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A Quantitative Assessment of the Sources and Fate of Petroleum Compounds in the Marine Environment [and Discussion]

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A quantitative assessment of the sources and fate of petroleum compounds in the marine environment

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Petroleum is complex, containing many thousands of compounds ranging from gases to residues boiling about 400 °C. Most (usually more than 75%) are types of hydrocarbons. Crude oils differ markedly in detailed composition, even during the lifetime of a single well, while distillates and petroleum products are enriched with certain compounds.

Thus petroleum-derived inputs vary considerably in composition; it is essential to bear this in mind when quantifying them in general terms such as an 'oil' or 'total petroleum hydrocarbons' measurement. However, to place the gross inputs in their proper perspective in an assessment of potential environmental effects, it is equally important to identify quantitatively those components that are potentially harmful or have long residence times. Additional sources of hydrocarbons such as other fossil fuels, combustion and the biosphere must also be distinguished, providing difficult analytical problems where the contribution of petroleum-derived constituents is small. Much less information is available on the non-hydrocarbon components.

Estimates of the total oil input to U.K. waters are, at best, approximate and range from 40 to 100 kt or more per year. Some contributions are more speculative than others, particularly the atmospheric input.

Usually, environmental effects are of local concern and it is more realistic and more meaningful to appraise the quantity and quality of the inputs on a local rather than a national or global basis. Such appraisal identifies potential 'hot-spots' or areas of concern to which the results of studies on the distribution of hydrocarbons can be related broadly.

The complexity of the inputs is matched by the range of properties of the components and the physical, chemical and biochemical processes that contribute to the distributive pathways and determine the fate of the inputs.

INTRODUCTION

International interest in oil pollution has been evident since the 1920s. The Workshop organized by the Ocean Affairs Board at Airlie, Virginia, in 1973, identified petroleum and its products as a major marine pollutant, the global annual input being 6 Mt (N.A.S. 1975). Currently, that study, which remains the best attempt so far to quantify sources of oil pollution, is being updated by the National Academy of Sciences (N.A.S.). The convenience and simplicity of the all-embracing phrase 'oil pollution' belies the many forms and sources of oil inputs to the marine environment, particularly the complex chemical composition of the crude oils and products composing those inputs. Our paper attempts to quantify sources of oil and reviews their fate in the context of the marine environment around the British Isles to provide a background to this Discussion Meeting on long-term effects of oil pollution. Before considering inputs, the nature of oil and the implications for assessment of inputs, fate and effects are examined briefly.

The nature of oil

All crude oils contain similar molecular species: thousands of compounds (Speers & Whitehead 1969) ranging from gases to residues boiling above 350 °C (table 1). They vary markedly in detailed composition, even during the lifetime of a single well. The principal elements are carbon and hydrogen with lesser amounts of sulphur, nitrogen, oxygen and metals, particularly nickel and vanadium. They form the various chemical classes: simple *n*-paraffins (alkanes); branched paraffins; cycloalkanes (naphthenes); aromatics, benzene (one-ring), naphthalene (two-ring) and their alkyl derivatives; polynuclear aromatics (PAHs), containing three or more fused rings; naphtheno-aromatics; organosulphur compounds; acids; phenols; pyridines; pyrroles; and the highly complex asphaltenes thought to contain ten or more fused aromatic rings, some heterocyclic, with aliphatic and naphthenic side chains (Posthuma 1977; Clark & Brown 1977). Most of the compounds (usually > 75%) are types of hydrocarbons but total analysis is not possible. Crudes, distillates and petroleum products are enriched in certain types of compounds (table 2) and 'cracking' introduces olefins, essentially absent in crudes.

Table 1. General composition of some crude oils relevant to the U.K. industry

(Modified from *Our industry, petroleum*, B.P. Co. Ltd, 1977.)

			North African	North Sea	Middle East	South American
			relative density			
			0.80	0.84	0.87	1.00
fraction	boiling point range/°C	relative density	yield by mass of distillates (%)			
petroleum gases	—	—	3.2	2.0	1.3	0.0
light gasolines:						
petrol	0–70	0.70	8.8	5.8	4.7	0.1
naphtha:						
feedstock	70–140	0.75	16.0	11.0	7.9	1.1
kerosene:						
paraffins, aviation and domestic	140–250	0.80	26.3	18.6	16.4	4.4
diesel fuel:						
gas oils	250–350	0.82–0.85	18.2	19.1	15.3	9.6
residue:						
heavy fuel oils	> 350	*ca.* 1.00	27.5	43.5	54.4	84.8

Whether the input is an oil, oil product, oily water discharge, derived effluent or product of combustion, it is usually a multicomponent system. The components have a wide range of physical and chemical properties. Consequently, they participate to differing extents and at different rates in both the progressive compositional changes of the input and the concurrent redistributive processes brought about by the interaction of physical, chemical and biochemical factors such as: evaporation, dissolution, dispersion, adsorption, sedimentation; photochemical or chemical oxidation and degradation; uptake and depuration, trophic transfer, metabolism and biodegradation by biota. Some changes and processes are rapid, others are slow; they are discussed in detail later.

There are great difficulties in quantifying 'oil' at all stages from input, through distribution to fate because the mixture is complex. It is progressively altered, dispersed and redistributed, resulting in a sharp decrease in concentration of the individual components and large changes in their relative concentrations. Indeed, real amounts of 'oil' representing what remains of the actual input cannot be measured in the environment. Different methods are used depending on the concentrations expected or type of sample (Clark & Brown 1977). At high concentrations, gravimetric methods may suffice. Water content is also important, e.g. emulsions and tar-balls. At concentrations down to 1 mg l^{-1} (e.g. oily water discharges), infrared absorption methods are commonly used. At low concentrations, sophisticated methods of gas chromatography or gas chromatography – mass spectroscopy analyse solvent extracts and identify specific compounds at concentrations of 1 ng l^{-1} or less, usually hydrocarbons (alkanes, aromatics and PAH) less frequently, non-hydrocarbons (e.g. alkyl sulphides, mercaptans and dibenzothiophenes). The total number of compounds measured routinely represent a small fraction of the total hydrocarbon array in oil because many are not amenable to analysis (Malins & Clark 1978). There are many potential sources of hydrocarbons in environmental samples other than petroleum and its products (table 3). Thus the contribution of the petroleum hydrocarbons in the analysis should be identified to avoid misinterpretation of the supposed petroleum sources (Tripp & Farrington 1981). There are guidelines (Clark & Brown 1977), but it is not always easy or unequivocal at low concentrations and the analyst may have to resort to the identification of specific stereoisomers only likely to be present in crude oils such as certain isoprenoid alkanes, hopanes and triterpanes (Gassmann 1981; Quirk *et al.* 1980). The problem of grossing up to an oil value remains. None of the methods available is entirely satisfactory. Selection represents a degree of compromise.

TABLE 2. MAJOR GROUPS OF COMPOUNDS (PERCENTAGE COMPOSITIONS) IN CRUDES AND PRODUCTS

(Large variations can be expected: the cycloalkanes in a light crude may be as high as 60 %; diesel fuel (*a*) is blended and has an exceptionally high aromatic content; the aromatic content in blended petrols may be as high as 25 %.)

	light crude	heavy crude	diesel fuels (no. 2 fuel oils) (*a*)	diesel fuels (no. 2 fuel oils) (*b*)	blended petrol	blended kerosene
n-alkanes	23.3	0.9	8.1	30	50	35
isoalkanes	12.8	3.2	22.3			
cycloalkanes	41.0	19.2	31.4	45	40	50
aromatics	6.4	9.2	38.2	25	10	15
naphthenoaromatics	8.1	27.9†				
heterocyclics (resins)	8.4	23.1				
asphaltenes		16.5				

† Includes sulphur compounds.
Data taken from Clark and Brown (1977).

TABLE 3. PRIMARY SOURCES OF HYDROCARBONS CONTRIBUTING TO ANALYSES

1. *petroleum, petroleum products, coal*
   unburnt coal in coastal sediments has an aromatic fingerprint similar to light crude or diesel fuel
2. *combustion products of fossil fuels*
   the PAH fraction tends to have a greater proportion of parent compounds relative to the alkyl substituted derivatives
3. *biosynthesis: terrestrial and marine*
   fairly well characterized array of relatively simple structures
4. *natural seeps and exposed bituminous shales*
   similar composition to oil, differentiated by specific stereoisomer distribution
5. *weathering and diagenetic processes*

Which components of oil and products are most important in terms of fate and effects but relevant to this discussion? Anderson (1979) concluded that toxicity is due primarily to concentrations of one-ring and two-ring aromatic hydrocarbons. Varying proportions are present in crudes and refined products. The general pattern of toxicity is related to the degree of alkyl substitution and the water solubility of the compounds. Toxicity appears to increase with the degree of alkylation of the parent compounds benzene, naphthalene and phenanthrene. Solubility decreases as the ring structure increases and the degree of substitution increases. Four-ring and five-ring aromatic hydrocarbons such as chrysene and benzo[*a*]pyrene are virtually insoluble in sea water and relatively non-toxic during the short-term exposures over which most toxicity data have been accumulated. Toxic non-hydrocarbons in petroleum include cresols, xylenols, naphthols, naphthaquinones, carboxylic acids, quinoline and substituted quinolines and pyridines. Other components of interest, but less studied, are in the complex naphthene fraction, which is difficult to fractionate and analyse.

