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of Marine Pollution (GESAMP)

Impact of oil and related chemicals on the marine environment

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Notes

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Definition of marine pollution by GESAMP:

Pollution means the introduction by man, directly or indirectly, of substances or energy into the marine environment (including estuaries) resulting in such deleterious effects as harm to living resources, hazards to human health, hindrance to marine activities including fishing, impairment of quality for use of seawater and reduction of amenities.

Members of the GESAMP Working Group on the Impact of Oil, Individual Hydrocarbons, and Related Chemicals on the Marine Environment, Including Used Lubricating Oils, Oil Spill Control Agents, and Wastes from Offshore Petroleum Operations

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Foreword

In 1977 GESAMP published its study *Impact of Oil on the Marine Environment* (Rep. Stud. GESAMP (6)). Since that time there have been many advances in the fields of marine pollution research and combating pollution respectively. The International Maritime Organization (IMO) therefore requested GESAMP to prepare a new synopsis of current knowledge on oil pollution supplementing the previous GESAMP review. IMO and the other sponsoring agencies of GESAMP agreed that, besides oil and individual hydrocarbons, this study should include dispersants and other control agents in oil spill responses as well as wastes from offshore petroleum operations.

In order to achieve this objective, GESAMP, at its nineteenth session in 1989, established a sub-group to its Working Group on the Review of Potentially Harmful Substances, asking it to operate under the terms of reference of the Working Group as follows:

1 to prepare short referenced reviews on selected substances which include an assessment of the following factors:
   - (a) the total of particular substances which reach the marine environment (on a local, regional and global scale) with particular attention being given to the relative importance of land-based sources;
   - (b) the fate (transfer, distribution and transformation) of these substances in the marine environment;
   - (c) the effects of these substances on the marine environment and adjacent coastal areas, both direct and indirect, on living resources and human health; and

2 to produce a scientific evaluation of the harmful effect of substances released into the marine environment on living resources, human health, aesthetics and other legitimate uses of the marine environment and adjacent coastal areas.

The Group was jointly sponsored by IMO, the Food and Agriculture Organization of the United Nations (FAO), the United Nations Educational, Scientific and Cultural Organization (UNESCO) and the United Nations Environment Programme (UNEP).

The Group first met in March 1990 under the chairmanship of Dr. P.G. Wells and subsequently twice before presenting its final report to the twenty-second session of GESAMP in March 1992, which adopted the report for publication in the GESAMP Reports and Studies series.

Part I – Executive Summary

Scope and intent of the review

GESAMP, at its nineteenth session (April 1989), agreed that a group would be established to prepare a summary review which would update the previous GESAMP (1977) review *Impact of Oil on the Marine Environment.* It would cover oil and individual hydrocarbons, used lubricating oils, chemical control agents for oil spills, and wastes from offshore petroleum operations. It would consider all major knowledge generated since the mid-1970s, primarily through the use of existing syntheses on the topic; the presentation was to be concise, and to include recommendations for further work.

The Working Group covers their topics comprehensively, from a consideration of the composition, sources and inputs of oil to its ecological and human health effects and its effects on man's use of the sea. The review addresses several key questions on the present levels of contamination, the impact of hydrocarbons and related chemicals on marine biota, the recovery potential of marine ecosystems exposed to these contaminants, the degree of protection required for marine ecosystems known to be vulnerable and sensitive, and recommended research and other actions to fill gaps in knowledge.

The review describes the hazards of marine oil pollution and associated chemicals and wastes as they are understood currently, and clarifies the importance of reducing oil inputs in coastal and offshore waters. It assists in considering fundamental questions, asked by the public and decision-makers alike, such as: how much oil is entering our oceans, and how much harm is it doing?

Summary, conclusions, and recommendations

1 Oil and individual hydrocarbons

1.1 Summary

1.1.1 The input of oil from anthropogenic sources into the marine environment has decreased during the past decade. This is largely due to measures required by international conventions on the prevention of marine pollution by oil from shipping. Although the spatial density of sampling and duration of time series are different in various parts of the world, there are indications that reduction of oil contamination has occurred on a global scale. Estimates in 1981 showed that 3.2 million tonnes of oil per year enter marine environments from all sources; the estimate for 1990 is 2.35 million tonnes. Annual amounts can vary greatly, depending upon accidents and acts of war. There is increasing evidence that the input of oil from land-based sources has so far been underestimated; enclosed and semi-enclosed coastal areas receive far higher amounts than have been indicated in global estimates.

1.1.2 The fate of oil in the marine environment has been studied extensively in both qualitative and quantitative detail over the past 15 years. The ecological impacts of oil are also better understood – many biological effects have been measured and some toxicological patterns have become apparent. Marine birds and mammals are visible victims of oil spills, and concern for chronic sublethal effects caused by spills in low-energy, shallow coastal waters and shorelines is increasing. Some habitats, such as exposed rocky shorelines, recover quickly from oiling events. Other ecosystems, such as mangroves, salt marshes, seagrasses and coral reefs, and polar habitats, are particularly vulnerable and sensitive to oil spills, and may take years to recover.

1.1.3 Oil can affect man's use of the sea. Spills have low or negligible impacts on fish populations but can taint fish and invertebrates, although there is little or no evidence of tainting of fish and shellfish, even by such events. In addition, tar can coat shorelines and harbours, and boats and fishing gear may be oiled during spills. The impacts of spills, large or small, are clearly better understood now than in the mid-1970s and, although there are major efforts worldwide to improve response capabilities, it is generally acknowledged that prevention is the best way of reducing the known impacts of oil on the marine environment and its resources.

1.2 Conclusions

1.2.1 The best current estimate is that 2.35 million tonnes of oil per year enter the marine environment from all sources. This estimate is highly influenced by number and size of shipping spills each year. At least 15% comes from natural oil seeps. Anthropogenic sources include chronic discharges from storage facilities and refineries, discharges from tankers and other shipping along major routes, and accidental events such as oil spills and ruptures of pipelines.

Sources also include river-borne discharges, diffuse discharges from industrialized municipal areas, offshore oil production, and the atmosphere. The sources vary in importance geographically but the primary inputs are generally from land-based sources (refineries, municipal wastes, urban run-off). Recent wars have resulted in major inputs (i.e. Arabian/Persian Gulf). Although oil spills and tar on beaches are highly visible, inputs of oil from land-based sources are of increasing concern, especially near urban centres.

1.2.2 Due to measures required by international conventions on prevention of oil pollution, the input of oil into the marine environment from maritime operations has decreased during the past three decades. In this regard, the entry into force of MARPOL 73/78, Annex I, in 1983 has had a substantial positive impact in decreasing the amount of oil that enters the sea from transportation activities, inputs decreasing from 1.47 million tonnes in 1981 to 0.54 million tonnes in 1989 (IMO, 1990). However, the input has varied by more than a factor of 10 from year to year, with 1979 (IXTOC blowout), 1983 to 1988 (Iran–Iraq war), and 1991 (the Gulf conflict) showing extra inputs which were many times the average of intervening years. Total floating tar observed in 1985 in shipping lanes and their associated surface currents was one-fourth or less of that observed in 1971–72, based on measurements in the Sargasso and Mediterranean Seas. Tanker accidents contribute to 5% of oil input, based on 1990 estimates, but volumes spilled annually are highly variable, making the identification of trends difficult. Tar continues to impair amenity beaches and coastlines in many parts of the world.

1.2.3 Physical, chemical and biological fates of hydrocarbons from spilled oils are better understood now in qualitative and quantitative terms. Many new methods of analysis for hydrocarbons in seawater, sediments and biological tissues have been developed. Investigations have addressed transformation (photo-oxidation, metabolic) by-products of specific hydrocarbons, and other basic characteristics of oils in the environment are better understood. Recent research on the polar fractions of dissolved oil residues has shown the presence of large numbers of oxygenated derivatives of aromatic hydrocarbons; their concentrations often exceed those of each parent hydrocarbon and their toxic effects to marine organisms are largely unknown. Quantitative modelling is most advanced in the areas of transport of slicks, evaporative weathering of slicks and uptake of components of slicks in selected species. Many new biochemical, physiological and toxicological techniques have been developed and applied in research and monitoring.

1.2.4 Reproductive, developmental and behavioural processes are very sensitive to exposure to hydrocarbons. Generally, young life stages are more sensitive than adults, and many juvenile and adult crustaceans and echinoderms are more sensitive than juvenile and adult fish. It is well established that different oil types vary in their toxicities, and that acute toxicity is largely due to components of the water-soluble fractions and dependent upon exact conditions and duration of exposure to them. Chronic sublethal effects caused by petroleum hydrocarbons spilled or discharged in low-energy, shallow coastal waters remain a valid concern.

1.2.5 Marine wildlife (turtles, seabirds, mammals) are often the most conspicuous victims of oil spills. Diving and surface-dwelling populations of seabirds, and sea otters and polar bears in particular, are now known to be vulnerable and sensitive to oiling. Documentation from the field on the effects of oiling on other mammals, especially cetaceans, is scarce.

1.2.6 Short-term impacts of spills are well understood. Except for wildlife, biological concerns largely centre on shallow near-shore areas and coastlines. There is some evidence that petroleum causes long-term effects on populations and communities at spill sites. Some habitats (e.g. low-energy marshes and mangroves) can require decades to return to their pre-spill condition of population, species diversity and habitat quality, while others recover relatively quickly (months to one or two years). Such recovery depends upon degree of oiling, oceanographic regime, and type of habitat and species affected.

1.2.7 Oil spills have low or negligible impacts on fish populations. Significant impacts on local populations generally occur only in shallow waters with poor circulation. In such locations, only small proportions of total regional populations are usually affected.

1.2.8 Tropical coastal ecosystems, such as mangroves and coral reefs, as well as seagrasses in all locations are particularly vulnerable and sensitive, due to greater retention of oil and the exposure of many species and life stages year-round. Damaged coastlines may prematurely erode and important habitats may be lost. Little is known about the time-scales and the recovery patterns and processes of such ecosystems after acute or chronic oiling.

1.2.9 Although large and small spills often result in closure of fisheries by regulatory authorities, there is little or no evidence of tainting of fish or shellfish, even by major spills.

1.3 Recommendations

1.3.1 Controls of discharges of oil from sources other than shipping (e.g. land-based sources, offshore activities) should be strengthened, where necessary, within appropriate national and international systems. More information is required on the characterization of land-based inputs of oils and should be systematically collected by national governments.

1.3.2 More efforts should be made by the appropriate international industrial and intergovernmental bodies in assisting governments in effectively implementing existing oil-pollution conventions.

1.3.3 To diminish the impacts of oil spills, governments should be urged to ratify the recently adopted International Convention on Oil Pollution Preparedness, Response and Co-operation, 1990, which requires the establishment of oil pollution emergency plans on ships and offshore installations and at ports and oil handling facilities, together with national and regional contingency plans, as appropriate.

1.3.4 Global and regional monitoring programmes need to be continued in all marine environments to describe concentrations and distributions of hydrocarbons at the sea surface, and in coastal sediments and biota, and to verify trends.

1.3.5 A selection of important and representative areas worldwide where spills are most likely to occur should be the focus of appropriate pre-spill research and monitoring studies. Studies at experimental spill sites and spills of opportunity should be encouraged, for both science and testing of response equipment and methods.

1.3.6 Research is needed on the fate and effects of phototransformation by-products of oils and the nitrogen-, oxygen- and sulphur-substituted polycyclic aromatic hydrocarbons (PAHs) found in crude oils. If results indicate reasons for concern, methods should be developed for monitoring purposes.

1.3.7 Intertidal and sublittoral communities are at most risk from oil spills and there is limited information on their recovery rates. Sub-acute toxicity studies are required to define dose-response relationships for selected benthic organisms exposed to representative oils.

2 Used lubricating oils

2.1 Summary

2.1.1 Crankcase oils are an important source of PAHs and lead, as well as trace levels of other contaminants such as chlorinated dibenzodioxins, in the marine environment. Sediments contaminated with high levels of crankcase oils, having PAH concentrations in the range 3 to 5 μg/g, are expected to be toxic to selected marine species associated with sediment. The risk of either chemical contamination or the tainting of seafood by crankcase oil is expected to be low or negligible. Any environmental and human health concerns should be focussed on urbanized and industrial harbours. Bilge waters containing used crankcase oil and other lubricating oils are responsible for many bird kills in coastal waters and may be important contributors of beach tar in some regions. Except for possible point sources of contamination, it is expected that industrial oils other than used lubricating oils are of minor environmental importance.

2.2 Conclusions

2.2.1 Crankcase oils are important contributors to point sources of combustion-generated PAHs and lead, as well as trace levels of other contaminants such as chlorinated dibenzodioxins.

2.2.2 Acute toxic effects of crankcase oils in the marine environment are expected to be negligible. However, sediments contaminated with high levels of crankcase oils are expected to be chronically toxic to some marine species, especially those associated with sediment.

2.2.3 There is some evidence that combustion-generated sources of PAHs in sediment in the range 3 to 5 μg/g can produce adverse effects, including carcinogenesis, in some species. This range represents approximately 10 times the background concentration of PAHs.

2.2.4 The risk of either chemical contamination or the tainting of seafood by crankcase oils is expected to be low or negligible.

2.2.5 Any environmental and human health concerns about used lubricating oils and industrial oils should be focussed on urbanized and industrial harbours.

2.3 Recommendations

2.3.1 More information is needed on production volumes and quantities of industrial oils (hydraulic, rolling, cutting, etc.) entering the marine environment and on the sub-acute toxicity of selected additives.

2.3.2 More information is needed on the role of bilge (engine waste) discharges, as distinct from tanker ballast discharges, in the formation of persistent residues such as beach tar.

2.3.3 Chronic toxicity studies are needed to define dose–response relationships for benthic species exposed to sediments contaminated with crankcase oils.

3 Oil spill control agents, particularly dispersants

3.1 Summary

3.1.1 Chemical spill control agents include dispersants, demoussifiers (emulsion breakers), recovery enhancers, shoreline washing agents, herders, sinking agents and biodegradation enhancers. Essentially all research has concentrated on chemical dispersants, which are recommended as one of several response options to spills. Of the other agents, only recovery enhancers and emulsion breakers hold significant potential. Both of these agents have specific and limited applications. Recovery enhancers improve the efficiency of mechanical clean-up of lighter oils and fuels. Emulsion breakers have the specialized use of breaking viscous water-in-oil emulsions (mousses). Herders (surface-active agents which diminish the spreading pressure of oil slicks) can be helpful adjuncts to mechanical clean-up, but have significant limitations. Sinking agents may be useful in some circumstances but the sunken oil is harmful to benthic organisms. Biodegradation enhancers have shown good performance in the laboratory but erratic performance in the field. Burning *in situ* has been considered as an alternative response technique and is discussed here; mechanical response techniques are not.

3.1.2 Assessments of the effectiveness of dispersants in responding to real spills have shown that the amount of oil removed from the sea surface is highly variable, never 100%, and often much less. Dispersants are most effective when applied to freshly spilled oil. However, the reduced adhesion to surfaces and the reduced biological impact in some situations (e.g. mangroves) make dispersed oil a generally less harmful pollutant than untreated oil. The most effective strategy for protecting sensitive coastlines is to disperse the oil offshore.

3.2 Conclusions

3.2.1 Dispersants, properly applied, can help remove oil from the water surface and dilute it to non-toxic concentrations. This reduces the impact of oil on surface wildlife and the risk of contamination of the shoreline. More valuable, but less well-known, is that the application of dispersants to oil before it strands on a shoreline can reduce the adhesion of oil to structures, sediments and organisms and can reduce environmental impact, particularly to mangrove habitats.

3.2.2 Chemical dispersant formulations currently in use have a lower acute toxicity than many crude and refined oils. The toxicity of chemically dispersed oil is no greater than that of mechanically dispersed oil at the same concentrations.

3.2.3 Application of dispersant or hot water to oil that is stranded on structures or rocky shores can re-mobilize the oil, but the dispersed oil may be transported to the sublittoral zone. Application of dispersant to oil stranded on a sandy beach tends to increase its penetration into the sediment.

3.2.4 Dispersal of oil in shallow water with poor circulation increases the exposure of benthic and subsurface organisms and can intensify acute toxic effects at or near the point of application, yet can reduce chronic effects due to decreased residence time.

3.2.5 Elasticizer additives may improve the efficiency of mechanical clean-up, particularly for small spills. Gelling agents are useful for reducing fire hazard in enclosed spaces, by reducing the loss of volatiles.

3.3 Recommendations

3.3.1 Laboratory and field studies should be conducted to quantitatively elucidate the roles of adhesion and absorption in the environmental impact of oil and dispersed oil.

3.3.2 Internationally organized laboratory and field studies should continue to document the long-term effects of dispersed oils on shallow-water marine communities, at all latitudes.

3.3.3 Long-term studies of the recovery of selected ecosystems from exposure to oil and dispersed oil and other countermeasures would be particularly useful if carried out at sites where the effects of oil and dispersed oil have already been studied on a shorter time-scale. Both experimental sites and sites of accidents should be included in such studies.

3.3.4 Internationally organized experimental oil spills are needed for a number of purposes: to develop remote sensing techniques, to improve application techniques for dispersants, to study the technique and environmental impact of burning *in situ*, to develop quantitative measures of the effectiveness of dispersants, and to evaluate techniques for bioremediation.

3.3.5 Research is needed on additives which improve the efficiency of mechanical clean-up.

4 Wastes from offshore oil exploration and exploitation

4.1 Summary

4.1.1 Since the previous GESAMP review of this topic (1977), the enormous growth of the offshore oil and gas industry and its steady advance into deeper waters has raised concerns about the impacts of its activities on the marine environment, fisheries, and other legitimate uses of the sea. Any evaluation of these impacts needs to take into account environmentally significant factors such as relative quantities of discharges, differences between single-well exploration drilling and multi-well development and production activities, the spatial extent of effects, potential for recovery, and special environmental sensitivities. The following discharges are major in size: drilling muds and cuttings, production water, storage displacement water and ballast water. Minor discharges arise from cooling water, deck drainage, domestic sewage, well-treatment fluids, produced sand, desalination waste, and pipeline treatment fluids. Atmospheric emissions and fallout from flaring remain largely unquantified.

4.1.2 Concerns have been focussed on hydrocarbons in drilling muds and production water, heavy metals from drilling wastes, surfactants, biocides and the possibility of fish and shellfish around offshore installations becoming tainted. The extent and severity of ecological impacts and the potential and time-scale for recovery once drilling discharges cease have caused intense debate. The systems of regulatory controls, for both the states bordering the North Sea and the North American continent, are therefore changing very rapidly as new evidence becomes available and monitoring around discharge sources covers longer periods of drilling and post-drilling history. These changes have implications for regulatory controls elsewhere in the world.

4.1.3 The possibility of tainting in fish and shellfish has been of particular concern. Surveys for tainting of fish have been carried out at exploration and production sites where oil-based muds have been used. Only a few surveys, of varying quality, have so far been reported. Tank studies of tainting have also been conducted.

4.2 Conclusions

4.2.1 The environmental impacts in the marine environment of operational discharges of wastes from oil and gas exploration and production activities are circumscribed, and smaller than those from other human marine activities (e.g. fishing, dredging, offshore disposal of waste). From a regional perspective, the total area of the affected seabed is very small.

4.2.2 Data from both the North Sea and the Gulf of Mexico show that biological changes have occurred in benthic communities as much as 5 km from production sites, mainly attributable to the discharge of drilling wastes, including cuttings.

4.2.3 Major biological changes around production sites have been reported to extend to maxima of 500 to 1,000 m from source, and contamination by hydrocarbons to maxima of 8 to 12 km.

4.2.4 There is no evidence that discharges of production water, in the absence of other wastes, affect benthos. Their chemical composition and the dilution regimes around offshore installations mean that this effect could only be significant in shallow inshore areas.

4.2.5 The effects of drilling discharges from single-well exploration and from multi-well development and production activities are similar quantitatively, but differ greatly in magnitude, spatial extent and predicted recovery rates.

4.2.6 Recovery of impacted sites begins soon after cessation of drilling, as shown for a number of sites in the North Sea.

4.2.7 Given their typical chemical composition and the amounts discharged, there is no reason to expect any hazard to human health from the discharge of chemical wastes from offshore exploration and production.

4.2.8 The discharge of oil-based drilling muds and cuttings from exploratory drilling has the potential to taint flatfish. The highest risk of tainting of fish would occur in the immediate vicinity of the disposal site for the cuttings, and any effect would not be expected to last for long.

4.2.9 A small proportion of flatfish caught in the vicinity of some North Sea production installations where oil-based drilling mud had previously been used were found to be tainted. Although the discharge of production water from platforms has the potential to taint fish on the basis of initial concentration, dilution of the discharge plume within 1,000 m of the discharge site renders the risk negligible.

4.3 Recommendations

4.3.1 Information on impacts, additional to the existing offshore data from sites in the North Sea and near North America, should be obtained from a larger variety of environments and latitudes in more vulnerable localities, such as shallow or enclosed waters and the Arctic marine environment.

4.3.2 Monitoring of chemical and biological effects of production sites should continue to strengthen the data base for long-term ecological change in the peripheral zones of effects, to better differentiate the effects of water-based from oil-based drilling muds and of mineral-oil-based from non-mineral-oil-based muds, and to evaluate recovery of the impact zones.

4.3.3 The nature and scale of the inputs from flaring need to be established.

4.3.4 On the basis of the few existing studies, and only from a few areas, there should be further scientific surveys of benthic resource species (e.g. flatfish and shellfish) in the vicinity of drilling installations to assess and document the risk of tainting.

4.3.5 Regulations for the control of discharges of wastes and other matter from offshore platforms and installations have to be established on the national, regional and global level.

Part II – Resource Document

Chapter 1 Introduction

1.1 The sponsoring agencies of GESAMP requested an updated study of *Impact of Oil on the Marine Environment*, following from the GESAMP oil report of 1977 (*Reports and Studies No. 6*, GESAMP, 1977) and the brief coverage of oil pollution in the recent report *State of the Marine Environment* (GESAMP, 1990). Besides considering petroleum oils and their component hydrocarbons, the present working group was asked to assess the impacts of used lubricating oils, spill control chemicals (especially dispersants), and wastes from offshore petroleum operations.

1.2 There have been many advances since the mid-1970s in the field of marine oil pollution research and response, and in the petroleum sector itself. Several thousand new scientific papers and reports have been published on the topic of sources, characterization, fate and effects of oil and its components (see, for example, the bibliographies by Samson *et al.*, 1980; NRC, 1985; Seakem Oceanography, 1987; and Young, 1986). This work was stimulated by the occurrence of accidental spills of all sizes during the 1970s and 1980s; by the need for effective countermeasures to reduce environmental and amenity damage wherever possible; by the adoption of the MARPOL 73/78 Convention; by the continuation of oil exploration and exploitation in offshore areas worldwide; and by the scientific, fisheries, management, regulatory and public concerns about the impacts of marine oil pollution. There has also been increased awareness that oils such as used lubricating oils and industrial oils reach the sea from many land-based sources (see Chapter 3).

1.3 Several key questions about oil, hydrocarbons and related chemicals and wastes are addressed in the different sections of this review and they form a basis for the summaries and recommendations:

- UNDERSTANDING. How well do we now understand the sources (and total amounts), fate (transport, distribution and transformation), and effects (direct and indirect) of hydrocarbon inputs into the sea? Do we have sufficient knowledge about land-based sources of hydrocarbons to the sea, especially in enclosed seas and shallow coastal waters? What are the relative hazards and risks of spilled oils to coastal and offshore marine ecosystems?
- IMPACTS. What are the impacts of oils, used oils, oil spill control agents, and wastes produced by the offshore oil industry? What are the relative hazards of these materials to coastal and offshore ecosystems?
- PRESENT SITUATION. How much damage to living resources, human health, aesthetics and other legitimate uses of the seas is sustained from oil inputs? Where is the situation getting worse? Where is it improving?
- ECOSYSTEM RECOVERY. How rapidly and by what mechanisms do oiled marine ecosystems at different latitudes recover from acute and chronic exposures to hydrocarbons? How reliable is the evidence of recovery?

