



CHAPTER II

PETROLEUM HYDROCARBONS IN THE MARINE ENVIRONMENT

2.1 The Composition of Petroleum Hydrocarbons

Crude oils and most of their distillation products are extremely complex mixtures containing thousands of compounds, comprised mostly of hydrocarbons, but often containing some sulfur, nitrogen and oxygen. Hydrocarbons can be classified into four categories (Figure 2-1) as follows:

1. Aliphatic Hydrocarbons

1.1 n-alkane. Crude oils often contain homologous series of n-alkanes extending from C_2 to beyond C_{60} with a smooth distribution between odd and even numbered carbon chain lengths.

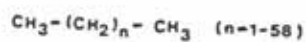
1.2 Branched alkanes (isoalkanes). Crudes contain many parallel homologous series of isomers including series of isoprenoid alkanes.

2. Alicyclic Hydrocarbons (Naphthenes) They are the complex mixture of cycloalkane including substituted and unsubstituted hydrocarbons.

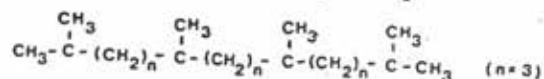
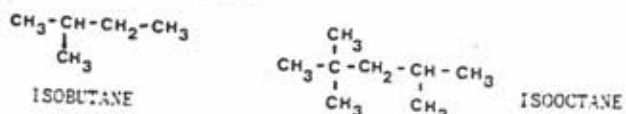
3. Aromatic Hydrocarbons Aromatics are complex mixtures including mono and polyalkyl-benzenes, naphthalenes and polyaromatics with multiple alkyl-substitution.

1. ALIPHATIC HYDROCARBONS

1.1 n-ALKANES

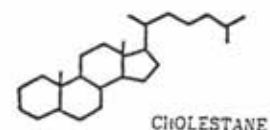
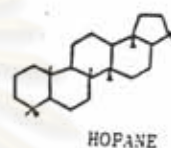
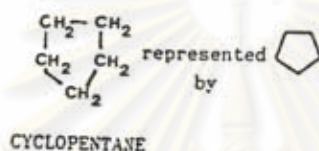


1.2 ISOALKANES

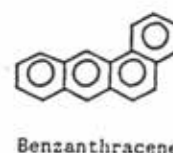
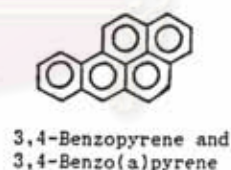
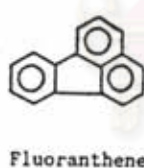
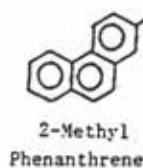
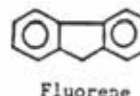
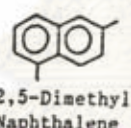
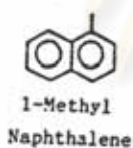


PRISTANE
(an isoprenoid hydrocarbon)

2. CYCLOALKANES

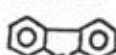
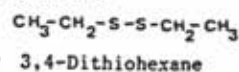
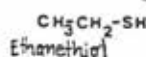


3. AROMATIC HYDROCARBONS



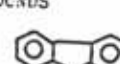
NSO COMPOUNDS

SULFUR COMPOUNDS



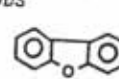
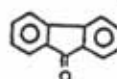
Thiocyclohexane Thiophene Dibenzothiophene

NITROGEN COMPOUNDS



Pyridine Quinoline Indoline Carbazole

OXYGEN COMPOUNDS



Fluorenone Phenol Dibenzofuran

Figure 2-1 CHEMICAL STRUCTURES OF PETROLEUM HYDROCARBONS.

4. Olefinic Hydrocarbons (Alkene) Absent in crude oils but often present in refined products.

Crude oils contain about 30% alkanes, 50% cycloalkanes, 15% aromatics and 5% nitrogen, sulfur and oxygen derivatives. The composition of oils from different global regions can vary tremendously.

Refined petroleum products are made by fractional distillation of crude oils and are thus discrete cuts or subsets of boiling range of starting crude. The composition of distilled oils are shown in Table 2-1

Table 2-1 Composition of distilled oils. (Hunts, 1979)

| Molecular size | Volume percent |
|---|----------------|
| Gasoline(C ₅ to C ₁₀) | 27 |
| Kerosene(C ₁₁ to C ₁₃) | 13 |
| Diesel fuel(C ₁₄ to C ₁₈) | 12 |
| Heavy gas oil(C ₁₉ to C ₂₅) | 10 |
| Lubricating oil (C ₂₆ to C ₄₀) | 20 |
| Residuum(> C ₄₀) | 18 |
| Total | 100 |

2.2 Origin of Hydrocarbons in the Marine Environment

Hydrocarbons enter the marine environment via three general processes. (Farrington and Meyer, 1980)

1. Biosynthesis : (Biogenesis Hydrocarbons)

Marine organisms can 1) synthesize their own hydrocarbons, 2) obtain them from their food sources, or 3) convert precursor compounds obtained with their food. These hydrocarbons may be released during metabolism or upon the death and decomposition of the organisms. Normal alkanes in organisms often exhibit a characteristic predominance of odd-numbered homologs over even-numbered ones. Odd carbon preference may be expressed by the ratio between the total weight of odd-carbon homologs and the weight of the even-carbon homologs. This ratio is known as the Carbon Preference Index (CPI), (Yen, 1975 and Sleeter et al, 1980) and is calculated as follows:

$$\text{CPI}_{x \rightarrow y} = \frac{\left(\sum_{n=x}^{n=y} \text{HC}_{\text{odd}} \right) D}{\left(\sum_{n=x}^{n=y} \text{HC}_{\text{even}} \right) N}$$

where D = number of even-numbered homologs between x and y, inclusive; and N = number of odd-numbered homologs between x and y, inclusive.