Marine inputs

The area considered is defined in figure 1, bounded to the west by the continental shelf and the Irish coastline, to the east by the median line in the North Sea and to the south by latitude 49 °N and the southern coastline of the English Channel. Only sources along the coastline of the U.K. and in waters surrounding the U.K. are considered in detail. The main aim of the paper is to quantify oil inputs. The biogenic inputs of hydrocarbons are only referred to later to give perspective to the oil inputs.

Sources of oil

Potential sources are summarized in table 4. Specific sources include accidental spills of oil or products as well as operational losses or licensed inputs such as oily water discharges, industrial and municipal effluents and dumped wastes. Some are continuous, although the oil content may fluctuate widely hour by hour; others occur at intervals. Dredged spoil from waterways is usually dumped at sites in outer estuaries or nearby coastal waters. It represents a redistribution of bulk material, the oil content being the product of a multiplicity of inputs. It may also act as a source in the sense that contaminated pore waters are probably released and some resuspension occurs. Non-specific sources include the river inputs to estuaries and the background of unspecified inputs in estuarine waters, such as urban runoff, on which the more specific sources are superimposed. Rainfall and dust deposition from the atmosphere represent a complex source resulting from differing stages of degradation of a variety of emissions, both biogenic and anthropogenic. Degradation in the atmosphere is a fate of volatile components of oil and combustion products. Other important fates are permanent burial in the sediments and biodegradation in the water column and sediments (A.I.B.S. 1976).

Production and transport of oil

The pattern of U.K.-related traffic in oil and products around the shores of the U.K. has changed substantially in the last 5 years as dependence on imported crude oil has diminished with the expansion of production in the North Sea. However, with adverse economic changes, the total volume of our consumption of oil has declined in recent years. Refinery capacity has begun to decline. Table 5 summarizes the picture in 1980. The trends continued in 1981. In 1980, oil inports were about 50% of consumption. About 80% of North Sea production in the U.K. sector was brough ashore by pipeline. Approximately 25% of the total inland deliveries of product was carried by coastal tanker traffic. In total, some 112 Mt of oil and products was shipped around the U.K. coasts in U.K.-related traffic but, in addition, nearly 1 Mt of oil was shipped through the English Channel every day to satisfy the trade pattern of northwest Europe (Royal Commission 1981, p. 127).

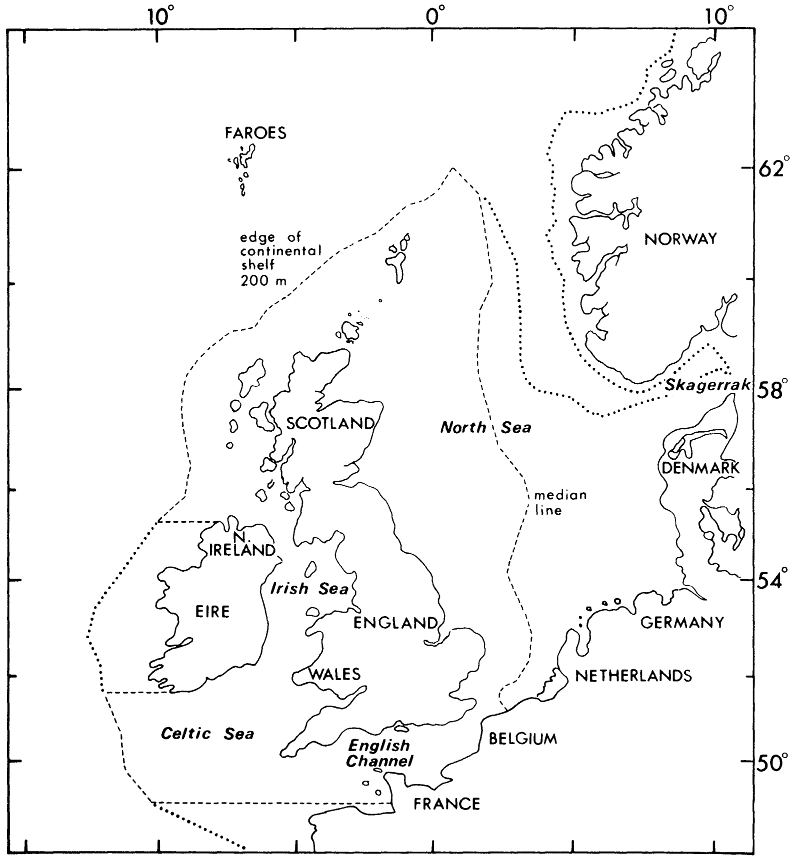

FIGURE 1. Area around the U.K. considered for inputs. Total area of North Sea including Skagerrak, 575000 km^2 (Kossinna 1921); broken line encloses area considered; dotted line, 200 m depth (the positions are approximate). Within the area enclosed areas are: northern North Sea (north 56° N), 215000 km^2; southern North Sea (south 56° N), 105000 km^2; Irish Sea, 45000 km^2; English Channel, 80000 km^2 (U.K. Petroleum Industry Association).

Global estimates of oil inputs

The N.A.S. Report (1975) has been quoted widely. The forecast for the early 1980s and the degree of confidence in the estimates is referred to less frequently (table 6). It anticipated a reduction of about 25% in the estimates derived for the mid-1970s. The original N.A.S. estimates were updated (Cowell 1978) and derived for Europe and the U.K. (table 6) based on their consumption as a proportion of the world production of oil (Europe, 0.33; U.K., 0.033). The trends assumed by both sources were an increase in the application of 'load-on-top' operations for oil tankers, a decrease in oil discharged by refinery effluents, and an increase in offshore exploration and production. The global totals are similar, but note the differences, particularly in those categories where changes were expected.

TABLE 4. POTENTIAL SOURCES OF PETROLEUM COMPOUNDS FOR THE MARINE ENVIRONMENT

1. *natural marine seeps of oil*
   low potential geologically
2. *offshore activity for oil exploration and production*
   accidental or operational losses (production or formation water, displacement water, disposal of drill cuttings)
3. *shipping: tankers and non-tankers*
   accidental or operational losses (loading or unloading fuel and cargo, bilges and cooling water, fuel oil sludge, tank washing and deballasting)
4. *coastal and estuarine effluents*
   refineries, sewage works, industrial (cooling water, waste products)
5. *dumping of wastes at sea*
   sewage sludge, industrial wastes (dredge spoil represents redistribution)
6. *coastal and estuarine urban runoff*
7. *rivers: inputs to estuaries*
8. *atmosphere*

TABLE 5. U.K. RELATED PRODUCTION AND MOVEMENT OF OIL, 1980 (MEGATONNES PER YEAR)

(Data from Department of Energy and United Kingdom Petroleum Industry Association.)

refinery capacity	130
crude oil refined	80
total inland deliveries of product	72
oil imports	40
North Sea production	78
Norwegian production	40–50
North Sea oil to U.K. refineries	39
North Sea oil to shore by tanker	15
oil exports	39
products delivered inland by tanker	18

Estimates for the United Kingdom

National estimates derived from global estimates only have limited usefulness. Where possible, such estimates should be based on actual experience. In table 7, we have put together a range of recent estimates, based as far as possible on the situation in 1980, and obtained or derived from data made available from a wide range of sources, acknowledged later. We have derived 'best estimates' from these (table 7) where the background information is sufficiently firmly based.

Natural seeps

Geologically, the continental shelf of the British Isles has low potential for oil seeps (0.05–2 kg km^{-2} annually) (Wilson 1974). Very small but unquantified seeps are known onshore near coasts in Dorset, Fife and Lancashire. Bituminous shales are present in Lothian and the south coast and are exposed along 30 miles of coast in the Bristol Channel. Erosion of the exposed shales contributes up to 40% of the hydrocarbons extractable from the mud in the estuary (S. Rowlands, personal communication). Estimates of the input from seeps depend on the rate and the area selected.

Offshore oil activity

Inputs tend to increase as the volume of formation or production water increases, but offshore production has not expanded as rapidly as predicted. The average concentration of oil in

Table 6. A comparison of estimated annual inputs of petroleum hydrocarbons (kilotonnes)

source	global (a) N.A.S. forecast for early 1980s†	global (b) N.A.S. estimates updated‡	U.K. derived from (b)‡
natural seeps	600**	600	negligible
offshore oil activity	200***	60	2
transportation	800***	1380	45.8
refineries	20***	60	2
municipal or industrial effluents	450***	450	15
urban runoff	300**	400	13.3
rivers	1600**	1400	46.7
atmosphere	600*	600	20
total	**4570**	**4950**	**145**

Annual world production crude oil: *ca.* 3 Gt; U.K. consumption of crude oil (1977): *ca.* 0.1 Gt.
Confidence: ***, high; **, medium; *, low.
† N.A.S. (1975). ‡ Cowell (1978).

