of the isoprenoids pristane and phytane.

There are possible sources of UCM other than human activities. UCM is synthesized by some anaerobic non-photosynthetic bacteria[60] and green algae, Chlorella valgaris[270]. Bacteria and green algae such as chlorella spp. are widely distributed in natural environments. Page et al.[271] reported that biodegraded mangrove

leaves contributed to the UCM in extracts of near shore sediments that had not been contaminated with fresh petroleum. In addition, unburned coal is a potential source of resolvable lower molecular weight n-alkanes, isoprenoid, and aromatic compounds, as well as polycyclic aromatic hydrocarbons (PAHs), to marine sediments and deposit feeding organisms (272-274).

Contribution from these and other soruces can be differentiated by high resolution GC and GC/MS techniques.

The chromatograms shown below illustrate some common features in petroleum hydrocarbon analysis. Figs. 47 and 48 are examples of petroleum contaminated sediments, with a smooth curve distribution of n-alkanes (no odd-carbon predominance) and the presence of UCM, they are both weathered but Fig. 48 showed oil heavily weathered than Fig. 47. A mixture of petrogenic and biogenic is indicated in Fig. 49, while Fig. 50 showed a bimodal distribution of n-alkanes, which suggest a mixed input having a varied boiling point range

The distribution pattern of the hydrocarbon of some representative sediment samples are shown in Fig. 51. Some of the samples showed the presence of pristane and phytane. The samples showed different stages of weathering - disappearance of the lower hydrocarbons and majority of the samples have prominent peaks between C_{21} and C_{29}.

Under hydrocarbon source characterization, it is pertinent to mention that the petroleum hydrocarbons present in some of the samples may be from different sources such as crude and refined oils. The results of individual hydrocarbons present in the analyzed samples made it difficult to have an easy classification because most of the samples have carbon range between n-C_{17} and n-C_{34}. Crude oils have n-alkanes covering this range while refined oils have hydrocarbons over narrower boiling ranges than the corresponding crude oils as dictated by refining processes. This point is clearly expressed in the chromatograms of some Nigerian crude and refined oils shown below Figs. 52–60.

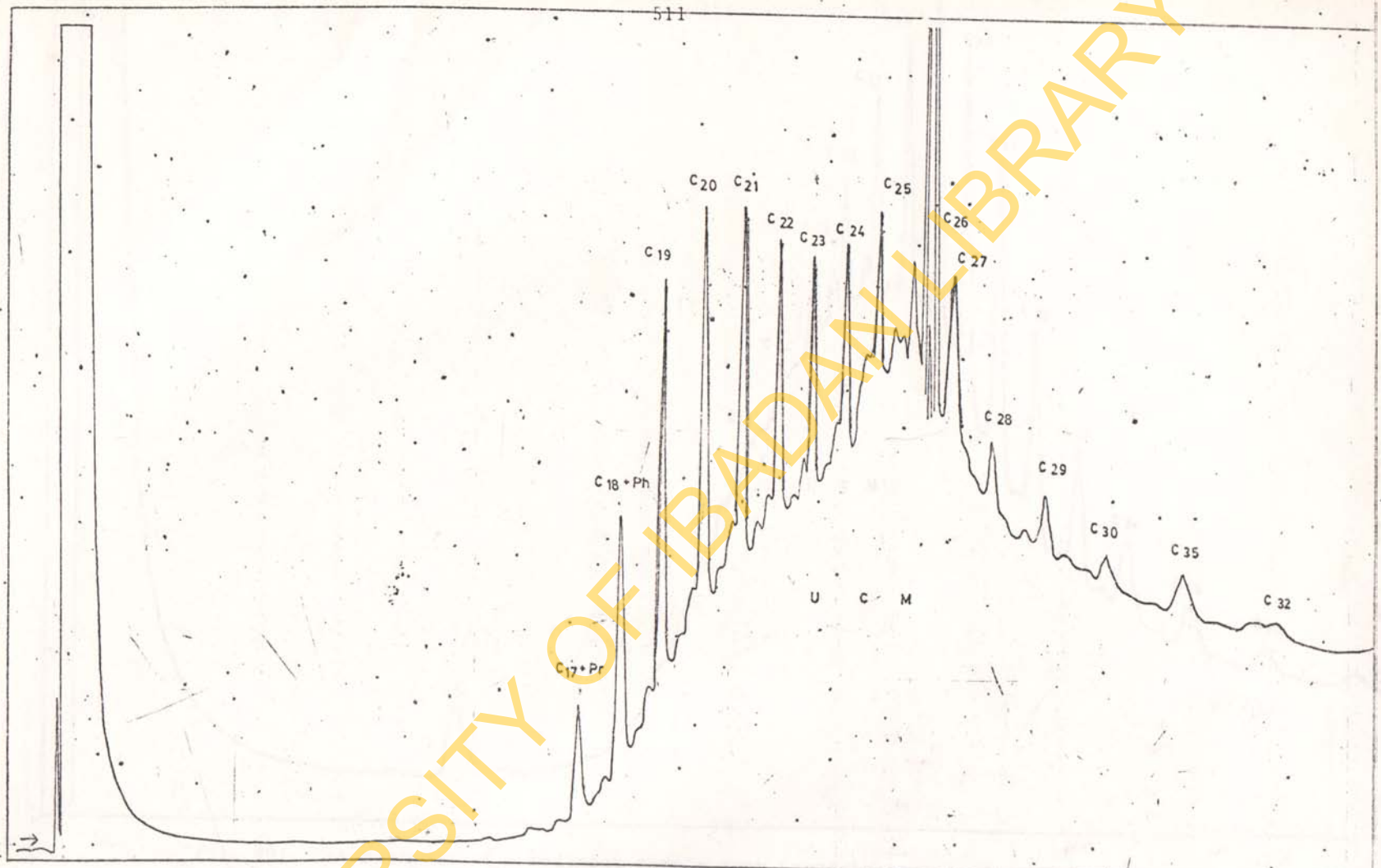


Fig. 47: Chromatogram of a petroleum contaminated sediment sample from Ogharife effluent channel.

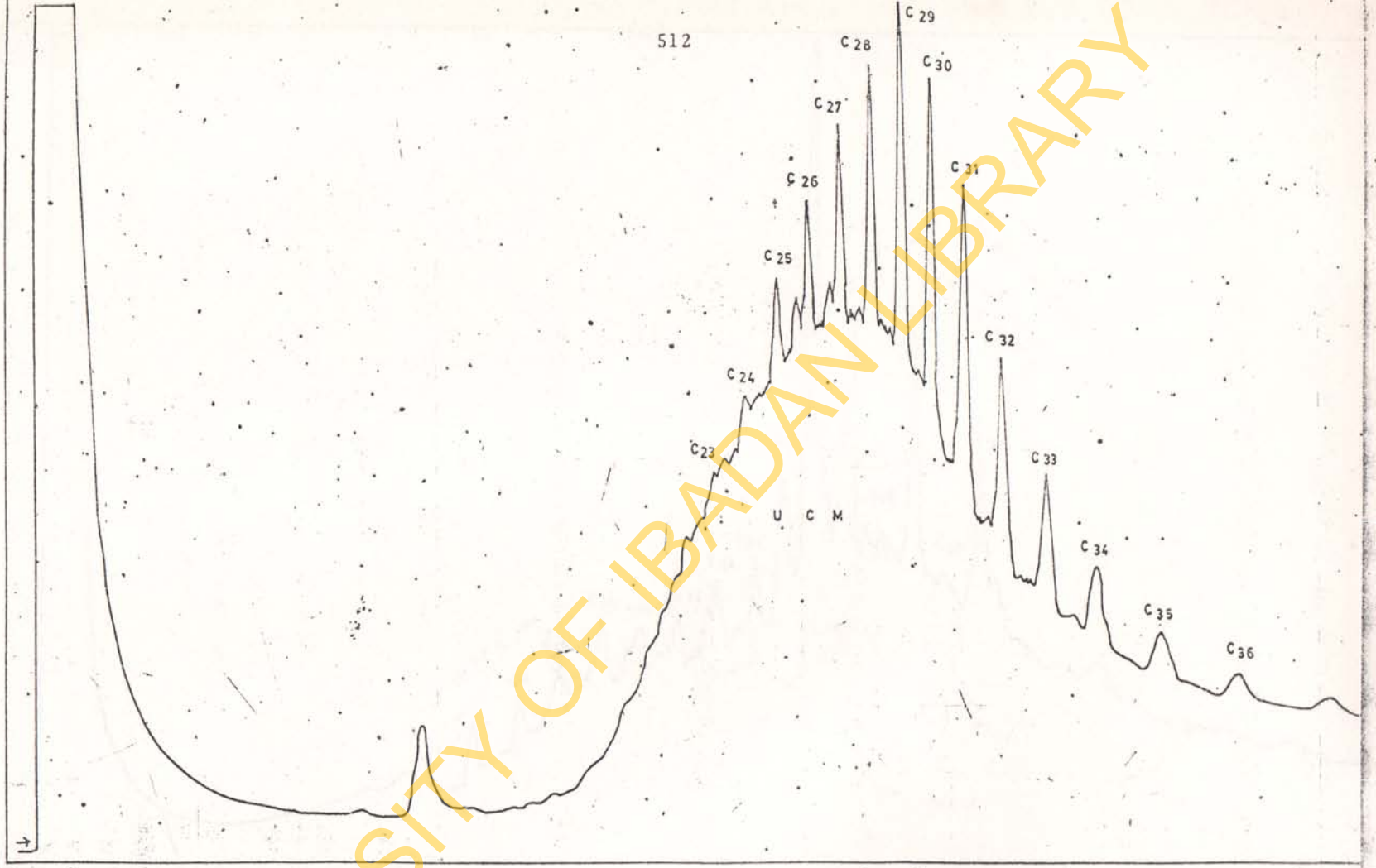


Fig. 48: Chromatogram of a sediment sample from Lagos lagoon showing weathered oil.

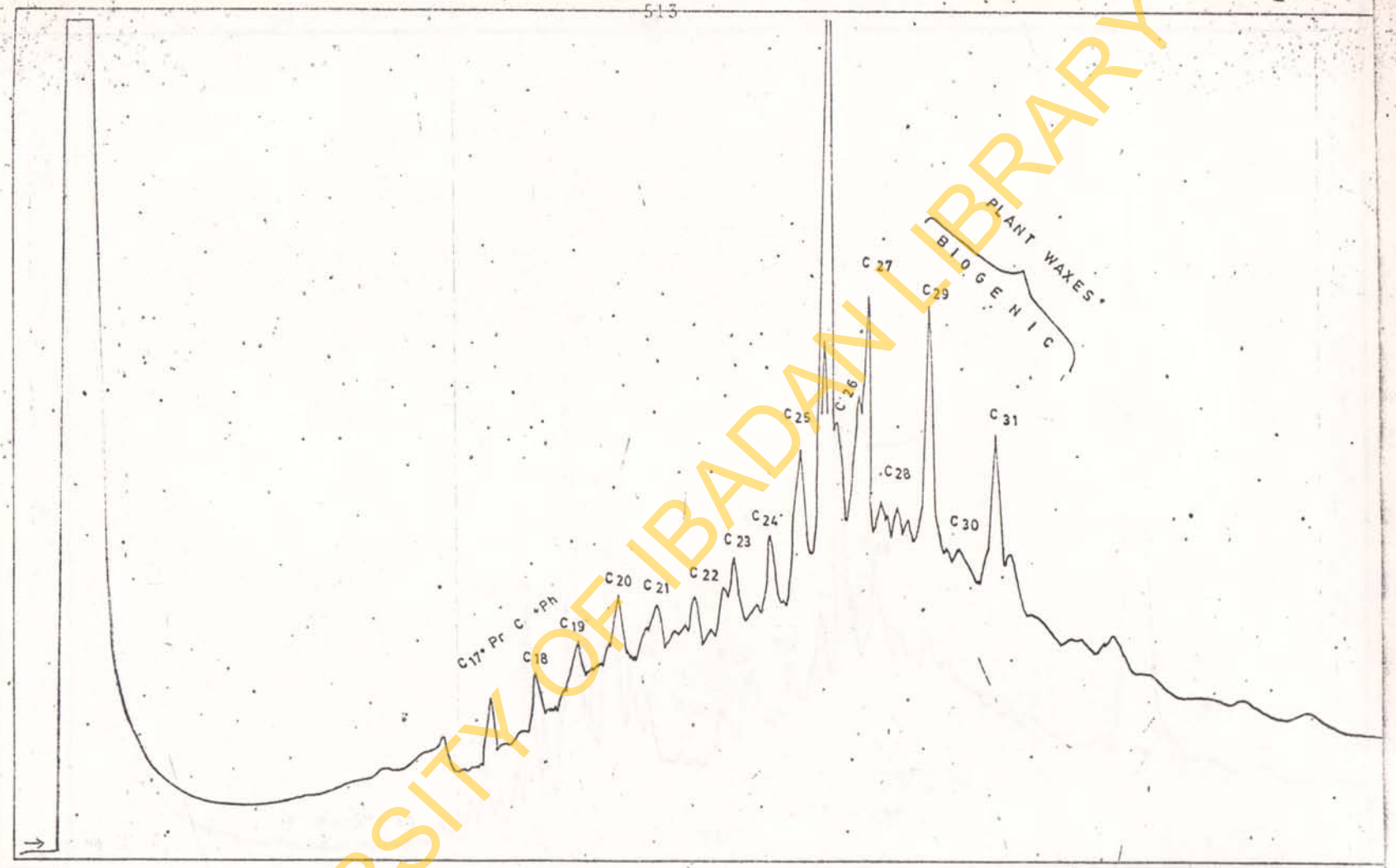


Fig. 49: Chromatogram of sediment sample showing the presence of both petrogenic and biogenic n-alkanes.

