

ENVIRONMENTAL POLLUTION ASSOCIATED WITH OIL DRILLING  
OPERATIONS IN SUMATRA, INDONESIA

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## TABLE OF CONTENTS

Introduction	1
Section 1	
THE PRESENT SITUATION IN RIAU PROVINCE, INDONESIA	1
SAMPLING	2
Sample sites	3
Map of sampling points	4
Sample preparation and analysis	5
Gas chromatography method	5
Fingerprinting of oil extracts	5
SAMPLING RESULTS	6
Distribution graphics	7
DISCUSSION	10
CONCLUSION AND RECOMMENDATIONS	12
Section 2	
POLLUTION FROM CRUDE OIL DRILLING AND REFINING	
CRUDE OIL	14
Typical crude oil components	14
Identification of crude oil	15
Indonesian crude oil composition	16
DRILLING FLUIDS	16
PRODUCED WATER	17
REFINING OF CRUDE OIL	17
PATHWAYS OF OIL INTO FRESHWATERS	17
BIODEGRADATION	18
BIOLOGICAL EFFECTS	
Aquatic environment and bioaccumulation	19
Sediments	21
Atmospheric emissions	22
Weathering	22
Wildlife	23
Plants	23
REFERENCES	24

## **INTRODUCTION**

The Indonesian Archipelago lies between the Pacific and Indian oceans. Dense, sweltering, primary rainforests dominate Sumatra, Kalimantan, Sulawesi and Irian Jaya. These blanket approximately 65% of Indonesia's total land area of two million square kilometres. The export of timber from these forests is of great importance to the Indonesian economy alongside rubber, copper, bauxite, palm oil and petroleum products.

Sumatra is the third largest island in Indonesia with a land area of some 473,400 km<sup>2</sup>. It is an island of enormous regional diversity, that for administrative purposes was divided into eight provinces. One of these, Riau Province, covers some 94,500 km<sup>2</sup> and comprises 3,214 islands. It contains four of Sumatra's largest rivers, and the greatest expanse of tropical rainforest on the island. Riau also contains the most productive oil fields in Indonesia.

The search for hydrocarbons in Indonesia was initiated in the 1890s. After almost 80 years of exploration on land, offshore activity began in 1967 with oil being first discovered in 1969 (Pulunggong *et al.* 1976). Since then exploitation of oil resources has expanded rapidly, with over 100 established gathering stations, mainly owned by American companies. The construction of each of these has necessitated clearance of large forest areas, both for the gathering station sites themselves and supply roads.

Almost all of the oil is pumped to the port of Dumai on the east coast for onward shipment (Oey *et al.* 1991). According to the Annual Statistics from Riau for 1991/1992 (Riau Dalam Angka 1992), the export of crude oil from the province in 1991 was 23,952,109,000 kg, worth 3,334,459,074 US\$. Refined petroleum products in the same year totalled 6,303,673,000 kg with a value of 696,114,655 US\$.

This report provides a short description of the environmental pollution attributed to oil drilling operations in Riau Province and a broader description of oil extraction operations. Section 1 presents analytical results collected from field studies undertaken during the period 18-23 June 1993. The significance of the emissions and impact on the region is discussed. Section 2 contains more general information on the substances and processes used in the extraction and refining of crude oil.

## **SECTION 1**

### **THE PRESENT SITUATION IN RIAU PROVINCE, INDONESIA**

The current investigation centres on five sites containing six American-owned gathering stations on the mainland of Riau Province. All discharges, except

one example, flow into small streams which transport the effluent into the Siak River. Deposits of oil could be frequently observed alongside the streams. The dense rainforest and swamp terrain encountered in these areas often made progress from one sampling point to another slow and required considerable effort to achieve an effective sample network. It was possible, however, to obtain samples of production water effluent from all but one gathering station (Beruk) and sediment samples from the receiving stream systems also with one exception (Minas III).

Oil drilling operations generate very large volumes of produced or formation waters. These contain a complex mixture of sub-surface water with solid and liquid geological/engineering materials, including crude oil, drilling fluids, drilling cuttings, and treatment chemicals as well as other geological materials (Boesch et al. 1985). The produced water may contain elevated levels of various inorganic (trace metals) and organic (petroleum hydrocarbons) substances of a potentially toxic nature.

At the sites investigated, the production water is discharged into settling lagoons in which the separation of oil and water takes place. With time the separation of the production water results in a stratification of surface oil underlain by an oil-water emulsion which in turn is underlain by water. The separated water is then discharged into the environment without further treatment to remove dissolved hydrocarbons or heavy metals. It is clear that the effectiveness of the oil-water separation ongoing in these lagoons controls the quality of the final discharge, a process that from personal observation and independent analytical evidence warrants immediate improvement.

The settling lagoons do not appear to contain a protective undercoating or sealant to prevent oil seepage into the soil below. The average temperature of the effluent from the lagoons has been measured to be approximately 80°C, sufficiently high for the evaporation of volatile organic compounds (VOCs) such as the short chain hydrocarbons and low molecular weight aromatics, (e.g. the toxic compounds benzene, toluene, and xylene). Evaporation will also take place under ambient temperature conditions, albeit more slowly. Whilst partially cleansing the immediate discharge site of these components the fractionation of these hydrocarbons into the atmosphere raises concern for air quality and the effects that such contaminants may exert when rained out.

The high temperatures of the discharged waters persist for a considerable distance downstream from the point of discharge. For example, water samples obtained approximately 2 miles from the effluent were still in excess of 60°. The high effluent temperatures mean that for some distance downstream of these discharges it is unlikely that microbial degradation will operate to successfully break down the hydrocarbon discharge and remove harmful components.

#### **SAMPLING**

Samples of water and sediment were obtained from 5 different areas. See figure 1 overleaf.

**Sample site 1. Pusaka Gathering Station (GS)**

One effluent sample:

MI3166 Effluent from discharge pipe entering stream

Four sediment samples:

MI3168 500 m downstream from discharge pipe

MI3169 1 km downstream from discharge pipe

MI3170 1.5 km downstream from discharge pipe

MI3167 1 km upstream of discharge stream (background sample)

Two drinking water samples:

MI3189

MI3190 both from the village of Deca Sungai Limau near the GS at Pusaka

**Sample site 2. Beruk GS**

No effluent sample was obtained from this site.

Three sediment samples:

MI3172 ≈ 4 km downstream from the GS

MI3173 ≈ 3 km downstream from the GS

MI3174 ≈ 2 km downstream from the GS

**Sample site 3, Minas II and Minas III GS**

Two effluent samples:

MI3175 from the discharge pipe (Minas III)

MI3176 from the discharge pipe (Minas II)

Four sediment samples from around Minas II:

MI3177 (background sample from nearby area)

MI3178 400m downstream of the GS

MI3179 800m downstream of the GS

MI3180 1.2 km downstream from the GS

**Sample site 4, Sintong GS**

One effluent sample:

MI3181 from the discharge pipe

Three sediment samples:

MI3182 upstream of settling lagoon

MI3183 ≈500m downstream of settling lagoon

MI3184 ≈1km downstream of settling lagoon

**Sample site, 5 Kota Batak GS**

One effluent sample:

MI3185 from the discharge pipe

Three sediment samples:

MI3186 ≈500m downstream of discharge pipe

MI3187 ≈2km downstream of discharge pipe

MI3188 ≈3km downstream of discharge pipe

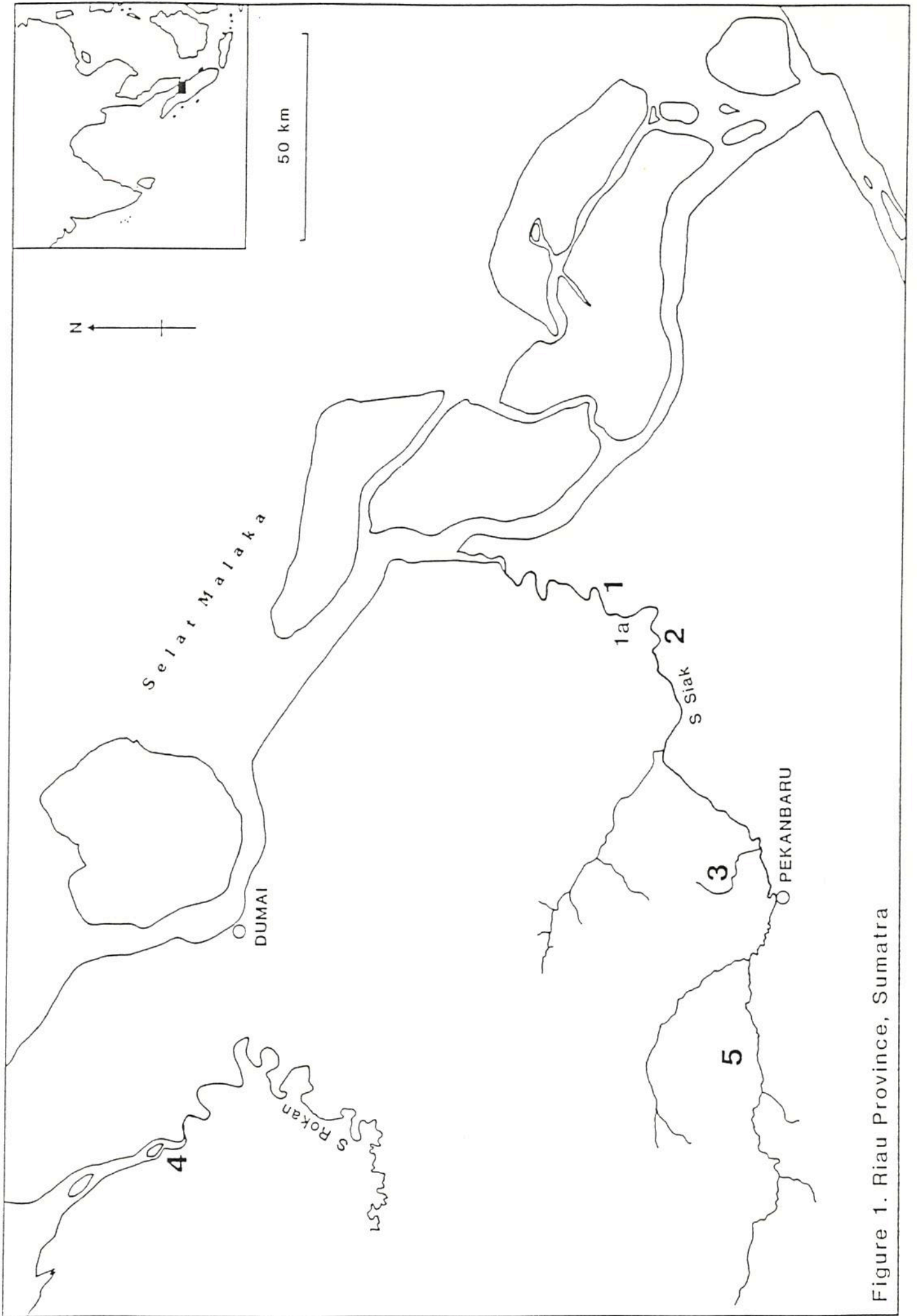


Figure 1. Riau Province, Sumatra

### **Sample preparation and analysis**

The preparation and analysis of effluent and sediment samples was conducted by SAL laboratories, Manchester, U.K.

Both sediment and effluent samples were essentially prepared and analysed using the same procedure. The sediment samples were dried prior to extraction.

Aliquots of the sediment ( $\approx 1\text{g}$ ) and effluent samples ( $\approx 500\text{ml}$ ) were repeatedly extracted with 3 separate 50ml volumes of dichloromethane in an ultrasonic bath. The solvent layers were decanted and combined before being concentrated under a stream of purified nitrogen.

The sample extract was then added to an activated silica column and fractionated into saturate, aromatic and NSO (compounds containing nitrogen, sulphur or oxygen) portions, using a system of solvent elutions. The three fractions were then transferred to weighed vials, allowed to come to complete dryness under a stream of purified nitrogen and then reweighed. The weights obtained constitute the basis of the quantification, with confirmation of the extract composition being performed by gas chromatography with flame ionisation detection (GC-FID).

The saturate fractions were resuspended in known volumes of dichloromethane and set aside for confirmation of their mineral oils content by GC-FID. A method blank was prepared in the same way.

### **Gas chromatography method**

A 1  $\mu\text{l}$  aliquot of each extract was injected, in the split mode, onto a 60m J&W DB-5 fused silica capillary column. Detection was by FID.

The GC conditions for the analysis were as follows:

Injector Temperature: 250°C  
Initial Temperature: 60°C  
Ramp Rate: 10°C/minute  
Final Temperature: 300°C, held for 15 minutes.

### **Fingerprinting of oil extracts**

The distribution patterns of n-alkanes in the saturate fraction provide a graphical "fingerprint" which clearly illustrates the makeup of the oil. These used to identify and compare oils from different sources, and in different media.



## SAMPLE RESULTS

The results tabulated below show the quantitation of the "mineral oil" (saturate fraction) and the total oil (sum of all three fractions) obtained from the gravimetric determination outlined above. Confirmation that the saturate (mineral oil) fraction contained the expected components was achieved by gas chromatography. Figures 2-7 show n-alkane profiles as described above.

Effluent results are quoted in mg/l

Gathering station	PUSAKA	BERUK	MINAS III	MINAS II	SINTONG	KOTA BATAK
Site number	1	2	3	3	4	5
Sample number	MI3166	no sample	MI3175	MI3176	MI3181	MI3185
Mineral oil	7.8	n/a	7.8	150	6.8	0.2
Total oil	12.0	n/a	12.0	190	9.4	4.4

Sediment results are quoted in mg/g dry weight

Gathering station	PUSAKA	BERUK	MINAS II	MINAS III	SINTONG	KOTA BATAK
Site number	1	2	3	3	4	5
Background samples						
	MI3167		MI3177			
Mineral oil	1.4		2.8			
Total oil	8.4		4.7			

sediment samples\*

Sample number	MI3168	MI3174	MI3178	no samples	MI3182	MI3186
Mineral oil	12	11	160	n/a	18	4.4
Total oil	20	14	230	n/a	26	9.2
	MI3169	MI3173	MI3179		MI3183	MI3187
Mineral oil	4.2	17	3.4	n/a	26	20
Total oil	14	21	5.4	n/a	42	26
	MI3170	MI3172	MI3180		MI3184	MI3188
Mineral oil	6.1	20	16	n/a	19	6.0
Total oil	14	25	23	n/a	30	8.9

\* listed in order of increasing distance from each gathering station

Drinking water samples are quoted in mg/l

Sampling site	1a	1a
	MI3188	MI3190
Mineral oil	0.8	1.0
Total oil	1.4	3.0

### MI 3166 and MI 3170 n-Alkane Distributions

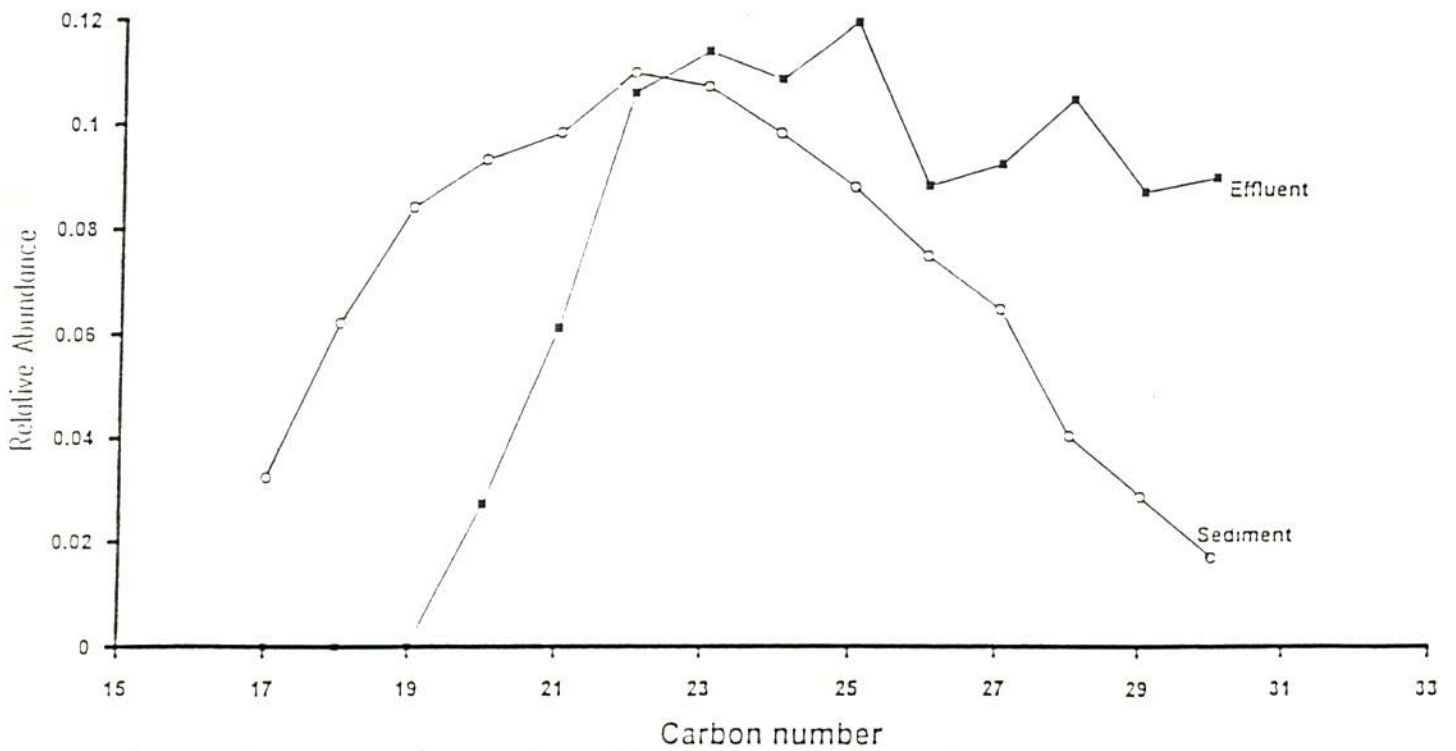


Figure 2. Comparison of n-alkane compositions in effluent and sediment 1.5km downstream from Pusaka gathering station (site 1).