Marine algae are characterized by n-alkanes where predominant at C₁₅, C₁₇, C₁₉ and C₂₁. In marine phytoplankton, the normal alkanes

with 15, 17, 19 and 21 carbon atoms are most abundant. (Anderson et al., 1981; Risebrough et al., 1983; Readman et al., 1986; Siron et al., 1987). Some bacteria are found to contain even- and odd-carbon-numbered C₂₅ to C₃₂ n-alkanes.

Branched alkane, including isoprenoids pristane (C₁₉),

have been found in uncontaminated recent sediments and organisms. Isoprenoids pristane are resolved from the normal C₁₇. Pristane is commonly found in plankton, especially in copepod, and various marine animals (Farrington and Meyer, 1980).

The most common isoprenoids, pristane and phytane, are found in several marine organisms, especially in plankton such as copepod and in recent sediments. They are derived from degradation products of the phytol chain of chlorophyll. Reducing conditions are necessary for a transformation of phytol to phytane, producing dihydrophytol and phytane as intermediates; oxidizing conditions assist a conversion of chlorophyll into pristane (Ikane et al., 1975) (Figure 2-2). Pristane have been found in uncontaminated recent sediment. A biochemical pathway for converting chlorophyll into pristane but not into phytane has been expressed below. The ratio of pristane/phytane is a useful indicator of a redox conditions in sediments. Simoneit (1977) reported the values of the pristane/phytane being vary from 0.85 (0.4 m depth) to 1.43 for anoxic Black Sea sediments. In this study the ratio pristane/phytane for sediments are concerned.

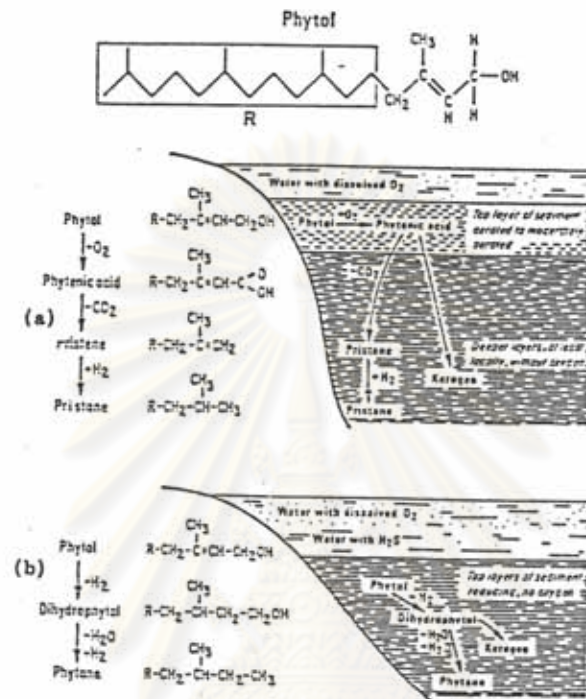


Figure 2-2 Diagenetic pathways from phytol to pristane and phytane
 a) in the presence of oxygen
 b) in the absence of oxygen
 (after Ikane et al., 1975)

ศูนย์วิทยทรัพยากร
 จุฬาลงกรณ์มหาวิทยาลัย

2. Geochemical Processes

There are a number of geochemical processes introducing hydrocarbons into the marine environment. The natural seepage of oil is an obvious example of this category. Weathering of ancient sediments and the resulting transport of the sediment and associated ancient hydrocarbons to the marine environment by fluvial or aeolian processes can result in introduction of an assemblage of hydrocarbons and other compounds similar to the composition of hydrocarbons. Two other processes, forest fires and early diagenesis of organic matter deposited to surface sediments, must also be considered (Farrington, et al., 1980)

Submarine and coastal land oil-seeps release petroleum hydrocarbons to the marine environment. Weathering of soils and sediments and transport of some of the hydrocarbons in these sediments to the marine environment should also be considered as an input, although probably small when compared to other sources because of a slow degradation of the hydrocarbons during the weathering process. There are chemical synthesis processes which are sources of hydrocarbons. Forest fires inject hydrocarbons into the atmosphere. There are also chemical reactions occurring during the diagenesis of organic matter in sediments which yield hydrocarbons (Farrington and Meyer, 1980).

3. Anthropogenic Inputs (Petroleum Contamination)

Anthropogenic inputs are the inputs of hydrocarbons from accidental and intentional discharge of fossil fuel to the marine environment and the input of hydrocarbons from atmosphere. The important group of hydrocarbons are polycyclic aromatic hydrocarbons.

2.3 Differentiation of Petroleum Hydrocarbons from Biogenic Hydrocarbons.

It is particularly important to know technics for distinguishing between petroleum and biogenic hydrocarbons for the determination of petroleum contamination in sediments, organisms and water. Those criteria are as follows (Farrington, 1980):-

1. Petroleum contains a much more complex mixture of hydrocarbons, with much greater ranges of molecular structure and weight.

2. Petroleum contains several homologous series with adjacent numbers usually presents in nearly the same concentration. The approximate unity ratio of even- and odd-numbered alkanes is an example of the homologous series of C_{12} to C_{23} isoprenoid alkanes.