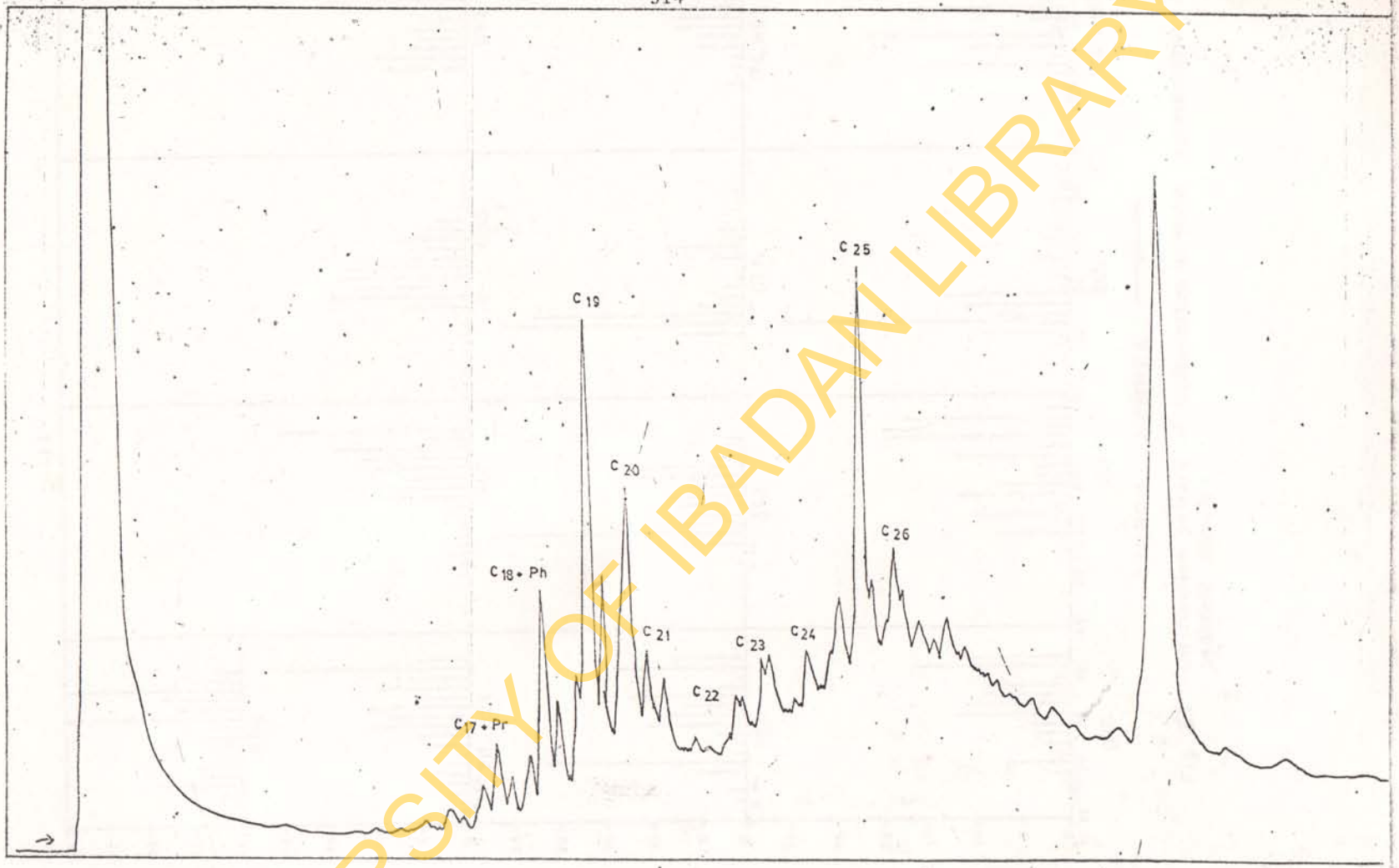


Fig. 50: Chromatogram showing a bimodal distribution of n-alkanes.

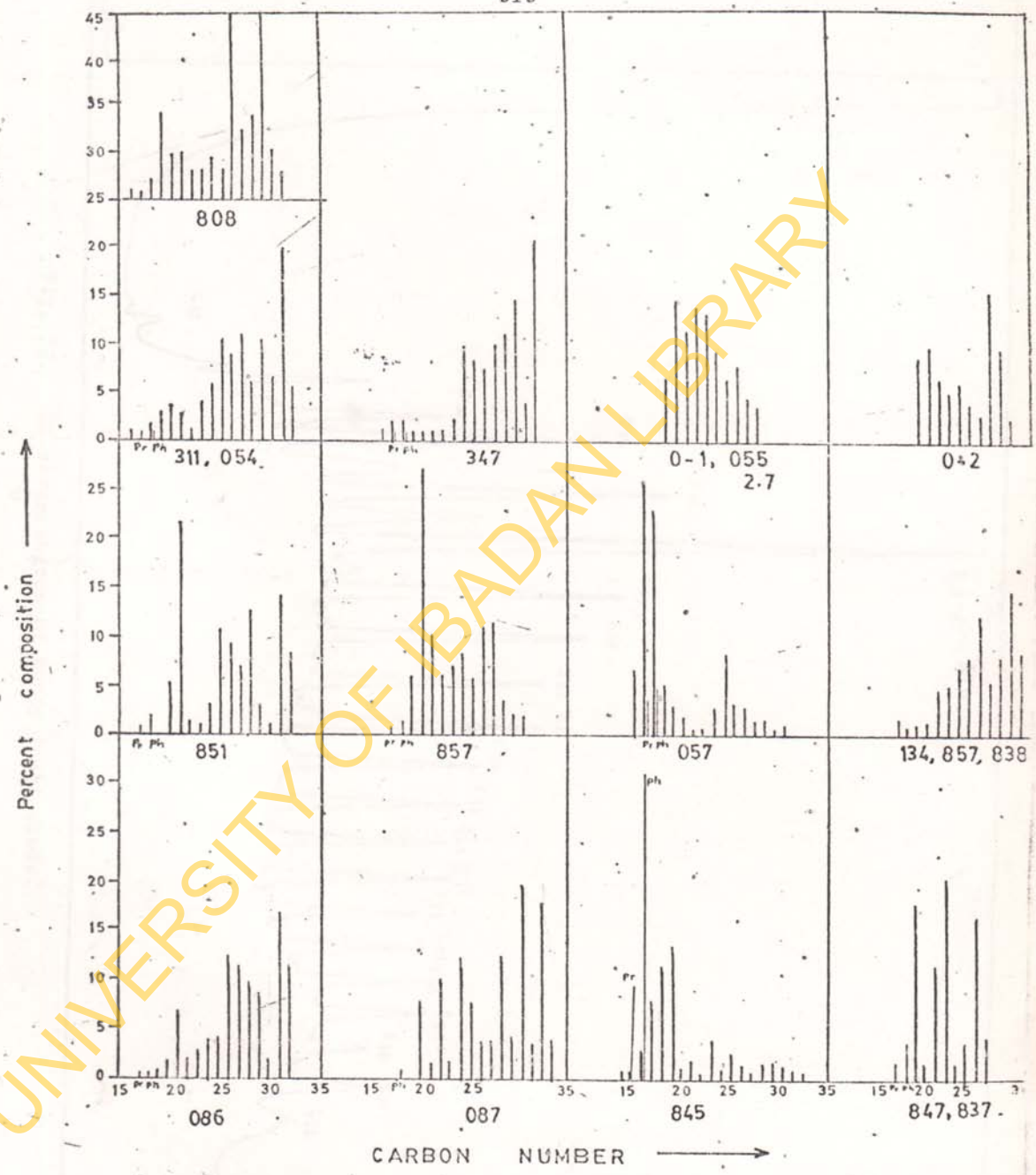


Fig. 51: Distribution pattern of hydrocarbon in some representative sediment samples

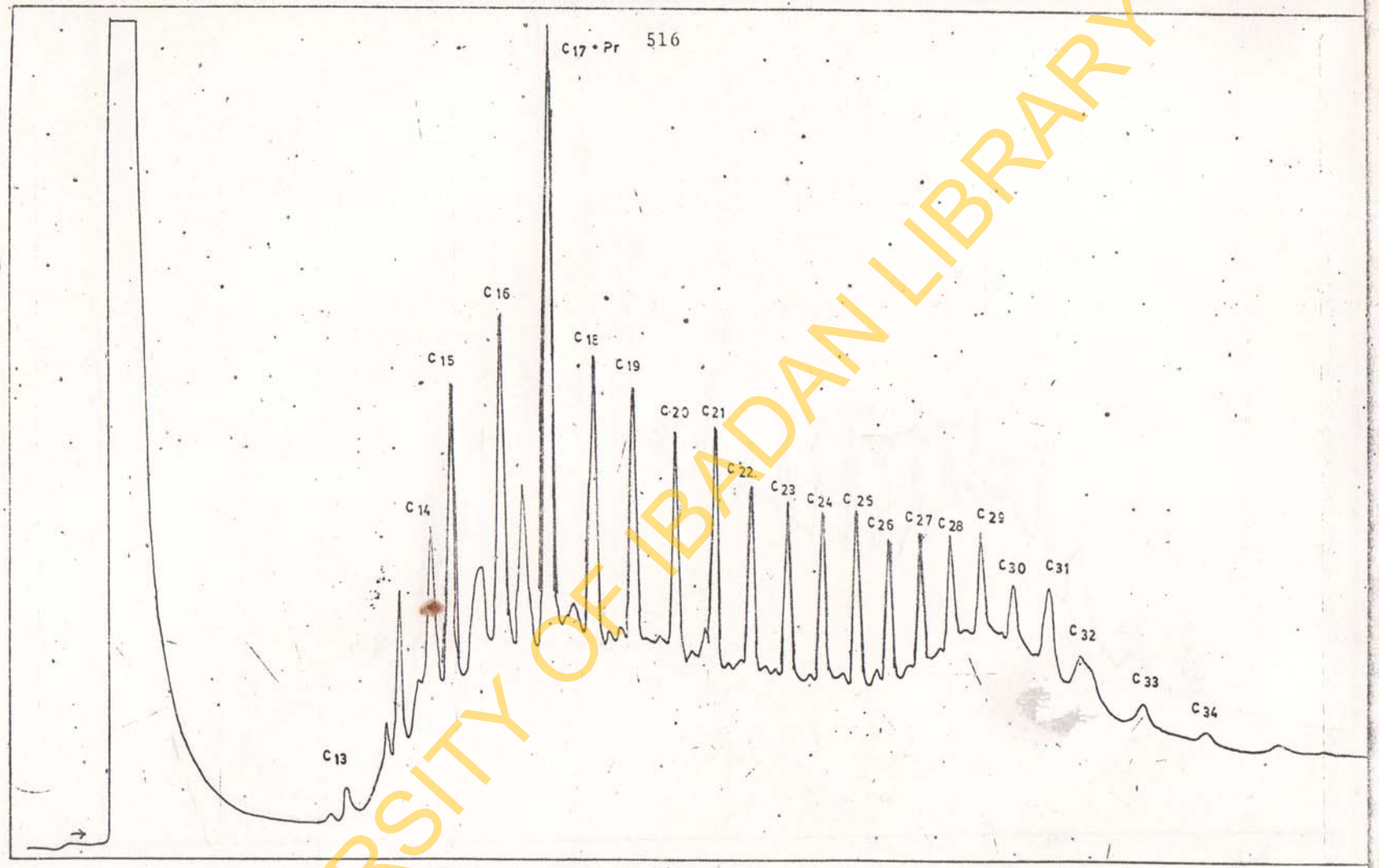


Fig. 52: GC chromatogram of Bonny light crude.

