ASPECTS OF THE LONG-TERM FATE OF PETROLEUM HYDROCARBONS IN THE MARINE ENVIRONMENT

by

DAVID ROBIN GREEN

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Department of OCEANOGRAPHY

The University of British Columbia 2075 Wesbrook Place Vancouver, Canada V6T 1W5

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ABSTRACT

The longterm fate of petroleum in four marine environments was investigated:

The fate of petroleum on the surface of the ocean was elucidated by undertaking a detailed study of petroleum residues polluting the Pacific Ocean. First, the extent of contamination of the Pacific by petroleum residues was assessed by measuring the amounts of tar in 2092 neuston tows over a nine-year period (1967-1975). The South Pacific was found to be free of tar; the Northeast Pacific was slightly polluted, with an average of 0.03 mg/m². The Northwest Pacific, particularly the Kuroshio current system, was the most severely polluted area: all 55 tows between 25° and $40^{\circ}N$ in the Northwest Pacific were contaminated. The average concentration in that area was 2.1 mg/m^2 , representing a standing stock of about 25,000 metric tons of tar. Chemical analyses of the tar as well as its distribution pattern strongly imply that it originates primarily from tanker traffic, and from tanker sludge in particular. The pollutants appear to be discharged by tankers on the very large Middle East to Japan tanker route, then become entrained in the Kuroshio current and create a plume of contamination which extends downstream for 7000 kilometers across the Pacific. Initially evaporation is the most important weathering mechanism acting on the tar, removing components up to the volatility of pentadecane over a period of days or perhaps weeks. Thereafter, microbial degradation is dominant, probably acting for over a year on many particles. Both of these processes increase the density of the residues, and this effect, combined with the overburden of fouling growth that develops, eventually results in the slow sinking of the tar into the depths of the ocean.

The fate of petroleum in the intertidal environment was studied by following the natural degradation of the oil after a small (200 ton) oil

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spill of #5 fuel oil. The most important weathering process was microbial degradation. Evaporation played only a minor role, while photo-oxidation and dissolution had no apparent effect. The microbal attack took approximately one year to complete the degradation of the n-paraffin fraction of the spilled oil, leaving a thin asphaltic residue on the beach. The combined effect of microbial degradation and abrasive weathering removed roughly 95% of the oil from the beach over the period of a year.

The fate of oil in the benthic environment was studied by treating 500 ml quantities of crude oil with a commercial sinkant, then placing the oil on soft sediments in about 6 meters of water. Again in the benthic environment, microbial action was the process responsible for the degradation of the oil. Evaporation had no opportunity to act, dissolution was ineffective, and photo-oxidation did not occur because of the low energy and intensity of the light reaching the sediment. The benthic petroleum samples were slow to degrade: the oil remained unchanged in chemical composition for at least 6 months, and after 16 months the n-paraffins were only partly degraded.

Oil dissolved in the water column was investigated by adding a spike of #2 fuel oil to an enclosed column of water 2 m in diameter by 15 m deep, and monitoring its fate by fluorescence spectroscopy. For water a meter or two in depth, exchange with the atmosphere played the dominant role in removing the hydrocarbons from the water column, but at 7 m and below, microbial degradation and sedimentation were the more important processes. The disappearance of the oil approximately followed an exponential decay curve. The half life for a large dissolved oil spike was about 3 days (less for a smaller spike) so that 95% removal occurred within 2 weeks.

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To those who wove the social fabric of my graduate student years: the girl who loved people; the friend from pathology; the lady from Africa; the woman of the woods; and the river travellers. xii

INTRODUCTION

In contrast to most previous work, which was done under artificial laboratory conditions, this thesis examines the fate of petroleum under natural conditions in the marine environment - as residues on the surface of the open ocean; as an oil spill in an intertidal area; as sunken oil on the sediment in about 6 meters of water; and as dissolved oil mixed into the water column.

Since much of the background information required in a discussion of oil pollution problems is not common knowledge or readily accessible in the literature, a considerable effort has been made to review the relevant aspects of oil pollution research. The first two chapters summarize subjects which provide background information for the rest of the thesis: the composition of petroleum, and the sources of oil to the marine environment. Chapter 3 then thoroughly reviews the literature dealing with the weathering processes which affect oil.

A small preliminary experiment is described in Chapter 4 in which various oils were weathered under controlled conditions so that only evaporation and photo-oxidation could occur. The effect of these processes on the composition of the oils is assessed.

Chapter 5 reports the results of the first major research topic: persistent petroleum residues in the Pacific Ocean. The distribution of pelagic tar on the surface of the North and South Pacific and the Beaufort Sea is reported and a map of tar contamination of the Pacific is presented. The source of the tar is identified from the distribution pattern and by chemical analyses. The eventual fate and the prime mechanism of degradation of the petroleum residues are also inferred from the analyses. The standing stock of tar in the north-western Pacific is calculated, and the ecological effects of the tar are discussed.

In Chapter 6 the long-term fate of oil in the intertidal environment

is researched. An oil spill was sampled over a year-long period, and gas chromatographic analyses were used to assess both the rate of degradation of the oil and the prime mechanism of degradation. In Chapter 7, the same analytical technique and reasoning were used to investigate the degradation of oil sunk by treatment with a sinking agent and left to weather for an extended period (18 months) in about 6 meters of water.

Finally, Chapter 8 deals with the degradation of oil dissolved in the water column. The experiments were carried out using a trapped water column as a part of the Controlled Ecosystem Pollution Experiment. This was the most difficult of the four projects in terms of analytical method, because of the low levels at which hydrocarbons dissolve in water. The gas chromatographic investigations were not a success, for reasons that are discussed, so the disappearance of the oil was monitored using fluorescence. The results give an indication of the rate and the mechanisms of removal of the oil from the water column.

Five appendices are included giving some useful technical information, a review of the biological effects of petroleum, a theoretical discussion of hydrocarbon exchange rates between ocean and atmosphere, an opinion, and a list of symposia and books dealing with oil pollution. The thesis concludes with an extensive bibliography of the literature relevant to oil pollution research.

CHAPTER 1

SUMMARY OF THE COMPOSITION OF PETROLEUM

Introduction

The term 'petroleum', here as elsewhere, is used interchangeably with 'mineral oil' and 'crude oil'. It is derived from the Latin <u>petra</u>, for rock, and oleum, for oil.

The fate of petroleum in the marine environment depends on its composition, so a discussion of the main chemical components is required. The complexity and variation of composition is immense, but some generalizations can be made.

The elements found in petroleum are carbon (83-87%), hydrogen (11-15%), oxygen (0-5%), sulfur (0-6%), nitrogen (0-0.5%), and trace amounts of metals, chiefly vanadium, nickel, iron, sodium, calcium, and copper, totalling 0.1 to 100 ppm (percentages are from Frankenfeld, 1973b). The main class of compounds present is hydrocarbons, which comprise 75-98% by weight of crude oil. The remainder is made up of nitrogen-, sulfur-, and oxygen- containing compounds (NSO compounds) which are generally of high molecular weight and complex structure.

No single crude has ever been completely analysed into its individual components. The most complete analysis has been performed on Ponca City crude oil, under the auspices of the American Petroleum Institute research project 6, which, by 1959, had identified 169 hydrocarbons comprising 46% of the crude (Rossini and Mair, 1951, 1959). By 1967, several hundred hydrocarbons and two hundred sulfur compounds had been identified in crude oils (Mair, 1965; Mair and Ronen, 1967; Hunt and O'Neal, 1967; Bestougeff, 1967). Recent analytical developments, such as interfaced gas chromotography - mass spectrometry and nuclear magnetic resonance spectroscopy, have greatly enlarged the number of compounds which can be identified (Coleman et al, 1973), but complete identification of a crude oil is still not possible, nor, perhaps, worthwhile. This is not meant to imply, however, that the composition of petroleum is infinitely complex. It appears that definite, regular processes have produced petroleum, with the result that the total number of isomers, although high, is only a negligible percentage of the total number of theoretical structures (Bestougeff, 1967).

Examples of the underlying order in petroleum are: (a) the presence of sets of homologous series of compounds in all petroleums (Bestougeff, 1951); and (b) the consistent finding that older Palaeozoic petroleums are more aliphatic, and newer Tertiary petroleums more cyclic in composition suggesting an orderly process of ageing (Bestougeff, 1967).

The sequence of events which has lead to this complex but nevertheless orderly composition of petroleum is succinctly summarized by Ehrhardt and Blumer (1972):

The geochemical processes responsible for the formation of crude oil lead to the production of an immense number of individual hydrocarbons, including many isomers and members of different homologous series. Each petroleum is an individual product whose composition reflects the chemistry of its source materials. In addition, it carries the indelible imprint of the geochemical subsurface processes that have lead to its formation. The time-temperature history and the inorganic components of the source beds affect the crude oil composition in a way that is understood in general terms but not in molecular detail. Further alteration of a crude oil may take place in a reservoir, either through thermal cracking after deep submergence or through bacterial alteration in shallow traps.Many structures formed by living organisms (four and five ring naphthenes, porphyrins, etc.) survive in crude oil. Their composition is strongly affected by the intensity of the chemical processes responsible for the formation of petroleum. Thus, the very small number of tetrapyrrole pigments may be converted by geochemical processes into thousands of different fossil porphyrins whose structures are a unique reflection of the subsurface conditions.

Table 1 gives a very approximate summary of crude oil composition by molecular size and molecular class. Table 2 lists some of the predominant compounds in crude oil, and their percentage occurrence. Detailed comparative analyses of crude oil are available (Martin et al, 1963).

TABLE 1: Average Composition of Crude Oil By Class of Compounds

By Molecular Size:		By Molecular Class:	
gasoline (C ₅ -C ₁₀)	30%	paraffins	15-35%
kerosine $(C_{10} - C_{12})$	10%	olefins	0%
light distillate (C ₁₂ -C ₂₀)	15%	naphthenes	30-50%
heavy distillate $(C_{20}^{-}-C_{40}^{-})$	25%	aromatics	5-20%
residual (C ₄₀)	20%	polar NSO cmpds	2–15%

(From Petroleum in the Marine Environment, 1975, p.43)

(From Zobell, 1973, p.5)

TABLE 2: No. Series and hydrocarbon Carbon atom Percent of crude oil Predominant number min. Constituents of max. Petroleum Normal paraffins Pentane 1 Сs 0.2 3.2 2 Hexane **C**6 0.04 2.6 3 Heptane C7 0.03 2.5 4 Octane-Decane C8-C10 n 1.8-2.0 5 Undecane-Pentadecane C11-C15 0 0.8-1.5 6 Hexadecane and higher C16 and higher 0 <1.0 **I**soparaffins 2-Methylpentane 1 C6 0.2 1.16 2 3-Methylpentane C₆ 0.06 0.9 3 2-Methylhexane C7 0.03 1.1 4 3-Methylhexane C7 0.02 0.9 5 2-Methylheptane C₈ 0.03 1.0 6 3-Methylheptane C₈ 0.02 0.4 7 2-Methyloctane C9 0.02 0.4 8 3-Methyloctane C۹ 0.01 0.2 C_{10} 9 2-Methylnonane 0.3 10 3-Methylnonane C10 0.1 11 4-Methylnonane C10 0.1 12 Pristane (isoprenoid) C19 1.12 **Cycloparaffins** 1 Methylcyclopentane Ç6 0.11 2.35 2 Cyclohexane Co 0.08 1.4 3 Methylcyclohexane C7 0.25 2.8 4 1, trans-2-dimethylcyclopentane C_7 0.05 1.2 5 1, cis-3-dimethylcyclopentane C7 0.04 1.0 6 1, cis-3-dimethylcyclohexane **C**₈ 0.9 7 1, cis-2-dimethylcyclohexane C₈ 0.6 8 1, 1, 3-trimethylcyclohexane C۹ 0.7 Aromatics Benzene 1 C₆ 0.01 1.0 2 Toluene C7 0.03 1.8 3 Ethylbenzene C₈ 0.01 1.6 4 m-Xylene C₈ 0.02 1.0 5 1-Methyl-3-ethylbenzene C۹ 0.3 1, 2, 4-Trimethylbenzene 6 C9 0.6 7 1, 2, 3-Trimethylbenzene C9 0.4 1, 2, 3, 4-Tetramethylbenzene 8 C10 0.3 9 2-Methylnaphtalene CII 0.3 (From Bestougeff, C18 10 2, 6-Dimethylnaphtalene 0.4 1967, p.80) **C**13 11 Trimethylnaphtalene 0.3

The Hydrocarbons

The hydrocarbons in crude oil are grouped into four main classes: paraffins, olefins, naphthenes and aromatics. The paraffins include all noncyclic alkanes, ranging from five up to fifty carbon atoms per molecule. They are of lower density and solubility than the other classes. Of particular prominence are the homologous series of normal alkanes and of isoprenoid compounds. The distribution of normal paraffins in two crude oils is illustrated in Figure 1. Clearly, the paraffinic content varies widely (note the differing y-axis expansions).

The isoprenoid compounds deserve special mention. They were first identified in petroleum in the early 1960's through the application of the new technique of gas chromatography (Bendoraitis et al, 1962). The discovery was exciting because it provided long-sought evidence for the biologic origin of petroleum: the isoprenoids are directly related to the biochemicallysynthesized terpenes. The most abundant of the isoprenoids in petroleum are pristane (2, 6, 10, 14 - tetramethylpentadecane) and phytane (2, 6, 10, 14 tetramethylhexadecane). Both are thought to derive from the phytol group in chlorophyll (Bendoraitis et al, 1963). Their concentrations vary from 0.05% to 0.5% of crude oil, and generally are within a factor of 2 of the concentrations of alkanes of similar boiling point (Martin et al, 1963).

Olefins, or alkenes, are found only in trace amounts in crude oil. A measure of the olefin content is the sometimes quoted 'bromine number' of oils. Olefins are, however, formed in the cracking process at refineries, and so occur to a limited extent in refined products, particularly gasoline.

The naphthenes include all compounds with saturated ring structures, that is, all the cycloalkanes. This broad range of compounds extends up to as many as six rings, and includes enormous varieties of alkyl side chains.

FIGURE 1: Distribution of n-Paraffins in Crude Oil



In Kawkawlin crude oil:

In Uinta Basin crude oil:



(From Martin et al, 1963, pp. 255-6)

The aromatics include all compounds which contain an aromatic ring structure. Again, there is a very rich variety of compounds with up to six aromatic rings arranged in various fashions, substituted with a wide array of alkyl side chains. The aromatics are the most soluble, the most dense, and the most toxic of the hydrocarbon classes.

Figure 2 shows the relationship between the classes of hydrocarbons in crude oil. Typically crudes are paraffinic below about C-20, and become aromatic at higher carbon numbers (Martin et al, 1963).

FIGURE 2: Hydrocarbon Types by Carbon Number in a Crude Oil



(From Martin et al, 1963, p.251. The oil is Kawkawlin crude.)

The four groups of hydrocarbons and their permutations (eg naphthenoaromatic) include all the possible hydrocarbons. However, practical usage has lumped the high-molecular weight hydrocarbons of uncertain structure into a portion of crude oil termed the asphaltic fraction.

The Asphaltic Fraction and the Non-hydrocarbons

The asphaltic portion of crude oil includes high molecular weight compounds (above about 500 MW) both hydrocarbon and non-hydrocarbon. The detailed structure of the compounds is still not known, so the definition is based on physical properties rather than chemical structure. The definition varies (Erdman, 1965; Witherspoon and Winniford, 1967), a commonly-used one being the residue remaining after non-destructive distillation up to $371^{\circ}C$ $(700^{\circ}F)$.

Within the asphaltic fraction, several terms are used to describe different fractions.Resins are the components soluble in n-pentane but insoluble in benzene. Asphaltenes are insoluble in n-pentane but soluble in benzene. Carbenes, or coke, are the heaviest components, consisting of highly condensed aromatic rings tied together by short chains. Carbenes are insoluble in n-pentane, and only poorly soluble in benzene (Erdman, 1965).

The asphaltic fraction of petroleum contains most of the non-hydrocarbons, i.e. the sulfur-, nitrogen-, and oxygen- containing compounds. Sulfur may exist as free sulfur (from 2-30% of total S), but most is in organic sulfur compounds such as sulfides and thiophenes. Disulfides and mercaptans occur in much lower concentrations (Constantinides and Arich, 1967). The sulfur compounds are dealt with in detail by Thompson et al (1965).

Oxygen is present largely as organic acids. Phenols are present in smaller amounts, usually less than 0.1%, and ketones occur only in traces (Constantinides and Arich, 1967).

All crude oils contain at least traces of nitrogen compounds, but never more than 1%. Their distribution is strongly skewed towards the highest molecular weight fraction of crude. Only basic nitrogen compounds have been completely identified since they are more easily isolated. About 25% of





metalloporphyrin

(From Atlas, 1972, p.22.)

nitrogen compounds are basic, and are made up of alkylated pyridines, pyrroles, quinolines, indoles and others. Another 20% of the nitrogen appears as metalporphyrin complexes (Constantinides and Arich, 1967).

Both the oxygen and nitrogen compounds are comprehensively reviewed by Lochte and Lettman (1955), all non-hydrocarbons by Constantinides and Arich (1967), and asphaltics in general by Dean and Whitehead (1963), Erdman (1965), Sergienko (1965), and Witherspoon and Winniford (1967).

Characterization of Crude Oils and Refined Products

Since crude oils and their products vary a great deal in their composition, various parameters are used to indicate the general nature of their density. Specific gravities of crude vary over the range 0.75 to 1.0. In the petroleum industry the density of oils is referred to in degrees of API gravity. The relationship to the specific gravity is given by:

$$API = \frac{141.5}{\text{Sp. Gr.}} - 131.5 \text{ (at 60}^{\circ}\text{F)}$$

API gravities vary from about 45 (light, specific gravity 0.8) to 10 (heavy, specific gravity 1.0).

Crudes are also classified by their sulfur content. Low sulfur petroleums are referred to as sweet, and high sulfur as sour, for obvious reasons. The line of demarcation is about 1% sulfur (Schmidt, 1969).

Viscosity is a third parameter widely used for characterizing oils. The metric measure of viscosity is the poise: the ratio of the shearing stress in dynes/cm² to the rate of shear in \sec^{-1} , which is a constant according to Newton's law. It is a measure of the liquid's resistance to flow. Here, as in other matters, the petroleum industry has gone its own way, and uses units based on convenience of measurement. Viscosity is given in seconds required for 60 cc of oil to flow through a standardized tube (Saybolt Universal viscometer) at a definite temperature. More recently the kinematic viscosity has been used. Happily, it is reported in cgs units, the centistoke (stoke = poise : density of fluid).

A fourth parameter used is the pour point. It is defined as the temperature $5^{\circ}F$ above the point at which the oil becomes solid (approximately the temperature at which the kinematic viscosity reaches 300,000 centistokes). The oil congeals primarily because of the formation of wax crystals (Schmidt,

Crude oils are also classified by the chemical composition. There are nine classifications: paraffinic, naphthenic, aromatic, asphaltic, and combinations of these. The percent composition for each is specified (see Sachanen, 1945).

Table 3 lists a variety of crude oils and their characteristics. Other lists are available (Dean, 1968; Fallah et al, 1972).

TABLE 3: Some Characteristics of Crude Oils

Crude oil	Specific gravity	Sulphur content, % wt	Kinematic viscosity, 100° F cS	Pour point, °F	Wax content, % wt	Asphalt- enes % wt	Vanadium content, ppm	Acidity mg KOH/ g	Residue > 700° F % wt on crude	Residue > 700° F pour point °F
Libyan	0.829	0.51	4.13	45	11.4	0.13	5	0.10	37.5	100
Zelten					•	•				
Nigerian Light	0.867	0.10	5.16	5	8.2	0.2	5	0.14	35.8	110
Iran Light (Agha Iari)	o·854	1.33	5.6	-5	7.0	0.2	36	0.07	42.7	80 .
Iran Heavy (Gach Saran)	o·869	1.28	8.83	10	6.7	1.9	107	0.13	47.8	80
Iraq Kirkuk	0.845	1.88	4.75	-30	6.5	°1.3	25	0.12	39.8	80
Kuwait	o·869	2.2	9.6	25	5.2	1.4	27	0.15	51.3	70 [·]
Venezuela Tia Juana Medium	o·896	1.24	33.75	-30	4.8	3.02	170	0.41	57.7	50

(From Berridge et al, 1968, p.49)

Refined Products

Several of the refined petroleum products are important from the point of view of marine pollution. The refined products most likely to reach the marine environment in large quantities are those used as fuels: gasoline, kerosine (#1 fuel oil), diesel fuel (#2 fuel oil) and heavy fuel oils. The characteristic boiling ranges of each are given in Table 4.

TABLE 4: Boiling Ranges of Petroleum Products

Fraction	<u>Boiling Range</u> (^O C)
Gasoline	30 - 200
Kerosine (#1)	150 - 250
Diesel fuel (#2)	160 - 400
Fuel oil (#5 & 6)	320 - 540

The grades of fuel oil are frequently bandied about in the petroleum pollution literature, and perhaps deserve some clarification. There are in fact five grades of fuel oil, designated as numbers 1, 2, 4, 5 and 6 (#3 was combined with #2 by decree in 1948). Fuel oils #1 and #2 are referred to as distillate oils since they can be distilled at moderate temperatures $(150^{\circ} - 350^{\circ}C)$ at atmospheric pressure. Fuel oil #1 (kerosine) is characterized by being sufficiently volatile to burn in vapourizing burners. #2 fuel oil is familiar as diesel oil, and less familiar as gas oil. #4 fuel oil is used only to a limited extent, mainly for small boilers in schools and apartments. It is not significant as a marine pollutant. Fuel oils #5 and #6 are referred to as residual oils, since they are obtained mainly from the residue left after distillation. They are characteristically heavy, black, and of complex composition. Fuel oil #6 is differentiated from #5 by the fact that it requires

preheating for handling and burning (#5 may require preheating in cold climates). These fuels are used on freighters where they are referred to as grades of bunker oil. For example, bunker C is equivalent to fuel oil #6.

The composition of the various refined products most likely to reach the marine environment, and their physical properties, are summarized in Table 5. An important variable affecting the composition is the method of refinery production. Straight-run distillates are obtained directly by distillation from crude oil, whereas cracked products are obtained by decomposing the heavy end of crude. Catalytically-cracked products have a higher aromatic and lower paraffinic content than straight-run distillates, due to dehydrogenation of the paraffinic and naphthenic compounds during cracking. The olefinic content is slightly increased. Thermally-cracked oils have still higher olefinic and aromatic content, but since they are easily oxidized to form sludge, they are not usually marketed without further processing. Further information on the fuel oils is available in Schmidt (1969), from which most of this subsection was drawn.

	Bunker (#6 Fuel	C 0i1)	Diesel (#2 Fuel Oil) Kerosine	Virgin Gasoline	Blended Gasoline	
Paraffins	15%		30%	35%	50%		
Olefins	0		trace	trace	0	0 - 30%	
Naphthenes	40%	•	45%	50%	40%		
Aromatics	25%		25%	15%	10%	20 - 30%	
Polar NSO Cmpds	15%		0	0	0		
Specific Gravity	1.00		.825850	.800	.700		
Viscosity (cps, 38 [°] C)	1,000		40	1-2	< 1		
Pour Point (^O C)	21 ⁰		-20.5°				
Carbon Numbers	^C 30 ⁺		C ₁₂ -C ₂₅	^C 10 ^{-C} 12	c ₅₋ c ₁₀		

TABLE 5: Average Composition of Refined Products

(From Petroleum in the Marine Environment, 1975, p.43)

Distinguishing Petroleum Hydrocarbons from Biogenic Hydrocarbons

Petroleum pollution monitoring, especially in the analysis of tissue, requires the analyst to be aware of the characteristic differences between crude oil hydrocarbons and the naturally-occurring hydrocarbons in organisms.

In general, petroleum contains a much more complex mixture of hydrocarbons, with greater ranges of molecular weight, than the natural hydrocarbons found in organisms. Specifically, the alkyl-substituted ring compounds, common in petroleum, have not been reported in organisms. Examples are the series of mono-, di-, tri-, and tetramethyl benzenes, and the mono-, di-, tri-, and tetramethyl naphthalenes. Neither have the naphthenoaromatic nor most of the NSO compounds prevalent in petroleum been found in organisms (<u>Petroleum in the Marine Environment</u>, 1975).

The most often-cited difference between petroleum and biogenic hydrocarbons is, however, in the spectrum of alkanes. Most petroleums show no predominence of odd-carbon over even-carbon alkanes (Martin et al, 1963). Organisms, however, often show a strong odd-carbon predominence, particularly in the C-15 to C-21 alkanes (Clark, 1966; Blumer et al, 1971).

Conclusion

The foregoing discussion of the composition of petroleum and its products provides the background information against which the modification and degradation of oils by the various weathering processes can be evaluated and understood. These mechanisms are discussed in detail in Chapter 3. However, before proceeding, there is some additional background information which needs to be presented.

CHAPTER 2

SOURCES OF OIL TO THE MARINE ENVIRONMENT

The estimation of oil reaching the oceans is a complex and speculative matter in which opinion plays a significant role. It has been stated, for instance, by a British researcher (Victory, 1973), with reference to American figures on sources of oil, that "...there is one characteristic which can always be guaranteed: that the figures coming from the other side of the Atlantic will have a factor of the magnitude of 2 or 3 above those from this side".

Despite the opinion of Mr. Victory, the most comprehensive and careful estimates of the amounts of oil reaching the ocean were arrived at by the U.S. National Academy of Sciences (<u>Petroleum in the Marine Environment</u>, 1975). Previous estimates of petroleum inputs were reviewed, and the uncertainties and assumptions were carefully stated. The tables of estimates prepared by the Academy of Sciences is presented in Table 6. Table 7 compares the figures with estimates from two other studies.

The estimates range from well-documented to undocumented. With reference to Table 6, the transportation sources are supported by years of data. However, at the other end of the spectrum, the hydrocarbon quantities contributed by the atmosphere are arrived at by cumulative black magic which involves estimating the amount of hydrocarbons lost to the atmosphere, the amount of reaction occurring in the atmosphere, and the amount of precipitation of unreacted hydrocarbons into the marine environment, none of which have much supporting data.

It is important to realize that the various sources introduce quite different fractions and forms of oil into the oceans. The sources listed in Table 6 as coastal refineries, atmosphere, coastal wastes, and run-off produce dissolved hydrocarbons and some thin slick contamination. In contrast, natural seeps and marine oil transport can produce thick slick contamination

	Input Rate (mta) ^a			
Source	Best Estimate Probable Range			
Natural seeps	0.6 0.2 - 1.0	·		
Offshore production	0.08 0.08 - 0.15			
Transportation				
LOT tankers Non-LOT tankers Dry docking Terminal operations Bilges, bunkering Tanker accidents Nontanker accidents	$\begin{array}{cccccccccccccccccccccccccccccccccccc$			
Coastal refineries	0.2 0.2 - 0.3			
Atmosphere	0.6 0.4 - 0.8			
Coastal municipal wastes	0.3 -			
Costal, Nonrefining, industrial wastes	0.3 -			
Urban runoff	0.3 0.1 - 0.5			
River runoff	1.6 -			
TOTAL	6.1			

TABLE 6: Budget of petroleum Hydrocarbons Introduced into the Oceans

a_{mta, million metric tons per annum}

(Table from Petroleum in the Marine Environment, 1975, p.6.)

TABLE 7: Comparison of Estimates of petroleum Hydrocarbons Annually

Entering the Oceans, Circa 1969 - 1971

	Authority (Authority (Millions of Tons per Annum)			
Source	MIT SCEPT Report (1970)	USCG Impact Statement (1973	NAS Workshop (1973)		
Marine transportation	1.13	1.72	2.133		
Offshore oil production	0.20	0.12	0.08		
Coastal oil refineries	0.30		-		
Industrial waste	_	1.98	0.3		
Municipal waste	0.45	· · · · ·	0.3		
Urban runoff	-		0.3		
River runoff ^a	_	-	1.6		
SUBTOTAL	2.08	3.82	4.913		
Natural seeps	? ь	?	0.6		
Atmospheric rainout	9.0	?	0.6		
TOTAL	11.08	?	6.113		

"PHC input from recreational boating assumed to be incorporated in the river runoff value.

^bBased upon assumed 10 percent return from the atmosphere.

(Table from Petroleum in the Marine Environment, 1975, p.6)

and persistent oil residues. It is these sources of persistant oil which are most relevant to this discussion.

Marine oil seepage has been reviewed by Wilson et al (1974). The amount of natural seepage is estimated by quantifying known seeps, then multiplying by the area in which seepage is likely to occur at that rate. Figure 4 shows the areas of low, moderate, and high estimated seepage in the Pacific. The number of marine oil seeps actually observed is very small, so that the amount of extrapolation involved is very large. Blumer (1972) has calculated that if oil seepage is on the same sort of magnitude as anthropogenic inputs, marine reservoirs of oil would have long ago been exhausted. By this line of reasoning, the estimate by Wilson of 0.6 mta (million metric tons per year) is much too high, which points out the uncertainty in the extimate, but does not otherwise clarify the situation.

FIGURE 4: Oil Seepage Potential of the Pacific Ocean Basin



(From Wilson et al, 1974)

The second major source of persistent oils is marine oil transportation. In Table 6 this has been broken down into six subsections. The first three of these can be lumped together as routine tanker operations. They contribute 1.33 mta to the marine environment, an amount that is both large and well documented. The pollution occurs because of the clingage of oil to walls of the tanks in which it is carried. The clingage factor can vary anywhere between 0.1% of the cargo for refined products up to 1.5% for residual fuel oils (<u>Petroleum in the Marine Environment</u>, 1975). However, crude oil is the primary cargo of tankers (see Figure 5), and the clingage factor for crude varies from 0.3 to 0.4% (Kirby, 1968; Holdsworth, 1971). The clinging oil becomes mixed with sea water when the tanker ballasts or cleans its tanks. It is then pumped overboard prior to taking on the next cargo unless the load-on-top (LOT) procedure is utilized.

The LOT procedure consists of allowing the oil-water mixture to separate, then pumping the water out until the oil-water interface is reached. The oil slops are kept on board, and the next cargo is merely added on top. It is up to the refinery to deal with the problem of removing the remaining salt water from the cargo. The efficiency of LOT varies with the weather conditions (since rough weather makes separation of the oil and water phases more difficult) and with the degree of care taken in the pumping operation. The reduction in oil pollution resulting from adoption of LOT procedures is estimated to vary from 80% (Porricelli et al, 1971) to 99% (Kirby, 1968; Holdsworth, 1971) depending on these parameters. About 80% of the tanker fleet makes use of LOT (Victory, 1973). Non-adherence occurs for several reasons:

- 1. Irresponsible operation.
- 2. The delivery of crude to smaller refineries which refuse to accept salt-contaminated residues.
- 3. Short passages in which there is insufficient time for separation of oil and water to occur.
- Combination carriers, which may carry crude followed by ore or grain.
 Carrying of fuel oil cargoes, which cannot be contaminated with salt water since the fuel is not further refined before use.
- 6. Entering dry dock, which requires precleaning of all tanks.





The graph shows the exponential increase in the amount transported by sea as well as the increase in the percentage of total oil transported which is crude instead of refined products. The maps show changes in tanker routes. The width of the path is proportional to the amount transported. Since the closing of the Suez Canal in 1967, a substantial fraction of all traffic has been diverted from the Mediterranean to the Atlantic Ocean.

(Figure from Butler et al, 1973, p.86.)

Some of these problems can be overcome by the provision of facilities in ports for the reception of oil residues (IMCO, 1972). For further reference to LOT and its problems, see Kirby (1968), Holdsworth (1971), Porricelli et al (1971) and Victory (1973). The international regulations are dealt with in IMCO (1972) and IMCO (1973a).

Referring again to Table 6, the next transportation source is 'Terminal operations'. This has been estimated from two studies of the Milford Haven tanker terminal in Britain (Dudley, 1968; Dudley, 1971). It is too small a source to be significant in the context of open ocean pollution.

The fourth source is listed as "Bilges, bunkering'. 'Bilges' refers to oil which reaches ship bilges and eventually the ocean. It is generally of a dissolved and thin slick nature which does not form persistent oil pollution. 'Bunkering' refers to the fuelling of ships. Oil pollution results from spillages when fueling, which contribute to harbour but not open ocean pollution.

Tanker accidents contribute 0.2 mta, and all ship accidents contribute 0.3 mta of petroleum to the marine environment. This is only 23% of the amount lost by operational discharges each year, but of course the losses are localized and dramatic, and so attract publicity. The nature of tanker accidents has been investigated by Porricelli et al (1971), Keith and Porricelli (1973), and Wardley Smith (1973). Oil spillage is primary due to structural failures (48% of total outflow), which generally occur offshore, and groundings (28% of total), which, not too surprisingly, tend to occur near shore (Keith and Porricelli, 1973).
CHAPTER 3

WEATHERING OF PETROLEUM IN THE MARINE ENVIRONMENT

Introduction

Both the chemical composition of petroleum and its sources to the marine environment have already been discussed. The long-term fate of this petroleum depends on a variety of environmental factors which combine to 'weather' the oil.

The environment may alter the state of the oil purely by physically disturbing it, causing emulsification or sinking. This I term physical weathering - no change in the chemical composition of the oil takes place. Chemical weathering, on the other hand, refers to environmental alteration of the chemical composition of the oil, such as by evaporation, dissolution, auto-oxidation, and biodegradation. Each of these weathering processes and its effect on oil in the marine environment is discussed below.

Physical Weathering: Emulsification

Two types of emulsion occur as a result of turbulence and agitation of oil at sea by wind, wave, and tide action: oil-in-water emulsions in which water is the main phase, and water-in-oil emulsions in which oil is predominant. Oil-in-water emulsions characteristically consist of fine droplets of oil, 5 μ m to several mm in diameter (Forrester, 1971), dispersed through the water column to an extent dependent on the violence of the turbulence. All oils will form oil-in-water emulsions given sufficient agitation, but they are of limited stability: fine dispersions containing about 1 ppm oil will persist for several weeks; dispersions of 30 ppm and above separate out in a matter of half an hour (Parker et al, 1971). Bacterial growth on the oil aids in its emulsification and enhances its stability, apparently because the metabolic products possess properties of surfactants (Zajic and

Supplisson, 1972). In oil spill situations, detergents have been widely used (e.g. Smith, 1968); they function as emulsifying agents, and maintain the oil in a stable emulsion (Silsby, 1968). Oil-in-water emulsions tend to be more toxic than slicks, since higher concentrations of hydrocarbons are dispersed into the water column. However, as a result of the greatly increased surface area of the oil as an emulsion, the rate of degradation increases, ingestion and sedimentation of the fine droplets by filter feeding zooplankton can occur, and association of droplets with detritus results in sedimentation (Parker et al, 1971).