### MI 3172 and MI 3174 n-Alkane Distributions

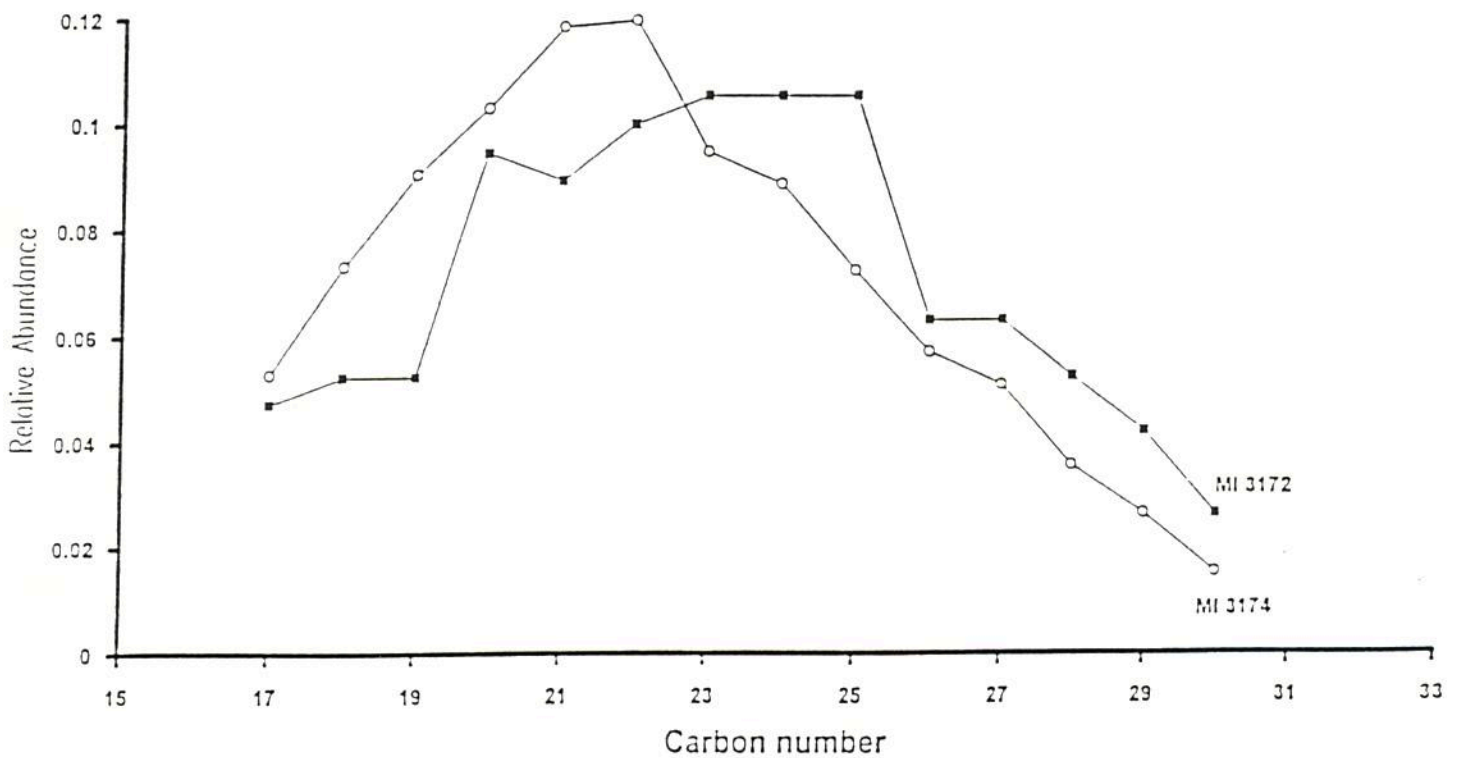


Figure 3. Comparison of n-alkane compositions in two sediments 2 and 4km downstream from Beruk Gathering station (site 2).

### MI 3176 and MI 3178 n-Alkane Distributions

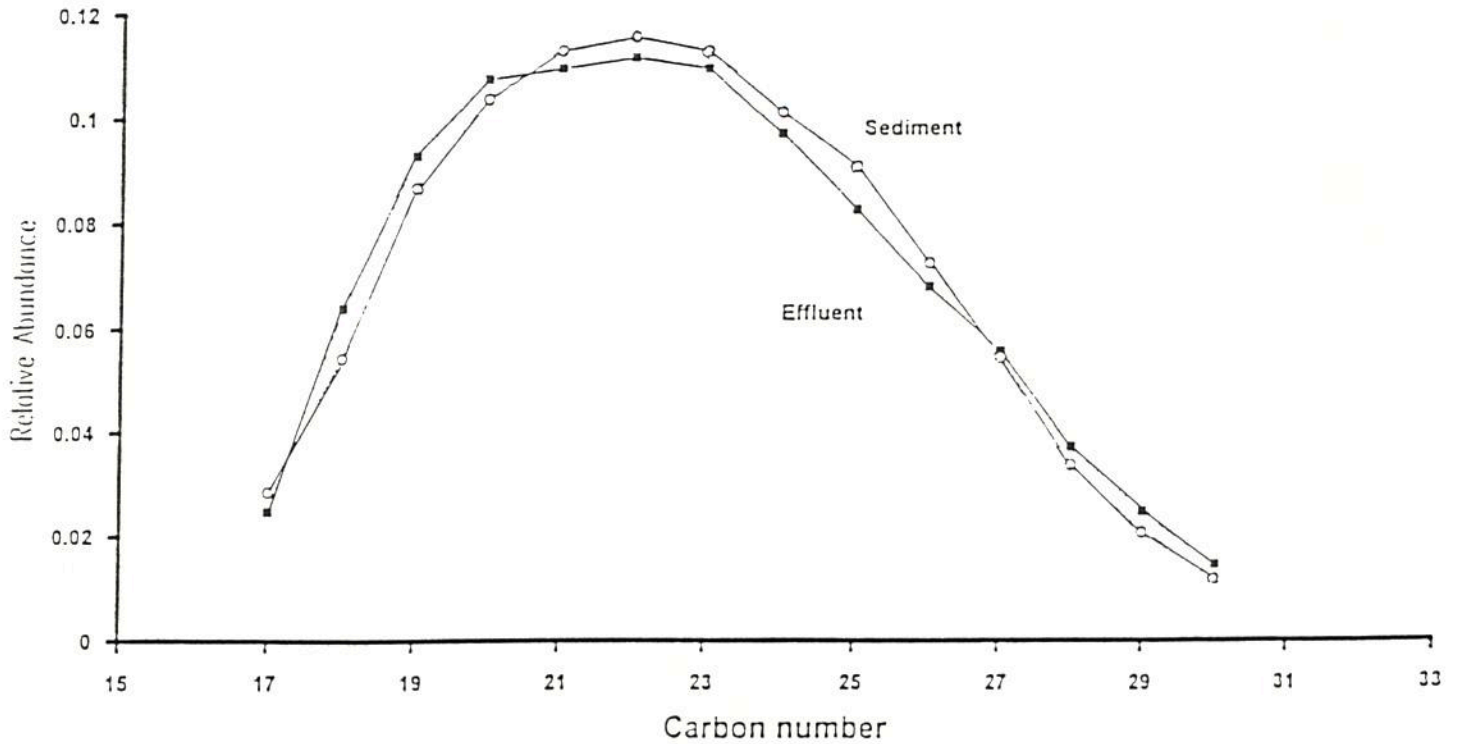


Figure 4. Comparison of n-alkane compositions in effluent and sediment 400m downstream from Minas II gathering station (site 3).