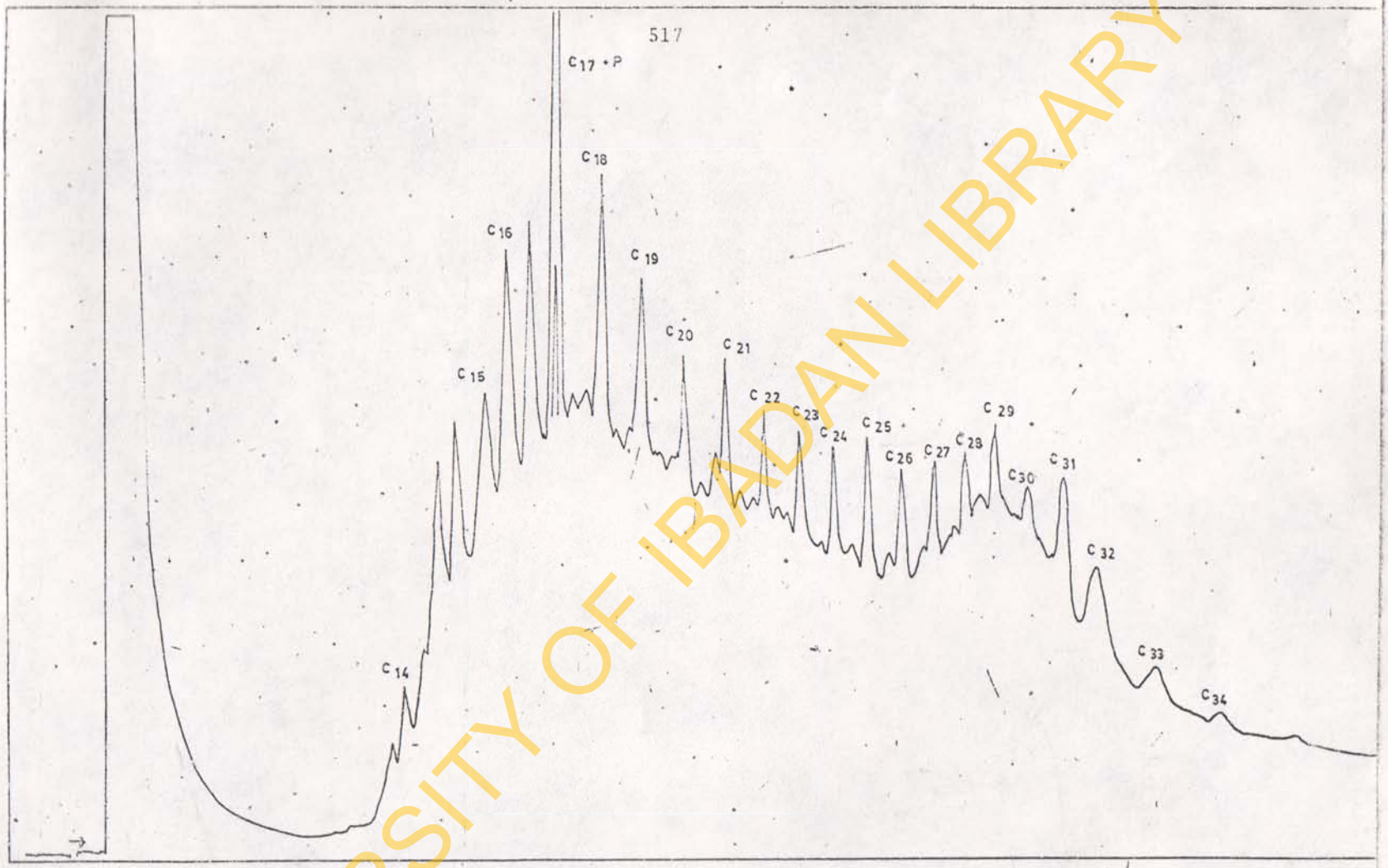


Fig. 53: GC chromatogram of Bonny medium.

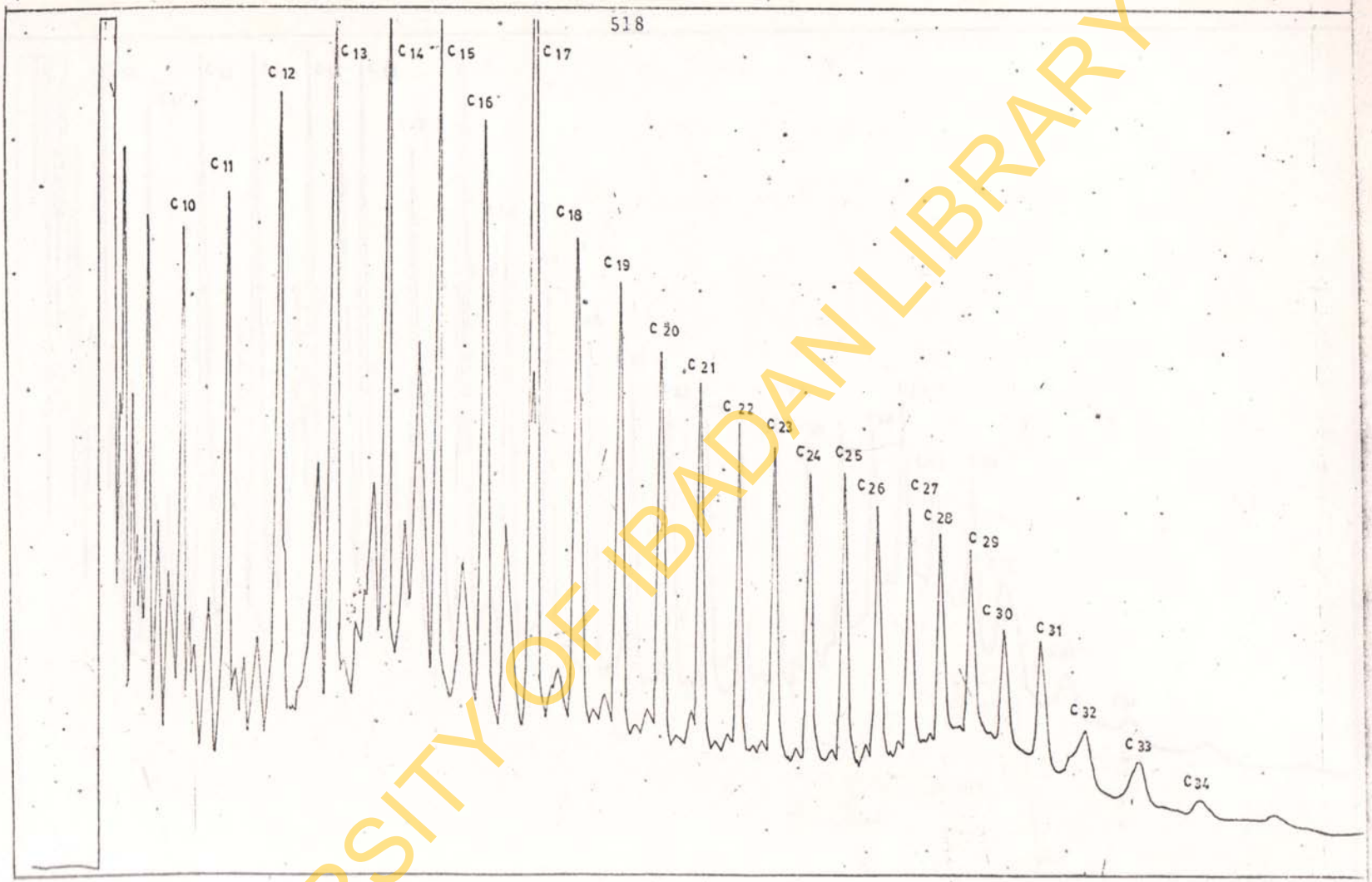


Fig. 54: GC chromatogram of Brass crude.

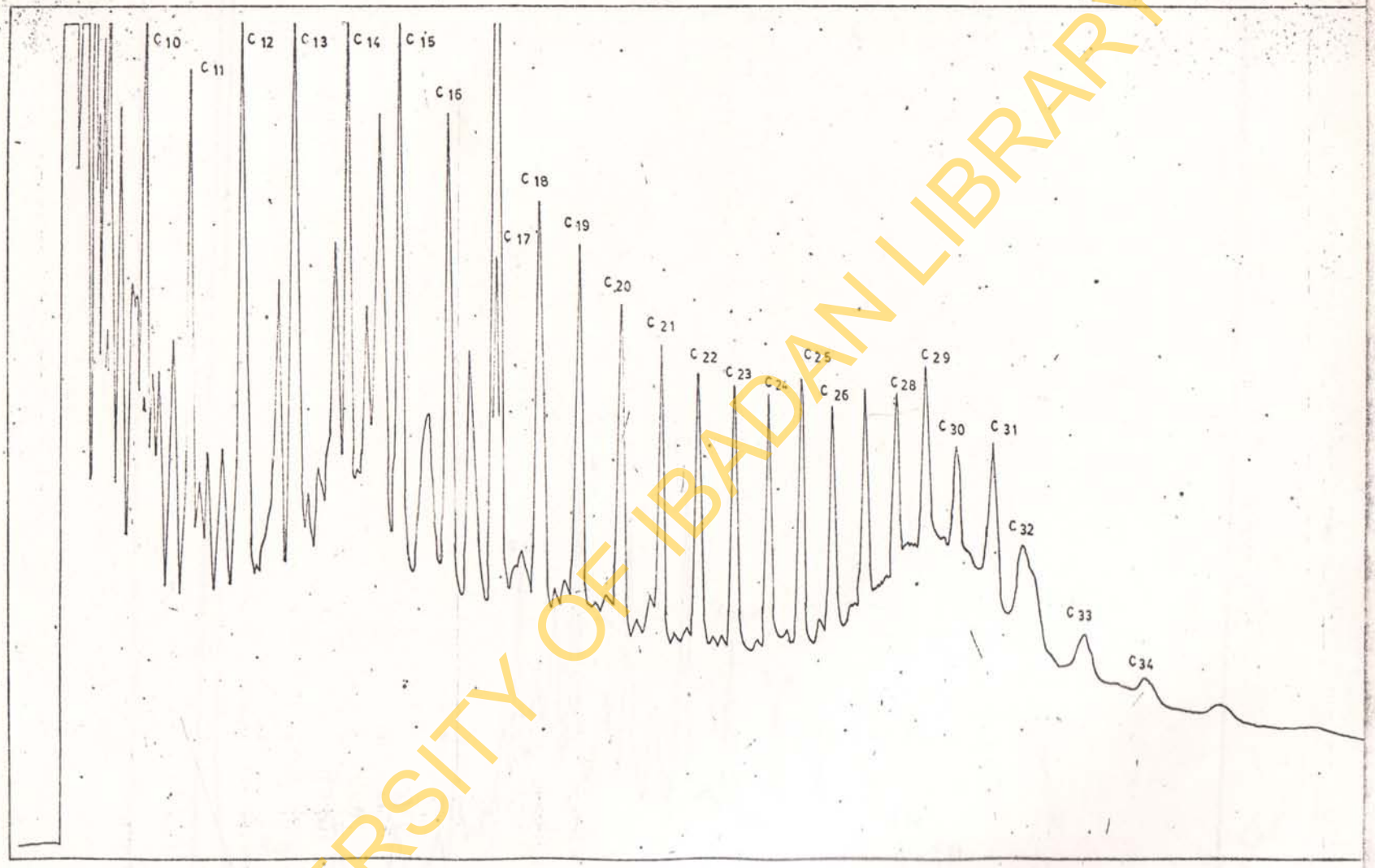


Fig. 55: GC chromatogram of Qua Iboe crude ($n\text{-}C_{10}$-$n\text{-}C_{34}$)