This means that marine organisms have a strong predominance of odd-numbered C_{15} through C_{21} alkanes.

3. Petroleum contains more kinds of cycloalkanes and aromatic hydrocarbons than biogenic hydrocarbons. Also the numerous alkyl

substituted ring compounds have not been reported in organism. Examples are the series of mono-, di-, tri-, and tetramethyl benzenes and the mono-, di-, tri-, and tetramethyl naphthalenes.

4. Petroleum contains numerous naphthenoaromatic hydrocarbons have not been reported in organisms.

2.4 Fate of Oil Entering the Sea

A variety of physical, chemical and biological processes affect the fate of spilled oil (Figure 2-3). Physical and biological processes rapidly act on oil slicks which generally results in their disappearance within a few days. Components of oil which enter the water also have a short residence time with some being carried to the bottom by sedimentation. The bottom sediments, thus are ultimate sinks for undegraded oil. The details are as follows:-

1. Fate of oil in slicks

After discharging, an oil slick forms due to the low water solubility of most components. Current, waves and winds act to spread the oil slick into thin film. The spread depends on the volume of oil spilled and its physical properties, i.e., heavy viscous oils do not spread as rapidly as less viscous types. In an open sea, wind often determines the direction and speed with which a slick moves with oil drift velocity about 3% of the wind velocity. In near shore areas tidal forces are able to control the oil movement.

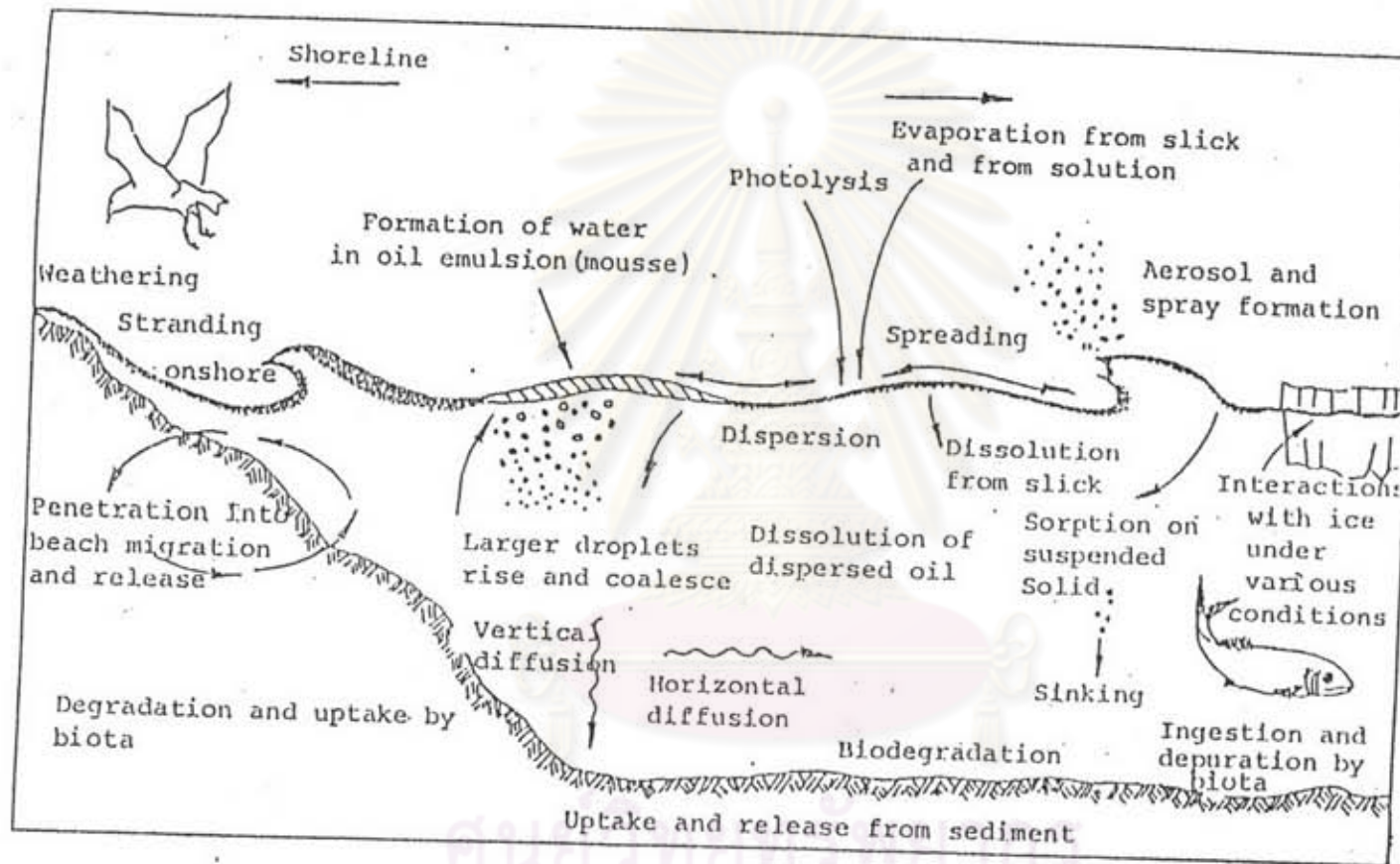


Figure 2-3 Fate of oil in the marine environment.