### MI 3181 and MI 3182 n-Alkane Distributions

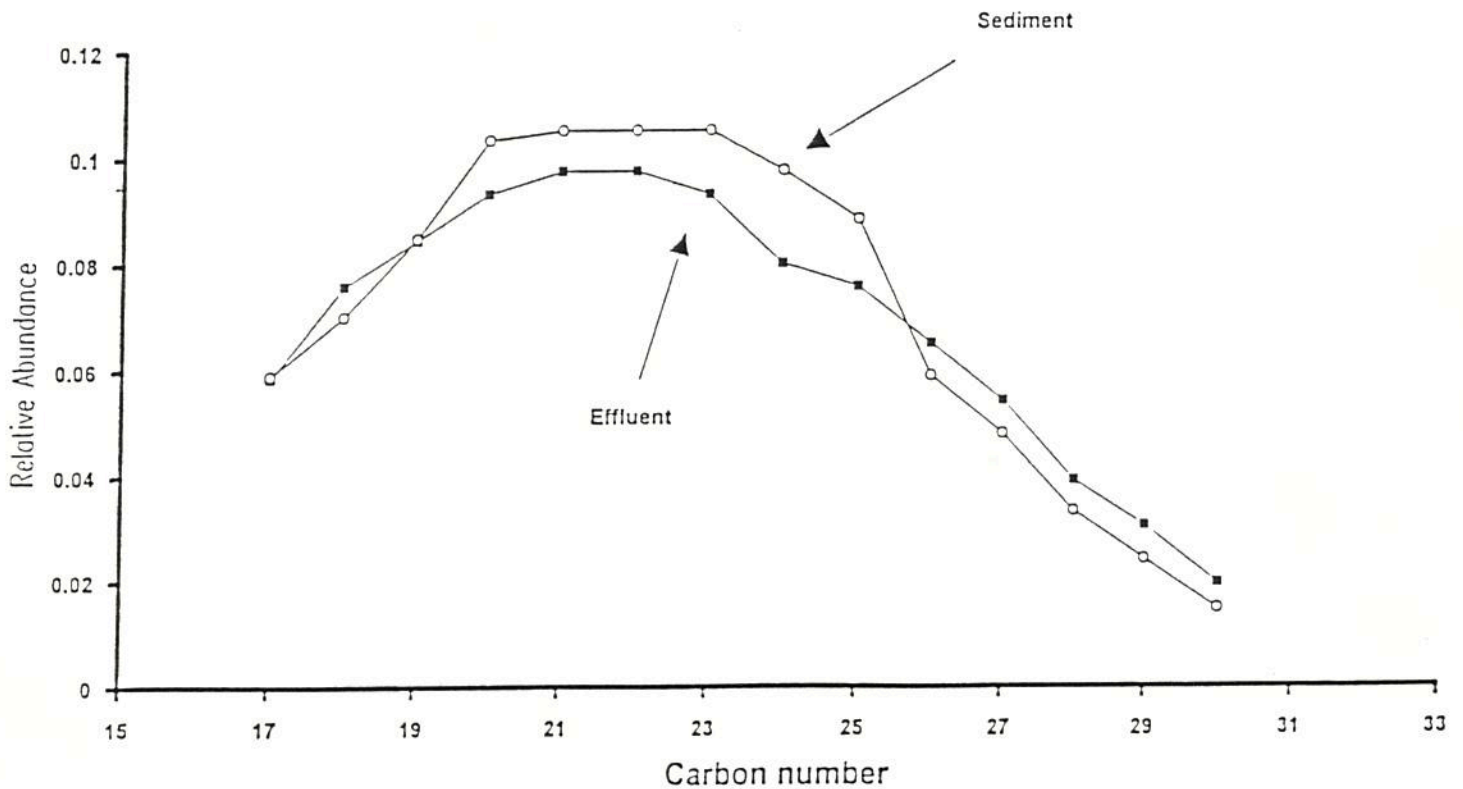


Figure 5. Comparison of n-alkane compositions in effluent and sediment between Sintong gathering station and settling lagoon (site 4).

### MI 3185 and MI 3187 n-Alkane Distributions

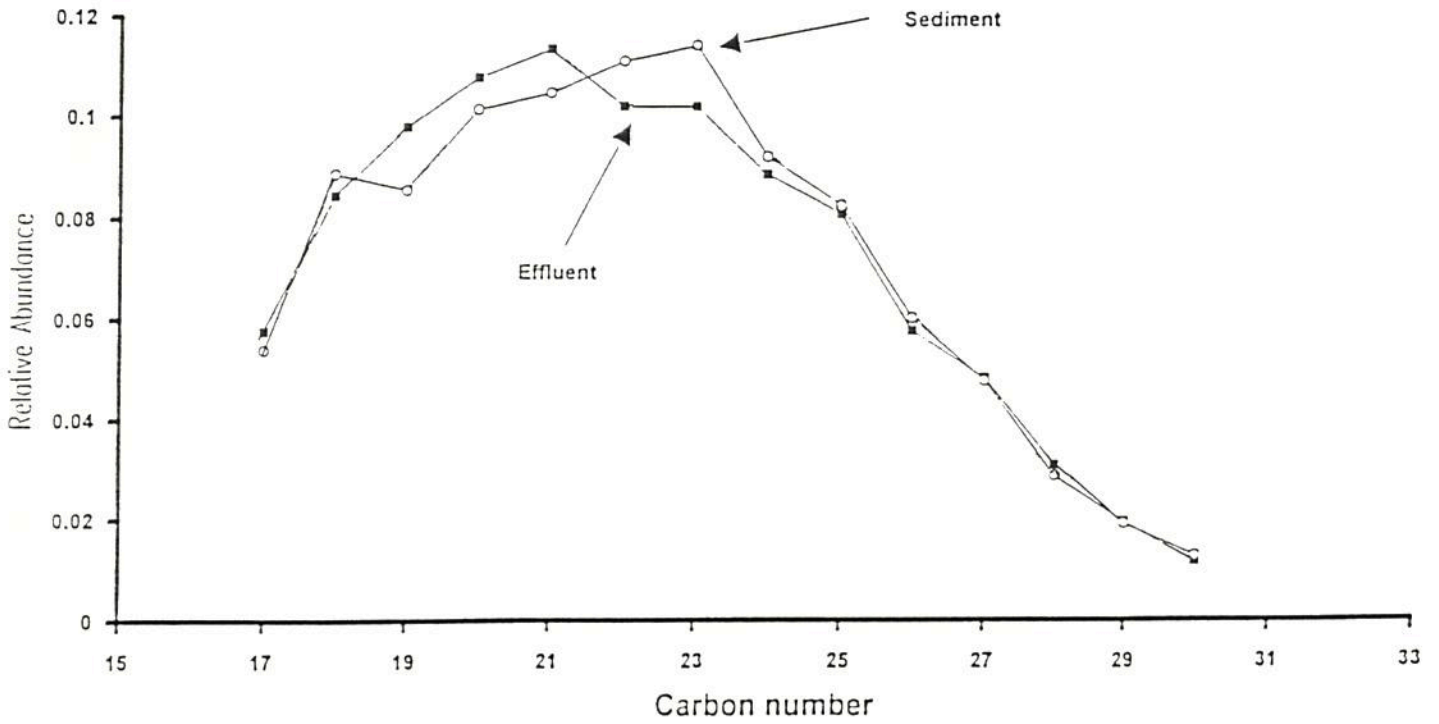


Figure 6. Comparison of n-alkane compositions in effluent and sediment 2km downstream from Kota Batak gathering station (site 5).

### MI 3189 n-Alkane Distribution

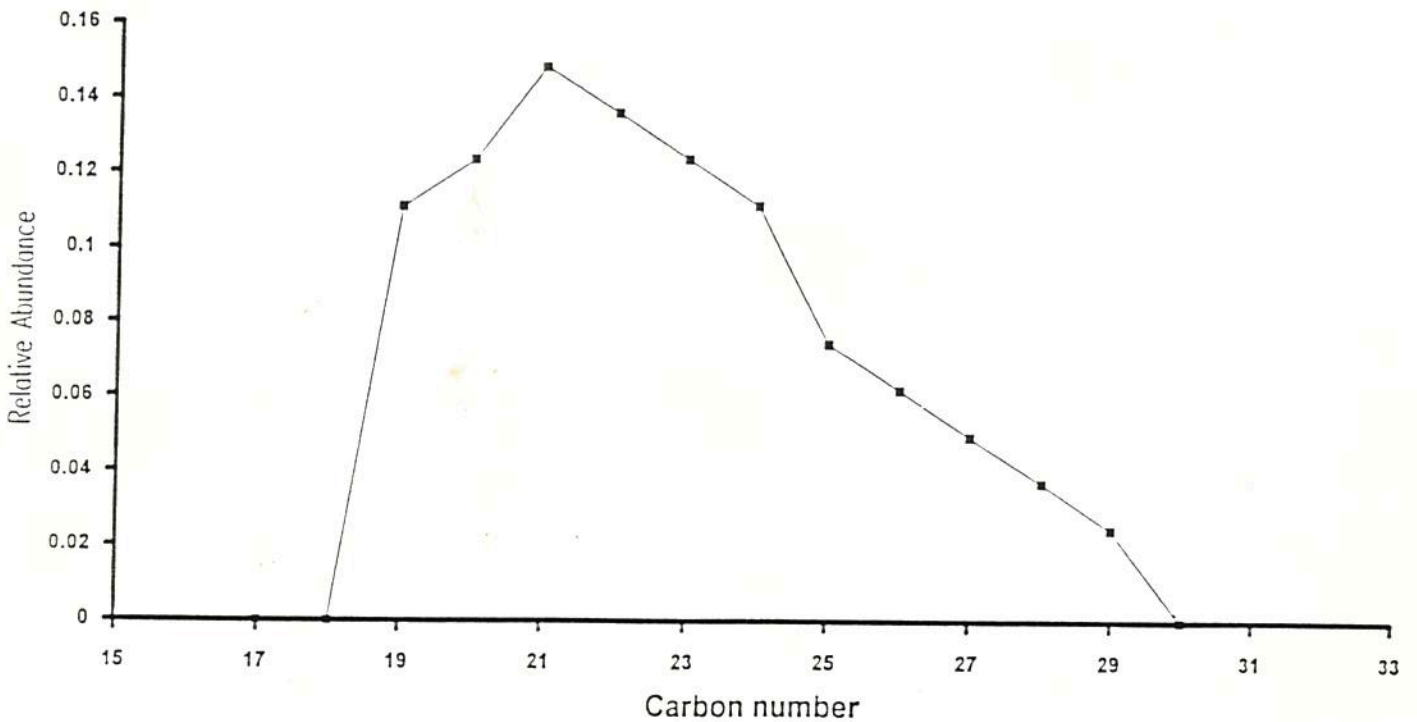


Figure 7. n-Alkane composition in drinking water from Deca Sungai Limau (site 1a) near the gathering station at Pusaka.

## DISCUSSION

All production waters showed a high degree of oil contamination, ranging from 4.4-190mg/l of total oil, with an average of 45.5mg/l. Discharge volume figures are not available and hydrocarbon concentrations in effluents would be expected to fluctuate with time, so an exact estimate of tonnages of oil discharged via this route cannot be made. However, the concentrations measured in the effluents and their temperatures will render them acutely toxic to all forms of life for considerable distances downstream. Toxicity of production waters to freshwater and marine life is discussed further below.

Of the six gathering stations investigated that at MINAS II is the largest and shows the highest concentration of oil contained in the discharged water. This is reflected in the sediment concentrations 400m from the point of discharge, which were the highest recorded in the survey, and almost ten times higher than the highest concentrations measured at other gathering stations. Clearly pollution control at this station is particularly lax.