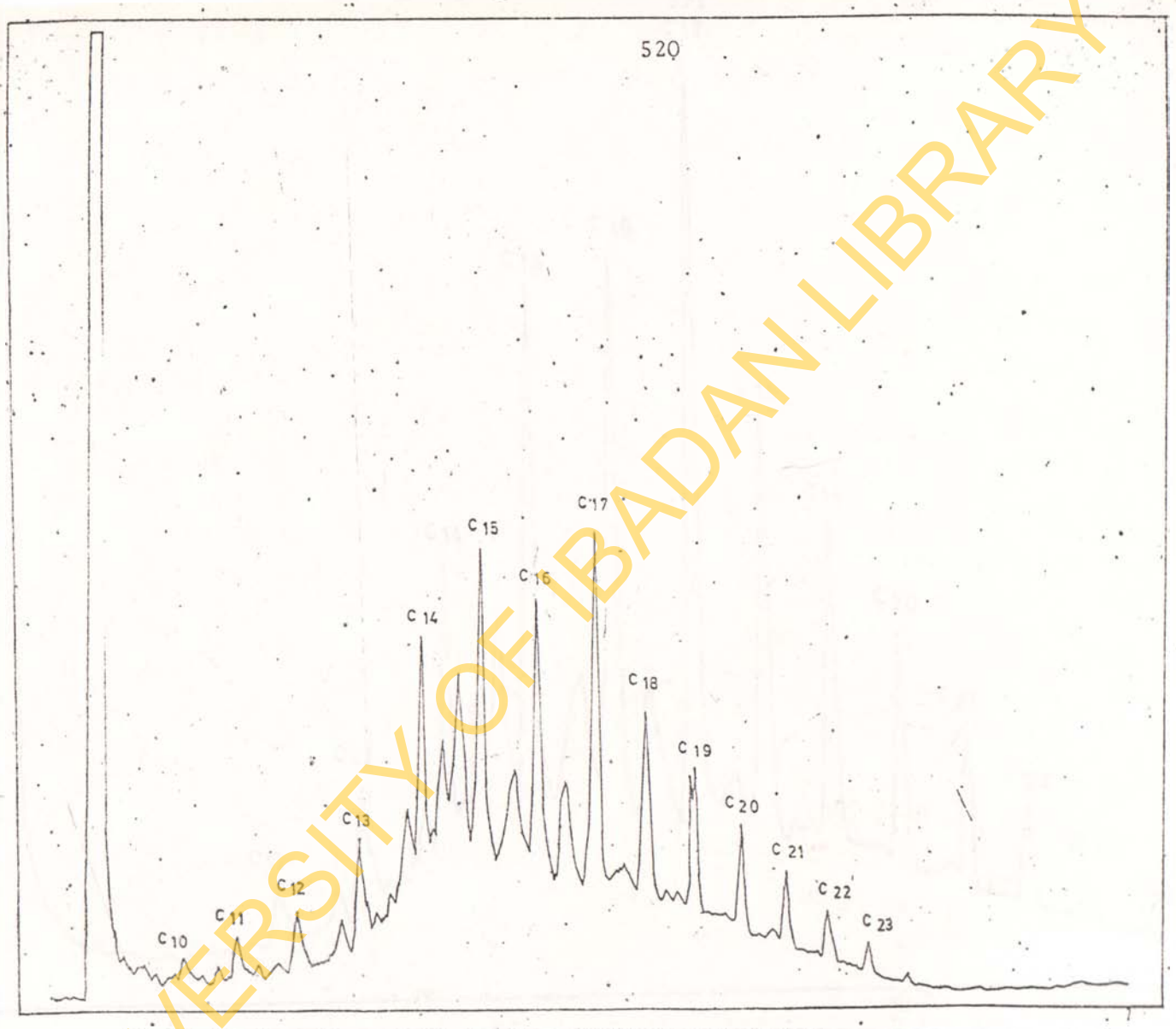


Fig. 55: GC Chromatogram of Nigerian Diesel Oil (Refined) ($n\text{-}C_{10}$-$n\text{-}C_{23}$).

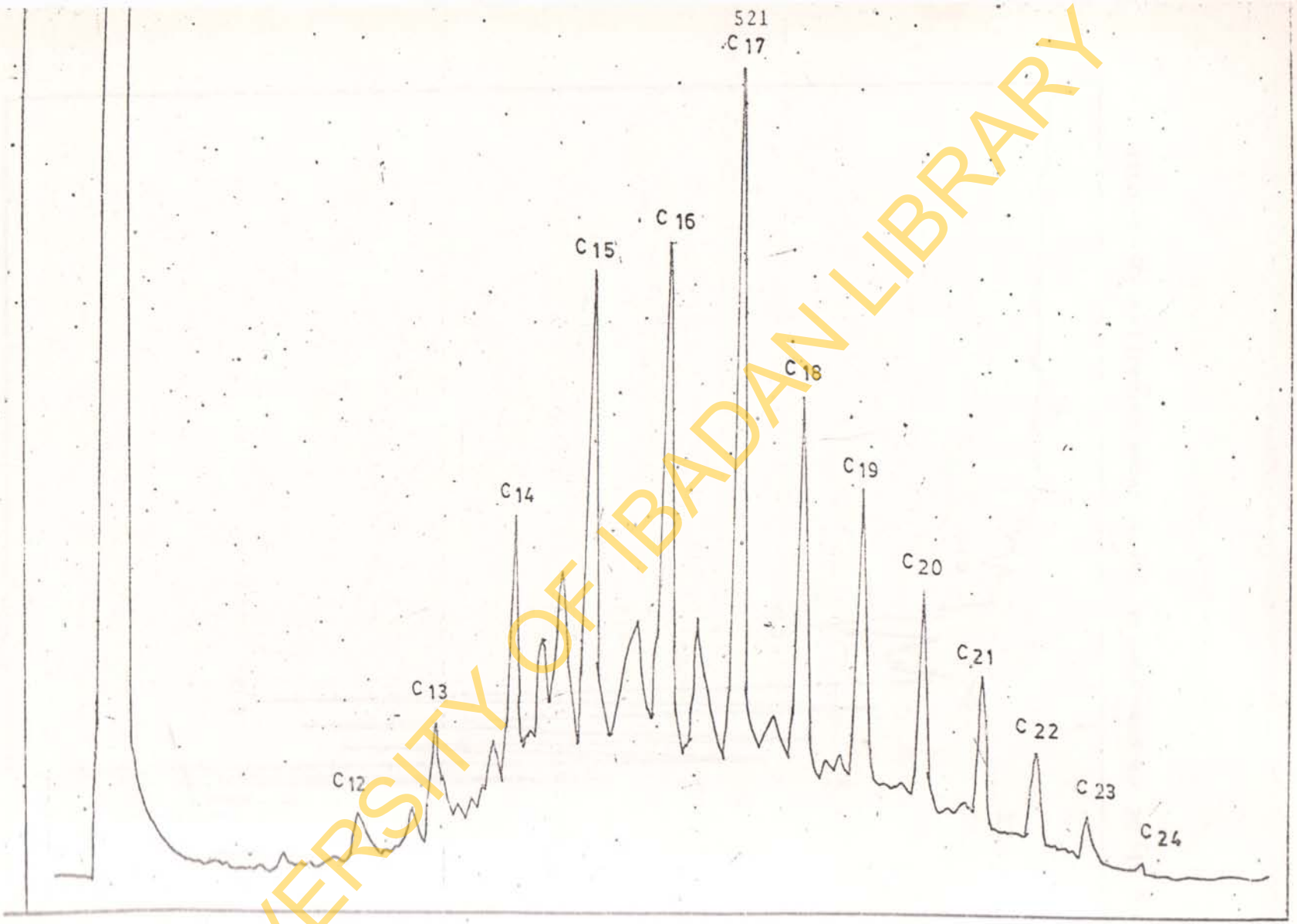


Fig. 57: GC Chromatogram of Automotive Gas Oil (Refined) (n- C_{12} -n- C_{24}).

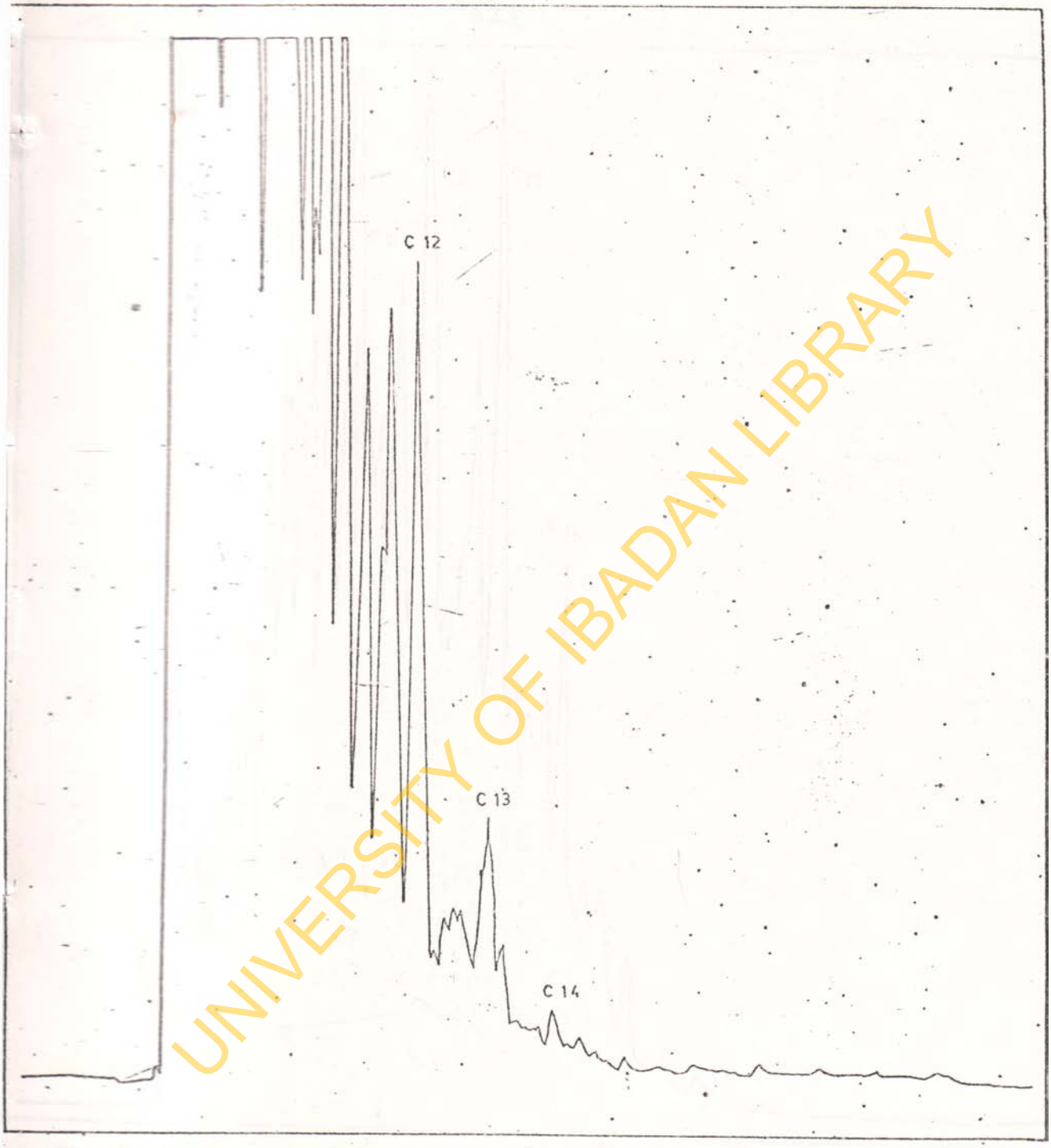


Fig. 58: GC Chromatogram of Nigerian Petrol (Refined) (< n - C10 — n - C 14).