Water-in-oil emulsions also occur. Only oils which contain the asphaltic components of crude will form such emulsions (Berridge et al, 1968), but they can form spontaneously and be extremely stable. The water content is usually about 80% (Berridge et al, 1968), with the rate of formation under similar conditions varying widely between crudes depending on their asphaltic content (Dodd, 1971). The agent causing emulsification was isolated but not fully identified by Mackay et al (1972) as a type of asphaltenic compound.

Water-in-oil emulsions are extremely viscous: the viscosity of the emulsion formed by the Bunker C oil spilled in the 'Arrow' accident was 30,000 poise (32°F) compared with 700 poise for the original oil (Mackay et al, 1973). These stable, viscous emulsions pose intractable problems in oil spill cleanup. The emulsion formed by the crude oil spilt in the 'Torrey Canyon' accident became notorious and a household word as 'chocolate mousse'.

Tank washing and pumping operations on tankers are ideal for the formation of water-in-oil emulsions (Holdsworth, 1970), so that tank washings are discharged as stable lumps of emulsion. This reduces the surface area drastically, since the oil would otherwise exist as a slick. Photo-oxidation is severely limited; evaporation and dissolution are hindered. Biodegradation is the only process which is available to degrade the oil. It proceeds

because of the water available to encourage bacterial growth within the micro-environment of the emulsion (Kinney et al, 1969). Since the degradation by bacteria in a nutrient-poor situation is very slow, water-in-oil emulsions form longlived pollutants that travel the seas as tar lumps. These will be further discussed in Chapter 5.

Sedimentation

The specific gravity of crude oils varies from 0.75 to 1.0; and sea water from 1.024 to 1.030. Thus virtually all crude oils, and all refined products except for the heaviest of residual oils, will float at sea. However, the various weathering processes all act to increase the density of oil. Water-in-oil emulsification immediately increases the density of the emulsified lump to a weighted average of the oil and seawater. Evaporation and dissolution preferentially remove the lighter components up to boiling points of about 370°C. The residual of crude oil boiling above 370°C has a density about 10% greater than the original crude (see Table 5). Bacterial degradation preferentially removes the paraffins (Blumer et al, 1973), which are the lightest class of compounds, and so further increases its density. The actual cell weight of the bacteria also increases the density of the oil-bacterial mass. Spooner (1971) reported that bacteria created a brew of approximately neutral buoyancy in laboratory experiments, and after several weeks found the oil largely on the bottom, entangled with bacterial masses. Kinney et al (1969) observed the same of water-in-oil emulsions in the natural environment.

Actual fouling growth on floating tar can increase its density to the point that it sinks. The fouling community can become quite large and varied - see Chapter 5 - but is doomed by its own luxurious growth. In coastal areas the sorption of oil onto silt and detritus may lead to sedimentation (Lisitzin, 1972; Spooner, 1970). Furthermore, fine grained clay minerals can absorb or adsorb dissolved hydrocarbons from the water column (Suess, 1968; Meyers, 1972).

Sedimentation may also occur for indirect reasons. Filter-feeding zooplankton can injest dispersed droplets of oil and sediment them in their feces (Parker et al, 1971; Conover, 1971). The rate at which this form of

sedimentation occurs depends on a variety of factors, but is significant and can reach 0.3 $g/m^3/day$ (Parker et al, 1971).

Whatever the mechanism, sedimentation of oil does occur. Marumo and Kamada (1973), Kinney et al (1969), Morris (1963) among others have observed tar below the surface hovering at neutral bouyancy. Blumer and Sass (1972) documented the incorporation of oil into the sediments after the 'Florida' spill, as did Kolpack et al (1971) after the Santa Barbara spill.

The sinking of oil has received attention and some use as a method of dealing with oil spills. A variety of materials which are oleophilic and dense enough to sink oil are available. The method is reviewed by Brown (1971) and tests of various materials are summarized and evaluated by Houston et al (1972).

Chemical Weathering - Evaporation

Evaporation preferentially removes the low-boiling components of oil. Since the vapour pressures of hydrocarbons decrease logarithimically with increasing carbon number(see Table ⁸), the evaporative losses decrease rapidly for higher members of homologous series. Little or no fractionization will occur between hydrocarbons of the same volatility that belong to different structural families (Blumer et al, 1973a).

Simulated evaporation experiments in the laboratory (Krieder, 1971) indicate that all hydrocarbons containing less than about 15 carbon atoms (boiling point 270° C) volatilize in about 10 days from a 0.5 mm slick. Hydrocarbons in the C-15 to C-25 range (boiling range $270^{\circ}-400^{\circ}$ C) show limited volatility and are retained for the most part. Above C-25 (boiling point above 400° C) there is very little loss (see Figure 6). These results are similar to those obtained by Lieberman (1973), again with simulated weathering apparatus, who found virtually all evaporation from #4 and #5 fuel oils occurred within 10 days.

In the natural environment the rate of evaporation may be much faster, but with the same ultimate results: Smith and MacIntyre (1971) found greater evaporation in six hours at sea than in 40 hours in a laboratory bubbler apparatus, and Sivadier and Mikolaj (1973) showed that natural seep oil lost the majority of its volatile fractions in 1-2 hours in sea state four conditions. The rate of evaporation is dependent mainly on wind speed and air temperature, with water temperature only a minor factor (Frankenfeld, 1973b). Whitecapping aids evaporation, producing a large loss of low-boiling compounds (Smith and MacIntyre, 1971). The rate of evaporation is also increased by the spreading of an oil slick (Hoult, 1972).

Whatever the rate of evaporation, there is a clear trend for rapid initial evaporation, and asymptotic approach to an ultimate weight loss



Effect of time on weathering, 0.5 mm initial film thickness.

(From Kreider, 1971, p. 120).





Test 1: sea state 2-3. Test 2: sea state 4.

(From Sivadier and Mikolaj, 1973, p. 483).

FIGURE 6: Simulated Weathering of Crude Oil

(Sivadier and Mikolaj, 1973; see figure 7). All studies agree that evaporation is slow to affect any hydrocarbons above C-15 (boiling point 270° C), and that, above about C-23 (boiling point 380° C), the effects of evaporation are insignificant (Blumer et al, 1973a; Brunnock et al, 1968).

The resultant effect of evaporation on an oil is thus very much dependent on its boiling point composition. Evaporation alone will remove less than 10% of a heavy residual oil, up to 50% of a crude oil, about 75% of #2 fuel oil, and virtually all of kerosine and gasoline (<u>Petroleum in</u> the Marine Environment, 1975).

In comparison with other weathering processes, evaporation is the most important process for the first 1-3 days when evaporation is very rapid (Frankenfeld, 1973b). Dissolution competes directly with evaporation, affecting the same compounds, but is definitely less than 50% of the rate of evaporation, and perhaps as low as 1% (Harrison et al, 1975).

Theoretical treatments of evaporation have been proposed. Blokker (1964) and Hoult (1971) arrived at predictive models for oil slicks which gave good agreement with experimental data from wind tunnel simulators when the weight loss was greater than 15%. Butler (1975) has proposed a model for evaporative weathering of petroleum residues such as tar lumps. Semiquantitative agreement was obtained for crude oils weathered artificially, and crude residues weathered on rocky shores. Application of the model to tar lumps required that tar be fragmented from much larger and older masses.

Dissolution

The effects of dissolution on the chemical composition of oil is qualitatively similar to evaporation - the low-boiling components, which are also the most solu^{ble}, are preferentially removed. Under natural conditions, the rate of evaporation is considerably greater than the rate of dissolution (Harrison et al, 1975). However, dissolution has importance not only as a weathering process, in which its role is limited, but also because it is the dissolved compounds which reach marine biota and are responsible for oil's toxicity.

The solubilities of hydrocarbons drop drastically with increasing carbon number (see Table 8). For example, the solubility of pentane is 27.6 ppm and of decane is 0.052 ppm, a decrease of about an order of magnitude for each two carbon atoms added. The relationship is that, for each homologous series, the solubility in water is a linear function of the hydrocarbon molar volume (McAuliffe, 1966). For hydrocarbons with the same number of carbon atoms the solubility increases in the order: n-alkanes, iso-alkanes, cycloparaffins, and aromatic hydrocarbons. The high-molecular weight NSO compounds which occur in petroleum, although surface active, are apparently not appreciably more soluble than hydrocarbons of comparable molecular weight (Koons, 1973). The solubilities of hydrocarbons are enhanced by the presence of natural dissolved organic matter in seawater (Boehm and Quinn, 1973).

The competing process of evaporation and dissolution lead to a fractionation of the dissolving petroleum that cannot be predicted purely by solubilities. Smith and MacIntyre (1971) found that medium molecular weight aromatics, particularly the methyl- and dimethyl-naphthalenes, comprised the greatest proportion of the dissolved oil, whereas the saturated hydrocarbons were not detectable. These results can be attributed to the

fact that the dissolution of the low-molecular weight paraffins and aromatics is offset by their high rate of evaporation, whereas the dissolution of the high-molecular weight aromatics, the medium and the high-molecular weight paraffins is limited by their solubility. (Medium weight paraffins are much less soluble than medium weight aromatics: decane solubility is 0.052 ppm whereas the corresponding aromatic, naphthalene, is 31.2 ppm soluble.) Thus, of the major groups of hydrocarbons, medium molecular weight aromatics have the best combination of solubility and volatility for entering the water column.

Anderson et al (1974) also have documented the enriched aromatic content of the water-soluble fraction of oil. Comparing the ratio of aromatics to paraffins in the water-soluble fraction to the ratio in the original oil, they calculated 'aromatic enrichment factors' ranging from 15 to 125 for two crudes, Bunker C, and #2 fuel oil.

Over longer time periods, the processes of biodegradation and photo-oxidation begin to affect the oil, causing oxidation of hydrocarbons to alcohols, aldehydes, and acids, all of which are more soluble than the parent hydrocarbons. For instance, n-octane (solubility 0.43 ppm) can be oxidized to <-octanol (solubility 600 ppm; Seidell, 1941), and naphthalene (31 ppm) to <-naphthol (740 ppm; Seidell, 1941). Frankenfeld (1973 a and b), using a weathering simulator, demonstrated that dissolved organics increase with weathering, and determined that the increased dissolved organics were chiefly oxygenated aromatics.

TABLE 8: Melting Points, Boiling Points, Vapour Pressures, and Solubilities of Selected Hydrocarbons

Melting points were taken from the <u>Handbook of Chemistry and</u> <u>Physics</u>, 55th Edition, CRC Press, 1974-75.

Vapour pressures were obtained from the <u>Handbook</u> and from Wilhoit and Zwolinski (1971). Antoine's equation was used to determine vapour pressures at 25^oC. A graph of vapour pressure as a function of carbon number is presented in Appendix A.

Solubilities were obtained from a variety of sources: Sutton and Calder (1974); McAuliffe (1963, 1966, and 1974); Price (1973): and Bohon and Claussen (1951). When more than one value appeared in the literature for solubility at 25°C, the most recent value was taken. When solubilities in sea water were available, they were quoted and indicated by an asterisk. Otherwise, values are for distilled water. Hydrocarbon solubilities in sea water are probably not more than 12 to 30% lower than those in distilled water (Harned and Owen, 1958).

The information in this table was assembled by Wendy Richardson under contract to Ocean Chemistry, Ocean and Aquatic Sciences, Department of Environment, Victoria, B.C., Canada.

NORMAL PARAFFINS

NAME	FORMULA	MELTING PT. (°C)	BOILING PT. (^O C)	V.P. at 25 ⁰ C (atmospheres)	SOLUBILITY @25 ^o C ppm (wt/wt)	
29 ³		······································			- <u></u>	`_
pentane	с ₅ н ₁₂	-129.7	36.1	6.75x10 ⁻¹	27.6*	
hexane	с ₆ н ₁₄	-95	68.9	1.99×10^{-1}	9.5	· .
heptane	с ₇ н ₁₆	-90.6	98.4	6.03x10 ⁻²	2.2	
octane	с ₈ н ₁₈	-56.8	125.7	1.86×10^{-2}	.43	
nonane	^С 9 ^Н 20	-51	150.8	5.64×10^{-3}	.12	
decane	C10 ^H 22	-29.7	174.1	1.72×10^{-3}	.052	
undecane	с ₁₁ н ₂₄	-25.6	195.9	3.15x10 ⁻⁴		•
dodecane	C12 ^H 26	-9.6	2.6.3	1.55×10^{-4}	.0029*	
tridecane	с ₁₃ н ₂₈	-5.5	235.4	4.37×10 ⁻⁵	· .	
tetradecane	^C 14 ^H 30	5.9	253.7	1.26×10^{-5}	.0017*	
pentadecane	C ₁₅ H ₃₂	10	270.6	3.46×10^{-6}		
hexadecane	^C 16 ^H 34	18.2	287	8.85×10 ⁻⁷	.0004*	
heptadecane	C ₁₇ ^H 36	22	301.8	2.67×10^{-7}		
octadecane	C18 ^H 38	28.2	316.1	7.34x10 ⁻⁸	.0008*	
eicosane	с ₂₀ н ₄₂	36.8	343	2.15x10 ⁻⁹	.0008*	
hexacosane	C ₂₆ ^H 54	56.4	412.2	7.22×10^{-14}	.0001*	
					•	

* indicates solubility in sea water, all others are solubilities in distilled water.

ISOPARAFFINS

NAME	FORMULA	MELTING PT. ([°] C)	BOILING PT. ([°] C)	V.P. at 25 ⁰ C (atmospheres)	SOLUBILITY *25°C ppm (wt/wt)
2-methylpentane	с ₆ н ₁₄	-153.7	60.3	2.76×10^{-1}	13.0
3-methylpentane	^C 6 ^H 14		63.3	2.50×10^{-1}	13.1
2-methylhexane	с ₇ н ₁₆	-118.3	90	8.67×10^{-2}	2.5
3-methylhexane	^С 7 ^Н 16	-119	92	8.10×10^{-2}	2.6
2-methylheptane	с ₈ н ₁₈	-109	117.7	2.71×10^{-2}	
3-methylheptane	с ₈ н ₁₈	т. Т	115.8	2.57×10^{-2}	.79
4-methylheptane	^C 9 ^H 20	-113.2	142.4	8.91x10 ⁻³	.11

CYCLOPARAFFINS

NAME	FORMULA	MELTING PT. (°C)	BOILING PT. (°C)	V.P. at 25 ⁰ C (atmospheres)	SOLUBILITY @25°C ppm (wt/wt)
cyclopentane	с _{5^н10}	-93.9	49.3	4.18x10 ⁻¹	160
methylcyclopentane	С ₆ ^Н 12	-142.4	71.8	1.81x10 ⁻¹	29.2*
cyclohexane	C6H12	6.55	80.7	1.28x10 ⁻¹	67.5
methylcyclohexane	с ₇ н ₁₄	-126.6	100.9	6.10×10^{-2}	16
ethylcyclopentane	C ₇ H ₁₄	-138.4	103.5	5.25x10 ⁻²	
1,trans-4-dimethylcyclohexane	C ₈ H ₁₆	-37.0	119.3	2.98×10^{-2}	3.84
1,cis-3-dimethylcyclohexane	с ₈ н ₁₆	-75.6	120.1	2.83x10 ⁻²	
1,cis-2-dimethylcyclohexane	C ₈ H ₁₆	-50.1	129.7	1.90×10^{-2}	6.0
ethylcyclohexane	C ₈ H ₁₆	-111.3	131.8	1.68×10^{-2}	
propyl cyclopentane	с ₈ н ₁₆	-117.3	131.0	1.62×10^{-2}	2.0

* indicates solubility in sea water, all others are solubilities in distilled water.

AROMATICS

NAME	FORMULA	MELTING PT. (°C)	BOILING PT. ([°] C)	V.P. at 25 ⁰ C (atmospheres)	SOLUBILITY @25°C ppm (wt/wt)
benzene and de la companya de la com	C ₆ H ₆	5.5	80.1	1.25x10 ⁻¹	1391*
toluene	с. С ₇ н ₈	-95	110.6	3.74x10 ⁻²	402*
ethyl benzene	с ₈ н ₁₀	-94.5	136.2	1.25×10^{-2}	152
p-xylene	с ₈ н ₁₀	13.3	138.4	1.15×10^{-2}	157
m-xylene	с _{8^н10}	-47.9	139.1	1.09×10 ⁻²	134
o-xylene	с ₈ н ₁₀	-25.2	144.4	8.71×10^{-3}	167
isopropylbenzene	C9 ^H 12	-96	152.4	6.03x10 ⁻³	48.2
n-propylbenzene	с _{9^н12}	-99.5	159.2	4.43×10^{-3}	
1-methy1-3-ethylbenzene	С ₉ н ₁₂		· · · · ·	3.86x10 ⁻³	
1,2,4-trimethylbenzene	с ₉ н ₁₂	-43.8	169.4	2.67x10 ⁻³	51.9
isobuty lbenzene	с ₁₀ н ₁₄	-51.5	172.8	2.45×10^{-3}	10.1
1,2,3-trimethylbenzene	с ₉ н ₁₂	-25.4	176.1	1.96x10 ⁻³	•
1,2,4,5-tetramethylbenzene	^C 10 ^H 14	79.2	196.8	6.50x10 ⁻⁴	3.48
naphthalene	с ₁₀ н ₈	80.6	218	3.07x10 ⁻⁴	31.2
1,2,3,4-tetramethylbenzene	^C 10 ^H 14	-6.2	205	4.44x10 ⁻⁴	
biphenyl	C ₁₂ H ₁₀	71	255.9		7.08
acenaphthalene	с ₁₂ н ₁₀	96.2	279		3.88
fluorene	с ₁₃ н ₁₀	116	293		1.90
phenanthrene	C ₁₄ H ₁₀	101	340	9.56x10 ⁻⁷	1.18
anthracene	с ₁₄ н ₁₀	216.2	340	2.68x10 ⁻⁶	.075

* indicates solubility in sea water, all others are solubilities in distilled water.

Vapour Pressures of Hydrocarbons as a Function of Carbon Number N



The regression line predicts $\log_{10}{\rm P}$ for normal alkanes within 95% confidence limits of \pm 0.08 .

(From Butler, 1975b, p. 11)

Biological Degradation

Introduction:

The literature dealing with the microbial degradation of hydrocarbons is extensive. The original interest in the problem was purely academic and scientific. It was first noticed in 1895 that bacteria degrade the supposedly inert paraffin used as a support in cultures, and over the years much work was done, usually using pure hydrocarbons under culture conditions. A large body of literature now exists dealing with the types of hydrocarbons attacked and the pathways of oxidation. This literature has been reviewed by Zobell (1946), Treccani (1965), McKenna and Kallio (1965), and Van der Linden and Thijsse (1965).

A second source of interest in petroleum microbiology originated from the discovery that microbes could be used to prospect for petroleum. It was also discovered that microbes caused decomposition of petroleum and refined products, especially jet fuels, under storage conditions, and that this decomposition also led to tank and pipe corrosion. These discoveries, and the interest in establishing the genesis of petroleum, inspired an extensive investigation into petroleum microbiology by the rapidly growing petroleum industry. This body of knowledge has been reviewed by Davis (1967).

Thirdly, and most recently, interest in the microbial degradation of hydrocarbons has come from increased environmental awareness and the burgeoning problem of oil spills, particularly in the marine environment. Some recent literature deals specifically with this problem, using mixed cultures with crude and refined oils, and attempting to understand the microbial ecology of the hydrocarbon oxidizers in the marine environment (Zobell, 1969 and 1973; Atlas, 1972; Floodgate, 1972). Hydrocarbon Degradation:

It has been established that microbes will attack the spectrum of hydrocarbons from aliphatic to aromatic (e.g. Treccani, 1965). Alkanes are preferentially degraded, and aromatics more resistant (Zobell, 1969). Within each hydrocarbon class the very lightest components, such as C-5 to C-8 in the paraffins, cyclohexane, toluene, and phenol, are bactericidal or bacteriostatic to most species (Klug and Markovitz, 1971; McKenna and Kallio, 1964). The medium molecular weight compounds are most easily attacked, and the high molecular weight compounds become increasingly more resistant, apparently because their very low solubilities present a logistical problem to the micro-organisms (Zobell, 1969). Highly condensed cyclic hydrocarbons, asphaltenes, and non-hydrocarbon NSO compounds are especially recalcitrant (Bailey et al, 1973).

The isoparaffins do not fit into this scheme. It has been shown that the ease of degradation of isoparaffins is very much dependent on the extent of branching. For instance, one methyl group attached to an alkane slows the rate of degradation. Two methyl groups on the same carbon atom, especially if they are on the penultimate carbon atom, essentially block degradation (McKenna and Kallio, 1964). Thus the isoprenoids pristane and phytane, which each have four methyl branches, are much more slowly degraded than the corresponding alkanes. Indeed, it appears that degradation of pristane and phytane in a mixed culture does not occur until the alkanes have been exhausted (Bailey et al, 1973).

The mechanisms of degradation have been worked out in some detail (Van der Linden and Thijse, 1965; Treccani, 1965; McKenna and Kallio, 1965). The detail of the mechanisms is much too voluminous to summarize here; suffice it to say that the products of degradation are primarily alcohols, aldehydes, and acids, but also include hydroperoxides, ketones, and esters (Zobell, 1973). Some of the degraded hydrocarbons are mineralized to carbon dioxide and water, and the remainder are assimilated to form bacterial biomass, or remain as intermediate products (Atlas and Bartha, 1972 a, b). Figure 8 shows the effect of a mixed population of micro-organisms on a crude oil under culture conditions.

Types of Micro-organisms:

Over 200 species of bacteria, yeasts, and filamentous fungi have been shown to metabolize one or more kinds of hydrocarbons. These species are diversified, being drawn from 28 genera of bacteria, 30 genera of fungi, and 12 of yeasts (Zobell, 1973). No single species of micro-organism has been found capable of attacking the full range of hydrocarbons. Instead, there is a great deal of specialization, and most effective degradation of a crude oil occurs with mixed cultures (Soli and Bens, 1972). The single most successful hydrocarbon-degrader which has been isolated is the fungus <u>Cladosporium resinae</u> (Cooney and Walker, 1973). Certain species, such as <u>C. resinae</u>, have constitutive enzymes for hydrocarbon degradation, but more commonly the enzymes are inducible (Zobell, 1973).

Ecology of Hydrocarbon-degraders in the Marine Environment:

Degradation of hydrocarbons is primarily an aerobic process. Some anaerobic degradation can occur, but the rates are apparently very slow (see Floodgate, 1972).

The hydrocarbons provide a carbon and energy source for microbes. However, a great many environmental factors, and some nutritional requirements, influence the rate at which degradation will occur. Since most work of hydrocarbon degradation is done under culture conditions, which are optimal, there





Gas chromatograms of crude oil at O-time (top), after 6 hours (centre), and 26 hours (bottom) of incubation with a mixed population of micro-organisms. Note change in attenuation in top chromatogram. (From Mechalas et al, 1973, p. 71).

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is not a great deal known about the influences of the various environmental factors, but some basic information has been obtained.

Hydrocarbon-degrading microbes are common in near shore waters (Gunkel, 1973; Zobell, 1969) but the concentrations vary widely, depending primarily on the levels of contamination by hydrocarbons (Mironov, 1970b). In the open ocean, Zobell (1969) reports that only 5% of several hundred samples contained oil-oxidizing bacteria, and none contained oil-oxidizing molds or fungi. Anderes (1973) obtained hydrocarbon-utilizing bacteria in 24% of 173 samples but no molds or fungi.

Despite these low concentrations in some environments, natural innoculation of oil spills always seems to occur, with complete colonization occurring within 1-2 weeks (Pilpel, 1968). Pilpel concludes that there is little to be gained by artificially innoculating oil slicks.

The environmental factor which most commonly limits the degradation of oil in the marine environment is a shortage of nitrate and phosphate nutrients (Bridie and Bos, 1971; Atlas and Bartha, 1972b). These nutrients are always in short supply in the open ocean, and it is not surprising that they limit growth in the intensive blooms of microbes which occur in oil. A promising method of oil spill treatment is the addition to oil slicks of an oleophilic nitrate and phosphate rich compound to encourage microbial degradation (Bartha, personal communication).

Oxygen can theoretically be limiting to degradation since the BOD of oil is high, especially if it is completely mineralized (Zobell, 1973). Oxygen does not appear to be the limiting factor in oil slick situations where atmospheric oxygen is readily available (Friede et al, 1972). Oxygen limitation may, however, be a problem in areas of chronic oil pollution where gas exchange is limited.

Temperature also affects the rate of degradation. It has been

established that oil is degraded at all marine temperatures from $-2^{\circ}C$ up to as high as $70^{\circ}C$ (Zobell, 1973). However, most species are active in the mesothermic range of 20° to $25^{\circ}C$, and degradation rates decrease markedly at lower temperatures. Psychrophilic bacteria oxidize oil at $-1.1^{\circ}C$ at only 5 to 10% of the rate of mesothermic species at $25^{\circ}C$ (Zobell, 1973). Kator et al (1971) found that oxidation of paraffins was proportional to the incubation temperature, doubling with an increase of $10^{\circ}C$.

Increasing depth reduces microbiological activity. In fact, petroleum residues deposited at several thousand meters depth may remain 'preserved' indefinitely (Jannasch and Eimhjellen, 1972).

Finally, the concentration of dissolved petroleum may be important to the rate of its microbial oxidation. In fact, there may be a threshold concentration below which autochthonous bacteria are unable to utilize dissolved hydrocarbons as a substrate (Jannasch, 1969). For masses of oil, the rate of microbial oxidation is very dependent on the surface area available to microbiological attack.

Various other factors influence the rate of degradation, such as: salinity; pH; turbulence; other organic matter; microbial predators; and accumulation of intermediate products. The relative effects of all these parameters have not been unravelled.

The net result of these various environmental factors determines the rate at which oil degrades in the marine environment. Measurements of the net degradation rate are of great interest, but are not common. The only direct observation of biological degradation is by Blumer et al (1973), who observed the partial biodegradation of stranded crude oil in the intertidal environment over a 16 month period. Other publications, such as Blumer and Sass (1972b), give an indirect idea of the rate of degradation. It is one of the purposes of this thesis to provide information on the rates of

biodegradation in the marine environment.

Macrobiological Degradation:

We have so far ignored any role which might be played by macroorganisms in the metabolism of oil. Various marine organisms have been observed to take up dissolved and particulate hydrocarbons from sea water (Lee 1972a, b, 1975; Stainken, 1975; Neff and Anderson, 1975; Conover, 1971). Lee reports that various dissolved polyaromatic hydrocarbons are taken up by zooplankton, mussels, and fish. In some cases the hydrocarbons are metabolized, and in other cases dissolved hydrocarbons are merely stored, and released into clean water (Lee, 1972a; b; Neff and Anderson, 1975). Particulate hydrocarbons appear to pass directly through zooplankton into their feces (Conover, 1971).

It is evident that various macro-organisms are capable of metabolizing various fractions of oil. However, from the point of view of contributing to the overall degradation of oil in the marine environment the role of macro-organisms must be assumed to be small. This statement is based less on experiment than on an appreciation of the microbes, with their enormous reproductive capabilities, as the primary degraders and mineralizers in the environment.

Auto-Oxidation

Chemical weathering of oil can occur purely by chemical reaction of oil with atmospheric oxygen. The process can be initiated either thermally or by photolysis. Under the thermal regime of the oceans, thermal reaction is extremely slow, so that, when there is reasonable exposure of oil to light, photolysis is the main process.

The absorption of light, or the thermal decomposition of impurities, creates free radicals. A chain reaction follows, since the products of reactions (hydroperoxides) themselves decompose to form more free radicals (Parker et al, 1971). These oxidation reactions are strongly catalysed by ions of variable valence, such as vanadium. They are inhibited by sulfur compounds due to the chain-breaking reactions of sulphoxide formation (Berridge et al, 1968).

The oxidation reactions may proceed in two different ways. The hydroxy compounds formed by decomposition of peroxides may undergo further dehydrogenation to yield aldehydes, ketones and acids. Alternatively, products of higher molecular weight may be formed by combination, condensation, or esterification (Parker et al, 1971). The products of lower molecular weight are much more soluble than the parent hydrocarbons (see dissolution section) and so are rapidly removed from the slick. Products of higher molecular weight are likely to form viscous gums or tars.

The chain reaction process depends on the extraction of a hydrogen atom by a radical. Therefore, hydrocarbon compounds containing weakly-bound hydrocarbon atoms should be preferentially oxidized. Since hydrogen atoms bound tertiary carbons are more weakly bound than those attached to secondary carbons, isoparaffins should be selectively degraded ahead of paraffins, cycloparaffins, and aromatics (Berridge et al, 1968). This conclusion is based on theoretical considerations rather than experiment. Hansen (1975), working with a light fraction of crude oil, found experimentally that isoparaffins appeared to be preferentially photo-oxidized relative to paraffins, but that aromatics were most effectively oxidized. He did not venture to explain this phenomenon. Hansen also found that most of the photo-oxidation products were carboxylic acids which appeared to be related to their parent hydrocarbons by the

relation: $C_{xy} + 0_2 \rightarrow C_{x-1}H_{y-2}$ COOH

The rate at which oil is photo-oxidized depends, like everything else, on a number of factors. The most important is probably the surface area of the oil. Oil spread as a thin film obviously absorbs much more radiant energy than oil lumped in a water-in-oil emulsion. The experimental work which has been performed has dealt with oil as a thin slick. The experiments of Freegarde and Hatchett (1970) indicate that complete photooxidation of a 2.5 μ m slick would take about 100 hours of sunlight, or 1 μ m per 40 hours. Hansen (1975), on the basis of his experiments, made an estimate of about three years continuous sunlight to degrade a 0.4 mm slick, which works out to 1 μ m per 100 hours. Both estimates indicate that photolysis is slow, even under the best of circumstances.

The rate of photo-oxidation is also very much dependent on the wavelengths of the irradiating light. Both Hansen (1975) and Parker et al (1971) obtained much faster degradation using shorter wavelengths than are found in sunlight (i.e. less than about 300 nm). Hansen could get no degradation to occur with wavelengths longer than 340 nm, and Parker et al also found the most effective portion of sunlight was the ultraviolet light of wavelength 300-350 nm. Ultraviolet light has a very high extinction coefficient in the ocean and does not penetrate more than a very few meters (Parsons and Takahashi, 1973), so that any oil dispersed below about two meters in the water column should not undergo photo-oxidation. This has not been investigated experimentally.

Thirdly, the composition of oil may affect the rate of degradation. Since sulfur compounds inhibit the reaction process, it is to be expected that high-sulfur oils should degrade more slowly than low-sulfur oils.

Finally, the optical density of the oil in the ultraviolet region may be an important variable (<u>Petroleum in the Marine Environment</u>, 1975). Neither of these last two factors have been studied.

Summary of Weathering

All of the significant weathering processes have been discussed in some detail. However, the relative rates and effects of the various mechanisms have not been drawn into focus, and that is the purpose of this section.

The processes of evaporation and dissolution affect the lightest components quickly, in a matter of a few hours under most conditions, and then their effect diminishes exponentially. Of the two, evaporation is usually the dominant process, but dissolution is important for the aromatics of medium molecular weight, and for the products of oxidative degradation.

Photo-oxidation and biodegradation are slower processes which take a matter of months to remove significant quantities of oil under natural conditions. They can oxidize the full spectrum of petroleum compounds, but since the light components are quickly removed by evaporation and dissolution, they primarily affect the medium and heavy molecular weight compounds. Microbial degradation preferentially removes the paraffins, whereas photooxidation preferentially removes the isoparaffins. Of the two processes, biodegradation is dominant in situations where there are reasonable conditions for microbial growth.

The interrelationships between the various weathering processes as they affect a floating crude oil slick are illustrated in Figure 9. The rate at which the processes act is very much dependent on the exposed surface area of the oil. Oil spread as a very thin slick allows the combined degradative processes to work to maximum effect. This is the reason the world's oceans are not covered by a thin film of petroleum hydrocarbons. Conversely, oil which is lumped in a water-in-oil emulsion is not degraded efficiently by any of these processes. In situations between these two extremes, the relative rates of the chemical weathering processes depend on the location and state of the oil.



FIGURE 9: Processes Leading to the Degradation of Crude Oil at Sea



The composition of the oil is also of great importance to the relative rates. Light refined oils are most affected by evaporation and dissolution, whereas residual oils must wait for the slow oxidative processes to occur. The heaviest, asphaltic portion of petroleum is virtually impervious to chemical weathering, and in fact asphaltics are formed from lighter compounds during the weathering process. The asphaltic fraction forms a long-lived, nearly inert environmental pollutant.

The fate of the isoprenoids pristane and phytane can be compared with the fate of the C-17 and C-18 n-alkanes to provide an analytic tool which reveals the relative rates at which an oil is affected by weathering processes.

The boiling points of pristane and phytane are almost identical to the C-17 and C-18 n-alkanes respectively. Thus the isoprenoids can be expected to evaporate at the same rate as the paraffins. However, the low molecular weight compounds C-17 and pristane are considerably more volatile than C-18 and phytane (vapour pressures: C-17 = 2.7×10^{-7} atm.; C-18 = 7.3 $\times 10^{-8}$ atm @ 25° C). Evaporation will preferentially remove the more volatile compounds so causing a decrease in the C-17/C-18 and pristane/phytane ratios in the weathered oil.

The solubilities of the isoprenoids are not known, but can be inferred from their polarity. They are, if anything, slightly less polar than the C-17 and C-18 n-alkanes a fact which is experimentally demonstrated by the slightly quicker rate at which the isoprenoids elute from polar columns in gas chromatography (e.g. Bailey et al, 1973; Ehrhardt and Blumer, 1972). The solubility of the n-alkanes is extremely low (0.0008 ppm), so the solubility of the isoprenoids is presumably lower still. Dissolution is, therefore, very unlikely to be a significant weathering process for any of these compounds.

Photo-oxidation is expected to oxidize the isoprenoids preferentially. This has been experimentally verified by Hansen (1975) whose results are summarized in Table ⁹. No fractionation between compounds of the same class has been observed or is expected.

TABLE	9:	Effect of Photo-oxidation on Isoprenoid/Alkane Ratios	in
		Crude Oil	

	· · ·		
Hours of Irradiation		<u>pr/C-17</u> (%)	<u>ph/C-18</u> (%)
0	· ·	50.5	36.2
4		50.5	34.5
53		50.0	33.0
126		49.4	32.7
170		47.9	31.8
295		46.8	30.9
462	· · ·	45.4	26.7

(From Hansen, 1975, p. 187).