(source : Smith, 1983)

Processes responsible for the disappearance of a slick include evaporation, dissolution, emulsification, photochemical oxidation and microbial degradation. A first order equation describes changes of oil concentration resulting from these processes is (Geyer,1980):

$$dc/dt = (K_v, K_e, K_d, K_p, K_b)C$$

K_v , K_e , K_d , K_p and K_b are evaporation, dissolution, photochemical, emulsification and biological decay coefficients, respectively.

Spreading theory of an oil on a water surface has been studied. Basically the approach of the theory bases on an assumption that a constant volume of spill of a single component petroleum spreads out radially with a monotonically decreasing thickness. Initially the oil spreads in a buoyant lens with gravitational spreading balanced by inertial forces, i.e., an accelerated mode that lasts only for a short period of time. A second nonaccelerated phase follows, in which gravity forces are balanced by viscous retardation set up by the boundary layer flow in the water underneath the oil slick. Rapidly the slick thins to a point where surface tension becomes the dominant spreading agent, with viscous drag against the retarding force. The slick diameter D in this final and by far most significant regime is dependent on the air-water surface tension, time since inception of spill, and the density and viscosity of water. Murray(1982) cited Milgram(1978) who emphasizes that oil does not spread uniformly, as assumed in this theory, but characteristically

separates into thick (>0.5 mm) and thin (<0.1 mm.) regions with varying levels of spreading pressure. Fractionation of a real oil slick into its various components is cited as the case of this phenomenon.

Effects of winds and tides on spilled oil at continental shelves and coastal waters were studied by various researchers. They have shown that the dominant role of winds and weather systems are on forcing the motion on these waters. In the Torrey Canyon spill off the west coast of England, large scale winds were a controlling factor. The Argo Merchant spill was largely controlled by oceanic processes and strong tidal currents were important only in the immediate vicinity of the wreck (Murray, 1982). A year ago, the Exxon Valdez supertanker ran aground on Bligh Reef in Alaska's Prince William Sound and 11 million gallons of crude oil pushed by tides and wind slapped against the base of the Alaska Peninsula, 650 km away (Hodgson, 1990).

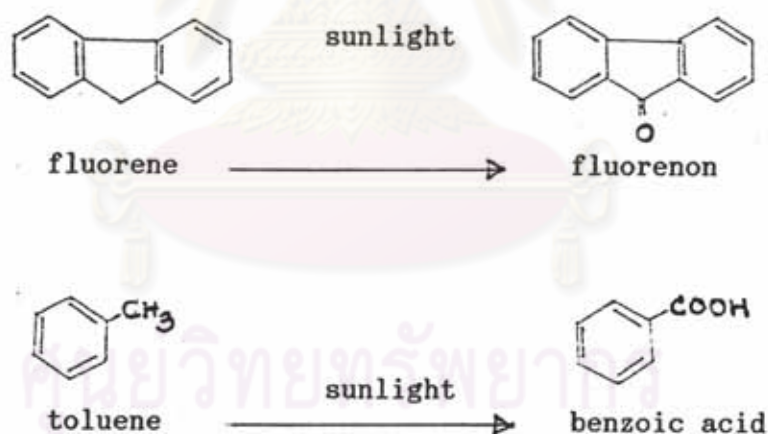
Dispersion and diffusion theory have also been applied to oil slick spreading. Basically this approach assumes that the physical spreading related to oil slick properties such as surface tension and buoyancy effects are secondary to the effect of the shear on the oil slick exerted by turbulent motions of the underlying water. It is concluded that both spreading and dispersion processes are likely to be important in the growth of real oil slicks in nature. And the importance of these two processes will vary depending on the site, the local physical oceanography, and the type of oil.

Evaporation is a process by which low to medium molecular weight components of low boiling point oil are volatilized into the atmosphere. It is also recognized as a significant removal of oil from the sea surface. Murray (1982) cited Milgram (1978) that if a relative volatile oil is spilled under warm conditions half of the oil can evaporate in a day or two. According to Ehrhardt and Blumer (1972) the lower-boiling point aromatic hydrocarbons are removed less rapidly by evaporation at ambient temperature than the n-paraffins of the same boiling point. The higher boiling point aromatics on the other hand, should evaporate more rapidly at ambient temperature than the corresponding n-paraffins. These phenomena have been observed in situ by Blumer et al., (1973) for two light paraffinic crude oils, and by Butler (1975) for samples of pelagic tar collected near Bermuda. Sivadier and Mkolaj (1973) measured evaporation rates over natural oil seeps and found that most of the volatile components were lost in 1 to 2 hours. They noted that wind speed and sea surface roughness exerted significant control on the rate of evaporation. In general, evaporation will also be a function of slick area and thickness, temperature, the concentrations of the various components of the oil, and their vapor pressure. Harrison et al., (1975) pointed out that, as many of the volatile components of spills are toxic, this rapid evaporation is biologically advantageous. Caution is advised on this point, however, as evaporation in thick spills may form a surface crust that traps volatile toxicity underneath until mechanical forces such as wave action break a crust and restart the evaporation cycle.