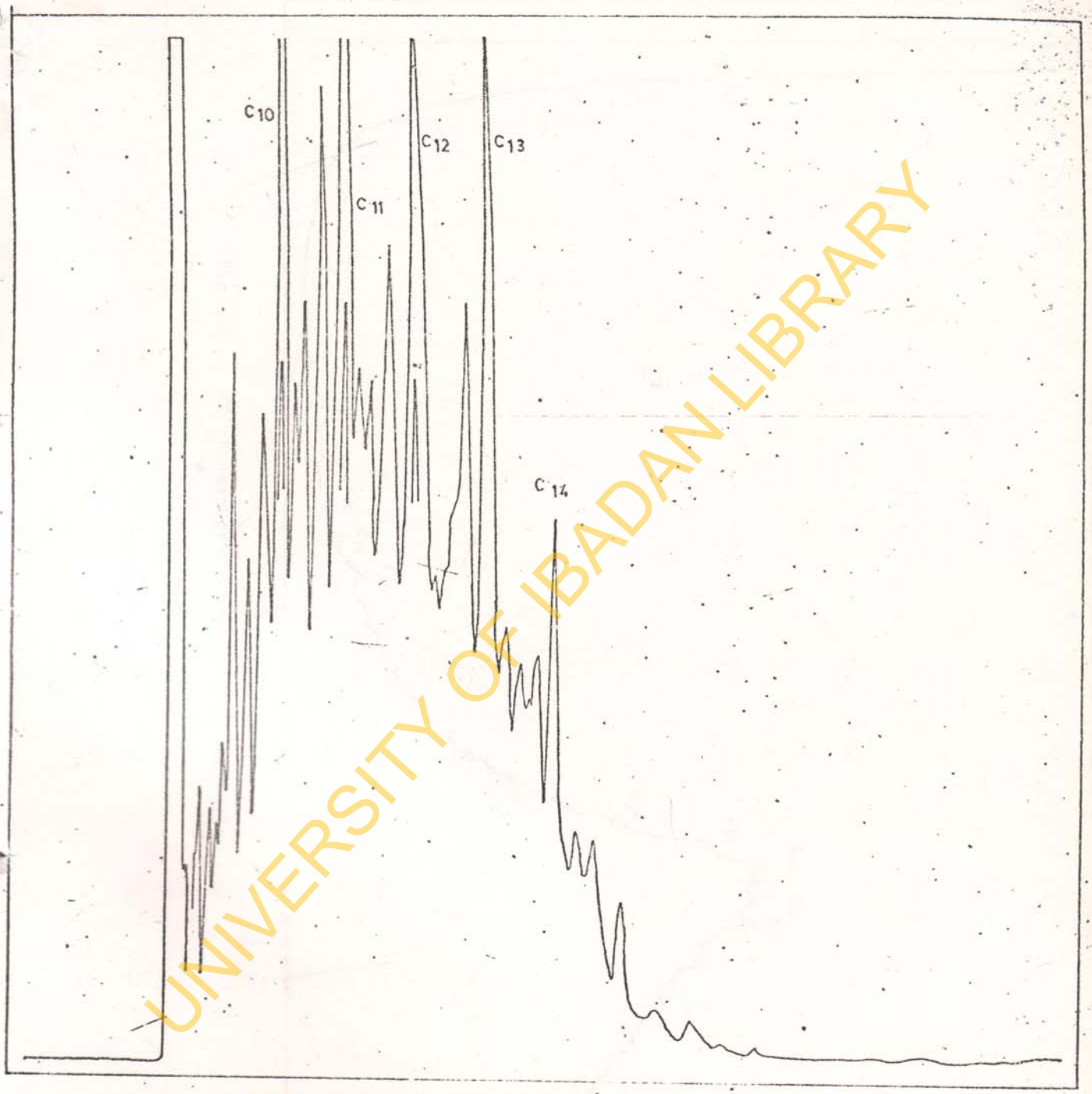


Fig. 59: GC Chromatogram of Kerosine (Refined) (< n - C10 - n C14).

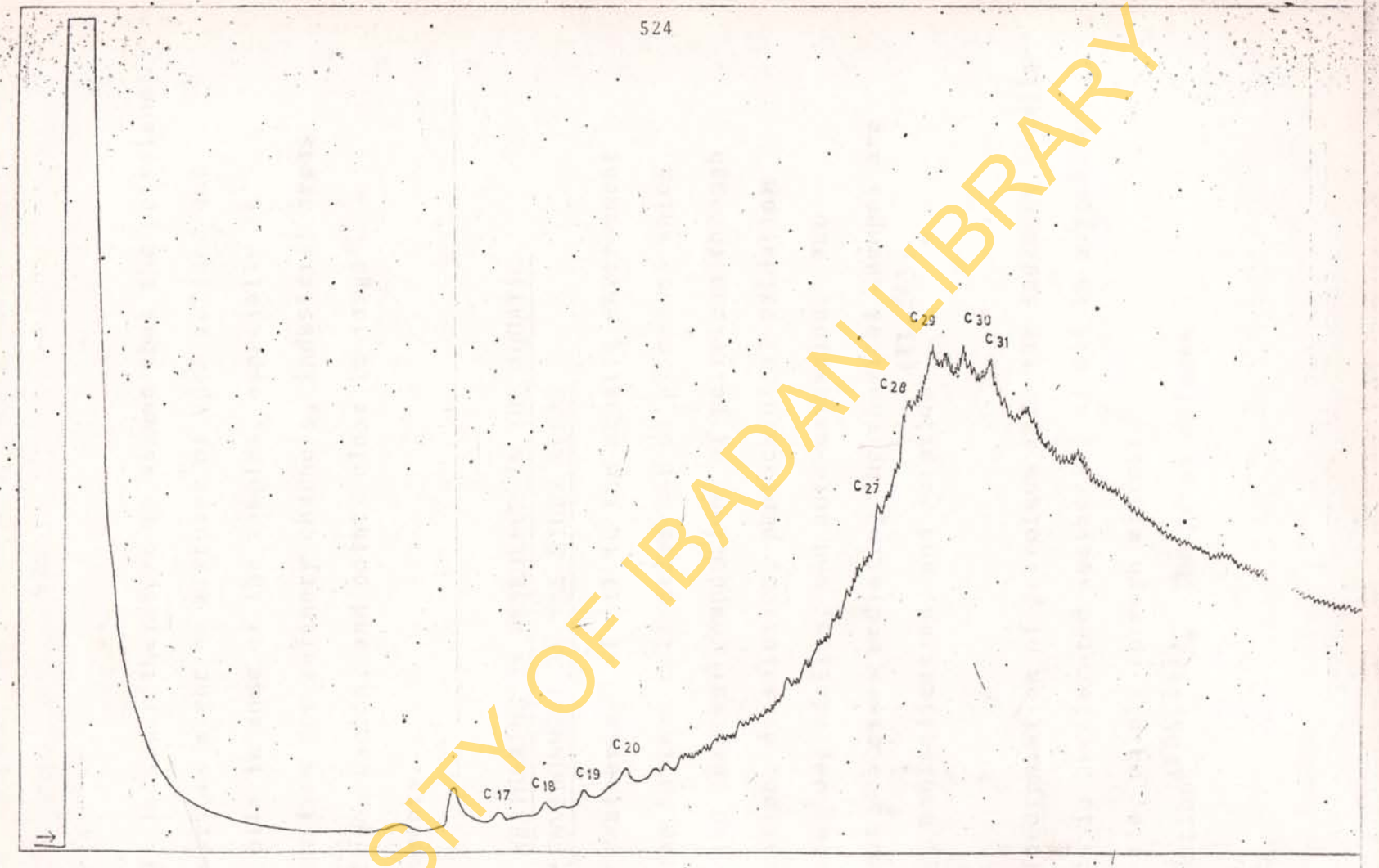


Fig. 60: GC chromatogram of engine oil (refined).

It is safer therefore to assume that the petroleum hydrocarbons might be mixtures of both refined and crude oils in some of the samples, especially in samples from the refinery channels, industrial areas e.g. Lagos Lagoon, and points close to large settlements.

4.12 WEATHERING OF PETROLEUM IN THE AQUATIC ENVIRONMENT IN THE STUDY AREAS

"Weathering" of oil in the aquatic environment pertains to that collective set of processes which alter the chemical composition of petroleum through evaporation, dissolution, photochemical oxidation, microbial degradation, and auto-oxidation. The physical processes mediating the chemical changes are mixing, emulsification, and sorption (11,265).

Incorporation of petroleum into the sediment usually results in accelerated weathering of oil in oxygenated substrate, mainly through microbial degradation (208,265). The gross effects

of these processes on the chemical composition of oil can be predicted[45,244]. Some indicator parameters have been used to determine the weathering age of oil in the aquatic environment. These include the ratios of UCM to the total n-alkanes, UCM to total resolved, the UCM (long-term) to the sum of n-alkanes from n-C_{14} to n-C_{23} (C_{14-23} - recent hydrocarbon introduction). The n-alkanes are more susceptible to degradation than the isoprenoid, acyclic, and aromatics, as the weathering age of the oil increases, the values of the ratios increases due to decrease in the amount of n-alkanes left in the oil.

Isoprenoid hydrocarbons are generally more resistant to bacterial degradation than the n-alkanes, thus the ratio of phytane and its neighbouring n-alkane, C_{18}, is provided as a rough indication of the relative state of biodegradation in samples. The ratio of pristane and n-C_{17} can also be used although the pristane has contributions from both petroleum and biogenic sources.

The results of these parameters for the analyzed sediment samples are shown in Tables 68 to 72. These results indicated that the samples were contaminated with heavily weathered oil because the low-boiling n-alkanes have been lost in most samples, the n-alkane up to n-C_{19} have been lost as can be seen in Fig. 48. The ratios given above involving the UCM and n-alkanes increased with increase weathering rate because n-alkanes are preferentially lost. The Pr/nC_{17} and Ph/nC_{18} ratios also increase with the weathering age of the oil as n-alkane are eliminated faster than the isoprenoids.

Some samples showed the presence of fresh oil from the carbon range in their chromatograms and the low values for the weathering ratio (i.e. UCM/n-alkanes, UCM/ C_{14-23}). Examples of such sample are Lever Brothers' discharge point (845), Asagba (134), Jones creek (360), Chanomi creek at confluence of unnamed creek draining Egwa field (858), Orughene creek (870), Bakana (807), Port Harcourt harbour (233a), Umuochi (020) and Berger/National Oil/Ijora (Stn 20 Lagos Lagoon).

TABLE 68: - n-ALKANES AND UNRESOLVED COMPLEX MIXTURE (UCM) PARAMETERS OF SEDIMENT SAMPLES FROM LAGOS, NIGER DELTA, KADUNA AND IBADAN AREAS OF NIGERIA

SN	Code	n-alkanes	Total Resolved	Pr / $n\text{-}C_{17}$	Ph / $n\text{-}C_{18}$	UCM	Total Aliphatic	% Resolved	UCM / n-alkanes	UCM / Resolved	Recent Alkanes $n\text{-}C_{14}^{23}$	Long term; recent UCM / $n\text{-}C_{14}^{23}$
1	LAGOS -LEKKI LAGOONS.											
	086	0.28	0.35	0.98	1.46	10.22	10.57	3.31	36.50	29.20	0.04	255.50
	087	0.10	0.22	-	0.55	9.19	9.41	2.34	91.90	41.77	0.02	459.50
	845	4.73	10.84	3.49	4.23	80.23	91.07	11.90	16.96	7.40	1.92	41.79
	847	0.56	0.67	10.73	23.84	37.65	38.32	1.75	67.23	56.19	0.31	121.45
	851	0.45	0.70	2.36	6.99	19.34	20.04	3.49	42.98	27.63	0.14	138.14
	856	-	-	-	-	-	-	-	-	-	-	-
	857	0.16	0.39	0.66	1.95	18.15	18.54	2.10	113.44	46.54	0.08	226.88
2	BENIN											
	057	1.20	1.79	0.14	0.21	-	1.79	100.00	-	-	0.80	-
	134	0.86	1.11	17.24	-	3.21	4.32	25.69	3.73	2.89	0.19	16.89
	311	0.15	0.16	0.98	0.28	1.83	1.99	8.04	12.20	11.44	0.02	91.50
	347	0.06	0.06	0.24	0.27	1.08	1.14	5.26	18.00	18.00	0.01	108.00
	835	0.04	0.04	0.47	1.10	-	0.04	100.0	-	-	0.01	-
	837	0.96	0.99	13.32	-	3.01	4.00	24.75	3.14	3.04	0.10	30.10
	838	0.28	0.28	-	-	7.23	7.51	3.73	25.82	25.82	0.07	103.29

TABLE 68 (contd.)