Progressing downstream from the points of discharge at the gathering stations, no well-defined concentration gradient is observable. There are several factors that explain this observation. Firstly, the freshwater stream system comprises a complex network of interconnected channels and variation of total stream flow at different times of the year means that different channels will be subject to varying proportions of the total effluent burden according to changes in rainfall and runoff. The degree of emulsification of oil and water components of the effluent will influence the behaviour of the hydrocarbons and the distance they are carried downstream. Further to this, specific components of the complex hydrocarbon mixture discharged partition between environmental compartments at different rates and thus total deposition would not be expected to be uniform. Analysis of the sediments, however, clearly indicates chronic and widespread pollution of an extremely severe nature.

The extent of the environmental contamination is also reflected in the "background" samples taken at Pusaka (sample site 1; MI3167) and Minas II (sample site 3; MI3177), which approach concentrations recorded in some of the downstream sediments. Indeed the background sample taken from 1km upstream of Pusaka exceeds one of the samples obtained downstream from Minas II and approaches two of those downstream from Kota Batak. The possible sources of input to areas not directly impacted by wastewater discharges include; oil spills, surface runoff during rains; and wet and dry atmospheric deposition.

No information is available on the ecological effects of the Riau gathering stations. Most of the research carried out pertains to marine systems and is discussed separately (see section 2). Nance *et al.* (1991) investigated the effects of produced water on benthic populations in small stream-like bayou systems in Texas, USA. The effects produced by hydrocarbons contained in the sediments followed a classical pattern of community depression and stimulation upon the benthic population. The sample stations characterised as within the zone of depression all contained an average sediment hydrocarbon concentration greater than 2.0 mg/g dry sediment. During the 12 month study, a major depression of the benthic community was observed at those stations that averaged hydrocarbon concentrations above 5.0 mg/g dry sediment whilst a moderate depression was observed at those stations that averaged hydrocarbon concentrations between 2.0-3.5 mg/g dry sediment. Both zones of moderate and severe depression suffered loss of biodiversity, with species diversity values below 0.5, and average abundance levels below 190 individuals/m<sup>2</sup> in the severely depressed area. The zones of stimulation were found at least 1486m

downstream and 381m upstream from the discharge sites. The level of hydrocarbons in the sediments at these stations were between 0.2-0.3 mg/g dry sediment above the surrounding stations external to the zone of depression. Calculations have shown that the total area for the zone of stimulation was approximately 5 times larger than that for the zone of depression. The benthic loss within the zone of depression was estimated at 20,500 individuals, while the benthic gain within the combined zones of stimulation was 45,500 individuals. Both depression and stimulation are indicative of ecological modification, and though the extent of the changes over the longer term have not been investigated, widespread perturbation of species assemblages is likely to occur.

All sediment concentrations measured in Riau, with the exception of the background sample at Minas II, were above 5mg/g and so would be expected to experience severe depression as described by Nance *et al.* above (1991), with the associated losses of species diversity and abundance. The area under this level of stress thus extends at least 1 km downstream from all stations, and over 3 and 4 km at Kota Batak (site 5) and Beruk (site 2), respectively. Zones of moderate depression and stimulation will be far greater. In the zones of greatest impact close to the Riau gathering stations the combination of high temperature, with resulting loss of dissolved oxygen, and constant exposure to greatly elevated pollutant levels will probably cause loss of all animal life. Some plant life is evident in the highly polluted areas, but progressive die-back of some tree species alongside the streams is occurring. In one of the few studies of the impact of oils on tropical plant life, Getter *et al.* (1985) described mortality and abnormal leaf formation within two weeks of an oil spill in two species of black mangroves. Exposure in this case was for a comparatively short period and recovery only took place as oil concentrations decreased.

Due to the retention of oils in the sediments and their continued penetration into soil, the impact zone around the gathering stations will continue to spread even if emissions are curtailed. The behaviour of the different hydrocarbons in the vadose zone is variable and will be dependent upon temperature, groundwater chemistry and movement, soil structure and composition. These influence complex reactions which operate in the subsurface environment, the migration of contaminants and trends of toxicity. In general, the non-soluble compounds tend to be retained on soil particles whilst the more soluble compounds will tend to travel with the groundwater through the contaminated area. The movement of the lighter fraction of oils (soluble and volatile compounds) may also supply a significant organic contribution to the recharge zones of aquifers and may also enter the soil gas environment (Jyer *et al.* (1989). It is inevitable that "spilled" petroleum hydrocarbons will create a major source of contamination in both soil and aquifer systems.

Figures 2-7 illustrate fingerprinting of the n-alkane fractions of samples of sediments and effluents. It should be noted that the n-alkane fingerprinting is only a preliminary correlation tool and detailed analysis of other components are required for unambiguous correlation. However, the closeness of the correlations between samples from sites 3-5 strongly implies that the measured environmental contamination derives directly from the production waters.

Further downstream from the gathering stations, correlations are not as close. Differential partitioning of oil fractions, weathering and biodegradation would all contribute to changing the pattern. Also, the composition of oil

from a single well may change over time, and differences in fingerprints may also reflect oil discharged at different stages in the operation of the gathering station. This is exemplified by figure 2 which shows effluent and sediment from Pusaka (site 1). Figure 3, illustrates two sediments taken two kilometres apart below Beruk gathering station (site 2). The closer sample (MI3174) was taken from the effluent channel where there was a high flow rate of undiluted production waters at high temperature. MI3172 was taken from a stream polluted by the same effluent, but changes in temperatures and flow rate were significantly different. These differences in physical/chemical characteristics between the two sites would cause selection amongst the hydrocarbons and hence alter the profile of deposited compounds.

Mineral oils are also present in the two drinking water samples indicating that domestic supplies have been highly contaminated. The American National Academy of Sciences and National Academy of Engineering recommended in 1972 that public water supply sources should be free from oil and grease (Ram *et al.* 1986). These recommendations were reinforced in the USEPA guidelines on water quality criteria (Train 1979) which stated that the domestic water supply should be "virtually free from oil and grease, particularly from the tastes and odours that emanate from petroleum products".

The relationship between water quality and health with reference to hydrocarbon compositions and their toxic potential in other drinking water samples have been detailed in Packard *et al.* (1990). The following suspected and known carcinogenic (C), mutagenic (M) and promoter (P) hydrocarbons were identified; benzene (C), n-decane (P), n-dodecane (P), eicosane (P), fluoranthene (M), octadecane (P), phenanthrene (M), phenol (P), tetradecane (P), undecane (P).

Whilst it was possible to sample produced water, there will also be releases of crude oil from the gathering process, and drilling muds, which contain a wide variety of organic and metallic contaminants, will be generated. It was not possible to obtain samples of either of these for analysis. They will, however, add to the environmental burden in the vicinity of the gathering stations. A description of the composition and toxicity of crude oils and drilling muds are given in section 2 below. The disposal of drilling muds should be investigated, since they are a potentially large source of heavy metals. Another environmental problem associated with drilling operations was discovered recently. Salt deposition from formation waters creates scale on the internal surfaces of pipes and other equipment. Regular descaling is a routine operation necessary to prevent pipe blockage. However, it is now known that the scale can contain an accumulation of naturally occurring radionuclides (Wilson & Scott 1992) and must therefore be handled as low-level radioactive waste.

#### **CONCLUSION AND RECOMMENDATIONS**

The results and observations show with clarity the environmental impact exerted from onshore oil drilling operations. The inadequacy of effluent treatment processes adopted in Riau and the resulting large scale releases of hydrocarbon contaminants into the freshwater system have led to irreparable environmental damage resulting in severe long term hazards to human health and the quality of both surface and subsurface freshwater environments.

Settling lagoons show no apparent marginal sealing and receive effluent loads which are then poorly confined. Gravity driven separation of the undissolved oil components will result in hydrocarbon contamination of the underlying soil

column and ultimately poses a serious threat to groundwater quality. Under the tropical climate experienced in Sumatra, massive, uncontrolled discharges of uncleaned waters can also occur by flooding of the settling lagoons during the rainy season.

The rate and direction of hydrocarbon transport in soil will be largely dependent upon the degree of water saturation, the character of the soil components, the groundwater level, the chemistry of the soil water and the nature of the hydrocarbon contaminants. Clearly, predicting the effects from hydrocarbon contamination when few, if any, of these factors in the discharge areas are known is impossible. Any assessment of the extent and persistence of present contamination surrounding the settling lagoons and gathering stations is impaired by an inadequate knowledge of the chemistry and dynamics of the soil water and surface water systems in Riau.

In view of the high discharge temperatures ( $\approx 80^{\circ}\text{C}$ ), hydrocarbon evaporation almost certainly creates local atmospheric pollution and rainfall contamination. At present, elevated temperatures are maintained considerable distances downstream from the discharge sites. Remedial action by lowering the outflow temperatures will improve dissolved oxygen levels and encourage biological degradation although the persistence of the more volatile compounds, particularly aromatics, can counter this benefit by causing severe toxic effects on plant and animal life.

The high suspended sediment loads transported in the river systems of Riau have made the province noted for its "chocolate coloured" rivers. Suspended particulate matter in the water column are known to provide favourable substrates for hydrocarbon compounds and thus create an additional mode of contaminant transport in these river systems.

Indonesia still contains a rainforest, although in decline and already decimated by the impact of onshore drilling operations and oil production. The sensitivity of this region is made even more precarious by poor confidence in predicting the environmental responses to further development, forced by the paucity of knowledge detailing the effects of oil operations in tropical regions.