Microbiological degradation, in contrast to photo-oxidation, preferentially removes the paraffins since the methyl groups on the isoprenoids impede degradation. This has been observed by many (e.g. Bailey et al, 1973; Blumer et al, 1973a). Again there is no significant fractionation between compounds of the same class (Mechalas et al, 1973).

Three conclusions can be reached by observing the isoprenoid/ paraffin ratio in oil undergoing chemical weathering:

1) A decrease in the pristane/phytane or C-17/C-18 ratio indicates evaporation is occurring.

2) An increase in the C-17/pristane and C-18/phytane ratio indicates that photo-oxidation is the dominant process.

3) A decrease in the alkane/isoprenoid ratio indicates microbial degradation is the dominant process.

These conclusions will be utilized throughout the experimental investigations to ascertain the mechanisms of petroleum degradation in various situations.

CHAPTER 4

THE WEATHERING OF PETROLEUM UNDER CONTROLLED CONDITIONS

Introduction

An experiment was conducted under controlled conditions, by weathering oil in tanks, to provide a control for comparison with the field observations. Gas chromatographic analyses were used to reveal the rate and mechanisms of chemical weathering of the oil samples.

Experimental Method

Three kinds of oil were placed in outdoor tanks 3 meters across, and ¹/₂ meter deep. Tanks were filled with seawater, and 5 gallons (23 1) of oil were poured in each tank, giving a layer of oil about 3mm thick, and an oil-to-water ratio of 1 to 156. The oils used were an Alberta crude oil, an intermediate fuel oil (Esso fuel 46 which is a #5 fuel oil), and diesel fuel. No exchange of water was provided, so that there was no source of nutrients for microbial growth and limited opportunity for dissolution - chemical weathering was thus restricted to evaporation and photo-oxidation. The tanks were left undisturbed, except for occasionally siphoning out rainwater, from October 1973 to January 1974. Samples were taken from the tanks periodically over this 3¹/₂ month period and analysed by gas chromatography to determine the extent of chemical weathering that had occurred. For these analyses about 0.3 g of sample was dissolved in 5 ml of carbon disulfide and injected onto a Dexsil column programmed to 400°C. The instrumental parameters are given in Table 18. Representative chromatograms are presented in Figures 10, 11, and 12.



FIGURE 10: Chromatograms of Artificially Weathered Crude Oil



1) Original fuel oil (Esso Fuel 46)





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Results of the Controlled Weathering Experiment

The results of the controlled weathering experiment are summarized in Table 10. The parameters listed there are calculated from the gas chromatograms. They are chosen to reveal the mechanisms by which the oil is chemically weathered during its $3\frac{1}{2}$ month exposure in experimental tanks. The first two parameters, $C_n^{10\%}$ and $C_n^{50\%}$, are measures of the shape of the envelope; they are defined as the equivalent n-paraffin carbon numbers at which the unresolved envelope reaches 10% and 50%, respectively, of its maximum amplitude. A high value of these parameters indicates a large loss of the low-boiling components making up the envelope, which in turn indicates the extent of weathering by the evaporation and dissolution.

The third parameter listed in Table 10 is the C-17/C-18 peak height ratio. Since the chromatograms do not separate the isoprenoids from the normal paraffins, the C-17 peak measures the amount of n-heptadecane and pristane, while the C-18 peak measures the amount of n-octadecane and phytane. A lower-ing of the C-17/C-18 ratio indicates the preferential loss of the lower-boiling homologs, and so provides a measure of the extent of evaporation and dissolution occurring at the boiling points of these compounds $(302^{\circ}C \text{ and } 316^{\circ}C)$.

The C-18/C-19 ratio compares the relative amounts of phytane and nonadecane. Photo-oxidation and biodegradation are processes which act over much wider ranges of molecular weight than evaporation and dissolution, but their effects are very much dependent on the structure of the hydrocarbons (see Chapter 3). Under microbial attack the isoprenoids are resistant, and the paraffins are preferentially removed, resulting in an increase in the C-18/ C-19 ratio. Photo-oxidation has the opposite effect, preferentially removing
the isoprenoids and so decreasing the C-18/C-19 ratio. Some ambiguity exists since, if both photo-oxidation and biodegradation occur, their relative effects will tend to cancel. The final parameter in Table 10, the C-18/env. ratio reduces the ambiguity by comparing the height of the C-18 peak to the height of the envelope. If both photo-oxidation and biodegradation are occurring, substantial decreases in the C-18/env. ratio should occur.

TABLE 10: Characteristics of Artificially Weathered Oils

Length of	10%	50%			· · · · · · · · · · · · · · · · · · ·
Exposure		· C _n	C-17/C-18	C-18/C-19	C-18/env.
	· ·				
Crude oil					
original	ind.	ind.	1.60	1.25	1.88
2 days	10.0	11.2	1.56	1.24	1.78
1 month	12.5	14.0	1.57	1.29	2.12
3^{1}_{2} months	12.7	14.3	1.51	1.30	2.18
		·			
#5 fuel oil					
original	12.3	13.2	1.29	0.92	1.51
2 days	12.5	13.7	1.32	0.93	1.67
1 week	12.5	14.0	1.13	0.97	1.37
7 weeks	13.5	15.0	1.00	0.96	1.64
3^{1}_{2} months	13.5	14.6	1.24	0.94	1.53
					· · · · ·
Diesel fuel					· .
original	11.0	15.9	1.12	1.45	2.42
2 days	11.0	16.0	1.11	1.45	3.10
1 week	11.8	16.0	1.14	1.45	3.00
7 weeks	15.5	17.0	1.16	1.44	2.42
9 weeks	16.3	17.2	0.87	1.41	2.64
<u> </u>		J	L	<u>t</u>	L

Discussion of the Controlled Weathering Experiment

As already discussed, the experiment was designed to eliminate the weathering effects of dissolution and biodegradation, and so to concentrate on the effects of photo-oxidation and evaporation. Each of these processes will be discussed in turn.

Dissolution: It is not possible to state, from the experimental evidence, that dissolution did not act on the oils in the tanks, because the effects of evaporation and dissolution overlap, and can only be resolved by comparing components of differing solubility but similar volatility. This involves more detailed analyses which were not performed. However, because of the very high ratio of oil to water that was used, and the very low solubilities of hydrocarbons (see Table 8) it is assumed that dissolution did not affect the composition of the oils.

Biodegradation and photo-oxidation: No biodegradation of the petroleum was expected because of the lack of nutrients. The C-18/C-19 ratio confirmed this expectation, but also revealed what was not expected: that photo-oxidation also had no affect. There was no change in the C-18/C-19 ratio, nor any change in the C-18/Env. ratio (other than 'noise') in any of the three oils over the $3\frac{1}{2}$ months of the experiment, implying that neither biodegradation nor photooxidation of the oils occurred. The experiment indicates that photo-oxidation is not effective as a weathering mechanism for oil spread as a layer (3mm thick) under the radiative conditions in British Columbia from October to January.

Evaporation: The role of evaporation is revealed most clearly by the parameters which measure the shape of the unresolved envelope: $C_n^{10\%}$ and $C_n^{50\%}$. All three oils show significant increases in these parameters. Crude oil, in particular, undergoes rapid initial removal of the lightest components, with a large portion of the evaporation occurring in the first two days. This was

FIGURE 30 (copy): Effect of Evaporation on a Thin Film of Crude Oil

A glass rod was dipped in Prudhoe Bay crude oil, then placed in a fume hood for 25 hours, with the following results:



#1 Prudhoe Bay
crude oil

#2 Thin film of Prudhoe Bay crude oil exposed for 25 hours. also the period in which the crude lost its pronounced odour. After about a month, the chromatograms indicate that stabilization occurred, with virtually no loss of additional components over the next 2½ months of exposure. No significant change in the C-17/C-18 ratio occured over the 3½ months of exposure, implying that evaporation did not affect components boiling above 300°C. During the course of the experiment the crude oil did not change in general appearance, but it became noticeably more viscous. No formation of tar lumps or sinking of the crude oil occurred.

The importance of the surface area in determining the rate and extent of evaporation is demonstrated by a comparison of Figure 10, which depicts crude undergoing evaporation in a 3mm thick layer, and Figure 30 which shows evaporation from a thin film. The following values are taken from these two Figures.

	Time of Exposure	c_n^{10%}	c_n	<u>C-17/C-18</u>
Oil as 3mm la	yer 3½ months	12.7	14.6	1.6 → 1.5
Oil as a thin	film 25 hours	14.2	16.0	1.4 + 1.1

All three indices indicate that very much more evaporative weathering occurs in 25 hours from a thin film than occurs in $3\frac{1}{2}$ months from a 3mm layer. The rate enhancement appears to be about 3 orders of magnitude, although it is not clear that evaporation would <u>ever</u> remove as much of the oil from a layer as it did in 25 hours from a film, since the layer appears to stabilize after about a month.

The intermediate fuel oil contained far less of the lower boiling components than crude oil, and so was less effected by evaporation. Neither its appearance nor its viscosity changed noticeably during the course of the experiment. Evaporation, as revealed by the gas chromatograms, was not evident in the initial week, and stabilization occurred after 7 weeks, with no detectable

change occurring thereafter. Again, no evaporation was detected by the C-17/C-18 ratio throughout the experiment.

The diesel fuel showed a markedly different weathering pattern from the other two oils. No stabilization of the oil occurred; instead, the $C_n^{10\%}$ and $C_n^{50\%}$ values showed a steady rise with continued exposure. After 9 weeks the effect of evaporation had extended through almost the complete spectrum of alkanes, the C-17/C-18 ratio was 'feeling' the effect of evaporation, and the layer of diesel oil on the surface of the tank had been depleted to a thin scum. A large amount of oil was emulsified and dissolved in the tank water, and the remainder had apparently evaporated. The very different behavior of the diesel from the other two oils is not understood, but apparently is a reflection of the presence of emulsifying agents in the diesel fuel, and the lack of high-boiling components to retain the lower-boiling fractions.

Conclusions

1. Photo-oxidation is not an effective weathering mechanism for oil in a moderately thick layer.

2. The rate of evaporation from a layer of oil is very much dependent on the surface volume ratio, varying over at least 3 orders of magnitude from a thin film to a 3 mm layer. It appears that reduced surface area may result in less absolute loss, no matter how long the oil is exposed.

3. Evaporation has a limited effect on heavier oils, reaching a point where stabilization occurs and further evaporation is negligible, but this stabilization does not occur for lighter oil such as diesel fuel.

4. Evaporation alone is not sufficient to produce tar lumps and cause sinking of crude oil. In a similar experiment performed by Ohya et al (1973) crude oil formed tar lumps and sunk after 200 days of exposure in a

tank. The difference was that continuous circulation was provided, so that sufficient nutrients for microbial growth were supplied. Apparently microbial degradation is crucial for the formation of tar lumps and eventual sinking of crude oil.

CHAPTER 5

PETROLEUM RESIDUES ON THE SURFACE OF THE PACIFIC AND ARCTIC OCEANS

Introduction

The first quantitative report of petroleum residues in the marine environment was the result of a study commissioned by the American Petroleum Institute in 1958 (Dennis, 1959). A year-long measurement was made of oil coming ashore at three locations near Miami, Florida. Oil came ashore on 341 days out of 355, and it appeared that the oil was always present offshore, since east winds always brought it in.

The presence of pelagic petroleum residues was first reported by P.M. David in 1965, although he had casually observed them since 1954 in the Mediterranean Sea and in the Atlantic and Indian Oceans (Horn et al, 1970). In 1970, Horn et al published the first quantitative information on pelagic tar, giving the concentrations observed on a cruise in the Mediterranean and adjacent Atlantic.

It was, however, Thor Heyerdahl on his 'Ra' expeditions in 1969 and 1970 who dramatically focussed public attention on marine pollution, and particularly on the presence of tar in the Atlantic. Heyerdahl published a book, popular articles, two scientific papers (see Heyerdahl, 1971), and received widespread coverage of his voyages in the mass media. He persistently stressed the shocking, virtually continuous oil pollution he had observed on his two journeys. A considerable amount of scientific work followed on the heels of Heyerdahl's observations. A chronological summary of the literature dealing with the distribution of tar in the marine environment is presented in Table The concentrations reported in these papers are summarized in Table 13. 11. Also, the chemical composition of tar has attracted attention in an effort to determine its source. The papers dealing with chemical composition are briefly reviewed in Table 12.

A quick scan of the literature cited in the above tables shows the

heavy emphasis which the Western Atlantic and the Mediterranean have received. At the time this project was instigated, in 1972, there was no information available on petroleum pollution in the Pacific Ocean. This dearth of research presumably stemmed from the fact that tar pollution of recreational beaches was not a problem in the Pacific, so that the impetus for investigation was not great. At the time of writing (Dec., 1975) there are three papers dealing with oil pollution in the Pacific, all in Japanese. Two of these deal with the waters in the immediate vicinity of Japan, and the third presents a great deal of data on the Western Pacific (see Figure 18), but all of it is of a qualitative nature. No chemical analyses nor source determinations of tar in the Pacific have been made. The research presented in this chapter addresses these problems.

With respect to the Arctic Ocean, no information exists other than that reported here.

TABLE 11: Tar in the Marine Environment: A Literature Summary

•		
Author and Date	Location	Observations
Dennis, 1959	Beaches in Miami, Florida	Oil came ashore whenever there was an east wind on 341 days out of 355.
Dennis, 1959	U.S. Eastern seaboard beaches	Generally free of oil except for shorelines in the vicinity of major harbours.
Horn et al, 1970	Mediterranean and adjacent Atlantic	Tar was present in 75% of 734 neuston tows. Associated biota: bacterial film, isopod <u>Idotea</u> <u>metallica</u> , & <u>Lepas</u> barnacles. Hardness was measured. Age was estimated to be at least 2 months for some.
Oren, 1970	Israel and Levant Basin	Beach pollution was severe.
Heyerdahl, 1971	North Atlantic crossing (between 15 ⁰ and 30 ⁰ N.)	Visible tar pollution on 40 of first 43 days on Ra 11 expedition.
Morris, 1971	Northwestern Atlantic near Canada	Tar conc. in 20 tows. Estimated total tar in Atlantic at 27,000 tons.
Polekarpo et al, 1971	Mediterranean	Associated biota: blue-green algae, diatoms, isopods, (<u>I.metal-</u> <u>lica</u>), crabs, shrimp, & <u>Lepas</u> barnacles. Size classification of tar. Patchiness.
Anon, 1971	Mediterranean	Beach pollution severe, especially in Italy.
Wellman, 1973	North Atlantic crossing(40 ⁰ -60 ⁰ N)	Tar in each of 18 tows.
Morris and Butler, 1973	Northwestern Atlantic and Sargasso Sea	Time series near Bermuda and on Bermuda beaches. Standing stock in Atlantic estimated at 85,000 tons Degradation probably takes years.
Finnerty et al, 1973		Electron micrographs of bacteria growing on tar lumps.
Butler et al, 1973	North Atlantic, especially Sargasso Sea	Reviewed information on Atlantic. History of beach tar pollution in Bermuda.
· · · ·		

67.

(Table 11: Tar in the Marine Environment: A Literature Summary, continued)

		•
Author and Date	Location	Observations
Marumo & Kamada, 1973(in Japanese)	Pacific near Japan	First to report tar quantities in subsurface tows. Made series of tows at lm. depth intervals, to 8m. Most tar in top 4 m .Associ- ated biota: blue-green algae, stony corals, bryozoa, copepods, and Lepas barnacles.
Ohya et al, 1973 (in Japanese)	Pacific near Japan	389 neuston tows. Tar conc. cor- related with oceanographic condi- tions. Artificially weathered crude oil: after 200 days tar lumps had formed, and 70% had sunk.
Butler & Morris, 1974	Sargasso Sea	Patchiness of tar: despite efforts to cancel out effects of Langmuir circulation, tar varied up to 10x between successive tows.
Jeffrey et al, 1974	Gulf of Mexico and Caribbean	Tar from 104 neuston tows. Analyses of beach, pelagic and abyssal tar.
Dwivedi and Parulekar, 1974	Indian coastline	57 of 59 beaches investigated were polluted with tar; $conc.$ ranged up to 4.5 kg/m ² .
Saner & Curtis, 1974	Florida beaches	l yr. study of tar coming ashore.
McGowan et al, 1974	North Atlantic	214 neuston tows made at ocean weather stations B,C,D, and E. High variability, but concentra- tions were definitely higher to the south in the Sargasso Sea.
Sherman et al, 1974	Gulf Stream	379 tows.
Sleeter et al, 1974	N.E. Atlantic	14 tows. Observed occasional long windrows of tar.
Sleeter et al, 1974	West Sargasso Sea.	15 tows.
Wade & Quinn, 1975	Sargasso Sea	Suggested h.c. in the water column and surface microlayer were par- ticles of weathered tar sized 0.3 µm to 1.0 mm.
•		

(Table 11: Tar in the Marine Environment: A Literature Summary, continued)

Author and Date Location Observations Nasu et al, 1975 Western Pacific & Results of 3 yrs.(1971-73) of (in Japanese) neuston tows for tuna fisheries re-Indian Oceans search program. Not quantitative: tar given as not present, present, or abundant. Butler, 1975 General review of pelagic tar for Scientific American. Mediterranean 48 tows. Compared results with Horn Morris et al. et al(1970). Source: tanker 1975 traffic. N.E. Atlantic Used high speed catamaran neuston Ehrhardt & net. Analyzed 49 samples by G.C. Derenbach, No correlation of comp. with 1975 location. Microbial degradation minimal. Evaporation minimal, apparently limited by diffusion rate from tar ball nucleus. Sargasso Sea Observed tar specks in the Morris et al, water column. Estimated 4 times 1976 as much tar in the water column (0-100m) as at surface. Caribbean 61 tows made. Beaches contamin-Sleeter et al, ated on windward shores. High 1976 pelagic tar.

Canary current

Low levels of pelagic tar. Equatorial Atlantic

TABLE 12: Chemical Analyses of Petroleum Residues: A Literature Summary

Reference	<u>Observations</u>
Drunnock et al, 1968	Analyzed two English beach tar samples and one pelagic tar sample. Noted high wax content. Gas chromatograms had bimodal distribution of paraffins typical of crude oil sludges from tankers. Also determined S, viscosity, and specific gravity.
Adlard, 1972	Reviewed the analytical techniques which could be applied to analysing persistent hydrocarbon pollutants.
Butler et al, 1973	Published large number of gas chromotograms of tar from the Sargasso Sea.
Attaway, et al, 1973	Anomalously high iron conc., greater than 0.1%, in 67% of 35 tar samples from the western North Atlantic. Suggested this indicated an anthropogenic source.
Jeffrey et al, 1974	Determined S, asphaltenes, and did gas chromotography of beach, pelagic, and abyssal tar from the South of Mexico and the Caribbean.
Feldman and Cawlfield, 1974	Used neutron activation analysis to measure V, Mn, Na, and Co in tar for use in identifying the specific source oil.
McGowan et al, 1974	Water content of tar samples from the North Atlantic ranged from 0-51%, average 21%.
Butler & Harris, 1975	Published normal paraffin profiles of tar from North Atlantic, and concluded it was mainly residues of waxy, paraffinic crude oil.

Mommessin and Raia, 1975 Used infrared, S content, & gas chromatography to categorize tar from the western North Atlantic.

TABLE 13: Tar Concentrations Reported in the Literature

All reported concentrations have come from the North Atlantic. They are listed here by geographical location beginning roughly in the central northern area, proceeding clockwise right around the North Atlantic, and concluding with the centre, the Sargasso Sea.

<u>Location</u>	Concentration (mg/m ²)	No.of tows	<u>Reference</u>
Ocean Station			· .
B (56°N, 51°W)	0.00	50	McGowan et al, 1974
C (53 ^o N, 35 ^o W)	0.1	50	McGowan et al, 1974
D (44 ^o N, 41 ^o W)	1.2	50	McGowan et al, 1974
N.E. Atlantic	6.	14	Sleeter et al, 1974
Mediterranean	37.	41	Horn et al, 1970
<i>.</i> •	9.7	48	Morris et al, 1975
Canary Current	2.0	9	Sleeter et al, 1976
	3.9	?	Polekarpov etal,1971
Equatorial Atlantic	0.1	22	Sleeter et al, 1976
Caribbean	0.7	20	Jeffrey et al, 1974
	1.4	61	Sleeter et al, 1976
Gulf of Mexico	1.2	84	Jeffrey et al, 1974
N.Antilles & Bahamas	4.4	86	Sherman et al, 1974
N.CFlorida	0.8	80	Sherman et al, 1974
Va. to Cape Cod	0.5	157	Sherman et al, 1974
Gulf Stream	2.2	16	Butler et al, 1973
Sargasso Sea	9.4	34	Butler et al, 1973
· .	16.	15	Sleeter et al, 1974
Northern Sargasso Sea	a 2.6	50	Sherman et al, 1974

(35°N, 48°W)

Distribution of Petroleum Residues on the Surface of the Pacific

The investigation began with a trans-Pacific cruise from Tokyo to Victoria, B.C., Canada, in 1972. Surface tows were made at 37 stations along the cruise track using a floating net with dimensions of 80cm x 30.5cm mouth and a mesh size of 150 um. The net was rigged so that it would tow off to the side of the ship through water undisturbed by the ship's wake. The research ship, CSS Parizeau, left Tokyo on 10 October, 1972, proceeded east along 35°N to near the California coast, then turned north along 125°W to reach Victoria, B.C. on 2 November, 1972. The cruise track is shown in Figure 13.

FIGURE 18: Transpac-72. Cruise Track and the Surface Circulation Pattern in the North Pacific.



..... cruise track → warm surface currents ⇒ tanker route to Japan ------ cold currents

Tar was present in thirty of thirty-three tows along $35^{\circ}N$ as black or brownish black lumps up to 3cm in diameter. Its concentration was consistently higher in the Western Pacific with a maximum of 14 mg m⁻² wet weight, and an average of 3.8 mg m⁻². The concentration in the Eastern Pacific was an order of magnitude lower on the average. No tar was found on the final leg of the cruise up the coast of North America along 125°W.

The tar distribution is shown in Figure 14 and summarized in Table 14.

FIGURE 14: Distribution of Tar and Plastics Along 35°N in the Pacific Ocean



---- tar distribution ---- plastic distribution

Tows covered an area of 1,800 \pm 300 m².

TABLE 14: Summary of the Results of Neuston Net Tows Along 35°N Latitude

		· · · · · · · · · · · · · · · · · · ·				
Material found in neuston net tows	Northwest Pacific (West of 172.5 ⁰ W)	Northeast Pacific (East of 172.5 ⁰ W)				
tar	in all tows	in 15 of 18 tows				
plastics	in 9 of 15 tows	in 13 of 18 tows				
average wet weight conc.of tar(mg/m ²)	3.8	0.4				
average conc. of plastics(mg/m ²)	0.2	0.3				
average wet weight conc.of organisms (mg/m ²)	4.7	11.2				
(No contaminants of any sort were present in the final 4 tows on the line north up 125°W.)						

The tar aggregates were often colonized by a biological fouling community which included a bacterial film, blue-green algae, bryozoa, goose barnacles (<u>Lepas sp</u>), and the eggs of <u>Halobates</u>, the marine water strider. Crabs, mostly still in the megalops stage, and, more frequently, the isopod <u>Ideotea metallica</u> were present on the lumps.

The amount of plastic in the tows was also recorded, and is indicated in Figure 14 and Table 14. Plastic was present in 21 of 33 tows along $35^{\circ}N$ as small (1-3 mm diameter), round, colourless pellets weighing 20-50 mg each. In contrast to tar, the maximum concentration of plastic was found in the Eastern Pacific (3.5 mg m⁻²). The maximum number of pieces observed was 62, corresponding to 34,000 pieces km⁻². Smaller plastic pieces did not support a fouling community, although the larger ones had similar organisms to tar lumps.

Some paper, elastic bands, and wood were found in the first few tows off Japan (up to 500 miles from Tokyo). None were found in the remaining 9,000 kilometer journey.

The oceanographic data collected on the cruise provided some insight into the reasons for the tar distribution pattern shown in Figure 14. The surface layer (0-300m) temperatures are plotted in Figure 15, together with the locations of the tar peaks. The zones of apparent influx of colder subarctic water from the north are indicated by the letters. It appears that the tar is associated with the warmer subtropical water of the North Pacific current (the extension of the Kuroshio current). Where intrusions of colder, subarctic water is not polluted by tar, and that, when it mixes with the polluted water of the Kuroshio system, it causes a drop in tar concentrations.

More recent experience has shown that tar is very patchy, so that repeated tows in the same area may give tar concentrations that vary over an



The temperatures are in [°]C. The zones of influx of colder subarctic water (A, B, C, D) and the locations of the peak concentrations of tar are indicated.

order of magnitude. Therefore the detailed pattern of peaks in Figure 14 may have little meaning, and the correlation with the cold water intrusions in Figure 15 may be coincidental. However, further data, which is presented below, has indicated that the basic premise is correct: the tar is associated with the Kuroshio current system, and the subarctic water is essentially free of contamination.

The results from the Transpac cruise pointed out that there was significant contamination of the Pacific Ocean by petroleum, which had gone unnoticed amidst the proliferation of information on the Atlantic Ocean (Table 11). The decision was made to pursue the investigation to determine the extent of the tar contamination of the Pacific, its source and fate.

A second cruise was undertaken in mid-summer, 1973, to perform another transect of the Pacific. The cruise, which was a part of the research program of Dr. McGowan at Scripps Institution of Oceanography, was chosen because the cruise track passed through the centre of the Pacific subtropical

gyre.

In the North Atlantic, tar and <u>Sargassum</u> accumulate in the subtropical anticyclonic gyre (the Sargasso Sea) apparently because of the downwelling that occurs at its centre (Butler et al, 1973). In order to determine if the same concentrating effects occur in the corresponding oceanic feature of the Pacific, a second cruise, Tasaday-3, was undertaken in mid-summer, 1973. The Tasaday-3 cruise, which was a part of the research program of Dr. McGowan at Scripps Institution of Oceanography, crossed the Northwest Pacific along 28° N, (Honolulu to Tokyo) passing directly through the centre of the subtropical gyre in the North Pacific. The results of the cruise are summarized in Figure 16.





Other than the anomaly at $177^{\circ}E$, it is clear that the values are lower than were found on the more northerly transect (Figure 11). The average value obtained along $28^{\circ}N$ (west of $172.5^{\circ}W$) was 1.4 mg m⁻¹, which compared with the average of 3.8 mg m⁻² obtained along $35^{\circ}N$. As for the higher values at the westernmost stations in Figure 16, one is in the Kuroshio current, and the other is nearby, which indicates that it is the Kuroshio current which is most contaminated with tar. Thus the concentrating effect observed in the Sargasso Sea is not observed in the Pacific. This can be attributed to the fact that the gyre effect is much weaker in the larger Pacific Ocean than in the Atlantic. Presumably this is also the explanation for the lack of a characteristic <u>Sargassum</u> community in the Pacific.

To further clarify the extent of contamination of the Pacific by petroleum residues, permission was obtained to look through the extensive collection of neuston samples at the Scripps Institution of Oceanography (see acknowledgements). 1944 tows were examined, and any tar present was removed, weighed, and kept for analysis. Concentrations were obtained by dividing the wet weight of the tar by the area covered during the tow (obtained from the record of the ship's speed, the time towed, and the dimension of the net). For the Scripps samples, tows covered an average area of roughly 2,000 m², and ranged from 1,000 to 28,500 m². Mesh sizes varied from 150-505 μ m. The information obtained from all these samples has been condensed into Figure 17, which indicates the amount of tar by a letter symbol, and the number of tows made in that location by the sides of a box. Table 15 summarizes the information from the various cruises, and indicates the average concentrations from the various regions. The full record is on file at the Ocean Chemistry Division, Ocean and Aquatic Sciences, D.O.E.

On the basis of the information available, which includes cruises from 1967 to 1972, the South Pacific contains virtually no tar. When it was

FIGURE 17: Distribution of Tar in the Pacific Ocean



LEGEND: A letter indicates the concentration of tar in a given location. The sides of the box around the letter indicate the number of tows which have been averaged to give that concentration. The meaning of the symbols is as follows:

Number of Tows Concentration Т trace, one tow zero 0 trace, less than 0.1 mg/m^2 T trace, average of 2-4 tows \mathbf{T} medium, 0.1 to 1 mg/m^2 М T trace, average of 5-9 tows T heavy, 1 to 5 mg/m Н trace, average of 10-20 tows extra-heavy, greater than 5 mg/m^2 T Х trace, average of > 20 tows

The table summarizes information from cruises made during the period 1967-1974 (see Table 15 for summary of cruises).

TABLE 15: Summary of Cruise Information and Average Tar Concentrations By Area in the Pacific

NORTHEAST PACIFIC (North of Equator, east of 160°W)

L'			· · · · · · · · · · · · · · · · · · ·				·
Identification	<u>Year</u>	<u>0</u>	<u>T</u>	M	H	<u>x</u>	<u>Total Tows</u>
Alaminos 14	1967	39	-		_	-	39
Oceanographer	1967	· 17	·-	_	_	-	17
Jordan 20	1967	72	37.	1	_	-	110
Jordan 30	1967	86	20	-	-		106
Washington 45	1967	54	11	-	-	. –	65
Rockaway 47	1967	64	-	· -	1	-	65
Argo 11	1967	45	8	2	-	-	55
Jordan 12	1967	53	13	2	-	-	68
Rockaway 13	1967	71	4	1	-	- ·	76
Jordan 50	1967	95	14	-	-	- '	109
Rockaway 77	1967	66	1	-	-	-	67
Jordan 60	1968	82	16	-	_ ·	-	98
Washington 75	1968	55	- ·	-		-	55
Jordan 76	1968	58	1.	-	-		59
Townsend Cromwell	1970	5		-	-	-	5
Aries 1	1970	4	-	-	-	-	4
Jordan 57	1970	18	-	-	-	- .	18
Jordan 65	1971	8	÷ –	-	_ ·	-	8
Jordan 65A	1971	8	1	-	-	-	9
Jordan 60	1971	21	-	-	-		21
Transpac-72	1972	7	6	4	1 .	-	18
CALCOFI	1972	81	87	5	1	1	125
Tasaday l	1973	· -	5	. 4	1.	-	10
SOTW-13	1973		18	8	2	-	28
Weathership	1973-74	28	4	.1 .	- .	-	33
TOTALS		1037	196	28	6	1	1268
PERCENTAGES		81.8%	15.5%	2.2%	0.4%	0.1%	
AVERAGE	0.0	3 mg/m^2	· · ·				

TABLE 15: (Continued)

NORTHWEST PACIFIC

KUROSHIO AREA

 $(25^{\circ}N \text{ to } 40^{\circ}N, 140^{\circ}E \text{ to } 160^{\circ}W)$

Identification	Year	0	Т	M	Н	х	Total Tows
Transpac-72	1972	-	1	6	8	4	19
Tasaday 3	1973	-	10	19	4	3	36
TOTALS		-	11	25	12	7	55
PERCENTAGES		0%	20%	45%	22%	13%	
AVERAGE	2	.1 mg/m ²					
				· · · · · · · · · · · · · · · · · · ·		· · ·	
REMAINDER							
Identification	Year	0	T	M	Н	X	Total Tows
Antipode	1970	3	4	_	-		7
Hakuho Maru	1971	4	5	. 4	1	1	15
SOTW	1972	-	2	-	-	-	2
TOTALS		7	11	4	1	1	24
PERCENTAGES		29%	46%	17%	4%	4%	
AVERAGE		! 10.4 mg/m ²					
	+		+			T	

TABLE 15: (Continued)

SOUTH PACIFIC

Identification	Year	0	Т	М	Н	Х	Total Tows
Argo 11	1967	13	-	· ••	-	-	13
Jordan 12	1967	48	-	 ·		× 	48
Rockaway 13	<u>1</u> 967	_ 63	2	-	-	-	65
Jordan 30	1967	19	2		-	-	21
Washington 45	1967	24	1	-	-	-	2.5
Rockaway 47	1967	. 89	1	1	-	-	91
Alaminos 14	1967	57	2				59
Oceanographer	1967	32	· -	-	-	-	32
Jordan 20	1967	18	-	-	-	· <u>-</u> ·	18
Jordan 50	1967	10	1		-	-	11
Jordan 60	1968	13	1	- .	-	-	14
Jordan 76	1968	41	1	_	-	_	42
Washington 75	1968	69	1	-	_	· _ ·	70
Rockaway 77	1.968	87	3	-	-	-	90
Piquero	1969	14			_	_	14
r rquero	1,0,	·					· · · ·
Townsend Cromwell	1970	13	-	-	-	_	13
Antipode	1970	4	-	-	-	_	4
Aries l	1970	32	-		-		32
Aries 3	1971	22	2		· · -	-	24
Jordan 60	1971	3	-	. –	-	_	3
Jordan 65	1971	28	_	- `	-	-	28
SOTW-3cetc	1972	10	-	-	-		10
Cato 2	1972	16	2	_ ·	-	-	18
TOTALS		725	19 .	1	- ·	-	745
PERCENTAGE		97.3%	2.6%	0.1%	-	· –	
AVERAGE		0.0003 mg	g/m^2		۰ ۰		

found in the preserved samples, the tar was present in very minute quantities only (about 1 mg per sample) and may have been contamination from the research ship.

In the Northeast Pacific, obvious cases of polluted samples occur, mainly offshore between 25° and 40° N. The concentrations decline to the south (occasional traces of tar) and to the north (traces of tar in 5 of 33 tows at ocean weather station P: 50° N, 145° W).

The area of heavy contamination is in the Northwest Pacific, particularly between 25° and 40° N. All 55 tows in this area (made during 1972-73) contained tar, many containing more tar than biological material (maximum catch: 50.5 g tar in a 40 minute tow, or 16.3 mg m⁻²). There is insufficient data to clearly delineate the northern and southern limits of contamination, but the qualitative information reported by Nasu and Ueyanagi (1974) (see Figure 18) indicates that the frequency of tar in the Western Pacific decreases markedly below 20° N, and is hardly ever present in tows south of 5° N. The area of heavy contamination corresponds to the area directly affected by the Kuroshio current and its extension, the North Pacific current.

Summary of Distribution of Pacific Tar (from Table 15)

Area		Number of	Tows	· ·	Averag	<u>e Concentra</u>	tion
South Pacific		745	с. 1917 г. – С		· · · · · · · · · · · · · · · · · · ·	0.0003	n ta Tha a
Northeast Pacific	· · · .	1,268		· · ·	•	0.03	. ·
Northwest Pacific: Outside Kuroshio area (25 ⁰ -40°N, 140°E-160°M	1)	24				0.4	
Kuroshio area		55				2.1	
Total Tows		2,092	· · ·				





(From Nasu and Ueyanagi, 1974, p. 17 and 19)

Time Series Observations of Tar Concentrations at Ocean Weather Station 'P'

A regular oceanographic program is funded by the Canadian government on the weatherships manning ocean weather station 'P' (50°N, 145°W) in the Northeastern Pacific. Beginning in 1973, neuston tows were made a part of the weathership program in order to investigate surface pollution in the waters off the west coast of Canada, and to establish a baseline before tankers begin plying the route from Alaska down the coast. Since 1973 tows have been conducted on a recurring (but not regular) basis on the line out to the weather station, and on station (see Figure 19 for locations).