- PRINCIPLES AND CONCEPTS OF OIL POLLUTION. How well can we predict the impacts of future pollution from oil and its refined products? What are the main principles and concepts emerging from current knowledge on this topic?
- MINIMIZING IMPACTS. Can marine resources, especially fisheries, wildlife and sensitive habitats, be protected by spill countermeasures and measures to control the discharge of hydrocarbons and wastes?
- RESEARCH NEEDS. What research is being done (especially in the wake of recent large accidents) or needs to be conducted worldwide (such as better documenting land-based sources of oil to the sea)?

Consideration of these questions helps to define the hazards of marine oil pollution, and associated chemicals and wastes, as they are understood currently, and clarifies the importance to be attached to reducing oil inputs to coastal and offshore waters. The review should also assist in answering the popular questions, asked continuously by public and administrators alike: How much oil is in our oceans and how much harm is it doing? What are the main sources, and what can be done to eliminate or reduce them?

1.4 This report is a synopsis of current knowledge on oil pollution, supplementing the previous GESAMP review (GESAMP, 1977). It is based on reliable reviews and other significant materials published since 1977 and the knowledge and critical evaluation of the Working Group. Intentionally, this report is not an exhaustive treatise. Instead it provides a documented up-to-date summary and hazard assessment of oil and related chemicals and wastes. The Working Group has strived for condensation and generalization wherever possible, supported by original analysis, summary tables and figures, and an extensive bibliography. The earlier literature, listed in GESAMP Report No. 6 (1977), is not recompiled nor re-evaluated, with the exception of the sections on tainting of biological resources.

1.5 Sources of information and experience abound and provided a challenging task of summarizing the major facts. Experimental studies have continued, although at a slower pace by the late 1980s. Many recent oil spills have been extensively studied and reported upon (e.g. *Amoco Cadiz* 1978, *Bravo* 1978, *Eleni V* 1978, IXTOC 1979, *Kurdistan* 1979). The 1989 *Exxon Valdez* spill in Alaska is being intensively studied now (Baker *et al.*, 1990; Maki, 1991). Major experimental oil spills under natural conditions have taken place for scientific study (e.g. BIOS 1980–84 (in Sergy, 1987); Panama spills (in API, 1987); Searsport spill in Maine and many others with oil and dispersants, (NRC, 1989)). The literature includes research papers, bibliographies, conference proceedings, newsletters, and technical reports on countermeasures. Most importantly, a number of reviews on oil, used oils, spill control agents, and offshore chemicals have been published since the 1977 report and form, in large part, the basis of this review (see Table 1.1). Such reviews contain a large body of information and new understanding that was unavailable for the 1977 GESAMP review. Recent papers and reviews also illustrate the influence of newer techniques (chemical, biological, computer modelling, remote sensing, etc.) that have been used to assess the sources, fate, transport and effects of hydrocarbons in marine waters, sediments and biota in recent years. They illustrate the evolution of scientific fields such as ecotoxicology that enable more accurate hazard assessments to be made of chemicals in general. They also emphasize the importance of land-based sources of oil components to the sea, although much less information is available.

1.6 It is hoped that this report, with its summary nature and extensive references to important recent work, will contribute to a better scientific, public and governmental understanding of the status of oil and related chemicals and wastes as marine pollutants. Priority should be given to filling key gaps in that understanding and, above all, preventing such materials from entering the sea.

Table 1.1 ***Reviews of marine pollution by oil and related chemicals since GESAMP (1977) – a selection***

Reviews	References
OIL AND HYDROCARBONS	
Effects of petroleum on Arctic and subarctic marine environments and organisms	Malins (1977)
Petroleum hydrocarbons in the marine environment	McIntyre and Whittle (1977)
Polycyclic aromatic hydrocarbons in the aquatic environment	Neff (1979)
Fate and weathering of petroleum spills in the marine environment	Jordan and Payne (1980)
The long-term effects of oil pollution on marine populations, communities and ecosystems	Clark (1982)
Petroleum in the marine environment	Marine Technology Society (1984)
The fate and significance of oil in the sea	Lange (1984)
Oil in the sea: inputs, fates, effects	NRC (1985)
Petroleum effects in the Arctic environment	Engelhardt (1985)
Fate and effects of oil on marine ecosystems	Kuiper and van der Brink (1987)
Sea mammals and oil. Confronting the risks	Geraci and St. Aubin (1990)
Contaminacion del Mar por Petroleo	Lopez and Laseca (1991)
DISPERSANTS	
Oil and dispersants in Canadian seas	Sprague *et al.* (1982)
Using oil spill dispersants in the sea	NRC (1989)
WASTES FROM OFFSHORE PETROLEUM OPERATIONS	
Long-term environmental effects of offshore oil and gas development	Boesch and Rabalais (1987)
Ecological impacts of the oil industry	Dicks (1989)
The environmental impact of North Sea oil	Jones (1989)
Drilling wastes	Engelhardt *et al.* (1989)

Chapter 2 Oil and individual hydrocarbons

2.1 Introduction

2.1.1 Reason for the concern

Most public concern between 1950 and the early 1970s about marine pollution concentrated on problems associated with oil. It was recognized that oil pollution of the sea was a problem requiring international control measures. A number of multilateral conventions were adopted at that time specifically addressing the problem, especially from shipping.

Although it is generally agreed that there has been "no evident irrevocable damage to marine resources on a broad oceanic scale" (NRC, 1985) from either major spills or chronic sources of oil and oil-derived hydrocarbons, i.e. discharges from ships and industry, oil contamination is highly visible, whether in the form of tar balls which foul beaches, of dead seabirds which have been washed ashore, or of oil slicks in coastal areas after accidental spills. Other major concerns are related to the potential effects of spilled oil on commercial fisheries and aquaculture projects and to the loss or change of habitats. This may indeed result in economic consequences (e.g. the closure of fishing areas due to potential impacts on human health, tainting of seafood, or fouling of fishing gear). Effects on the use of seawater for industrial purposes (e.g. cooling of power plant) and domestic purposes (e.g. desalination plants) as well as on wildlife and their sanctuaries (e.g. breeding grounds of birds) and marine parks have been of considerable concern. There have also been questions about the chronic long-term accumulation of hydrocarbons in coastal and estuarine waters and their contribution to a gradual change of ecological systems.

GESAMP, in its report on the State of the Marine Environment (GESAMP, 1990), concluded for oil that "notwithstanding the impact of large accidental spills, its main global impact is due to tar balls which, although generally harmless to marine organisms, may foul beaches and interfere with recreational activities, sometimes with major economic consequences in tourist areas. The presence of petroleum hydrocarbons in seawater and particularly in sediments, however, continues to be a matter of concern locally after accidents have released large amounts of oil that accumulate in sheltered areas, affecting amenity and living resources, especially bird life. While the damage is not irreversible, recovery can be slow." In addition, there are many land-based sources of oil, and although such sources need better characterization, they may now be the major source of oil to the sea, especially enclosed seas (see sections 2.2, 2.3 and 3).

There are continued accidental spills, posing threats to marine resources and ecosystems, and there is increased concern about land-based sources of petroleum-derived hydrocarbons. Hence, coastal states place "oil" high on their lists of marine pollutants and make efforts to address the problems concerned by establishing national, regional and global legislation to prevent and control oil pollution.

2.1.2 Applicable agreements and conventions

Since 1954 a number of global agreements dealing with marine pollution from oil have been adopted. These are:

.1 International Convention for the Prevention of Pollution of the Sea by Oil, 1954; amended 1962, 1969 and 1971;

.2 International Convention Relating to Intervention on the High Seas in Cases of Oil Pollution Casualties, 1969;

.3 International Convention on Civil Liability for Oil Pollution Damage, 1969;

.4 International Convention on the Establishment of an International Fund for Oil Pollution Damage, 1971;

.5 International Convention for the Prevention of Pollution from Ships, 1973, as modified by the Protocol of 1978 relating thereto (MARPOL 73/78);

.6 International Convention on Oil Pollution Preparedness, Response and Co-operation, London 1990 (not yet in force).

The above Conventions adopted by the International Maritime Organization (IMO) are supplemented by a number of codes and recommendations designed to complement the requirements contained in the Conventions or to assist their implementation. The Conventions and recommendations tackle the problem of marine oil pollution in a number of ways, including the following:

.1 *Reducing accidents:* this is principally achieved by introducing and enforcing strict standards and navigational procedures on a world-wide basis (e.g. through the International Convention for the Safety of Life at Sea, 1960 and 1974 (SOLAS) and the Convention on the International Regulations for Preventing Collisions at Sea, 1972 (COLREG)). While principally designed to make shipping safer, these measures have a secondary advantage in that they also help cut pollution resulting from accidents. Despite all the technical advances of the past few decades, the human element remains the most vulnerable component in shipping. For example, the "Elf" oil company estimates that the human element causes 80% of its accidents (Leroy, 1991). (See also: Survey carried out by the Department of Transport, U.K. through Tavistock Institute for Human Relations, 1991.) In this respect the International Convention on Standards of Training, Certification and Watchkeeping for Seafarers, 1978 (STCW) is of particular importance.

.2 *Reducing the consequences of accidents:* measures have been introduced which are designed to decrease the amount of pollution resulting from an accident (for example, by describing positions and by limiting the size of tanks and thereby limiting the amount of oil entering the sea in the event of a tanker going aground or being involved in a collision).

.3 *Combating major oil pollution incidents:* IMO, in November 1990, adopted the International Convention on Oil Pollution Preparedness, Response and Co-operation, recognizing that, in the event of a pollution incident, prompt and effective action is essential.

.4 *Preventing operational pollution:* preventing, for example, the discharge of oil–water mixtures resulting from tank cleaning directly into the sea. This has been done by introducing anti-pollution measures into the design, equipment and operation of ships.

.5 *Protecting special geographic areas:* special protection from potential damage by shipping is provided in larger enclosed or semi-enclosed areas being designated as Special Areas. Six such areas have so far been designated. Special protection to smaller sea areas can be provided by a scheme adopted by IMO for identification of Particularly Sensitive Areas (e.g. Great Barrier Reef Park).

.6 *Providing compensation:* the costs of pollution can be enormous. A series of measures has been adopted to enable victims of pollution incidents to be provided with compensation for their losses.

.7 *Helping implementation:* IMO has provided technical and other assistance to governments in developing contingency plans for countering pollution and other aspects.

A number of regional conventions and protocols to regional conventions have been established concerning co-operation in dealing with pollution by oil and combating pollution emergencies. In several regions these agreements are reinforced by the establishment of bilateral agreements, subregional contingency plans, and regional emergency centres and equipment bases. In several regions oil company co-operatives have been established to facilitate a rapid and efficient response to oil spills beyond the immediate capabilities of one company and in areas of joint concern.

There are also a number of regional agreements regulating discharges of oil and other hazardous substances from land and offshore installations. However, there has so far been no globally applicable convention established for the control of these sources, although they create 50% of the input of oil into the marine environment.

2.2 Composition of hydrocarbon mixtures from different sources

2.2.1 Sources of hydrocarbons

Hydrocarbons, i.e. chemical compounds composed exclusively of the elements carbon and hydrogen, are the principal components of fossil fuels. Crude oil and oil products, however, are not the only sources of hydrocarbons. Other sources exist which contribute to the hydrocarbon load of the marine environment. These derive from incomplete combustion processes and recent biosynthesis. These have been included in the list as follows:

.1 petroleum (crude oil) or its constituents and fractions originating from:
  (a) transportation, including normal tanker operations, dry-docking, discharged bilge and fuel oils, losses in tanker and non-tanker accidents;
  (b) municipal and industrial wastes, urban run-off and riverine discharges, i.e. land-based sources of oils;
  (c) natural sources such as marine seeps and erosion of sediments;
  (d) offshore oil production;

.2 incomplete combustion processes; and

.3 recent biosynthesis.

The diverse sources of hydrocarbons can be differentiated by their characteristic compositions.

2.2.2 Compositional characteristics of different sources

2.2.2.1 Chemical composition and physical properties of crude oils

Crude oil or petroleum*, a transformation product of fossil (often marine) organisms, is a liquid mixture, occurring underground, of many thousands of organic compounds amongst which hydrocarbons predominate. Some of its component hydrocarbons are the same as contemporary biosynthetic products, and many are products of transformation into compounds more stable thermodynamically under the conditions to which oils are exposed in source rocks and reservoirs. In addition to hydrocarbons, i.e. compounds composed exclusively of the elements carbon and hydrogen, sulfur, oxygen and nitrogen derivatives of hydrocarbons are also present in mineral oils in varying proportions, as are complexes of organically bound nickel, vanadium and cobalt. Nickel and vanadium are often present in μg/g quantities (NRC, 1985) and their ratios can be used to characterize a crude oil. Depending upon source materials, the history of pressures and temperatures during formation and the structure and chemical composition of source rocks, and the migration to and the conditions in reservoirs, the compositions of crude oils may vary widely (Figure 2.1). Figure 2.2 shows some types of compounds found in crude oils. More detailed information of the composition of crude oil may be found in Petrov (1984), NRC (1985), Neff (1990) and Lopez and Laseca (1991).

The specific gravity of whole crude oils usually is less than 1.0, i.e. they float on water. All oil components are, to a certain degree, soluble in water. Aqueous solubility depends on the structural type, with normal alkanes being least and aromatic hydrocarbons being most soluble in water (ca. 0.7 grams of benzene dissolve in 1 kg of water). Solubilities in water are also inversely proportional to molecular weights (McAuliffe, 1966). Therefore, the fraction of an oil which, upon release on the surface of a natural water body, dissolves in it has a composition different from the original oil, with an enrichment of the more water-soluble low-molecular-weight aliphatic and aromatic components (Shiu *et al.*, 1990). General methods for characterizing spilled oil samples are well described (Butt *et al.*, 1986).

2.2.2.2 Composition of mixtures of combustion-generated hydrocarbons

Whenever materials containing carbon and hydrogen atoms in their molecular structures are combusted, hydrocarbon mixtures are formed in which aromatic hydrocarbons predominate. These materials include oil and oil products, wood, garbage, coal, and paper. In contrast to the relatively mild conditions during the formation of crude oil, which are conducive to the generation of alkyl-substituted aromatic hydrocarbons, the relatively high temperatures of combustion processes favour the formation of non-alkylated polycyclic aromatic hydrocarbons (PAH). Figure 2.3 illustrates the temperature dependence of alkyl substitution. Based upon these compositional characteristics, it has become, to a certain extent, possible to differentiate between aromatic hydrocarbons in seawater originating from direct oil inputs and those that are derived from incomplete combustion processes and reach the sea via the atmosphere. There is some evidence, however, to suggest that microbial degradation as well as photo-oxidation attack alkyl-substituted aromatic hydrocarbons in preference to

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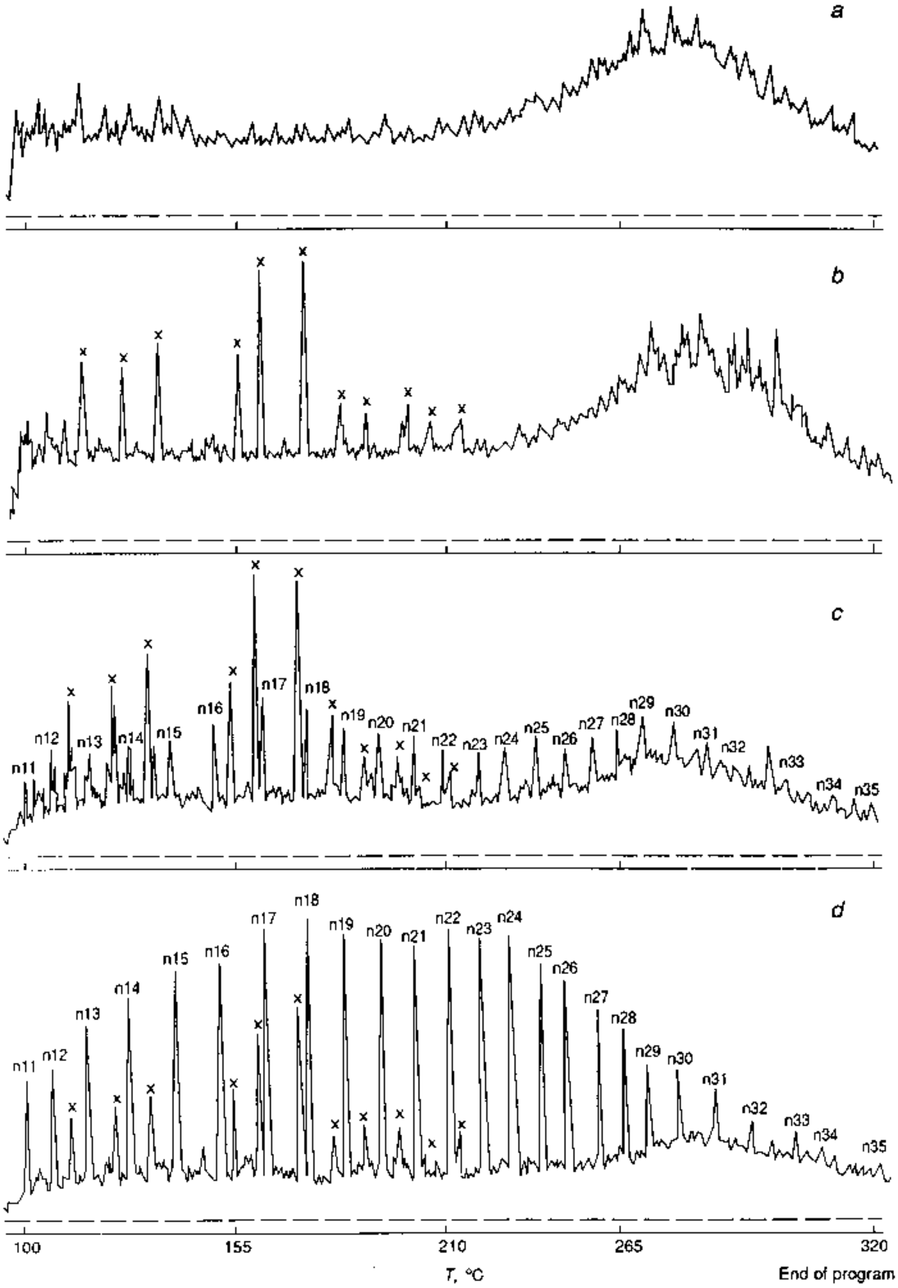
* *Crude oil* and *petroleum* are synonymous terms, as are *fossil hydrocarbons*, *petrogenic hydrocarbons* and *petroleum hydrocarbons*.

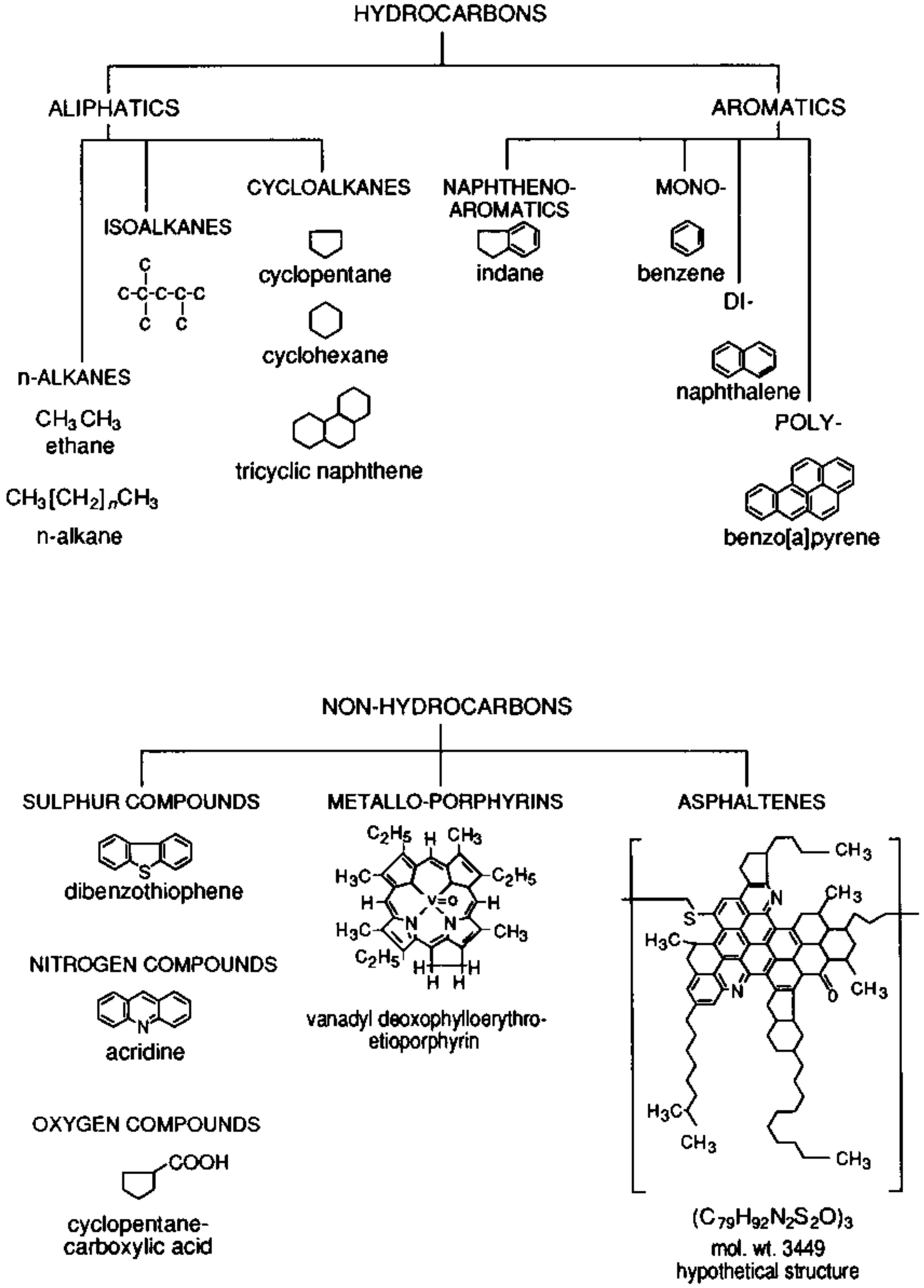
their non-alkylated parent compounds. (Davies and Tibbets, 1987; Ehrhardt *et al.*, 1992). Environmentally degraded oil residues could therefore resemble combustion-generated hydrocarbon mixtures in their composition.

Figure 2.1: ***Gas chromatograms of different types of crude oil. Deposits: (a) Surakhanskoe; (b) Balakbanskoe; (c) Kotur-Tepe; (d) Samotlor. The number of carbon atoms in the molecules is indicated. X denotes isoprenoid alkane peaks. Capillary column 30 m, Apiezon; linear temperature programming, 100→3°C/min***



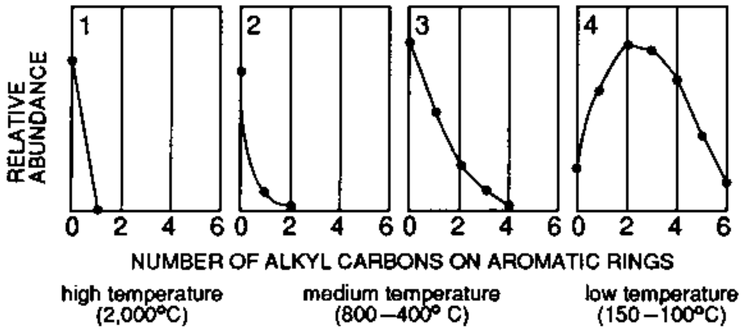
Source: Petrov (1984)

Figure 2.2: ***Examples of the chemical structure of some common components of crude oil***



Source: Miller, G.J. and D.W. Connell (1982)

Figure 2.3: ***Relative abundance of parent aromatic compounds and alkyl substituents as influenced by temperature of formation***



Source: NRC (1985).