SN	Code	n-Alkanes	Total Resolved	Pr / $n\text{-}C_{17}$	Ph / $n\text{-}C_{18}$	UCM	Total Aliphatic	% Resolved	UCM / n-Alkanes	UCM / Resolved	Recent Alkanes $n\text{-}C_{14}^{23}$	Long term: Recent UCM / $n\text{-}C_{14}^{23}$
	0-1	0.08	0.08	0.73	0.36	-	0.08	100.00	-	-	0.05	-
	0-2	4.24	4.32	57.91	126.95	36.90	41.22	10.48	8.70	8.54	1.58	23.35
3	ESCRAVOS											
	054	0.47	1.06	0.34	0.35	57.39	58.45	1.81	122.11	54.14	0.16	358.69
	055	0.38	1.76	-	-	-	1.76	100.00	-	-	0.10	-
	360	1.08	1.20	0.12	0.85	2.46	3.66	32.79	2.28	2.05	0.21	11.71
	362	0.33	0.56	1.69	3.31	8.16	8.72	6.42	24.73	14.57	0.08	102.00
	831	0.52	0.87	2.63	-	-	0.87	100.00	-	-	0.07	-
	839	0.86	1.06	3.67	1.46	-	1.06	100.00	-	-	0.06	-
4	FORCADOS -WARRI											
	040	0.08	0.08	0.25	0.18	0.20	0.28	28.57	2.50	2.50	0.01	20.00
	049	0.08	0.14	-	-	0.97	1.11	12.61	12.13	6.93	-	-
	050	10.03	15.84	-	-	-	15.84	100.00	-	-	0.64	-
	052	0.17	0.18	-	-	0.45	0.63	28.57	2.50	0.08	0.08	5.63
	053	0.73	1.04	1.88	4.19	26.64	27.68	3.76	36.49	25.62	0.08	333.00
	351	0.09	0.13	1.09	1.61	1.50	1.63	7.98	16.67	11.54	0.05	30.00
	352	2.62	6.65	2.88	3.58	-	6.65	100.00	-	-	0.98	-
	353	0.14	0.15	0.52	1.54	2.30	2.45	6.12	16.43	15.33	0.03	76.67

TABLE 68 (contd.)

SN	Code	n-Alkanes	Total Resolved	Pr / $n\text{-}C_{17}$	Ph / $n\text{-}C_{18}$	UCM	Total Aliphatic	% Resolved	UCM / n-Alkanes	UCM / Resolved	Recent Alkanes $n\text{-}C_{14}^{23}$	Long term: Recent UCM / $n\text{-}C_{14}^{23}$
	372	1.15	1.22	0.75	0.37	2.95	4.17	29.26	2.57	2.42	0.31	76.67
	858	12.07	16.19	7.05	8.42	53.33	69.52	23.29	4.42	3.29	1.08	49.38
	860	0.21	0.26	-	-	4.64	4.90	5.31	22.10	17.85	0.05	92.80
	862	0.09	0.56	0.85	4.27	3.76	4.32	12.96	31.78	6.71	0.03	125.33
	863	2.71	5.52	1.46	6.61	-	5.52	100.00	-	-	1.43	-
	864	0.25	0.31	-	-	3.75	4.06	7.64	15.00	12.10	0.03	125.00
	865	3.10	3.68	-	0.42	28.76	32.44	11.34	9.28	7.82	0.95	30.27
	866	0.06	0.06	-	-	2.00	2.06	2.91	33.33	33.33	0.01	200.00
5	RAMOS											
	038	1.63	8.06	1.69	1.05	27.04	35.10	22.96	16.59	3.35	0.13	208.00
	382	2.52	5.81	0.19	0.17	-	5.81	100.00	-	-	1.74	
	869	0.07	0.19	-	0.70	6.80	6.99	2.72	97.14	35.79	0.02	340.00
	870	2.35	5.98	2.42	5.37	60.93	66.91	8.94	25.93	10.19	0.98	62.17
	871	0.06	0.07	-	-	-	0.07	100.00	-	-	0.01	-
6	NUN-EKOLE-BRASS											
	036	-	-	-	-	-	-	-	-	-	-	-

TABLE 68 (contd.)

SN	Code	n-Alkanes	Total Resolved	Pr / $n\text{-}C_{17}$	Ph / $n\text{-}C_{18}$	UCM	Total Aliphatic	% Resolved	UCM / n-Alkanes	UCM / Resolved	Recent Alkanes $n\text{-}C_{14}^{23}$	Long term Recent UCM / $n\text{-}C_{14}^{23}$
	043	0.19	0.21	-	-	13.61	13.82	1.52	71.63	64.81	0.03	-
	281	0.20	0.26	0.61	6.64	-	0.26	100.00	-	-	0.08	-
	872	0.07	0.12	-	-	3.79	3.91	3.07	54.14	31.58	0.01	379.00
	873	0.15	0.16	-	-	3.24	3.40	4.71	21.60	20.25	0.01	324.00
7	ORASHI											
	012	0.16	0.17	-	-	-	0.17	100.00	-	-	0.09	-
	013	0.20	0.20	0.37	0.12	1.05	1.25	16.00	5.25	5.25	0.04	26.25
	014	1.09	1.23	0.93	0.77	2.85	4.08	30.15	2.61	2.32	0.59	4.83
	016	0.42	0.47	5.62	0.28	3.41	3.88	12.11	8.12	7.26	0.18	18.94
	021	0.20	0.20	-	-	4.83	5.03	3.98	24.15	24.15	0.02	241.50
	035	0.56	0.58	0.37	0.14	-	0.58	100.00	-	-	0.14	-
	250	0.13	0.13	0.74	0.44	-	0.13	100.00	-	-	0.05	-
	251	0.07	0.08	0.37	0.14	1.56	1.64	4.88	22.29	19.50	0.02	78.00
	252	1.95	1.95	0.74	0.44	-	1.95	100.00	-	-	0.17	-
	262	0.32	0.32	0.38	0.14	0.63	0.95	33.68	1.97	1.97	0.15	4.20
	801	0.44	1.25	-	-	-	1.25	100.00	-	-	0.21	-
	802	0.25	0.25	1.07	0.61	1.90	2.15	11.63	7.60	7.60	0.09	21.11

TABLE 68 (contd.)

SN	Code	n-Alkanes	Total Resolved	Pr / $n\text{-}C_{17}$	Ph / $n\text{-}C_{18}$	UCM	Total Aliphatic	% Resolved	UCM / n-Alkanes	UCM / Resolved	Recent Alkanes $n\text{-}C_{14}^{23}$	Long term: Recent UCM / $n\text{-}C_{14}^{23}$
	821	0.16	0.16	0.74	0.61	-	0.16	100.00	-	-	0.05	-
	824	0.02	0.02	-	-	-	0.02	100.00	-	-	0.00	-
8	BONNY - NEW CALABAR											
	020	0.48	0.87	-	-	0.34	1.27	71.90	0.71	0.39	0.14	2.43
	121	0.24	0.24	0.49	0.28	-	0.24	100.00	-	-	0.02	-
	233a	0.55	0.55	0.86	0.55	6.76	7.31	7.52	12.29	12.29	0.12	56.33
	807	0.95	3.69	0.85	0.80	13.55	17.24	21.40	14.26	3.67	0.13	104.23
	808	0.45	0.59	0.99	0.28	1.41	2.00	29.50	3.13	2.39	0.13	10.85
	810	0.87	0.88	-	-	-	0.88	100.00	-	-	0.21	-
9	IMO											
	128	0.18	0.20	0.05	0.03	8.55	8.75	2.29	47.50	42.75	0.06	142.50
	813	0.27	0.29	-	-	1.06	1.35	21.48	3.93	3.66	0.15	7.07
	817	0.24	0.25	0.37	0.14	-	0.25	100.00	-	-	0.12	-

TABLE 68: (contd.)

SN	Code	n-Alkanes	Total Resolved	Pr / $n\text{-}C_{17}$	Ph / $n\text{-}C_{18}$	UCM	Total Aliphatic	% Resolved	UCM / n-Alkanes	UCM / Resolved	Recent Alkanes $n\text{-}C_{14}^{23}$	Long term; Recent UCM / $n\text{-}C_{14}^{23}$
10	CROSS RIVER - CALABAR											
	071	0.47	0.57	0.48	1.60	2.10	2.67	21.35	4.47	3.68	0.28	7.5
	811	0.22	0.22	0.74	0.44	-	0.22	100.00	-	-	0.04	-
	812	0.46	0.46	2.97	0.22	-	0.46	100.00	-	-	0.10	-
	827	0.44	0.44	0.34	0.28	3.35	3.79	11.61	7.61	7.61	0.03	111.67
11	KADUNA											
	141A	0.25	0.25	0.13	0.06	20.25	20.25	1.22	81.00	81.00	0.06	337.50
	141B	0.84	0.84			16.26	17.10	4.91	20.36	20.36	0.24	71.25
	843	0.15	0.15	0.36	0.22	0.43	0.58	25.86	2.87	2.87	0.04	10.75
	844	0.52	0.64	0.14	0.22	8.56	9.20	6.96	16.46	13.38	0,06	142.67
12	IBADAN											
	Ag-1	0.67	0.67			27.12	27.79	2.41	40.48	40.48	0.52	52.15
	As-2	1.78	1.78			5.07	6.85	25.99	2.85	2.85	0.40	12.68

TABLE 69: n-ALKANES AND UNRESOLVED COMPLEX MIXTURE (UCM) PARAMETERS (OKPARI RIVER) (1984)

SN	Code	n-alkanes ($ug\ g^{-1}$)	Total Resolved	UCM	Total Aliphatic	% Resolved	UCM / n-alkanes	UCM / Resolved	Recent alkanes $n\text{-}C_{14}^{23}$	Long-term: recent UCM / $n - C_{14}^{23}$
1.	B	24.07	28.78	85.27	114.05	25.2	3.5	3.0	0.164	520.0
2.	D	1.70	2.27	103.63	105.90	2.1	61.0	45.7	0.311	333.2
3.	E	2.96	3.18	23.19	26.37	12.1	7.8	7.3	0.079	293.5
4.	G-1	4.48	5.24	37.38	42.62	12.3	8.3	7.1	0.383	97.6
5.	G-2	4.43	4.81	35.53	40.34	11.9	8.0	7.4	0.809	43.9
6.	G-3	4.92	12.55	39.32	51.87	24.2	8.0	3.1	0.058	677.9
7.	G-4	9.21	21.53	102.56	124.09	17.4	11.1	4.8	0.631	162.5
8.	R-1	3.11	8.31	86.42	94.73	8.8	27.8	10.4	0.172	502.4
9.	R-2	1.79	3.27	148.46	151.73	2.2	82.9	45.4	0.391	379.7
10.	R-3	0.97	2.11	91.01	93.12	2.3	93.8	43.1	0.229	392.4
11.	O-1	12.10	18.38	222.90	241.28	7.6	18.4	12.1	0.992	224.7
12.	O-2	9.52	26.14	150.66	202.93	12.9	15.8	5.8	0.312	482.9
13.	N	0.35	0.74	44.00	44.74	1.7	125.7	59.5	0.149	295.3
14.	V	0.72	3.89	11.06	14.95	26.0	15.4	2.8	0.061	181.3
15.	K-1	1.32	3.04	7.38	10.42	29.2	5.6	2.4	-	-
16.	K-3	16.22	46.26	99.76	146.02	31.7	6.2	2.2	0.757	131.8
17.	T	4.89	6.54	83.38	89.92	7.3	17.1	12.7	0.54	153.8
18.	U	0.76	1.23	55.45	56.68	2.2	73.0	45.1	0.221	250.9

TABLE 70 n-ALKANES AND UNRESOLVED COMPLEX MIXTURE (UCM) PARAMETERS (OKPARI RIVER, FEBRUARY 1985)

SN	Code	n-alkanes ($\mu g\ g^{-1}$)	Total Resolved	UCM	Total Aliphatic	% Resolved	UCM / n-alkanes	UCM / Resolved	Recent alkanes $n\text{-}C_{14}^{23}$	Long-term recent UCM / $n - C_{14}^{23}$
1.	B_{1-1}	0.053	0.064	7.336	7.400	0.9	138.4	114.6	0.045	163.9
2.	B_{2-1}	0.085	0.093	2.135	2.228	4.2	25.1	23.0	0.006	385.4
3.	C-1	ND	ND	ND	ND	ND	ND	ND	ND	ND
4.	D	0.055	0.058	0.467	0.525	11.0	8.5	8.1	0.005	94.3
5.	E_{1-1}	0.362	0.373	2.369	2.742	0.1	6.5	6.4	0.085	27.8
6.	E_{2-1}	0.255	0.316	5.741	6.057	5.2	22.5	18.2	0.084	68.1
7.	F	ND	ND	ND	ND	ND	ND	ND	ND	ND
8.	K-2	0.034	00.38	0.577	0.615	0.1	17.0	15.2	0.009	65.7
9.	N	0.029	00.32	0.693	0.725	4.4	23.9	21.7	0.001	1474.5
10.	0-1	0.011	0.013	0.244	0.2257	5.1	22.2	18.8	0.001	369.7
11.	0-2	0.009	0.009	0.134	0.143	6.3	14.9	14.9	0.001	418.8
12.	0-3	0.378	0.378	0.703	1.081	35.0	1.9	1.9	0.059	11.9
13.	R-1	ND	ND	ND	ND	ND	ND	ND	ND	ND
14.	R-2	0.175	0.272	0.562	0.834	32.6	3.2	2.1	0.002	231.3
15.	T	1.134	1.134	6.947	8.081	14.0	6.1	6.1	0.740	9.4