Table 7. Estimated annual inputs (tonnes) of petroleum hydrocarbons to waters around the British Isles

	range of estimates†		‘best estimates’	
natural seeps	*35–1400*		*< 300*	
offshore oil activity	*3405–4510*		*3410–3560 +*	
formation and production water		750–900		750–900
displacement water		45–300		50
accidental spills		100–300		100‡
platform runoff		10		10
drill cuttings		2500–3000		2500
transportation	*3905–16340*		*7550–9000 +*	
tankers: large spills		3000–15000		1900–2200§
small spills				50–100
non-tanker spills				< 1000
operational losses from ships		—		4000–5000
shore terminals				
refinery terminals		80–140		100–200
coastal storage depots		20–50		
crude loading terminals		5–50		
oily water discharges		800–1100		500
refineries	*2000–13300*		*6000–6500*	
municipal and industrial effluents	*16010–28010*		*15510–16910*	
sewage effluent to tidal waters		500–9000		500–1400
sewage sludge dumped at sea		4500–8000		6500–7000
industrial waste dumped at sea		< 10		< 10
industrial effluent urban runoff to tidal waters		11000		8500
rivers	*< 5000–50000*		*< 7500*	
atmosphere	*9000–60000*		*30000*‖	
[*dredge spoil*]¶	[*2800*]			
total/kt	**39.3–212.9**		**70.3–73.8**	

† Taken from a wide variety of sources; see acknowledgements.
‡ Plus large spills from major incidents.
§ Plus massive spills from major incidents.
‖ Maximum estimate 250000.
¶ Not included in inputs total, redistribution rather than input.

displacement water is assumed to be 10 μg g^{-1} (Read & Blackman 1980); 15 Mt was transported from the oil-fields by tanker (table 5). The maximum annual input would be 150 t, but calculations based on the oil-field operators' experience, representing 80% of oil reserves in the U.K. sector, suggest about 50 t (Read & Blackman 1980). The background level of small accidental spills (*ca.* 100 t annually) has decreased from higher values in the early stages of production. Experience is insufficient to estimate soundly the annual contribution from infrequent large spills, which may range from 100 t to tens of thousands of tonnes. Drill cuttings contaminated with oil are disposed of at platforms and high concentrations are likely when oil-based drilling muds are in use. The speculative estimate based on wells drilled and the amount and average concentration of oil in the cuttings disposed of suggests that this input may be quantitatively the most important source in offshore operations. Overall, the inputs from offshore activities are small in comparison with others (table 7).

Transportation

Shipping. Tanker spills vary markedly year by year. The records of the International Tanker Owners Pollution Federation Ltd give estimates of quantities lost by all tanker spills greater than 7 t. Analysis for the seas surrounding the British Isles, our shores and those of our maritime neighbours shows that for the 10 years from 1971 to 1980 the average annual loss due to spills greater than 7 t was 22500 t. The annual average for the 5 years from 1976 to 1980 was 42000 t and, for spills less than 7 t, 130 t. The averages over the same 10- and 5-year periods for the U.K. area (figure 1) were each *ca.* 2000 t for large spills and *ca.* 60 t for small spills. These averages do not reflect the exceptionally massive incidents, e.g. *Torrey Canyon* and *Amoco Cadiz*, but are more realistic as background values for tanker spills. In deriving such estimates, important factors are the years taken for averaging, the area defined for analysis of the spill data, and the spill size categories used to group the data. Assigning of unquantified small spills has little significance to the total. No attempt was made to correct for amounts recovered in clean-up operations or dispersed by natural or artificial processes, since the estimates represent actual inputs. Amounts recovered and dispersive processes represent aspects of the fate of oil considered later. A recent statistical analysis of worldwide tanker accidents from 1969 to 1978 (Goldberg *et al.* 1981) shows a downward trend in annual spill incidents but a rise in annual spill quantities and in the amount spilled in each incident, partly attributable to steadily increasing tanker size.

Analysis of the spill records of the last few years from the Annual Reports of the Advisory Committee on Oil Pollution of the Sea (Acops) suggests a background of small spills (less than 250 t) ranging from 2000 to 3000 t annually, on which larger incidents are superimposed. Comparison with tanker losses (less than 250 t) suggests that up to *ca.* 1000 t annually is spilt from sources other than tanker accidents. It was not possible to isolate accidental spillage from non-tanker shipping. Figure 2 illustrates the pattern of spills around the British Isles based on our compilation of H.M. Coastguards' reports of marine spills, 1974 to mid-1981; it compares well with the Acops reports.

Operational discharges from ships (table 4) are difficult to quantify. The trend in building diesel rather than turbine-powered ships leads to larger operational losses per ship. There are about 300 shipping movements in the Straits of Dover each day included in a total of 2700 in the waters around the U.K. (Eashams Ltd, personal communication). From a recent analysis of shipping to and from British ports (Garratt & Wingfield 1981) it can be deduced that on average each day there are 610 ships in British ports and 400 ships at sea. It has been estimated that operational daily discharges from ships in port average for all ships about 3 kg oil per ship (Knap 1978) and, at sea, about 30 kg oil per ship (N.A.S. 1975). All crude oil delivered to the U.K. by sea from offshore oilfields is carried in segregated ballast tankers. Inputs from tank washings and oily ballast discharges from tankers are thought to be small.

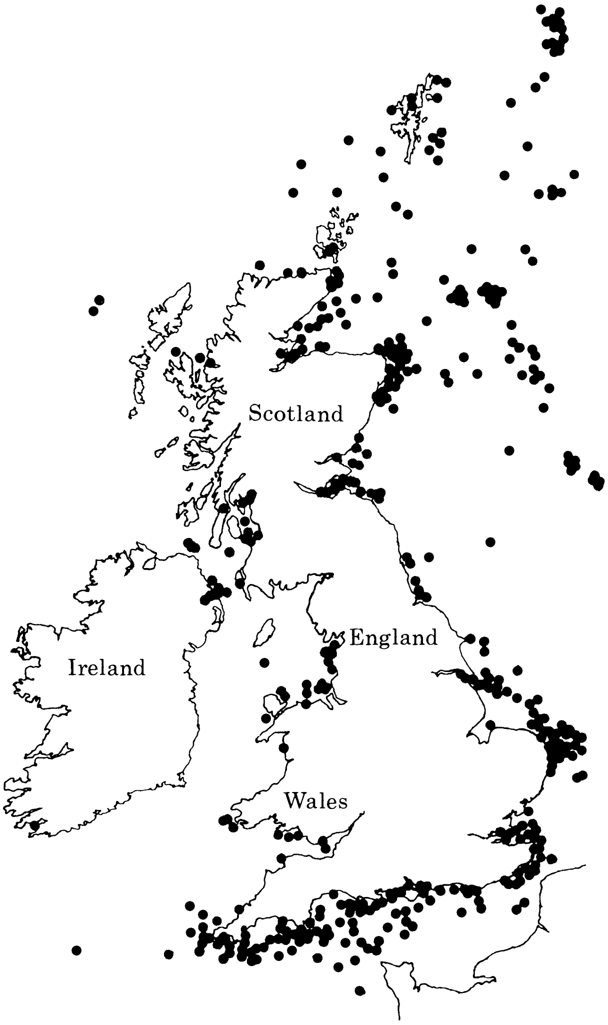

FIGURE 2. Marine oil spills around the British Isles, 1974 to mid-1981, compiled from the reports of marine spills from H.M. Coastguard. A dot in the denser areas may represent multiple spills; 405 spills are recorded on the diagram.

Shore terminals. Estimates of handling losses at terminals are based on a percentage loss (0.00008–0.00015%) of the total annual oil movement at coastal storage depots, refinery terminals and crude-loading terminal (130 Mt; table 5). To these are added oily water discharges from treatment facilities for crude oil washing, production or formation water and ballast water. An increasing proportion of tankers using the crude-loading terminals have segregated ballast systems, resulting in smaller discharges of oily water from ballast treatment facilities.

Refineries

Refineries discharge effluents to tidal waters (for locations see Royal Commission 1981, p. 79). Older refineries (pre-1960) use large volumes of water and release considerable quantities of oil in the effluent (e.g. 0.009% of refining capacity). Those built more recently lose on average one-tenth to one-fifteenth of the amount of oil, as a percentage of refinery capacity (Concawe 1979). Thus, in the U.K. nearly 95% of the oil input is contributed by about half the total refinery capacity. Currently, refinery capacity is tending to decline. The throughput of crude oil is declining steadily and may fall below 70 Mt in 1981. Both the volume of effluent and the concentration of oil have decreased at older refineries such as Fawley (approximately 13% of total capacity) with the introduction of improved treatment facilities (Dicks & Iball 1981; Dicks & Hartley, this symposium). Overall, refinery inputs are decreasing.

Municipal or industrial effluents to tidal waters

The annual volume of sewage effluent discharged to tidal water in the U.K. is about 1.4 km^3. Some 25% is classified as unsatisfactory. Few data are available for oil or hydrocarbon concentrations in effluent. It has been suggested that the average upper limit is 1 mg l^{-1}, a tenfold reduction being expected in satisfactory effluents for which a few analyses suggest a range, 25–250 μg non-volatile hydrocarbons per litre (Knap 1978).

Approximately 9.5 Mt of wet sewage sludge is dumped annually at licensed sites in U.K. coastal waters. Analyses by M.A.F.F. and D.A.F.S. of samples representative of most sludge dumped suggest an overall average oil content in wet sludge of about 0.07%.

Excluding refinery effluent, power-station cooling water represents by far the largest volume of industrial effluent (16×10^9 m^3 annually). No analytical data are available and estimates depend on the assumed oil concentration, 10–100 μg l^{-1}. Some estimates include industrial effluents with urban runoff, which can be influenced strongly by storms. Again, there is insufficient information for the U.K. but experience in the Los Angeles area suggests that the urban contribution is about 2.5 times higher than the non-urban (Eganhouse & Kaplan 1981). Alternatively, global estimates of inputs of oily waste from shore-based industry and rivers combined (including urban runoff) are about 2.5 times higher than refinery inputs, which, on the basis of our pessimistic 'best estimate' (table 7) would be about 16000 t annually. Adjustment with our pessimistic input from rivers (table 7) provides a highly speculative annual input from non-refinery industrial sources and urban runoff of 8500 t.