2.2.2.3 Composition of recent biosynthetic hydrocarbon mixtures

Due to the specificity of biosynthetic pathways, the number of individual hydrocarbons synthesized by organisms is very much smaller than that found in crude oil or oil products. Among aliphatic hydrocarbons synthesized by organisms, those containing an odd number of carbon atoms predominate. Olefins occur frequently and at relatively high concentrations, whereas aromatic hydrocarbons are scarce.

The main producers of biogenic hydrocarbons are phytoplankton (Blumer *et al.*, 1971; Clark and Blumer, 1967), zooplankton (Blumer and Thomas, 1965a,b; Avigan and Blumer, 1968; Blumer *et al.*, 1969) and benthic algae (Clark and Blumer, 1967; Youngblood *et al.*, 1971; Youngblood and Blumer, 1973). A detailed review is found in NRC (1985).

Based on estimates of primary production and the proportion of hydrocarbons to other cell constituents, the global input of biogenic hydrocarbons may far exceed that of petrogenic hydrocarbons. However, not only are the molecular compositions of the two sources different, but also the input kinetics. Biogenic hydrocarbons are generated slowly and over vast areas; their input thus matches the degradative capacity of hydrocarbon-utilizing micro-organisms. The harmful effects of oil pollution, to a large extent, rest on the fact that substantial quantities of hydrocarbons are introduced in limited areas over short periods of time, conditions that often result in the build-up of toxic concentrations.

2.3 Inputs of oil and its hydrocarbons

2.3.1 Changes in inputs over the past two decades

The National Academy of Sciences (NAS) of the United States estimated in 1973 that 6.1 million tonnes of petroleum annually enter the ocean (NRC, 1975). In 1981 the Academy estimated that 3.2 million tonnes of petroleum hydrocarbons enter the sea every year (NRC, 1985). This does not mean necessarily that the quantity was nearly halved in about ten years, but that, besides reductions due to measures taken in accordance with control requirements, the estimating methods have also improved. While there are disparities between these sets of figures and similar estimates made by other bodies, there is general agreement as to the sources and the relative contributions of each.

Estimates of inputs of petroleum to the world oceans carried out by the National Academy of Sciences in 1973 and 1981, together with other estimates, are shown in Table 2.1.

Table 2.1: ***Estimates of inputs of petroleum hydrocarbons per year to the world's oceans (in thousands of tonnes)***

(ranges shown in parenthesis)

Source:	Year:	1973	1979	1981	1981
	Ref.: Source	NRC (1975)	Kornberg (1981)	Baker (1983)	NRC (1985) (Also see Table 2.3)
Urban run-off and discharges		2500	2100	1430(700-2800)	1080(500-250)
Operational discharges from tankers		1080	600	710(440-1450)	700(400-1500)
Accidents from tankers at sea		300	300	390(350-430)	400(300-400)
Losses from non-tanker shipping		750	200	340(160-640)	320(200-600)
Atmospheric deposition		600	600	300(50-500)	300(50-500)
Natural seeps		600	600	300(30-2600)	200(20-2000)
Coastal refineries		200	60	–	100(60-600)
Other coastal effluents		–	150	50(30-80)	50(50-200)
Offshore production losses		80	60	50(40-70)	50(40-60)
Total discharges		6110	4670	3570	3200

Source: Adapted from Freedman (1989)

The relative contributions of each of the recognized sources for global inputs of petroleum hydrocarbons into the world oceans are shown in Table 2.1. However, the situation differs in the various marine areas; major sources depend on such factors as the degree of industrialization of coastal States, population in coastal areas, density of shipping and offshore activities. Figures reflecting the special situation in the North Sea, as submitted to the Second International Conference on the Protection of the North Sea (Anon. 1987), in the Danish Sea area and in the Baltic Sea (Jensen and Jörgensen, 1984; Baltic Marine Environment Protection Commission, 1987) are shown in Table 2.2.

Table 2.2: ***Relative contributions of petroleum hydrocarbon inputs to the world oceans, the North Sea, the Danish Sea area and the Baltic Sea***

	Global 1985 (%)	North Sea 1987 (%)	Danish Sea area 1983 (%)	Baltic Sea 1984 (%)
Natural sources	8	2	–	–
Offshore production	2	28	15.7	?
Maritime transportation	45	3	22.8	7.8
Atmosphere	10	12	10.5	1.3
Land-based discharges and run-off	34	43	51.8	90.6
– refineries			(1.1)	(2.4)
– municipal waste water			(17.5)	(15.4)
– industrial waste water			(5.2)	(0.9)
– urban run-off			(6.1)	(13.1)
– rivers			(21.9)	(58.8)
Dumping at sea	1	12	–	

Sources: Jensen and Jörgensen (1984); NRC (1985); Baltic Marine Environment Protection Commission (1987); Pettersson and Broman (1990).

The U.S. National Academy of Sciences, at the request of the International Maritime Organization (IMO), conducted a new study in 1990, updating the 1981 estimates of inputs of petroleum hydrocarbons into the ocean due to marine transportation activities. The Academy concluded that the estimate of oil entering the sea from marine transportation activities has been reduced from 1.47 million tonnes in 1981 to 0.57 million tonnes in 1989 (IMO, 1990). The marine transportation sources were subdivided as shown in Table 2.3.

Table 2.3: ***Estimated inputs of petroleum hydrocarbons into the ocean due to marine transportation activities (U.S. National Academy of Sciences)***

	1981 (million tonnes)	1989 (million tonnes)
Tanker operations	0.7	0.159
Tanker accidents	0.4	0.114
Bilge and fuel oil discharges	0.3	0.253
Dry-docking	0.03	0.004
Marine terminals (including bunkering operations)	0.022	0.030
Non-tanker accidents	0.02	0.007
Scrapping of ships	–	0.003
TOTAL:	1.47	0.57

Sources: NRC (1985); IMO (1990).

The best known cause of oil pollution is that arising from *tanker accidents*. Although these contribute a comparatively small percentage of the total oil entering the sea in a year, the consequences of an accident can be disastrous to the immediate area, particularly if the ship involved is a large one and the accident occurs close to the coast. The wrecks of the *Torrey Canyon* (1967), *Amoco Cadiz* (1978), *Exxon Valdez* (1989) and *Braer* (1993) are examples.

The most common pollution incidents occur during *terminal operations* when oil is being loaded or discharged. Because they occur close to shore and often in a confined area, such as ports, their environmental damage to the immediate vicinity can be considerable. In tonnage terms, such accidents provide only a small proportion of the total amounts of oil entering the sea.

In 1973 and again in 1981 the largest single source of oil from transportation activities entering the sea was estimated to be from *tanker operations*, usually associated with the cleaning of cargo residues when the ship is ballasting and cleaning its tanks for the return voyage from the port of discharge. In the new estimate for 1989 the largest single source of oil entering the sea through shipping activities is estimated to be from *fuel oil sludge and machinery-space bilges*. This is largely attributable to the worldwide lack of adequate reception facilities.

The years since the late 70s have seen major changes in the oil industry and in the movement of oil by sea. World oil consumption in 1988 was over 3,038 million tonnes – less than the record 3,141 million tonnes of 1979, but still a substantial increase on the 2,103 million tonnes consumed in 1965.

The world tanker fleet in 1989 was smaller than it was in 1980. However, it still consisted of nearly 250 million deadweight tons compared with some 64 million tons in 1960 and about 170 million tons in 1970. In 1980 the world's tanker fleet was about 340 million deadweight tons (after *Lloyd's Register of Shipping* Tables).

The ships themselves have also changed dramatically in size. In the 1950s, ships of 30,000 dwt were regarded as very large; today, tankers of 250,000 dwt are commonplace. The stranding of the *Exxon Valdez*, carrying 170,000 tons of oil, in the Prince William Sound off Alaska, which resulted in a spill of 11 million US gallons of oil, naturally led to a public outcry and requests that some action be taken by governments to prevent such damages. The adoption of the 1990 International Convention on Oil Pollution Prevention, Preparedness and Co-operation should accordingly be seen as a direct result of newly rising concerns. In this connection it should be pointed out that, according to the IMO Steering Group on Casualty Statistics (IMO, 1989), the rate of accidents involving oil and chemical tankers per 100 ships of 6,000 GT and above has declined since 1971; the annual casualty rate until 1980 was 2.6% and from 1980 to 1988 about 2.2%. In 1988 the rate was 1.92%. For tankers of the size 100 to 5,999 GT the average rate since 1978 is 1.26 per year and there have been virtually no changes over the years 1983 to 1989. This is probably due to the incomplete reporting of casualties involving smaller ships.

Statistics from other sources support the view that the situation is improving. The International Tanker Owner's Pollution Federation reported in 1986 (also see UNEP, 1990) that the average incidence of oil spills of above 5,000 tons in the 1980s was 70% lower than in the previous decade. There were on average 26 such spills a year in the 1970s, and this had dropped to only eight annually in the 1980s. As shown by Table 2.3, not only has the number of tanker and non-tanker accidents decreased, but the amounts of spilled oil from most transportation sources also have declined. From Figure 2.4, it is evident that, over the 13 years from 1978 to 1990, contributions by oil spilled from tankers were highly variable and markedly decreased overall.

Although tanker accidents and other accidental as well as intentional discharges of oil at sea are highly visible and therefore in the focus of public attention, the data in Tables 2.1 and 2.2 afford evidence that municipal and industrial waste waters are globally important and in some places the predominant local sources of non-biogenic hydrocarbons. Their entry into the sea is much less conspicuous, because the major part of these hydrocarbons, which are released more or less continuously at moderate concentrations, is dissolved and therefore detectable by chemical analysis only. In contrast with dramatic, largely short-term effects of episodic large-scale releases, the impact of such continuous releases of oil on biota is chronic and likely to be at least as disruptive. Shallow coastal areas may be affected where the volume of water available for dilution and degradation is limited. These areas, if unaffected, are often highly productive biologically and provide shelter for sensitive young stages of many marine organisms. The fact that, in many parts of the world, especially south-east Asia, they are also the sites of extensive aquaculture emphasizes the importance of protecting them.

In the case of these discharges the material summarized as 'hydrocarbons' usually is much more diverse in composition than crude or fuel oils which constitute the bulk of hydrocarbon contaminants at sea. Lubricating oils, industrial cutting oils, wear and abrasion of automobile tyres and street surfaces, and non-volatile combustion products are examples of its constituents. To date, no universally applicable method exists for bulk measurements other than ultraviolet fluorescence, the limitations of which, aggravated by the non-uniform compositional complexity, are discussed under 2.4.1. A clear need exists here for the development of analytical methods.

2.3.2 Estimated inputs from shipping (The 1990 review of inputs from shipping and their relation to other input sources)

The figures for transportation inputs, organized as in the 1981 estimate of the National Academy of Sciences, have changed in the recent 1990 estimate (see Table 2.3). Assuming that figures from other sources can still stand, the total estimated input would be 2.35 million tonnes per year rather than 3.25 million tonnes. The relative inputs would change as follows:

1	Municipal and industrial (i.e. primary land-based sources)	50% (1,175,000 tonnes)
2	Transportation	24% (564,000 tonnes)
3	Atmosphere	13% (305,500 tonnes)
4	Natural sources	11% (258,500 tonnes)
5	Offshore production	2% (47,000 tonnes)

2.3.3 Extent of oil pollution in selected regional seas and coastal waters

2.3.3.1 Europe

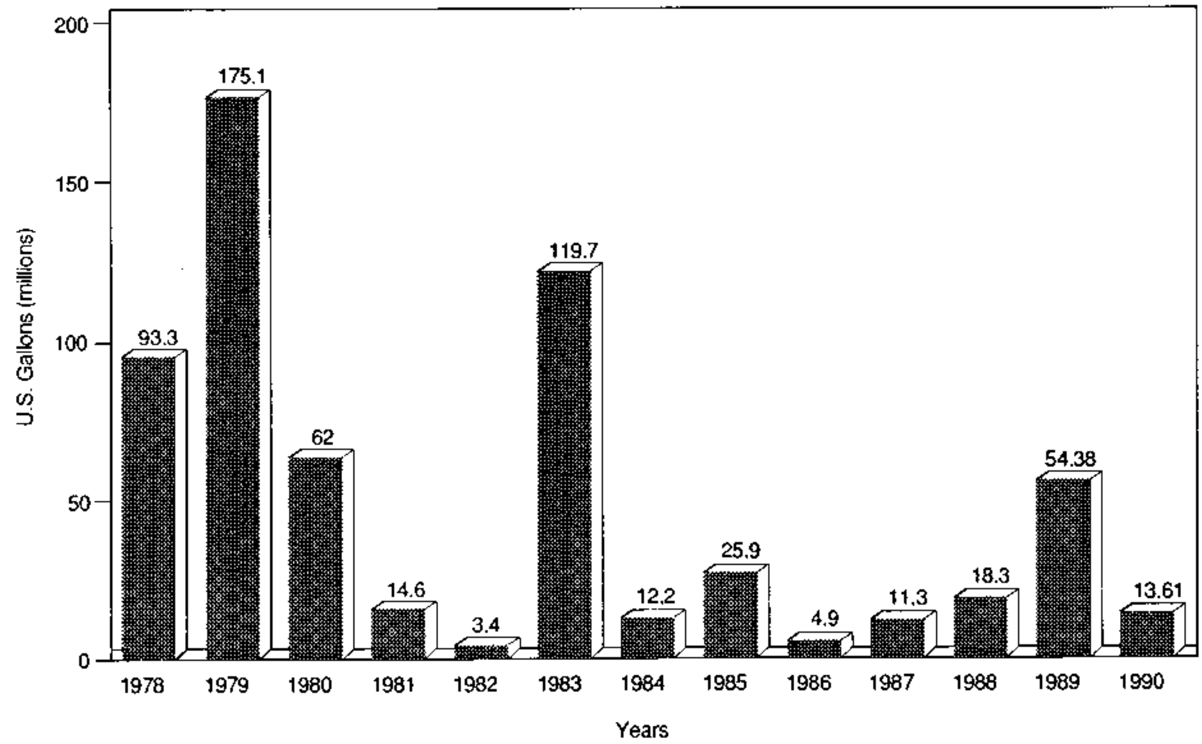
North Sea

An estimated maximum of 260,000 tonnes of oil enters the North Sea from all sources annually, with shipping, rivers and offshore oil production being the greatest contributors. There are many coastal spillages from shipping, and frequent oiling of coastlines, especially in the southern part of the North Sea. Concerns are for amenity beaches, sensitive coastal areas and fisheries and aquaculture, especially the tainting of fish. A recent North Sea Conference concluded that "while oil causes gross pollution after a large spill, and poses problems in localized areas and to sensitive organisms, it is in general not a 'major threat' to the North Sea" (*Proceedings of the North Sea Conference 1987*, Anon., 1987).

Jones (1989) described the major sources of petroleum hydrocarbons into the North Sea as being the atmosphere, river and land run-off, the coastal oil industry, and oil and gas developments. Quantifying the inputs is a complex task, but Bedborough *et al.* (1987) provided estimates showing that about 20% comes directly from discharges from offshore production (about 20 kt per annum up to 1985). Inputs are often diffuse and very variable.

McIntyre (1987) drew some conclusions regarding the impact of North Sea gas and oil development. "First, in the absence of any major oil spill, there has been no widespread biological pollution from the oil itself. Fish stocks have not been affected, and impacts on plant and animal communities have been confined to the immediate vicinity of inputs. Most populations of birds, probably the main target organisms, have been increasing in the North Sea, although some populations of the most susceptible species could be at risk if subjected to continued chronic oiling... Any build up of oil is confined to localized hot spots, such as round some oil platforms or in industrialised estuaries. Oil slicks are common, and although they do not cause general disruption to sea-surface processes, they are responsible for effects on birds and for tarry residues on beaches."

Figure 2.4: ***Oil spilled by tankers, 1978–1990***



Sources: Anon. (1989) and Anon. (1991a)

Westaway (1987) decribed the estimated annual inputs of hydrocarbons to the North Sea and the extent of effects from the petroleum industry as a whole on the North Sea. The total inputs range between 107,000–165,000 tonnes, with approximately half originating from rivers and land runoff. Regular monitoring of the areas surrounding the North Sea production installations indicates that operations have led to very few measurable impacts. Monitoring in areas surrounding the discharge outlets of refineries has shown that localized effects may occur in some cases, particularly where effluent dispersion in the receiving environment is poor. Spills from pipelines occur and two major ones have occurred since 1974; one slick from a 3,000 tonne spill moved across the North Sea and approached the Norwegian coastline – only minor effects were reported. Where major spills such as Ekofisk B in 1977 have occurred, no lasting effects have been recorded at sea.

Shears (1989) described the frequency, location and magnitude of oil spills around the British Isles, and evaluated their environmental damage. "Between 1979 and 1987, 516 spills were recorded which released 21,530 tonnes of oil. Offshore oil rigs were the dominant source (48% of spills); oil tankers the second major source (19% of spills). Incidents were concentrated within the northern North Sea oilfields, the heavily industrialized mainland estuaries, and major oil ports. Environmental effects were only reported in 41% of the recorded incidents. Actual effects were confined to a minority of spills, and were mostly the disturbance of tourist and amenity activities, and the oiling of seabirds. Analysis of oiling incidents affecting seabirds recorded by the RSPB showed that, between 1979 and 1987, 82 incidents occurred, killing approximately 34,500 birds, mostly auks. Most cases of oil pollution affecting seabirds occurred in winter, probably due to the wider distribution of auks at this time which brings the birds to the more polluted southern waters."

Baltic

The extent of oiling of the Baltic has been described by recent Swedish reports (SPEA, 1990; SPEA, unknown date; Pettersson and Broman, 1990). The largest identified source of marine oil pollution in Sweden is riverine input (load of 2 kt/yr), followed by atmospheric deposition (1 kt/yr), discharges from municipal treatment plants (0.5 kt/yr), and discharges from shipping accidents or illegal discharges from vessels (0.5 kt/yr) (SPEA, 1990). The largest cumulative loading on the sea is caused by continuous input (at least 90%), rather than by one-time events such as accidents. There is also a major input of industrial oils into the Baltic, as yet unquantified (Ladner, pers. comm.; also see Chapter 3). It is estimated that Swedish sources account for approximately 5000 tonnes of oil into the Baltic (SPEA, 1990). Clearly, the largest concern is with land-based sources of oil (Jensen and Jörgensen, 1984; Ladner, pers. comm.).

Enckell (1987) also described the oil pollution load on the Baltic Sea, hydrocarbons entering from all of the well-known sources (coastal effluents, urban and industrial; sea transport; offshore oil production; river run-off; and the atmosphere). The best estimate is that 21,000 to 66,000 tonnes per year enter the Baltic from all sources, with urban and river discharges being most important. Progress is occurring, with increased control of discharges and oil spills from ships (*National Geographic*, May 1989), and many studies of the transport, fate and effects of PAHs (Broman, 1990; Broman *et al.*, 1990) have been made.

Mediterranean

Oil is found nearly everywhere in the Mediterranean (Hinrichsen, 1990), although oil pollution is thought to be decreasing due to the installation of oil-waste handling facilities in different ports. Through the 1970s, tar was ubiquitous on the sea surface. Estimates from Malta are that between 500,000 and one million tons of oil and oil-related products are flushed into the Mediterranean each year (Hinrichsen, 1990). Concentrations of dissolved/dispersed hydrocarbons in seawater are generally below 10 $\mu g/\ell$ in offshore waters, and sometimes as high as 40 $\mu g/\ell$ in coastal waters; tar can be as high as 100 mg/m^2; hydrocarbons are in sediments and biota, but few data are available yet (Hinrichsen, 1990; UNEP, 1988b; UNEP, 1989b).

Ehrhardt and Petrick (1989) demonstrated the generally very low concentrations of dissolved/dispersed fossil-fuel residues in eastern Mediterranean surface waters, being in the range of several tens ng/ℓ to less than 200 ng/ℓ, and increasing shoreward, demonstrating that most of the oil pollution is concentrated in coastal waters. Pelagic tar was monitored in an extensive study in 1987 (Golik *et al.*, 1988); it showed that the most tar-contaminated sea is in the north-east, between Cyprus and Turkey, and in the Gulf of Sirte, off the coast of Libya, where the mean tar contents were 1,847 and 6,859 $\mu g/m^2$. There has been a general decline in tar concentrations with time for the Mediterranean, going from 37,000 $\mu g/m^2$ (1969) to 9,700 $\mu g/m^2$ (1974) to 1,175 $\mu g/m^2$ (1987), although there is still a high level of tar pollution off the Turkish and Libyan coasts. Mass-balance calculations were made by Burns (1986).

2.3.3.2 North-west Atlantic

The North-west Atlantic is heavily trafficked by tankers and other shipping, and is bordered by many areas of moderate to high population and industrial activity, from the Atlantic provinces of Canada to Cape Hatteras. There are many small spillages recorded each year (e.g. 2,284 spills, of 28,700 tonnes in total, between 1974 and 1984 in Atlantic Canada) and occasional larger accidents involving tankers, such as off New England in 1989. Industrial harbours are often affected from oil input from refineries, and sometimes have heavily oiled shorelines and seabird kills from accumulated small spillages. Floating tar is evident at and near shipping lanes and often on beaches. Spill sites such as those from the *Florida* (1969) in Buzzards Bay and the *Arrow* (1970) in Chedabucto Bay have been slow to recover from oiling, whereas others, such as from the *Kurdistan*, in the Cabot Strait, and the *Argo Merchant*, off Cape Cod, caused little impact. Considerable concern exists concerning oil-spill impacts and oil and gas development on economically important fishing banks and their fisheries stocks, and on marine wildlife, especially seabirds, from Georges Bank to the Grand Banks (Environment Canada, 1988; Wells and Rolston, 1991).

Considerable scientific research has been conducted in this region to describe the extent of contamination from petroleum oils, from natural and man-made sources (Levy, 1980, 1983, 1984a,b, 1985, 1986; Levy and Walton, 1976; Levy *et al.*, 1981); background data are now available for the entire east coast of Canada, including Baffin Island, Hudson Strait, Foxe Basin and Labrador Shelf areas, the Grand Banks, and the Scotian Shelf. Natural seepages have been described, as well as distributions of dissolved/dispersed oil in the water column. Studies have continued at oil spill sites, such as the *Arrow* (Vandermeulen, pers. comm.) and the *Florida* (Teal *et al.*, 1992).

2.3.3.3 Wider Caribbean (Caribbean Sea and Gulf of Mexico)

The extent of oil pollution in the Caribbean has been described by Hinrichsen (1990), Atwood *et al.* (1987a,b), Jones and Bacon (1990), and Pequegnat and Jeffrey (1979). Hinrichsen (1990) states that "on average every year, about 7 million barrels of oil are dumped into the Caribbean, about 50% of it from tankers and other ships in violation of IMO treaties, and significant amounts from offshore oil rigs and exploratory drilling". There are huge (12 billion metric tonnes) oil reserves and currently 73 refineries in the region, handling over 12 million barrels per day. The result has been many devastated ecosystems in the major oil-producing areas and along tanker routes – mangroves, seagrasses and coral reefs have been affected or destroyed, beaches are heavily contaminated with tar balls and oily residues, and marine life has often been killed, particularly the especially vulnerable sea turtles (Hinrichsen, 1990).

Atwood *et al.* (1987a,b) have extensively described oil pollution in the Caribbean. Their summary follows: "A significant level of petroleum pollution exists throughout the Wider Caribbean. Manifestations of this pollution include serious tar contamination of windward exposed beaches, high levels of floating tar within the major currents system, and very high levels of dissolved/dispersed hydrocarbons in surface waters. The sources of petroleum pollution in the region include oil entering from the adjacent North Atlantic (50%) and tanker ballast washings (50%). Effects in the Caribbean include tar levels on many beaches that either prevent recreational use, or require expensive clean-up operations; probable distress and death to marine organisms, such as endangered turtles who feed on floating tar; and responses in the enzyme systems of marine organisms that have been correlated with declines in reproductive success." Other studies have described the weathering of oil from a major blow-out, IXTOC-1, in 1979 (Atwood and Ferguson, 1982) and the distribution, sources and fates of floating tar residues in the Eastern Gulf of Mexico (Van Fleet *et al.*, 1984).