Because of the large size of the weatherships, and the very high distance from the water at which one is obliged to work, the conventional floating neuston net is not very handy. Another net was used based on the design of Sameoto and Jaroszynski (1969). This net rides up on adjustable fins, angles away from the ship automatically, and can be towed somewhat faster than the conventional floating neuston nets. Six of these nets were built out of aluminum and used for the weathership program.

From the beginning of 1973 to September, 1975, 113 tows were performed. Of these, 31 contained tar, usually in minute amounts, and 5 contained plastic. The average concentration of tar was 0.04 mg/m^2 , with a range from 0 to 1.9 mg/m^2 . The results are summarized in Table 16. There is no evidence that any particular trend is occurring with time.

Further information on baseline levels of tar in the waters off the British Columbia coast was obtained from the Superintendent of the Pacific Rim National Park on the west coast of Vancouver Island (49°00'N, 125°45'W). The park has about 20 miles of sand beaches directly exposed to the open Pacific. In 1971 the Ocean Chemistry Division, Department of Environment, visited Long Beach at the park to investigate very large tar balls up to 40 cm in diameter which had appeared on the beach. In October, 1973, a letter was

Cruise	Dates	No.Tows	# Tows c Tar	Ave. Tar	∦ Tows c Plastic
	1973	· · · ·			
73-001	JanFeb.	6	3	.03	1
73-003	MarApr.	9	0	0	0
73-004	May-June	7	0	0	0
73-006	AugSept.	6	0	• 0	· 0
73-007	Nov.	1	0	0	0
73-009	DecJan.	6	2	0.2	0
. .	1974			· . · ·	· · ·
74-002	FebMar.	17	11	.09	1
74-005	May-June	7	2	.04	0
74-007	AugSept.	6	3	.01	1
74-008	Nov.	3	1	.01	0
	1975				·
75-003	AprMay	10	2	.001	1
75-004	May-June	18	7	.007	1
75-005	July	13	0	0	0
75-007	Sept.	4	0	0	0
	TOTALS	113	31		5
Summary of To	ows by Quanti	ty:	. *		
Quantity: (mg/m ²)	Zero	Trace (<.1)	Medium (.1-1)	Heavy (1-5)	Extra (>5)
No. of tows:	82	26	3	2	0
Average Tow	Area:	800 m^2	/m ²	• •	
Range:		0 to 1	,	11.7	
nauge.		0 10 1.	a mg/m ber re	w.	

TABLE 16: Summary of Weathership Time Series of Neuston Tows

written to the Superintendent of the park asking if any further such incidences had occurred, and requesting that a log of oil and tar contamination of the beach be maintained. The Superintendent replied that he was not aware of any problem of contamination, but that a log would be maintained. By June, 1974, only two incidents of oil pollution had been reported, and no tar. A further letter to the Superintendent in July, 1975, failed to elicit a response. The tentative conclusion which can be reached from this correspondence, and by casual examination of the beach by the author, is that noticeable tar contamination is not occurring on a regular basis. Sporadic or low-level tar pollution may be occurring.

The levels of tar and plastic contamination will continue to be monitored as tanker traffic begins to move down the coast from Alaska to determine if changes occur.



FIGURE 19:

Tar Distribution in Local Waters

The inshore waters of British Columbia were not travelled by crude oil tanker traffic in 1972. However, there is heavy urbanization and industrialization in the Strait of Georgia, three refineries in Burrard Inlet, and a great deal of commercial and pleasure boat traffic. In addition, large quantities of refined products are shipped by barge and small tankers. The lack of crude oil tanker traffic, the presence of many other possible sources of petroleum contamination, and the impending tanker route from Alaska through these waters, made it worthwhile to investigate the local waters for tar contamination. Neuston tows were made in the Straits of Juan de Fuca, the Strait of Georgia, and in Burrard Inlet directly past the refinery operations, during a three day cruise of the research vessel C.S.S. Vector, 28-30 November, 1972.0f 36 tows, 32 contained no tar, and the remaining four had minute traces too small to qualify. The locations of the tows are indicated in Figure 20.

The absence of tar in the neuston tows left open the possibility that tar was being quickly deposited on the extensive shorelines in this enclosed area, leaving the surface waters virtually uncontaminated. A study was therefore commissioned by the Ocean Chemistry Division, Department of Environment, to We Healdath Consultants to investigate the local beaches. Nine beaches on Vancouver Island were checked once by a transect down the beach, and twice by walking the beach, during June and July of 1973. The location of these beaches is indicated in Figure 20. No tar was found on the surveyed beaches, although incidental occurences of oil pollution and very occasional tar pollution were observed by the contractor in other locations. Specifically, tar was noted on one occasion adhering to logs and on two occasions adhering to rocks in the Gulf Islands. The very low incidence of tar on the shorelines, and the lack of tar in the surface waters indicates that virtually no tar pollution of the inshore waters is occurring.

The significance of this finding in relation to the identification of the source of the tar found in the open Pacific will be discussed in a later section.

FIGURE 20: Locations of Neuston Tows and Beach Surveys in Local British Columbia Waters



Tar and Plastics in the Beaufort Sea

During the summer of 1974 and 1975 the Ocean Chemistry Division made two cruises to the Beaufort Sea in the Arctic Ocean to perform environmental baseline studies. As a part of this program, neuston tows were made to investigate surface pollution: in 1974, four one hour tows were made; in 1975, 17 tows were made. The locations of the tows are shown in Figure 21.

No tar or plastics were found in the 1974 investigation. In 1975, a piece of stryafoam was found in one tow, and very small black pieces 0.1 to 2mm in diameter occurred in 11 of the 17 tows. The number of particles varied from about ten up to several hundred per sample. These black particles consisted of seeds, ash, dark terrestial detritus such as fragments of bark, flying insects caught in tows, and occasionally what appeared to be tar specks. However, the tar-like material would not dissolve in carbon disulfide, and so was probably terrestial detritus from the Mackenzie River run-off, which is a dominant oceanographic feature of the Beaufort Sea.

Beaches in the Beaufort Sea were also surveyed for tar and plastic pollutants in 1974 under a contract from the Department of Environment (see acknowledgements). 26.4 km of beach were surveyed in the locations indicated in Figure 21. No tar contamination was found, but plastics were a common contaminant. Ironically, most of the plastic was related to oil exploration, such as surveying flagging and plastic containers used for explosives in marine seismic work (Wong et al, 1974). (It should be noted that many of the Arctic beaches are composed of coarse-grained material, so it is impossible to see small particles of tar.) In conclusion, the Beaufort Sea is more severely contaminated with plastic than with tar. The plastic is found mainly on the beach, rather than in neuston tows and so must be rapidly blown ashore. Tar may be present as very minute particles in surface tows, but the concentration is definitely less than 0.001 mg/m^2 and may be zero. Tar has not been observed on the beaches.





Unnumbered dots indicate tows made during the summer of 1974. Numbered tows tows were made in 1975. Cross-hatching indicates beaches surveyed during 1974.

Variability of Tar Concentrations

Spatial Variations:

The variation that is obtained in tar concentrations when replicate neuston tows are made is very large. Table 17 shows the results of replicate tows made on the Tasaday-3 cruise. The concentrations vary over as much as an order of magnitude, a result which has been observed in other locations (Butler and Morris, 1974). These variations are not random in nature. This is demonstrated by the data from the Tasaday-3 cruise which is plotted as a histogram in Figure 22a. If we assume that the Western Pacific along 28° N is randomly contaminated with tar, then the frequency distribution of concentrations should follow a Poisson distribution curve. It is clear from Figure 22a that the Poisson distribution and the observed distribution differ markedly, particularly in the first frequency class, and in fact the goodness of fit is unacceptable ($p(\chi^2) \ll .005$). The discrepancy in the first frequency class indicates that the tar concentrations are clumped rather than being randomly distributed (Archibald, 1948). The distribution may follow Neymann's contagious distribution. more closely.

Neymann's distribution assumes that if one individual (a tar lump in this case) is present this increases the probability of other individuals being present (Neymann, 1939). Neymann was dealing with larvae hatching from clumps of eggs and gradually spreading out from the location of the eggs. He assumed that the egg clumps were randomly distributed, and that the number of eggs per clump was a random variable. The analogy is that the egg clumps are patches of tar lumps left behind by tankers cleaning their tanks (see section on sources of tar). The surface turbulence then distributes the tar in a manner similar to the movements of larvae away from egg clumps. Unfortunately there is insufficient data to ascertain the two parameters required to calculate the Neymann distribution: the mean number of patches per unit area; and the mean concentration per patch.

TABLE 17: Variability of Tar Concentrations in Replicate Tows

			<u> </u>
Location	Area of Tow (m ²)	Tar Concentration (mg/m ²)	Variation Factor $\left(\frac{\text{highest conc.}}{1 \text{ owest conc.}}\right)$
			,
28°N, 160°E	4800 6800	0.81	
	3100	0.26	
	8100	0.22	
	5600	0.12	· ·
	3600	0.18	5.2
4	3600	0.01	· ·
	4000	0.38	· · · ·
· · · ·	6700	0.49	
	5800	0.48	
	3400	0.73	
		· · · · · · · · · · · · · · · · · · ·	
28 [°] N, 170 [°] W	1900 3300	0.01 0.01	1.0
	·	· · · · · · · · · · · · · · · · · · ·	· · · · · · · · · · · · · · · · · · ·
280N 1750W	1600	0.26	
20 N, 175 W	2300	0.48	1.8
	2300	0.40	
280N 1700E	1600	0.07	
20 N, 170 E	2300	0.10	1.4
	2.300	0.10	
			······································
00 ⁰ 1/(⁰	2600	0.17	
28 N, 140 E	3600	0.17	2.4
	3700	0.41	
0 . 0			
30 [~] N, 143 [~] E	3100	16.3	12.5
	3600	1.3	
34 [°] N, 140 [°] E	1900	5.6	43
	2200	1.3	4.5

(Data are from the Tasaday-3 cruise.)

FIGURE 22: Histograms of Tar Concentrations from the Western Pacific along 28°N



a) Histogram of Tar Concentrations and the Poisson Distribution





LOG TAR CONCENTRATION

Langmuir circulation may also affect the distribution and patchiness of tar. It will tend to regroup tar into windrows spaced from 10 to 50 m apart. Butler and Morris (1974) eliminated this effect by making tows in a circle of about 1 km diameter, but tar concentrations in replicate tows still varied over an order of magnitude. This indicates that Langmuir circulation is not the prime factor influencing the patchiness of tar. Polekarpov et al (1971), working in the Northeast Atlantic and using a statistical method which is not clearly described in the translation of their paper, estimated that tar was distributed in patches of about 200 to 3000 m^2 area. The combined evidence suggests that Neymann's model of dispersal from random point sources may be appropriate.

Those who have considered the distribution of tar in the literature have concluded that the distribution is close to log normal (Morris, 1971; Polekarpov, 1971; Morris et al, 1975). This route is simpler mathematically than attempting to deal with Neymann's distribution, but reveals less of the nature of the processes occurring. It is useful primarily for establishing the confidence limits of mean concentrations, and for determining if different oceanic areas have statistically different concentrations of tar. For example, Figure 22b displays the data from 22a as frequency classes of the log of tar concentration. The distribution is approximately log normal, and has a geometric mean of 0.25 mg/m² with 66% confidence limits of .05 to 1.15 mg/m². The arithmetic mean is 1.2 mg/m^2 . Further north in the Western Pacific along $35^{\circ}N$ (Transpac-72 cruise), the arithmetic mean concentration of tar is 4.6 mg/m², and the geometric mean is 2.9 mg/m^2 with 66% confidence limits of 1.0 to 8.5 mg/m². Thus the mean concentration is significantly higher (66% confidence level) along $35^{\circ}N$ than along $28^{\circ}N$.

The geometric mean provides a measure of central tendancy. Its uncertainty can be decreased by increasing either the length or the number of neuston tows. The arithmetic mean is not a statistic of a log normal distribution and 60
confidence limits cannot be calculated directly from the variance. Nevertheless the arithmetic mean is the appropriate statistic for estimates of absolute abundance, and so it is used throughout this chapter.

Temporal Variations:

The variation of tar concentrations with time at the same location has been investigated by Butler and Morris (1974) using time series data from station S (32⁰10'N, 64⁰30'W) in the Sargasso Sea. Spectral analysis indicated a cycle of 10 weeks duration which they attributed to an unknown feature of ocean circulation. The time series data from station P presented in a previous section is too irregular for application of spectral analysis. No cycle of any significance is apparent from a perusal of the data.

Size Distribution of Pelagic Tar Particles

Tar particles ranged in size from a few tenths of a millimeter in diameter up to five centimeters (34 g). The spectrum was presumably curtailed on the small end by the mesh of the neuston nets, which varied between 150 and 505 um depending on the cruise. The tar obtained on the Transpac-72 cruise was size classed, and the following distribution was found (150 um mesh net):

Largest Dimension (mm)	No. of Particles
<1	237
1-5	442
5-10	345
>10	106

Most particles were in the 1-5 mm range, and most of the mass in the 5-10 mm range. The size distribution was apparently consistent across the Pacific with no significant tendency for smaller particles to occur either in the east or the west.

Polekarpov et al (1971), working in the central Atlantic, found a similar size distribution of particles (most particles in 4-8 mm size range), although larger pieces were more common in that location than in the Pacific. They explained the size distribution by postulating that tiny particles of tar 'snowball' to form larger pieces until a dynamic equilibrium is reached (in the 4-8 mm range) where the disruptive forces of wave action equal the cohesive forces of the tar pieces. This explanation is not very satisfactory because tar does not conglomerate in the laboratory purely by colliding. Morris et al (1976) found tiny particles of tar in the water column, and theorized that tar lumps eventually disintegrate under the weathering process to produce very fine particles. If such a process were occurring in the Pacific, small particles would be expected to be more common in the eastern regions remote from the main source (see section on sources), and in the Western Pacific near the source tar pieces should be fresher and larger. No such pattern of size distribution is evident in the data.

The theory presented here is that tar neither disintegrates nor snowballs, but is produced at the source in roughly the same size distribution as it is found in the ocean, and is removed by sinking in a manner which is not size selective (see section on physical fate of tar).

Chemical Analysis of Tar

Determination of Water Content:

Nine tar samples from the Transpac-72 cruise were dried by placing each tar sample in an evacuated chamber together with molecular sieves for several days. The molecular sieves trapped water vapour, but not volatile hydrocarbons because of size exclusion. In this manner it was possible to dry the tar without removing any volatile hydrocarbons.

Analysis by Gas Chromatography:

The tar samples (0.2-0.5g) were dissolved by vigorous shaking in 5ml of carbon disulfide, centrifuged, and stored in glass vials with teflon septums in a refrigerator.

The samples underwent two different gas chromatographic analyses. 84 samples were run on a Dexsil column. Dexsil 300 is a non-polar, hightemperature packing which can be programmed up to 400°C with very little bleed. This gave a 'full' chromatogram of the oil on a stable baseline.

Secondly, some of the samples were run on a polar FFAP column to separate isoprenoid peaks (pristane and phytane) from the corresponding paraffin peaks (C-17 and C-18). FFAP is not very temperature-stable, so that the chromatograph could only be programmed up to 250°C, giving a 'partial' chromatogram.

The detailed instrumental parameters used in the analyses are given in Table 18.

TABLE 18: Instrumental Parameters for Gas Chromatographic Analyses

Full (high-temperature) chromatograms:

A Varian Aerograph 1400 gas chromatograph was used. The working parameters were as follows:

Sample size: 5 to 40 ul Carrier gas: N_2 Column: length 10' by 1/8" diameter 3% Dexsil 300 on 100/120 mesh Chromosorb W (acid-washed) ml/min: Carrier 20 H₂ 50 Air 350 Inj. port: 300°C Detector: 400°CColumn Conditions: Programmed Initial temp: 70°C, for two minutes Final temp: 400°C, hold Program rate: 8°/min Chart speed: 0.5 IPM Detector: FID Sensitivity: variable within 10^{-10} range

Chromatograms for isoprenoid/paraffin ratios:

The same parameters were used except for the column and the temperature programming:

```
Column: <u>length 10' x 1/8" diameter</u>
12.5% FFAP on 80/100 mesh Chromosorb G (acid-washed, DMCS treated)
Column Conditions: <u>programmed</u>
Initial temp: <u>100<sup>o</sup>C for 2 minutes</u>
Final temp: <u>250<sup>o</sup>C</u>
```

Analysis by Flame Atomic Absorption Spectophotometry:

104 tar samples were analysed for their iron and nickel content using flame atomic absorption spectrophotometry. 0.2 to 0.5g of tar were digested in a mixture of 75% HNO_3 and 25% $HC1O_4$ for approximately 2 hrs. at $150^{\circ}C$ using teflon-lined digestion bombs. The dissolved metals were then made up to 50 ml in 4N HNO_3 , and the solution was analysed for Fe and Ni on a Jarrell-Ash model 810 atomic absorption spectrophotometer.

Results of Chemical Analysis

Water Content:

For the nine tar samples dried by the use of molecular sieves, water was found to represent an average of 22% of the weight of the tar, and varied from 13% to 29%.

Gas Chromatograms:

The 84 full chromatograms are presented in Figure 23. The most important parameters from these chromatograms are summarized in Table 19.

The partial chromatograms for isoprenoid/paraffin ratios are presented in the discussion.

Iron and Nickel Content:

The results of the analysis by atomic absorption spectrophotometry are listed in Table 20.

FIGURE 23: Chromatograms of Pelagic Tar

Chromatograms of 84 pelagic tar samples are presented on the following pages. They are organized by cruise, and within the cruise, in chronological order by the date on which the neuston tow was made. The chromatograms are numbered for reference purposes, and next to the number is a line of information about the sample. The information is listed as follows: cruise; tow identification; location of tow; date of tow; method of storage of sample; date of analysis; chromatogram run number. Below this line of information is a description of the sample if one was noted when the sample was prepared. The dashed lines indicate the baseline.

The instrumental parameters used to obtain the chromatograms are given in Table 18. The chromatograms are summarized in Table 19.







10. Tranpac-72; Tow 9; 35N, 165E; 15/10/72; frozen; 11/7/75; 60. (outside section of a large brown ball)



11. Transpac-72; Tow 10; 35N, 170E; 16/10/72; frozen; 7/2/74.
 (first sample)



12. Transpac-72; Tow 10; 35N, 170E; 16/10/72; frozen; 20/2/74. (second sample)





13. Transpac-72; Tow 10; 35N, 170E; 16/10/72; frozen; 10/7/75; 56. (outside section of large black lump, no growth except small barnacles)





15. Transpac-72; Tow 12; 35N, 180; 18/10/72; frozen; 1/7/75; 64. (one black lump)





16. Transpac-72; Tow 13; 35N, 178W; 18/10/72; frozen; 6/3/74. (first sample, ten lumps with little growth)

17. Transpac-72; Tow 13; 35N, 178W; 18/10/72; frozen; 9/4/74. (second sample, numerous tiny lumps)



18. Transpac-72; Tow 13; 35N, 178W; 18/10/72; frozen; 10/7/75; 57. (third sample, end section of large brown lump)







23. TSDY 3; Tow 1; 28N, 163W; 22/7/73; frozen; 16/8/75; 161.



29. TSDY 3; Tow 10; 28N, 178E; 28/7/73; frozen; 27/2/74. (five lumps, no growth)



30. TSDY 3; Tow 11; 28N, 175E; 28/7/73; frozen; 21/8/75; 202. (two lumps, no growth)



31. TSDY 3; Tow 12; 28N, 175E; 28/7/73; frozen; 27/2/74. (1/3 of largest lump, bacterial covering)







113 -







47. TSDY 3; Tow 36; 34N, 140E; 6/8/73; frozen; 27/3/74. (one lump, fresh)



48. TSDY 3; Tow 37; 34N, 140E; 6/8/73; frozen; 10/7/75; 57.







50. Weathership 73-009; Stn 4; 8/12/73; frozen; 6/3/74. (very fresh oil)











58. Weathership 74-007; Stn 4; 17/9/74; frozen; 13/8/75; 151.

59. Weathership; Bowie Seamount; 53N, 136W; 19/11/74; frozen; 13/8/75; 154.









TSDY 1; A5 63; 28N, 155W; 26/6/73; formalin; 23/8/75; 219. 65.







77. SOTW 13; Stn 22, tow 106(?); 32N, 124W; 19/2/73; form.; 23/8/75; 229. (three pieces with small amount encrusting)



78. SOTW 13; Stn 24, tow 106; 32N, 124W; 19/2/73; form.; 23/8/75; 226. (several small pieces, no growth)







CALCOFI 7210; 30-80; 42N, 129W; ?/10/72; formalin; 11/7/75; 65. 82.
TABLE 19: Summary of Chromatograms of Pelagic Tar

This table summarizes key parameters of the chromatograms presented in Figure 23. The information is listed in mine columns which follow this format:

Column 1: #. Gives the number of the chromatogram in Figure23 that is being summarized. Brackets indicate samples from the same tow, and asterisks indicate samples from the same tar lump.

Column 2: 'Description'. Summarizes the description of the sample which was noted at the time of sample preparation. The following terms are used:

fresh: no growth or bacterial covering, soft, and sticky

black: no growth or bacterial covering, but hard

brown: covered with a thick bacterial layer

no grouth. May or may not have bacterial covering, but not encrusted or otherwise overgrown

p. encr.: partially encrusted with bryozoa

encr.: completely encrusted with bryozoa

ins.: inside of tar lump

outs.: outside scraping of a tar lump

frag.: fragment taken indiscriminately from a larger mass

half; one; two; etc.: the number of lumps used to make up the sample

Column 3: C-17/C-18. The height of the C-17 peak divided by the height of the C-18 peak. A ratio substantially less than one is an indication of evaporation.

Column 4: C-18/C-19. A large ratio of these peak heights (above 2.0) indicates that biodegradation is occurring.

Column 5: C first. The first clearly identifiable peak in the chromatogram.

Column 6: C max. The highest paraffin peak measuring from the envelope up.

Column 7: C end. The last clearly identifiable paraffin peak.

Column 8: 'Location'. The position of the neuston tow from which the sample was obtained. A bracket indicates samples are from the same tow.

Column 9: 'Comment'. Used to indicate samples that may be from natural seeps, analysis dates of samples from the same lump, and if the sample sinks in fresh water.

			•	• '	•			
#	Description	<u>C-17</u> C-18	<u>C-18</u> C-19	$^{\rm C}_{\rm first}$	C _{max}	C _{end}	Location (35°N)	Comment
Trar	nspac-72			. ·				
l.	several, fresh	1.18	2.5	15	38	46	140° E	
2.	ins., p. encr.	•74	∞	17	38	47	141° E	
3.	ins., p. encr.	•57	8	17	37	43	142°E	
4.	half, fresh	1.04	1 . 6	13	36	48	143°E	
5.	one	1.06	1.5	16	29	50	145°E	
6.	one	1.67	4.	17	29	50	150° E	
7.	fragment	1.08	2.2	17	33	51	155°E	
8.	one	•86	-7.	17	44	53	160°E	
9.	· ·	•45	1.6	17	38	47 }	ו גנ ⁰ ד	
10.	outside	1.13	1.3	15	17	44 }	10 J	
11.		1.50	1.3	16	27	47)	· .	
12.		1.39	1.1	14	17	35	170°E	seep?
13.	outs., black	1.26	1.2	15	37	48)	· ·	
14.	twelve, encr.	1.29	6.	17	17	51	175°E	
15.	one, black	1.15	•96	14	27	41	180°	
16.	ten, p. encr.	1.30	1.1	14	27	41		
17.	numerous	1.21	1.1	14	17	36	178°W	seep?
18.	end, brown	1.0	6.	17	42	53)		
19.	one, encr.	•86	5.8	17	18	47	175°W	
20.	several, encr.	1.31	1.1	15	27	51	148°W	
21.	one	1.11	4.3	13	37	47	142°W	
22.	two, p. encr.	•75	1.0	15	33	49	138 [°] W	

#	Description	<u>C-17</u> C-18	<u>C-18</u> C-19	C _{first}	C _{max}	°end	Location (28°N)	Comment
Tasa	day-3			• •			• .	
23.		1.13	1.0	15	27	42	163°W	
24.	· ·	1.33	1.1	16	27	38	165°W	
25.		1.30	1.1	16	27	38	168°W	
*26.	outside	1.32	1.1	12	27	49)		an. 2/74
*27•	outside	1.29	1.1	12	27	45	ם <i>ממ</i> ידי	an. 8/75
* 28•	inside	1.27	1.1	12	27	45 /	• 178 Г	an. 8/75
29.	five, no gr.	1.33	1.0	12	27	48)		an. 2/74
30.	two, no gr.	1.33	2.0	17	27	35	175 [°] E	
31.	1/3, brown	1.32	1.2	15	32	50 }	ז <i>יקנ⁰</i> ד	•
32.	· .	•83	10.	17	44	50	т() п	
33•	four, p. encr.	1.0	1.6	17	27	48	172°E	
34•	two, fresh	•89	2.3	17	34	50	165°E	• .
35.	one	•95	1.3	15	34	48	160°E	
36.	several, fresh	1.05	1.3	15	37	49	11	
37.	one, fresh	•71	2.6	17	37	49	11	
38.	fragment	•98	1 . 4	15	42	49	11	
39•		•95	2.3	16	37	45	**	
40.	two, no gr.	in.	in.	35	39	49	155°E	
41.		1.62	\otimes	17	36	44	148°E	
42.	frag., brown	•64	\sim	. 17	36	46	146°E	
43.	two	1.42	1.2	13	17	35)		seep?
.44•	•	1.06	1.0	15	27	47 }	31N , 143E	
45.		1.00	3.	17	37	49 ∫		
46.	three, fresh	1.07	1.1	16	27	40 ·	. 11 - 11	
47.	one, fresh	•91	0.9	17	27	43	34N,140E	
48.		1.59	1.4	17	27	36	11 11	

#	Description	<u>C-17</u> C-18	<u>C-18</u> C-19	C _{first}	C _{max}	C _{last}	Location	Comment
Weath	ership					· · ·	•	
49•	one	.65	2.7	17	26	32	Stn P	seep?
50.	v. fresh	1.37	1.5	15	17	31	Stn 4	seep?
51.		1.00	5.	17	32	38	Stn 12	· · ·
52.	five, no gr.	1.09	2.0	13	31	46 }	Stn 9	
53•		•75	3.2	17	32	48 J	, bon ,	
54.		1.46	2.4	16	17	38	Stn 11	
55•		•60	∞	18	37	46	Stn P	subsur.
56.	5	•43	∞	18	37	42	**	subsur.
57.		•50	\sim	17	37	45		subsur.
58.		1.14	1.8	14	35	46	Stn 4	· ·
59•		•96	1.5	16	18	34	53N,136W	seep?
	· .			:	: 			
Tasad	ay-l		н на селото се на селото село			• • • _		
60.	one, encr.	1.04	1.0	15	27	40.}	28N,155W	· ·
61.	one, black	1.17	1.2	15	36	44. S		
62.	fragment	1.26	1.1	14	27	45	¥\$ \$\$	
63.	• • •	1.11	1.4	14	17	27	11 11	seep?
64.		•57	09	17	38	48	98 98	
65.	one, fresh	1.17	1.2	15	40	50	28N.155W	
66.	one, p. encr.	1.32	1.1	15	27	45 ∫	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	
67.	one, p. encr.	1.22	1.1	15	31	45	11 11	
South	tow-13				· .			
68.	half, encr.	1.02	0.95	15	27	35		
69.	one, no gr.	•96	1.4	14	35	49	28N,155W	· .
70.	fragment	•91	1.6	15	38	48)		
71.	one	1.09	1.5	14	35	45	17 17	
72.		•90	1.4	15	36	48	88 8 1	
73•	one, no gr.	1.07	1.4	14	36	45	fi fi	
74•	one, no gr.	1.06	1.4	14	34	40	11 11	· ,
75•	ten	•95	1.0	16	27	45	91 19	
76.	many, brown	1.00	1.3	15	27	45	31N,137W	
77•	three, p. encr.	1.08	1.0	15	26	35	32N,124W	seep?
78.	some, no gr.	1.19	1.1	15	17.	47	18 18	seep?

#	Description	<u>C-17</u> C-18	<u>C-18</u> C-19	C _{first}	C _{max}	C _{end}	Location	Comment .
CALCO	FI 7210			:			· .	
79.	half, encr.	1.11	1.7	14	35	47)		sank
80.	one, brown	•95	1.5	15	38	45 }	39N,145W	
81.	one, black	•94	2.2	15	38	47)		
82.	one, black	1.08	· 1.3	13	35	48	42N,129W	
83.	two, p. encr.	1.25	1.2	13	36	52	?	
Rocka	way 47-507		·		•		•	
84.	one, brown	•42	0.8	17	22	35	7N,95W	seep?

135

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TABLE 20: Iron and Nickel Content of Tar Samples

Note:

When more than one sample has been analyzed from the same tow, the results are listed consecutively.

SAMPLE	IRON CONC. (ppt)	NICKEL CONC. (ppt)
Natural seep	0.2 0.1 0.30	0 0 0.09
Prudhoe Bay crude	0 0.01	.14 0
Aries 9 Queer	2.3	0
Aries 9 Quit	2.1	0
TSDY 1 A1 NR 16	1.4 3.1	0 0
TSDY 1 A2 #30	6.9	0
TSDY 1 A3	8.2	0
TSDY 1 A3 #43	12.0	0
TSDY 1 A4 53	1.3 0.5	0 0
TSDY 1 A5 #63	0.6 32.6	0 0
TSDY 1 A5 NR 28	1.3 6.0	0 0
TSDY 1 A6 NR 73	6.9	0
TSDY 1 A6 #75	0.8 0.3	0 0
TSDY 1 A3 NR 41	0.8 0.9	.17 0
CALCOFI 7210 39.145	1.1 0.5	0 0
CALCOFI 7210 31.145	13.1	0
CALCOFI 27.141	0.1 2.6	0 0
CALCOFI 35.133	1.5 0.4	0 0
CALCOFI 31.137	0.5 0.4	0 0
SOTW 13 Stn 22, 106	1.3	0
SOTW 13 #88	7.0	0
SOTW 13 #89	2.1	0
SOTW 13 Dipnet	0 0	0.06
SOTW 13 Stn 22. 105	0.7 1.1	0 0
SOTW 13. 7. #83	0.5	0
ARCO 11 11-044	0.8	0
NIGO IT IT-044		

TABLE 20: (Continued)

SAMPLE	IRON CONC. (ppt)	NICKEL CONC. (ppt)
FASADAY 3		
-Tow 2	1.2	0
-Tow 3	0.9	0
-Tow 5	12.6	0
-Tow 7	4.6	0.01
-Tow 10	7.1 0.6 6.3	0 0 0
-Tow 11	2.7	0.1
-Tow 12	3.5	0
-Tow 14	10.4	0.01
-Tow 15	13.5	0
-Tow 17	1.8 2.3	0 0
-Tow 18	0 0.5	0 0
-Tow 19	13.6 4.1	0 0
-Tow 20	9.4	0
-Tow 21	5.4	0.01
-Tow 22	8.6	0.02
-Tow 23	7.0 18.6	0 0
-Tow 24	5.6	0.01
-Tow 25	2.9	0.01
-Tow 26	8.0	0
-Tow 27	4.2	0
-Tow 28	4.0	0
-Tow 29	27.6	1.3
-Tow 30	5.7	0
-Tow 31	5.3 3.7	0 0
-Tow 32	5.8	0.01
Tow 33	13.0 13.5	0 0
-Tow 34	13.9	0
-Tow 35	0.2 2.4	0 0
-Tow 36	7.1	0
-Tow 37	1.4	0

TABLE 20: (Continued)

SAMPLE		IRON C	ONC. (p	pt)		NICKEL	CONC.	(ppt)
Transpac	1	15.8				0		
	3	49.4				0		• .
	4	3	7.5			n	0.3	
	5	.4	0.4	•		n	0	
	6	13	27	5		n	n	0
	7	37.9		•		0		
	8	9.8	1.7			n	0	
	9	4.9				0		
	10	4	2.2		· .	n	0	
	11	3.2				0		
	12	2	15.0		•	n	0	
	13	6	0			n.	0	
	14	11.5				0.03		
	16	5.7		• •		0		
	17	4.4				0		
	18	0.6				0		
	23	10	3.3			n	0	
	25	23.2				0		
	26	6	2.3			n		
ŀ							,	,

n = not determined

Discussion of Chemical Analyses

Water Content:

The water content of the nine tar samples is considerably less than the typical percentage of water in a fresh water-in-oil emulsion, which is about 80% (Berridge et al, 1968). However, the average value of 22% agrees well with the amount found by McGowan et al (1974) of 21% (range 0-51%) in tar samples from the Atlantic.

Gas Chromatograms:

Residue.

The tar would not completely dissolve in carbon disulfide. The residue in six samples averaged 15% of the weight of the tar, and ranged from 5 to 24%. Residues were obviously organic in nature, and were similar in appearance to the original tar. They seemed to be composed of high molecular weight asphaltic compounds.

Reproducibility of Chromatograms.

The reproducibility of chromatograms from day to day, with different operators, and with different Dexsil columns was excellent. Although the attenuation varied, the pattern of peaks was always clearly reproduced. An example is shown in Figure 24. A second and more impressive example is to be found in chromatograms 26 and 27 (Figure 23) of different samples from the same lump. The analyses were performed by different operators one and a half years apart on different Dexsil columns. The chromatograms are identical as nearly as the eye can see.

The general observation over fifty-odd duplicate runs was that the reproducibility was excellent over the carbon number range of about C-12 to C-40; below and above this range the relative peak heights sometimes changed. The

FIGURE 24: Reproducibility of Chromatograms

CALCOFI 7210; 39-145; 39N, 145W; 20/10/72; formalin; 25/8/75.

a) Run #241



Two chromatograms of the same sample run on the same day with the same instrument. Six other samples were analyzed between the two runs. Note the excellent reproducibility of the pattern and relative heights of the peaks. position of peaks eluting from the column near the very beginning of the program (before C-12) also was variable, apparently because of the instability of the thermal regime of the gas chromatograph in this region. However, this was not a problem with tar lumps, which seldom contained paraffins less than C-12 in carbon number.

Limitations of the Method.