TABLE 71: n-ALKANES AND UNRESOLVED COMPLEX MIXTURE (UCM) PARAMETERS (OKPARI RIVER, 3RD SAMPLING)

SN	Code	n-alkanes ($\mu g\ g^{-1}$)	Total Resolved	UCM	Total Aliphatic	% Resolved	UCM / n-alkanes	UCM / Resolved	Recent alkanes $n\text{-}C_{14}^{23}$	Long-term recent UCM / $n - C_{14}^{23}$
1.	A-1	0.131	0.131	2.091	2.222	5.9	16.0	16.0	0.012	174.3
2.	B	1.014	1.188	62.766	63.954	1.9	60.9	52.8	0.232	270.5
3.	C-2	0.091	0.116	2.830	2.946	3.9	31.2	24.4	ND	-
4.	C-3	0.242	0.275	2.879	3.154	8.7	11.9	10.5	0.017	169.4
5.	D	2.938	4.066	15.016	19.082	21.3	5.1	3.7	0.054	333.7
6.	F	2.404	3.880	14.468	18.348	21.1	6.0	3.7	0.070	206.7
7.	G-1	1.155	1.184	14.165	15.349	7.7	12.3	12.0	0.095	149.1
8.	J-1	0.454	0.454	5.988	6.438	7.0	13.1	13.3	0.066	90.7
9.	J-2	2.136	2.628	12.565	15.193	17.3	5.9	4.8	0.061	206.0
10.	J-3	9.505	15.072	33.007	48.079	31.3	3.5	2.2	0.269	122.7
11.	K-2	0.951	1.167	7.760	8.927	13.1	8.2	6.6	0.026	298.5
12.	M	1.387	3.476	11.205	14.681	23.7	8.1	3.2	0.059	189.9

TABLE 71 (contd.)

SN	Code	n-alkanes ($\mu g\ g^{-1}$)	Total Resolved	UCM	Total Aliphatic	% Resolved	UCM / n-alkanes	UCM / Resolved	Recent alkanes $n\text{-}C_{14}^{23}$	Long-term recent UCM / $n - C_{14}^{23}$
13.	N	0.545	0.841±	21.798	22.639	3.7	39.9	25.9	0.122	178.7
14.	0-1	0.282	0.958	13.488	14.446	6.6	47.8	14.1	0.028	481.7
15.	0-2	2.453	5.113	16.999	22.112	23.1	6.9	3.3	0.185	91.9
16.	0-3	1.726	1.844	20.580	22.424	8.2	11.8	11.2	0.181	113.7
17.	P	0.060	0.061	1.929	1.990	3.1	32.2	31.6	0.014	137.8
18.	R-1	0.016	0.021	-	0.021	100.0	-	-	0.002	-
19.	R-2	3.274	3.358	21.384	24.742	13.6	6.5	6.4	0.302	70.8
20.	R-3	0.249	0.556	3.115	3.671	15.1	12.5	5.1	0.044	70.8
21.	T	3.288	4.824	47.750	52.574	9.2	13.8	9.9	0.238	200.6
22.	U	3.145	3.358	23.332	26.690	12.6	7.4	6.9	0.585	39.9
23.	V	4.649	8.861	37.035	45.896	19.3	8.0	4.2	0.110	336.7

TABLE 72: n-ALKANES AND UNRESOLVED COMPLEX MIXTURE (UCM) PARAMETERS LAGOS LAGOON (1985)

SN	Code	n-Alkanes	Total Resolved	Pr / $n\text{-}C_{17}$	Ph / $n\text{-}C_{18}$	UCM	Total Aliphatic	% Resolved	UCM / n-Alkanes	Recent Alkanes $n\text{-}C_{14}^{23}$	Long-term recent UCM / $n\text{-}C_{14}^{23}$
1	LS-1	1.928	1.928	-	-	21.878	23.806	8.1	11.348	1.410	15.52
2	LS-2	0.404	0.574	-	-	11.211	11.785	4.9	19.531	0.178	62.98
3	LS-3	0.306	0.306	-	-	-	0.306	100.0	-	0.088	-
4	LS-32	4.590	4.666	-	0.08	33.582	38.248	12.2	7.197	1.398	24.02
5	LS-4	0.912	1.154	-	-	-	1.154	100.0	-	0.714	-
6	LS-42	1.722	2.222	-	-	-	2.222	100.0	-	0.434	-
7	LS-5	1.034	1.324	-	0.31	15.832	17.156	7.7	11.958	0.328	48.27
8	LS-52	0.162	0.170	-	-	-	0.170	100.0	-	0.032	-
9	LS-6	1.310	1.540	-	-	15.074	16.614	9.3	9.788	0.386	39.05
10	LS-62	ND	ND	-	-	ND	ND	-	-	-	-
11	LS-7	7.150	7.296	1.41	0.06	124.604	131.900	5.5	17.078	4.258	29.26
12	LS-72	33.816	25.124	-	-	-	25.124	100.0	-	15.950	-
13	LS-82	1.400	1.630	-	-	-	1.630	100.0	-	0.344	-
14	LS-92	4.168	4.660	-	-	-	4.660	100.0	-	0.660	-
15	LS-10	4.820	5.192	-	-	-	5.192	100.0	-	1.038	-
16	LS-102	0.406	0.408	-	-	-	0.408	100.0	-	0.032	-
17	LS-11	0.818	1.198	0.11	1.38	11.304	12.502	9.6	9.436	0.378	29.90
18	LS-112	1.076	1.260	-	-	7.150	8.410	15.0	5.675	0.416	17.19

TABLE 72 (contd.)

SN	Code	n-Alkanes	Total Resolved	Pr / $n\text{-}C_{17}$	Ph / $n\text{-}C_{18}$	UCM	Total Aliphatic	% Resolved	UCM / n-Alkanes	Recent Alkanes $n\text{-}C_{14}^{23}$	Long-term: recent UCM / $n\text{-}C_{14}^{23}$
19	LS-12	0.438	0.484	-	-	-	0.484	100.0	-	0.160	-
20	LS-132	40.222	43.596	-	0.13	163.964	207.560	21.0	3.761	2.416	67.87
21	LS-14	1.446	1.476	-	-	-	1.476	100.0	-	-	-
22	LS-142	0.186	0.186	-	-	-	0.186	100.0	-	-	-
23	LS-15	3.880	3.880	-	-	-	3.880	100.0	-	3.400	-
24	LS-16	6.682	7.596	-	-	20.504	28.100	27.0	2.699	1.704	12.03
25	LS-17	0.652	0.792	0.67	2.8	28.424	29.216	2.7	35.889	0.312	91.10
26	LS-173	0.552	0.624	-	-	-	0.624	100.0	-	0.066	-
27	LS-175	0.254	0.254	-	-	-	0.254	100.0	-	0.060	-
28	LS-18	1.706	2.046	-	-	22.788	24.834	8.2	11.138	0.936	24.35
29	LS-184	ND	-	-	-	-	-	-	-	-	-
30	LS-185	6.180	8.299	0.07	0.08	-	8.299	100.0	-	4.846	-
31	LS-19	14.940	18.558	-	-	-	18.558	100.0	-	2.392	-
32	LS191	5.152	5.830	0.87	0.42	89.400	95.230	6.1	15.334	4.546	19.67
33	LS-192	0.722	0.722	-	-	22.728	23.450	3.1	31.479	0.520	43.71
34	LS-195	4.094	4.116	-	-	-	4.116	100.0	-	1.060	-
35	LS-20	28.842	29.868	0.39	0.50	488.722	518.59	5.8	16.363	23.114	21.14
36	LS-201	8.454	9.342	-	0.49	387.360	396.702	2.4	41.464	5.002	77.44
37	LS-202	126.978	179.226	0.47	1.58	2524.154	2703.380	6.6	14.084	114.920	21.96
38	LS-203	0.402	0.804	-	-	11.966	12.770	6.3	14.883	0.234	51.14

TABLE 72 (contd.)

SN	Code	n-Alkanes	Total Resolved	Pr / $n\text{-}C_{17}$	Ph / $n\text{-}C_{18}$	UCM	Total Aliphatic	% Resolved	UCM / n-Alkanes	Recent Alkanes $n\text{-}C_{14}^{23}$	Long-term; recent UCM / $n\text{-}C_{14}^{23}$
39	LS-205	11.232	11.876	0.18	0.20	381.526	393.402	3.0	32.126	8.810	43.31
40	LS-21	2.282	4.336	-	1.43	23.920	28.256	15.3	5.517	1.748	13.68
41	LS-22	1.120	1.574	0.18	0.26	20.764	22.338	7.0	13.192	0.764	27.18
42	LS-222	1.364	1.914	0.31	0.24	17.304	19.218	10.0	9.041	0.718	24.10
43	LS-225	0.256	0.466	-	-	-	0.466	100.0	-	0.096	-
44	LS-23	6.154	10.564	2.28	0.81	101.742	112.306	9.4	9.63	2.968	34.28
45	LS-232	40.164	41.112	1.40	2.39	174.010	215.122	19.1	4.23	4.00	43.39
46	LS-233	ND	ND	-	-	-	ND	-	-	-	-
47	LS-234	6.854	6.854	-	-	152.446	159.300	4.3	22.242	0.646	235.98
48	LS-24	16.270	17.494	0.71	0.51	120.390	137.884	12.7	6.882	11.374	10.58
49	LS-242	0.170	0.710	-	-	-	0.710	100.0	-	0.106	-
50	LS-245	4.394	5.518	0.31	0.42	44.470	49.988	11.0	8.059	1.560	28.51
51	LS-251	20.170	20.170	-	-	19.000	39.170	51.5	0.942	10.496	1.81
52	LS-252	0.756	1.338	-	-	-	1.338	100.0	-	0.278	-
53	LS-26	2.378	3.510	-	-	-	3.510	100.0	-	0.740	-
54	LS-262	36.116	59.748	-	-	-	59.748	100.0	-	9.474	-

These ratios have also been used for source identification of the hydrocarbons present in sediment samples. As earlier indicated under the MOPI section, higher numerical values of these ratios is a pointer to the presence of petroleum hydrocarbons.

4.13 ACCUMMULATION OF PETROLEUM HYDROCARBONS

The levels of petroleum hydrocarbons in water column most of the time reflect recent introduction of the hydrocarbons into the aquatic environment because the resident time for hydrocarbons (e.g. alkanes and light aromatic) in water is relatively short. The physical and chemical processes (e.g. current, temperature, chemical and microbial degradation) would always act to eliminate the hydrocarbons. The insoluble fractions (alkanes and some aromatics) are taken down to the bottom sediment to be incorporated in the sediment matrix. The ratio of the hydrocarbon concentrations in the two compartments is a good indicator of the pollutional trend. Some results are shown in Table 73, below to illustrate this point.

The concentration factor can correctly reflect if the introduction of petroleum hydrocarbons has been on for a long period, the nature of the sediment in terms of absorptive capacity and aeration levels nature of the water (water type), a black water type with its characteristic high level of organic matter will accelerate the rate of sedimentation and thereby hasten the rate of accummulation of the adsorbed and absorbed hydrocarbons. Then more importantly is the speed of the water. A fast flowing water would not to some extent support fast accummulation of petroleum hydrocarbons within the immediate surroundings of the point of introduction.

For a point to be able to accummulate a reasonable level of petroleum hydrocarbon, it has to combine factors such as fine sediment particles (clay and mud) known for high absorptive capacity, high level of suspended organic matter, slow moving water body, and the level of introduction of petroleum hydrocarbon into the water system, which has to keep pace with the rate of degradation because if the latter outpace the rate of introduction, there would not be anything left to accummulate.