Oil pollution along Jamaican coasts has been extensively described. Stranded tar residues on beaches are very persistent, and the east coast and Kingston Harbour are subjected to constant and relatively large amounts of fresh tar, in contrast to other coasts except where oil spills have taken place (Jones and Bacon, 1990). The north and west coasts suffer tar from much more than 100 g per metre of beach, far in excess of acceptable levels for tourism, and much higher than current amounts found on Bermudan beaches (Butler, pers. comm.).

There are also natural petroleum seeps in several deep benthic areas of the western Gulf of Mexico (Pequegnat and Jeffrey, 1979), and a "rich and varied bottom fauna found to be associated with large amounts of plant material and oil" in such locations. Most recently, studies on the continental shelves in the Gulf of Mexico have shown, for the first time, "a direct link between natural seepage in a deep water marine setting and sea slick and tar ball formation", and suggest, along with other studies, that natural liquid and gaseous hydrocarbon seepages are a widespread phenomenon in the marine environment in this region (Kennicutt *et al.*, 1988).

2.3.3.4 Africa

West Africa and Central Africa

Oil pollution along these coasts has been described by both UNEP (1984a) and Hinrichsen (1990). Coastal waters of the Gulf of Guinea are contaminated with oily wastes and tar balls, spills have killed mangroves along Nigerian coastlines, and the Niger delta is contaminated with oil residues from offshore drilling and transport (Hinrichsen, 1990).

South Africa

South Africa is adjacent to a major oil shipping route and experiences many accidental spillages and illegal discharges of oil from bilge waters (Moldan and Dehrman, 1989). They are being monitored between Cape Town and north of Durban, and occur throughout the year. Illegal discharges are primarily from bulk carriers and general cargo vessels. Spillages cause considerable coastal damage, especially to seabirds (Moldan *et al.*, 1979; Moldan *et al.*, 1985).

East African Region

The extent of oil pollution has been described by UNEP (IMO/UNEP, 1982, 1985), Bryceson (1990) and Hinrichsen (1990). IMO/UNEP (1982) describes damages to coastlines for each country down the coast. Major oil pollution comes from oil tankers moving between the Middle East and Europe through the Mozambique Channel and flushing their tanks at sea; less important sources include land-based discharges from garages, thermal power stations and industries (IMO/UNEP, 1982). Tar pollution on beaches is serious in Kenya, tar concentrations on beaches varying with seasons. The 1982 report leaves little doubt that tanker traffic is the main source of oil pollution. Bryceson (1990) indicates that major and continued discharges of oil have continued from tankers, that tar lumps are commonly washed up on beaches in the region, that harbours are subjected to discharges and spills of oil from vessels during loading and unloading, and that spills occur at local refineries. Local spills have destroyed mangroves and their associated biota in several areas. Chronic seepages from shipwrecks have also occurred on reefs.

2.3.3.5 Middle East

Red Sea and Gulf of Aden

The Red Sea suffers from considerable oil pollution, especially around the oil fields in the Gulf of Suez, in Egyptian waters (Hinrichsen, 1990). Tar balls and slicks are common, and fouling of beaches is extensive, with some beaches thought to be beyond recovery. Extensive damage has occurred to coral reefs and seagrass beds in the region. The Gulf of Aden is also oiled due to ships pumping ballast waters and cleaning tanks (Hinrichsen, 1990).

Arabian/Persian Gulf

This gulf is probably the most oiled area in the world (approximately 1.2 million barrels per year (Oostdam, 1980)), especially in the wake of the recent Iraq–Iran war and the Gulf War in 1991 and the subsequent release of several million (see below) barrels of oil from the Kuwaiti oilfields into the northern Gulf. Hinrichsen (1990) states that many beaches are tarred, but background levels in biota and sediments are not exceptionally high, due to rapid weathering, biodegradation and flushing. The recent war has left productive areas of Saudi Arabian coastline heavily contaminated and many wildlife killed (Canby, 1991). Scientific studies include those by El-Samra (1989), Emara (1990), Burns *et al.* (1982), El-Samra *et al.* (1986), El-Samra and El-Deeb (1988), Fowler (1985), Grimalt *et al.* (1985), Oostdam (1980) and Oostdam and Anderlini (1978). The most recent ones have estimated an oil budget of 30,000 tonnes for the western Gulf coastal waters (El Samra, 1989); generally, the levels of hydrocarbons in the water column were not exceptionally high compared with other areas of the world, being 4.4 to 63 $\mu g/\ell$ ($\bar{x} = 15 \mu g/\ell$) (Emara, 1990). Another study, on oil inputs from coastal refineries, has shown that the Omanian Refinery adds 160.4 tons of Omanian crude oil wastes and refined products annually to Mina Al Fahal waters, where it is situated (Awad *et al.*, 1990), with adjacent tank farms adding another 140 tons.

Inputs of crude oil released into the waters of the Persian Gulf due to hostilities during the 1991 Gulf War are currently (November 1991) estimated to be between 6 and 8 million barrels (approximately 6.4 million) (*Sci.Amer.*, October 1991). The releases were from different sources, including oil tankers and terminals (MEPA, 1991). Early descriptions of the extent of the spillages (Anon., 1991b; Canby, 1991) showed that the slicks have affected at least 500 km of coastline in Saudi Arabia, with estimates of large loss of wildlife, especially seabirds, and probable loss of all coastal mangroves and most of the salt marshes (MEPA, 1991; McKinnon and Vine, 1991). Coral reefs and seagrass beds are also heavily impacted. Some self-cleaning by blue-green microbial mats has begun (Sorkhoh *et al.*, 1992).

2.3.3.6 Indian Ocean

Surface oil and tar accumulations and distributions along Indian beaches have been described by Gupta *et al.* (1989). Oil slicks are very common in the northern Indian Ocean, mostly from shipping. Beach tar along the west coast of India is a chronic problem, with total deposits of 750 and 1000 tonnes per year for 1975 and 1976 respectively. Many harbours have high (up to 100 $\mu g/\ell$) concentrations of hydrocarbon in the water.

Hinrichsen (1990) has described oil pollution in South Asia seas – Arabian Sea and Indian Ocean. "The problem is the routine discharge of dirty ballast waters, bilge slops and tank washings from oil tankers and other ships plying the shipping lanes of the Indian Ocean. It has been estimated that approximately 5 million tonnes of oil enters the Arabian Sea each year, while the Bay of Bengal gets 400,000 tonnes. Tar balls and oily residues are a common sight on most beaches bordering the Indian Ocean. Coral reefs have been coated with oil residues in the Andaman and Nicobar island archipelagos in the Andaman Sea, reducing income from tourism."

2.3.3.7 South-East Asia

The sources and extent of oil pollution in the East Asian Seas Region have been recently described (MSPE, 1988). Oil originates from a number of sources – activities on land, natural seepage from submarine reservoirs, and offshore operations. Shipping and shipping accidents are a particularly important source. Research and survey data describing the problem and its overall effects are scarce. The Marine Pollution (Petroleum) Monitoring Pilot Project (MAPMOPP) of the Integrated Global Ocean Survey System (IGOSS) (Levy *et al.*, 1981) provides the only overview of oil contamination in the East Asian Seas (MSPE, 1988). "The hydrocarbon concentrations range from 0.01–4 ppb with both extremes occurring in the southern part of the South China Sea. The Malacca Straits, eastern South China Sea, Celebes Sea, and northern Philippine Seas give values of 0.06–0.07 ppb." Other surveys have been done, but data are impossible to compare due to different methods being used. It is clear from the MSPE (1988) report that South-East Asian waters, including the South China Sea, are continuously contaminated with oil (dispersed/dissolved in the water column, floating oil lumps, stranded tar balls) and that areas such as the Straits of Malacca and the South China Sea are most vulnerable due to both constant deballasting activities and accidents such as collisions in shallow waters. Surveys and monitoring of South-East Asian waters are being continued to assess the extent of oil pollution; few reliable data exist to quantify the current status and to enable trend analysis.

Few effects data for South-East Asia are available (Chansang, 1988). The *Showa Maru* spill affected mangroves in Indonesian waters, especially in sheltered bays, with recovery times being greater than 2.5 yr. Chronic discharges of crude oil at a terminal in Brunei reduced intertidal invertebrates, and tainting has occurred in Jakarta Bay due to chronic oil pollution and in Surabaja due to discharges from a petrochemical plant (see Chansang, 1988). There is a general lack of information on the ecological impacts of oil pollution in marine waters in South-East Asia.

2.3.3.8 South-east Pacific

A programme of research, monitoring and control of petroleum pollution has been conducted from Panama to Concepcion in Chile (Ramorino, 1989?), with attempts being made to estimate amounts of hydrocarbons entering the sea from land-based sources, shipping, offshore exploration and drilling, and accidents. Spills from all sources have taken place along the coast, affecting the benthos and intertidal zones and amenity beaches. Residues in the water, and in biota, and beach tar, are being monitored in the regional programme. Cabrera (in press) states that pollution from petroleum hydrocarbons in the south-east Pacific, covered by the South-east Regional Seas Action Plan of UNEP, is mainly concentrated in areas where oil extraction, processing and trans-shipment activities are carried out, although no evidence is given. Due to the importance of the problem, a draft programme of research and surveillance of marine pollution in the south-east Pacific, incorporating the determination of oil-derived hydrocarbons in seawater and sediments, has been prepared (Escobar, in press).

2.3.3.9 North-east Pacific

The north-east Pacific has been subjected to recent oiling episodes (*Exxon Valdez*, *Nestucca*, and others) in coastal sites. The *Exxon Valdez* oiled 1740 km of shoreline, with many acute effects on wildlife (Maki, 1991). The *Nestucca* spill heavily oiled 2–3 km of the 150 km of oiled shoreline of western Vancouver Island (Harding and Englar, 1989). Most reported spills along the coast of British Columbia are petroleum-related (79%).

Waldichuk (1983) summarized the extent of pollution from petroleum hydrocarbons in the Strait of Georgia, British Columbia/Washington State. "It has been estimated that there is an annual total spillage from all Canadian sources into the Strait of Georgia – Jan de Fuca Strait system of about 22,000 bbl (3000 tons) compared with about 41,000 bbl (5600 tons) from United States sources (Oceanographic Institute of Washington, 1980). Sources of oil included tankers in transit and at berth, storage tanks, pipelines, tank barges, non-oil-transporting vessels, and land sources, including those from coastal refineries, municipal wastewater, urban runoff, and marine and land transportation facilities. It was concluded that, in the continuing absence of major oil spills in the Strait of Georgia or in its contiguous waters, the amount of oil in the water, sediments and biota will probably remain small" (Waldichuk, 1983).

In recent years, however, there have been major spillages of crude oil off Port Angeles, WA, and the 1988 *Nestucca* spill off the Washington coast oiled more than 150 km of the coastline of Vancouver Island, killing thousands of seabirds, contaminating fish habitats and closing fisheries, and coating otter colony sites. On Vancouver Island, oil continued to appear in small quantities on the beaches even after the extensive clean-up (Wykes *et al.*, 1989).

2.3.3.10 Polar seas

Arctic Ocean

There have been many small spillages of oil and even gas blowouts in the Arctic areas where oil is either shipped or being developed and produced in the offshore (Engelhardt, 1985, among others). In Canadian waters, between 1973 and 1989, oil companies drilled 130 offshore wells in the Beaufort Sea, Arctic Islands, Davis Strait and Hudson Bay (Wells and Rolston, 1991); if these areas become producing ones, there will be all of the attendant risks associated with production in ice-covered waters in harsh climates. Diesel oil in drilling fluids is discharged routinely to the sea under the ice; for example, 18 wells used an average of 23,000 litres of diesel oil per well as lubricant, which was then discharged. There are chronic fuel spills associated with the offshore oil and gas drilling activities, and some localized impacts (Packman and Shearer, 1988). Shipping occasionally causes spills, some of which have been documented (see Engelhardt, 1985). Natural oil seepages also occur in the eastern Arctic (Levy 1980).

Antarctic Ocean

There have been two recent shipping spills, the *Bahia Paraiso* in January 1989 and the *Humboldt* in February 1989, and two land-based spillages in the Antarctic (ACOPS. 1990). The first spill was significant (the vessel carried 250,000 gallons of various fuel and jet oils), and threatened wildlife and caused mortalities of krill. A detailed assessment of the extent of oil discharges from research stations around the Antarctic and shipping in the area has not been reported to date.

2.3.4 Global oil pollution – its extent

The only known truly global survey of oil pollution was conducted in the late 1970s – the IGOSS (Integrated Global Ocean Station System) Pilot Project on Marine Pollution (Petroleum) Monitoring (Levy *et al.*, 1981; Levy, 1984b). This study made visual observations of oil slicks and sampled floating particulate petroleum residues, dissolved and dispersed petroleum residues, and tar stranded on beaches. One of the primary conclusions was that, based on nearly 100,000 observations and measurements at the sea surface, concentrations of dissolved/dispersed petroleum residues in the low $\mu g/\ell$ range were present nearly everywhere (Levy, 1984b); such concentrations, representing both natural and anthropogenic sources, are currently below known toxicity thresholds for aquatic organisms. In addition, "data demonstrate that floating forms of oil pollution [i.e. tar lumps] are closely associated with the tanker lanes and other areas of ship activity and that the distribution on a larger scale can be accounted for in terms of transport from these areas of input by surface ocean currents" (Levy *et al.*, 1981). This knowledge of oil distribution is based in part on observations from ships' crews, supplemented by wider chemical sampling and other observations across the oceans.

The truly global extent of the problem caused by oil spillages is well illustrated in the recent *State of the Earth Atlas* (Seager, 1990), which maps the distribution of recently reported spills from ships and oil platforms. No map has been attempted yet for land-based sources of oil contamination.

2.4 Physical, chemical and biological methods

2.4.1 Methods of chemical analysis

2.4.1.1 Sampling

The first requirement for analyses of mineral oil accidentally or intentionally released into the sea is the proper collection of samples. This operation is relatively straightforward in the case of bulk oil either floating on the water surface or washed up on a shore, so that no need was seen here for improvement of methods. However, as contaminating oil is distributed into various compartments of the environment (such as water, suspended particles, biota, and sediments) and concentrations decrease because of dispersion, evaporation, and chemical as well as biological decomposition, quantitative collection and avoidance of contamination of samples become more difficult. Recognition of these difficulties triggered the refinement of existing techniques and the development of new sampling techniques.

The collection of small-volume samples of near-surface water by weighted solvent bottles (UNESCO, 1984) has been tested in a number of intercalibration exercises and found to be reliable (e.g. Knap *et al.*, 1986; Ehrhardt *et al.*, 1990). For the collection of clean water samples at greater depths, a sampler that was designed originally by Bodman *et al.* (1961) has found widespread application in recent years, as has the Niskin bottle (Boehm and Fiest, 1982; Grzybowski *et al.*, 1987). Another interesting sampling device is a glass sphere of 10 litres capacity which is lowered empty and closed and is mechanically strong enough to withstand pressures corresponding to sampling depths of up to 2,000 metres (Stadler and Schomaker, 1977; Gassmann and Pocklington, 1984). A more recent development based on it has a capacity of 100 litres and a maximum sampling depth of 200 metres (Theobald, 1990, pers. comm.). The principal advantage of these samplers is the same as that of the weighted solvent bottle: hydrocarbons can be concentrated in them by extraction with a suitable solvent, thus minimizing the hazard of sample contamination which, in the first decade of open-ocean oil-contamination studies, appears to have led, on occasion, to erroneously high results.

Analysis of contaminating hydrocarbons in seawater on the single-compound level that is necessary, e.g., for source correlation and decomposition studies. normally requires concentration from large volumes of water. Because solvent extraction becomes impracticable beyond sample volumes of a few litres, methods have been developed to concentrate hydrocarbons, as well as other lipophilic material, by adsorption onto solid sorbents. Sorbent applications are described in Burns and Smith, 1980; Dawson and Riley, 1977; Dawson *et al.*, 1976; Derenbach *et al.*, 1978; Ehrhardt, 1987a,b; Harvey, 1972; Harvey *et al.*, 1973; Osterroht, 1974.

Josefson *et al.* (1984) investigated the use of Chromosorb T and Fluoropak 80 (two different brands of poly(tetrafluorethylene) adsorbents) for concentrating lipophilic organic compounds from water and compared their efficiencies with those of Amberlite XAD-2 and Amberlite XAD-8. Quantitative recoveries were obtained with Chromosorb T for a variety of solutes at concentrations around 50 μg per litre in water containing 2 mg of humic acids per litre.

Porous polyurethane foam has also been applied for concentrating hydrocarbons from dilute aqueous solution (de Lappe *et al.*, 1983; Albaigés *et al.*, 1984; Gomez-Belinchón *et al.*, 1988).

For a number of years, the use of solid adsorbents for hydrocarbon trace analyses was hampered by the presence in these materials of contaminants originating from their manufacture and, possibly, their degradation upon storage. Unfortunately, they include hydrocarbons of the type found in fossil fuels, such as alkylbenzenes, naphthalene, alkylnaphthalenes, biphenyls, and diphenylalkanes (in Amberlite XAD-2 and XAD-4) as well as, in Ambersorb XE-340, a number of non-alkylated polycyclic aromatic hydrocarbons (Hunt and Pangaro, 1982). However, extremely clean sorbent materials have recently become available commercially, and Ehrhardt (1987a) has described an apparatus and a procedure for cleaning solid sorbents.

In recent years porous silica, its surface modified by chemically bonded n-octadecyl groups, has found increasing use for contaminant studies in fresh water. Junk and Richard (1988) evaluated this sorbent material. It gave excellent recoveries of greater than 85% for pesticides and polycyclic aromatic hydrocarbons in water samples spiked at the concentration range of nanograms per millilitre.

Concern has been expressed sometimes regarding the stability of hydrocarbons sorbed onto solid materials that are used for their concentration from seawater. Green and le Pape (1987) found, however, that hydrocarbons accumulated on Amberlite XAD-2 and on octadecylsilanized silica gel remained unchanged for up to 100 days even in the presence of oleophilic bacteria.

2.4.1.2 Analytical methods

The preceding paragraphs emphasize the importance attributed to the recovery of hydrocarbons and their environmental degradation/oxidation products from trace concentrations in seawater and progress made in this respect. The combination of effective sampling techniques with high-resolution capillary gas chromatography and high-performance liquid chromatography (HPLC) and mass-spectrometric identification of compounds has been developed into a powerful analytical tool for investigating not only concentrations but also the chemical composition of fossil-fuel residues in seawater. Application of the latter methods to analyses of suspended particles, sediments, and organisms has also led to improved understanding of sources and the environmental fate of hydrocarbons derived from fossil fuels. Investigations of dissolved material in seawater that is more polar than hydrocarbons revealed the presence of numerous oxygenated derivatives of aromatic and aliphatic hydrocarbons. Model experiments have shown that these compounds probably are generated by sensitized photo-oxidation of hydrocarbon precursors (Ehrhardt, 1987b; Ehrhardt and Petrick, 1984, 1985; Ehrhardt and Weber, 1991).

Analysis of contaminant hydrocarbons with single compound resolution, useful and necessary as it is for studying their transformation in the environment, is often considered too complex, expensive, and time-consuming for surveillance and monitoring purposes. The bulk determination of fossil hydrocarbons by UV spectrofluorimetry, which was introduced as a monitoring tool in the mid 1970s (IGOSS Marine Pollution (Petroleum) Monitoring Pilot Project), continues to be used as a component of the Marine Pollution Monitoring Programme (MARPOLMON) and regional components such as the Caribbean Pollution Monitoring Programme (CARIPOL). It has been shown, in a number of intercalibration exercises (Baltic Oceanographers, Kiel, 1981; IOC/UNEP Workshop, Bermuda, 1984; IOC/CSIC/UNEP, Barcelona, 1984; IOC/UNEP River Input Workshop, Bangkok, 1986), to yield comparable data with a precision of ±30% (Kullenberg, 1986; Law *et al.*, 1988; Ehrhardt *et al.*, 1991). Comparability of the data is based, however, on the tacit assumption that the composition of the fluorescent material is more or less constant in time and space which, especially in the initial stages of weathering after a spill, probably is not the case. Therefore, a decrease in fluorescence intensity of samples taken shortly after a spill must not uncritically be equated with a proportional decrease in potential for harm. Recent experimental results (Ehrhardt *et al.*, 1992) indicate that many fluorescent hydrocarbons are merely converted into oxygenated derivatives with as yet unknown ecotoxicology and with fluorescence characteristics that prevent their detection by UV fluorescence methods in common use.

Detailed analyses by high-resolution techniques have also shown that aromatic hydrocarbons of petroleum origin are not the only fluorescent materials detected by the UV fluorescence method. Suites of structurally similar compounds generated in combustion processes often contribute to or exclusively generate the analytical signal. Thus, UV fluorescence analysis can be used safely as a monitoring tool only if the sources and composition of the fluorescent material are well characterized. Its capacity to yield large numbers of data at relatively little expense within short periods of time makes it useful for detecting unusual events, which can then be investigated in detail.

Because UV spectrofluorimetry with a fixed excitation wavelength reveals little information on sample composition, John and Soutar (1976) proposed to use synchronous excitation for more detailed characterization of samples. By simultaneous scanning of excitation and emission wavelengths with a fixed wavelength difference of 15 to 25 nm, fluorescence signals are generated successively of mono-, di-, tri-, tetra-, and penta-cyclic aromatic compounds, whose relative concentrations, thus accessible, may be used to typify samples. The method has been used in a number of cases for characterizing lipophilic extracts from seawater and sediment (Boehm and Fiest, 1982; Boehm *et al.*, 1987; Dahlmann and Lange, 1981; Ehrhardt and Petrick, 1989; Koerting-Walker and Buck, 1989; Mille *et al.*, 1983). Graphic presentation of synchronous excitation fluorescence spectra in computer-generated quasi-three-dimensional contour plots is a further refinement of the method. It has been used by Keizer *et al.* (1977) and should become more easily applicable as modern spectrofluorimeters increasingly feature electronic data-processing capability.

2.4.1.3 Weathering

Research over the past 15 years has revealed considerable information on chemical and biologically mediated compositional alteration of spilled oil. Thus, Oudot (1984), investigating the decomposition of a light Arabian crude with a mixed, quasi-continuous culture of oil-degrading bacteria during an experiment of two months duration, found that rates are structure-related; 74% of normal and branched-chain alkanes were degraded, 50% of aromatic hydrocarbons, 30% of asphaltenes, and greater than 5% of resinous material. Rates of degradation differ even within groups of structurally related compounds. These findings are corroborated by results of a study on the fate of oil in sublittoral sediments (Davies and Tibbetts, 1987) and agree with earlier work (Saltzmann, 1982). Both investigations hint at a phenomenon that is of potential importance for interpreting the composition of the aromatic fraction of what is usually referred to as dissolved/dispersed oil residues. In many such samples, unsubstituted PAHs are more highly concentrated than their alkyl derivatives, which may indicate incomplete combustion as sources originating via atmospheric deposition. This is because combustion processes have been shown experimentally to generate unsubstituted PAHs in much higher abundance than their alkyl derivatives. However, there is evidence that alkyl-substituted PAHs are degraded biologically and photochemically (Ehrhardt *et al.*, 1992) at slightly faster rates than their unsubstituted parent compounds, which could lead, eventually, to the latter's preponderance.