Dissolution is the dispersal of oil into water. This includes dissolved compounds and small dispersed oil droplets. The solubility of hydrocarbons drops exponentially as a function of their molecular volume so that low weight aromatics have relatively high solubility. The solubility of hydrocarbon with the same number of carbon atoms. The solubility increases in the order: n-alkane, iso-alkane, cycloparaffins and aromatic hydrocarbons. Some typical solubilities of petroleum hydrocarbons in water expressed in part per million (ppm) are as follows: n-pentane (40), n-hexane(10), n-octane(1), n-dodecane(0.01). Benzene, Toluene, naphthalene, propylbenzene, phenanthrene and chrysene are an aromatic series with an increasing number of rings and solubilities in distilled water which are 1800, 515, 50, 32, 1, and 0.002 mg/l, respectively. Seawater solubility is some 12-13 % lower than the distilled water solubility. Thus, under oil slicks the predominant component compounds are low weight aromatics such as a benzene, toluene and xylene. The rate of dissolution is affected by temperature, turbulence, naturally occurring surfactant such as humic acids and fatty acids, which tend to be concentrated in the surface microlayer. Hardy et al, (1990) suggested that the surface contamination in the Chesapeake Bay is potentially toxic to floating fish eggs and other surface organisms. However, the enrichment factors of concentrations between surface to bulk water can determine the present degree of aquatic surface microlayer pollution at the selected site (Hardy, et al, 1990). Solar radiation can photochemically degrade certain oil components to polar, surface active molecules which promote the dissolution of the oil.

Surface-active components in crude oil such as porphyrins and carboxylic acids helps to form water-in-oil emulsion, sometime referred as 'chocolate mousse.' This stable emulsion floats on the water and can be carried ashore by wind and waves. Strong turbulent mixing can drive emulsified oil into the water column. Fuel oil and other refined petroleum products with no surfactants do not form water-in-oil emulsions. The time required for this formation varies from a few hours to several days depending on the nature of the oil.

Photo-oxidation and microbial degradation are primary processes responsible for degrading the compounds in oil slicks. Energy from sunlight can transform hydrocarbons into oxygenated compounds (Sivadier and Mkolaj, 1973).



Because of their relatively high water solubility, the products of photo-oxidation, including carboxylic acids, alcohols, ketones and phenol are detected in water below oil slicks which have been exposed to ultraviolet irradiation. The aromatics hydrocarbons in oil are degraded by light more rapidly than aliphatic, and branched

chain aliphatics are degraded more rapidly than straight chain aliphatics. Photo-oxidation products which have been isolated include fluorenone and benzoic acid. The ultraviolet and near ultraviolet areas of the spectrum are responsible for degradation since exposure to light above 350 nm does not result in oil degradation. Very thin oil films can be photochemically degraded by energy from sunlight in a few days.

Because of the time needed for initiation of microbial degradation of slicks, which have short lifetimes, it is assumed that microbial degradation is less important than other processes above-discussed in slick removal. Once the oil is dispersed into fine droplets or particle in water or deposited on sediment, microbial degradation becomes of great importance.

Emulsification in the formation of a colloidal suspension of one liquid in another. Oil can form two types of emulsion. The first is an oil-in-water emulsion, in which the water is the continuous phase. This is considered a "good" emulsion in that the microscopic size of the oil droplets provided much more surface area for microbial degradation than would be true if they were to remain in the underside of an oil slick. The second type is water in oil emulsion, containing up to 80% water. This is a different problem, as this type of emulsion floats on water and agglomerates into large masses bearing resemblance to a chocolate mousse, hence the nickname "mouse". The incorporation of water into slick through this process

considerably enlarges its size and impact. It was found that the volume of slick impacting on beach after the Torray Canyon spill was greater than the original spill volume. Such emulsions resist weathering and take on physical properties quite different from those of surface oil.

The remainder oil, after evaporation, formation of emulsions, microbial degradation, activities, etc., turns into a very viscous sheet and breaks apart due to winds and wave action. Eagle et al., (1979) found that tar lump formed rapidly within a few days after the oil interacted with sea water. These tar lumps may sink and be deposited on the sea bottom or they may be washed ashore. Finally, tar lumps deposited on the shore and exposed to sunlight gradually lose their original properties and become one of three categories of tar ball. The first type is fresh tar which is soft, sticky and almost free of sand. It may be newly washed ashore tar. The second type is sand coated tar which is relatively soft and coated with sand. It may contain entrained sand since it has been exposed to and mixed with sand on the beach for some time. The last type is aged tar which is hard and brittle and may contain sand and shell fragments as it has been retained on the beach and exposed to air for a long period of time. The lifetime of tar balls is on the order of several months to a year.

2. Fate of Oil in Water

Oil can enter the water phase by dissolution. The concentration of oil components decreases exponentially due to evaporation, adsorption to suspended particles, sedimentation, photochemical oxidation, uptake by zooplankton or biodegradation.

Higher weight aromatics and aliphatics in water adsorb to suspended particles because of their low water solubility while lower weight hydrocarbons and more polar components remained dissolved in water. Sedimentation of particles carries hydrocarbons to the bottom. In estuarine areas most dissolved hydrocarbons adsorb to detrital particles, which are mixtures of organic matter, living bacteria and small clay particles (Lee, 1977). Presumably these surfaces provide hydrophobic areas for hydrocarbon adsorption.

Oil slick and dispersed oil globules adsorb to clays and fine suspended sediments in seawater. These sediments, with attached oil globule or oil films, are carried to the bottom.