The results in Table 73 show some points to have very high concentration factor - Warri river above Keremo (863) - 5520, Port Harcourt Harbour (233a) - 7310, Bakana (807) - 1077.5. Other points with relatively high concentration factors are Lever Brothers' discharge (845) - 435.7. Okobaba Sawmill (847) - 294.8, Warri river field (053) - 814.1, Chanomi creek below mouth of Oyeye creek (351) - 815 and Lower Orashi river (819) - 185.7. All these points are located in areas where the introduction of petroleum hydrocarbons is more or less on a regular basis either through operational source, intentional or accidental discharges. They also have mud sediment which can effectively retain organic compound including petroleum hydrocarbon and the sediment matrix is not well aerated to allow for oxidative degradation of the petroleum hydrocarbons.

Points like North of NNPC Facility on Lagos Lagoon (087) have a concentration factor of 34.6. Benin City on Ikpoba river (311) - 79.6, Oguta Pontoon Crossing (016) - 60.6, Umuochi (020) - 55 and Azumini river at

TABLE 73: COMPARISON OF THE ALIPHATIC HYDROCARBONS (BY GC) IN WATER AND SEDIMENT SAMPLES FROM SAME SAMPLING SITE

Sample Code	Sample Lithology	Water mg/l	Sediment µg/g	Concentration Factor
		LAGOS LAGOON		
086	Mud	0.141	10.570	75.0
087	Fine sand	0.272	9.410	34.6
845	Mud	0.209	91.070	435.7
847	Mud	0.130	38.320	294.8
		BENIN RIVER SYSTEM		
134	Mud	0.904	4.320	4.8
311	Coarse sand	0.025	1.990	79.6
		ESCRAVOS RIVER SYSTEM		
055	Mud	0.151	1.760	11.7
833	Mud	0.265	2.800	10.6
		FORCADOS-WARRI RIVER SYSTEM		
053	Mud	0.034	27.680	814.1
351	Mud	0.002	1.630	815.0
863	Mud	0.001	5.520	5520.0

TABLE 73 (contd.)

Sample Code	Sample Lithology	Water mg/l	Sediment µg/g	Concentration Factor
		ORASHI RIVER SYSTEM		
016	Fine	0.064	3.880	60.6
035	Mud	0.060	0.580	9.7
819	Mud	0.007	1.300	185.7
		BONNY-NEW CALABAR RIVER SYSTEM		
018	Mud	0.039	0.50	12.8
020	Coarse sand	0.022	1.21	55.0
233a	Mud	0.001	7.31	7310.0
807	Mud	0.016	17.24	1077.5
808	Fine sand	0.041	2.00	48.8
810	Sand/pebbles	0.543	0.88	1.6
		IMO RIVER SYSTEM		
814	Fine sand	0.046	1.350	29.3

Aba - 29.3. These are points having sand particles with poor absorptive capacity and where oxidative degradation is also a likely process to degrade the petroleum hydrocarbons.

4.14 COMPARISON OF LEVELS OF PETROLEUM HYDROCARBONS IN SEDIMENTS OF NIGERIAN COASTAL WATERS WITH SIMILAR RESULTS FROM OTHER COUNTRIES

In order to assess the quality of the Nigerian coastal environment in terms of petroleum hydrocarbons pollution as a result of the activities of the various industries e.g. oil companies, the results reported in this study must be compared with results reported for similar work in other parts of the world.

The results of this study are presented alongside other results from other countries in Table 74 below. The results are collections of data from different systems - harbours, bays, lakes, islands and rivers. The results from Lagos Lagoon sediments are comparable to those of highly contaminated sediments. That is, total hydrocarbons in the sediments near the densely

populated lake shore of Lake Zug in Switzerland have been estimated to be 240-290µg/g (189). In Lake Washington, U.S.A., Wakeham and Carpenter have reported that most surface sediments contain an average of about 1400µg/g total aliphatic hydrocarbons (265). Thus the Niger Delta area is not seriously contaminated. Apart from some scattered points that are located within the oil production areas or next to some urban settlements, most of the points recorded values that are comparable to the unpolluted sediments of Rothernemere (UK) - 37µg/g reported by Thompson and Eglinton (1978), Barrier Islands (Gulf of Mexico) had 0.10-2.8µg/g (Palacas et al, 1976) and Chichinjima Island, Japan, 54µg/g (275).

The Okpari river (a case study) was polluted in 1984 as a result of an oil spill from a ruptured pipe but the river quickly recovered in 1985 (see Table 62) with the average concentration of total hydrocarbons dropping from 101.66 µg/g (1984) to 20.62 µg/g (1985).

Therefore, the high contents of hydrocarbons for the sediments from the marine water (represented by Lagos Lagoon) can be attributed to our daily urban - industrial activities, including industrial effluents, ship and boat traffic, sewage disposal and probably oil seeps (underground tanks). The Lagoon is well known for its poor circulation system and low levels of freshwater input which prevent effective flushing. Consequently, pollutants e.g. petroleum hydrocarbons, accummulate in the water column and sediments.

The low contents of hydrocarbons recorded for the sediments from Niger Delta (fresh water) may be explained by factors such as proximity of some of the points from oil activity areas, lithology of the samples, tidal influence and the water circulation systems. Most of the river systems in the Niger Delta are well served with good circulation system and reasonable level of freshwater input. The rivers are also fast flowing in most of the points involved.

TABLE 74: COMPARISON OF PETROLEUM HYDROCARBON (ALIPHATIC FRACTION) LEVELS IN SEDIMENTS OF NIGERIA COASTAL WATER WITH SIMILAR RESULTS FROM OTHER COUNTRIES

Station	Aliphatic (µg/g)	Reference	Comment
Wild Harbour	250-1,600	Blumer and Sass (1972)	Subtidal, oil spil polluted
Buzzards Bay, Massachusetts, USA	50-70	Blumer and Sass (1972)	Polluted
River Blyth (UK)	3,320	Cooper et al.(1974)	Intertidal polluted
Lake Zug, Switzer land	240-900	Giger et al.(1974)	Polluted
Lake Washington, USA	1,600	Wakemar and Carpenter (1976)	Subtidal polluted
Barrier Islands (Gulf of Mexico)	0.10-2.8	Palacas et al.(1976)	Unpolluted
Buzzards Bay USA	110	Farrington et al.(1977)	Subtidal polluted
Wide Wall Bay	0.125-0.486	Mavron Kas (1978)	Unpolluted
South Forties	3.84- 8.48	Mavron Kas (1978)	Unpolluted
Grangemoult	147-483	Mavron Kas (1978)	Intertidal polluted
Rothernemere, U.K	37	Thompson and Eglinton (1978)	Unpolluted
Chedabucpo, Bay	5-2,092	Keizer et al.(1978)	Subtidal polluted
Narragansett Bay	2.3-5,410	Van Vleet and Quinn (1978)	Subtidal polluted
Long Cove, Maine	3-1,647	Mayo et al.(1978)	Oil leakage
Bermuda Seamount	0.6-1.5	Sleeter et al.(1979)	Subtidal unpolluted
New York Bight,(USA)	308	Koons and Thomas (1979)	Subtidal, oil spill
New York Bight, (USA)	35-2900	Wakeham and Farrington (1980)	Sewage Sludge and dredge

TABLE 74 Cont.

Station	Aliphatic (ug/g)	Reference	Comment
Kinneil	250-1,000	Hartley (1980, 1981)	Spoil dumping subtidal polluted
Tana river, Tokyo, Japan	266-1,194	Matsumoto (1983)	Polluted
Chichi-jima Island, Japan	54	Matsumoto (1983)	Unpolluted
Lagos and Lekki: Lagoon, Nigeria	0.2-2703.4	This Study (1984-85)	Polluted
Niger Delta, Nigeria	0.02-69.52	This Study (1984-1985)	Intertidal unpolluted to slightly polluted
Okpari river, Nigeria	10.42-241.23	This Study (1984)	Oil spill, polluted.
Okpari river, Nigeria	0.02-63.95	This Study (1985)	Oil spill slightly polluted

4.15 CONCLUSION

The results of this study indicated that petroleum hydrocarbons are present both in the water column and the underlying sediments of Nigerian river systems to varying degrees.

The levels of petroleum hydrocarbon in both water and sediments varying between samples to reflect the site activity and the nature of the river system. Samples from oil activity areas recorded higher levels of petroleum hydrocarbons - 55.41-2766.27 (221.05) $\mu g g^{-1}$ than those from more remote areas ND - 64.13 (40.07) $\mu g g^{-1}$ Apart from oil installations, boat traffic also showed its impact as high concentration of petroleum hydrocarbons in some locations can best be explained with reference to the volume of boat traffic along such routes. Industrial effluents, urban settlements - waste oil from petrol stations and mechanic garages are other sources identified especially around Lagos Lagoon.

Seasonal variation was indicated in the results of the petroleum hydrocarbons in water samples in

favour of the wet period over the dry period. This may be due to river and urban run-off with their loads of pollutants including petroleum hydrocarbons. Mixing which may occur as a result of turbulent movement in the water body also help to re-suspend the already adsorbed or assimilated petroleum hydrocarbon from the sediments, this would invariably boost the levels of petroleum hydrocarbons in the water column during the wet season.

On the other hand, the variation in petroleum hydrocarbons levels in sediments did not follow a clear course like those of the water because quite a lot of factors that are interwoven are responsible for the control of the levels of petroleum hydrocarbons available in sediments.

Comparing the different river systems, Lagos Lagoon showed higher level of contamination ND - 2766.27 (52.19) μgg^{-1} than the delta river systems 0.05 - 74.05 (9.07) μgg^{-1}. It implies that there are other sources of petroleum hydrocarbons into the coastal water, especially around Lagos Lagoon that also needs deserve

attention as the one being focus on the Delta area. Some sources such as the industrial effluents and the surreptitious release of oil from the numerous petrol service stations, mechanic workshops etc. have not been given adequate attention.

Lagos Lagoon with its poor circulation is under heavy stress from these sources. Hence, the high level of contamination from petroleum hydrocarbon found around the Lagoon.

Hydrocarbon pollution of the Niger Delta while not yet as calamitous as in the western Mediterranean Mediterranean(276) is nevertheless significant. The area contains oil terminals, two oil refineries (the third is underway), petrochemical industries, and busy ports. Lagos also has very busy ports and many industries.

Barring any major disaster, severe problems from oil pollution can be expected to arise in the near future in Nigerian coastal waters unless effective measures are taken to reduce the rate at which oil is spilled during normal operations. If the statistics

of oil spills given earlier in Tables 14 and 15 are anything to go by, then we need to re-examine the industrial practice of the various oil companies and make it mandatory for them to update their production technology. Waste-water discharges also need strict control and monitoring.

In attempts to assess the actual effect of petroleum hydrocarbon discharge on a particular ecosystem, it is essential that we understand the range of natural fluctuation that can be expected within the ecosystem, that is, a measure of the background level against which we are going to attempt to measure the pollution-linked effect. There must be a sufficiently critical scientific base for responsible environmental protection policy. It is essential that we use what reliable data and experience we have to ensure the maintenance of the best practical environmental policy.

The results of this study have shown that infrared spectrophotometric method and the gas chromatographic method are well suited for the monitoring of petroleum hydrocarbons in our environment, there is a positive

correlation between the two values (r = 0.668) and the two components used as indicators - water and sediments have proved quite adequate. They can be used to complement the results of a third component - particulate-feeding biota, notably shellfish (e.g. mussels) to obtain a complete picture of the petroleum hydrocarbons pollution levels in our environment.

In conclusion, since there has not been any previous baseline study on the present distribution of petroleum hydrocarbons in water and sediments of the Nigerian coastal waters, the results obtained in this study would therefore represent baseline levels for future work on petroleum hydrocarbons in water and sediments in Nigerian coastal waters.

4.16 SUGGESTIONS FOR FUTURE STUDY

The results of this work will in no doubt serve as a springboard for those who are going to work in this area of petroleum hydrocarbon pollution study. The results can be used as a guide for the selection of 'hot spots' where more attention would need to be focussed.

Aromatics determination by glass capillary Gas Chromatography (GC)[2] and mass spectrometry (MS) for detail study of individual aromatic hydrocarbon especially the polynuclear aromatic hydrocarbons is very necessary because of their importance.

Apart from the river systems, underground waters in areas like Lagos and some locations very close to oil facility should be included in future programmes.

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