Qualitative analysis of environmentally degraded oil, for purposes of source correlation, has always placed considerable demands on the analyst's skill, because readily recognizable chromatographic signals are lacking. However, persistent and characteristic concentration ratios of hydrocarbons with direct genetic relationships to biological precursor compounds (biomarkers) have become accessible through the use of selected-ion-monitoring (SIM) GC/MS analyses (e.g. Brakstad and Grahl-Nielsen, 1988; Farran *et al.*, 1987; Grahl-Nielsen and Lygre, 1990). Gough and Rowland (1990) described a degradation procedure, involving oxidation with chromic acid, which forms a limited number of oxygenated derivatives for gas-chromatographic analysis. The method is especially useful for characterizing lubricating oils in marine environmental samples as no proven analytical method exists at the present time.

2.4.1.4 Analytical challenges

Since the previous report (GESAMP, 1977), analytical methodology has seen considerable progress and development. Recognition and avoidance of extraneous sources of contamination have made sample collection much more reliable. Results of intercalibration exercises provide the basis for rational interpretation of data. The compositions of hydrocarbon assemblages from different sources are now known in much greater detail, enabling more reliable source correlation and risk assessment. Finally, degradation pathways and products have been elucidated.

Kinetic measurements of biotic as well as abiotic (photochemical) reaction rate-constants and half-lives under various natural conditions are still scarce, but these are much needed for impact predictions and mass-balance calculations. There is also a need to investigate the chemical nature and biological properties and effects of degradation products of hydrocarbons, on which information is very limited. What are they? What are their concentrations in water? Are they accumulated by organisms? How toxic are they? If adverse effects should be detected, methods must be developed for easy and reliable determinations in various matrices, such as seawater, organisms, and sediments.

2.4.2 Tainting

A "taint" is defined by the ISO as "an odour or flavour foreign to the product" (International Standards Organisation, 1983a). This definition of taint makes no reference as to whether the taint is pleasant or unpleasant; while it is true that most pollutants would impart an unpleasant flavour to fish, this need not be the case for some contaminants. Nevertheless, even if the contaminant improved the flavour of fish, tainting should be considered an effect in the context of the impact of oil pollution on the marine environment. Any procedure for assessment of taint should therefore seek to detect and measure a change in flavour rather than an impairment of flavour.

A taint is a sensory experience and can only be measured directly by a sensory procedure, using human assessors. The property of most relevance to tainting is the chemical's ability to stimulate the chemical senses, predominately the olfactory organ which gives rise to the sense of smell. This property can be conveniently summarized by the compound's detection threshold, which is the minimum concentration in the medium – usually air or water – that can be detected. Detection thresholds in air and/or water have been measured for many substances, including some hydrocarbons and other chemicals found in oil, and values can be found in compilations of values (Fazzalari, 1978; Van Gemert and Nettenbreijer, 1977). Jardine and Hrudey (1988) have measured detection thresholds in fish flesh of chemicals that might be associated with tainting of fish by oil-sands operations.

There are broadly two circumstances in which assessment of taint is required and which require different approaches to the sensory evaluation of the samples:

.1 detection and measurement of taint in fish exposed to contamination under experimental conditions, for example in measuring the potential of an oil to induce taint; and

.2 detection and measurement of taint in fish harvested from the wild, for example in monitoring the impact of discharges of oil.

A major problem in the sensory analysis of fish is that the natural flavour of fish varies both between and within species. Variations within species are the result of ground and feed effects, and biological and physiological processes, and are not easily described and codified. They are greater in wild populations than in cultured. When investigating tainting of fish under experimental conditions, fish from the same batch as the test material and subject to the same cultural conditions other than the regime under test are usually available as reference samples. Sensory methods involving direct comparisons can then be used and the effects of variations in intrinsic flavour are minimized.

There is very little experimental data on the ability of chemical substances, oils or otherwise, to taint fish, and available data have been obtained by a variety of procedures and may not be entirely comparable. The GESAMP Working Group on the Evaluation of Hazards of Harmful Substances Carried by Ships (EHS) issued draft guidelines for measuring the ability of a chemical to taint fish as a contribution to developing standardized procedures for measuring an index of tainting capacity analogous to LC_{50}, which is used as an index of a substance's aquatic toxicity. The principles of the procedure are to expose the fish to known concentrations of the chemical for 24 hours, harvest and cook the fish, and assess the test fish in comparison with the control for a difference in odour or flavour. The triangular test procedure (International Standards Organisation, 1983b) was recommended for detecting any difference between the test sample and reference samples.

These draft guidelines were elaborated by an ECETOC Task Force and subjected to a ring test with five industrial chemicals (European Chemical Industries Environmental and Toxicological Centre, 1987; Poels *et al.*, 1988). The GESAMP EHS Working Group later published a more extended version of its guidelines (GESAMP, 1989).

These guidelines were developed for the testing of industrial chemicals; an example of the GESAMP guidelines being used for measurement of tainting by 2,4-dichlorophenol is given by Howgate (1989). Measurement of tainting of cod and scallops by water-soluble fractions of crude oils and condensates, using the ECETOC guidelines, has been reported (Carter and Ernst, 1989; Ernst *et al.*, 1987, 1989a & b) and the tainting threshold of diesel has been measured essentially by the GESAMP procedure (Davis *et al.*, 1992).

There are no guidelines for the assessment of tainting in fish caught in the wild. The major difficulty in this type of investigation is that it is usually not possible to obtain valid reference material, and comparison tests (such as the triangular test that is used in the guidelines described above) are not suitable. The assessors must evaluate samples with reference to their past experience of the normal flavours of the species under test. Under these circumstances, the reliability of detection of taint will be influenced by the experience of the assessors. It is likely that assessors who are experienced in evaluating the flavour of the test species, and hence who are familiar with its normal range of intrinsic flavours, will be more able to detect a foreign flavour, and will be more consistent in their assessments, than would inexperienced assessors.

Unfortunately, reports of tainting of fish by acute or chronic discharges of oil or oil-related chemicals rarely include details of the experimental procedures that were used to evaluate the taint or of the selection and training of the assessors. Howgate *et al.* (1977), Parker *et al.* (1990) and Scarratt (1980) give reasonably full descriptions of the selection and training of assessors for detection of taint that has been induced under laboratory conditions. Otherwise, reports of tainting of fish by discharges of oil or oil-related chemicals into the sea state only that the fish were tainted, without presenting any quantitative data on the proportion of the fish that were tested which were affected or of the intensity of the taint. McGill *et al.* (1987) used panels of eight to ten experienced assessors and a majority vote approach; a sample was designated as tainted if more than half of the members of the panel detected a taint in it. Other accounts, however, do not usually state the size of the panels, the extent of training (if any) of the assessors or the criteria for deciding if a fish, or a batch of fish, is tainted.

The range of sensory procedures that have been used to evaluate taint in fish, and the lack of experimental detail in the reports, make it very difficult for a reviewer to compare data across reports, or to evaluate the validity of the data and the soundness of the conclusions. There is a need for more systematic research into tainting by oil, but a prior requirement is that there should be research into experimental procedures for investigating the effect.

2.5 Fate of spilled oils

2.5.1 Physical and chemical fate

Although the particular composition of a crude oil in its natural reservoir may be stable over geological time spans, its composition changes once it is exposed to water, oxygen, sunlight, micro-organisms, and other factors. Change occurs rapidly in the initial stages, but with diminishing speed as thermodynamic equilibrium with conditions in the environment is approached. Volatile components evaporate, at rates depending upon vapour pressure and mass-transport conditions, leaving behind a residue which may become dense enough to sink (Payne and Phillips, 1985).

Some low-API-gravity residual fuel oils, called "LAPIO", are, to a very limited extent, being used for generation of electric power. These fuels have a density very near to or higher than seawater, and are expected to sink immediately, causing problems with their recovery if spilled.

With vigorous wave action, water-in-oil emulsions (chocolate mousse) are formed with an oil content of approximately 30%, and oil is dispersed into the water as fine droplets. Soluble components enter the aqueous phase, and energetic photons from the short-wavelength band of the solar spectrum trigger chemical reactions (oxidation, decomposition, polymerization) in the well illuminated surface layer, whose thickness is inversely proportional to the turbidity of the water. A number of photo-oxidation products of oil components have been identified as alkylated derivatives of tetralin hydroperoxide, tetrahydronaphthols, alkylphenols, carboxylic acids (Larson *et al.*, 1979), dibenzothiophene sulfoxides (Patel *et al.*, 1979), quinones, phenylalkanones, phenylalkanols, dialkyl ketones, methyl alkyl ketones (Ehrhardt and Petrick, 1984, 1985; Ehrhardt, 1987b; Ehrhardt *et al.*, 1990) and low-molecular-weight carbonyl compounds such as acetone, acetaldehyde, and formaldehyde (Ehrhardt and Weber, 1991).

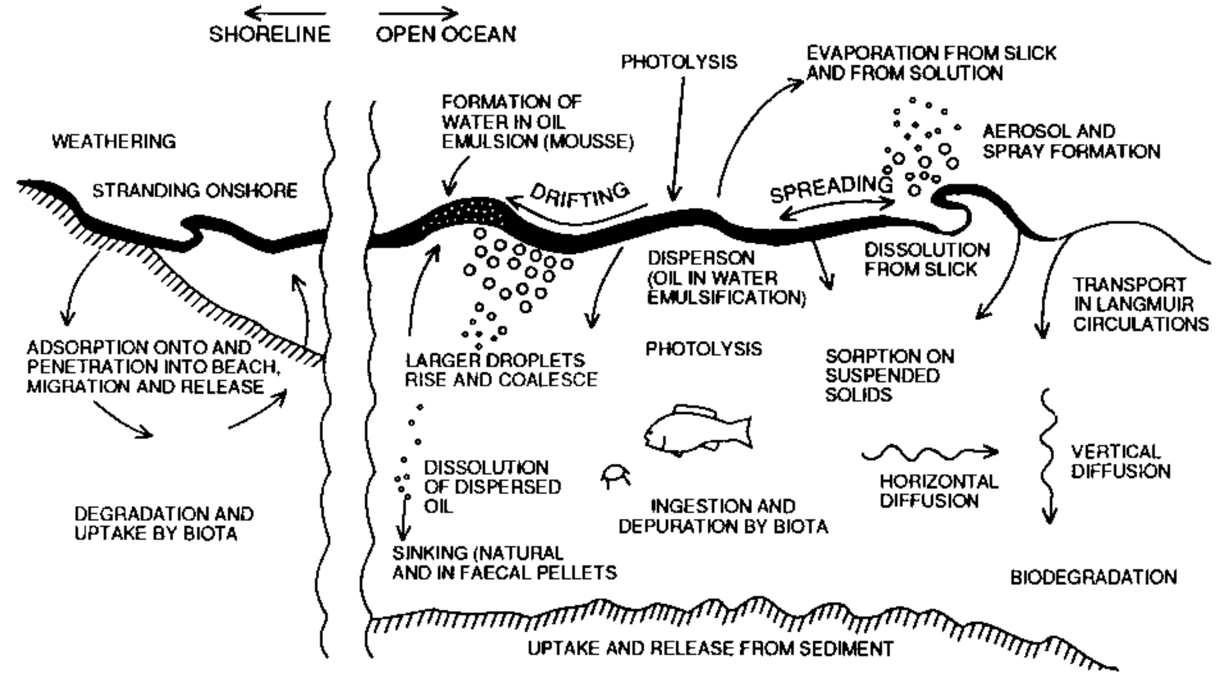
In aqueous solution, and especially in particulate form, either suspended or deposited on the seafloor (Burns, 1986), components of oil are degraded microbially. Sufficient nitrogen and phosphorus compounds are needed to sustain the growth and metabolism of oil-degrading micro-organisms. Rates of microbial decomposition depend upon structure and molecular weight, with rates decreasing in the order n-alkanes > branched-chain alkanes > aromatic hydrocarbons > alicyclic hydrocarbons, and with increasing molecular weights (Watkinson, 1978).

Thus, the composition of a given oil not only reflects its origin but also, if spilled, the duration of exposure to and the conditions in the environment. The tarry oil deposits that are often found on beaches are rather stable residues which are composed of high-boiling components and largely protected against microbial decomposition by their small surface/volume ratios.

Figure 2.5 schematically represents the fate of oil spilled on the sea surface and on shorelines, identifying key processes such as dissolution, advection, evaporation and sorption onto suspended solids.

A great deal has been learned about the physical, chemical, and biological fate of spilled oil from investigations of accidental blowouts from oil wells and ship accidents. For example, studies of processes and effects after the grounding of the tanker *Amoco Cadiz* near Portsall in Brittany, France, in the night of 16 to 17 March 1978 (Marchand, 1981) have been extensive. Spillage of most of her cargo of 223,000 tons of a mixture of "Arabian light" (100,000 tons) and "Iranian light" resulted in the worst incident of oil pollution to that date but which eventually also became one of the best investigated.

Figure 2.5: ***Schematic diagram of oil spill processes at sea and shorelines***



Source: MacKay (1985) in Engelhardt (1985)

Like many spilled crude oils, the oil from the *Amoco Cadiz* formed a stable water-in-oil emulsion, with a water content of approximately 30%, soon after it escaped into the sea. Due to the large proportion of low-boiling components, a considerable fraction of the spilled oil evaporated (approx. 30%). Roughly 14% dissolved in the water, 8% was incorporated into sediments, and 28% was washed up on the shore. The dissolved oil was rapidly degraded microbially, as shown by the decreasing concentrations of dissolved oxygen, nitrate and phosphate in the water column. Investigations under controlled conditions showed, however, that only a sizeable fraction of the straight-chain alkanes is completely remineralized and converted into carbon dioxide and water (10–15%). Not more than 2 to 6% of the branched-chain isoprenoid alkanes pristane and phytane were remineralized, as was only a very small fraction of the aromatic hydrocarbons. Despite extensive microbial decomposition, only a small fraction of the oil was converted into compounds known to be innocuous (Marchand, 1981).

At the *Amoco Cadiz* spill, the fate and effects of the oil which reached the shore depended very much on the shoreline's physical consistency and on the exposure or not to wave action on the affected substrate. Thus, exposed rocky shores were almost free of oil a few weeks after the accident; erosion rocky platforms took a few months to clean themselves; medium to coarse sand beaches took one to three years to become clean because of penetration of oil into the ground; pebble and gravel beaches were not clean for three to five years, also because of penetration of oil into deeper layers. Under sheltered conditions, physical removal and breakdown of oil took proportionally longer periods of time. Oil on erosion platforms lasting three to five years, and in sheltered mud flats, enduring for more than 10 years, were the extremes (Berne *et al*,. 1980).

Once oil has come ashore, its persistence and longevity depend on a number of factors, such as the type of oil, the season, the geomorphology of the coast, and the degree of exposure. The latter two parameters have been used to classify entire coastlines according to their vulnerability or sensitivity to oil, with the first such classification being proposed by Gundlach and Hayes (1978). This followed their observations of the variable impact sustained by different coastal types following a spill event. Vulnerability has since been determined, with minor modifications, for a number of coastal environments from the Arctic (Michel *et al.*, 1978) to the tropics (Gundlach and Murday, 1989) and to the Antarctic (Gregory *et al.*, 1984). The classification does not take into account the ecological or other values of the coast and is based exclusively on coastal geomorphology, degree of exposure to wave action, and the likely persistence of oil, if it came ashore. Integration of the coastal index with ecological resources and amenity values has been undertaken for New Zealand (Tortell, 1981). However, the complex nature of such an approach permitted the recognition of only three broad categories of coastal environments, namely those that merited high priority, those of medium priority, and those of only low priority.

Davies and Tibbetts (1987) investigated the depuration of an experimentally oiled sediment under natural conditions. The total concentration of the oil initially decreased quite rapidly (approx. 80% of the oil was lost during the first 40 days of the experiment). However, it was mainly dissolution of oil into the water which accounted for its disappearance, microbial decomposition being far less effective. After four months 95% was lost, but concentrations then remained fairly constant during the following eight months. Lopez and Laseca (1991) have presented an extensive discussion of physical, chemical and biological fates of spilled oil.

2.5.2 Oil spill trajectory modelling

Several oil spill trajectory modelling applications and prototypes are available today. A list of models, not intended to be exhaustive, is in Table 2.4. From evaluations done by various groups, many supporting their models, and industry/government papers, it is obvious that the weakest link in all of the models is the availability of accurate and timely input data. The input data that are needed are normally divided into two components, environmental and oil. The environmental data usually include wind, current, tides, temperature, and ice information (if present) and water characteristics. The oil data include oil type, physical and chemical properties, and characteristics of the spill, such as amount spilled and rate of spilling. The data that are needed to predict the trajectory of a slick accurately are not available for most of the world. In all cases reviewed, there were data that, when known (usually after the fact), would have enhanced the predictive results significantly.

The more detailed the available survey data are for any given geographic area, the better the predictive models can provide a reasonable assessment of the track, location, shape and weathering of a spill. Even in studies where reasonable accuracy was stated, the accuracy achieved (Venkatesh *et al.*, 1988) was not sufficient to give a response coordinator confidence that he could rely on the predicted location for planning response actions. For example, there are no night-time operations, due to the inability to maintain contact with or locate the slick at night. If the models were as accurate as the authors claimed, operations would be possible during the night.

Current oil-spill models can predict the movement and weathering of a slick over time with very good correlation, but only if very accurate input data are available. This is especially true when the input data are obtained in real time. Detailed research on location-specific characteristics that influence the needed input data, such as floor topography and unique shoreline interactions, is needed.

2.6 Marine ecosystems and oil – effects and recovery

2.6.1 Introduction

There has been a major research effort over the past 20 years to understand better the biological effects of oil and its constituents in the sea. This work has been extensively reviewed (e.g. Clark, 1982; Howarth, 1987; Jackson *et al.*, 1989; Karinen, 1988; NRC, 1985; Farrington, 1985; Vandermeulen, 1982; Engelhardt, 1985). It adds substantially to what was previously known about the magnitude, the impacts of oil spills (Nelson-Smith, 1972; GESAMP, 1977; NRC, 1975; Malins, 1977a,b).

There are new insights and understanding about the degree and persistence of oil impacts. Chief amongst the new insights is identification of the most sensitive and vulnerable shorelines (low-energy, marshes, seagrasses, mangroves); recovery time of oiled coastal areas (up to 10 years or more in boreal and temperate seas, and often two or more decades in sub-tropical and tropical systems such as coral reefs and mangroves); threshold effect concentrations for various species and different hydrocarbons and their mixtures in water (as low as a few $\mu g/\ell$, but often well above measured or predicted concentrations in the water column); the effects of different oils; sensitivity of young life stages (very sensitive, but variable with stage); differential sensitivity of different species (crustaceans versus fish); and the impact

Table 2.4: ***Selected models to predict the trajectory and fate of an oil spill***

MODEL	MODEL TYPE	DEVELOPER
AES OIL SPILL MODEL	EMERGENCY RESPONSE	ATMOSPHERIC ENVIRONMENT
ASA PC OIL SPILL MODEL	EMERGENCY RESPONSE	APPLIED SCIENCE ASSOC.
ASA ATOM	EMERGENCY RESPONSE CONTINGENCY PLANNING	APPLIED SCIENCE ASSOC.
ASA COASTAL SEA MODEL SYSTEM	EMERGENCY RESPONSE CONTINGENCY PLANNING HINDCAST	APPLIED SCIENCE ASSOC.
ASA COZOIL	COASTAL INTERACTION	APPLIED SCIENCE ASSOC.
CHEMSPIL	EMERGENCY RESPONSE	SHELL OIL COMPANY
CHI/VKI MODEL	EMERGENCY RESPONSE	DANISH HYDRAULICS LABORATORY
DOOSIM	EMERGENCY RESPONSE HINDCAST	OCEANOR
ECO OIL SPILL MODEL	EMERGENCY RESPONSE CONTINGENCY PLANNING	ENGINEERING COMPUTER OPTECNOMICS (ECO)
ENSR OSP MODEL	CONTINGENCY PLANNING EMERGENCY RESPONSE	ENSR CONSULTING AND ENGINEERING
HACS	EMERGENCY RESPONSE	U.S. COAST GUARD
OILBRICE	EMERGENCY RESPONSE	ATMOSPHERIC ENIV. SERV. FLEET TECHNOLOGY, LTD.
OIL IN ICE MODEL	EMERGENCY RESPONSE	DOME PETROLEUM LTD.
OSRA	CONTINGENCY PLANNING	MINERALS MANAGEMENT SERV., U.S. DEPT. OF INTERIOR
OSSM TACTICAL AND RECEPTOR MODE	EMERGENCY RESPONSE CONTINGENCY PLANNING	N.O.A.A.
PC OIL SLICK SIMULATION	EMERGENCY RESPONSE CONTINGENCY PLANNING	SCICON ENERGY
TRANSPIL	EMERGENCY RESPONSE	DELFT HYDRAULICS
S.L. ROSS OIL SPILL MODEL	CONTINGENCY PLANNING	S.L. ROSS ENVIRONMENTAL RESEARCH LTD.
SHORT TERM USGS MODEL	EMERGENCY RESPONSE	U.S.C.G. R&D CENTER
SLIKTRAC	CONTINGENCY PLANNING	E & P FORUM
SPILLCALC	EMERGENCY RESPONSE	SEACONSULT MARINE RESEARCH LTD.
WARREN SPRING MODEL	EMERGENCY RESPONSE	UNIVERSITY COLLEGE OF NORTH WALES

Source: F.R. Engelhardt, pers. comm.

of oil on coastal and tropical environments (mangroves are often devastated) (see NRC, 1985; Farrington, 1985). There are continued gaps in our understanding – especially extrapolating from laboratory studies on fate and effects to field predictions of impact, an "intractable problem with the 1985 National Academy review", according to Farrington (1985), and a difficult and critical problem generally (Cairns, 1986).

Studies of the past 20 years also show the new important technical advancements for assessing impacts of oil spills in both laboratory and field. They include:

- production and control of more realistic exposure concentrations/ compositions of hydrocarbons in laboratory experiments assessing hydrocarbons in water, and their use in toxicity studies (measurements of composition and concentration of hydrocarbons are essential);
- use of a wider range of species and young life stages, especially through culture, for experiments – microscale toxicity and QSAR (quantitative structure–activity relationships) approaches allow rapid evaluations;
- studies of critical factors (physico-chemical and biological) controlling persistence, exposure, uptake, bioaccumulation, and toxicity and metabolism of hydrocarbons (fate and effects models are being linked);
- measurement of a wide range of toxicity response variables in sublethal experiments (many highly sensitive techniques now exist);
- conduct of experiments involving oiled sediments in laboratory and field, examining bioavailability and toxicity of sediment-bound hydrocarbons (behavioural responses are particularly sensitive);
- microcosm, mesocosm and controlled field approaches for studying oil impacts (this has been the major step in testing laboratory predictions of impacts);
- biomonitoring approaches with individual organisms and benthic communities, including statistical considerations (considerable progress has been made in design); and
- hazard-assessment approaches applied to the prediction of oil impacts in marine systems (exposure assessment and toxicity have been considered together).

Biological responses to exposures to hydrocarbons are of many types, often complex, most often non-specific, and closely dependent upon precise exposure conditions, making generalization difficult and often erroneous. The following sections describe the most sensitive processes; the most sensitive and vulnerable species and life stages; the responses and the ranges of recovery times of specific habitats and ecosystems; the impact of oil in special places, such as polar and coastal seas; the impacts of major spills; and the effects on fisheries.

2.6.2 Impacts of oil in the sea

It is well established that oil and its related compounds enter the sea from many sources, ships and land-based activities being the primary ones (see sections 2.2 and 2.3). The effects of used lubricating oils and industrial oils are considered in Chapter 3, and hydrocarbons from offshore operations in Chapter 5. Most research to date on toxicology and effects on ecosystems has been conducted within a ship-spill context, involving crude and refined oils or individual hydrocarbons. Highlights of our current understanding about impacts, within this context, are presented below.