Rivers

The total annual river flow in the U.K. is about 150 km^3. Rivers are classified on a scale of 1–4 with increasing deterioration in quality. Data on oil or hydrocarbon concentrations are very sparse. Concentrations of extractable organics above the tidal reach are usually less than 1 mg l^{-1} and most fall in the range 0.1–0.2 mg l^{-1} (Department of Environment), but non-volatile hydrocarbon concentrations may be as low as 10 μg l^{-1} in class 1 rivers (Knap 1978). A ratio of oil to extractable organics of 1:2 is usually assumed, but this is unlikely to apply throughout the classification. Our speculative maximum input to the tidal waters assumes an average concentration, 0.15 mg l^{-1}.

Atmospheric

Estimation is difficult because the inputs have not been measured. Table 8 estimates the relevant emissions. Emission from any single source is variable. Thus the choice of a single conversion factor to derive emissions from reasonably accurate consumption data introduces considerable uncertainty in the estimates. The conversion factors suggested for mobile sources vary from 0.031 (used in our estimates) to 0.0195. Emissions comprise gas, liquid and solid phases. The first three listed in table 8 are primarily gaseous. Some partitioning to liquid and solid particulate matter occurs, but the major portion should remain in the gas phase from which losses occur by, for example, adsorption to rain, snow or precipitating dust, direct adsorption to surfaces such as soil or vegetation, photochemical reactions or partition across the sea water interface. The information available (Duce 1978; Brice & Derwent 1978; Eisenreich *et al.* 1981) is insufficient to give a quantitative assessment of the possible inputs to the marine environment. However, the input may be estimated on the basis of ideal physical assumptions on the concentration and distribution of the gaseous emissions in the atmosphere and rapid equilibration with the surface layer of the sea. It probably lies between 2 and 20% of the total emission. In sunshine, photochemical reactions may reduce the lifetime of a large proportion of the gaseous emissions to 6–11 h (Brice & Derwent 1978), which decreases the amount available for equilibration with the sea but over the whole year the effect should be less marked. Loss also occurs by precipitation, particularly of emissions close to the ground. Annually some 10% of the gaseous emissions from mobile sources and 1% or less of the others are precipitated mainly over the land.

TABLE 8. ESTIMATED MAJOR ANNUAL EMISSIONS (KILOTONNES) FROM U.K. SOURCES

sources	hydrocarbons†	Particulate organic carbon‡
mobile sources	780	36
industrial processes	295	9
solvent evaporation	310	—
stationary combustion	42	154
waste disposal	35	23
total	**1462**	**222**

† Calculated after Brice & Derwent (1978) by using oil consumption data for 1980 (Department of Energy, Institute of Petroleum).

‡ Calculated after Duce (1978), except stationary combustion calculated from smoke emission data (Department of the Environment).

Particulate organic carbon contains a wide variety of petroleum or petroleum-like substances, including high molecular mass aliphatic hydrocarbons and PAH, depending on the source. In diesel exhaust, 80% of the particulate organic carbon is thought to be carbon itself, compared with 20% for petrol engines. Roughly half the particulate emissions are probably less than 1 μm (Duce 1978), having an average residence time of 37 days compared with 2 days for the larger particles. Assuming a prevailing wind of 32 km h^{-1}, approximately 24000 t of particulates are deposited within 320 km of the source. They may contain 50% hydrocarbons by mass and, perhaps, up to 50% will be deposited in the sea. The total PAH in the particulates is unknown. It may be about 0.1% of the total hydrocarbons, contributing about 70 t to the sea.

Biogenic hydrocarbons

The main sources are production by the marine biomass and a proportion of terrestrial biogenic emissions that reaches the sea. The annual inputs may be 100–200 kt. Estimates have been derived for the U.K. from global estimates (Royal Commission 1981, p. 14) of phytoplankton production and atmospheric inputs, totalling about 110 kt. In addition, marine biogenic inputs have been calculated for the North Sea from average hydrocarbon concentrations for the biomass of phytoplankton and zooplankton, benthos and fish by using assumed turnover times (R. Johnston, personal communication). The annual estimate after extrapolation for U.K. waters (figure 1) is about 165 kt.

Inputs in a local environment

Table 7 shows clearly the wide range of the estimates of petroleum-derived inputs for the U.K. They can be compared with those derived from global inputs (table 6) that fall within the ranges in table 7 for the most part but appear to overestimate transportation losses and underestimate offshore activity and refinery inputs, the latter being equivalent to the Fawley refinery alone (figure 3 and Dicks & Iball 1981). Many estimates, particularly the diffuse inputs,

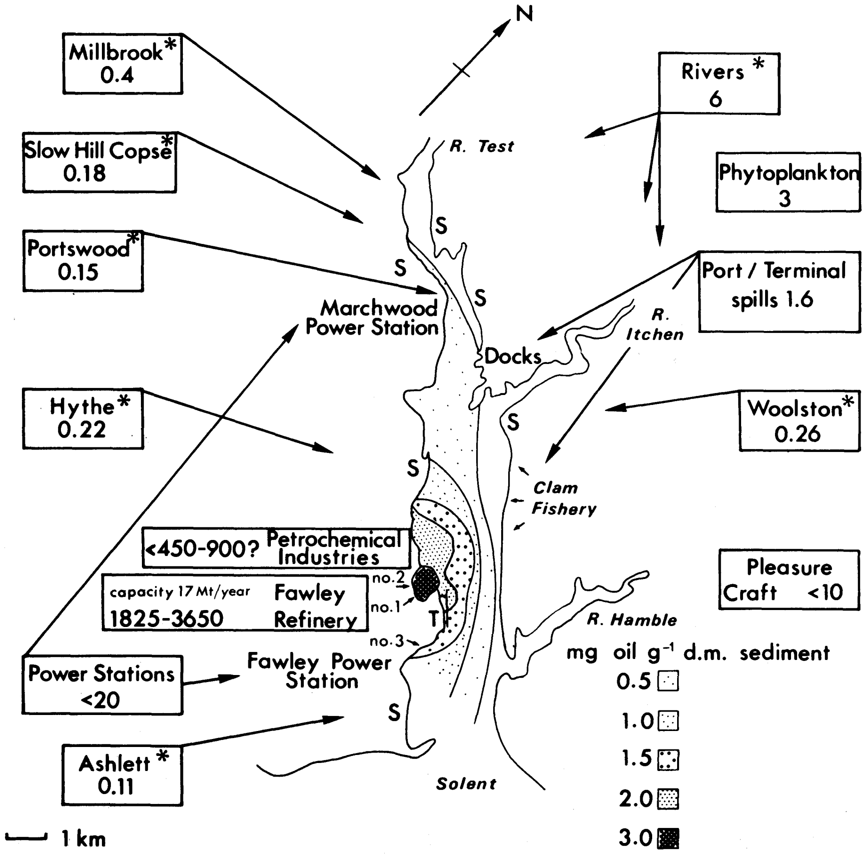

Figure 3. Maximum estimates of inputs of hydrocarbons to Southampton Water, 1974–6 (tonnes per year) (data from A. H. Knap, P. J. Le B. Williams & E. Lysiak, University of Southampton). S, sewage outfalls, Millbrook, Slow Hill Copse, Portswood, Hythe, Ashlett, Woolston; T, oil terminal; *, non-volatiles only; no. 1 to no. 3, refinery discharges. The 'terminal spills' refer to Fawley, T. The petrochemical input is speculative.

are both speculative and potentially large. The sparse data base makes it difficult to draw up a coherent national picture. Nevertheless, the potential effects of specific oil inputs or discharges are local. Indeed, it is far more meaningful to characterize the local inputs in any environmental assessment rather than attempt to extrapolate from national or global estimates, and it can be done with greater precision.

Unfortunately, there are few areas in the U.K. for which there are sufficient data to characterize and quantify all the inputs to an estuary for instance. Williams (1976) derived a carbon budget for Southampton Water and, building on this, Knap (1978) quantified the gross hydrocarbon inputs. These are summarized in figure 3 together with sediment analyses that demonstrate the localized deposition of hydrocarbons from the refinery outfalls. Details of the study, the hydrocarbon budget and model are to be published (A. H. Knap and P. J. Le B. Williams, personal communication). The refinery makes by far the largest contribution. The estimate agrees well with those derived independently by using different analytical techniques which also show, over a much longer time series, the influence of improved treatment facilities (Dicks & Iball 1981; Dicks & Hartley, this symposium). Difficulties still remain in quantifying some inputs despite simplification to a local environment. Estimates for power stations, pleasure-craft and petrochemicals are speculative. Quantifying the components most likely to be implicated in potential effects in a local environment remains a major task, but some progress has been made in an estuary (Readman *et al.* 1982) and offshore (Massie *et al.* 1981).

PATHWAYS AND PROCESSES OF FATE

Some inputs or incidents such as spills, oily water discharges or industrial and municipal effluents are specific and localized. They may be insignificant, chronic or acute, but continuous or occasional. Others, such as the atmospheric input, are dispersed continuously over the whole area at low but not necessarily uniform concentrations. As a prelude to considering potential effects later in the meeting, we need to predict the physical and chemical behaviour of oil inputs. We need to quantify the rates of the different redistributive processes and determine how the different chemical constituents participate.

What happens to the inputs? What are the pathways of distribution and fate of the petroleum-derived materials that lead to the concentrations of 'oil', groups of compounds or individual compounds that we can measure in the marine environment? In this context, it is necessary to be aware of the important background oceanographic features reviewed by A. J. Lee (1980). The extent of penetration of North Atlantic water varies seasonally. The coastal residual surface current circulation in the North Sea is anticlockwise, but in the central areas of north and south, surface circulation is essentially wind-driven. Recent estimates suggest that the North Sea water mass may be renewed annually.