It should be understood that the method has two distinct limitations. It is limited at high carbon numbers because of the upper limit to which the chromatograph can be programmed, and because the high molecular weight compounds have a limited solubility in the solvent, carbon disulphide. Secondly, the column provides only low resolution. All the aromatics, cyclo-paraffins, and heterocycles appear as a broad envelope onto which the paraffins are added. The resolution is not sufficient to distinguish the isoprenoids from the paraffins, so that pristane and phytane appear lumped in the same peaks with C-17 and C-18 respectively.

Despite these limitations the chromatograms do provide a great deal of information on the tar samples, particularly on their paraffin content.

Storage of Samples.

Tar samples were stored by refrigeration and in formalin. Both appeared to be entirely satisfactory. Chromatograms 26 and 27 (Figure 23) show that refrigerated tar does not change detectably over a year and a half of storage. Similarly there is no indication of any systematic change occurring in the samples stored in formalin. Contamination of samples by trace hydrocarbons in the formalin, although a potential problem in trace tissue analysis, does not affect the analysis of the tar because of the great excess of tar hydrocarbons. Characterization of Tar Chromatograms.

From the information revealed in the gas chromatograms five parameters have been chosen as being especially informative. These parameters have been listed in Table 19. They are: the C-17/C-18 ratio; $C_{\rm first}$, the carbon number of the first clearly identifiable peak; $C_{\rm max}$, the largest paraffin peak; and $C_{\rm end}$, the last clearly identifiable peak. A description of the sample and the location of the neuston tow are also listed.

Other authors have used other parameters to characterize chromatograms. For instance, Blumer, Erhardt, and Jones (1973) characterized repeated chromatograms of stranded crude oil with six ratios as well as the carbon numbers at which the envelope reached 10% and 50% of its maximum value. The parameters used here were chosen to reveal the weathering of the oil by biodegradation (C-18/C019), and by evaporation (C-17/C-18 and C_{first}), and to distinguish natural seeps from tanker residues (C_{max} and C_{end}). In general the envelope shape was not found to be useful in making these distinctions. The mean values of the five parameters for various subclasses of tar samples are listed in Table 21.

C-17/C-18: The average ratio for the 82 tar lump samples was 1.05 \pm .27, which compares with the average found by Martin et al (1963) for seventeen crude oils of 1.25. Although the difference is not statistically significant, the lower ratio in the tar samples may reflect the preferential loss of the lower boiling heptadecane and pristane by evaporation. Some support for this interpretation comes from the correlation between the C-17/C-18 ratio and specific subclasses of tar. The subclasses listed in Table 21 that consist of older tar have lower C-17/C-18 ratios, suggesting that the removal of the C-17 peak occurs with prolonged exposure. Specifically the ratio is lower for C_{first} = 17 than for C_{first} = 15, and for C_{max} = 36-38 than for C_{max} = 27. Similarly, tar which is extensively degraded by bacteria (C-18/C-19 = ∞) has a low ratio. TABLE 21: Average Composition of Subclasses of Pelagic Tar

	•						
Description of Subclass	No. of Samples	<u>C-17</u> C-18	<u>C-18</u> C-19	C _{first}	C _{max}	Cend	Location (long.)
Average of all tar	82	1.05 <u>+</u> .27	2.9	15.7 <u>+</u> 2.6	31 <u>+</u> 7	44 <u>+</u> 6	170°W <u>+</u> 32
C _{first} = 15	25	1.10 <u>+</u> .16	1.3	15	31 <u>+</u> 7	45 <u>+</u> 5	164°W <u>+</u> 29
C _{first} = 17	25	0•92 <u>+</u> •35	5.1	17	33 <u>+</u> 7	46 <u>+</u> 6	174 [°] E <u>+</u> 33
$C_{max} = 27$	21	1.18 <u>+</u> .17	1.2	15.2 <u>+</u> 1.4	27	43 <u>+</u> 5	177 [°] W <u>+</u> 25
C _{max} = 36-38	24	0•90 <u>+</u> •30	4.6	15.8 <u>+</u> 1.5	37.0	47 <u>+</u> 2	173 [°] E <u>+</u> 32
$\frac{C-18}{C-19} = \infty$	8	0.71 <u>+</u> .38	8	17.3 <u>+</u> .5	37.0 <u>+</u> .8	45 <u>+</u> 2	178 [°] E <u>+</u> 37
Natural seeps	10	1.08 <u>+</u> .33	1.3	15.0 <u>+</u> 1.3	19 <u>+</u> 4	35 <u>+</u> 5	142°₩ <u>+</u> 28
Weathership (without seeps)	8	0.87 <u>+</u> .36	5.6	16.3 <u>+</u> 1.8	32 <u>+</u> 7	44 <u>+</u> 4	140 [°] พ <u>+</u> 6
Western Pacific (west of 172°E)	29	1.06 <u>+</u> .31	3.3	16.6 <u>+</u> 3.8	32 <u>+</u> 7	39 <u>+</u> 9	153 [°] E <u>+</u> 11
fresh, black	14	1.07 <u>+</u> .17	1.6	15.1 <u>+</u> 1.3	33 <u>+</u> 6	45 <u>+</u> 5	178 [°] Е <u>+</u> 34
brown, p. encr. encr.	, 20	1.01 <u>+</u> .27	3.2	15.6 <u>+</u> 1.3	30 <u>+</u> 7	45 <u>+</u> 6	170°W <u>+</u> 34
small pieces (< 0.l g)	14	1.15 <u>+</u> .13	1.7	14•9 +1•4	27 <u>+</u> 6	45 <u>+</u> 5	
large pieces (>0.5 g)	15	1.02 <u>+</u> .23	3•4	15.2 <u>+</u> 1.6	34 <u>+</u> 7	47 <u>+</u> 4	

FIGURE 25 : Pristane and Phytane in Pelagic Tar

a) TSDY 3, Tow 10; 28N, 178E; 28/7/73; formalin; 1/8/75; 127.

(Compare with chromatograms 26, 27, and 28 in Figure 23)



b) TSDY 3, Tow 19; 28N, 160E; 1/8/73; formalin; 7/8/75; 131.

(Compare with chromatogram 36, Figure 23)



c) Weathership 74-002; 50N, 143W; 18/2/74; frozen; 8/8/75; 135.

(Compare with chromatogram 51, Figure 23)



C-18/C-19: This ratio (henceforth termed the biodegradation index) is a measure of the extent to which microbial action has degraded the tar sample. The C-18 peak reflects both the amount of octadecane and the amount of phytane, whereas the C-19 peak reflects only the amount of nonadecane. Since the paraffins are more easily degraded than the isoprenoids (see Chapter 2), the C-19 peak may be reduced to zero by microbial action, while for the C-18 peak only the octadecane is removed and the phytane remains. Thus a high value of the biodegradation index is an indication that microbial degradation is occurring. The partial chromatograms in Figure 25 illustrate this effect by separating the isoprenoids from the paraffins. Chromatogram (a) shows fresh tar in which the paraffins have not been degraded, and chromatogram (c) shows a tar sample which has undergone extensive microbial degradation leaving only the isoprenoids. The average value of the biodegradation index for seventeen crude oils was 1.5 (calculated from data in Martin et al, 1963)*, whereas for the tar samples the average value was 2.9. Of the 82 tar samples, 33% had values greater than 2, indicating that microbial degradation is an important factor in the degradation of tar at sea.

C_{first}: The frequency of occurrence of the carbon numbers of the first identifiable peaks are shown in Figure 26. The first peak varies from dodecane (C-12) to C-35. The two most common paraffins forming the first peak were pentadecane (C-15) and heptadecane (C-17). These two initial peaks distinguish two quite different subclasses of tar samples: C-15 indicates a 'younger', less degraded sample; C-17 an older, degraded sample.

C_{max}: The carbon numbers of the largest peaks are also shown in Figure 26. They vary from hexadecane (C-16) to C-45. Most commonly C-27 is the largest peak, particularly in tar samples with little microbial degradation while C-36 to C-38 occur as the largest peaks in chromatograms of extensively degraded

tar.

* see Appendix A.

 C_{end} : The carbon numbers of the last clearly indentifiable peaks are also shown in Figure 26. They range between C-27 and C-54, with an average of C-44. The upper limit is probably imposed by the analytical method as already discussed.



Metal Analyses of Tar

Of the 104 tar samples analysed for iron, 77% had concentrations of iron greater than 1 part per thousand in wet weight of tar. In contrast, crude oils have less than 0.1 ppt (International Petroleum Encyclopedia, 1974).

The concentration of Ni in 94 of the 104 samples was also determined to indicate if general metal enrichment was occurring in the tar by scavenging of metals from the sea water or by concentration of the metals in the original oil during the weathering process. In 90 of 94 samples the nickel was below the detection limit of 0.01 ppt, and in the other four samples the highest amount obtained was 0.17 ppt. Ni concentrations in crude oil are in the range of 1 to 100 ppm (International Petroleum Encyclopedia, 1974; Brunnock, 1968). These consistently low values for Ni indicate that general metal enrichment was not occurring.

	Fe Conce (wt. Fe/m		
	> 10 ppt	<u>1-10 ppt</u>	<1 pp1
No. of samples	21	59	24
% of samples	20%	57%	23%

TABLE 22: Summary of Fe Concentrations in Pelagic Tar

Source of Pelagic Tar

In Chapter 1 the sources of petroleum to the marine environment were reviewed. The three major sources from which tar residues could originate are tanker traffic, natural seepage, and land run-off.

Run-off from land sources is least likely to result in tar formation since there is no obvious mechanism by which formation of tar can occur from the dissolved or slick contamination characteristic of land sources. Local tows made in Vancouver harbour near a heavily industrialized area with three refineries contained no tar (Figure 20) and tows off the heavily populated Los Angeles area of California (Figure 17) also gave low values, evidencing that land sources do not lead to tar formation.

The remaining likely sources are tanker traffic and natural seepage. The major tanker lane in the Pacific is the massive Middle-East to Japan route (Figure 27 - 5,570 thousand barrels or 758,000 metric tons per day in 1972). The area of heavy tar contamination in the Pacific (shaded in Figure 17) can be explained by assuming tar wastes are discharged by tankers south of Japan, become entrained in the Kuroshio current (Figure 28) and create a plume of contamination which extends downstream across the Pacific. The decreasing quantities of tar found to the east can be attributed to the gradual dispersal, degradation, and eventual sinking of the tar.

The absence of tar from the South Pacific and the Arctic correspond with the absence of crude oil tanker traffic in these areas. Natural seepage, on the other hand, is of the same order of magnitude in the North and South Pacific (see Figure 4) and also occurs in the Arctic, so the tar distribution does not correlate with the areas of natural seepage.

The gas chromatographic analyses provide a second indication that tanker traffic and not natural seepage is responsible for the pelagic tar contamination in the Pacific. Of the 82 tar samples analysed, 72 contained long-chain, waxy



Numbers indicate the quantities of crude oil transported in thousands of barrels barrels per day (1 barrel = 0.137 metric tons). (Rearranged from International Petroleum Encyclopedia, 1973)







Continuous arrows indicate the tanker route to Japan. Solid lines indicate warm surface currents. Dashed lines indicate cold surface currents. paraffins (higher carbon number than C-25) in much greater abundance than they are normally found in crude oil. This high wax content is typical of tanker residues. The precipitate or sludge remaining in the tanks of crude oil carriers after unloading normally has an enriched wax content of 20-30% above that of the crude cargo (Holdsworth, 1970), the amount of wax coming out of solution depending on the wax content of the crude and the length and temperature conditions of the loaded voyage. Typically the residues amount to about 0.4% of the cargo carried (Holdsworth, 1970), and they are discharged overboard during the deballasting and tank-washing procedures on tankers that do not employ the load-on-top (LOT) technique. The waxy sludge has a great propensity to form a tight water-in-oil emulsion under the action of the washing jets and subsequent pumping, and so is ideal for the formation of pelagic tar lumps.

Figure 29 illustrates the evidence provided by the chromatograms that tanker residues are the major source of pelagic tar. The first chromatogram is of Prudhoe Bay crude oil. Like most other crudes, it has little paraffin content above C-25. The second chromatogram shows the same crude oil after it has been exposed for 25 hours. Note that the paraffins up to C-15 have evaporated, but above C-17 the spectrum is unchanged. The third chromatogram is of a sample that apparently came from a natural seep (the sample was dip-netted near Santa Barbara, an area of extensive natural seepage). The trace is very similar to that of evaporated crude oil, except that microbial degradation has removed most of the paraffins, leaving only the isoprenoids at C-17 and C-18. No long-chain paraffins are evident. The fourth chromatogram is of a typical tar lump, and shows an abundance of long-chain paraffins. The contrast at high carbon numbers with both the crude and the natural seep oil is very clear. Of the 82 tar samples analysed, 12% looked akin to chromatogram #3 and may have come from natural seeps, while 88% were comparable to chromatogram #4 and presumably originated from tanker residues. Thus the presence of long-chain, waxy paraffins



points to tanker sludge as the usual source of pelagic tar.

The metal analyses of 104 tar samples also indicate that tankers, and not natural seepage, are responsible for most of the pelagic tar. 77% of the samples contained greater than 1 part per thousand of iron. This represents an enrichment of at least one order of magnitude over the levels of iron in crude oil (20% of the samples showed at least two orders of magnitude enrichment). In contrast, the nickel concentrations were not detectably above the levels in crude oil, indicating that general metal enrichment was not occurring in the tar due to scavenging of metals from sea water or concentration of metals during the weathering process. The alternative is that the iron has an anthropogenic source. Specifically, it is likely that it originates from the pickup of rust particles from tankers during the tank-washing process when the sludge is peeled off with high-pressure water jets (Butterworthing).

Tar with low iron and wax contents may originate either from natural seeps or from spilt crude oil. The formation of tar from both these sources has been observed: around the Santa Barbara oil seeps tar is common on the beaches (eg. Coal Oil Point); and O'Sullivan (1971), among others, has observed the formation of tar lumps after a crude oil spill. It is not possible to distinguish between these two sources using the analytical techniques described here, and no attempt has been made to do so. In Tables 19 and 21, the oil industry has been given the benefit of the doubt, and tar with low wax content (12% of the samples) has been tentatively attributed to natural seeps.

In summary, the correlation of tanker traffic to tar presence in the Pacific, the presence of long-chain paraffins, and the high concentration of iron in many of the samples all indicate that pelagic tar contamination in the Pacific originates primarily from tanker traffic, and from tanker sludge in particular. The standing stock of tar in the Kuroshio current system is, very approximately, 25,000 metric tons, assuming 2.1 mg m⁻² average contamination

over the area bounded by 20°-40°N, 140°E-160°W. The residence time of the tar in this area, assuming a drift eastwards of 15 km/day (Dodimead et al, 1962), is about one year. Thus the yearly input to the area must be on the order of 25,000 metric tons. This amounts to only 0.01% of the annual volume of crude oil travelling the tanker route to Japan. That such a small percentage of the transported oil should reach the ocean is not unlikely: 0.4% of crude cargoes in non-LOT tankers and 0.02% in LOT tankers are estimated lost during deballasting and tank-washing (Anon, 1971b). However, given the vast quantities being transported and the persistence of the tarry fraction, even a very small percentage loss results in significant contamination of the surface waters.

Chemical Weathering of Pelagic Tar

Evaporation:

Evaporation removes the lower-molecular weight components from pelagic tar up to about pentadecane quite rapidly (probably over a period of several days for small particles, longer for larger masses) and reduces the amount of components up to the volatility of heptadecane (C-17). Figure 30 illustrates the effect of evaporation on a sample of crude oil exposed to the atmosphere in a fume hood at room temperature. The exposure increased C_{first} from less than nonane (C-9) to pentadecane (C-15), and reduced the C-17/C-18 ratio from 1.4 to 1.1, indicating that these parameters are indeed measures of the effect of evaporation (the biodegradation index remained unchanged at 1.5).

FIGURE 30: The Effect of Evaporation on the Composition of a Crude Oil

#1 Prudhoe Bay
crude oil

#2 Prudhoe Bay crude oil exposed for 25 hours



The chromatograms in Figure ²³ reveal the effect of evaporation on pelagic tar. The lightest paraffin compound in any tar sample was dodecane (C-12) which was found in a large lump and a smaller piece in the middle of the North Pacific $(28^{\circ}N, 178^{\circ}E)$. The most common first peaks in the chromatograms were C-15 and C-17. Apparently the components up to C-15 are removed quite quickly, since no biodegradation is evident in samples with $C_{first} = 15$ (average biodegradation index of 1.3). The loss of paraffins above C-15 does occur purely due to evaporation in some samples, but more commonly an initial peak of C-17 is associated with extensive microbial degradation. Clearly, the loss by evaporation of components above C-15 is slow, and the process is usually overtaken by microbial attack.

It is curious that small particles show no greater effect of evaporation than larger particles. In fact, the C-17/C-18 ratio indicates less evaporation, if anything, for small particles (see Table 21). Furthermore, the analyses of samples from inside and outside a large lump failed to show the expected gradient of lighter compounds. It was expected that more light compounds would be found in the centre of the lump than in the exterior, but no difference in the composition could be distinguished. (See chromatograms 26, 27, and 28 in Figure 23.)

Several observations made here contradict the model for evaporative weathering of pelagic tar proposed by Butler (1975). For the purpose of further discussion, the contradictions will be noted. Butler's model assumes that the evaporation rate is proportional to the equilibrium vapor pressure P of each compound and to the fraction of that compound remaining:

$$\frac{dx}{dt} = -kP(x/x_0)$$

where x is the original amount

x is amount remaining at time t k is an empirical rate coefficient that varies with a variety of factors, including the size of the tar lump.

Such a model, when applied to the small particles of pelagic tar, requires either that they be very fresh, or that they have recently broken off larger, older lumps. The small particles cannot all be fresh, so Butler is forced to assume that they have broken off larger crude oil masses with a median size of 1000 cm³. He concludes that the principal weathering processes are a combination of evaporative weathering and physical fragmentation to particles thousands of times smaller than the original oil mass.

Neither the extensive evaporative weathering nor the physical fragmentation is evident from the data collected here: evaporation appears to consistently remove paraffins up to C-15 over a period of time, but beyond this the effect is minimal, and is overshadowed by the effects of microbial degradation. Similarly, the size distribution of particles does not indicate that physical fragmentation is occurring as the tar gets older. Furthermore, small particles do not show the effect of greater evaporative weathering that is predicted, and the expected diffusion gradient in the large tar lump is missing. Since pelagic tar is almost completely submerged in water at sea, and since it has a very small surface area, it may be that the rates of evaporation are very much reduced, leaving microbial degradation as the prime mechanism for long-term weathering.

Dissolution:

The effect of dissolution has not been distinguished from that of evaporation since the two processes affect the same components of petroleum. Evaporation has been shown to be the more effective process for weathering surface slicks (Harrison et al, see Chapter 3), but this may not be the case for tar lumps. In the absence of any information to the contrary, it has been assumed that evaporation is predominant. Hence, in the previous section, the removal of the lightest components from pelagic tar has been attributed to evaporation rather than dissolution, whereas in fact some partitioning probably occurs.

Photo-oxidation:

As described in Chapter 3, photo-oxidation removes the isoprenoids from petroleum before the paraffins, resulting in the values for the C-18/C-19 ratio being decreased below the values found in crude oil. This effect is not evident in any of the tar samples analysed; instead, the ratio is often substantially increased by the effect of microbial degradation. Thus the chromatograms indicate that photo-oxidation does not play a significant role in the degradation of pelagic tar. This result is not surprising in view of the very limited surface area which is available for absorption of light, and the opaque nature of the tar, which prevents light from affecting anything but the surface layer of the particles.

Biodegradation:

The C-18/C-19 ratio from the chromatograms provides clear evidence that microbial degradation is important in the weathering of pelagic tar. The average value of the ratio for seventeen crude oils was 1.5 (based on data from Martin et al, 1963), whereas the average ratio for the pelagic tar samples was 2.9 (33% of the samples had indices above 2). The average value of the index at the weather-

ship, far from the probable source in the Western Pacific, is 5.6 indicating that by the time the tar reaches this portion of the Pacific, extensive degradation has occurred. Unfortunately, the index is not a clear function of the longtitude as one would expect if all the tar originated from the tanker route near Japan and was carried eastward by the prevailing currents. Figure 31 shows a plot of the index versus the longtitude at which the sample was obtained. Highly degraded tar is found in the western Pacific near the postulated source,

FIGURE 31: Biodegradation Index (C-18/C-19 ratio) as a Function of Longtitude



Dots indicate samples which appear to be natural seeps. Triangles indicate regular tar samples. Numbers indicate more than one sample from same location with same biodegradation index.

as well as in the eastern Pacific. This very weathered western tar may have originated in the Indian Ocean, or have travelled around the gyre in the western Pacific.

The most degraded tar, with an index of ∞ , has a remarkable consistency of composition (see Table 21). All eight samples were very similar despite coming from widely differing locations. Typically these samples have a C-17/C-18 ratio well below 1 (indicating the effect of prolonged evaporation); the first peak is 17; the maximum occurs at C-37, and the final peak is C-45.

Tar which visually appears older, being brown or encrusted, has a significantly higher degradation index than tar which is black and fresh-looking. Thus the visual appearance does correlate to some extent with the chemical weathering. Interestingly enough, small particles of tar are usually less degraded than larger pleces. Small pieces less than 0.1 g have an average index of 1.7, whereas pieces larger than 0.5 have an average index of 3.4. The reason for this phenomenon is not known.

Physical Weathering and Fate of Tar

Tar pollution of the Atlantic and Mediterranean has resulted in extensive contamination of beaches in some areas. It appears that the final resting place of much of the pelagic tar in those locations is in the sand on beaches. In the Pacific, however, tar pollution of beaches is not common. Thus it is not satisfactory to assume that the tar floats until it is washed ashore.

An experiment was conducted to determine the density of tar as a function of its apparent age and chemical composition. Tar samples were placed in beakers of fresh water to determine which lumps would sink. It was possible to observe definite classes of tar. Some was exceedingly bouyant, some was marginal, and 4% of the particles sank. Although not all of the bouyant lumps appeared fresh, all of the samples which sank were very weathered. There was no size selection in the sunken tar, some particles being large and some small. A chromatogram of sunken tar is shown in Figure 32: it reveals an advanced stage of decomposition. Also shown is a sample of abyssal tar dredged from the bottom of the western Gulf of Mexico (collected by Dr. Jeffrey of Texas A&M University). The abyssal tar is extensively degraded, having lost virtually all its paraffin components so that only the unresolved envelope remains. Since the paraffins are the lightest class of compounds in petroleum, their loss (by microbial action) increases the density of the tar lumps. In the case of the abyssal tar sample, the loss of the paraffins apparently resulted in the sinking of the tar. Chromatogram 79 in Figure 23 shows the composition of a second tar sample which sank in fresh water. It shows some degradation, but is not as degraded as the sample in Figure 32; however, the lump was heavily encrusted with fouling organisms. Three samples obtained at ocean weather station P were obtained from tows made just below the surface. The chromatograms (#56, 57 and 58 in Figure 23) indicate that all three samples were in a state of advanced decomposition: presumably they had a near neutral bouyancy, and were mixed below the surface by turbulence. The

FIGURE 32: Chromatograms of a Pelagic Tar Sample with High Specific Gravity and of an Abyssal Tar Sample



Abyssal tar obtained by dredge from the western Gulf of Mexico (sample courtesy of Dr. L.M. Jeffrey, Texas A&M University)



actual increase in density required to sink pelagic tar is not large: the average specific gravity of crude oils is about 0.85 (tanker residues are probably slightly denser), while the specific gravity of oceanic surface water is about 1.025. Therefore an increase in density of approximately 20% is required for pelagic tar to attain a negative bouyancy.

Some supporting observations exist in the literature to suggest that the ultimate fate of pelagic tar is sinking: Kinney et al (1969) observed that a water-in-oil emulsion eventually became heavier than water due to bacterial action; Spooner (1971), in a laboratory experiment, found that bacteria sank crude oil masses after several weeks; Heyerdahl (1971) observed tar as far below the surface as he could see during the Ra II expedition; and Marumo and Kamada (1973) repeatedly found tar in tows made at a few meters depth.

In conclusion, the preliminary evidence indicates that the ultimate fate of pelagic tar is to sink due to the gradual removal of the lighter components of the tar by the weathering processes, and the accumulation of an overburden of fouling organisms. The time required for sinking to occur is presumably a function of the density and composition of the original oil, the time of innoculation of the tar with appropriate micro-organisms, and the fouling growth that develops. Judging from the distribution pattern of the pelagic tar, some particles must drift for periods on the order of years before eventually sinking.

Ecological Effects of Pelagic Tar

The extensive contamination of the surface waters of the oceans by tar residues raises the question of the environmental impact that the residues have on the ocean ecosystem. Although no research on this matter was pursued during the course of this degree program, some comments can be made on the basis of general observations and information that has accrued in the literature.

From observations made on the tar lumps collected in the Pacific, it is evident that tar lumps enrich the biota of the surface layer by providing a substrate on which organisms can live and reproduce. The colonizing community typically includes bacteria and other micro-organisms (especially blue-green algae), chlorophyta, byrozoa, and <u>Lepas</u> barnacles. Isopods (<u>Idotea metallica</u>) are commonly found on tar lumps, and their colouring suggests that they may have adapted to this environment. Crabs are also found. They are usually still in the megalops stage, suggesting that they do not grow to maturity in their precarious habitats. Finally, the eggs of the oceanic water strider <u>Halobates</u> occur on about 2% of the tar lumps, so the tar apparently encourages this species as well.

Beyond this superficial observation of the substrate role of tar, some more negative aspects must be considered. It is possible that organisms living on tar are not healthy, but suffer from sublethal effects that are not immediately evident. Some support for this proposition can be drawn from the observation of hyperplasia in bryozoa growing near coal tar (Powell et al, 1970). However,

Morris (1973) found that barnacles growing on tar were not severely contaminated by hydrocarbons. A second consideration is that tar may be injested by surface feeding organisms. This has been observed with copepods after an oil spill (Conover, 1971) and could result either in sedimentation of the tar in the feces, or passage up the food chain. The second possibility has not been documented.

More directly relevant to the human condition is the occurrence of tar on the beaches over large portions of the globe. Tar is a pollutant around most

of the coastline of the Mediterranean (Anon, 1971), in southern Africa (personal documentation), the Caribbean (Sleeter et al, 1976), Bermuda (Butler et al, 1973), Florida (Dennis, 1959), Brazil (personal documentation) and around the entire coastline of India (Dwivedi and Parulekar, 1974). Many of these areas have very substantial tourist industries, for the seashore is perhaps the favorite play-ground of the human race. The presence of tar reduces the recreational potential of beaches severely: highly contaminated beaches are not pleasant to walk along even in shoes because of the heavy accumulation of tar which occurs; towels cannot be laid on the beach ; playing in the sand results in hands covered with tar, presenting an intractable cleaning problem without the use of organic solvents; resort owners in many locations provide solvents for their guests to clean their feet after venturing on the beach. Clearly the presence of tar damages the esthetic appeal and recreational value of a treasured environment.

A final consideration is that the presence of tar must be taken as an indication of hydrocarbons entering the water column. Although the partition coeffficient between crude residues forming tar and components entering the water column is unknown, the presence of high concentrations of tar probably indicates that sizeable quantities of hydrocarbons are entering the water column. The biological effects of soluble hydrocarbons are considerably more serious than those of the non-soluble tar (see Appendix B). The presence of tar may signal that hydrocarbons are entering the water column in sufficient quantities to disturb the balance of species and alter the food chain dynamics (Parsons et al, 1975; Fisher, 1976: see Appendix B).

Conclusions

1. On the basis of 2092 surface tows between 1967 and 1975 the following conclusions were reached about the distribution of tar in the Pacific:

- a) Petroleum residues are not a significant pollutant in the surface waters of the South Pacific.
- b) In the Northeast Pacific occasional contamination of surface tows occurs (average concentration is 0.03 mg/m²).
- c) The Northwest Pacific is the most contaminated area, particularly in the Kuroshio current system between 25° and 40° N. The average concentration in this area is 2.1 mg/m², which represents a standing stock of 25,000 metric tons of tar.

2. Plastic is a widespread contaminant on the North Pacific Ocean, but generally in lower quantities than tar. It usually occurs as round, colourless pellets weighing 20-50 mg each.

3. The Beaufort Sea in the Arctic Ocean is not contaminated by tar. Plastic, however, is a common contaminant on the beaches.

4. The distribution of the tar in contaminated areas is patchy, so that replicate tows catch widely varying quantities of tar which approximately follow a log normal distribution. This patchiness cannot be explained on the basis of windrows, and probably is a result of the tar gradually spreading out from point sources. The tar distribution may be best represented mathematically by Newmann's contagious distribution.

5. Most tar particles were in the 1-5 mm range, but most of the tar mass was in particles in the 5-10 mm range. The largest tar lump was 5 cm in diameter and weighed 34 g.

6. The average water content of the tar was 22% by weight, which is considerably less than the amount of water in a fresh water-in-oil emulsion (80%).

7. Tar samples stored for a year and a half by refrigeration

or in formalin did not show any detectable change in composition.

8. Surface tows and beach surveys made in local British Columbia waters in an area of heavy urban and industrial development (including three oil refineries) detected no petroleum residues, implying that the source of tar is not from run-off or refinery outfalls.

9. High iron concentrations of greater than 1 ppt were found in 77% of the 104 tar samples analysed (iron in crude oil does not exceed 0.1 ppt). Nickel concentrations, however, were not detectable above those in crude oil, so general metal enrichment did not occur. The anomalously high levels of iron strongly imply an anthropogenic source of the tar.

10. Gas chromatographic analyses provided a second and more precise indication of the source of the tar. 88% of the 82 samples analysed contained long-chain, waxy paraffins of higher carbon number than C-25 in much greater abundance than they are normally found in crude oil. These longchain paraffins are typical of the sludge discharged by tankers when they clean their tanks after carrying crude oil. This tanker sludge is probably the source of most of the pelagic tar in the Pacific.

11. The chemical analyses, combined with the distribution pattern of the tar, imply that most of the pelagic tar contamination in the Pacific originates from tankers on the very large Middle East to Japan tanker route, then becomes entrained in the Kuroshio current south of Japan and creates a plume of contamination which extends downstream for 7000 kilometers across the Pacific.

12. The standing stock of tar in the Northwest Pacific (25,000 metric tons) represents a loss of only about 0.01% of the oil carried on the Japanese tanker route. However, because of the vast quantities being transported and the persistance of the tarry fraction, even a very small percentage
loss results in significant contamination of the surface waters.

13. Photo-oxidation does not detectably contribute to the degradation of tar. The role of dissolution is uncertain, but from theoretical considerations is presumed to be small.

14. Evaporation removes compounds up to the volatility of pentadecane (C-15) from the tar: 73% of the 82 samples analysed had lost all n-alkanes up to C-15. Above C-15 the evaporative losses become very slow and the process is usually overtaken by microbial attack.

15. At least 33% of the tar samples analysed by gas chromatography showed clear evidence of microbial degradation.

16. Small particles of tar did not show any tendency to be further affected by evaporation or microbial attack than larger lumps. No gradient of lighter compounds between the inside and outside of a large tar lump could be detected, indicating that evaporation is not diffusion-limited.

17. Both evaporation and microbial degradation increase the density of the tar particles, and this effect combined with the weight of the fouling community that develops, results in the eventual sinking of the tar into the depths of the ocean.

18. Tar particles provide the biota of the surface of the ocean with a substrate on which they can live and reproduce.

19. Tar occurs as a pollutant on a very large portion of the world's beaches, including nearly all of the popular seaside resort areas. The presence of the tar severely reduces the recreational and esthetic value of sandy beaches.

CHAPTER 6

OIL IN THE INTERTIDAL ENVIRONMENT

Introduction

Although contamination of the intertidal environment by oil has received a great deal of attention during and after various oil spill calamities, the scientific investigations are usually biological in nature and attempt to assess the biological damage. The number of chemical studies is far fewer: Blumer, Ehrhardt, and Jones (1973) followed the fate of stranded masses of petroleum in Massachussetts and Bermuda; Betancourt and McLean (1973) studied the weathering of intertidal oil left after the Arrow spill (the method of analysis - vanadium and nickel concentrations - did not allow them to determine the mechanisms of weathering). These are the only two studies which deal specifically with the chemical weathering of intertidal oil. The purpose of this research was to determine the rate and mechanisms of oil degradation in the intertidal environment under local conditions, so as to provide some relevant information for the conduct of clean-up operations, and for the design of means for enhancing the natural degradation of oil.

The Alert Bay Oil Spill

The study of the weathering of intertidal oil was conducted by examining the degradation of fuel oil spilled by a freighter which grounded near the northern end of Vancouver Island, British Columbia. The accident occurred late on 24 January, 1973, when the freighter Irish Stardust ran aground near Haddington Island and spilled roughly 200 tons of heavy fuel oil into Broughton Strait (see Figure 33). The majority of this oil was deposited along the shores to the east by the receding high tide on the morning of 25 January (high tide of 14.6'). The town of Alert Bay on Cormorant Island was the community most affected. Major clean-up operations were conducted on the beaches of Cormorant Island and other islands further to the east. However, one of the contaminated bays was sufficiently isolated that it could be left undisturbed for scientific study. This bay was code-named Reserved Bay, and five visits were made to it over the period of a year to obtain chemical samples and observe the natural degradation of the heavy fuel oil.

Description of the Study Area

Reserved Bay is a semi-exposed bay situated on the west side of the largest island of the Pearse group. The north and south sides of the bay are bounded by vertical rock faces five to ten feet in height. Its head is bordered by a lowland of meadow and marsh grasses. A small stream flows onto the south end of the beach. The low-tide zone consists of a clay-based mudflat; the midtide zone of stone, sand, and pebble areas; and the high-tide zone of rock faces and patches of sand, stone, and pebbles. The area surrounding the stream is mostly a sand-clay mixture.

Rockweed (Fucus distichus) extends from high to mid-tidal areas. The low-tide mudflat harbours eelgrass beds (Zostera marina). Brown algae (Alaria <u>marginata</u> and Laminaira sp.) grow on logs which are partially embedded in the mud. Mud holes suggest the presence of clams, polychaete worms, and/or shrimp. Barnacles (Balanus glandulus), shore crabs (Hemigrapsus nudus and H. oregonensis), amphipods (Orchestia sp), periwinkles (Littorina sitkana and L. scutulate), and turban snails (Calliostoma sp.) frequent mid-tidal areas; while the latter three and the limpets (Acmaea spp.) are the prominent fauna in the higher tidal zones. A peculiar characteristic of the bay is the absence of the typical scattering of barnacles at the higher tidal levels.