In marine systems, micro-organisms are the predominant type of biotic decomposer of oil. There are more than 25 genera each of hydrocarbon-degrading bacteria and fungi. The proportion of hydrocarbon-degrading species to the total heterotrophic community varies widely. It is clear, however, that prior adaptation to hydrocarbons in the environment enhances the subsequent rate of degradation of hydrocarbons, as shown at natural oil seeps. The physical form of the petroleum (tar ball, slick, mousse, etc.) greatly affects the rate of breakdown of hydrocarbons, mainly through a simple surface-area relationship (Leahy and Colwell, 1990). Temperature, oxygen concentration, nutrients, salinity, pressure, water activity of sediments and pH all affect the rate of biodegradation (Leahy and Colwell, 1990). Low-temperature environments often, but not always, have slow microbial responses to exposure to petroleum, but such limited rates of biodegradation of hydrocarbons are due as much or more to the availability of nutrients, i.e. nitrogen and phosphorus, and the lack of oxygen (often the limiting factor) than to the low temperatures (Horowitz and Atlas, 1977; Atlas, 1985). In fact, recent Norwegian work has "clearly shown that bacterial degradation at low temperatures in the Barents Sea occurs at the same rates as further south such as in the North Sea" (Gray, pers. comm.). Clearly, microbial degradation of oil and its constituents at sea is an important but highly variable mechanism for breakdown and removal (Neff, 1990).

The effects of both chronic discharges and accidental releases of petroleum hydrocarbons have been studied with a wide variety of organisms and ecosystems and biological processes. Generally, the broad types of biological effects are similar in tropical, temperate and polar marine environments for related or similar groups of organisms (Percy and Wells, 1984), although more is known about oil pollution in temperate areas. Environmental impacts may differ due to factors that affect the distribution and composition of the petroleum hydrocarbons, especially their weathering and persistence and, consequently, their bioavailability. In open bodies of water, currents and diffusion can decrease concentrations of contaminants rapidly. At shorelines, however, this is more difficult, especially in low-energy environments (e.g. some sandy beaches, estuaries, marshes and protected coves). Once oil encounters a shoreline, several factors determine its persistence: properties of the oil, porosity of sediments (type of material, particle size and percent organic matter), presence of animal (e.g. worm and crab) burrows, wave and erosion activity, type of vegetation, etc. Oil coats rocks, often forming a tough tarry skin that protects pools of oil underneath; these liquid pools can persist for decades. Aquatic macrophytes are highly susceptible and often constitute the dominant vegetation affected in the impacted ecosystem. Many animals will be killed outright or experience sublethal effects that may cause delayed mortality.

The recovery of these shoreline ecosystems is dependent upon the type, amount, and duration of hydrocarbons persisting in the water and sediments, and the life histories of the organisms initially affected. The time scales of recovery may vary from species to species, dependent upon the generation time, the availability of recruits and sensitivity to the remaining hydrocarbons. For example, often a shift from a grazing to a detrital-based food web has been observed, as petroleum provides an additional carbon source (NRC, 1985). Mussels, barnacles and some algae may re-inhabit a previously oiled environment within months, whereas populations of decapod crustaceans may take longer. Relatively little is understood about these patterns and rates of recovery, and the key influencing factors, and they are a subject of considerable study at some major spills such as the *Exxon Valdez* (Maki, 1991; Baker *et al.*, 1991a,b).

Capuzzo (1987) reported that the biological effects of petroleum hydrocarbons on marine organisms are a function of several factors: persistence and bioavailability of the hydrocarbons, ability of the organism to accumulate and metabolize them, and how much the contaminants interfere with normal metabolism. She categorized effects on four levels of biological organization: biochemical and cellular, organismal, population and community. Evaluation of community effects has been hampered by a lack of satisfactory descriptors of the community structure and the high levels of natural variability. In addition, it has been difficult to identify a clear relationship between the amount of hydrocarbon in key tissues, toxic effects and how these effects are reversed when hydrocarbons are released from tissues.

The chemical complexity of petroleum has undoubtedly complicated the evaluation of its biological effects (Daling *et al.*, 1990; Shiu *et al.*, 1990). Toxicity is a deleterious effect, whether lethal or sublethal, to an organism, population and community (NRC, 1985). Toxicity is generally greatest for the compounds with the highest molecular weight within homologous series; however, in water, the lower-molecular-weight components (C_{12} to C_{24}) cause most acute toxic effects because of their greater solubility and therefore greater bioavailability and penetration to the sites of toxic action (Abernethy *et al.*, 1986). For these reasons, and for others pertaining to their physico-chemical properties, there can be major differences in toxicities between different oil types and between fresh and weathered oils (Mackay and Wells, 1981; Maclean and Doe, 1989; Baker, pers. comm.). Constituents of oils can also affect different species differentially; the lowest-molecular-weight compounds in a homologous series are most toxic to marine plants, whereas the opposite is true for microcrustaceans (Abernethy *et al.*, 1986; Baker, pers. comm.). As for many other chemicals, exposure conditions may be a more important variable than species differences in toxicity when determining the hazard of oils and their constituents in the sea. The toxicities of products of photolysis and biodegradation of oil are currently of interest, within this context.

There is only rudimentary evidence that there have been long-term effects at the population level and at the community level from petroleum pollution in the sea (Howells *et al.*, 1990). Often, up to 10 years is needed for biological communities to recover to their pre-spill state (NRC, 1985), but this time is highly variable, being less in cold-water, high-energy, temperate and sub-Arctic areas and greater in low-energy, tropical regions (e.g. Prince William Sound, Alaska (Baker *et al.*, 1991a,b), 2 to 3 years; tropical areas (Thorhaug, 1991), 2 to 3 decades).

Birds are often the most conspicuous victims of an oil spill, with many thousands of casualties frequently occurring after spills. However, there is controversy concerning long-term effects on the population level of seabirds. It has been difficult to delineate natural versus oil-related mortalities over several generations of a seabird population. Laboratory studies show a very wide array of effects induced by petroleum hydrocarbons for a large number of species. There has been great difficulty, however, in extrapolating these results from confined laboratory experiments to complex field communities where there may be many thousands of pathways of cause and effect operating simultaneously.

In addition, little is yet known about the impacts of oiling and low-level oil contamination on some groups of wildlife such as turtles, which are suspected to be particularly vulnerable during egg-laying and hatching.

There is increasing evidence of mutagenic and carcinogenic effects of petroleum compounds, especially high-molecular-weight PAHs, and the ecological risk of chronic sources of petroleum contamination may be much larger than anyone has yet estimated (NRC, 1985).

Establishing ecological effects from chronic pollution, or establishing recovery from a spill, depends on having reliable reference sites and on having a sufficiently long series of measurements at the site of concern so that effects of pollutants can be distinguished from natural variability. For this purpose, it would be desirable to have a comprehensive ecological–pollution data repository, a theoretical framework to help organize and evaluate the data, and a mechanism for periodic critical evaluation of these data.

Laboratory and field studies carried out in the 1970s and 1980s demonstrated acute and chronic effects in adult fish exposed to waters and sediments contaminated with high levels of petroleum hydrocarbons. Petroleum spills generally have a low acute toxicity potential for adult fish (Rice, 1985), but fish kills may occur due to high exposure to emulsified oil in shallow waters (e.g. *Braer* spill, January 1993, Shetland Islands). Fish may avoid oil at sea, although little documentation exists and some of it is contradictory, e.g. few estuarine fish were observed along the oiled shorelines at *Amoco Cadiz* (Wells, pers. observ.), but migratory behaviour of salmon was unaffected by experimental exposures to oil (McAuliffe, pers. comm.). "There is no evidence so far that any oil spill has significantly affected adult fish populations in the open sea" (Baker, 1991). However, chronic exposure of bottom-dwelling species to highly contaminated intertidal/near-shore sediments is of concern. For example, dose–response relationships have been evaluated in winter flounder (*Pseudopleuronectes americanus*) chronically exposed to sediments contaminated with petroleum and adverse effects were noted at concentrations commonly found to occur under oil-spill conditions. Although effects are expected to be quite localized, it is reasonable to assume that heavily contaminated sediments will have adverse effects on such flatfish (Payne *et al.*, 1988).

With respect to fish larval kills and attendant impacts on population levels, modelling studies indicate that large numbers of larvae would have to be destroyed to affect recruitment (Reed *et al.*, 1984; Hurlbut *et al.*, 1991). In the event of major spills, the possibility exists for impacts on stocks spawning in shallow-water areas having poor water circulation. However, only small proportions of any population will be likely to be impacted, with relatively small or insignificant resource losses.

A recent comparison of toxicity data for acute and sublethal effects of petroleum pollution on many different types of organisms showed that effects are similar for marine and freshwater environments (Vandermeulen, 1987). Acute effects are better understood than sublethal ones. Vandermeulen (1987) hypothesized that sublethal effects caused by a chronic long-term discharge would more probably have effects at the population level than merely be restricted to the level of individual organisms. However, this hypothesis is most plausible if the effects are harmful, not merely adaptive, and present in a large proportion of the population. An ecological risk analysis of a seabird population, comparing effects at the population level of both chronic and accidental discharges, has not supported this hypothesis (Lane, 1985). Both types of discharges can affect aquatic populations over several generations, depending on their specific life history and the nature of the environment and of the contaminant discharge.

Mesocosm and field (controlled) experiments have also added insight to the impacts of hydrocarbons in marine ecosystems, especially in bridging field and laboratory results, and allowing comparisons between the effects of accidental oil spills, chronic oil pollution, and oil exposures in the mesocosms themselves (Teal and Howarth, 1984; NRC, 1985; Gray, 1987; Howarth 1989; NRC, 1989). A number of such experiments have been conducted in North America and Europe, including the CEPEX (Controlled Ecosystem Pollution Experiment) study in British Columbia, the MERL (Marine Ecosystem Research Laboratory) project in Narragansett Bay, Rhode Island; the planktonic bag experiments in Scotland (Davies *et al.*, 1980); and the benthic mesocosms in Oslo, Norway (Gray, 1987). Collectively, the experiments have shown the wide range of chronic sublethal effects that occur at numerous trophic levels while the hydrocarbon exposures persist (NRC, 1985; Howarth, 1989). For example, one MERL experiment involved a six-month dose of water-dispersed No. 2 fuel oil averaging 180 μg/ℓ, with 75 μg/ℓ of total aromatics (NRC, 1985). Effects were observed in bacterioplankton, phyto- and zoo-plankton and the benthos at concentrations as low as 90 μg/ℓ and for plankton at levels of 40 μg/ℓ of total hydrocarbons. Nanoplankton dominated, bacterioplankton increased and zooplankton populations decreased in this experiment. Collectively, mesocosm experiments with zooplankton, to date, have shown the type and variability of toxic responses (lethality, lowered feeding and reproduction, and community changes) that might be expected among natural zooplankton communities when continuously exposed to low levels of oil-derived hydrocarbons (Wells, 1981; NRC, 1985; Wells and Percy, 1985). In addition, recent studies of benthos in mesocosms in Norway have shown clear long-term effects of oil doses; in a hard-bottom mesocosm, effects were noted on algal growth, recruitment of periwinkles and byssus secretion of mussels, all of which are detrimental in the natural environment (Gray, 1987). Hence, mesocosms are proving to be a very useful method for studying the processes of impact and recovery from oiling events.

Two of the most publicized oil spills in temperate environments were the *Torrey Canyon*, off the coast of Cornwall, U.K., in which 95,000 tons of oil were lost in 1967, and the *Amoco Cadiz*, off the Brittany coast, which discharged 220,000 tons in 1978. Both spills resulted in massive bird kills. For the *Amoco Cadiz* wreck, large amounts of oil were stranded on the beaches and 321 km of shoreline were impacted. There were some mortalities of fish up to 10 km from the wreck, but changes in commercial finfish species were insignificant while aquaculture was harmed (NRC, 1985). Page *et al.* (1989) followed the decomposition of the hydrocarbons in the sediments for seven years and showed that all but the most heavily impacted areas were in the final stages of degradation by 1986. Forty percent of benthic biomass was eliminated in some of the impacted areas. Berthou *et al.* (1987) documented that, seven years after the same spill, oyster areas remained polluted with aromatic hydrocarbons and animals exhibited lesions of the digestive tract and gonads. Dauvin (1987) reported that amphipod populations had not returned to pre-spill levels in eight years following the *Amoco Cadiz* spill. These effects are expected to persist for several more years. There were changes in species composition in the intertidal communities and considerable additional damage was incurred during clean-up (Baca *et al.*, 1987). Some of the low energy environments, such as the Île Grande saltmarsh, are expected to take longer to recover (from oiling and clean-up techniques) and are still undergoing remediation efforts.

Because of the increasing need to identify new petroleum reserves, there is continued interest in oil exploration and production in polar environments. Some estimates have arctic petroleum reserves equal to all others in the world (Engelhardt, 1985). There has been a long-standing controversy on what is an acceptable level of environmental risk in proceeding with arctic oil development. To date, much of the production has been on land or in near-shore marine areas, with transport of oil by tanker or pipeline.

Polar environments have special features, such as low temperatures, long periods of ice cover, a short summer and ice-free season, low species diversity and under-ice algal/crustacean communities, that make them particularly vulnerable and sensitive to oil-spill impacts (NRC, 1985). Polar waters are often shallow and air temperatures can be − 55 °C, with ice-covered seas. Low temperatures increase the viscosity of spilled oil and inhibit the mixing of oil in water. Microbial degradation of stranded oil may occur more slowly in arctic environments than in their southern counterparts. Microbial degradation of subtidal oil may also be hindered by inadequate nutrients and low oxygen. Constituents of petroleum can be very persistent in beaches and subtidal sediments in cold environments; natural degradation of oil may take decades rather than months to years (Atlas, 1985; Sergy, 1987). Low-energy coastlines are particularly vulnerable to long-term oiling, and spilled oil can harden into persistent asphalt pavements on intertidal surfaces (Sergy, 1987).

Polar food webs are short, with low species diversity, as compared to those of other ecosystems. Marine birds are a conspicuous component of these food webs, and several thousand dead birds may be collected after an oil spill. As elsewhere, this number may represent only a small portion of the total mortality at sea, which can be devastating to local populations. Following a spill, others die as their ability to thermoregulate is impaired by very small amounts of oil encountered on the water surface. Others drown as their oiled feathers lose buoyancy. Besides external effects, birds can ingest oil when preening oiled feathers and eating contaminated food. This can cause direct toxicity and can lead to decreased survival, density, and fecundity of bird populations. Several physiological effects have been noted. Birds are especially vulnerable not only because of the small amounts of petroleum that are toxic to them but also because many of their activities (such as breeding, feeding, overwintering, and migration) are undertaken in parts of the marine ecosystem vulnerable to oil pollution, i.e. tidal flats, coastlines, surface waters, polynyas.

The Arctic Ocean has relatively few productive fish stocks, and marine mammals and seabirds constitute the top predators in the marine food webs (Percy and Wells, 1984). Fish rearing and spawning areas are sensitive to oiling, especially in confined bays and harbours. Eggs and larvae are the most vulnerable; developmental malformations can occur *after exposure of hours to days* at concentrations of less that 1 $\mu g/\ell$ (NRC, 1985; Rice, 1985). However, there have been no documented cases of a fish stock being greatly reduced following an Arctic oil spill.

A large proportion of the world's marine mammals inhabit polar waters for at least a part of the year. These animals use the estuaries, shores, ice and air–sea interfaces, which are all areas where they could encounter a spill. For many species there are only fragmented data on the effects of oil and these organisms are not conducive to laboratory experimentation. Thus, field information will continue to be very important. Ice tends to concentrate oil in breathing holes and ice leads. Wind moves oil between ice-floes and against ice edges. Engelhardt (1985) has reported on the vulnerability of several mammals, such as during the birth and post-natal care of ringed seals (which occurs in air pockets under the ice), and when bowhead whales depend on ice leads for migration. In addition, external oiling and ingestion of contaminated food can cause lethal and sublethal effects. As with birds, there are no definitive quantitative predictions that link mortality in marine mammals with exposure to spilled oil (Engelhardt, 1985). Body-temperature problems probably do not affect oiled cetaceans but do affect polar bears and sea otters after they have been oiled (Geraci and St. Aubin, 1990).

On 24 March 1989 the *Exxon Valdez* went aground in Prince William Sound, Alaska, and discharged 42 million litres of Prudhoe Bay crude oil. Although damage is still being assessed (Maki 1991, pers. comm.), the oil had severe effects on wildlife, especially otters and seabirds, in the short term. Several thousand kilometres of shoreline were oiled. Recovery of the Sound is being evaluated (Baker *et al*, 1990). Prince William Sound possesses some of the best colonies of sea otters in the world. Approximately 2–3,000 of the 10–11,000 animals were killed outright and undoubtedly many more subsequently perished (Waldichuk, 1990). Although there were valiant rescue efforts, many otters died from ingesting oil, causing liver damage associated with low blood sugar and low body temperature. Once a sea otter is in contact with fresh oil, the animal has only a 50% probability of survival (Waldichuk, 1990); later in the spill, after the oil had weathered and lost much of its acute toxicity, survival of oil-contaminated and cleaned otters was much higher (Lindstedt-Siva, 1991, pers. comm.). Tens of thousands of seabirds died, including 150 bald eagles (Hodgson, 1990). Clams, mussels and finfish were contaminated (Hodgson, 1990).

At least two oil spills have occurred in Antarctic waters, in 1989 and 1990, involving fuels from ships and land stations (ACOPS, 1990; Kennicutt *et al.*, 1990). These were the *Bahia Paraiso* (various fuels and petroleum) and McMurdo station (various fuels, petrol) (ACOPS, 1990). Concerns include acute effects on the unique wildlife, especially seabirds such as penguins, and longer term effects on euphausiids (i.e. krill) and other plankton which support the southern food webs. Oils in ice-infested waters are very difficult to recover and clean up, and hydrocarbons may persist if trapped in sediments on shorelines or subtidally. Some countries, such as Britain, are considering special studies of oil hazards in Antarctic waters (John Sproule, British Antarctic Survey, pers. comm.).

Many tropical ecosystems, such as coastal mangrove swamps and coral reefs, are particularly vulnerable to petroleum pollution (Vandermeulen and Gilfillan, 1984; Ballou *et al.*, 1987; Ballou and Lewis, 1989). There is still a great deal that is not known on how these systems function naturally, as well as under contaminant stress.

The vulnerability and sensitivity of mangroves has been summarized by NRC (1985) and has been the subject of a number of specific studies over the past decade (see Ballou *et al.*, 1987, 1989; Ballou and Lewis, 1989; Teas *et al.*, 1989). Mangroves are a major component of tropical coastal productivity, occurring along approximately 75% of shorelines between 25° north and 25° south, and providing protection against erosion and shelter for innumerable species. Mangrove swamps and systems are highly vulnerable to oiling and oil residues; they are permeable to tidal waters, are low-energy environments, and have many channels and fine sediments. Hence they trap oil. The aerial roots are easily oiled and suffer clogging and choking. Seedlings are very sensitive to hydrocarbons. Young trees are more sensitive than mature trees, but large, old trees can be killed by oil too. Oiled forests suffer leaf loss and partial to complete defoliation. Recovery rates vary highly, taking as long as 20 years. Global losses of mangroves due to oiling are unknown. More needs to be understood concerning recovery rates and processes and the success of rehabilitation programmes after oiling (Teas *et al.*, 1989).

The responses of corals and their communities to oil have been extensively studied. Using their own observations from the reef flat at Eliat in the Red Sea, Loya and Rinkevich (1980) demonstrated the importance of sublethal effects of oil pollution on vital processes such as growth, development, feeding behaviour and reproduction of corals. Most of the effects noted in the early studies were considered temporary (ITOPF, 1985). However, Bak (1987) noted that sub-lethal effects of oil pollution on coral reefs may not become manifest except over very long periods of time. A Caribbean study showed that the results of chronic oil pollution (such as spills, clean-ups, etc.) are clearly discernible over a distance of 10 to 15 km along the reef. Bak (1987) and Ballou *et al.* (1989) also pointed out that there is differential sensitivity to oil among species; one coral reef species (*Diploria strigosa*) is relatively tolerant to dispersed oil in terms of long-term effects on growth and survival.

Burns and Knap (1989) described the Bahia las Minas crude oil spill on the Caribbean coast of Panama in April 1986 that caused extensive mortality of subtidal reef corals and infauna of seagrass beds. Eight million litres of medium-weight crude oil spilled from a ruptured storage tank at a refinery site into a region of mangroves, seagrasses and coral reefs (Burns and Knap, 1989). This location was near the *Witwater* spill eighteen years earlier (Jackson *et al.*, 1989). There was uptake of dissolved/dispersed hydrocarbons by subtidal corals, primarily from the water (as indicated by GC patterns), verifying the many laboratory observations of uptake of hydrocarbons. In contrast, oil in sediments may not be available for uptake by the corals. In addition to documenting the incorporation of petroleum hydrocarbons into coral tissues and demonstrating a positive correlation between tissue burden and mortality, the data also suggested a possible modification in the protein to lipid ratios in corals that are heavily stressed by oil (Burns and Knap, 1989). Such "alterations in the lipid metabolism would also be expected to have profound effects on the physiology and reproductive success of corals". Jackson *et al.* (1989) described the ecological effects of the spill. There was extensive damage to mangroves and intertidal seagrasses. Most subtidal seagrass communities survived intact. Fringing reefs were greatly damaged on their seaward side. In total, infauna and epifauna and members of all trophic levels of both intertidal and subtidal communities were harmed. There was mortality of subtidal corals and seagrass infauna, a new observation. The authors cautioned against extrapolation of laboratory and short-term field experiments to natural communities. They concluded that sublethal effects are more important than initial mortality in regard to the future recovery of oiled reef populations.

Oil spills in Egypt, Indonesia, Curacao and Panama have shown a series of species of corals, in various oceans, to be sensitive to oil (Thorhaug, 1991). It would appear that emerged coral reefs are clearly more vulnerable to oil than those submerged (Bak's work 1981, quoted in Thorhaug, 1991).

Enclosed water bodies, such as industrialized lagoons and inlets in tropical regions, often are exposed to chronic oiling and suffer the cumulative effects of low-level hydrocarbon concentrations. However, it is difficult to separate oil impacts from those of other chemicals in such locations.

The largest accidental spill to date (November 1990) in a tropical/semi-tropical environment has been the blowout of the IXTOC 1 exploration well off the coast of Mexico in 1979. It took ten months to cap the well. Oil was lost at between 20,000 and 40,000 barrels per day (2,740–5,480 tonnes/day) (Gourlay, 1988). Because of the duration of the spill, scientists were able to study it in more detail as an open-ocean spill. Oil formed a chocolate mousse with upwelling burning gas at the centre. The mousse provided a vehicle for transport of the aromatic compounds long distances from the spill. Exposed U.S. coasts have been better studied than the open ocean and Mexican coasts. Although populations of hydrocarbon-degrading bacteria were more abundant in the vicinity of the mousse, nutrient limitation slowed their action. Consequently, the major weathering of the oil was attributed to physical and chemical processes. Along U.S. coastlines, it is thought that there were significant declines in benthic, intertidal and subtidal communities; however, there was little evidence of effects on the economically important shrimp populations. Oil from the spill was tracked to the north-eastern Gulf of Mexico; the fate of the largest amount of spilled oil, remaining at sea or entering the atmosphere, remains unknown.

The restoration and rehabilitation of oiled coastal ecosystems has become an important activity, especially with marshes, seagrasses and mangroves. Work after the *Amoco Cadiz* spill in France in 1978 showed some of the problems involved in re-establishing species in an oiled marsh sediment, and work on mangroves shows that weathering of oil influences restorative capacity. Sites in the United Arab Emirates (mangroves), Jamaica (seagrasses) and the Philippines (seagrasses) have apparently been successfully restored.

2.7 Effects on human health

The greatest hazard to human health of oil spills is from explosion and fire at the spill site. While other hazards to people are from hydrocarbons from the oil, at various distances and times from spill sites (especially during clean-up operations), and may be serious, they are not of the magnitude of the fire/explosion risks. Fires and explosions have obvious effects and are not covered further in this review.