These reconnaissance investigations highlight the fragility of tropical regions exposed to oil contamination and form a basis to prompt research initiatives into the toxicological effects upon the freshwater ecosystem from onshore drilling operations. Comprehensive monitoring and assessment programmes are necessary to establish the scope and the scale of the existing problem with an view to remediation and in order to protect against such problems arising in other areas. A vital component of this programme would be the emplacement and rigorous enforcement of progressive legislation requiring emissions monitoring and reduction of pollutant loads to this irreplaceable ecosystem.



## SECTION 2

### POLLUTION FROM CRUDE OIL DRILLING AND REFINING

#### **CRUDE OIL**

Crude oil is formed over a period of millions of years from organic materials which have been exposed to great heat and pressure beneath the earth's surface (Katsouras *et al.* (1991). It consists of thousands of different organic molecules, the majority of them are hydrocarbons with between 4 and 26 atoms per molecule. In addition, crude oil contains sulphur and nitrogen compounds, and metals such as vanadium and nickel (Mason *et al.* (1991). Oil from different sources have very different compositions. The major types of hydrocarbons are alkanes, cycloalkanes and aromatics.

Two systems of nomenclature exist to describe the structure of these compounds. The most comprehensive is the I.U.P.A.C. system whilst the other consists of older or trivial terms more commonly employed by petroleum geologists. It is not unusual to find these two systems of terms mixed in the literature.

The I.U.P.A.C system is most commonly used by chemists and is as follows:

- |                     |                                                                                                                                     |
|---------------------|-------------------------------------------------------------------------------------------------------------------------------------|
| <i>Alkanes</i>      | Open chain single carbon/carbon bonded molecules; two forms n-alkanes having straight chains and isoalkanes having branched chains. |
| <i>Cycloalkanes</i> | Alkane rings.                                                                                                                       |
| <i>Alkenes</i>      | Similar molecules to above but unsaturated (ie with double bonds).                                                                  |
| <i>Arenes</i>       | Hydrocarbons with one or more benzene rings.                                                                                        |

The alternative scheme frequently used by petroleum geologists and those chemists frequently responsible for typing crude oils use the terms paraffins for alkanes, naphthenes or cycloparaffins for cycloalkanes, olefins for alkenes, and aromatics for arenes. However, the term aromatics instead of arenes, has received greater usage by all chemists.

The most useful and widely used terminology for petroleum hydrocarbons is;

*Saturated hydrocarbons:* Straight chained and branched alkanes (paraffins) and cycloalkanes (naphthenes) also called aliphatics

*Aromatic hydrocarbons:* Aromatics, polycyclic aromatics, cycloalkanoaromatics (naphthenoaromatics) and cyclic sulphur compounds.

*Resins and asphaltenes:* High molecular weight polycyclic fractions containing nitrogen, sulphur and oxygen (NSO compounds). Both have a high polarity (asphaltenes > resins) and are of low solubility (resins > asphaltenes).

#### **Typical crude oil components**

(abstracted from Gill R.A. and Robotham P.W.J. 1989)

*n-Alkanes:* make up approximately 15-20% of crude oils with a carbon number from n-C1-C40 and above, with a proportional bias towards the lower molecular weight. Degradation of crude oil by microbial action results in their reduction to compounds of lower molecular weight.

*Isoalkanes*: Many possible isomers exist and constitute approximately 1-2% rising to 15% in heavily biodegraded crude oils. The majority of isoalkanes exist as small C6-C8 forms.

*Cycloalkanes*: 50-55% of these occur as mono and dicyclic forms with 20% tricyclic and 25% tetracyclic. Together they can constitute approximately 31% of the crude oil.

*Aromatic compounds*: These occur normally as alkylated homologues from single ring compounds up to polycyclic aromatic forms, with a predominance of the smaller alkylated compounds. This group includes the highly volatile and frequently highly toxic benzene, toluene and xylene compounds.

Other compounds, such as aromatics combined with naphthene rings are also present, as are heterocyclic aromatic sulphur compounds and aromatic nitrogen compounds. Most crude oils have a low sulphur content (up to 2%) whilst nitrogen typically ranges from 0.094 - 0.65% sometimes reaching 1.24% in degraded asphalts. The nitrogen mostly occurs bound to the high molecular weight and low volatility fractions.

Resins and asphaltenes are complex arrangements of polycyclic or naphthenoaromatic nuclei with chains and heteroatoms of oxygen, nitrogen and sulphur. They constitute between 10% in light paraffin oils up to 60% in heavy degraded oils. Low concentrations of metals such as vanadium and nickel are common associations.

#### Identification of crude oil

The precise composition of a crude oil or oil product serves to uniquely characterise it from other oils or products. It is claimed that crude oils from nearby wells are distinguishable, even when samples taken from the same well at different times may show clear differences in composition (Clark and MacLeod *et al.* 1977).

Since the normal paraffins are the compounds most rapidly affected by biodegradation it is considered preferable to identify crude oils on the basis of their pristane/phytane ratio (Duckworth *et al.* 1986).

The isoprenoids, nor-pristane, pristane and phytane are abundant in petroleum products and are commonly found in petroleum polluted biotic and abiotic samples (Porte *et al.* 1990). They are also rather resistant to metabolic degradation, to the extent that the ratios among these homologues have been frequently used for characterisation of oil spillages in the marine environment (Albaiges *et al.* 1976, Gomez-Belinchon *et al.* 1991) Certain generalisations can be made concerning the chemical components of crude oil. These have a bearing upon the understanding of formation and degradation processes which in turn are frequently the basis for fingerprinting identification systems.

However, the composition of oil can be altered rapidly by weathering, and because many hydrocarbon components are also produced by other sources, the precise identification by analysis is not always possible. Instead, most workers use methods of "fingerprinting" in which the combination of various methods of qualitative and quantitative, or semiquantitative, analysis is applied, making use of the key identifying features of particular components.

Fingerprinting represents a practical approach to the analysis of oil and its products, and gives usable and useful results. Some of the common applications of fingerprinting are:

- a) identifying the pollutant (identification may range from the general to the absolutely specific),
- b) estimating the amount of pollutant present,
- c) estimating the extent of pollution (e.g. area of polluted water),
- d) determining the type and extent of weathering of the pollutant,
- e) estimating the time at which a spill occurred, or the period of contamination,
- f) tracking the physical migration of pollutant through a system,
- g) tracking the movement of pollutant through the compartments of an ecosystem (Gill *et al.* 1989).

#### **Indonesian crude oil composition**

According to Oudot *et al.* (1989) the Indonesian crude oil "Handil" is highly paraffinic and contains a high amount of long chain *n*-alkanes in the C20-C35 range. The pristane Pr (C18 isoprenoid) concentration is unusually high (*n*-C17 pristane 0.55), but is typical of Indonesian crude oils. Other characteristic features are the homologous series in the isoalkanes spectrum and the presence of the biological markers; polycyclic alkanes, steranes and terpanes. The main aromatic resolvable by chromatography are alkyl-naphthalenes (NPH). The unresolved complex mixture which lies under the baseline of the chromatogram contains the polycyclic alkanes and aromatics.

#### **DRILLING FLUIDS**

Abstracted from Edwards, (1989)

Drilling muds are circulated into the borehole to remove cuttings, lubricate the drilling bit, and provide hydrostatic pressure to prevent the well from blowing out. Chemical constituents of the muds and fluids also function to control corrosion (copper carbonate, sodium arsenite, alkyl phenoethylene oxide, imidazoline, abiethylamine and sodium sulfite), bacteria and scale formation (Tab. 1). Many of the constituents and chemicals are added to maintain essential physical and chemical properties, such as weight, viscosity, and pH.

Of the suite of heavy metals used during the drilling and completion of oil and gas wells, the most important are lead, arsenic and chromium (Kerr *et al.* 1981). Lead is the primary component of drill collar and pipe joint thread compounds, commonly referred to as "pipe dope". During the drilling operation, the trips of the pipe string in and out of the bore hole require the use of many pounds of "pipe dope" to treat the pipe joints. These compounds often contain greater than 30% lead (Edwards *et al.* 1985; Edwards *et al.* 1985; Monlux *et al.* 1971). In addition, chromates and arsenicals have been used extensively as corrosion inhibitors and additives in drilling muds and fluids. (Edwards *et al.* 1985; Gray *et al.* 1980; Kerr *et al.* 1981).

Tab 1. Partial list of components of oil well drilling muds and fluids

Arsenic	Diatomaceous earth	Potassium hydroxide
Asbestos	Gilsonite	Quebracho
Asphalt	Guar gum	Sepiolite
Attapulgite	Hog hair	Sodium bicarbonate
Bagasse	Lignite	Sodium chloride
Barite	Lignosulphonates	Sodium dichromate
Bentonite	Magnesium chloride	Sodium phosphate
Calcium Bromide	Magnesium oxide	Sodium sulfite
Calcium Carbonate	Mica	Starch
Calcium Chloride	Mineral Wool	Tannins
Calcium hydroxide	Olive Pits	Vermiculite
Calcium oxide	Organic polymers	Wood shavings
Calcium sulfate	Organophosphates	Xanthan gum
Chromic chloride	Pecan shells	Zinc bromide
Chromium potassium sulfate	Polyphosphates	Zinc carbonate
Coal	Potassium carbonate	Zinc chromate
Cottonseed hulls	Potassium chloride	Zinc sulfate

#### PRODUCED WATER

Other contaminants will also be expected to occur in production water effluents. Daniels *et al.* (1990) investigated the characterisation of the chemical contaminants present in produced water collected at two discharge sites in South Louisiana. Their results show that the major volatile constituents found in produced water were benzene (1200-2000  $\mu\text{g/l}$ ), toluene, ethylbenzene and xylenes, together with phenol (1600, 1800  $\mu\text{g/ml}$ ), *p*-creosol, *m,o*-creosol and benzoic acid. In their analyses various other saturated and unsaturated hydrocarbons (PAHs, primarily alkylated analogues of naphthalene and phenanthrene), cyclic hydrocarbons, ketones, low molecular weight alcohols) and various acids were also detected. Benzoic acid was the most abundant single organic constituent overall at the two discharge sites (3100  $\mu\text{g/l}$  and 4000  $\mu\text{g/l}$ ) whilst the greatest concentration of PAH detected in sediment samples at a single discharge site was 25 000 ng/g.