In general, this species composition is typical of intertidal life in a British Columbia semi-exposed habitat. Also, the physical characteristics of the bay are common to thousands of inlets and bays along the complex coastline of British Columbia and Alaska. Reserved Bay, then, provides a good 'case study' of the environment which would be affected by an oil spill on the west coast.





Observations

Reserved Bay was visited five times over a one year period to collect samples for chemical analysis. On each visit the extent of oil contamination and the appearance of the oil were recorded, and a log of the more obvious biological events was kept. These observations are summarized in Table 23.

•

Date	Observations of 011	Observations of Biota
30 Jan.73 (5 days after spill)	An oily sheen was on the surface waters of the cove; oil-soaked material and thick black patches of oil floated near the beach. A band of oil covered a vertical height of approxi- mately 2 meters downwards from the high tide mark. Coverage was continuous over rocks,rock faces, logs and seaweed, with a coating 1 to 5mm thick. The sand was oily but not coated. A thick bed of detached, heavily-oiled rock- weed (Fucus distichus)covered the high tidal area. Below the band of contamination the beach appeared to be totally oil-free.	
9 Mar.73 (6 weeks after spill)	The areas of beach and rock contaminated by oil were unchanged from the first visit. No migration of oil down the beach or to adja- cent unoik/areas had taken place. In general appearance the oil looked remark- ably similar to the first visit, except for being slightly less glossy and sticky.	Smothering had killed many limpets (<u>Acmaea spp.</u>) on the heavily-oiled rockfaces (42 dead limpets were found at the base of a rockface 1 m ² in area. Many oil-covered amphipods (<u>Orchestia sp.</u>) were found. Most were alive but exhibited slow re- strained movements. Periwinkles (<u>Littorina spp</u> .) among the oiled rocks were lying free on the ground with their opercula tightly in position. Marsh grasses at head of beach were heavily oiled. The fauna and flora of the unoiled portions of the beach appeared to be unaffected.
5 Jun.73 (4 ¹ 2 months after spill)	The location of oil contamination was un- changed. The oil had a dull,black, asphalt- like appearance, but still stuck to one's feet, leached a film of oil into the water, and appeared fresh in crannies and under rocks.	Nearly all limpets had died and fallen off heavily oiled rockfaces. A few appeared to be success- fully grazing on the oiled rock. Meiofauna popu- lations in the sand were of normal diversity.
28 Aug.73	Oil was still very evident on rock and gravel portions of the beach. It was no longer noticeable in the sand. Exposed oil was as- phalt-like in appearance. However, an oil slick was still leached onto the advancing tide wherever the beach was disturbed.	Oil coverage of marsh grass was more weathered, and plants no longer stuck together in clumps. In spite of a sticky, oiled substrates, very high densities of amphipods were found ($1000/m^2$). No recolonization of rockfaces by limpets or littorinids was evident.

Date Observations of 011

26 Jan.74 (1 year after spill) Superficially, the oil had disappeared. It was no longer evident on the small stones of the beach, and on the rock walls the dark stains of oil were nearly gone. No oil was evident in the sand, and the oiled rockweed at the top of the beach had disappeared. Rocks and gravel could be handled without the need for plastic gloves, although an unobtrusive thin black coating of oil was still present on rocks in some places. A few portions of the gravel beach were still immobilized by weathered, coagulated oil. Oil still leached into the water when the beach was disturbed.

Observations of Biota

The oiled marsh grass was reduced in height relative to unaffected stands, but was still alive. Limpets were beginning to recolonize portions of the rockfaces. Periwinkles were found in areas previously devoid of them.

Chemical Analysis

Oil samples from each visit to Alert Bay were analysed by gas chromatography to determine the chemical changes that occurred in the oil due to the effects of weathering. Roughly one gram of material was weighed out from each sample into a centrifuge tube. Five milliliters of carbon disulfide were added and vigorously shaken to dissolve the oil. The tube was centrifuged to remove sand and other particulate material, then the CS₂ solution was decanted into a glass vial and refrigerated until analysed.

The samples were run on two different columns: full chromatograms were obtained using Dexsil 300 - a non-polar, high-temperature packing which can be programmed up to 400°C with very little bleed; separation of isoprenoid compounds from paraffins was accomplished on FFAP, a polar packing. The analytical parameters were the same as those used for pelagic tar analyses (see Table 18). Table 24 gives the specifications of the fuel oil of the Irish Stardust, as obtained from the fuelling report.

TABLE	24:	Specifications of Fuel Oil Spilt at Al	ert Bay
		Specific gravity at 15°C	0.9412
•		Vis. R.W. No.1	465
		Carbon	9.0%
		Flash Point	91 [°] C
		Pour Point	-10 ⁰ C
		Sulfur	2.41%

(Above information is from the fuelling report, Osaka, Japan. The fuel falls into the classification of No.5 fuel oil.)

FIGURE 34: Chromatograms of Fuel Oil Weathering in an Intertidal Environment



2) After 5 days (thick slick floating near the beach)



3) After 6 weeks
(thick oil between the rocks)





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FIGURE 35: Isoprenoid/Paraffin Ratios in Fuel Oil Weathering in an Intertidal Environment

Results of Chemical Analyses

Representative chromatograms from each visit to Reserved Bay are presented in Figures 34 and 35. The parameters which indicate the effect of the various weathering mechanisms were calculated from these chromatograms and are listed in Table ²⁵.

TABLE 25: Characteristics of Fuel Oil Weathering in an Intertidal Environment

	<u> </u>	From Fig	gure 34	From Figure 35			
Length of Exposure	c_n^10%	c _n ^{50%}	17/env	25/env	17/Pr	18/Ph	Pr/Ph
Original	11.6	16.5	4.7	1.0	1.9	2.2	1.3
5 days	11.0	16.3	4.6	1.4	1.9	2.2	1.3
6 weeks	11.6	16.3	4.1	1.3	1.7	1.8	1.0
4 ¹ 2 months	14.8	18.0	3.0	3.1	1.2	1.2	.9
8 months	14.2	17.0	1.6	• .1	.3	.2	.8
l year,#1	14.3	17.2	1.7	.2	.3	.2	.8
1 year,#2	14.0	17.1	1.5	1.0	.2	.3	.8

Note:

 $C_n^{10\%}$ and $C_n^{50\%}$ refer to the equivalent n-paraffin carbon numbers at which the unresolved envelope reaches 10% and 50% respectively of its maximum amplitude.

Discussion of Intertidal Weathering

The chromatogram of oil from the tanks of the Irish Stardust is virtually identical to that obtained 5 days later near the beach at Reserved Bay. If the source of the polluting oil had been in doubt, these two chromatograms would have provided convincing evidence that the oil came from the Irish Stardust. Virtually no evaporation or dissolution occurred over the first 6 weeks, the $C_n^{10\%}$ and $C_n^{50\%}$ values remained unchanged. Between 6 weeks and $4\frac{1}{2}$ months the values suddenly increased. This coincides with the summer season, and is perhaps due to the increased temperatures in the sun-heated oil, causing increased evaporation. After $4\frac{1}{2}$ months no further evaporation or dissolution is evident.

The ratio of paraffins to isoprenoids began to decline after 6 weeks and dropped markedly between 4½ months and 8 months, indicating the pronounced effect of microbial degradation. If any photo-oxidation occurred, its effect on the paraffin/isoprenoid ratios was competely masked by microbial degradation. The chromatograms show the steady advance of degradation until, after about a year, the paraffins were completely degraded, leaving an unresolved envelope. By comparison, bacteria under culture conditions can completely remove paraffins from oil within 24 hours (see Figure 8).

Blumer, Erhardt, and Jones (1973) found that the alkanes were depleted from intertidal crude oil within 4 months when nutrients were available (from decaying plant material) but were not degraded during the 16 months of the study for samples on rock. The two chromatograms of one year samples (Figure 34, #6) also show some variations by locale. Both are samples from oiled gravel, but one is considerably more degraded than the other (25/env ratios: 0.2 vs. 1.0), which presumably is a result of differing surface areas or availability of nutrients.

The chromatogram of the $4\frac{1}{2}$ month sample (Figure 34, #4) has an inter-

esting anomaly - there is an enrichment of the longer-chain paraffins relative to the original sample (the 25/env ratio has tripled). There is no known weathering mechanism which cause polymerization of alkanes, so this sample apparently had an inclusion of wax resulting from wax precipitation either in the tanks of the Irish Stardust or after the spill.

Conclusions

- Microbial degradation was responsible for the chemical weathering of the spilt oil at Reserved Bay. Evaporation played only a minor role; photooxidation and dissolution did not appear to have any effect.
- 2. Microbial attack took approximately 1 year to complete the degradation of the paraffins in the spilled oil, leaving an asphalt-like residue on the stones of the beach. The asphaltic residue was apparently more susceptible to physical weathering than the original oil.
- 3. The combined effects of chemical and physical weathering removed about 95% of the spilled oil from the cove over the period of one year.

Several factors must be considered in applying this measurement of the degradation rate to other situations:

- a) Since microbial action is the prime mechanism for degrading intertidal oil, a source of nutrients is essential. In Reserved Bay an ample supply was available from the decaying rockweed at the head of the beach. Bare rock is the poorest environment for nutrient supply. There it may be most efficient to add nutrients in the form of an oleophilic solution to encourage degradation, rather than attempt financially and ecologically expensive clean-up procedures such as sand-blasting, steam-cleaning, or the application of detergents.
- b) The rate of degradation is very much a function of the amount of oil spilled per unit area. The time required for degradation does not appear to vary

linearly with increasing oil contamination, but <u>exponentially</u>, partly because of the decreased surface area per unit volume for evaporation and microbial attack, but also because heavy contamination may result in 'immobilization' of the beach. Immobilization occurs when the asphaltic residue from spilled oil effectively paves the intertidal area, preventing natural beach overturn and so eliminating most of the physical weathering. Several beaches were immobilized by the Arrow spill (Task Force - Operation 0il): a measurement of the extent of weathering by Betancourt and McLean (1973) indicated that about 20% loss of material occurred over a one year period, after which chemical weathering appeared to have stopped.

- c) The rate of natural degradation is dependent on the type of oil spilled. Light petroleum products such as diesel fuel disappear more quickly because of the increased importance of evaporation and dissolution, but have more severe biological effects.
- d) The rate of weathering depends on the exposure of the beach. Intertidal areas with open ocean exposure should purge themselves of oil contamination considerably more quickly than the semi-exposed location at Reserved Bay: the greater energy of the beach leads to increased physical weathering, thereby increasing the surface area of the oil and the rate of chemical weathering.

CHAPTER 7

OIL IN THE BENTHIC ENVIRONMENT

Introduction

There have been a number of publications dealing with sinking agents as a method of treating oil spills (Houston et al, 1972; Arthur D. Little, Inc., 1969; Warren Spring Laboratory, 1972; Water Quality Laboratory, 1969; Brown, 1971). These publications compare the effectiveness of various sinking agents, and evaluate the general effectiveness of the method in comparison with other oil treatment procedures.

Several of these publications indicate the need to know something of the rate of degradation of oil which has been artificially sunk, but nothing has appeared in literature to date dealing with this problem. The information is necessary to establish the propriety of using sinking agents, and it also provides further insight into the manner in which the natural environment deals with the sudden intrusion of petroleum chemicals.

The purpose of the experiment described in this chapter was to determine the rate at which crude oil degradation took place under ideal conditions in a previously pristine environment, and to establish the mechanisms of degradation.

Method

Two liters of seawater were placed in a four liter container lined with a plastic bag. 500 ml of Peace River crude oil were added, giving a surface slick 2 cm thick. 1000 - 2000 ml of sinking agent - a dried, untreated volcanic ash - were added to the container, sinking the oil. The water was poured off, and the bag tied closed. Four samples were prepared in this manner.

The four bags of sunken oil were taken to Dodger's Cove, in Barkley Sound, a shallow (5-7 m) silty area with currents of up to 1 knot. The contents of each bag were spread by divers over individual quadrats of about 0.25 m², and covered with $\frac{1}{2}$ inch mesh fish netting which was staked into the silt to prevent drifting and to mark the site. The sites were sampled according to the following schedule:

Time after
Commencement of experiment:9 Feb. 1974First sampling:7 Mar. 19741 monthSecond sampling:25 Jul. 19745½ monthsThird sampling:7 Jun. 197516 months

Samples were preserved both with formalin and by refrigeration (-18°C).

The samples were analyzed by gas chromatography. About 0.5 g of sample were shaken with CS₂, centrifuged, and 5-40 ul were injected into a Varian Aerograph 1400 gas chromatograph. Two columns were used, a high-temperature Dexsil column for obtaining a full chromatogram, and a polar FFAP column for separating the isoprenoid compounds from the alkanes. The technical data is the same as for the analyses performed on pelagic tar as detailed in Table 18.

Observations

When the oil was released from its bag on the bottom and spread over the quadrat, some of the oil escaped and bubbled to the surface. The percentage loss is hard to estimate, but was probably in the neighbourhood of 5-10%. One month later, all four quadrats bubbled oil to the surface when disturbed. After 5½ months, at the time of the second sampling, one quadrat bubbled oil, and all showed obvious oil contamination which appeared fresh. By the time of the third sampling, 16 months after contamination, all quadrats were covered with about a centimeter of silt. The oil contamination was no longer obvious, and no oil escaped to the surface when the sediment was disturbed. It was difficult to tell what to sample when diving, and upon reaching the surface, the only way of determining if oiled sediment had been obtained was by the smell of the oil. The odour of oil was still clearly evident in the sediment samples.

Results of Chemical Analyses

The full gas chromatograms obtained from the samples are shown in Figure 36, and the chromatograms obtained with the polar FFAP column are shown in Figure 37. The parameters calculated from these chromatograms are tabulated in Table 27.

It was discovered during this investigation that formalin preserves heavily-oiled samples more effectively than refrigeration. The evidence for this conclusion is presented in Figure 38. (All chromatograms in Figure 36 and 37 were of samples preserved in formalin.)





FIGURE 36: continued



FIGURE 37: Isoprenoid/Paraffin Ratios in Crude Oil Weathering in a Benthic Environment



Preservation of Heavily-Oiled Samples

To check on the integrity of the methods of storage of oil samples, duplicate samples of heavily-oiled sediment from the benthic experiment were stored in formalin and by freezing for $10\frac{1}{2}$ months, analysed in the usual manner, and the chromatograms compared with an analysis made on the fresh sample. The chromatograms of the samples stored by the two methods are compared in Figure 38, and summarized in Table 26. It is immediately clear that the frozen sample lost some of its volatile components over the period of storage despite the cold temperatures and screw-top glass container in which it was kept - three-quarters of the C-9 and C-10 peaks were lost relative to C-17, and the effects of evaporation extended up to and included C-13. The sample preserved in formalin, however, did not change in composition. Thus, although formalin may contain trace hydrocarbons that make it unsuitable for preserving sediment and tissue for trace analysis, it is sufficiently pure for preserving heavily-oiled samples, and very effectively eliminates evaporative losses.

TABLE	26:	Comparison of	Refrigeration	and	Formalin	as	Methods	of	Preserving
		Heavily-Oiled	Samples						· _ ·

Storage	9/17	<u>Pe</u> 10/17	ak Height 11/17	s Relativ 12/17	ve to C-17 13/17	14/17	15/17
None	.82	.81	.88	.93	.96	.94	.84
10 ¹ ⁄2 months in formalin	.85	.76	.98	1.02	1.00	.99	.89
10½ months frozen	.26	.27	.65	. 79	.88	.93	.86

- FIGURE 38: Chromatograms showing the Effect of Storage on Preserved Oil Samples
- Sample preserved for eleven months in formalin (sampled 25/7/74; formalin; anal. 12/6/75; #25 - no change from original chromatogram)



2) Sample preserved for eleven months by refrigeration at -18°C (sampled 25/7/74; freezing; anal. 12/6/75; #23 - note loss of lower-boiling components)



Discussion

None of the four quadrats of sunken oil underwent any change in chemical composition during 5½ months of exposure on the bottom of Dodger's Cove. The rate of degradation was so slow that the quadrats were not sampled again for nearly a year. After 16 months the oil had begun to degrade. Chromatograms #4 and #5 (Figure 36) show the range of degradation which had occurred. In sample 1, alkanes up to about C-20 were removed and partial losses occurred up to C-25 (see Table 27). The degradation of the sample is clearly caused by microbial attack, since the paraffin/isoprenoid ratios drop drastically for this sample (17/Pr from 1.4 to 0.1; 18/Ph from 1.6 to 0.3). As in one sample from the intertidal experiment, this sample shows a mysterious enrichment of the long-chain paraffins between C-25 and C-35 (C-30 ratio double the original oil sample ratio - see Table 27). Again, this must represent some sort of wax inclusion caused by precipitation of waxes.

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The second chromatogram of a 16 month sample is from the least degraded of the quadrats. In this sample the alkanes had only been reduced up to about C-20, but again there is clear evidence that microbial attack is responsible.

The degradation process was slower in the benthic environment than in the intertidal situation already discussed. The reason may be that, in the benthic environment, evaporation has no opportunity to remove the toxic short chain components (C-5 to C-8) which are bactericidal to many species of microbes (Button, 1971). Dissolution did not appear to be effective in removing these volatile components: for 5½ months the composition of the oil did not change - if no dissolution occurred over this long period, it is unlikely that it occurred at all. More likely, the toxic components were eventually removed by microbial action. Since only a few species are capable of degrading the lightest components of petroleum, the seeding time is long and the degradation slow. Once the lightest components are degraded, seeding of the oil by many other

TABLE 27: Characteristics of Crude Oil Weathering in a Benthic Environment

Length of Exposure	11	15	17	20	25	30
Original 1 month	.89 .95	.87 .88	1.03 1.00	.31 .31	.20 .21	.07
$5\frac{1}{2}$ months	.88	.78	.89	.35	.14	.05
16 months - sample 1 - sample 2	.05	.10	.39	.05 .22	.12 .20	.16 .09
•						

a) From full chromatograms (Figure 36):

(for each chromatogram, peak heights have been normalized by dividing by 4 times the height of the envelope at C-17.)

b) From partial chromatograms (Figure 37):

Length of Exposure	17/Pr	18/Ph	Pr/Ph	Pr/env	Ph/env
Original	1.43	1.63	1.48	.83	.56
5½ months	1.38	1.64	1.47	.90	.58
16 months	.14	.29	1.62	1.07	.59

strains of bacteria, fungi, and mold can occur, and microbial attack can begin in earnest. Thus the slow degradation of the benthic oil can be explained as an initial delay followed by the same process of microbial degradation as occurred in the intertidal environment, probably at about the same rate (1 year to remove the paraffins).

It will be noted that photo-oxidation has not been mentioned as a weathering process in this discussion. The paraffin/isoprenoid ratios show clearly that microbial degradation is the dominant process, and any photo-oxidative effects are completely masked. Since light of the correct wavelength (less than 300 nm) will only penetrate a few meters into the ocean, it is unlikely that any photo-oxidation of the petroleum occurred.

Finally, it should be noted that pristane occurs widely in sediments (Blumer and Sass, 1972b). Caution must be exercized, therefore, in assuming that the pristane quantities in the benthic oil samples are conservative. The pristane/envelope ratio (Table ²⁷) increased by about 29% over the period of the experiment. Since the phytane/envelope ratio did not change, some enrichment of the samples by pristane from the sediment is indicated.

Conclusions

- Heavily-oiled samples should be preserved in formalin if they are to be stored for any length of time prior to analysis, since the formalin not only prevents bacterial alteration, but also eliminates evaporative losses which can occur if the samples are stored by refrigeration.
- 2) The degradation of the benthic crude oil resulted almost entirely from microbial action. Evaporation had no opportunity to act; dissolution was ineffective; and photo-oxidation was not possible because of the low energy and intensity of the light reaching the sediment.

- 3) The benthic petroleum samples were slow to degrade: the oil remained unchanged in chemical composition for at least six months; even after 16 months the paraffins, which are the fraction most susceptible to attack, were only partially degraded.
- 4) The pattern of degradation appeared to consist of an initial delay while bactericidal components were dealt with, followed by microbial degradation of the remaining oil at roughly the same rate as in the intertidal experiment - one year to remove the paraffin components.

The following factors limit the generality of the measured rate of degradation of the oil in this experiment:

- a) The conditions in Dodger's Cove are ideal for microbial growth. The sediment is thick, soft, and aerobic, with an abundant supply of detritus. A gentle tidal current maintains flushing and a supply of nutrients. In other situations, such as at great depth or in areas of nutrient limitation, the conditions for microbial growth may be less suitable, and result in slower degradation.
- b) The sunken oil was a fresh crude, and so contained a high percentage of light components in the C-5 to C-8 carbon number range. These compounds are toxic for most species of microbes, and so greatly inhibit microbial degradation. If the sunken oil had been a heavy fuel oil or a weathered crude, then the bactericidal components would not have been present, and bacterial degradation would have proceeded more efficiently.
- c) Dodger's Cove is in a pristine area distant from any industrial or urban centre, so there is no adaption of the bacterial fauna to petroleum degradation. In areas chronically polluted by petroleum, seeding and consequent bacterial degradation should be considerably more rapid.

CHAPTER 8

OIL IN THE WATER COLUMN

Introduction

The purpose of the experiment described in this chapter was to determine the fate of hydrocarbons that enter the water column, and to test in a controlled situation the validity of the analytical methods that are employed in hydrocarbon determinations.

The determination of the quantities and composition of hydrocarbons in the water column is a difficult analytical problem because of the immense diversity of the hydrocarbons, the very low levels at which they dissolve, and the complex matrix of organic compounds from which they must be separated.

Sampling oceanic waters for hydrocarbons requires a degree of caution which has frequently not been exercised in reported studies. Gordon et al (1974), in a classic demonstration of the hazards of hydrocarbon sampling, found that they obtained the same concentrations of hydrocarbons whether or not they actually collected water samples with their Knudsen bottles. They recommended that the surface of the sampler not come in contact with any water except that being sampled, and that the sampler be rinsed with solvent after sampling to recover hydrocarbons adsorbed on the walls. The rinsing of the sampler with solvent precludes the use of plastic containers because of the danger of contamination by plasticizers.

The most common analytical methods for the detection of hydrocarbons in seawater are: infrared absorbance (Brown, 1973, 1975; Monaghan, 1973); fluorescence spectroscopy (Levy, 1971, 1972; Gordon et al, 1974; Cretney and Wong, 1974); and gas chromatography (Barbier et al, 1973; Hardy et al, 1975). Of the three methods, fluorescence is the most sensitive, but responds only to very specific polyaromatic compounds, gives little information on composition, and is prone to interference from non-hydrocarbons such as chlorophyll. Infrared spectroscopy detects a broad spectrum of hydrocarbons in a single signal (CH3- or CH2- groups) but again gives little information on composition and is prone to interference from non-hydrocarbons. Both the infrared and the fluorescence method require the use of an arbitrary calibration standard to convert instrument response into concentrations. Gas chromatography can reveal much information on the composition of the hydrocarbon extract, but thereby sacrifices sensitivity and requires more time and skill for analyses. The problems of interference can be overcome by using column chromatography (Cretney and Wong, 1974; Brown et al, 1973, 1975) or thin layer chromatography (Barbier et al, 1973); sensitivity can be enhanced by extracting larger quantities of water (Barbier et al extracted approximately 100 1 using 9 liters of solvent!). However, the preparative methods and the increased volumes of water increase the ever-present risk of contamination. The utmost caution is required: solvents often are not sufficiently pure even after multiple distillation; atmospheric hydrocarbons may contaminate samples left open; glassware must be meticulously cleaned and transfers minimized; plastics must be scrupulously avoided; and all chemicals must be soxhletextracted before use. Filtration can have pronounced effects on the results because much of the 'dissolved' hydrocarbon material occurs adsorbed on silt and other particulate material. Furthermore, adsorption on the filter may occur. Finally, the samples must be guarded against microbial degradation and evaporation (especially during roto-evaporation of solvents). In general, the sampling and analytical methods require very meticulous attention, and it may be that many of the values reported in the literature are unreliable (Gordon et al, 1974).

The methods and results of some of the more prominent investigations of hydrocarbons in the water column are summarized in Table 28. There has been a tendency for values to decline with later publications (Gordon et al,

Reference	Location	Depth	Concentration (ug/liter)	No. of Samples	Extraction Solvent	Analytical Method	Column	Filtra- tion?	Sampling Method
Barbier et al, 1973	European coast & off West Africa	0 to 4500m	10-137	(8)	CHCL ₃ (9 Litres)	g.c.	t.l.c. (silicic acid)	yes	130 liter teflon bottle
Hardy et al, 1975	North Sea & U.K. coast- al waters	surface film 1 m	$34 \pm 28 \text{ ug/m}^2$ 2. ± 2.0	(40) (85)	pentane	g.c. (alkanes only)	silicic acid	yes	s.s. screen bucket
Levy, 1972	Nova Scotia coast	2 and 10 m	1.7 ± .7	(24)	CC14	fluor. (Bunker C standard)	none	no	oceano- graphic bottles
Gordon et al, 1974	Halifax- °Bermuda section	0-3 mm 1 m 5 m	$20 \pm 61 \\ 0.8 \pm 1.3 \\ 0.4 \pm 0.5$	(43) (24) (24)	CH2C12	fluor. (Venezuelan crude standard)	none -	no	special device
Cretney & Wong, 1974	Northeast Pacific	Om	.018 ± .006	(9)	CH2C12	HPLC- fluor. (chrysene standard)	silica gel	no	bucket
Brown et al, 1973	Venezuelan tanker routes	0 m 10 m	8.9 ± 9.6 3.9 ± 3.6	(33) (25)	cc1 ₄	i.r. (crude oil standard)	silica gel	no	bucket sea water line (from tankers)
Brown et al, 1975	Mediterr. Mediterr. Deep Sea profile (nr Bermuda)	0 m 10 m 0-30 m 50- 2500m	$27 \pm 54 \\ 3.6 \pm 2.0 \\ 3.8 \pm 1.4 \\ 0.8 \pm 0.8 \\ $	(19) (15) (7) (16)	cci4	i.r. (crude oil standard)	silica gel	no	bucket sea water line 30 l Niskin 30 l Niskin

TABLE 28: Reported Concentrations of Nonvolatile Hydrocarbons in Oceanic Waters

. 195 1974) and this trend may continue. It has been established, however, that there is a surface film high in hydrocarbons (Duce et al, 1972), that surface waters from 0 to 10 m are relatively high in hydrocarbons (0.5 to 30 ug/1 depending on location and method), and that deep waters are relatively low in hydrocarbons (<1 ug/1, often below the detection limit).

A calculation can be made of the standing stock of hydrocarbons in oceanic waters based on these estimates of hydrocarbon concentrations. The following concentration profile is assumed: 0 m = 6 ug/l10 m = 3 ug/l

10 m = 3 ug/1 1000 m = 1 ug/1 2000 m = 0 ug/1(total volume of ocean = 1.37 x 10²¹ liters).

Integration of this profile gives an estimate for total hydrocarbons in the oceans of about 400 million metric tons. Petroleum input has been estimated at 6 mta (chapter 1) and biogenic hydrocarbon production at 3 mta (Revelle et al, 1971) to 10 mta (Button, 1971). These figures imply that the residence time of hydrocarbons in the water column is about 10 to 100 years.

The most important measurement required for environmental management is the distinction between biogenic and petroleum hydrocarbons. Direct differentiation is not possible at the present state of the art, but indirect inferences have been made. Two indirect approaches in particular have been attempted. Monaghan et al (1974) and Brown and Huffman (1976) relied on the determination of the hydrocarbon/lipid ratio in a clean environment (about 0.2), then attributed increases in the ratio to petroleum pollution. Barbier et al (1973) compared the spectrum of hydrocarbons in the water column to those in phytoplankton, attributing differences to the presence of petroleum hydrocarbons. Clearly both methods have many unknowns, and different conclusions have been reached. Brown and Huffman (1976) felt that most of the hydrocarbons they measured were anthropogenic, while Barbier et al noted the similarity in hydrocarbon composition of seawater and algae, and hypothesized that most oceanic hydrocarbons are natural products. The issue remains

unresolved.

Zsolnay (1973c and 1974b) has noted a correlation between chlorophyll and hydrocarbon concentration, suggesting that a portion of the regional differences in hydrocarbon concentrations is due to differences in photoplankton populations, rather than purely due to anthropogenic input. Boehm and Quinn (1973) have noticed that dissolved organic compounds in the seawater increase the solubility of alkanes but not aromatics. Anderson et al (1974) have shown that the spectrum of dissolved hydrocarbons present in the water column differs from the polluting oil by being enriched in aromatics relative to paraffins. Brown and Huffman (1976) speculate that, of hydrocarbons entering the water column, cycloalkanes are the most persistent, and aromatics the least (alkanes not considered). All of these considerations complicate the determination of the source and fate of dissolved hydrocarbons in the environment.

Experimental Method

The experiment was conducted in floating polyethylene enclosures 2 m in diameter and 15 m deep, filled with about 60 tons (60,000 l) of seawater. These large bags were available as a part of the Controlled Ecosystem Pollution Experiment (CEPEX) which is being conducted in Saanich Inlet. They are termed Controlled Ecosystem Enclosures (CEE's) and have been described by Parsons (1974) and Takahashi et al (1975). Two columns were used in this experiment, one of which was treated with oil ('G'), and the other kept as a control ('F').

Oil was added to enclosure G in the following manner: carboys containing 17 liters of seawater from the CEPEX site were stirred for 24 hours with 35 ml of #2 fuel oil (American Petroleum Institute standard); the phases were allowed to separate for 12 hours; then the water extract from each of 10 carboys was pumped through a diffusion ring into the water column of the enclosure. No surface slick resulted from this addition, indicating that the petroleum hydrocarbons remained dissolved. The date of addition was 11 June, 1975. A second addition of fuel oil was made a week later (20 June) following the same procedure except that 10% ethanol in seawater was used to increase the solubility of the oil, and so to decrease the volume of addition required. All of the oil was added at 8 meters using the diffusion ring; in this case a small amount of oil came to the surface as a slick, which disappeared in a few minutes.

Sampling:

Prior to the addition of the spike of fuel oil, sampling was conducted to establish the background levels. After the addition, both the control bag and the polluted bag were sampled on a regular basis at 1, 7, and 13 m depth. The program of sampling was repeated for the second spike of fuel oil. Samples were obtained by hand-lowering a Niskin bottle into the CEE's. The water samples were drained into 4 liter glass bottles with teflon-lined screw caps,

preserved with ca. 100 mg mercuric chloride, and stored in a cooler at 5°C. (Prior to use, the four liter bottles had been rigourously cleaned with chromic acid, distilled water, methanol, and pentane.) A larger volume of sample was desired for the gas chromatographic analyses. 20 liter carboys were filled using a diaphragm pump, preserved with HgCl₂, and stored in a cooler. Sediment samples were collected from the bottom of the CEE's every three days for hydrocarbon analyses, so that the extent of hydrocarbon sedimentation could be ascertained. Finally, an extensive program of biological and nutrient sampling was conducted by the staff of the CEPEX experiment. The parameters measured included: composition and abundance of major phytoplankton and zooplankton populations; nitrate, phosphate, and chlorophyll determinations.

Hydrocarbon Analyses:

Fluorescence analyses were conducted on the 4 liter samples collected with Niskin bottles. The samples were analysed by extracting 1.5 liters of water with 90 + 60 ml of methylene chloride in a separatory funnel. The extract was rotoevaporated to dryness, the residue taken up in 1 ml of hexane, and 0.5 ml injected into a high-pressure liquid chromatograph with a silica gel column (see Table 29 for operational parameters). The function of the column was to strip polar material, such as chlorophyll and other pigments, from the sample and pass only the hydrocarbons. The elutant from the column passed through an ultraviolet detector which measured absorbance at 263 nm, and through a fluorescence detector which excited at 308 nm and measured the emitted light (The fluorescence wavelengths are optimum for chrysene and suitable at 383 nm. for the detection of most oils - Johnson et al, 1973.) The fluorescent response was recorded on a Honeywell recorder, and quantified by calculating the peak area and comparing to a chrysene standard.

The samples for gas chromatographic analysis were extracted with pentane in a continuous liquid-liquid extractor which allowed large volumes to be extracted using moderate amounts of solvent (for a description of the

TABLE 29: Instrumental Parameters for Hydrocarbon Analysis of Seawater

Fluorescence Analyses

Instrument:	Waters Associates model 202/401 liquid chromatograph inter- faced with a Perkin-Elmer model 204 fluorescence spectro- photometer by a flow-through cell (0.1 ml internal volume)						
Column:	150 mm x 1.8 mm column packed with 5 micron silica gel (LiChrosorb Si-60, E. Merck Co.)						
Solvent:	hexane						
Flow rate:	1.2 m1/min						
Pressure:	Approx. 2000 psi						
Chart speed:	0.5 inch/min (Honeywell recorder)						
Fluorescence s	pectrophotometer settings: exciter wavelength 308 nm analyser wavelength 383 nm						

Gas Chromatographic Analyses

Instrument: Hewlett-Packard model 5710A

Column: 7' x 1/8" 2% OV-7 on 80/100 mesh Chromosorb W (HP)

Carrier gas: He

Temperature	programming:	initial	100°C (2 min)
		final	270°C (4 min)
		rate	8°C/min

Chart speed: 0.5 inch/min

Detector: FID

Sensitivity: variable

extractor see Werner and Waldichuk, 1962). For each carboy sample, two 5-7 liter subsamples were extracted with 300 ml pentane, the pentane rotoevaporated to dryness, and the residue taken up in 1 ml of hexane. 0.5 ml was then injected into the high-pressure liquid chromatograph with the same operating parameters and column used for the fluorescence analyses. The elutant from the liquid chromatograph was collected, rotoevaporated, the residue taken up in 500 ul of CS_2 , and 100 ul injected into the gas chromatograph (operating parameters as given in Table 29). Peaks in the gas chromatograms were identified by retention times, and quantified by peak heights relative to an internal standard.

Finally, a few infrared measurements were made to determine total nonvolatile hydrocarbons in a manner similar to that described by Brown et al (1973). Four liters of seawater were extracted with spectrograde CCl_4 ; the extract was concentrated to 1 ml and treated with activated Florisil to remove nonhydrocarbon material. Measurements were made on a Perkin-Elmer infrared spectrophotometer (Model 467) at 2930 cm⁻¹, which gave a measure of the aliphatic hydrocarbons present. The response was compared with fuel oil standards to give a measure of total hydrocarbons.

Discussion of Analytical Methods

One of the purposes of this investigation was to test the validity of the most common analytical methods for determining hydrocarbons under controlled conditions. The fluorescent and gas chromatographic methods were scrutinized to determine their reliability and to identify weaknesses and problems that occur in their practical application.