The NRC (1985) review covered human health comprehensively, based on the background paper by Laseter (1981). Concerns are three-fold: acute effects of contact with oil or its constituents; the carcinogenic potential of oil-derived hydrocarbons in humans; and, linked to the second, the potential for hydrocarbons to be transferred to humans via seafood. A major message of the NRC report was that "the effects of the majority of petroleum components on human health are unknown, and that studies with human subjects are largely lacking". The following specific points come from the NRC (1985) report:

- Acute exposures can take place after accidents, potentially affecting clean-up crews, regulatory and emergency officials, coastal residents, and members of scientific teams investigating the spill. Intake of hydrocarbons can be through inhalation, skin contact, and even accidental ingestion. The volatile aromatic benzene is of particular concern in that it has been established as a human carcinogen; there is clinical evidence that hyperplastic bone marrow leukemia is associated with exposure to benzene, and recent clinical evidence suggests that tank-cleaning personnel chronically exposed to petroleum vapours suffer chromosomal aberrations in bone-marrow cells (Hogstedt *et al.*, 1981). Direct skin contact with oil can lead to irritation and dermal corrosion. At spills, effects on people from exposure to oil and to oil fume include headaches, dizziness, nausea, sensation of inebriation, vomiting, abdominal pains, skin irritation and erythema after contact with oil, but no signs of changes in blood chemistry;
- the report clearly states that "specific hydrocarbon constituents commonly found in natural crudes, refined products, and other related fossil fuel sources can result in the induction of cancer in humans and animals". There is a concern that people may be exposed to carcinogens through the ingestion of hydrocarbon-contaminated seafoods. The hydrocarbons of concern are those in the PAH fraction

boiling above 350 °C, particularly benzo[*a*]pyrene (B(a)P) and closely related pyrenes and anthracenes and anthrenes. Levels in crude oils are small, but are enhanced in used oils (see Chapter 3). PAHs enter marine environments from many sources; discharges of crude oil and petroleum products may contribute about 10 to 20 tons of B(a)P each year, which is less than 5% of all inputs of B(a)P from all sources (Neff, 1979; NRC, 1985). Many marine organisms accumulate PAHs from the water and their food, and can be one source to humans of potentially carcinogenic materials.

- However, with one exception (Iceland), there "is no epidemiological evidence for an increased risk of human cancer from intake of PAH-contaminated food" (Lo and Sandi, 1978; NRC, 1985; IARC, 1983), as concluded in the 1977 GESAMP report. Some information shows that humans can rapidly absorb and excrete hydrocarbons, and that they do not accumulate in humans. The 1985 NRC Report concluded that "there is no demonstrated relationship that chronic exposures through eating petroleum-derived PAH-contaminated seafood are related to the incidence of cancer or other diseases in humans" (Cowell, 1976; GESAMP, 1977; King, 1977). Hence, the concern with contaminated seafoods that there may be a chronic non-occupational exposure through the accumulation and transfer of potentially harmful hydrocarbons from contaminated seafoods appears to be unsupported by evidence. That notwithstanding, there continues to be much use of fish from locally contaminated waters in many countries.

There is considerable concern about benzene as a toxic chemical and as a carcinogen (Infante and White, 1983; Kalf, 1987; Huff *et al.*, 1988; Goldstein *et al.*, 1989). There are suggestions of linkages between occupational exposures to benzene and the onset of leukemia in workers, including refinery workers (Infante and White, 1983). The mechanisms by which benzene works as both a myelotoxin and a carcinogen are being elucidated (Kalf, 1987). The toxicology of benzene as a leukemogenic agent is under increased scrutiny (Goldstein *et al.*, 1989), with the view of conducting more accurate assessments of exposure and risk. This volatile hydrocarbon and many others contact workers at spill sites unless they are protected with specialized respiratory equipment and outer clothing. Such protection seems judicious, considering the growing medical evidence of benzene's potency.

In the wake of the *Exxon Valdez* spill, there is continued concern about the effects on human health of large oil spills, especially coastal ones. Baringa (1989) briefly summarized oil's impacts on health: "Skin contact can cause acute dermatitis. Necropsies on dead sea otters at the *Exxon Valdez* spill revealed severe emphysema – presumably from breathing the fumes of the freshly spilled oil – as well as liver, kidney, intestinal, adrenal, and bone marrow abnormalities, similar to damage previously found in studies of laboratory rats." Reducing risks to humans takes place when the highly toxic components, the PAH compounds, evaporate from crude oil spills within several days, reducing the oil's carcinogenic potential, according to R. Florky, Exxon. There is a need for an independent assessment of the health effects and risks of oil spills. Only the low-molecular-weight PAHs evaporate easily, and concern centres on the chronic carcinogenicity potential of high-molecular-weight PAHs such as benzo[*a*]pyrene (also see Chapter 3).

2.8 Effects on man's use of the sea

2.8.1 Tainting of fish by oil

Five reviews of tainting of fish by oil have appeared since the 1977 GESAMP publication. Stansby (1978) published a brief review with 22 references. Whittle (1978), in a broad review of tainting of fish by chemicals, included a section on tainting by petroleum, with 25 associated references. Connell and Miller's (1981) review of sublethal effects of petroleum hydrocarbons in the aquatic environment included a section on tainting as an effect, with 23 relevant references. Motohiro's paper (1983) deals mainly with the chemistry of oils in relation to tainting and has only 11 references to tainting as a sensory effect. The Canada Oil and Gas Lands Administration commissioned a review of tainting of fisheries resources resulting from oil spills or hydrocarbon development activities (Tidmarsh *et al.*, 1985). The scope of the review was very wide and, in addition to collating reports of tainting incidents, the authors discussed associated topics such as procedures for sensory evaluation of foods, chemical analysis and composition of oils, composition of fish, uptake and release of chemicals into and from fish, and control measures. Consequently there are about 180 text references and a further 150 in a bibliography. However, only about 30 citations relate to taint as a sensory experience, and some of these are multiple reportings of single incidents. The literature on tainting by oil is very sparse, in contrast to literature on biological effects.

Table 2.5 summarizes reports of tainting by acute discharges, mostly tanker accidents; they are split approximately equally between spills of crude oils and spills of refined oils. Most of the spillages resulted from groundings of vessels, so it is not surprising to see that shellfish, both bivalve and crustacean, are often affected. Though this review is directed towards impacts in the marine environment, a report of tainting by diesel oil in fresh water (Mackie *et al.*, 1972) is relevant. These incidents are only a very small proportion of all spillages of oil in the period covered, and there might be many more incidents when fish were, or could have been, tainted but the fact was not reported nor the possibility investigated.

In most cases, even in the event of massive spills, descriptions of tainting are hardly more than anecdotal, and there do not seem to have been any formal laboratory evaluations of taint. For example, the summary report on the *Torrey Canyon* spill (Simpson, 1968) states that fish were tainted, but Smith (1968) makes no mention of it. Chassé (1978), when describing the environmental impact of the *Amoco Cadiz* accident, states that, 3 weeks or so after the spill, fish were 'most often untainted', implying that some were tainted at that time and perhaps a higher proportion at an earlier date. In none of the reports listed in Table 2.5 is there any information on the extent, either in space or duration, of any tainting effect, nor of the intensity of any taint. To some extent the scarcity of reports of tainting can be attributed to a low level of effort looking for the effect, but, even where the observers have specifically examined fish for tainting (for example, Grainger *et al.*, 1980; Mackie *et al.*, 1978; Scarratt, 1980), any effect has been very small.

Tainting of seafoods is perceived by the public, by fishermen, and by regulatory authorities as an inevitable and undesirable consequence of discharges of oils into the marine environment (McIntyre, 1982). Regulatory authorities will usually, and immediately, close fisheries in the area affected by an oil spill or condemn as unfit for human consumption any fish caught in the area. A justification for such actions is the presumption that the product will be tainted and thereby rendered unfit for consumption. However, though tainting has been reported at many spills (Table 2.5), there is no evidence from published reports of large, or even significant, amounts of tainting arising from oil spills.

Table 2.5: ***Tainting of marine organisms by acute incidents***

Materials	Incident	Species affected	Reference
A CRUDE OILS			
Kuwaiti crude (122,000 t) and dispersants	*Torrey Canyon*	Mackerel, sea trout, lobster, carp, plaice	Simpson (1968)
Kuwaiti crude	*Universe Leader*	Periwinkles, scallops, mussels, sea urchins	Golob (1975)
Arabian and Kuwaiti light crude (233,000 t)	*Amoco Cadiz*	Crab, mackerel	Chassé (1978)
Arabian light crude	*Metula*	Mussels, finfish	Golob (1975)
Arabian light crude	*Betelgeuse*	Scallop	Grainger *et al.*, (1980)
Iranian crude	*Northern Gulf*	Clams	Mayo *et al.*, (1974)
Crude oil	Coast of Bahrain	Unspecified fish	Linden (1984)
Crude oil (6,000 t)	*Juliana*	Salmon, mullet, black sea bream	Motohiro and Inoue (1973)
North Sea crude oil (20,000–30,000 t)	Ekofisk blowout	Unspecified fish	Mackie *et al.* (1978)
B REFINED OILS			
Petrol (3,000 t)	*Dona Marika*	Mackerel	Blackman *et al.* (1973)
Gas oil	*Wemeldinge*	Mussels	Kerkhoff (1974)
Diesel oil	*Florida*	Oysters, scallops	Blumer *et al.* (1970)
Diesel oil	Spill into a river	Trout	Mackie *et al.* (1972)
Diesel oil (2,200 t)	*British Mallard*	Herring, flounder, sea trout, salmon, haddock, saithe	Palmork and Wilhelmsen (1974)
Bunker C (1,500,000 gallons)	*Arrow*	Lobster	Wilder (1970)
Bunker C	Maine Maritime Academy Ship	Clams	Shenton (1973)
Bunker C	*Afran Zodiac*	Scallops, clams, sea urchins	Golob (1975)
Bunker C	Barge (STC-101) Chesapeake Bay	Oysters	Roland *et al.* (1977)
Bunker C	*Kurdistan*	Lobster	Scarratt (1980)

Table 2.6 summarizes reports of tainting by chronic discharges of oil and by the activities of the petroleum refining industry; the impacts of oil exploration and exploitation are dealt with in Chapter 5. The paper by Krishnaswami and Kupchanko (1969) concerns tainting in the fresh-water environment, but is relevant to this review.

Table 2.6: ***Tainting of marine organisms by chronic discharges***

Source	Species affected	Reference
Petroleum refinery wastes	Grey mullet, eel, flatfish, quilla, clams	Nitta *et al.* (1965)
Petroleum refinery wastes	Rainbow trout	Krishnaswami and Kupchanko (1969)
Petroleum wastes	Mullet	Connell (1971), (1974), (1978), (1979); Connell *et al.* (1975); Sidhu *et al.* (1970); Shipton *et al.* (1970); Vale *et al.* (1970)
Petroleum refinery wastes	Eels, grey mullet	Ogata and Miyake (1973)
Waste water	Various finfish	Thomas (1973)
Mineral oil	Mussels	Brunies (1971)

A group of Australian workers has described the tainting of mullet (*Mugil cephalus*) from inshore waters which was attributed to petroleum industry wastes discharged into rivers (Connell, 1971, 1974, 1978, 1979; Shipton *et al.*, 1970; Sidhu *et al.*, 1970; Vale *et al.*, 1970). The fish were reported to have a kerosene-like flavour, and gas chromatography of volatiles from tainted samples produced a hydrocarbon profile similar to that of kerosene (Shipton *et al.*, 1970). Several of the components of the chromatogram were identified but the authors do not attribute the taint to any single chemical or group of chemicals.

Brunies (1971) reported that mussels (*Mytilus edulis*) harvested near the East Frisian Islands had a strong diesel-oil flavour which rendered them unfit for consumption. Chemical analysis of edible tissue of the mussels and of the sediment showed the presence of 'mineral oil', but its nature was not determined.

Papers from Japan (Nitta *et al.*, 1965; Ogata and Miyake, 1973) refer to fish being affected by petroleum industry wastes and having an 'evil' or 'offensive' smell, but otherwise they give little information about the sensory evaluation of the taint. The paper by Thomas (1973), which is about procedures for measuring taint in fish, makes only passing reference to tainting by petroleum products in its preamble.

It is possible that chronic tainting of fish, particularly shellfish, is more widespread than these few reports would suggest. Though various national and international agencies monitor the marine environment for chemical and biological evidence of pollution, there does not seem to be any programme of monitoring for possible impacts on the edibility of seafoods. The sparseness of the literature on tainting by chronic discharges might reflect more the level of resources devoted to its investigation than the rarity or importance of the effect.

There is no doubt that fish can be tainted by acute or chronic discharges of oil into the marine environment, but the accounts of incidents provide little information about which components of petroleum are responsible for the effect, or on the quantities required to induce tainting. Nor do they provide information on rates of uptake or release of taints. Fortunately, there are a few studies, listed in Table 2.7, of tainting induced under laboratory conditions.

Table 2.7: ***Tainting of marine organisms under experimental conditions***

Material	Exposure conditions	Species used	Reference
North Sea and Kuwait crude oils	Crude oil mixed in bottom sediment	Plaice and crustaceans	Howgate *et al.* (1977)
Crude oil	Added to tank water	Greenfish	Deshimaru (1971)
Arabian light crude oil	Layered on surface of water	Eels	Ogata and Miyake (1975)
Louisiana crude oil	Layered on surface of tank water	Shrimp, crab	Knieper and Culley (1975)
Ekofisk crude oil	Layered on surface of water	Salmon, saithe	Brandal *et al.* (1976)
Arabian light crude oil	Layered on surface of tank water	Eels	Ogata *et al.* (1977)
Crude oils, distilled oil	Water-soluble fraction	Cod	Ernst *et al.* (1987); Ernst *et al.* (1989b)
Crude oil, gas condensate	Water-soluble fraction	Scallop	Ernst *et al.* (1989a) Carter and Ernst (1989)
Mineral oil	Water-soluble fractions	Eels	Ogata and Ogura (1976)
Gasoline, individual hydrocarbons	Added to tank water	Eels	Ogata and Miyake (1973)
Refinery waste water, oil, oil fractions	Water-soluble fractions and diluted waste water	Eels	Nitta *et al.* (1965)
Diesel oil	Injected into a flow-through system	Trout	Davis *et al.* (1992)

Many of the studies originate from a group of investigators in Japan. Descriptions of the sensory procedures used are sketchy and concentrations in the water phase are not always given, but the Japanese workers showed that a variety of individual hydrocarbons and crude oils tainted fish, some at concentrations down to 0.01 mg/ℓ. Ogata and Miyake (1973) found that gasoline tainted fish, with the most intense flavour being given by a cracked gasoline rich in olefins.

Brandal *et al.* (1976) exposed saithe (*Gadus virens*) and Atlantic salmon (*Salmo salar*) for up to 68 days to weathered Ekofisk crude oil layered on the surface of the tanks. Seawater was flowing through the tanks, but the authors report that oil concentrations in the water were 0.04 to 0.05 mg/ℓ with only a slight tendency for concentrations to decrease during the trial. Taint was detected in salmon after 4 days of exposure and in the saithe after 22 days.

Howgate *et al.* (1977) held plaice (*Pleuronectes platessa*) and crustaceans in tanks containing a sediment contaminated with North Sea crude oil or, in the case of brown shrimp only, topped Kuwait crude oil. A panel of assessors had been trained to rate the intensity of oil taint by tasting plaice flesh spiked with known amounts of crude oil. It was estimated that the minimum concentration of oil that could be reliably detected by this scalar technique was 10 microlitres/kg (equivalent to about 9 mg/kg). All species exposed to the North Sea crude were strongly tainted after 1 day of exposure. The brown shrimp (*Crangon crangon*) exposed to the topped Kuwait oil was tainted, but only just above the minimum detection level. It seems that loss of volatiles during topping had removed most of the tainting compounds.

Ernst *et al.* (1987) exposed cod (*Gadus morhua*) to water-soluble fractions of 3 crude oils – Brent, Amauligak, and Hibernia – and of a base oil. The base oil was a middle distillate consisting predominantly of cyclic and branched alkanes; n-alkanes and lower-boiling-point aromatics were not present. The experimental procedures for exposing the fish to the contaminant and for evaluating the exposed fish for taint followed the ECETOC guidelines (European Chemical Industries Environmental and Toxicology Centre, 1987). The authors conclude that the minimum concentrations of water-soluble compounds (based on hydrocarbon contents determined by GLC) that resulted in tainting after 24 hours of exposure were, for the Brent, Amauligak, and Hibernia crudes, 0.5 mg/ℓ, between 0.3 and 0.8 mg/ℓ, and between 0.5 and 2.0 mg/ℓ respectively, and between 0.7 and 1.2 mg/ℓ for the base oil. It is interesting to note that the tainting threshold for the base oil is not different from that of the crudes as a group, in spite of the fact that it was free of the lower-boiling-point aromatics. The minimum tainting concentration for exposure to water-soluble fractions of the crude oils for 7 days was around 0.2 mg/ℓ. Taint was depurated from the fish in 1 to 4 days, depending on the concentration of the original exposure.

In further trials, scallops (*Plactopecten magellanicus*) were exposed to water-soluble fractions of Scotian Shelf gas condensate (Ernst *et al.* 1989a) and of Ninian crude oil (Carter and Ernst, 1989). The condensate was rich in aromatic hydrocarbons, with benzene, toluene and xylenes predominating. Taint was detected in scallops exposed for 24 hours to 3.8 mg/ℓ of water-soluble hydrocarbons of the condensate, but not when they were exposed to 0.8 mg/ℓ. However, scallops exposed to 0.8 mg/ℓ for 96 hours were tainted. The tainting threshold of the Ninian crude was reported to be 0.5 mg/ℓ of water-soluble hydrocarbons. Again, depuration of taint from the scallops took 1 to 4 days, depending on the original exposure conditions.

Davis *et al.* (1992) exposed rainbow trout (*Oncorhynchus mykiss*) in a flow-through dosing system to marine diesel injected into the water flow and found the tainting threshold to be 0.076 mg/ℓ with 95% confidence limits of 0.040 and 0.14 mg/ℓ.

The amount of data from experimental studies and, less so, from observations made of acute and chronic discharges is small, but some conclusions can be drawn about factors governing tainting by oils. The conclusions probably can be used in modelling studies of the impact of discharges of oil on the activities of commercial fisheries, and could guide further research.

Experimental studies show that minimum total concentrations of oil components in water that will induce taint in exposed fish are in the range 0.01 to 1.0 mg/ℓ. The wide range possibly reflects differences among experimenters in measuring and expressing effective concentrations and in evaluating taint as an effect as much as it reflects differences among oils in their intrinsic potential to induce taint. Tainting concentrations are in the range below that causing acute effects in adult invertebrates and fish, but similar to that causing acute and sublethal effects in their embryonic and larval life stages.

Water-soluble fractions are enriched in the components that cause tainting compared with the original oil, possibly by more than 100-fold. Deshimaru's experiments (1971) showed that it required 50 mg/ℓ of crude oil to taint fish at 5 days' exposure. Ernst *et al.* (1987) found that tainted cod contained around 0.6 mg/kg of water soluble hydrocarbons whereas Howgate *et al.* (1977) considered that the minimum detectable amount of crude oil added to plaice flesh was around 9 mg/kg. Motohiro and Iseya (1976) reported that the minimum amount of Arabian crude oil detectable in scallop meat was 100 mg/kg.

So far, there is little information about which components of oil are responsible for its tainting effect. Experimental studies show that alkylbenzenes are capable of tainting fish, but this is not the only class of tainters in crude and refined oils. The Canadian trials show little difference in tainting potential among the water-soluble fractions from oils ranging from those that are rich in low-boiling-point aromatics to those that are free of this fraction.

Fish can be tainted very rapidly on exposure – within a few hours at concentrations above 1 mg/ℓ hydrocarbons in the ambient water. Information on depuration rates is conflicting. In the Canadian trials – which comprise the only quantitative data available on depuration of oily taints – tainted cod and scallop lost their taint within 1 to 4 days, depending on the original exposure conditions. However, both published and anecdotal accounts of the effects of spillages of fuel oils report that fish were still tainted days or weeks after the incident.

2.8.2 Other considerations

2.8.2.1 Contamination of fishing gear and aquaculture facilities

Floating and sunken oil has an impact on fishing and aquaculture activities by fouling gear. Apart from making the gear messy and awkward to handle, contact with fouled gear can contaminate the produce and render it unsuitable as food. Free-swimming fish can detect oil and might be in a position to avoid it, but caged fish and shellfish and cultured molluscs cannot avoid an affected area and thereby stand a high risk of being contaminated or tainted by soluble or dispersed oil fractions following a spill. Farmed marine fish have high unit value, and stocking densities in cages are high, so the commercial consequences of even a small spill in areas with high densities of aquaculture activities could be very large. Land-based coastal aquaculture systems, including hatcheries and rearing units, usually require continuous supplies of clean seawater for their operations, as do cleansing stations for shellfish and holding tanks. The plant and facilities at such sites could be fouled and damaged by floating oil and the edible flesh of produce could be tainted by dispersed oil and soluble components.

Moller *et al.* (1989) have summarized and discussed the impact of oil on fisheries and aquaculture, based on nearly 60 incidents over the 10 years to 1989. They give details of 30 incidents which occurred in the Far East, including the costs of clean-up and damage settlements. Table 2.8, taken from this paper, summarizes the authors' assessment of the sensitivity of fishing gear and aquaculture activities to damage by drifting oil. Eng *et al.* (1989) have also referred to the possible impacts of oil pollution on aquaculture in South-east Asia. White and Nichols (1979) have discussed the impacts of oil spills in the context of the U.K. mariculture industry. The study of the costs of the *Amoco Cadiz* spill (U.S. Department of Commerce, 1983) has a detailed description of the impact of the spill on the local shellfish industry.

Table 2.8: ***Sensitivity of fishing gear and aquaculture to damage by stranded or drifting oil***

A Fishing gear

Type of gear	Sensitivity
Brush traps, staked traps, baskets, fences	High
Lift nets, cast nets	Moderate
Gill nets, drift nets, tangle nets, trammel nets, push nets	Moderate
Purse seines, ring nets, beach seines	Moderate/low
Handlines, longlines, drift lines	Low
Trawls, dredges, sweep nets	Low

B Aquaculture

Cultivation method	Species	Sensitivity
Intertidal zone	molluscs	High
Ropework suspended at sea surface by floats or poles	sea laver, sea mustard	High
Onshore tanks	fish, crustacea, molluscs, seaweed	Moderate
Sea impoundments and ponds	prawns, fish	Moderate/low
Vertical ropes/cages supported below sea by floats	kelp, mussel, scallops, oyster, sea squirt, yellowtail, sea bream, bass, salmon	Moderate/low
Seabed	sea cucumber, abalone, arkshell	Low
Seabed enclosures	crab, lobster	Low

Source: modified from Moller *et al.* (1989)

2.8.2.2 Impact on tourism

The fouling of beaches, coastlines and visitor facilities has a profound effect on tourism in areas affected by, or even believed to be affected by, oil spills. The impact might last years after the original clean-up because oil which might have infiltrated beaches can be brought to the surface by later storm action. The U.S. Department of Commerce's study (1983) of the costs of the *Amoco Cadiz* spill describes costs incurred by the local tourist industry. Coastal areas and inshore waters throughout the world are often important tourist centres, or have the potential to be so, in part because of the opportunities for informal or intensive study of natural history. Some areas have been declared as land or marine nature reserves or national parks. Any damage to these areas above or below the water line, or any impoverishment of the flora and fauna, by oil pollution will reduce their tourist value as well as their biological value.

2.8.2.3 Impact on industrial uses

Some power stations and industrial processes use seawater for cooling or for processing purposes, and the presence of floating or dispersed oil can interfere with this activity (Nichols and Parker, 1989; Parker *et al.*, 1987). ACOPS (1990) describes a power station in Algiers having to shut down following a spill of bitumen in the harbour. Desalination plants producing drinking water, such as those in the Arabian/Persian Gulf, are particularly susceptible to interference from oil pollution (Kruth *et al.*, 1987).