Recently a number of excellent reviews have described various aspects of the fate of oil, including Wheeler (1978), Anderson (1979), R. F. Lee (1980), B.N.C.O.R. (1980) and Sprague *et al.* (1981). The general pathways and mechanisms are summarized in figure 4 and the approximate relative magnitudes of the processes redistributing spilled oil and their time-scales are shown in figure 5. Speculatively, with a knowledge of the nature of oil, a balance can be ascribed to the major processes of redistribution and degradation of the gross components of oil: evaporation, photooxidation, dispersion, dissolution, biodegradation and sedimentation (figure 6).

The models can be modified and improved as more real, quantified information is defined for these processes under different conditions. They represent redistribution of spilled oil. The behaviour of different oils or products with different physical properties and chemical composition will vary and the models can be adjusted accordingly. Other inputs, such as dispersed oils in oily water discharges, can enter the models at the appropriate point, e.g. the

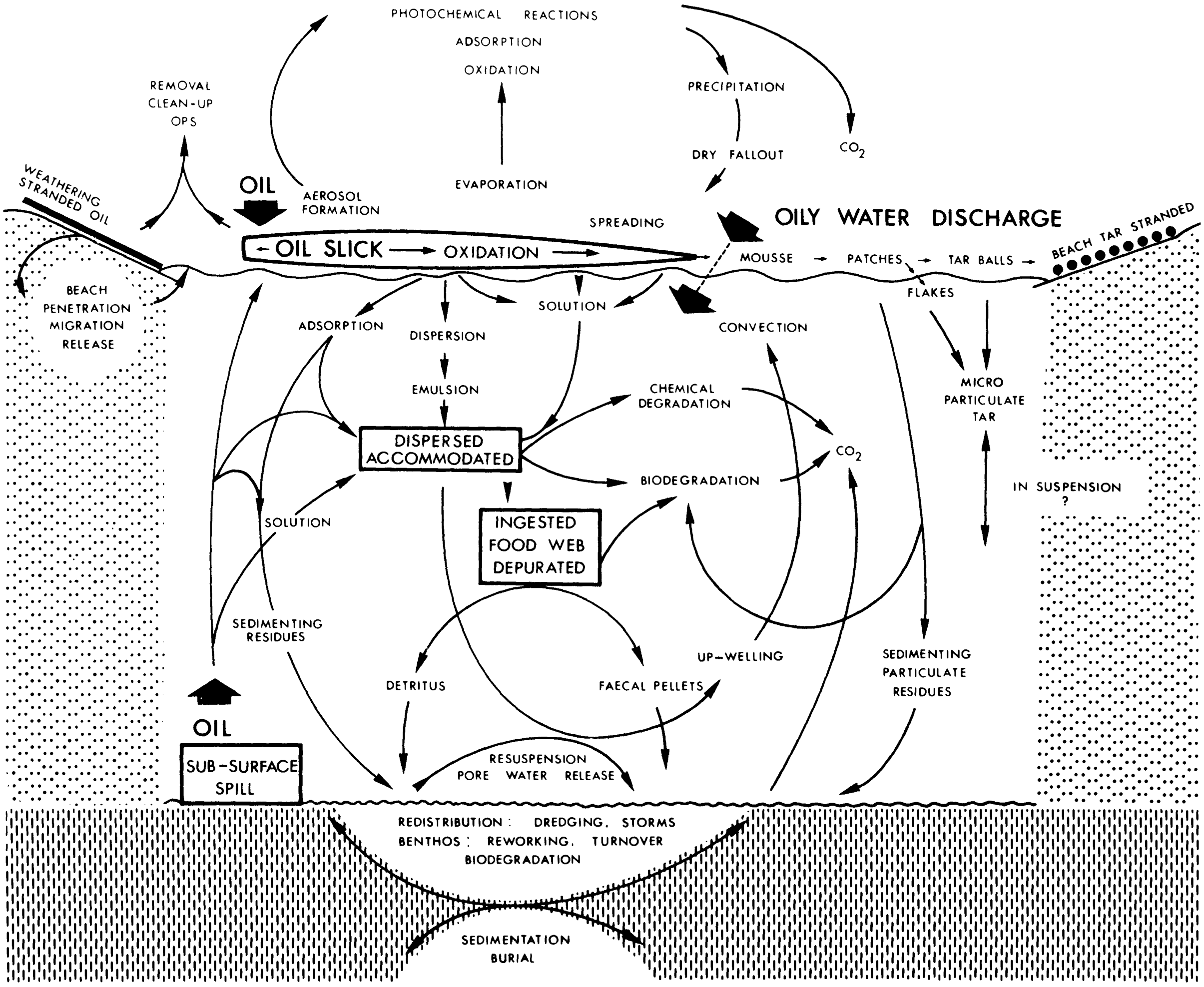

FIGURE 4. General pathways and mechanisms of the fate of oil. Modified after Burwood & Speers (1974) and Hardy *et al.* (1981).

petroleum-derived components of specific industrial effluents may be largely soluble or largely particulate depending on their origin. However, we wish to deal only briefly with the general picture. Rather, we wish to place it in the perspectives of U.K. waters and of potential effects and consider some of the more recent results of laboratory and field research on possible fates.

Spills

When oil is spilt on the sea surface a slick forms and it spreads. The factors involved are density, surface tension and gravitational, inertial and frictional forces. However, spreading and the other processes described above depend on the physical and chemical properties of the oil or oil product, the amount, and how and where the spill occurs (cf. various incidents: *Dona Marika*, 3000 t petrol, grounded in a sandy cove in Milford Haven in 1973; *Ekofisk Bravo*, *ca.* 14000 t Ekofisk oil, central North Sea platform blowout in 1977; *Eleni V*, 5000 t heavy fuel oil, collision off Norfolk coast in 1978; *Christos Bitas*, 3000 t Iranian crude, grounded on Pembrokeshire rocks in 1978). The use of detergents or other methods of dispersal or containment and retrieval, the ambient temperature, weather conditions and the local hydrography are also important. For instance, at the time of the Ekofisk blowout, the water column was completely mixed, aiding dispersion. Models of slick spreading are only relevant to the first few hours because the processes continuously modify the spilled oil *ab initio*. Simulations of oil drift use a proportion of wind speed (1–4 %) at a small fixed angle of wind direction to the right of the wind (usually less than 10°), but they are inadequate for coastal situations without reference to local winds and tides (B.N.C.O.R. 1980).

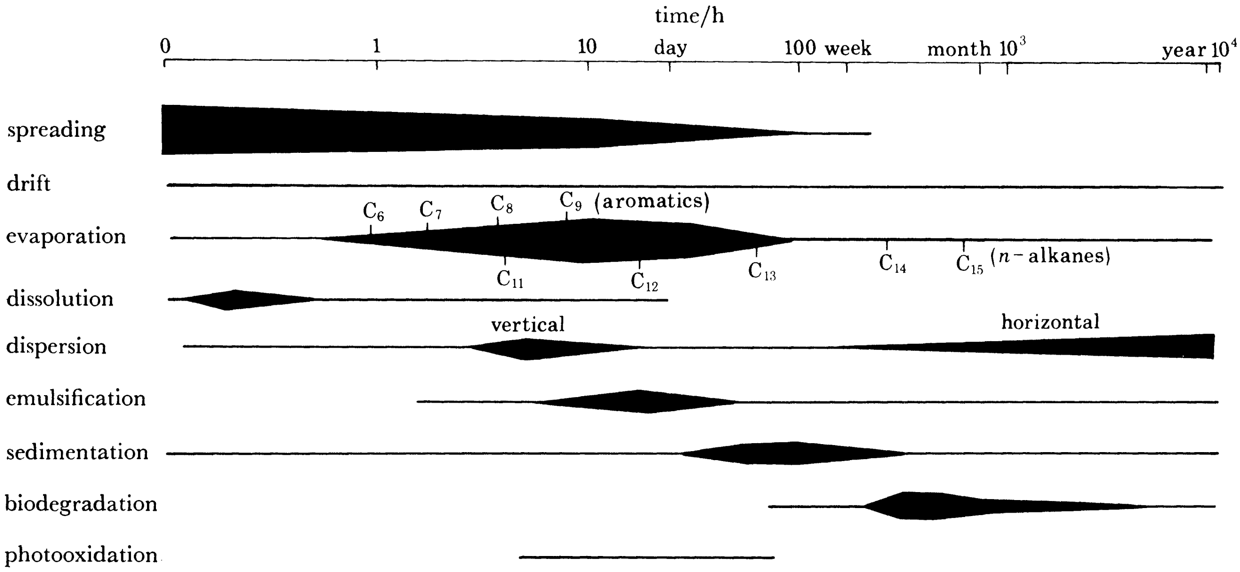

FIGURE 5. The relative magnitudes and timescales of the redistributive processes for the fate of oil spilled at sea (revised after Wheeler 1978; Wheeler, personal communication). The development of processes as time elapses after a spill: the line length indicates the probable timespan of a process; the line width shows the changes in the magnitude of a process with time and compares it with other contemporary processes.

Evaporation, dispersion, emulsification, adsorption and sedimentation are important in the first few hours. A large proportion of the hydrocarbons of light crude oils and the light and middle distillates are volatile. Carbon number range C_4 to C_{15} constitutes about 20–50 % of most crude oils and 75 % or more of many light fuel oils. The rate of evaporation is probably proportional to the percentage of volatile components. We have found that in calm spring weather some 35 % by mass of a thin Forties crude oil slick on sea water was lost by evaporation over 24 h from outdoor open tanks (Mackie & Whittle, unpublished observations). This compares with an estimated loss of about 25 % of a Kuwait crude over 24 h under so-called average English Channel conditions. In trials at sea, some 50 % of the crude oil deliberately added direct to the sea surface was lost to the atmosphere. An analysis of the rates of transport and fate of hydrocarbons from a diesel oil dispersed initially at about 150 $\mu g\ l^{-1}$ in a controlled ecosystem approximating to a temperate estuarine environment showed an exponential decrease of extractable total oil over 90 h (rate constant 0.0066 h^{-1}), some 60–90% of the loss being due to evaporation (Gearing *et al.* 1979).