#### REFINING OF CRUDE OIL

Crude oil is refined by a process essentially of distillation which separates the different fractions at increasing boiling points. At low temperatures, those compounds used in the production of petroleum are separated. At higher temperatures, naphtha, (which forms the basis of the petrochemical industry, separates) while at higher temperatures diesel oil, bunker oil (used to fuel ships and power-generating stations) and tars are separated. Further refinements to the distillation products are often necessary to produce commercial products (Mason *et al.* 1991).

#### PATHWAYS OF OIL INTO FRESHWATERS

There are many pathways in which oil can reach the freshwater environment. Amongst these are oil spills from wells or road vehicles, run off from roads and leakage from oil storage tanks or pipelines, all of which can lead to oil

filtering through the soil and contaminating groundwater. Oil tends to penetrate porous subsoils better wherein gravitational and/or capillary movement is the principal mechanism of penetration. The rate of penetration through the soil depends on the soil structure and the type of oil. For example, high viscosity oils penetrate less effectively compared to lighter, low viscosity oils. In areas where oil pools or accumulates on the surface the degree of penetration increases in response to a pressure head which encourages the movement of oil downwards.

Upon the introduction of petroleum hydrocarbons into the environment, immediate interaction occurs with the surrounding systems. Some of the major processes affecting hydrocarbon compounds include adsorption, chemical degradation, diffusion, volatilization and biodegradation. Separation and equilibration of these compounds will occur contributing a significant effect upon the chemistry of the soil and other freshwater environments, ultimately endangering aquifer systems and entering domestic water supplies.

### **BIODEGRADATION**

The biodegradation of oil may be accomplished via several pathways involving a complex series of chemical reactions including the metabolic function of microorganisms. The uptake of hydrocarbon components by microorganisms is converted to new cells and metabolic products, most commonly carbon dioxide and water.

Zo Bell *et al.* (1946) discovered a wide range of microorganisms capable of utilising hydrocarbons as their sole source of carbon and energy. More than 100 species representing at least 36 genera of bacteria, fungi, yeasts and one algal genus have since been shown to use hydrocarbons in this way.

The factors that control the rate of biodegradation of oil in different natural environments are oxygen supply, inorganic nutrients, temperature, light, water availability, pH, salinity, other gases and other carbon sources. The rate at which biodegradation of oil occurs is variable as some hydrocarbons are more susceptible to breakdown and can be utilised more readily than others (Morgan *et al.* 1992).

Generally, oil degradation by microorganisms occurs in the following sequence; aliphatics > aromatics > heterocyclics > asphaltenes.

Experiments conducted by Oudot *et al.* (1989) refined this classical order of biodegradability of petroleum components (i.e. *n*-alkanes > iso-alkanes > medium molecular weight polycyclic alkanes and aromatics). They confirmed that those compounds known to be more resistant to biodegradation (i.e. heavy polycyclic alkanes and aromatics, steranes-terpanes, resins and asphaltenes) were in part retained on the substrate used in their experiment indicating that in the natural environment these components would be expected to remain firmly bound to the mineral matrix of the soil or sediment.

Intensive research has been undertaken on isolating the pathways of biodegradation and selecting the right microorganisms to biodegrade crude and other oils (Gibson *et al.* 1984). Edwards *et al.* (1992) discovered the complete mineralization of toluene and the three isomers of xylene by aquifer-derived microorganisms in a gasoline-contaminated sediment which utilized sulfate under strict anaerobic conditions to produce CO<sub>2</sub> and biomass. However, under

these conditions benzene and ethylbenzene were not degraded. The persistence of benzene and ethylbenzene raises concern as these compounds, along with toluene and xylenes, are confirmed or suspected carcinogens, even at very low concentrations (Dean et al. 1985). Anaerobic conditions may easily be generated or accelerated after periods of oil spill or operations involving oil separation due to the ability of the oil to seal either the surface layer of the water column or the sediment surface.

In contrast, Tabak et al. (1981) have shown that benzene can be potentially biodegradable by microbial populations under aerobic conditions, however nitrogen could be a limiting factor in the biodegradation of benzene under certain conditions (Karlson et al. 1989). Other studies dealing with the effectiveness of benzene biodegradation include Vaishnav et al. (1987) and Korte et al. (1982).

## **BIOLOGICAL EFFECTS**

### **Aquatic environment and bioaccumulation**

Considerable research has been undertaken to evaluate the effects of off-shore drilling operations or oil spill on marine aquatic organisms. These studies have indicated that such events present a primary cause concern for the effects upon the marine ecosystem. It is noteworthy that few of these investigations have been conducted in the tropical region, consequently the environmental impact of drilling operations and oil spills are less predictable and have remained poorly assessed in these environments.

Research into the toxicity of crude oils upon aquatic microalgae has shown that acute toxic effects are mainly due to the water-soluble components in crude oils which are generally designated as the "water soluble fraction" (WSF) (Winters et al. 1976; Nunes and Benville 1979; Ostgaard and Jensen 1983; Bate and Crafford 1985; Siron et al. 1991). Comparatively little research has been directed towards the impact resulting from onshore drilling operations which include the discharge of produced waters into the freshwater environment.

Amongst the more mobile marine organisms, the variability shown in the toxicity of oils to fish in short-term tests have revealed a range of influences (Hedtke and Puglisi 1982). These may depend on the type of oil, differences between batches of the same oil, the changing nature of oil with time, the type of test system or the length of exposure.

Prasad et al. (1987) investigated the histochemical observations on crude oil poisoning in the respiratory epithelium of the fish species *Puntius sophore*. In the respiration process, mucus secretion is known to play an important function in the maintenance of the gill tissue for respiratory activities (Munshi and Singh 1968). The rate of secretion and the nature and quantity of the mucus responds to a variety of environmental and pathogenic agents. It follows that any change in the physico-chemical character of the ambient media (i.e. seawater) will cause aberration to the normal functioning of the mucus glands and in turn the respiratory mechanism.

Results indicate that the function of the mucus cells are highly susceptible to crude oil poisoning. Oil concentrations were found to be lethal at 2000ppm but still effective in respiratory disfunction at sublethal concentrations. Lethal extracts reduce the number and size of the mucus cells causing scanty

mucus secretion in short-term exposure (4 hours), culminating in the degeneration of the mucus cells when the exposure period is prolonged (12 hours). In contrast, sublethal extracts induce excessive mucus production resulting in the formation of a protective covering over the branchial epithelia.

Of the small number of investigations documenting the effects and impact of oil spill and off-shore drilling operations in the tropical region, Garrity and Levings (1990) examined the effects of an oil spill on the molluscs of a Caribbean intertidal reef flat where about 8 000 000 litres of medium weight crude oil were spilled in 1986. The results show that the mortality was extensive in some sections of the reef flat and that complete recovery had not been achieved up to three years after the spill. The separation of fluctuations in mollusc population by natural means from those caused by the oil spill, and the evaluation of the time required for final recovery of the population must await further study.

In other studies into the effect of oil discharge into the Caribbean, Jones *et al.* (19..) investigated the quantity of stranded beach tar on Jamaican beaches. Of the 26 beaches visited, sampled for 5 days in every month over a study period of 13 months, 61.5% were contaminated by tar at any one time. Tar values ranged from 0 g/m<sup>2</sup> to 11 940 g/m<sup>2</sup>; the most contaminated beaches showing tar residues in the form of aggregated lumps.

Given the frequency of inland oil spills, detailed investigations of this mode of contamination are few. Between 1979 and 1986, 179 inland spills were reported in the USA, the majority of these involving less than 100m<sup>3</sup> of oil (Cronk *et al.* 1990). The Ashland accident (1988) in Ohio discharged nearly 2700m<sup>3</sup> of no. 2 diesel fuel into the Monongahela River at the Ashland Oil Company's Floreffe River terminal, an oil storage facility 40km upstream of the head of the Ohio River. The spill is estimated to have killed between 10 000 to as many as 3 000 000 fish (CHMR 1989).

The effects of test on freshwater fish exposed to diesel oil indicate 50% mortality at emulsified diesel oil concentrations of between 0.9 - 6.2ppm over 4 days exposure, and 0.9 - 8.2 ppm over 1 day exposure (Rehwoldt *et al.* 1974).

Daniels *et al.* (1990) conducted cytogenetic assays using developing embryos of an estuarine fish, the sheepshead minnow (*Cyprinodon variegatus*) to determine the potential mutagenic and clastogenic threat posed to organisms residing in areas effected by discharged waters.

The results of their assays supports the hypothesis that production water discharged into semi-enclosed areas may pose a long-term ecological hazard for fishes inhabiting these waters. Produced water discharged at both sites was found to induce very high frequencies of clastogenic effects (i.e. chromosome gaps and breaks) in developing embryos of *C. variegatus*. Interestingly, the produced waters had to be diluted by a factor of 25 before the bioassays could be successfully performed. Since the observation of chromosomal aberrations is usually rare in the cells of *C. variegatus* and since cell replication and differentiation are maximal in the early developmental stages of this and other species of aquatic organisms, the results strongly suggest a potential for adverse effects of such discharges on estuarine productivity.