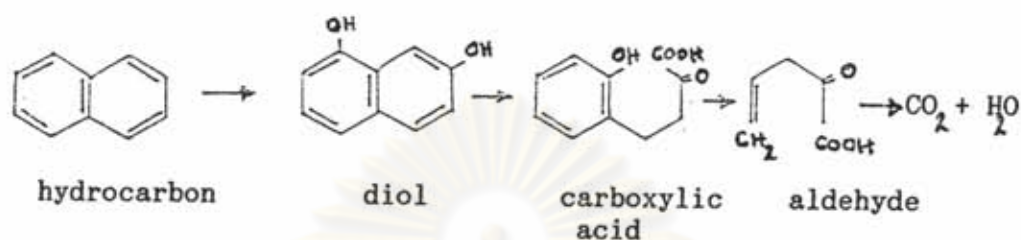
Photo-oxidation can also degrade components of oil in water. Ultraviolet light does not penetrate into water and many of short wavelengths present in the visible region attenuate a few meters below the surface. Some high molecular weight polycyclic aromatic hydrocarbons are degraded by light with wavelengths longer than 300 nm, e.g. benzo(a)pyrene, and can be completely photo-oxidized in seawater within a few days after exposure to sunlight.

After a sufficiently long resident time in the water, biological processes rapidly gain in significance. Over 90 species of bacteria and fungi have been identified that are capable of degrading oil by biological oxidation. Bacteria have been shown to accumulate hydrocarbons with concentration factors ranging from a few hundred to over fifty thousand for different compounds and species of microorganisms. They apparently store hydrocarbons in their cells in unmodified form and can produce more lipids when growing on hydrocarbons than on control media. Bacteria are capable of transforming or degrading hydrocarbon. N-alkanes are more easily degraded than the other hydrocarbon compounds; order of degradation being branched alkanes > cyclic > aromatic hydrocarbons. The rate of bacterial degradation, even for the n-alkanes, is probably much lower in the natural environment than under laboratory condition, where aeration, nutrients, agitation and elevated temperatures are controlled. These processes operate on a time scale of several months and, while greatly affecting the ultimate feature of the oil, they will play no role in the short-term physical processes (Blumer, 1972).

3. Fate of Oil in Sediments

Community of microbes, meiofauna and macrofauna is responsible for the degradation of sediment oil. The rate of microbial degradation are influenced by temperature and nutrient. Aromatic hydrocarbons undergo enzymatic hydroxylation to diols with subsequent ring fission to yield a variety of acids and aldehydes. Since the

hydrocarbons are used as sources of carbon for growth the final product is carbon dioxide.



Associated with the action of meiofauna, macrofauna and microorganisms, the formation of hydrocarbons from other related structures of the modification of preexistent hydrocarbons by reduction, decarboxylation or aromatization is induced by adsorption phenomena and a complex series of interactions between the mineral fraction of the sediment and the organic matter. The relative distribution and carbon number dominance of the n-alkanes in the upper sediment layers can be changed by early diagenesis, the bacterial activity or by a change in the lipid contribution.

Association of hydrocarbons with mineral particles or with particulate material can also greatly alter the form of hydrocarbons. Rough seas apparently increase chances that oil droplets dispersed into the water column. The droplets will contact and be absorbed onto particulate matter such as fecal pellets, dead and living organisms, silts, clays and shell material.

In the Santa Barbara channel spilled suspended sediment from the Ventura River served to sink large amounts of oil on contact,

while in the Argo Merchant case very little oil sank to the bottom. Once the oil is trapped on the bottom in the marine sediment, microbial degradation seems to be extremely slow; for example, Blumer and Sass (1988) report that the area of polluted bottom sediment was much greater 10 months after an oil spill on Cape Cod than it had been initially.

In addition, dissolved hydrocarbons may be adsorbed directly by the sediments. This association being controlled by the nature of the sediment and the content of indigenous matter such as humic acids (Meyers and Quinn, 1973). Thus, generally correlation between organic content of the sediment and hydrocarbon uptake is observed.

In shallow water areas masses of oil can be rolled along the bottom by waves and currents and eventually washing ashore to form hard, tarry masses. Also floating tar balls or emulsions oils can be washed ashore by these same forces. Stranded oil undergoes various weathering processes but the high boiling components in large masses of oil persist for many years.

In addition to movement on the bottom the oil can penetrate deeper into the sediment, be resuspended into the overlying water or be degraded. Turbulent mixing as a result of waves and other forces are probably responsible for the penetration of oil in shallow water.

Idle flow causes resuspension of sediments with their associated hydrocarbons. These resuspended sediments can be ingested by benthic filter feeders, such as clams, mussels and oysters. Oil in the feces of these animals can be released oil into the water.

In some coastal areas oil-derived hydrocarbons remain in the sediments for many years after a spill. Coarser bottom, i.e. composed of sand or gravel, allows greater penetration than fine unconsolidated sediments. The highest concentrations of oil can generally associated with silt sediment possibly because these sediments have a greater area for adsorption of oil. Coarser sediments, although allowing greater oil penetration, also have high biodegradation rates relative to fine sediments, possibly because of greater aeration and nutrient flow to the subsurface.

The main factor affecting the persistence of oil in sediments is the rate of biodegradation. Most rapid degradation occurs on the water-sediment interface.