The components lost to the atmosphere in the gas phase or dispersed as aerosols are prone to oxidative or photooxidative attack and may be adsorbed on particulates. The nature and extent of these reactions is unclear and relatively unstudied. There are no reliable estimates of the fate of this component. Undoubtedly, some proportion makes a contribution elsewhere, perhaps far removed, to the diffuse inputs of precipitation and dry fallout.

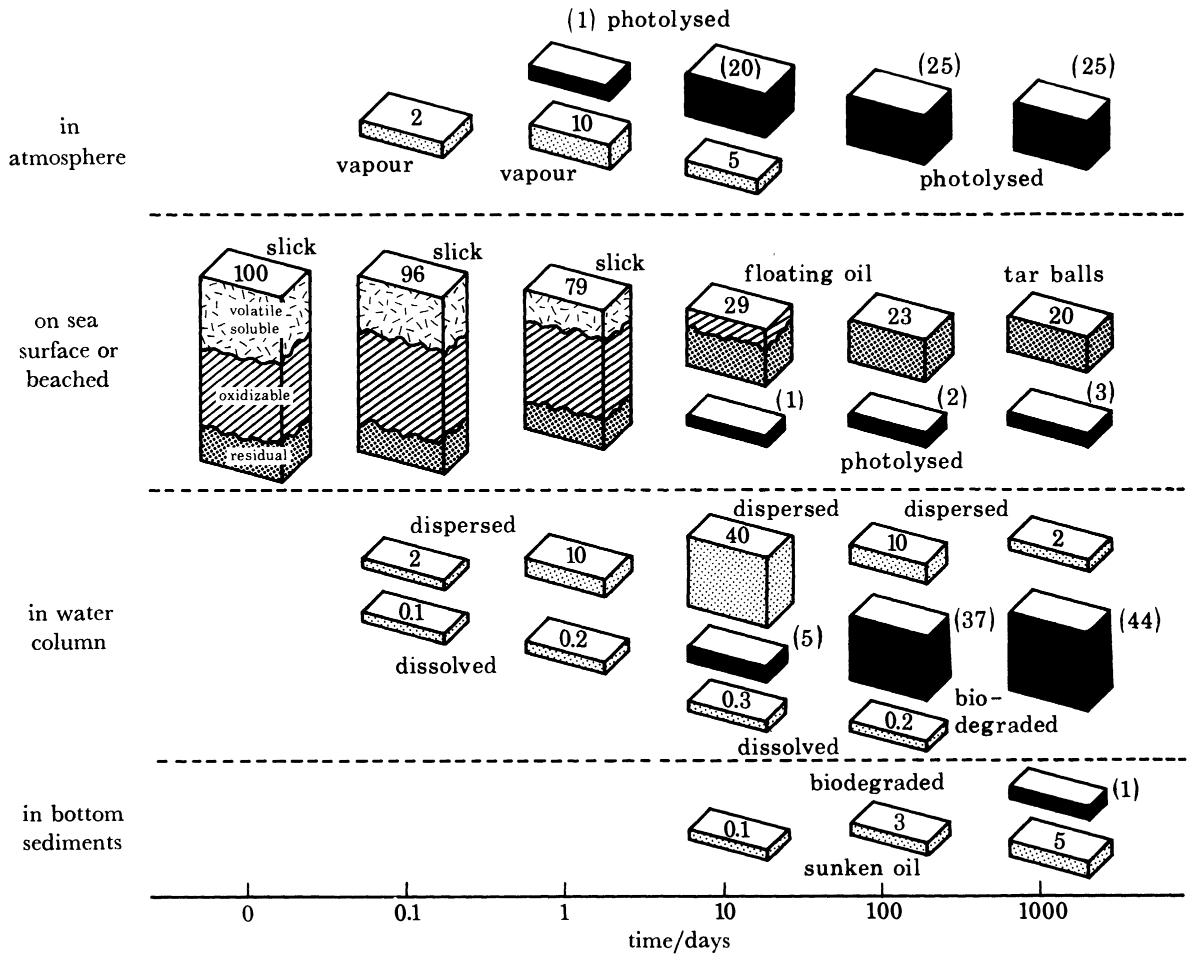

Figure 6. A mass balance with time for the major processes of redistribution of spilled oil and the fate of the gross fractions. This speculative mass balance illustrates the distribution and conversion of an initial 100 volumes of oil at various times after spilling. The black boxes represent oil converted to another chemical form (modified from a diagram by D. Mackay (chapter 2 of Sprague *et al.* 1981) and based on a similar diagram by J. N. Butler, Harvard University).

Components of the slick enter the water column by adsorption on particles, formation of oil–water emulsions and dissolution. The last two processes are enhanced by surfactants, e.g. the soluble charged products from photodegradation of the slick. In the water-dispersed fraction of crude oil, aliphatics are more likely to be associated with particulate materials than the more soluble low molecular mass aromatics (Blackman & Law 1980*a*). The combined processes may ultimately disperse as much as 20–40% of a slick into the mixed zone of the water column, resulting initially in 'oil' concentrations as high as 300 μg ml^{-1} immediately under the slick. Photooxidative decomposition is small, 0.7% per day being estimated from laboratory tests. More significant is the introduction of surfactant-type products of photochemical oxidation and the selective loss by this route of aromatic and sulphur derivatives, which will ultimately be degraded. In spite of enhancement of solubility by the presence of surfactants, it is unlikely because of its very nature that petroleum would contribute a large soluble fraction, although the water would be enriched in the lower molecular mass and more polar components, e.g. about 13% of a slick diesel oil evaporated over 40 h compared with some 0.053% lost by dissolution. Quantitatively, adsorbed and emulsified oil probably represent the major dispersed losses in the sea. The contribution that each makes is difficult to distinguish.

Introduction of dispersant, provided there is mixing in the water column, may result in a substantial increase in oil concentrations in the water and in the material settling out. At typical U.K. sea temperatures, concentrated dispersants are ineffective at oil viscosities above 5000–7500 cP† (R. F. Lee 1980), such as heavy fuel oils (Blackman & Law 1980*b*). Slicks (7 l) treated or untreated with dispersant in ecosystem enclosures 19 m deep over 8 days showed that 20% of the Forties oil was dispersed in the water column with 14% subsequently found in the settlement material, compared with less than 1% in the water column in the untreated system (Ward & Davies 1978).

The appearance of the slick changes quickly after the rapid and considerable losses to the atmosphere and water column during the first 24 h. It becomes more viscous and discontinuous. In terms of spreading, turbulence of the surface water and lateral shears in water motion become increasingly important and ultimately dominate as discrete floating patches or particles of oil develop. Some crudes form water–oil emulsions often referred to as 'chocolate mousse'. It has been said that some light North Sea crudes do not readily form mousse, but this did occur in the studies of Ward & Davies (1978). The detailed chemical and physical studies and comparisons of the weathering processes after the Ekofisk and Ixtoc blowouts (Haegh & Rossemyr 1980; Patton *et al.* 1981) demonstrate how the chemical components fractionate between the products of the various processes operating during weathering. After some 70–80 days weathering of Ixtoc oil, areas of small mousse patches with cracked, scaly skin flaked in turbulent seas, exposing relatively unweathered mousse, and released a surface sheen until a skin reformed. This process accelerates surface-dependent evaporative dissolution and photochemical weathering and enhances the rate of microbial colonization. The small mousse patches had lost almost all the alkanes eluting before n-C_{15} and had only low levels of naphthalenes. The flakes had few alkanes but were enriched in the polar components. The heavy fuel oil from *Eleni V* (relative density 0.94–0.97) behaved quite differently. It travelled underwater up to 1 km before reaching the surface and quickly formed patches of viscous brown mousse that barely floated. On the beaches, sufficient sediment adhered to sink the mousse patches, which then rolled about in the surf. Similar processes probably occurred in the turbid waters offshore, producing denser masses that travelled on or near the seabed and came ashore later (Blackman & Law 1980*b*).

The prevailing winds and surface circulation in U.K. waters suggest that residual weathered oil or tar-balls on the sea surface have a high probability of being stranded eventually along the coastline. Persistent, directional, strong winds would effectively clear the stock of floating

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† 1 cP = 1 mPa s.

oil to the coastline and must in part account for the low but variable concentrations of tar-balls found on the seas around the British Isles (usually less than 0.1 mg m^{-2}).

Stranded oil

Oil can be stranded ashore unweathered or at any stage of weathering and may be recovered (mostly in sheltered areas) by a variety of mechanical methods. After the *Eleni V* spill of heavy fuel oil, hydrocarbon concentrations of inshore waters and mussel tissues returned to 'normal' 300–400 days after an exposed and mechanically cleaned beach became visibly clean after winter storms. In contrast, oil stranded on a sheltered uncleared beach showed little overall degradation. It was protected by the rapid development of a surface crust within which the dense, viscous fuel oil was retained virtually unchanged (Blackman & Law 1981). After the *Amoco Cadiz* spill of light crudes from the Middle East, coastal processes and geomorphology played a major role in dispersal and accumulation once the oil came ashore. Exposed rocky coasts were cleaned of extremely heavy doses within a few days. Oil accumulated on sheltered rocky coasts, sheltered tidal flats and in estuarine marshes (Hayes *et al.* 1979).