The toxicity of production water appears to be greater in shallow water (< 10m), particularly around production platforms where the destruction of benthic populations has been noted. In deep water the effects of production

water have less effect because of dilution (Mackin, 1971, 1973). Although the measured variability in total toxic organic loads of different produced waters limits conclusions about their toxicity, these results serve to indicate the potential effects of such waters discharged from other sites. There is clearly a need for continued research on the toxic effects of chronic operational discharges of produced waters upon aquatic species in other estuarine environments.

### **Sediments**

In the marine environment, Wade et al. (1989) detailed the uptake of PAHs into organism tissues from areas of natural oil seepage containing a significant amount of polynuclear aromatic hydrocarbons (PAHs). In these areas the largest repository for these compounds was contained in the sediments which presumably acted as a favourable substrate for PAHs. It was found that those sediments containing the highest concentration of PAHs supports sedentary organisms (e.g. mussels and tube worms) which contain high levels of these compounds in their tissues. These concentrations were found to be much greater than those in the tissues of more mobile organisms (e.g. fish) in the area. In addition, the microbial biomass around the areas of natural oil seepage was found to be substantially enhanced. The existence of apparently healthy populations of sedentary organisms in areas of naturally introduced oil may indicate that certain organisms can show a marked tolerance to artificially introduced hydrocarbons, adapting well under conditions which other organisms experience stress.

In an attempt to monitor the contribution of carbon derived from natural oil sources to the biomass (Wade et al. 1989), the resolution offered by isotopic studies could not distinguish between this and the fractionation involved in chemosynthesis in providing the primary source of isotopically light carbon to the system. However, Wade et al. (1989) concluded that processes of oil biodegradation / bioassimilation by these organisms cannot be totally discounted. This indicates that a causal link between oil in the environment and hydrocarbon uptake by organisms may still need to be more positively reinforced.

Referenced to sediments have been superficially addressed in the foregoing discussion of the aquatic environment. It has already been mentioned that most of the remaining hydrocarbons after evaporation will reside in the first 15 cm of the sediment column (Oudot et al. 1989). Further to this, changes in the dynamics and chemistry of the aquatic system can be expected to force changes in the underlying sediment substrate.

Changes in the concentration of hydrocarbons in water column are affected by evaporation. This can produce an upward migration of hydrocarbons to the water surface. In response, stored hydrocarbons in the sediment are taken up into solution. Hydrocarbon transport in the reverse direction can occur in response to the resuspension of sediments by strong seasonal currents which effectively remove hydrocarbons together with the surface sediment, leaving the hydrocarbon concentration of the remaining substrate lower than the overlying water column.

Processes of physical mobilisation will also redistribute or back transfer stored oil compounds from the sediment into the water column. Here it becomes accessible to free-swimming organisms in addition to being subject to redistribution, posing a threat of further contamination at distance from the



site of discharge.

The transfer rate of oil between sediment and water will be dependent upon the degree of hydrocarbon saturation, the porosity, the grain size and the chemical composition of the sediment. PAHs are among the most commonly known compounds found in the sedimentary environment; their abundance reflecting the primary composition of the oil source. These compounds are sometimes highly toxic, a few known to be carcinogenic or mutagenic.

#### **Atmospheric emissions**

Evaporation occurs during the exchange of oil components across the air-water/oil interface and accounts for one of the principal outward pathways of oil from the aquatic environment (Liss and Slater, 1974). The rate of hydrocarbon evaporation depends upon the composition of the oil, the surface area of the oil spill, the solubility of the hydrocarbon in water, the water and air temperatures, and the wind speed and moisture content. Most oils possess a specific gravity less than 1 and therefore remain as a floating film in all but turbulent regimes (Herbes and Yeh, 1985).

Evaporation has been shown to be minimal in a flowing river system indicating the persistence of oil-spill contamination in these environments. Laboratory experiments indicate quite clearly that oil loss by evaporation is suppressed in flowing, turbulent waters compared to the higher transfer rates measured above stagnant waters (Mackay and Wolkoff 1973). Evaporation is most effective when oil lays undisturbed on the surface of the water and in contact with a flowing air stream. The rate of oil evaporation from flowing or turbulent waters is considerably reduced due to the removal of oil from the water surface and its redistribution through the water column. The mixing of oil and water, such as might be expected in flowing freshwater systems, imposes a delay upon the transfer of oil from the water body to the water surface thereby maintaining an ecological threat to the aquatic environment.

Once hydrocarbons have evaporated they are known to combine with atmospheric particles and to be precipitated in rain or snow (Katsouros *et al.* 1991). For example, the solubility of benzene in water (1.8 g/l) is sufficient to suggest that atmospheric benzene can be rained out onto land masses and water bodies (Nielsen *et al.* 1991). In fact, benzene has been detected in rainfall in the UK at concentration levels of 87.2  $\mu\text{g/l}$  (Colenutt *et al.* 1980).

Evaporated hydrocarbons also provides a source of reactive organic gases which when combined with emitted oxides of nitrogen (NO<sub>x</sub>) can, via a complex series of reactions, form ozone as a reaction product (Carter *et al.* 1990, Altshuller *et al.* 1991). Photochemical ozone formation continues to be an important air pollution problem in many urban and downwind areas.

#### **Weathering**

Oudot *et al.* (1989) studied the weathering and biodegradation of hydrocarbons in a tropical estuarine ecosystem in Indonesia. They detected a substantial reduction in the concentration of hydrocarbons in the first few days prior to a more regular decrease. The conclusions after the twelfth month of their investigation indicated that oil removal by weathering/biodegradation was highest in the lower intertidal zone, presumably the result of more active washing-out of oil by tidal flushing in the lowest areas of the experimental

field.

Analyses of the oil contaminated estuarine waters by gas chromatography showed that the lighter hydrocarbons up to C14 disappeared within the first three weeks after their introduction. This was attributed to evaporation both at the site and during processing of the samples.

### **Wildlife**

Edwards *et al.* (1989, 1991) conducted intensive studies into the environmental impact of the major steps involved in oil production (*viz* drilling, completion, production, transportation, etc.), covering the toxicity of petroleum hydrocarbons, drilling fluids, muds and additives upon both livestock and wildlife. The toxicological effects of these materials is complicated by the extensive compositional range of drilling muds, fluids and additives.

In most cases drilling fluids, well treatment solvents and other chemicals used in oil production are complex mixtures, are commonly toxic, and produce effects which may be additive or synergistic. Many of the fluids and additives are extremely caustic and produce rumenitis, whilst others are petroleum or solvent-based and can result in aspiration pneumonia and rumen dysfunction. In addition, some are methemoglobin inducers, and some contain phenolics and other hepatotoxins.

Perhaps the most visible impact of oil spills upon wildlife is the oiling of seabirds and waterfowl. These effects have been measured by McEwan and Koelink (1973) who found that the thermal conduction of oiled ducks increased from 74% to 98% and resulted in rapid heat loss and the onset of hypothermia. Growth rates, behaviour and egg production may also be adversely affected (Shales *et al.*, 1989) together with extensive organ damage (Khan *et al.* 1991).

It is common that birds which suffer contamination though not necessarily incapacitation by oiling, may nevertheless fail to breed successfully because of the toxic effects of oil transferred to the eggs during their incubation. An illustration of this was provided in Szaro (1979) in which a drastic reduction in the hatching success of mallard chicks was recorded from those eggs treated with a surface application of oil spread over the shell. A 100 per cent mortality was recorded in those eggs treated with a 10 $\mu$ l application; the toxicity probably being due to the aromatic components of the oil. The dead duck embryos showed a number of abnormalities including deformed bills, a reduction in liver size, incomplete ossification and incomplete feather formation (Hoffmann, 1979).

### **Plants**

The toxic effect of oil spills upon plant life can be adequately summarised from the work of Holt *et al.* (1987) wherein the impact of crude and diesel oil spills on plant communities in Northeast Greenland. Several interacting factors were cited which are considered to have influenced the ability of different vegetation types to recover after their decimation by oil spill contamination. These are;

- (1) resistance of the species to the direct toxic effect of oil
- (2) moisture conditions at the site (e.g. a high moisture content in the soil accelerates recovery)

- (3) exposure to physical secondary stresses such as desiccation and snow abrasion (e.g. wind-exposed sites without a protective snowcover during the winter showed a very low rate of recovery)
- (4) the duration of the latent toxicity of surface soils which prevents or reduces establishment of new seedlings.

The direct toxic effects of diesel oil was found to be more pronounced in the majority of the plant species compared to the effects of crude oil. Although a high degree of recovery in the plant cover occurred in those sites with high moisture within 4 to 5 years; the species diversity can be expected to be reduced for a longer period of time. In contrast, the drier plots located in a physically harsh environment showed a very low rate of recovery in the plant cover and can be expected to be affected by the oil spills for several decades.

Laboratory tests into the impact from oil spill upon black mangrove showed that except for the production of anomalous lateral foliage, all stress symptoms, or mortality, in two species of black mangrove was manifested within 2 weeks of oil treatment (Getter *et al.* 1985). From this, it is indicated that the toxicological effect from petroleum-hydrocarbon on mangrove seedlings occur within a relatively short time. Subsequent field trials showed that most damage to both adult and seedling trees had occurred within four months with no further effects observed after that time.

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