Fluorescent Method:

1) Sampling: Gordon et al (1974) found that open Knudsen samplers were not suitable for hydrocarbon sampling, since they got the same fluorescent values whether or not they tripped the bottles. Undoubtedly some hydrocarbon

material adsorbed on the walls of the containers when they passed through the surface film. The remaining fluorescence probably was due to plasticizers extracted from the bottles when they were rinsed with solvent. In this experiment an ordinary 5 liter Niskin bottle was used to obtain samples as per Gordon et al, but the bottle was not rinsed with solvent after obtaining a sample. The data indicates that no significant contamination occurred during sampling. This can be seen from the background samples, which are uniformly low, and from the surface samples taken after the second spike (see Figure 46). The surface samples are all low in hydrocarbons, while deeper samples have much higher values. This result would not be possible if contamination of the bottle was occurring as it passed through the surface film. Two factors probably contributed to the successful use of the Niskin sampler in this experiment: the levels of hydrocarbons tended to be high compared to those being measured by Gordon et al, due to the spike of oil added; and the sampler was not rinsed with solvent, which minimized contamination by plasticizers in the P.V.C. plastic.

2) Temperature of extraction: some preliminary observations indicated that the temperature of extraction influenced the extraction efficiency. Although this relationship was not rigorously investigated, all samples were extracted at 5° C to eliminate this variable and improve the precision of the results.

3) Formation of emulsions: the extraction of samples of CEPEX water resulted in the formation of a water-in-solvent emulsion which would not separate despite prolonged standing in a separatory funnel. These emulsions apparently result from natural emulsifiers which are present in the water column in biologically productive areas (the effect does not occur in off-shore samples). A glass wool plug was placed in the spout of the separatory funnel to physically break the emulsion. Some water was still present in the eluted dichloromethane, and this was merely left in the roundbottom flask after
rotoevaporation, where apparently it did not interfere with the analyses.

4) Use of heat gun: water from the emulsion described above was left in the roundbottom flask after rotoevaporation, together with the residue of the extracted material. This water was driven off with a heat gun until it was found that the heat gun had a drastic effect on the fluorescent material. 90 seconds exposure to the heat gun reduced the fluorescence to 2% of its original value. The use of the heat gun was discontinued, all the analyses were repeated, and water was allowed to remain in the roundbottom flask after rotoevaporation. Apparently it did not interfere with analyses.

Time of Exposure	Fluorescence	
to near gun	(ng/i chrysene equiv.)	
0	561	
45 sec	101	
90 sec	13	

5) Solvents: Low blanks for dichloromethane (residue of 150 ml) were consistently difficult to obtain. Repeated distillation often resulted in <u>increasing</u> contamination of the solvent with fluorescing material. Eventually, Caledon glass-distilled solvents were purchased, and these gave low blanks without requiring distillation.

6) Glassware: glassware was cleaned in chromic acid, rinsed with distilled water, and washed with high grade acetone. Before use, it was rinsed once with spectrograde hexane. Leaving out any of these steps resulted in contamination problems. The ground-glass area was the prime source of contamination.

7) Syringe carryover: a 1 ml syringe was used to inject into a high-pressure liquid chromatograph. Contamination from a syringe previously used on a concentrated sample can carry over for up to 10 injections. A single syringe contamination resulted in erroneously high values for 5 CEPEX samples, and possible contamination of six more, all of which had to be repeated. Great care must be taken in syringe handling and cleaning.

Linearity of response: during these analyses a great deal of 8) information was lost because of a non-linearity in the slide wire driving the recorder pen. As a result of this problem, a careful check of the linearity of the instrumental response was made. Figure 39 shows the response as a function of the chrysene concentration injected: the response was very linear on the two sensitivities checked. Peak area, but not peak heights, were conserved when switching from one range to the other.

FIGURE 39: Linearity of Fluorescence Response for Determination of Hydrocarbon Concentrations





9) Precision of results: Figure 39 implies good precision of response, but over periods of time longer than a few hours the precision of the fluorescence method was not particularly good. The standard concentration of chrysene used to calibrate the CEPEX measurements gave disc integrator response that varied between 14.3 and 17.8 over the nine days in which the measurements were performed. The largest variation for a single day was almost as large: 14.9 to 17.8. The mean and standard deviation for 10 determinations over 9 days was 16.2 ± 1.2 . Some of the uncertainty may have resulted from variations in the volume injected by the syringe, but the most likely source of variation is the light source. It is possible that a double beam instrument would be required to improve the precision of the results.

10) Column performance: from time to time the column interacted with samples in such a manner that delayed peaks were detected 5 to 15 minutes after the main fluorescent peak. The area of the secondary peaks was sometimes substantial, and interfered with subsequent analyses. The secondary peaks complicate the analyses, and raise the question whether or not the first peak is the only one which should be quantified. Further work is required to clarify this matter.

11) Chrysene standard: all measurements of oil in the CEPEX bags were made in terms of chrysene equivalents. Chrysene was used as a standard because it was in general use at the laboratory as a standard for all oceanic determinations of hydrocarbons. It was originally chosen as a standard for several reasons: a pure organic compound - available in unlimited supply and exhibiting an unaltering fluorescent spectrum - was desirable to facilitate comparisons of oil concentrations. Since heavy oils generally show a fluorescence excitation maximum in the region 290-330 nm and an emission maximum in the region 360-400 nm, the standard was chosen to have a similar response. Chrysene fluoresces in the right range and is readily available at low cost

in high purity, so it was chosen as a standard. 1 ng/l chrysene is the fluorescent equivalent of $118 \pm 3 \text{ ng/l}$ of #2 fuel oil.

12) Simultaneous U.V. detection: the elutant from the liquid chromatograph passed through an ultraviolet as well as a fluorescent detector. The ultraviolet response was monitored, but it was difficult to get good blanks for both the U.V. and the fluorescent detectors. The results were not consistent and are not presented here. However, with some development, both detectors could be used simultaneously.

Gas Chromatographic Analyses:

The problems with the gas chromatographic analyses were never fully resolved, and the results obtained were without pattern or significance. The reasons for this dismal performance are discussed below.

1) Extraction: in order to perform extractions on large quantities of water without using correspondingly large concentrations of solvent, a continuous extraction apparatus was constructed similar to that described by Werner and Waldichuk, 1962. The apparatus required about 300 ml of solvent which was refluxed through a steady flow of sample water (counter current extraction). Although the published efficiencies of the extractor were quite high (44% - 75% depending on conditions) it was found that the extraction efficiencies for the particular parameters used in this experiment were very low - about 5%. This low extraction efficiency, which was not noticed until most of the analyses had been performed, presumably was a major factor in the poor results obtained.

2) Solvent purity: 300 ml of pentane were used in the extractions. The chromatogram of an undistilled pentane blank is shown in Figure 40. A large contaminating peak eluting at 252°C is evident (labelled 'S'). Distillation of the pentane did not improve its purity, but instead increased the contamination, adding several more peaks and increasing the size of the 'S' contaminant. Distillation was abandoned, and undistilled pentane was used in the extractions. The 'S' peak was removed by the silica gel column (see Figure 42) indicating that it was not a hydrocarbon.

FIGURE 40: Effect of Distillation on Solvent Blanks

Pentane blank (residue of 300 ml): a) prior to distillation



b) after distillation



3) Distilled water blank: using the extraction apparatus to extract distilled water gave the chromatogram in Figure 41. The solvent peak 'S' is again apparent, as well as two additional peaks. One was apparently present in the distilled water, while the other (labelled 'R') was a contaminant either from the atmosphere or the apparatus, and appeared in all extracted samples.

FIGURE 41: Distilled Water Blank



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4) Effect of column pretreatment: Figure 42 shows the effect of first injecting the sample into the high-pressure liquid chromagraph (silica gel column) as opposed to direct injection into the gas chromatograph. The column removes the contaminating peaks R and S, and enhances the aliphatics relative to the envelope.

FIGURE 42: Effect of a Preparative Silica Gel Column on Gas Chromatographic Analyses

CEPEX carboy sample #4B: a) without silica gel column preparative step

b) with silica gel column

5) Replication of analyses: Figure 43 shows duplicate analyses of a CEPEX water sample. Despite the most careful attention to possible sources of contamination, the chromatograms are wildly different. Use of the preparative HPLC step reduced the variations by removing some contaminants, but nevertheless there was never, in eleven sets of duplicate analyses, a clear similarity between chromatograms. The reasons for these rather spectacular variations in results are not understood.

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FIGURE 43: <u>Replication of Gas Chromatographic Analyses of Water Samples</u>a) Subsample A, CEPEX carboy #2.



b) Subsample B, CEPEX carboy #2.



6) Contamination: the cruelest insult came from the final sample analysed, which was from the control enclosure F. This sample, which was supposed to be hydrocarbon-free, gave a clearer alkane spectrum than any of the samples taken from the polluted enclosure. The source of this contamination, which found its way to the sample despite the most scrupulous clean-room conditions, is indeed perplexing.



This experience with gas chromatographic analyses emphasizes the difficulties of analysing water samples. Some of the problems undoubtedly result from the extraction apparatus, which was not very successful. The very irregular nature of the results, and the constant contamination problems cannot be accounted for purely by the extraction apparatus, however. Some possible contributing factors are: the sampling procedure, which involved pumping the water to the surface using a diaphragm pump; rotoevaporation, which may have caused varying losses of lighter components; and contamination from the atmosphere during the continuous extraction procedure. Beyond these three explanations, it is difficult to see how so much contamination and variability occurred, since all glassware was thoroughly cleaned, and all manipulations and transfers were carefully performed in a 'clean room'.

Results

A gas chromatogram of the #2 fuel oil used in the experiment is given in Figure 45, together with a chromatogram of the seawater extract of the oil which was added to CEPEX enclosure. The results of the fluorescent analyses are presented in Figure 46, and in Table 30.



MN = methylnapthalene. Identification of peaks is based on retention times and is tentative.

Note enrichment of napthalene compounds relative to paraffins in the seawater extract.



FIGURE 46: Fluorescence Results for CEPEX Hydrocarbon Experiment

TABLE 30: Results of Fluorescent Determinations of Hydrocarbons in the CEPEX Enclosures

First Experiment

Location	Depth	Time after Contamination	Value (ng/l chrysene	equiv.)
G	7 m	before	80.5	
	,	15 min	586	
		$1\frac{1}{2}$ hr	452	
		$3\frac{1}{4}$ hr	418	
	1	7 hr	356, 339	
		15] hr	198, 306	
		25 hr	173	
١		4 days	117	
G	13 m	25 hr	29•7	
outside CEE	7 m	5 days	17.7	

Second Experiment

Location	Depth	Time after Contamination	Value (ng/l chrysene	 equiv.)
G	lm	4 hr	283]
		21 hr	114	
		36 hr	115	
		55 hr	119	
		3 days 3 hrs	120	
		7 days 5 hrs	70	
G	7 m	before	117	
		0 hr	1898	
		4 hr	1990	
		11 hr	2680	
		21 hr	1325; 1708	
	·	36 hr	1375	
		55 hr	1213	
		5 days	684, 737; 561	
		7 days, 5 hr	550, 476	

.

TABLE 30 continued:

Second Experiment ((continued)	
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Location	Depth	Time after Contamination	Value (ng/l chr	ysene equiv.)
G	13 m	4 hr	246	
		21 hr	1710	
		36 hr	1115	
		55 hr	1798	
		3 days 3 hr	802	
control	7 m	4 hr	72	
•	1 m	7 days 5 hr	41	
outside	7 m	7 days 5 hr	33	

#2 Fuel Oil Equivalent

Determination #	Conversion factor for #2 fuel oil in hexane	
1	118.6 disc response chrysene	
2	115.5 "	
3	113.7 "	
4	120.8 "	

Average: Chrysene fluoresces 118 ± 3 times as much as the same concentration of fuel oil, when both are dissolved in hexane.

Discussion of Results

The chromatograms in Figure 45 show a pronounced enrichment of aromatics relative to alkanes in the water extracts of the #2 fuel oil. In particular, the ratio of methylnapthalenes to C-13 and C-14 alkanes increased from 0.80 in the fuel oil to 3.5 in the water-soluble fraction, an increase of 440% (this aromatic enrichment in the soluble fraction has been reported by others - see Chapter 3). The gas chromatographic analyses of CEPEX water samples were too unreliable to provide further information.

The background level of fluorescence in Saanich Inlet was 49 ± 27 ng/l chrysene equivalents, which compares with 18 ± 6 ng/l in the open Pacific (see Table 28). The spike of oil clearly shows in Figure 46: the maximum value obtained after the first addition was 586 ng/l chrysene equivalents, which corresponds to 69 ug/l of #2 fuel oil (the infrared method indicated a total of 50 ug/l of fuel oil). The hydrocarbons disappeared exponentially, and the curve can be parameterized by the following relation:

$$y = 452 e^{-.054t}$$

where y is the fluorescence response in ng/l above background, and t is the time after contamination in hours.

The coefficient of determination for this curve fit is 0.89 . The 'half-life' of the hydrocarbon spike was about 13 hours.

For the second addition of hydrocarbons, ethanol was used to increase the solubility of the oil, so that the added spike was about 100 times as concentrated as the first spike. The addition was made entirely at 8 m using a diffusing ring. The maximum concentration, 2680 ng/l chrysene equivalents, was not observed at 7 m until 11 hours after addition, presumably because of the delay in the oil mixing upwards (on the basis of equal distribution of the added oil throughout the water column of the enclosure, a peak value of 1370 ng/l is expected). Again the disappearance of the hydrocarbons was approximately exponential, following the relation: $y = 2050 e^{-.011t}$ (symbols as before) The coefficient of determination for this curve fit was 0.90. The 'half-life' of the peak was 63 hours.

The consistently low concentrations of hydrocarbons at 1 m after the second addition pose an interesting question: since all the oil was added at 8 m, it is possible that no oil was advected or diffused into the uppermost waters of the enclosure; alternatively, oil may have been evaporating as quickly as it reached the surface waters. On the basis of this data alone, it is not possible to distinguish between the two possibilities. However, using the model of gas exchange between ocean and atmosphere developed by Liss and Slater (1974) it is possible to get an estimate of the residence times of dissolved hydrocarbons (see Appendix C for full discussion). The half lives of polyaromatic fluorescing compounds at 1 m depth at the temperature of the water in the bags (about 20°C) would be about 1 day. (See Table 34 in Appendix C). This rate of exchange with the atmosphere is probably sufficient to keep the hydrocarbons which advect to the surface of the bag at a consistently low level. The half life increases linearly with depth (see Appendix C) so at 7 m the half life is about 7 days. Since the half life of the hydrocarbon spike was 3 days, other processes must have contributed to the removal of the oil. The hydrocarbon levels at 13 m remained low for least five hours after addition of the oil, but after 21 hours, had increased above the levels at 7 m. This result suggests that sedimentation of hydrocarbons was occurring. Ultraviolet examination of the sediment by Dr. R. Lee (see Lee et al, 1975) detected milligram quantities of naphthalenes after 4 days, whereas no naphthalenes were detected in the control bag sediment, thereby providing clear evidence that significant rates of sedimentation were occurring. Fluorescent analyses of the sediment gave high values in both the control and the hydrocarbon enclosures, so that the

degree of sedimentation of hydrocarbons could not be ascertained effectively in this manner.

To determine the extent of microbial activity, water samples were taken, and microbial degradation rates were measured using radiolabelled hydrocarbons. (This work was performed by Dr. Lee - see acknowledgements). After the addition of oil, degradation rates increased dramatically for most of the lighter hydrocarbons. For example, the napthalene degradation rate jumped from 0.1 to 2.5 ug/l/day. For the large polyaromatic compounds the change was not so pronounced. Fluorene and benzopyrene were not degraded before addition of the oil; after additon, degradation of benzopyrene, but not fluorene, was detectable. The chrysene degradation rates were not determined, but probably were also low. Microbial degradation, therefore, was important in the overall removal of the hydrocarbons, but its importance in the degradation of the polyaromatic compounds detected by the fluorescence method is less clear. It is possible that larger organisms fuch as zooplankton may have played a role in the degradation of these compounds (Lee, 1975).

Conclusions

1. High pressure liquid chromatography combined with a fluorescence detecter provides a reliable method of determining the concentrations of fluorescing hydrocarbons in seawater as long as stringent precautions are taken to guard against contamination.

2. Although there is some ambiguity in the data, it appears that exchange with the atmosphere was the dominant process in the removal of dissolved hydrocarbons from the uppermost meter or two of the water column, while in the deeper water microbial degradation and sedimentation were the most important processes.

3. The disappearance of the oil approximately followed an exponential decay curve: the half-life for a large dissolved oil spike was about 3 days (less for a smaller spike) so that 95% removal occurred within 2 weeks.

SUMMARY OF FINDINGS

Controlled Weathering Experiment:

 Photo-oxidation is not an effective weathering mechanism for oil in a moderately thick (3 mm) layer.

2. The rate of evaporation of volatile components from a layer of oil is very strongly dependent on the sunface/volume ratio, varying over at least 3 orders of magnitude from a thin film to a 3 mm layer. Apparently, reduced surface area may result in less absolute loss no matter how long the oil is exposed.

3. The effect of evaporation alone is not sufficient to produce tar lumps and cause sinking of crude oil - microbial degradation is required.

Pelagic Petroleum Residues:

4. On the basis of 2092 surface tows between 1967 and 1975 the following conclusions were reached about the distribution of tar in the Pacific:

- a) Petroleum residues are not a significant pollutant in the surface waters of the South Pacific.
- b) In the Northeast Pacific occasional contamination of surface tows occurs (average concentration is 0.03 mg/m²).
- c) The Northwest Pacific is the most contaminated area, particularly in the Kuroshio current system between 25° and 40° N. The average concentration in this area is 2.1 mg/m², which represents a standing stock of 25,000 metric tons of tar.

5. Plastic is a widespread contaminant on the North Pacific Ocean, but generally in lower quantities than tar. It usually occurs as round, colourless pellets weighing 20-50 mg each.

6. The Beaufort Sea in the Arctic Ocean is not contaminated by tar. Plastic, however, is a common contaminant on the beaches.

7. The distribution of the tar in contaminated areas is patchy, so that replicate tows catch widely varying quantities of tar which approximately follow a log normal distribution. This patchiness cannot be explained on the basis of windrows, and probably is a result of the tar gradually spreading out from point sources. The tar distribution may be best represented mathematically by Newmann's contagious distribution.

8. Most tar particles were in the 1-5 mm range, but most of the tar mass was in particles in the 5-10 mm range. The largest tar lump was 5 cm in diameter and weighed 34 g.

9. The average water content of the tar was 22% by weight, which is considerably less than the amount of water in a fresh water-in-oil emulsion (80%).

10. Tar samples stored for a year and a half by refrigeration or in formalin did not show any detectable change in composition.

11. Surface tows and beach surveys made in local British Columbia waters in an area of heavy urban and industrial development (including three oil refineries) detected no petroleum residues, implying that the source of tar is not from run-off or refinery outfalls.

12. High iron concentrations of greater than 1 ppt were found in 77% of the 104 tar samples analysed (iron in crude oil does not exceed 0.1 ppt). Nickel concentrations, however, were not detectably above those in crude oil, so general metal enrichment did not occur. The anomalously high levels of iron strongly imply an anthropogenic source of the tar.

13. Gas chromatographic analyses provided a second and more precise indication of the source of the tar. 88% of the 82 samples analysed contained long-chain, waxy paraffins of higher carbon number than C-25 in much greater abundance than they are normally found in crude oil. These longchain paraffins are typical of the sludge discharged by tankers when they clean their tanks after carrying crude oil. This tanker sludge is probably the source of most of the pelagic tar in the Pacific. 14. The chemical analyses, combined with the distribution pattern of the tar, imply that most of the pelagic tar contamination in the Pacific originates from tankers on the very large Middle East to Japan tanker route, then becomes entrained in the Kuroshio current south of Japan and creates a plume of contamination which extends downstream for 7000 kilometers across the Pacific.

15. The standing stock of tar in the Northwest Pacific (25,000 metric tons) represents a loss of only about 0.01% of the oil carried on the Japanese tanker route. However, because of the vast quantities being transported and the persistance of the tarry fraction, even a very small percentage loss results in significant contamination of the surface waters.

16. Photo-oxidation does not detectably contribute to the degradation of tar. The role of dissolution is uncertain, but from theoretical considerations is presumed to be small.

17. Evaporation removes compounds up to the volatility of pentadecane (C-15) from the tar: 73% of the 82 samples analysed had lost all n-alkanes up to C-15. Above C-15 the evaporative losses become very slow and the process is usually overtaken by microbial attack.

18. At least 33% of the tar samples analysed by gas chromatography showed clear evidence of microbial degradation.

19. Small particles of tar did not show any tendency to be further affected by evaporation or microbial attack than larger lumps. No gradient of lighter compounds between the inside and outside of a large tar lump could be detected, indicating that evaporation is not diffusion-limited.

20. Both evaporation and microbial degradation increase the density of the tar particles, and this effect combined with the weight of the fouling community that develops, results in the eventual sinking of the tar into the depths of the ocean. 21. Tar particles provide the biota of the surface of the ocean with a substrate on which they can live and reproduce.

22. Tar occurs as a pollutant on a very large portion of the world's beaches, including nearly all of the popular seaside resort areas. The presence of the tar severely reduces the recreational and esthetic value of sandy beaches.

Intertidal 0il:

- 23. Microbial degradation was responsible for the chemical weathering of the spilt oil at Reserved Bay. Evaporation played only a minor role; photo-oxidation and dissolution did not appear to have any effect.
- 24. Microbial attack took approximately 1 year to complete the degradation of the paraffins in the spilled oil, leaving an asphaltlike residue on the stones of the beach. The asphaltic residue was apparently more susceptible to physical weathering than the original oil.
- 25. The combined effects of chemical and physical weathering removed about 95% of the spilled oil from the cove over the period of one year.

Benthic Oil:

26. Heavily-oiled samples should be preserved in formalin if they are to be stored for any length of time prior to analysis, since the formalin not only prevents bacterial alteration, but also eliminates evaporative losses which can occur if the samples are stored by refrigeration.

- 27. The degradation of the benchic crude oil resulted almost entirely from microbial action. Evaporation had no opportunity to act; dissolution was ineffective; and photo-oxidation was not possible because of the low energy and intensity of the light reaching the sediment.
- 28. The benthic petroleum samples were slow to degrade: the oil remained unchanged in chemical composition for at least six months. Even after 16 months the paraffins, which are the fraction most susceptible to attack, were only partially degraded.
 29. The pattern of degradation appeared to consist of an initial delay while bactericidal components were dealt with, followed by microbial degradation of the reamining oil at roughly the same rate as in the intertidal experiment one year to remove the paraffin components.

Oil in the Water Column:

- 30. High pressure liquid chromatography combined with a fluorescence detector provides a reliable method of determining the concentration of the fluorescing hydrocarbon compounds in seawater, provided stringent precautions are taken to guard against contamination.
- 31. It appears that exchange with the atmosphere was the dominant process in the removal of fluorescing hydrocarbons from the uppermost meter or two of the water column, while in the deeper water (below 7 m) microbial degradation and sedimentation were the most important processes.
- 32. The disappearance of the oil approximately followed an exponential decay curve: the half-life for a large dissolved oil spike was about 3 days (less for a smaller spike) so that 95% removal occurred within 2 weeks.

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CONCLUSIONS

The research presented in this thesis provides some first order approximations of the rate at which, and the mechanisms by which, petroleum degrades in various marine environments under natural conditions.

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For the pelagic environment, the study of floating petroleum residues in the Pacific is revealing because, in contrast to the Atlantic, there is only one plausible source for most of the tar. This considerably simplifies the situation. Because of the very large size of the Pacific, proportionately less of the tar ends up on beaches, and therefore the evidence of microbial attack and eventual sinking is clearer than in other areas. The rate of microbial attack was not directly determined, but from the distribution pattern it is evident that some of the tar must remain afloat for periods on the order of one to two years. Thus the mechanism by which the pelagic environment deals with petroleum residues is a rather slow process, so that even a small percentage loss of petroleum cargoes results in significant and widespread contamination of the surface waters.

The study of oil in the intertidal environment was a unique opportunity to observe the degradation of a reasonably large (by experimental standards) quantity of oil under natural conditions. The opportunity was unusual since, in most areas, public use of the beach areas requires immediate clean-up of oil spills. At Reserved Bay the area is sufficiently uninhabited that the oil remained undisturbed by clean-up crews and the general public. The samples from the bay show very clearly the advance of microbial 'grazing' of the paraffin compounds in the fuel oil. The combined action of the microbes and abrasive weathering removed 95% of the oil on the beach over a period of a year, leaving an unobtrusive and essentially inert residue of asphalt on the stones of the beach. Even though there are a great many variables to be considered, this first order measurement of natural rate of oil removal is useful in determining the extent of clean-up that is required after an oil spill.

The measurements in the benthic environment of the rate and means of the degradation of petroleum are the first measurements of any sort to be published. The results are important primarily in assessing the propriety of using sinking agents to treat oil spills. The experiment shows that the degradation on the bottom, even under good conditions for microbial growth, is very slow to begin, with virtually no change in the composition of the oil occurring over a 6 month period . Such a slow commencement of the degradation process, if it is of general occurrence, would certainly weigh against the use of sinking agents.

The study of oil in the water column, while not as definitive a study as was hoped because of instrument difficulties and contamination problems, still did provide some indication of the rate at which, and mechanisms by which, hydrocarbons are removed from the water column. The relatively short life of a dissolved hydrocarbon spike in the water - a matter of one to two weeks for even the most persistent of the dissolved compounds - is in part a reflection of the very low levels at which hydrocarbons are soluble, and their preference to leave the water phase in favor of the atmosphere or adsoption on detritus.

In summary, the experiments described in this thesis show the slow but methodical manner in which the marine ecosystem deals with the intrusion of petroleum hydrocarbons, nearly always relying on the ultimate mineralizers, the microbes, to assimilate the non-volatile components of polluting oils.

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APPENDIX A: Conversion Factors and Quantities Useful in Oil Pollution Research

Conversion Factors

* These weight-volume conversions depend on the density of the oil. The stated conversions are for oil of specific gravity 0.86.

1 barrel	=	42 U.S. gallons	
	=	35 Imperial gallons	
	=	159 liters	
nautical mile	=	1854.4 m	
1 knot	=	0.514 m/sec	
1 mg/m^2	=	5.7 lb/sq. mile	
	=	0.14 ounces/acre	

Useful Quantities

Pristane and phytane ratios in various crude oils:

Crude oil	pristane/phytane	n-heptadecane/pristane	n-heptadecane/backgr.	N
Kuwait	0.48 + 0.01	5·75 ± 0·07	2.87 ± 0.06	6
Boscan	0.53 + 0.03	1.18 ± 0.02	0.80 ± 0.07	5
West Texas (high sulphur)	0.88 ± 0.01	1.65 ± 0.03	1.76 ± 0.02	4
La Rosa	0.89 ± 0.02	1.44 - 0.03	0.90 ± 0.02	- 5
Wilmington	1.37 ± 0.02	0.31 ± 0.01	0.34 ± 0.02	5
East Texas	1.41 ± 0.02	1.61 - 0.04	3.80 ± 0.06	7
South Louisiana	1.54 ± 0.04	1.48 ± 0.04	2.13 ± 0.06	6
Lagunillas	1.54 ± 0.06	0.81 ± 0.02	0.28 ± 0.02	10

N = number of gas chromatograms.

1

(from Ehrhardt and Blumer, 1972)

APPENDIX A continued:

	n-C ₁₇	Pristane	n-C18	Phytane
Alida	0.45	0.20	0.40	0.20
Beaver Lodge	0.60	0.20	0.55	0.15
Darius	0.55	0.10	0.50	0.15
Eola McLish	0.70	0.45	0.55	0.40
Eola Oil Creek	1.10	0.45	0.75	0.30
Hendricks	0.05	0.05	0.10	0.05
Kawkawlin	1.40	0.10	0.35	0.10
Lee Harrison	0.60	0.20	0.50	0.35
North Smyer	0.40	0.50	0.35	0.45
Penbina	0.65	0.50	0.55	0.25
Ponca City	0.85	0.40	0.55	0.20
Redwater	0.55	0.50	0.45	0.35
Swanson River	0.60	0.55	0.55	0.25
Teas	0.50	0.40	0.40	0.30
Vinta Basin	0.75	0.50	0.75	0.45
Wafra	0.05	0.10	· ·	0.15
Wilmington	0.10	0.25	0.15	0.20
AVERAGE	0.58+.35	0.32+.18	0.47 <u>+</u> .18	0.25 <u>+</u> .1

Pristane and phytane in various crude oils (% by volume):

(from Martin et al, 1963)

APPENDIX B: BIOLOGICAL EFFECTS OF OIL POLLUTANTS

The chemical complexity of oil and the biological complexity of marine ecosystems combine to make the study of oil pollution effects something of an experimental jungle. Oil composition, as has already been discussed, varies widely, both within the crude oils and between types of refined products. Bioassay experiments, the most straightforward way of studying biological effects, are influenced by differences between individuals in the same species, seasonal cycles of organisms, lifestage, and differences between species. Furthermore, bioassay techniques are not well standardized so that results may vary widely from one researcher to another.

Investigations into the more elusive sub-lethal effects must also account for narcotic, carcinogenic, and hormonal mechanisms. Ecological studies must deal with even more complex factors, such as relative effects of oil on competing species, effects of food chain dynamics, and stimulation as well as inhibition of productivity.

Research into the effects of petroleum began in the nineteenth century (Macadam, 1866), became more common in the 1920's, and blossomed after the Torrey Canyon oil spill in 1967. Much of the earlier literature consisted of bioassays with poor determination of concentration, state (dissolved, emulsion, or slick), and composition of the oil used. The investigations have become increasingly sophisticated, and now deal with complex sublethal effects such as interference with pheromone communication at concentrations in the parts per billion (ppb) range.

It is not the purpose of this review to summarize the very large amount of information available, but rather to present some generalizations which have been reached as a result of the accumulation of this broad spectrum of information.

The Relative Toxicities of Petroleum Compounds

The following generalizations have been made specifically for plants (see summary in Baker, 1971), but the same trends should also apply to animals because the mechanisms of toxicity are similar at the cellular level. 1) Toxicity increases with unsaturation, increasing from paraffins to naphthenes and olefins to aromatics (Havis, 1950). For example, 12-carbon paraffins are nearly non-toxic, 12-carbon olefins are quite toxic, and 12carbon aromatics are more toxic (van Overbeek and Blondeau, 1954). Similarly, toxicity of vapours to barley and carrot increases along the series hexane, hexene, cyclohexane, cyloxhexene, benzene (Currier and Peoples, 1954).

2) Within each class of hydrocarbons, the smaller molecules are more toxic than the larger. For example, within the paraffins, octane (C-8) and decane (C-10) are very toxic, while dodecane (C-12) and higher paraffins are nearly non-toxic (van Overbeek and Blondeau, 1954). As a consequence, refined products which tend to concentrate the lighter portions of crude oil (gasoline, light fuel oils) tend to be more toxic than crude oil. Conversely, petroleum products consisting of the residual heavy components of crude oil (fuel oil #5 and 6) are generally less toxic than crude oil; and weathered crude, which has lost its lighter, more volatile components, is generally less toxic than fresh crude oil. There are exceptions. Specifically, aromatics apparently increase in toxicity along the series benzene, toluene, xylene, trimethylbenzene, apparently because the increase in methyl groups promotes cell penetration (Currier, 1951). However, beyond this point increasing molecular size of aromatics results in decreased toxicity.

3) Within crude oils there is a correlation between the toxicity of the oil and the concentration of monocyclic aromatics that it contains (Ottway, 1971). Other compounds which have been implicated in the toxicity of crude oil are: acids and phenols, sulphur compounds (thiols, sulphides and thio-

phenes), and the carcinogenic polynuclear aromatic hydrocarbons (3,4-benzpyrene, 1,2-benzanthracene, chrysene, fluorene, phenanthrene, and dibenzthiophene). The concentrations of these toxic compounds in crude oil are given in Table 31.

TABLE 31: Percentage of Toxic Compounds in Crude Oils

(1)	Low molecular weight aromatics	0 - 8%
(2)	Phenols	0 - 0.1%
(3)	Acids	0 - 2%
(4)	Sulphur compounds	0 - 40%
(5)	Polynuclear aromatic hydrocarbons	0 - 0.1%

Effects at the Cellular Level

known.

The first work on the effect of petroleum compounds on cells was done as a part of investigations into using oils as herbicides, fungicides, and insecticides. These investigations established that, in acute oil toxicity, increased permeability of the plasma membrane is involved (van Overbeek and Blondeau, 1954). Apparently, hydrocarbon molecules of lower molecular weight are soluble in the membrane lipoproteins and cause swelling and disruption of the membrane. Increased permeability may result in increased uptake of water, or, in the extreme, may allow organic molecules to leak out of cell, causing collapse and death. The larger the size of the hydrocarbon molecules, the slower is the penetration into the membrane (van Overbeek and Blondeau, 1954).

Because of the wide variety of compounds in petroleum, it is not surprising that membrane disruption is not the only pathological effect. Manwell and Baker (1967) have demonstrated that crude oil interferes with the activity of enzyme systems from a wide variety of marine plants and animals. Powell et al (1970) observed hyperplasia in an estuarine bryozoan attributable to coal tar derivatives. Uncontrolled growth in ovicells apparently resulted from a carcinogen in coal tar. Goldacre (1968) reviewed work on the narcotic effect of the lower molecular weight paraffins on various cells, and suggested this was a result of interference with the cell membrane. He also speculated that hydrocarbon carcinogens cause permanent changes in the cell membrane leading to a breakdown in cell-cell communication and to cancer. Finnerty et al (1973), using electron micrographs, have shown that inclusion bodies or 'pools' of hydrocarbon are formed in the cytoplasm of bacteria, yeast, and fungi grown on pure hydrocarbons. The bacteria also undergo morphological transformations, specifically intracytoplasmic membrane synthesis and irregular formation of giant cells. The reasons for these bizarre effects are not

In summary, the effects of hydrocarbons on cells are not well understood, but most seem to be manifestations of interference with the membranes of the cell.

Effects at the Organism Level

The literature dealing with the effects of oils on various organisms is extensive. Papers deal with all forms of marine organisms from plankton to fish and birds, and with a variety of types of oils. However, the results sometimes are contradictory, and frequently are not comparable with one another because of differing test conditions. No attempt to completely survey this literature is made here. Literature reviews are available: Nelson-Smith (1970), Nelson-Smith (1972), and Butler et al (1974). Table 33 lists some of the numerical results which have been obtained by the authors reviewed in these literature surveys, to give some idea of variety and extent of the research. This table has been updated with some more recent results, but does not purport to summarize all the information available, much of which does not fit into a numerical or tabular format.