2.5 Effects of Petroleum Hydrocarbons in Organisms

Toxic hydrocarbons leached into water from floating oil can kill a wide variety of organisms existing in the water (Esso,1976). The impact on the ecological system will depend upon the type of organisms killed and the magnitude of the kill. If the lower forms of life such as plankton are killed in large numbers, the entire biologic system is endangered because the whole food pyramid of food web stands

on a base of enormous numbers of planktonic organisms. If the amount or type of hydrocarbons do not produce death in significant numbers of organisms, there is a possibility that the oil will become widely distributed in the foodweb. When plankton consume oil-derived hydrocarbons, their metabolic products will remain in the plankton. The plankton will be eaten by small fish, mollusk and those will be eaten by larger organisms, ultimately reaching even man. At each stage, some hydrocarbons may be retained in the tissue of the consuming animal, frequently with metabolic change. Exposed to sublethal concentration of petroleum hydrocarbons has been shown to affect metabolic energy changes in crustaceans (Laughlin and Linden, 1983). The water soluble fraction (WSF) contains a predominant diaromatic fraction (naphthalene and alkylnaphthalene) is thought to be the most toxic component of oil (Anderson et al., 1974).

Reduced growth and reproduction of animal exposed to oil may result from energetic changes which may include increased energy metabolism, altered feeding behavior or assimilation efficiency. Reduced growth has been observed in the shrimp Crangon crangon (Edwards, 1978) and in bivalve mollusks Modiolus demissus and Mytilus edulis exposed to WSF of crude oil (Gilfillan, 1975). The copepod Eurytemora affinis exhibits decreased egg production, brood size and total fecundity when exposed to WSF of crude oil (Berdugo, et al., 1977).

Apparently, aromatic hydrocarbons in marine environment can contaminate marine economical species of fish and shellfish. This might be harmful to human health as a top of food web.

Anderson (1974) tested toxicity of different sources of crude oil to post larvae grass shrimp Palaemonetes pugio and brown shrimp Penaeus aztecus. They found that toxicity of the crude oil could vary between 10 to 6000 ppm depending on types and sources of the crude oil.

However, the effects of oil spill will vary from amount of spilled oil. Amount may be thought of as a product of the concentration of oil and the time of the exposure or contact.

The type of oil is a major factor. Light products will evaporate soonest, leaving a minimal residue and fouling problem. But these may have the highest concentrations of the most toxic hydrocarbons, especially aromatics. For this reason, products such as gasolines, naphthas and middle distillates are most likely to produce acute toxic effects. Heavy oils may be the lowest in terms of concentrations of toxic constituents, but these will result in more fouling problems. Thus, bunker fuels are not likely to produce acute effects. Crude oils produce effects which are heavily dependent on the nature of the crude. The crude which are high in aromatics are likely to cause acute toxic effects, whereas those which are low in aromatics tends to produce highly viscous residues and emulsions which will result mostly in fouling problems.

Oceanographic conditions will exert a strong influence on effects. If oil spilled in the open ocean or in deeper water, biological effects will be minimal because there is a minimum biologic

community to impact. If the sea is turbulent, mixing will be rapid and this will tend toward rapid dilution and minimal impact (ESSO, 1976). Rough seas can also dispose toward emulsification and this can result in a more widespread distribution of the oil.

Meteorological conditions are very important and it will also dictate oceanographic conditions to the same degree. If the air and water are warm, evaporation will be increased. High winds causes evaporation. Bright sunlight can catalyze reactions in floating oil such as polymerization, and this would accelerate the formation of a more viscous mass. The directions of wind, tide and current will also determine whether the floating oil will move toward shore, possibly resulting in extensive shoreline contamination or move toward the open sea where most impacts would be minimized.

2.6 Sources of Oil Pollution in Thailand

Potential sources of oil pollution in Thai waters are as follows (Watcharasin, 1988):

1. Tanker and Ship Transportation

The monthly international tanker and ship vessel traffic including coastal tanker passing through the Gulf of Thailand and the western shoreline, totally about 301 and 7 vessels, respectively. It is anticipated that when Lam Chabang and Map Ta Phut Deep Sea Ports in the Eastern Sea Board are in operation, the vessels landed to the port will be about 180 and 51 vessel/months, respectively.

Oil may spill from oil vessels when they are involved in an accident or when oil tankers are cleaned, water discharging and so on. However, the most oil spill come from oil vessels.

2. Refineries

There are three refineries and tank farms in Thailand. One of the refineries is along the Chao Phraya River (Bangchak) and the other two are located on the shoreline of Sri Racha, namely Thai Oil and Esso Refineries. Oil contamination may occurs during oil transportation activities, tanker cleaning and deballasting by crude oil tankers and accidental discharges.

3. The Offshore Petroleum Exploration and Production

The activities may cause oil pollution from discharges from drilling mud during the exploration periods and accidental oil discharged during production processes.

At present, there are 8 companies who win the the petroleum concessions in the Gulf of Thailand namely:-

AMOCA Thailand

UNOCAL Thailand Inc.

PTT Exploration and Production Company Ltd.

Thailand Sun Oil

Triton Oil Company of Thailand

Thai Shell Exploration

BRITOIL (alpha) Ltd. and

PREMIER Oil Pacific

4. Ship-Breaking Industry

The demolishing processes may cause oil pollution. Oil can escape from machinery spaces, ballast tanks and fuel tank.

Record of major incidents of oil spills in Thailand according to Watcharasin (1988) are shown in Table 2-2. The worst oil spill incidents occurred in the world are summarized in Table 2-3.



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Table 2-2 Incidents of oil spills in Thailand.