Sedimentation

Quantitatively, this process is more important in estuarine and coastal areas where turbidity is high. However, after the Ekofisk blowout, sedimenting oil was observed at sea by using sediment traps. The daily oil flux was 0.3 mg m^{-2}, representing as much as 0.013% of the oil in the slick sedimenting daily (Mackie *et al.* 1978).

The penetration of oil into sediments is related to sediment type and composition. Coarser sediments allow greater penetration than fine unconsolidated sediments. They also have higher rates of biodegradation than fine sediments, perhaps because of greater aeration and higher nutrient concentration in the subsurface. Coarser sediments are also associated with more exposed coasts and more effective weathering processes. Consequently, the highest concentrations of oil are associated generally with silt-sized sediments, which have a larger surface area (R. F. Lee 1980). Resuspension and turnover of the surface sediments apart, remobilization can occur via the pore waters. Storms and dredging operations are major but occasional influences on these processes.

Processes in estuaries

Rivers carry a hydrocarbon load derived from terrestrial biogenic sources, characterized, in plants and insects, by *n*-alkanes with predominantly odd carbon numbered chain length members, some alkenes and a variety of cyclic monoterpenes and diterpenes. In addition, sewage, specific and non-specific industrial effluents and storm water runoff also contribute hydrocarbons that include petrogenic material. The hydrophobic and lipophilic hydrocarbons have low true solubilities, ranging from 10^2 to 10^{-23} mg l^{-1}. Dissolved organic and humic substances enhance solubility, perhaps by a few times, by aiding micellar formation. Much of the river load is associated with organic material and carried on particles, the amount depending on topography and weather conditions.

It is not easy to generalize about estuarine processes, nor is it advisable. No two estuaries are alike and it is difficult to distinguish between general principles and unique details. For instance, extreme conditions such as storms are often more important than average conditions in determining changes in estuarine sediments. In estuaries, dilution and removal processes occur; on dilution large pH and salinity changes occur, causing precipitation of the humic material, which is colloidal. Most humic material in estuaries is terrestrial and probably precipitates out within the estuary or close inshore. Flocculation is a potentially effective scavenging mechanism for the removal of lipophilic substances from surface waters. Thus much of the organic and particulate matter and the hydrocarbon load is likely to be deposited in estuaries. Colloidally dispersed micelles of oil form spontaneous associations in the presence of dissolved electrolytes, which may induce clay-particle flocculation so that a significant quantity of oil may be adsorbed to clays and, together with oily globules, sedimented (Bassin & Ichiye 1977). But the authors thought that the observed sedimenting of oils by clays in coastal waters is due more to electrolytic flocculation of sea water than to an affinity between oils and clays.

Fractionation of oil occurs during adsorption to particles and sedimentation. In investigations of estuarine ecosystems (5 m deep above silty clay sediments), a dispersion of diesel oil (*ca.* 95 $\mu g\ l^{-1}$) was added (Gearing *et al.* 1980). Fractionation resulted in the sedimentation of about 50 % of the relatively insoluble saturated hydrocarbons but less than 20 % of the more soluble aromatics. In other experiments, particulates adsorbed about 15 % of the added oil, and 7–16 %, depleted in the low molecular mass aromatics relative to the original oil, was ultimately found in the sediments. There the oil-derived hydrocarbons were gradually mixed through the bioperturbation zone. Biodegradation and other processes removed most of the hydrocarbons soon after addition of the diesel dispersion ceased, but a residue of 10–20 %, mainly in the form of branched and cycloalkanes as well as aromatic compounds, persisted more than a year later (Gearing *et al.* 1980). It was concluded from this and other work that hydrocarbons are lost from the water column according to their physical and chemical properties. Hydrocarbons associate with suspended particles inversely with the degree of aqueous solubility and with the size of the particles, but directly in proportion to the percentage of organic matter. Interestingly, in the case of the silty clay sediment above, adsorption of diesel to the sediment actually increased when the organic matter of the sediment was removed. Association depends on the prior physical state of the oil. Agglomeration of oil and particles occurs when the oil is dispersed as droplets at relatively high concentrations (1 $mg\ l^{-1}$ to 1 $g\ l^{-1}$) and little chemical fractionation of hydrocarbons occurs. Adsorption to sedimenting particles low in organic matter is insignificant in the presence of low concentrations of dissolved hydrocarbons. At the intermediate concentrations used in the work described above, most of the aromatics were either dissolved or solubilized whereas more than 90 % of the aliphatics was adsorbed on particles.

On average, the *n*-alkane contents of estuarine sediments around the British Isles are about six times higher than those in the open sea. Fluorescence measurements on extracts of the surface waters from the River Forth – Firth of Forth system extrapolated to notional crude oil equivalents show decreasing concentration towards the open sea as do total carbon measurements, a trend not necessarily shown by the *n*-alkanes.

The general characteristics of the freshwater plume leaving estuaries around our coasts are well known and predictable, and the effects are localized in coastal waters. Whatever the combination of processes in the estuary, the impact of the river hydrocarbon load on the open sea is very small indeed. The area of contamination of specific effluents inputs along the coastline such as refinery effluents is usually localized (figure 3).

Biodegradation

The different hydrocarbon classes degrade at different rates, tending to decrease as molecular mass and branching or substitution increases. The petroleum residues, which include the asphaltenes, are resistant to biodegradation. The initial rates of degradation are related to the initial populations of petroleum-degrading organisms and the previous exposure to petroleum inputs. Rates for water samples from experimental ecosystems were determined by adding radio-labelled substrates *in vitro*. Rates increased after prior exposure to oil (Lee & Takahashi 1977; Davies *et al.* 1980). Gunkel *et al.* (1980) found high populations in the North Sea near the Ekofisk oilfield and at the mouth of the Elbe. Table 9 compares mineralization rates for the water column and sediment in areas experiencing different inputs.

TABLE 9. COMPARISON OF DAILY MINERALIZATION RATES IN WATER (MICROGRAMS PER CUBIC METRE) AND SEDIMENT (MICROGRAMS PER SQUARE METRE) FROM AREAS EXPERIENCING DIFFERING INPUTS

(Data from Lee & Takahashi (1977), Davies *et al.* (1980) and Massie *et al.* (1981).)

	water		sediment	
areas	naphthalene	benzo[*a*]pyrene	naphthalene	benzo[*a*]pyrene
ecosystems	50–5000	0–10	—	—
Sullom Voe	14	0.1	113	1.0
North Sea	7	0.15	68	1.2
oilfields	0–20000	0.3	0–3130	0–3
Forth Estuary	200–16500	—	25–40	0.2–0.3

In sediments, microbial degradation of petroleum hydrocarbons is more rapid near the surface than in the lower layers, since oxic conditions are required. The decrease in *n*-alkanes (relative to branched and cyclic alkanes) with depth in sediment cores is attributed to the greater degree of biodegradation of the *n*-alkanes. Hydrocarbons buried in the sediments can be remobilized to the surface by diffusion in the pore waters, which may account for the tendency of aromatics of low molecular mass not to survive long-term accumulation. Factors affecting the degradation of individual compounds have been investigated. [^{14}C]Benz[*a*]anthracene was followed for 230 days in the experimental estuarine ecosystem described earlier (Hinga *et al.* 1980). It was transported rapidly to the sediment. The half-life in the water column was 24 h whereas that of the total activity including degradation products was 52 h. Most biodegradation probably took place in the upper layers of the sediment, with both biodegradation and biotransformation processes giving rise to various labelled products identified in the water column and sediment. In total, 29% was respired to CO_2, and the remaining extractable activity (43%) was evenly divided between the parent compound and intermediate metabolic products. The 20–30% unaccounted for was unlikely to have been lost by evaporation but, more likely, by poor extraction efficiencies. No estimate could be made of the absolute lifetime of benz[*a*]anthracene in the system. It was concluded that aromatics of high molecular mass are probably carried on particles and that the metabolites are present long enough to be available to organisms.

Benzo[*a*]pyrene deposited in reduced sediments, where facultative and anaerobic bacteria predominate, will persist longer than in surface layers, where aerobic bacteria predominate. Some of the difficulties in making realistic estimates of degradation in sediments were shown by Delaune *et al.* (1981), who compared the degradation rate in sediment in the presence of changing redox potential and pH and attributed differences of 100-fold to changes in these parameters. The organic carbon content of sediment is also a limiting factor since the degrading bacteria cannot use PAHs as their sole carbon source. Temperature, water–sediment exchange processes, rates of bioperturbation and the physical characteristics of the sediment all probably help to control rates of degradation.