The effects of oil on organisms can be grouped under a few mechanisms. Each of these will be briefly reviewed.

Smothering and Mechanical Damage:

Damage from crude and residual oils is primarily due to mechanical interference and smothering of organisms. Smothering mainly affects sedentary intertidal organisms such as macroalgae, barnacles, limpets, and mussels (see, for example, Chan, 1973 and 1975). Birds, particularly diving birds such as auks, suffer from mechanical damage. Their plumage is oleophilic, and, once contaminated, it loses its insulative properties. Death occurs primarily from exposure. The diving birds have very low reproductive rates, with the result that their populations have been severely depleted in some areas of the world (Clark, 1968; Bourne, 1968).

Poisoning:

Dissolved and emulsified hydrocarbons are toxic to a wide variety of

marine organisms. Toxicity is a function of composition as has been discussed: for example, high concentrations of low boiling aromatics are lethal to almost every species, whereas the high boiling paraffins are essentially non-toxic.

Quantitative investigations of the poisonous levels of oil have usually taken the form of bioassay experiments, many of which are summarized in Table 33. These bioassay experiments suffer from several chronic problems. Firstly, the experimental techniques frequently vary widely, making comparison of results difficult or impossible. Typical differences in experimental technique involve the method of measuring the concentrations of the oil, the method of exposing the organisms to the oil (surface slick, emulsion, dissolved) and the environmental conditions of exposure (running sea water, static water, nutrients added, temperature, etc.). Secondly, the concentration of the oil to which the organism is actually exposed is frequently not determined, and instead only the amount of oil added is given. Thirdly, the oil composition is frequently not characterized beyond 'crude' or 'no. 2 fuel oil', so that the nature of the oil components affecting the organisms is unknown. The reason for the last two problems is the difficulty of performing the necessary chemical analyses, which demand more skill and equipment than the actual bioassay experiment. Two papers which present bioassay results with thorough chemical analyses are Battelle (1973) and Anderson et al (1974).

Within the limitations imposed by these problems, the various median tolerance limits given in Table 33 are indications of the levels at which various organisms are poisoned by petroleum compounds. In general, concentrations of greater than 100 ppm of dissolved or emulsified crude oil are required for lethal effects, although the more sensitive species and lifestages (especially eggs) may be killed by concentrations of 10 ppm and (rarely) less. Most sublethal effects have been observed over a concentration range of 0.01

to 10 ppm. Refined products vary in toxicity roughly in accordance with their low-molecular weight aromatic content. For example, Anderson et al (1974) notes that, for six test species, dispersions of #2 fuel oil, which is rich in aromatics, were two orders of magnitude more toxic than dispersions of crude oil.

Sub-lethal Effects:

The sub-lethal effect first observed was the narcotic effect of dissolved hydrocarbons. Organisms show markedly reduced activity levels, an effect which is usually reversible when the organism is placed in clean water (Marsland, 1933).

Of greater concern, because it occurs at much lower concentrations, is the interference of mineral hydrocarbons with chemical communication in the oceans. Hydrocarbons have been shown to interfere with chemoreception in crabs (Takahashi and Kittredge, 1973), with the feeding behavior of lobster (Atema and Stein, 1972), with chemotaxis in snails (Jacobson and Boylan, 1973), with bacterial chemoreception (Mitchell et al, 1972), and to cause avoidance behaviour in salmon (Rice, 1973). Marine animals make wide use of 'smell' or chemoreception for mating, feeding, and navigation (Lucas, 1947), so that the effect of adding the spectrum of hydrocarbons from crude oil to the natural environment, even at ppb levels, could have widespread insidious effects.

The presence of carcinogenic hydrocarbons in crude oil has been verified by analysis, and by the unfortunate experience of machine operators who have suffered skin cancer from lubricating oils (Bingham et al, 1965). Most knowledge of the carcinogenic effects of various hydrocarbons has been gained from investigations of the health hazard of smoking. However, hyperplasia, apparently caused by a dissolved petroleum carcinogen, has been observed in bryozoans growing near coal tar (Powell et al, 1970). The prime concern to anthropocentric scientists is human cancer through eating petroleum-contaminated sea foods. The threat is moderated by the wide occurence of the same carcinogenic hydrocarbons from natural sources, mainly natural fires (Zobell, 1971; Youngblood and Blumer, 1975), and by the fact that a good many species of animals and most aquatic bacterial populations can metabolize and degrade carginogenic hydrocarbons (Zobell, 1971).

Many other sublethal effects on organisms are possible, such as those affecting reproduction, growth, metabolism, and behaviour. Generally, the findings are too few and scattered to be worth summarizing here. More complete reviews of sublethal effects are available in Nelson-Smith (1970b), Nelson-Smith (1972), and Butler et al (1974).

Ecological Effects

All the investigations of oil and organisms already discussed have implications at the ecological, or community level. However, direct observations of the effects of oil on communities are necessary to understand these implications and unravel the consequences for competing species that live in a complex and balanced web of life. Oil damage to a species is akin to a traffic accident at rush hour: in addition to being tragic in its own right, it has consequences that reverberate through the transportation system.

Most knowledge of the broad scale ecological effects of oil pollution has come from experience with oil spills. Table32 lists five of the major oil spills with a quick sketch of the biological damage that resulted from each. More complete discussions are available in the original references. Oil spill studies usually suffer from poor baseline information and lack of controls. /An exception is the Milford Haven oil port in Britain (Cowell, 1971)/A. Also, they generally deal with the intertidal and perhaps the benthic environment; the pelagic environment is neglected, being too difficult to study in an oil spill-situation.

The biological damage mentioned in Table32 ranges from short-term effects on a few species (Arrow) to long-term effects on virtually all species (Florida). The key variable is the composition of the spilt oil, a matter we have already discussed. The ecological changes vary from kill, recruitment, and recovery (Santa Barbara); to the rather complex sequence of events that took place at the Tampico Maru spill. Here there was an immediate severe kill of most species. Two or three months after the initial damage, young kelp plants began to appear, and grew at an alarming rate, eventually choking the entire bay. The explosive growth was the result of elimination by the oil of the sea urchins and abalones which feed on young kelp, and of

the filter-feeding mussels and scallops which feed on the spores. The grazers and their predator, a star fish, gradually repopulated the area, and a balance was once again established after about six years (North et al, 1965). The reduction in species and the proliferation of some resistant types is typical of polluted areas, particularly those suffering from chronic pollution.

The pelagic environment is best investigated by the use of captive ecosystems, since in open ocean situations it is very difficult to follow a specific water mass. The difficulties of maintaining a captive ecosystem are formidable, but the facilities exist as a part of the International Decade of Ocean Exploration project CEPEX (Controlled Ecosystem Pollution Experiment) (Parsons, 1974). Investigations of the effects of hydrocarbons at the parts per billion level have shown stimulation of microflagellates at the expense of diatoms (Parsons et al, 1975). Diatoms are large, and lead to a short, efficient food chain, whereas the smaller microflagellates lead to a long food chain of low efficiency (Ryther, 1969). Broad scale low level pollution by petroleum could result in a shift towards a microflagellate-based food chain with severe consequences for pelagic fisheries. There are some indications that this process has begun to occur in the North Sea (Fisher, 1976; Reid, 1975).

In addition to the disturbance of the balance of species, the dynamics of hydrocarbons in the food chain must be considered. It has been demonstrated that chlorinated hydrocarbons (such as DDT), which are widely used as insecticides, are concentrated as they are passed up the food chain (Risebrough et al, 1967). For mineral hydrocarbons it has been shown that they are sequestered by bacteria (Finnerty et al, 1973), that they can be found in the gut of zooplankton (Conover, 1971), and that they are incorporated into the tissues of filter feeders (Stainken, 1975; Lee, 1975; Neff and Anderson, 1975). However, passage of hydrocarbons up the food chain is less

well-documented. Blumer et al (1970) state that hydrocarbons, once incorporated into a particular marine organism, are stable and may pass through many members of the food chain without alteration. They speculate that poisonous hydrocarbons may be concentrated by the food chain with harmful results for animals at the top (humans). However, no one has been able to document either concentration up the food chain, or resulting harmful effects. For example, Scarrat and Zitko (1972) found evidence of oil in benthic species after the Arrow spill, but could not detect concentration of the oil by the food chain.

Spill	Locality	Date	Oil Spilled	Detergent Used	Damage
Tampico Maru (North et al, 1965)	Baja California, Mexico	March 29, 1957	Diesel, total 9380 m ³ (1/3 lost on stranding)	None	Very high mortality recorded one month after spill. Six years later recovery almost complete. Rocky cove $\frac{1}{2}$ mile 3/4 cove blocked.
Torrey Canyon (Bellamy et al, 1967) (Smith, 1968)	Isles of Scilly off Cornwall, England	March 18, 1967	96,000 m ³ Kuwait crude	2½ million gallons	Damage greatly increased where detergent was used. Subtidal damage blamed on detergent. Detergent on approx. 140 miles English beaches, 75 mi. French.
Florida (Blumer et al, 1970)	Falmouth, Mass., USA	September 16, 1969	650-700 m ³ No. 2 fuel oil	None	95-100% mortality in inter- tidal and subtidal areas to 10 meters. June 1970, inter- tidal marsh grass still dead and no sign of recovery in intertidal areas.
Oil Rig (Straughan, 1971)	Santa Barbara Channel, USA	January 28, 1969	Santa Barbara Crude Oil	43,010 gallons over 13 months at sea	Mortality patchy in inter- tidal and confined to areas covered with thick oil. Recovery of algae and sea- grasses and resettlement of barnacles commenced in

TABLE 32: COMPARISON OF CIRCUMSTANCE AND DOCUMENTED DAMAGE OF OIL SPILLS

Con't.

than toxic.

1969. Oil smothering rather

Spill	Locality	Date	Oil Spilled	Detergent Used	Damage
Arrow (Thomas, 1973)	Chedabucto Bay N.S. Canada	February 4, 1970	10,000 m ³ Bunker C	None	Fisheries, oyster harvest, algae, eelgrass, all apparently unaffected. Clams suffered approx. 20% mortality and beds were
		· .			closed as a safety measure. Several thousand birds apparently killed. Oil smothering rather than toxic. Much asthetic damage and nuisance - some beaches immobilized for
	· .				years.
	· .				
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Definitions

- M. T. L. (Median tolerance limit): the concentration of toxic material in the water which is lethal to 50% of its occupants over a specified time (usually 24, 48 or 96 hours).
- ppm (parts per million): this is an ambiguous measure which indicates different concentrations depending on whether it refers to parts by weight, parts by volume, or a combination of the two. However, the density of most oils is within about 20% of that of sea water, which is generally less than the experimental error in the measurement of concentrations, so ppm is used throughout to facilitate comparison and may refer to either wt/wt, vol/vol, or mg/l, depending on the original literature source.
- * indicates the reference is taken from the extensive literature review in <u>Oil Pollution and Marine Ecology</u> by Nelson-Smith, and is not listed separately in this bibliography.

<u>Notes</u>

1) Some of the oil concentration values given in this table have little meaning. Crude and residual oils are no more than 100 - 500 ppm soluable in seawater (Anderson et al, 1974), so any concentrations greater than this must refer to emulsions, or to test arrangements in which slicks occur on top of the water phase.

2) When authors present a spectrum of results, the lowest concentration with toxic effects is quoted.

CRUDE OIL

<u>Concentration</u> (ppm)	Toxic Effect	Reference
.0103	stimulates photosynthesis about 10%	Gordon & Prouse (1973)
0.01	<u>Rhombus</u> (fish) eggs survived to hatching, but this was irregular and took longer than usual	Mironov (1971)
0.01	can impart oily taste to oyster Crassostrea virginica. The taint may persist for six months after heavier doses.	Menzel (1948)*
0.05	water soluable components had no effect on the lobster <u>Homarus</u> americanus	Blumer et al (1973b)
0.1	M. T. L. (48 hours) for <u>Rhombus</u> eggs	Mironov (1971)
0.1-1	effects on five species of diatoms ranged from stimulation to no effect	Prouse et al (1975)
0.73	decreased growth of alevin fry after 10 day exposure	'Rice et al (1975)
1	causes decrease in net carbon balance of mussels	Gilfillan (1973)
1	little effect on 5 species of zooplankton	Mironov (1971)
1.6 (Prudhoe)	avoidance threshold (95% con- fidence level) for salmon fry in August	Rice (1973)
5	herring eggs and fry recorded mortalities of 70% to 100% within the first 3 or 4 days	Kuhnhold (1971)*
5 (Middle East)	herring larvae normally hatched and transferred to polluted water died within three days	Kuhnhold (1971)*
5 (Venezuelan)	thicker Venezuelan crude took 12 days to kill herring larvae	Kuhnhold (1971)*
6	M. T. L. (96 hours) of pink salmon fry	Rice et al (1975)

CRUDE OIL (Continued)

Concentration (ppm)	<u>Toxic Effect</u>	Reference
8.2	M. T. L. (24 hours) for the mysid <u>Mysidopsis</u> using water soluable fraction of Kuwait crude	Anderson et al (1974)
10 (slick)	effected behaviour and feeding time of the lobster <u>Homarus</u> <u>americanus</u>	Blumer et al (1973b)
10	reduces feeding of most sensitive form of coral (<u>Madracis asperula</u>) - no recovery	Lewis (1971)
15	M. T. L. (96 hours) for juvenile shiner perch	Battelle (1973)
10 - 100	cause larvae of a species of the barnacle <u>Balanus</u> and larvae of crab <u>Pachygrapsus</u> to develop abnormally.	Mironov (1971)
16.5	M. T. L. (48 hours) for mummichog <u>Fundulus</u>	LaRoche, Eisler & Tarzwell (1970)*
30 - 40	M. T. L. (50 hours) for newly fertilized Black Sea turbot eggs	Mironov (1967)
72	M. T. L. (24 hours) for the mysid <u>Mysidopis</u> using oil-in-water dispersion of Kuwait crude	Anderson et al (1974)
100	no immediate effect on nauplius larvae of the barnacle <u>Eliminius</u> after several hours exposure	Smith (1968)*
100	50% kill of nauplius larvae of the barnacle <u>Eliminius modestus</u> (contrasts with results of Smith)	Spooner (1968)*
100	kills 5 species of zooplankton within 24 hours	Mironov (1971)
100	100% mortality to Black Sea turbot eggs within 2 days	Mironov (1971)
100-500 fresh crude	harmed four species of coral	Lewis (1971)

CRUDE OIL (Continued)

Concentration (ppm)	Toxic Effect	Reference
110	M. T. L. (96 hours) for salmon fry at 11.5 ^o C in August (most sensitive time)	Rice (1973)
250	3 species of fish - <u>Sargus</u> , wrasse, and mullet remained normally active for several days	Mironov (1971)
400	'marked toxicity' to small carp	Veselov (1948)*
800-30,000	M. T. L. (168 hours) for repre- sentative groups of Red Sea macro fauna	Eisler (1975)
1,000 (Iranian & Kuwait)	no effect noticed on guppies within a test period of 15 days	Capart (1968)*
1,000 (Russian)	causes a 50% mortality to Black Sea topshells within 6-18 days	Mironov (1970)*
l,000 (Iranian)	does not kill brown shrimp, prawns or brine-shrimp	Nelson-Smith (1968) Capart (1968)*
1,000	20% mortality in hydroids (<u>Tubularia</u>)	Chipman & Galtsoff (1949)*
1,000	accelerates death of ragworms (<u>Nereis</u>) in sediment	Mironov (1970)*
7,000	M. T. L. (96 hours) Sculpin in sea water	Hebert, Kussat (1972)
10,000 (Kuwait)	causes a depression in the growth rate of the diatom <u>Rhaeodactylum</u> tricornutum	Lacaze (1967)*
>10,000	M. T. L. (96 hours) Coho fry in fresh water	Hebert, Kussat (1972)
25,000	retards multiplication of diatom <u>Nitzschia closterium</u> . Lower levels have a slight stimulatory effect.	Galtsoff et al (1935);
extracts from 50,000	rapidly toxic to a variety of American fresh water fish	Wiebe (1935)*

CRUDE OIL (Continued)

Concentration (ppm)	Toxic Effect	Reference
50,000	complete kill of hydroids (<u>Tubularia</u>) within 24 hours	Chipman & Galtsoff (1949)*
-	duck eggs treated with between 2mg and 36mg of medicinal 'paraffin' oil showed an aver- age hatch of 20% against 90% in controls	Hartung (1965)*
	underside of ducks smeared with 4-5 ml of oil before sitting resulted in no eggs hatching	Hartung (1965)*
Submergence in 20 different crude oils for one hour	mortalities in the snail <u>Littorina littoralis</u> over the 5 days following exposure varied from 1% to 89% at 16°C	Ottway (1973)*

GASOLINE

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Concentration (ppm)	<u>Toxic Effect</u>	Reference
91	M.T.L. (48 hours) for shad (fish)	Tagatz (1961)*
60-180	lethal threshold for trout	Zahner (1962)*

KEROSINE

0.1	retards the rate of cell divi- sion for the most sensitive species of diatom (<u>Ditylum</u>); other species much more resistant.	Mironov (1971)
3	appreciably depresses growth rate of micro-algae after exposure for several days	Aubert, Charra, Malara (1969)*
38	appreciably decreases growth rate of diatom <u>Asterionella</u> japonica	Aubert, Charra, Malara (1969)*
57	toxic threshold for diatom (Asterionella japonica)	Aubert, Charra, Malara (1969)*
100	kills diatoms within 24 hours (3 species)	Mironov (1971)
188	toxic threshold to unspecified micro-algae	Aubert, Charra, Malara (1969)*
300	unable to detect toxic effect to goldfish	Aubert, Charra, Malara (1969)*
10,000	some species of diatoms can tolerate up to this level for 24 hours	Mironov (1971)

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DIESEL OIL (No. 2 fuel oil)

Concentration	Toxic Effect	Reference
(ppm)		
0.04-0.4	stimulates diatom <u>Fragilaria</u> no effect on diatom <u>Dunaliella</u>	Prouse et al (1975)
.05	stimulates the growth of the flagellate <u>Chrysochromulina</u> <u>kappa</u> in a controlled ecosystem enclosure	Parsons et al (1975
.12	depressed photosynthesis to approximately 60% of controls	Gordon & Prouse (1973)
>0.3	can significantly inhibit marine bacterial activity, although	· ·
	it	Hodson et al (1975)
1.6	M.T.L. (24 hours) for the mysid <u>Mysidopsis</u> using water-soluable fraction	Anderson et al (1974)
2.6	M.T.L. (24 hours) for <u>Mysidopsis</u> using oil-in-water dispersions	Anderson et al (1974)
7.5	M.T.L. (96 hours) for adult shiner perch using dispersed oil	Battelle (1973)
100 (emulsion)	brief exposure irreversibly inhibits photosynthesis in California giant kelp. Effect appears after 7 days.	North, Neushul, & Clendenning (1964)*
100 (emulsion)	inactivates the tube-feet by which urchins move around. Exposure for more than an hour causes death.	North*
167	M.T.L. (48 hours) for shad (fish)	Tagatz (1961)*
300-4000	'lethal threshold' for trout	Zahner (1962)*
525 (-50°C pour point)	M.T.L. (96 hours) for sculpin in sea water	Herbert & Kussat (1972)

BUNKER C (No. 6 fuel oil)

Concentration (ppm)	Toxic Effect	Reference
6.3	M.T.L. for the mysid <u>Mysidopsis</u> using oil-in-water dispersion	Anderson et al (1974)
780	M.T.L. (96 hours) for Coho fry in fresh water	Herbert, Kussat (1972)
4,800	M.T.L. (96 hours) for sculpin in sea water	Herbert, Kussat (1972)
2,417	M.T.L. (48 hours) for shad	Tagatz (1961)*
10,000	M.T.L. for salmon at 15 ⁰ C	
10,000	M.T.L. for salmon at 5 ⁰ C	Task Force - Operation Oil (1970)
10,000	M.T.L. for flounder at 5 ⁰ C	
10,000	M.T.L. for lobster at 5 [°] C	

WEATHERED TANK SLUDGE

-	cultures of marine protozoans kept in contact with weathered sludge showed no ill effects	Elmhirst	(1922)*
	sea-urchin and sea star larvae showed abnormalities in devel- opment when kept in sea water over weathered sludge	Elmhirst	(1922)*
close proximity to coal tar derivatives	hyperplasmia induced in the estuarine hyozoan <u>Schizoporella</u> attributed to carcinogens in the petrochemicals	Powell et	al (1970)

AROMATICS

Because the aromatic fraction of oil is generally considered to be the most toxic, the individual aromatic compounds have been studied more closely than other fractions.

Concentration (ppm)	Toxic Effect	Reference
Pomo on c		
Benzene	•	
6.6-15.6	M.T.L. for pond-snails	Cairns & Scheier (1962)*
10	affects respiratory rate and induces a narcotic effect with prolonged exposure	Brocksen and Bailey (1973)
10	lethal to roach (fresh water fish)	Hubault (1936)*
10	barbel (fish) survive almost indefinitely	Toman & Stota (1959)*
20	lethal to sunfish (fresh water)	Turnbull, DeMann & Weston (1954)*
35-37	lethal to sunfish (fresh water)	Shelford (1917)*
100	barbel (fish) survive for 24 hours	Toman & Stota (1959)*
386-395	lethal to mosquitofish (fresh water)	from Wallen in McKee (1956)*
1,744	possessed sufficient acute toxicity, despite rapid rates of volatization, to be lethal to <u>Chlorella</u> (algal) cells	Kauss et al (1973)
Naphthalene		
.001	threshold of interference with chemoreception in crab <u>Pachygrapsus</u>	Kittredge (1973)
30	2 hours exposure reduces algal cells (Chlamydomonas) ability to photosynthesize to 11% of normal (fresh water)	Kauss et al (1973)
150-220	lethal to mosquito fish	from Wallen in McKee (1956)*
AROMATICS (Continued)

<u>Concentration</u> (ppm)	<u>Toxic Effect</u>	Reference
Toluene		
61-65	lethal to sunfish	Shelford (1917)*
505	sufficient acute toxicity, despite rapid rates of vola- tization, to be lethal to <u>Chlorella</u> (algal) cells	Kauss et al (1973)
Xylene	e	
47-48	lethal to sunfish	Shelford (1917)*
. 171	sufficient acute toxicity, despite rapid rates of vola- tization, to be lethal to <u>Chlorella</u> (algal) cells	Kauss et al (1973)
Cresols and Pher	nols	
5-10	causes 50% inactivation of kelp photosynthesis in four	Clendenning and

daysNorth (1960)17toxic to minnowsSchaut (1939)*19toxic to sunfishTurnbull, DeMann
& Weston (1954)*72toxic to mosquitofishfrom Wallen in

from Wallen in McKee (1956)*

APPENDIX C: EXCHANGE RATES OF HYDROCARBONS BETWEEN OCEAN AND ATMOSPHERE

(The following discussion is drawn from the Beaufort Sea Report, 1976, Ocean and Aquatic Sciences, Department of Environment, Canada, by C.S. Wong, R.W. MacDonald, W.J. Cretney, and P. Christensen).

The best treatment to date of gas exchange between the ocean and atmosphere has been given by Liss and Slater (1974). Using their model, it is possible to get an estimate of the residence times of various dissolved hydrocarbons. Consider that the exchange process is controlled by a two layer interface. The bulk atmosphere and bulk water column are considered to be well mixed with a homogeneous concentration of the diffusing compound. At steady state

$$F = k_{g} (C_{g} - C_{sg}) = k_{l} (C_{sl} - C_{l}) \text{ mole/m}^{2} hr$$
(1)

where F is flux out of the water, k_q and k_l are exchange constants (m/hr). The concentration of hydrocarbon is expressed as C where C_q refers to the atmosphere, C_l refers to the bulk liquid, and C_{sq} and C_{sl} refer to the concentration at the atmosphere and liquid side of the interface respectively. Defining K_l (the overall liquid exchange coefficient) as

 $\frac{1}{K_{l}} = \frac{1}{k_{l}} + \frac{RT}{k_{g}H}$

where R is the gas constant, T is the absolute temperature, and H is Henry's Law constant, then the flux across the atmosphere-ocean boundary can be expressed as

$$F = K_{l} \left(\begin{array}{c} C_{l} - \frac{P}{H} \end{array} \right) \text{ mole/m}^{2} \text{ hr}$$
 where P is the partial (3) pressure of the hydrocarbon in atm.

If it is assumed that the atmospheric concentration of the hydrocarbon is negligible (a valid assumption with the exception of methane), then

$$F = K_l C_l mole/m^2 hr$$

The flux can also be expressed as

$$F = \frac{dN}{dt} = -\frac{dC}{dt} = \frac{2 \text{ mole } / \text{m}^2 \text{ hr}}{dt}$$

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(5)

(4)

(2)

where Z is the depth of the water column considered to be exchanging with the atmosphere. Combining Equation 4 and 5 and integrating gives

$$C = C_{o} \exp \frac{-K_{g} C_{h}}{2} t$$
 (6)

so the half life of a spike of a hydrocarbon in the water column is given by

$$t_{\frac{1}{2}} = \frac{z}{K_{\theta}} \ln 2$$
 (7)

Liss and Slater have given typical oceanic values of the exchange constants as .02 m/hr for k_{χ} and 3.0 m/hr for k_{g} at 25°C. Using these values corrected for molecular weight and setting the depth to 1 m, the K_{χ} and $t_{\chi_{\chi}}$ values can be calculated. These are presented in Table 34 along with the values at 0°C. The lower temperature constants were calculated by assuming k_{χ} and k_{χ} were associated with activation energies of about 5 kcal/mole. The data of Schooley (1969) shows that this is a fair approximation. From Table 34 it is apparent that the half lives of hydrocarbons in the water increase by a factor of about 2 for most hydrocarbons on going from 25°C to 0°C. The polynuclear aromatics are extremely slow in being removed, t_{χ} for phenanthrene being 248 hours.

It has been shown that the exchange constants k, and k, are influenced by wind velocity. There is a linear increase in k, with wind velocity, while k, increases as the square of wind velocity (Liss and Slater, 1974). As a result, hydrocarbons will be removed by exchange faster at a high wind velocity.

If bubbles are injected by turbulence down into the water column, they can effectively strip some dissolved hydrocarbons from the water. Perhaps the easiest way to visualize this process is to examine the partitioning of various hydrocarbons between the gas and liquid phase when equal volumes of both phases are equilibrated. Table 35 presents this information for selected hydrocarbons at 0° C and 25° C. The volatile alkanes can be efficiently removed

from the water by bubbles, but the aromatics do not strip out very well and the higher molecular weight hydrocarbons cannot be removed at all well by this mechanism.

TABLE 34: Theoretical Half Lives of Dissolved Hydrocarbons Exchanging with the Atmosphere

			·	
Hydrocarbon	0 [°] C		25 ⁰ C	
	K _Į	$t_{\frac{1}{2}}$ (hours)	K,	$t_{\frac{1}{2}}$ (hours)
Hexane	.066	10.5	.143	4.82
Octane	.057	12.0	.124	5.56
Decane	.051	13.5	.111	6.22
Dodecane	.047	14.7	.102	6.76
Tetradecane	.044	15.9	.094	7.34
Hexadecane	.041	17.0	.0088	7.80
Cyclohexane	.067	10.3	.145	4.75
Benzene	.064	10.8	.143	4.82
Toluene	.061	11.3	.133	5.18
Ethyl Benzene	.068	12.0	.126	5.48
Cumene	.055	12.6	.119	5.80
Naphthalene	.0046	151.	.069	9.98
Biphenyl	.015	46.6	.077	9.01
Fluorene	.0049	137	.049	14.0
Anthracene	.0036	194	.086	8.1
Phenanthrene	.0028	248	.037	18.9

 TABLE 35:
 Partitioning of Hydrocarbons Between Equal Volumes of

 Gas and Liquid Phases

· · · · · · · · · · · · · · · · · · ·	% in gas	% in gas
Hydrocarbon	phase 0°C	phase 25°C
	· · · · · · · · · · · · · · · · · · ·	•
n-hexane	97.7	98.7
m-octane	98.3	99.5
n-decane	99.4	99.5
n-dodecane	99.4	99.7
n-hexadecane	99.3	90.1
Cyclohexane	67.2	86.9
Benzene	11.2	8.6
Toluene	17.8	20.3
Ethyl Benzene	24.5	29.2
o-xylene:	15.1	18.5
Durene	33.5	50.6
Naphthalene	0.10	1.71
Biphenzyl	0.44	2.54
Fluorene	0.12	0.95
Anthracene	0.08	6.32
Phenanthrene	0.07	0.60

APPENDIX D: A Personal Perspective on the Oil Pollution Problem

Petroleum is a natural product which has undergone chemical restructuring due to geological pressures, temperatures, and time scales. Many of the components of oil are analogs of present-day natural products, and are easily assimilated by the biological system, providing both an energy and a carbon source. Other components of oil are less familiar and more refractory. However, no component of oil has yet been isolated which cannot be degraded by some form of microorganism. Degradation of petroleum has been demonstrated to occur in a variety of marine environments in this thesis, albiet sometimes at slow rates.

My personal synthesis of all the masses of published work on the biological effects of oil pollution suggests to me the following: violent disruption of the environment by large oil spills from supertankers will continue to occur from time to time. The local flora and fauna (including humans) will be drastically effected, but the effects will be limited to the area receiving the spill, and recovery will occur over a period of years. Chronic pollution of near-shore waters will result in decreased diversity and productivity there. Unusually sensitive species may be severely affected by low levels of petroleum hydrocarbons, and be eliminated from areas of their range. However, the global marine ecosystem, which is a vast and stable structure, will probably not be noticeably perturbed by petroleum pollution.

The main impact of petroleum on the environment will, I think, come in quite another direction. The increasing use of petroleum over the last century has seen it become an integral part of our daily lives as a fuel, as chemicals, pharmaceuticals, plastics, synthetics of all descriptions. Our population and our expectations have risen exponentially with the exponential rise in the exploitation of oil. We have committed ourselves irrevocably to a dependence on a continued supply. The ramifications of our dependence have

been clearly felt over the last few years, requiring international co-operation on a scale never before seen. The network of petroleum production and utilization is so vast, integrating such a myriad of governments, international corporations, and social systems that the complexities have become well-nigh unmanageable. This complex balance of power will be seriously strained as supplies become harder and harder to obtain. Governments, caught between a populace angry at their falling standard of living, and an international situation in which they are powerless to act except by force, will have little option except to protect their own interests.

The importance of petroleum as a source of international tension and conflict cannot be underestimated, and the spectre of war over petroleum supplies is very real. Modern warfare with the use of nuclear, chemical, biological and powerful conventional weapons is the ultimate environmental hazard on a scale orders of magnitude above the prosaic problems of hydrocarbon pollution.

I argue that petroleum pollution is not and will not be, one of man's crucial problems. Instead, it is the effect on our <u>social</u> ecosystem, and the resulting potential for warfare, that is the crucial environmental problem posed by petroleum.

APPENDIX E: Symposia and Books Dealing with Oil Pollution

Ahearn, D.G.; and S.P. Meyers (eds.).1973. <u>The Microbial Degradation of Oil</u> <u>Pollutants</u>. Workshop held at Georgia State University, Atlanta, in December 1972. Lousiana State University publication no. LSU-SG-73-01.

Carthy, J.D. and D.R. Arthur (eds.), 1968. <u>The Biological Effects of Oil</u> <u>Pollution on Littoral Communities</u>. Proceedings of a symposium held at Orielton Field Centre, Penbroke Waters, 17-19 February, 1968. Field Studies <u>2</u> (supplement).

Alcan Shipping Services Ltd., 1971. <u>Pollution and the Maritime Industry</u>. 3 volumes. Prepared under contract to U.S. Dept. of Transport.

Cowell, E.B. (ed.). 1971. <u>The Ecological Effects of Oil Pollution on</u> <u>Littoral Communities</u>. Proceedings of a symposium held 30 November to 1 December, 1970. Institute of Petroleum, London.

Hepple, P. (ed.). 1968. <u>Scientific Aspects of Pollution of the Sea by Oil</u>. Proceedings of a symposium held 2 October, 1968. Institute of Petroleum, London.

Hepple, P. (ed.). 1971. <u>Water Pollution by Oil</u>. Proceedings of a seminar held at Aviemore, Scotland, 4-8 May, 1970. Applied Science, Essex, England.

Hoult, D.P. (ed.). 1969. <u>Oil on the Sea</u>. Proceedings of a symposium held at Cambridge, Massachusetts, 16 May, 1969. Plenum Press, New York.

IMCO, 1973. The Environmental and Financial Consequences of Oil Pollution from Ships. Report of study no. VI, submitted by the U.K. to the 1973 Intergovernmental Marine Pollution Conference.

Marine Pollution Monitoring (Petroleum). 1974. Proceedings of a symposium and workshop held at the National Bureau of Standards, Gaithersburg, Md., 13-17 May, 1974. National Bureau of Standards Special Publication 409, Washington, B.C.

Nelson-Smith, A. 1972. Oil Pollution and Marine Ecology. Elek Science, London.

<u>Oil Pollution of the Sea</u>. 1968. Report of proceedings of an international conference held in Rome, 7-9 October, 1968. Wykeham Press, England.

Prevention and Control of Oil Spills. 1969. Proceedings of a joint conference on 15-17 December, 1969, in New York. American Petroleum Institute, New York.

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Prevention and Control of Oil Spills. 1973. Proceedings of a joint conference on 13-15 March, 1973, in Washington, D.C. American Petroleum Institute, Washington.

<u>Prevention and Control of Oil Pollution</u>. 1975 Proceedings of a conference on 25-27 March, 1975, in San Fransisco, California. American Petroleum Institute, Washington.

Ruivo, M. (ed.). 1972. <u>Marine Pollution and Sea Life</u>. Proceedings of the Food and Agriculture Organization of the United Nations technical conference on marine pollution and its effects on living resources and fishing, held 9-18 December, 1970, at FAO Headquarters, Rome. Fishing News (Books) ltd. London.

Smith, J.E. (ed.). 1968. <u>'Torrey Canyon' Pollution and Marine Life</u>. A report by the Plymouth Laboratory of the Marine Biological Association of the United Kingdom. University Press, Cambridge.

Study of Critical Environmental Properties (SCEP). 1970. Man's impact on the global environment. Assessment and recommendations for action. MIT Press, Cambridge, Mass.

Symposium on Marine Pollution. 1973. Proceedings of a symposium held at the at the National Physical Laboratory, Teddington, 27-28 February, 1973. Royal Institution of Naval Architects, London.

Task Force - Operation Oil. 1970. Report of the clean-up of the Arrow oil spill in Chedabucto Bay, Nova Scotia, Canada. 3 volumes. Information Canada, Ottawa.