-
- In 1973 at Sattahip Port. Fired accident of a Thai's coastal tanker
- April 10, 1974. Accidental collision between a Thai's coastal tanker (Visahakit) and a Mexican's tanker (Tolvla) near the Chao Phraya River. 2,234,400 litres (1 gallon equal 4.45 litres) of oil released. Damages occurred to fishery resources of Samutprakarn Province.
- May 29, 1977. 300,000 litres of oil was released from the accidental collision between a Thai's coastal tanker (Tvchira) and a Japanese ship.
- April 16, 1978. Accidental discharges from a cargo ship (Delta Sigma PI) at the Chao Phraya river mouth.
1979. Spillage of oil from sinking Sunflower tanker near Ko Sichang, Chonburi.
- July 5, 1981. Spillage of oil and dispersant from Gota Gaja cargo ship sunk near Ko Sichang, Chonburi.
- November 1985. Discharged of oil from unidentified cargo ship. The oil sheet is 1km. in distance and 2 cm. in thickness.
- September 1987. Accidental discharges from Ship-breaking industry located at Prachaup Kirikun province. Spillage of oil and dispersant damage to aquaculture.
- July 22, 1988. Shintoku Cargo was collided in the Chao Phraya River and the oil was leaked.
- August, 1989. Offshore accidental discharge from an unidentified vessel. Spillage of oil and dispersant damage the tourism at Kata, Karon and Patong Beaches, Phuket Province.
- March 6, 1990. Spillage of oil from Chock Anan Tanker near Chong Non-see, in the Chao Phraya River Mouth. 7000 liters of diesel oil released.
- November, 1990. An unidentified discharges from Srichang Island. Damaged to the tourism at Pattaya Beach, Chonburi Province.
- February, 1991. An unidentified discharges in the Chao Phraya River, near Orientel Hotel, 1km. extent.
-

Adapted from Watcharasin (1988)

Table 2-3 The worst incidents of oil spills in the world.

In 1967, Torrey Canyon ran aground the British Island. 36 million gallons spilled.

In 1970, Othello was crashed at Voxholm city in Sweden and almost of its 30 million gallons oil leaked.

In 1972, 36 million gallons of oil from collided Sea Star was dumped in the Gulf of Oman.

In 1975, Jarco Maersk struck an underwater rock in Portuguese. 21 million gallons of oil leaked into the marine environment.

In 1976, Urquiolo ran aground and 21 million gallons of oil leaked at Spain.

In 1978, 68 million gallons of oil from Amoco Cadiz spilled when she ran aground at Britain offshore in France.

In June 1979, the worst event happened when offshore Ixtoc well called Bahia de Campeche of Mexican National Company blow out during drilling process. Everyone and every things were suddenly destroyed. Crude oil flowed out for a long period of time. In March of the next year of 1980 the oil could be blocked. 140 million gallons of oil discharged.

In 1979, Atlantic Empire was collided at Tabago, north of South Africa. More than 43 million gallons was discharged.

In 1979, about 29 million gallons of oil assaulted Eastonbul Port when Independenta was collided.

In 1980, Irenes Serenade discharged 37 million gallons of oil from unidentified blowers out on herself in Greek.

In February 1983, coastal well of Aramco Company was attacked from the Gulf of Persian War. More than 80 millions gallons of oil contaminated coastal and marine environment and could be blocked the spill within 7 month.

In 1983, 15.4 million gallons of oil discharged from Catillo de bellver at Cape Town in South Africa.

In 1985, 21 million gallons assaulted Persian the Gulf when Nova was collided.

In March 1989, 11 million gallons of oil assaulted Prince William Sound when the Exxon Valdez struck a reef. The spill drifted to the Alaska Pennsylvania and hit four national wildlife refuges, one national forest and three national park areas. More than 1,200 miles of shoreline were oiled. Herring spawning area, salmon terminal and harvest areas, salmon hatchery, sea otter and wild bird habitats were destroyed. It is the worst tanker spill in the U.S. history.

(cont.)

In January 1991, an underground pipeline used to offload oil from a ship docked near Puget Sound. 400,000 gallons of crude oil bubbled to the surface above the pipeline.

Adapted from Mineral Resources Gazette (1990).



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2.7 Study Area

2.7.1 Characteristic of Map Ta Phut Sea Coast

The coastline of Map Ta Phut, the study area, is about 10 kilometers long. It locates on the lower eastcoast of the Gulf of Thailand and lies in the east-west direction facing the open sea. In this area, the shoreline is rather straight. This region is under the influence of the predominant monsoons as follows:-

- south-west monsoon in the rainy season during the period of May to October
- north-east monsoon during the period of November to February

The bathymetric of the shore is steep slope in the nearshore region. Since the selected study site is under the influence of the monsoons, the wind speed and wind direction follow closely to the strength and the direction of the two monsoons from south-west and north-east with predominant wind from the south within a short day spat in March and April. Information on tide and tidal current of Rayong coast surveyed by the Hydrographic Department of the Royal Thai Navy in 1969 shows the mixed type and a tide level ranges of about 1.10 meters. The average strength of the current in the north-south direction offshore is about 0.5 knot (15.43 m/mins.) (ONEB, 1988)

2.7.2 Source of Petroleum Hydrocarbons in Map Ta Phut Area

1. Ship-Breaking Industry

In Rayong, Map Ta Phut area, the government's leading industrial complexes were established as planned by the National Economic and Social Development Board of Thailand (NESDB). In 1990, two enterprises are found to be located in this area which are the Thai International Steel Co.,Ltd. and the Thai Hua Lee Co.,Ltd.

2. Fishing Boats

The data obtained from the Fishery Statistic Section of the Eastern Marine Fisheries Development Center of Fishery Department indicated that there are 103 small diesel fishing boats in Ban Phala, Tambon Map Ta Phut.

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