Uptake accumulation and depuration in organisms, trophic transfer and metabolism

Aspects have been reviewed recently by Lee (1977), Malins (1977), Teal (1977), Corner (1978) and Anderson (1979). Marine organisms show selective uptake of aliphatic (Hardy *et al.* 1974) and aromatic (Varanasi & Malins 1977) hydrocarbons. The latter may be the result of differential rates of metabolism of aromatic compounds. Varanasi & Gmur (1981) exposed English sole simultaneously to benzo[*a*]pyrene and naphthalene in sediments containing 1 % crude oil. The bioconcentration of naphthalene in tissues was much greater after 24 h. After 7 days the naphthalene-derived activity decreased but the benzo[*a*]pyrene-derived activity increased. After transfer to clean sediment for 24 h, more activity from benzo[*a*]pyrene than naphthalene was retained. The liver metabolized benzo[*a*]pyrene to a much greater extent. Exposure of bivalves for 180 days to crude oil dispersions in sea water ranging from 0.03 to 3 mg l^{-1} showed that decreases in the tissue burden began 30–120 days after initial exposure and continued at least 60 days after exposure ceased (Anderson 1979). Fractionation of the components was markedly different. Branched and cyclic alkanes (C_{12}–C_{16}) were retained preferentially compared with *n*-alkanes. Aromatics of high molecular mass and substituted aromatics were concentrated selectively but aromatic sulphur compounds were not. Unfortunately it is not possible to extrapolate directly from one species to another with respect to uptake and release rates of aliphatic or aromatic hydrocarbons. Differences in uptake of *n*-alkanes may be due to the presence or absence of dispersed oil or oil adsorbed on particles and to the intrinsic fat metabolism of the animal. Uptake of alkanes is relatively small when only water-soluble compounds are available. When animals are exposed to oiled sediments it is difficult to distinguish between uptake from ingested sediment or from interstitial water containing hydrocarbons leached from sediment. Generally, the latter pathway is probably more important except perhaps in filter feeders. PAHs such as benzo[*a*]pyrene can be taken up by deposit feeding organisms. Naphthalenes and phenanthrenes are accumulated rapidly from solution but apparently are not taken up (or at least retained) significantly from oil-contaminated sediment. However, the concentrations of hydrocarbons in interstitial waters, derived from partly anaerobic sediments containing large amounts of aromatics, are important.

Part of the depuration process depends on the partitioning of hydrocarbons between the aqueous and lipoidal phases of tissues and retention tends to depend on the ratios of their water and lipid solubilities (Anderson 1979). The level of organ-system development in a species and its hydrocarbon metabolism also affect depuration rates. The pattern of release of specific compounds is similar. Invariably, the *n*-alkanes are released most rapidly possibly because they are incorporated in faeces or pseudofaeces. Usually, naphthalene is lost first from the aromatic fraction in contaminated tissues followed by the mono-, di- and trimethylnaphthalenes. The detailed differences among them and between the naphthalenes and phenanthrenes are not established. Rates of depuration appear to decrease from phenanthrene to chrysene and to benzo[*a*]pyrene.

There are few data on trophic transfer of hydrocarbons (Murray *et al.* 1977). Dobroski & Epifanio (1980) cultured diatoms in benzo[*a*]pyrene and fed them to clam larvae. The rate of uptake by the diatoms was much greater than the rate of transfer to the larvae, attributed to the higher efficiency of direct uptake and the larger quantity of benzo[*a*]pyrene available in the water. However, the authors concluded that the processes may be equally important in the accumulation of benzo[*a*]pyrene in natural populations.

The principal enzymic degradation pathways are the oxidation of alkanes to fatty acids, the hydroxylation of the aromatic ring via epoxide intermediates and the oxidation of alkyl side-chain substituents on the ring. Induction of these processes occurs during chronic exposure to petroleum or other organic pollutants. Thus the previous history of exposure is important. One substrate may influence the favoured metabolic route of another. The metabolism of 2,6-dimethylnaphthalene yields a number of products (Gruger *et al.* ,1981) that may or may not be conjugated principally as glycosides or glucuronides. The presence of alkyl substituents increases the proportion of biliary glucoside conjugates. The glucuronides yield two metabolites, the alcohol representing oxidation at a methyl substituent and the dihydrodiol representing oxidation of an aromatic ring. However, previous exposure to naphthalene or *p*-cresol, or both, significantly reduces the alcohol metabolite and increases the dihydrodiol, i.e. it favours the formation of the potentially damaging epoxides. There is a shift from side-chain oxidation to aromatic ring hydroxylation as a result of xenobiotic interaction (Gruger *et al.* 1981).

TABLE 10. 'OIL' CONCENTRATIONS IN WATERS SURROUNDING THE BRITISH ISLES

environment	concentration in water/($\mu g\ l^{-1}$)	concentration in sediment/($\mu g\ g^{-1}$ d.m.)
coastal		
free from apparent oil pollution	0.5–5	0.5–30
low contamination	5–20	5–50
high contamination	< 200	40–3000†
open sea	1–7	0.3–55
gas fields		
southern North Sea	10–20	2–120
oil fields		
northern North Sea	0.5–35	0.5–260

HYDROCARBON CONCENTRATIONS IN U.K. WATERS

We conclude our discussion of the inputs and fate of oil by briefly considering the distribution of hydrocarbons actually found in some sectors of the environment, the result of all the inputs. Table 10 summarizes hydrocarbon analyses accumulated over a number of years by the Fisheries Departments and grossed up to nominal 'oil' values. Similar results have been obtained by other groups (Gunkel *et al.* 1980; Grahl-Nielsen *et al.* 1979).

At least six different techniques have been adopted for petroleum hydrocarbon analysis. Among the physical methods, fluorescence measurements provide most data but different crudes have been used as reference, e.g. Ekofisk (Law 1981) and Forties (Davies *et al.* 1981). High values do not necessarily reflect significant oil inputs (Davies *et al.* 1981). The remaining methods depend on quantitative separation of alkanes and aromatic hydrocarbons, including PAHs. However, authors have measured different components within the range C_{11}–C_{33} for alkanes and 8–48 different PAHs and two-ring compounds. The concentrations and distribution of some PAHs, e.g. benz[*a*]anthracene, benzfluoranthene and cyclopentapyrene are more indicative of combustion products than oil, whereas the monomethyl to trimethyl substituted naphthalenes, phenanthrenes and dibenzthiophenes (NPD) are more representative of oil inputs.

The background 'oil' concentration of subsurface waters is 1–2 μg l^{-1}, equivalent to 0.2–0.5 μg l^{-1} alkanes and 0.02–0.05 μg l^{-1} NPD. The equivalent 'standing stock' of oil in the water column of the North Sea would be 55–110 kt. Concentrations in the water and sediment are generally low except in coastal areas and estuaries experiencing the inputs described earlier and in the immediate vicinities of specific discharges. Studies over the last 7 years, particularly an annual assessment of a line of stations from the Firth of Forth across the North Sea to the Forties oilfield, have failed to show any particular statistically valid trend in hydrocarbon concentrations (Hardy *et al.* 1981). Within the experimental variation the concentrations remain relatively constant year by year. An increase in input that leads to a doubling of the background or previous concentration should be detectable with confidence (Gearing *et al.* 1979; Grahl-Nielsen *et al.* 1979; Davies *et al.* 1981).

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Discussion

DALE STRAUGHAN (*University of Southern California, Los Angeles, U.S.A.*). In field studies, we have found that petroleum is distributed in a very patchy way and the ideal is probably to take a hydrocarbon sample with each biological sample. Does this variability occur in the type of situation indicated by the contour lines of hydrocarbon levels shown in Southampton water?

K. J. WHITTLE. Indeed, hydrocarbon concentrations are very variable in sediments, perhaps by as much as fivefold in adjacent cores. However, with sufficient numbers of samples, as in this case, it is possible to discern trends in concentration away from the discharge point, as it has been possible in other areas where discharges are high such as Narragansett Bay and New York Bight. The concentration range actually covers about 100-fold in Southampton Water and the distribution can be described approximately by the contours at that particular sampling time. This general trend away from the discharge also fits independent data of our colleagues in M.A.F.F., but they show at another point in time that the detailed contours would be drawn differently because of continual redistribution of sediments in the estuary.

D. J. Crisp, F.R.S. (*Marine Science Laboratories*, *Menai Bridge*, *Gwynedd*, *U.K.*). Dr Whittle has provided us with estimates of petroleum hydrocarbons in the marine environment. In addition to these man-made inputs, there are naturally occurring seeps of mineral oil – small in the U.K. but not negligible globally – and biogenic hydrocarbons, some of which are common to mineral hydrocarbons. I wonder whether Dr Whittle would expand our perspective by comparing the input of petroleum products with the natural input from living organisms.

K. J. Whittle. My talk was concerned primarily with petroleum-derived hydrocarbon inputs, but in our written paper we have briefly referred to estimates of the biogenic hydrocarbon input to broaden the perspective. It is large and probably of the order of 100–200 kt annually. It is important to remember that it comprises both terrestrial and marine sources and is composed of a quite characteristic suite of compounds much less complex than the petroleum input.

J. M. Baker (*Field Studies Council*, *Orielton Field Centre*, *Pembroke*, *U.K.*). Concerning variability in sediment oil contents, perhaps there are differences between chronic discharge areas such as Southampton Water and 'one-off' spill areas. Our recent field experimental data from plots initially oiled evenly certainly support Dr Straughan's comments on variability – there are orders-of-magnitude differences between cores from the same plot.

K. J. Whittle. I believe one should expect differences between distributions observed at chronic discharge sites and at one-off spill sites. We have noted large variations between adjacent cores in subsequent sampling of bottom sediments purposely oiled *in situ*, and at the same time it is also clear that one can define quite easily the degree of contamination of sediments in the vicinity of platforms using oil-based drilling muds, as a result of disposal of the drill cuttings.

W. N. Bonner (*British Antarctic Survey*, *Madingley Road*, *Cambridge*, *U.K.*). Figure 5 showed the fate of the components of an oil spill as time passed. Surely this must depend very much on the physical conditions, e.g. sea temperature and sea surface condition. An extreme example will occur in polar seas when the surface freezes and spilt oil becomes entrapped.

K. J. Whittle. I agree entirely. Our paper is concerned with inputs and fate with respect to the temperate environment around the British Isles. We have drawn attention to the variability in the progress of the various dispersive processes due to environmental conditions, not forgetting the nature of the oil and where it was spilt.