2.8.2.4 Costs of oil pollution

The social and economic costs of oil pollution have been reviewed by the EPA/Institute on Man and Science (1974) and the OECD (1982a, b). The U.S. Department of Commerce (1983) has reported in detail on the costs of the *Amoco Cadiz* spill. White and Nichols (1981) tabulate the costs and claims resulting from some oil spills from tankers. The Advisory Committee on Pollution of the Sea (ACOPS, 1990) lists incidents of pollution of the marine environment by oil (and other pollutants) and summarizes the activities of the various governmental and non-governmental bodies concerned with monitoring and dealing with oil pollution. It also refers to the amounts of monies paid as damages by the various compensation funds.

ACOPS (1990) has a brief description of the *Exxon Valdez* spill and refers to an estimate of US$ 1,280 million as the costs of clean-up by the end of July 1989 and continuing costs of US$ 40 million a week. By August 1991, the costs of clean-up of this spill had exceeded US$ 2,300 million (Exxon Corporation, pers. comm.).

2.9 Summary, conclusions and recommendations

2.9.1 Summary and conclusions

Petroleum and its products are complex materials that undergo many compositional changes in the environment. They are leading contaminants, in prevalence and quantity, in the ocean, due to their global production, transport, use, disposal and spillages.

A quantity of 2.35 million tonnes of oil per year enter the marine environment from all sources. At least 15% comes from natural oil seeps. Anthropogenic sources include chronic discharges from storage facilities and refineries, from tankers and other shipping along major routes, and from accidental events such as spills and pipeline ruptures. Sources also include river-borne discharges, diffuse discharges from industrialized municipal areas, offshore oil production, and the atmosphere. The sources vary in importance geographically but the primary inputs are generally from land-based sources (refineries, municipal wastes, urban run-off). Recent wars have resulted in major oil inputs (i.e. Arabian/Persian Gulf). Although oil spills and tar are highly visible, inputs of oil from land-based sources are of increasing concern, especially near urban centres.

Due to measures required by international conventions on prevention of oil pollution, the input of oil into the sea has decreased during the past three decades. In this regard the entry into force of MARPOL 73/78, Annex I, in 1983 has had a substantial positive impact in reducing the amount of oil that enters the sea from transportation activities, inputs decreasing from 1.47 million tonnes in 1981 to 0.54 million tonnes in 1989 (IMO, 1990). However, the input has varied by more than a factor of 10 from year to year, with 1979 (IXTOC blowout), 1983 to 1988 (Iran–Iraq war), and 1991 (the Gulf conflict) showing extra inputs which were many times the average of intervening years.

Total floating tar in shipping lanes and their associated surface currents observed in 1985 was one-fourth or less of that observed in 1971–2, based on measurements in the Sargasso and Mediterranean Seas. Tanker accidents contribute 5% of oil input, based on 1990 estimates, but volumes spilled annually from ships are highly variable, making trends difficult to predict accurately. Tar continues to impair amenity beaches and coastlines in many parts of the world.

Physical, chemical and biological fates of hydrocarbons from spilled oils are better understood in qualitative terms in 1990 compared to 20 years ago. Many new methods for analysis of hydrocarbons in seawater, sediments and tissues have been developed over the past 15 years. They particularly have addressed transformation (photo-oxidation, metabolic) by-products of specific hydrocarbons, and other basic characteristics of oils in the environment are better understood. Recent research on the polar fractions of dissolved oil residues has shown the presence of large numbers of oxygenated derivatives of aromatic hydrocarbons; their concentrations often exceed those of each parent hydrocarbon, and their toxicity to marine organisms is largely unknown.

Quantitative modelling is most advanced in the areas of transport of slicks, evaporative weathering and uptake in selected species. Many new biochemical, physiological and toxicological techniques have been developed and applied in research and monitoring.

Reproductive, developmental and behavioural processes are very sensitive to exposure to hydrocarbons. Generally, young life stages are more sensitive than adults, and many juvenile and adult crustaceans and echinoderms are more sensitive than juvenile and adult fish. It is well established that different oil types vary in their toxicities, and that acute toxicity is largely due to components of the water-soluble fractions and dependent upon exact exposure conditions and time. Chronic sublethal effects caused by petroleum hydrocarbons spilled or discharged in low-energy, shallow coastal waters remain a valid concern.

Marine wildlife (turtles, seabirds, mammals) are often the most conspicuous victims of oil spills. Diving and surface-dwelling populations of seabirds, and sea otters and polar bears in particular, are now known to be vulnerable and sensitive to oiling. Documentation from the field on the effects of oiling on other mammals, especially cetaceans, is scarce.

Short-term impacts of spills are well understood. Except for wildlife which frequents both coastal and open seas, biological concerns largely centre on shallow near-shore areas and coastlines. There is some evidence at spill sites of long-term effects on populations and communities. Some habitats (e.g. low-energy marshes and mangroves) can require decades to return to their pre-spill condition of population numbers, species diversity and habitat quality, while others recover relatively quickly (months to one or two years). Such recovery depends upon degree of oiling, oceanographic regime, and type of habitat and species affected.

Oil spills have low or negligible impacts on fish populations. Significant impacts on local populations generally occur only in shallow waters with poor circulation. In such locations, only small proportions of total regional populations are usually affected.

Tropical coastal ecosystems such as mangroves and coral reefs, as well as seagrasses in all locations, are particularly vulnerable and sensitive; damaged coastlines may prematurely erode and important habitats may be lost. Little is known about the time-scales and the recovery patterns and processes of such ecosystems after acute or chronic oiling.

Although large and small spills often result in closure of fisheries by regulatory authorities, there is little or no evidence of tainting of fish or shellfish, even by major spills.

2.9.2 Recommendations

Controls of discharges of oil from sources other than shipping (e.g. land-based sources, offshore activities) should be strengthened, where necessary, within appropriate national and international systems. More information is required on the characterization of land-based inputs of oils and should be systematically collected by national governments.

More efforts should be made by the appropriate international, industrial and inter-governmental bodies in assisting governments in effectively implementing existing oil pollution conventions.

To diminish the impacts of oil spills, governments should be urged to ratify the recently adopted International Convention on Oil Pollution Preparedness, Response and Co-operation, 1990, requiring the establishment of oil pollution emergency plans on ships and offshore installations, and at ports and oil handling facilities, together with national and regional contingency plans as appropriate.

Global and regional monitoring programmes need to be continued in all marine environments to describe concentrations and distributions of hydrocarbons at the sea surface, and in sediments and biota, and to establish and verify trends.

A selection of important and representative areas worldwide where spills are most likely to occur should be the focus of appropriate pre-spill research and monitoring studies. Studies at experimental spill sites and at spills of opportunity should be encouraged, for both scientific purposes and the testing of response equipment and methods.

Research is needed on the fate and effects of phototransformation by-products of oils and of the nitrogen-, oxygen- and sulphur-substituted PAHs found in crude oils. If results indicate reasons for concern, methods should be developed for monitoring purposes.

Intertidal and sublittoral communities are at most risk from oil spills, and there is limited information on their recovery rates. Sub-acute toxicity studies are required to define dose–response relationships for selected benthic organisms exposed to representative oils.

Standardized and validated procedures for measuring taint in fish should be developed.

Further research should be conducted to define minimum concentrations of oils that will induce taint in seafoods, so that criteria for closures of fisheries are better defined. Rates of uptake and depuration of taint, and the effects of dispersants on the tainting process, should also be investigated.

Chapter 3 Used lubricating oils

3.1 Introduction

Used engine oil contains high levels of combustion-derived polycyclic aromatic hydrocarbons and heavy metals such as lead. It is increasingly becoming a contaminant of concern because of the relatively large volumes entering the aquatic environment through sewers, urban run-off, highway run-off and other sources. A major cause of the concern about used engine oil stems from linkages between combustion PAHs and carcinogenesis, for which there is presently some circumstantial evidence in fish in highly polluted urban-associated waters (Malins *et al.*, 1987). The presence in used engine oil of relatively high concentrations of lead is also of interest, but this problem should diminish with the general phasing out of leaded gasoline in most countries. Various additives, including detergents, corrosion inhibitors, antioxidants and others, are found commonly in engine oils. Furthermore, waste oils are often contaminated with chlorinated solvents and polychlorinated biphenyls (PCBs); this is thought to be primarily related to poor segregation of used oils at source during collection (Franklin Associates, 1985).

The PAHs found in used engine oil principally originate from incomplete combustion and extraction of unburned fuel. Mutagenicity/carcinogenicity studies carried out with combustion by-products of diesel and petrol are of direct relevance when evaluating the carcinogenic potential of used oils. As noted by Schoket *et al.* (1989), studies on materials emitted from diesel and petrol engines have shown them to be mutagenic in bacterial assays and to be carcinogenic when applied to the skin of mice, when inhaled by rats and when implanted in the lungs of rats. Fractionation of exhaust condensates has implicated PAHs containing more than three fused benzene rings as accounting for as much as 91% of their carcinogenic activity. There also appears to be little contribution from the nitro-PAH fraction of the condensates, nor do the non-carcinogenic fractions show significant enhancing or inhibiting effects.

Used engine lubricating oils also contain PAHs and have demonstrable carcinogenic activity on mouse skin (IARC, 1984). As with exhaust condensates, a large proportion of the activity is attributable to PAHs with more than three rings (Grimmer *et al.*, 1982).

3.2 Sources and inputs

3.2.1 Production and consumption of lubricating oils

The production and consumption of lubricating oils have been recently reviewed by Vazquez-Duhalt (1989). The world production of lubricating oils is almost 1–2% of refined crude oil, and world consumption (excluding Eastern Europe and China) was 23.8 million tonnes in 1980. A good contemporary estimate of world consumption is 35–38 million tonnes of lubricating oil yearly. In Europe, the annual consumption of crankcase oil per car was 21.2 kg in 1975 and 12.5 kg in 1985. This decrease can be considered a consequence of the progress in motor technology and oil technology (refining and additives), which has lengthened the time between oil changes and decreased leakage and losses during combustion.

3.2.2 Production, input and fate of used lubricating oils

The production and fate of used oil has also been reviewed by Vazquez-Duhalt (1989). The production of used crankcase oil is estimated to be between 65% and 68% of the sales of new motor oil, with one-third of the oil being consumed by motors and lost. In the case of industrial oils, the production of used oil represents 30–57% of consumption.

The losses of oil when a motor is running comprise between 0.5 and 2.0 g hp^{-1} h^{-1}, which is equivalent to 1.5 or 2.5% of fuel consumption. A car with a four-cylinder engine of between 1 and 1.5 litres capacity loses from 0.2 to 0.3 litre of lubricating oil for each 1,000 km of roadway. These losses are not always so small, a level of 0.5 to 1.0 litre per 1,000 km being more common. In diesel engines with 9 or 10 cylinders, oil losses are between 0.5 and 23 g h^{-1}, according to loading and rotation speed.

The production of waste crankcase oil in the U.S.A. was estimated at more than 9 million tonnes in 1980. The world production of used motor oil can be estimated at almost 25–28 million tonnes in addition to 12–15 million tonnes lost yearly during engine operations.

At present, used motor oil has many fates: as auxiliary fuel; for re-refining; as road oil or a component of asphalt; disposed of in landfill; and unknown fates (Monenco Consultants, 1989; Vazquez-Duhalt, 1989). For example, in the U.S.A. the estimate is as follows: 31.7–50% of used motor oil is utilized as fuel; 11.0–16.7% is incorporated into asphalt for roads; 3.3–9.2% is re-refined; and 23.0-30.0% is directly disposed of into the environment. In developing countries, its loss to the environment remains an important environmental problem (Osibanjo, pers. comm.).

How much used engine oil enters the oceans? The world production and loss of used motor oil has been estimated to be in the range of 40 million tonnes per annum (Vazquez-Duhalt, 1989). In the meantime it has been estimated that input of oil from land-based sources worldwide is in the range of approx. 1,175,000 tonnes per annum (see Section 2.3.2). If it is assumed that all of the petroleum hydrocarbons in land-based sources are of engine-oil origin, this results in an approximate input to the oceans of 4.4% of the total production of used oil. This is probably a major overestimate, but is a useful figure for estimating 'maximal' inputs of combustion-associated hydrocarbons. It should be noted that a difficult problem in considering land-based inputs is in isolating combustion inputs from used oil inputs *per se*, but from a toxicological viewpoint the contaminants of concern in used engine oil are also primarily combustion by-products.

Of special interest are estimates of used oils for enclosed seas such as the Mediterranean and Baltic. UNEP (1989c) estimated the total year's production in the Mediterranean area to be in the range of 370,000 tonnes, which would translate, according to the above assumption of 4.4% of total production, into a maximum input of approximately 16,280 tonnes annually into the Mediterranean Sea. However, it is not known what proportion of the 370,000 tonnes produced in Mediterranean (or other) countries is re-refined or burnt. It is also not known what proportion of the estimated 21 to 60 thousand tonnes of petroleum hydrocarbons which enter the Baltic Sea annually is of engine-oil origin. Given that approximately 50% of total petroleum hydrocarbon inputs into the Baltic are from rivers and domestic sewage (Table 2.2), the inputs of used engine oil could be relatively high. The same situation may exist for other enclosed waters, emphasizing that inputs of hydrocarbons from land-based sources into enclosed seas need to be addressed.

3.2.3 Production and fate of industrial oils

The dominant lubricating oils entering the aquatic environment are used crankcase and engine oils. However, a number of industries, and especially the metal-working and transport industries, use a variety of cutting, lubricating, hydraulic and other industrial oils which can be expected to enter the environment at varying levels. Total use of oils in the metal-working industry in Sweden, for which information is available, is 1,000 tonnes per annum for cutting oils, 55,000 tonnes per annum for lubricating oils and 35,000 tonnes per annum for hydraulic oils (Landner, pers. comm.). In addition, oils containing degreasing and defoaming agents are likely contaminants in some coastal and inland waters. For instance, in Sweden about 20,000 tonnes of degreasing agents and 5,000 tonnes of defoaming agents are used annually. In contrast to crankcase and engine oils, inputs of industrial oils can generally be expected to be low on a worldwide scale, but more information is needed on amounts entering the oceans, especially enclosed seas.

3.3 Chemical composition and physical properties

Components of typical used automotive oils with respect to physical properties and concentrations of metals and organics are described in Table 3.1 while the concentrations of potentially hazardous constituents in used oils are given in Table 3.2. This information is based on U.S. data collected between 1979 and 1983. Table 3.3 provides a typical formulation of gasoline engine oil. It should be noted that, with the movement away from leaded gasoline in some countries, lead has become a minor contaminant in some used engine oils. Also, it is likely that chlorinated solvents are introduced into used oil through improper segregation during transportation and storage.

There is little information available on the concentrations of specific polycyclic aromatic hydrocarbons and chlorinated dibenzodioxins and furans in used motor oils. Table 3.4 provides a list of 'total' levels of various types of aromatics, both parent and alkylated compounds, in a sample of heavily used oil. Similarly, extremely toxic congeners of dioxins and furans are found at trace levels in combustion mixtures and can be expected to occur in used oils. The sample of oil analysed for aromatics was also analysed for dioxins and furans, and the results are given in Table 3.5 (analysis carried out by Seakem Oceanography for J.F. Payne, pers. comm.).

With regard to industrial oils, Tables 3.6 to 3.10 provide a perspective on the main components found in various oils, including grinding oils (Table 3.6), circulation oils (Table 3.7), cutting oils (Table 3.8), hydraulic oils (Table 3.9) and rolling oils (Table 3.10).

3.4 Physical, chemical and biological methods

The methods used for studying used engine oils are essentially similar to those used for petroleum and combustion sources of hydrocarbons and metals (e.g. see NRC, 1985).

3.4.1 Mutagenicity and other short-term tests

Payne *et al.* (1978) demonstrated that aromatic-hydrocarbon-enriched extracts of used but not virgin crankcase oils were mutagenic to the bacterium *Salmonella typhimurium*. Similar

Table 3.1: ***Characterization of used automotive oil***

Parameter	Measured value
Gravity API at 16 °C	24.0
Viscosity (cm^2/s)	0.99
Pour point (°C)	37
Flashpoint (°C)	140
Heating value (kJ/kg)	38,000
BS&W*, Vol. (%)	11.0
Sulphur (wt %)	0.43
Ash (wt %)	1.01
Arsenic (ppm)	5
Barium (ppm)	48
Cadmium (ppm)	3
Calcium (ppm)	1,850
Chromium (ppm)	7
Copper (ppm)	177
Iron (ppm)	1,025
Lead (ppm)	240
Magnesium (ppm)	559
Phosphorus (ppm)	1,250
Silver (ppm)	1
Tin (ppm)	58
Zinc (ppm)	480
Chlorinated solvents (ppm)	
dichlorodifluoromethane	20
trichlorotrifluoroethane	160
1,1,1-trichloroethane	200
trichloroethylene	100
tetrachloroethylene	105
Total chlorine (ppm)	1,600
Other organics (ppm)	
benzene	20
toluene	380
xylene	550
benzo[*a*]anthracene	12
benzo[*a*]pyrene	10
naphthalene	330
PCBs	5

* BS&W – bottom sediment and water

Sources: Franklin Associates Ltd. (1985); Rudolph (1978); PEDCo-Environmental Inc. (1984)

Table 3.2: ***Concentration of potentially hazardous constituents in used oils****

Parameter	Number of samples analysed	Samples with detected contaminants		Mean concentration** (ppm)	Median concentration*** (ppm)	Concentration at 75th percentile*** (ppm)	Concentration at 90th percentile*** (ppm)
		No.	%				
Metals							
Arsenic	537	135	25	17	5	5	18
Barium	752	675	89	132	48	120	251
Cadmium	744	271	36	3.1	3	8	10
Chromium	756	592	78	28	6.5	12	35
Lead	835	760	91	665	240	740	1,200
Zinc	810	799	98	580	480	872	1,130
Chlorinated solvents							
Dichlorodifluoromethane	87	51	58	373	20	160	640
Trichlorotrifluoroethane	28	17	60	62,900	160	1,300	100,000
1,1,1-Trichloroethane	616	388	62	2,800	200	1,300	3,500
Trichloroethylene	608	259	42	1,390	100	200	800
Tetrachloroethylene	599	352	58	1,420	106	600	1,600
Total chlorine	590	568	96	5,000	1,600	4,000	9,500
Other organics							
Benzene	236	118	50	961	20	110	300
Toluene	242	198	81	2,200	380	1,400	4,500
Xylenes	235	194	82	3,390	550	1,400	3,280
Benzo[*a*]anthracene	27	20	74	71	12	30	40
Benzo[*a*]pyrene	65	38	58	25	10	12	16
Naphthalene	25	25	100	475	330	560	800
PCBs	753	142	19	109	5	15	50

* Results determined from the analyses of 1071 samples of used oil.

** Calculated for detected concentrations only.

*** For the purposes of determining median and percentile concentrations, undetected levels were assumed to be equal to the detection limit.

Source: Franklin Associates Ltd. (1985)

Table 3.3: ***Typical formulation of gasoline engine oil***

Ingredient	Percent of volume
Base oil (solvent 150 neutral)	86
Detergent inhibitor (ZDDP, zinc dialkyl dithiophosphate)	1
Detergent (barium and calcium sulphonates)	4
Multifunctional additive (dispersant, pour-depressant, viscosity improver, poly(methyl methacrylates))	4
Viscosity improver (polyisobutylene)	5

Source: Weinstein (1974) in Monenco Consultants (1989)

Table 3.4: ***Concentration of polycyclic aromatic hydrocarbons in a typical used oil***

Compound	Concentration (μg/g, ppm
LPAHs (lower-molecular-weight polycyclic aromatic hydrocarbons)	
Naphthalene	52.0
Acenaphthalene	1.5
Acenaphthene	3.7
Fluorene	67.0
Phenanthrene	200.0
Anthracene	22.0
HPAHs (higher-molecular-weight polycyclic aromatic hydrocarbons)	
Fluoranthene	55.0
Pyrene	120.0
Benzo[*a*]anthracene	38.0
Chrysene	45.0
Benzofluoranthenes	46.0
Benzo[*e*]pyrene	32.0
Benzo[*a*]pyrene	15.0
Perylene	1.1
Indeno[1,2,3-*cd*]pyrene	14.0
Dibenz[*a,h*]anthracene	1.5
Benzo[*ghi*]perylene	72.0
Dibenzothiophene	1.9
Naphthalenes	
C_1 naphthalene	31.0
C_2 naphthalene	60.0
C_3 naphthalene	80.0
C_4 naphthalene	52.0
Phenanthrenes	
C_1 phenanthrene	300.0
C_2 phenanthrene	300.0
C_3 phenanthrene	140.0
C_4 phenanthrene	35.0

Source: J. F. Payne, 1990, pers. comm.

Table 3.5: ***Concentrations of polychlorinated dibenzodioxins and dibenzofurans in a sample of used engine oil***

Dioxins*	Concentration (pg/g)	(SDL)**	Furans***	Concentration (pg/g)	(SDL)**
T_4CCD: total	310	10	T_4CDF: total	660	3.2
2,3,7,8	NDR	10	2,3,7,8	370	3.2
P_5CDD: total	220	12	P_5CDF: total	170	8.1
1,2,3,7,8	80	12	1,2,2,7,8	79	8.1
			2,3,4,7,8	59	8.1
H_6CDD: total	440	18	H_6CDF: total	610	15
1,2,3,4,7,8	87	15	1,2,3,4,7,8	170	15
1,2,3,6,7,8	100	18	1,2,3,6,7,8	160	15
1,2,3,7,8,9	160	18	2,3,4,6,7,8	140	15
			1,2,3,7,8,9	81	15
H_7CDD: total	210	19	H_7CDF: total	320	14
1,2,3,4,6,7,8	0.5	0.2	1,2,3,4,6,7,8	190	14
			1,2,3,4,7,8,9	100	14
O_8CDD	2.3	0.2	O_8CDF	210	18

* T_4CDD = tetrachlorodibenzodioxins, P_5CDD = pentachlorodibenzodioxins, H_6CDD = hexachlorodibenzodioxins, H_7CDD = heptachlorodibenzodioxins, O_8CDD = octachlorodibenzodioxin

** SDL = sample detection limit

***T_4CDF = tetrachlorodibenzofurans, P_5CDF = pentachlorodibenzofurans, H_6CDF = hexachlorodibenzofurans, H_7CDF = heptachlorodibenzofurans, O_8CDF = octachlorodibenzofuran

Source: J.F. Payne, 1990, pers. comm.

Table 3.6: ***Main components found in grinding oils in an industrial survey in Sweden***

Component	Content in a 'typical' grinding oil (%)	Volume containing the component (m^3)*
Basic oil	10-100	320
Chlorinated paraffins	1-10	320
Aliphatic fatty acids	1-10	180
Alkenylsuccinic acid and alkyl orthophosphate	0.1-1	140
Sulphur	0.1-1	140
Petroleum sulphonates of alkali metals	10-100	180
Zinc dithiophosphate	0.1-1	140
Organic sulphur compounds	0.1-1	140
Silicone oil	0-0.1	140

* total amount 625 tonnes

Source: Wetterling (1984)

Table 3.7: ***Main components found in circulation oils in an industrial survey in Sweden***

Component	Content in a 'typical' oil (%)	Volume containing the component (m^3)*
Basic oil	10–100	620
2,6-Di-tertiary-butyl-4-methylphenol	0.1–1	380
Poly(alkyl methacrylate)	0–0.1	230
p,p'-Dioctyldiphenylamine	0–0.1	230
Benzotriazole derivatives	0–0.1	230
Monoester of substituted succinic acids	0–0.1	230
Polysiloxane	0–0.1	85
Zinc dithiophosphate	0.1–1	60

* total amount 630 tonnes

Source: Wetterling (1984)

Table 3.8: ***Main components found in cutting oils in an industrial survey in Sweden***

Component	Content in a 'typical' cutting oil (%)	Volume containing the component (m^3)*
Basic oil	10–100	420
Deionized water	1–10	200
Petroleum sulphonates of alkali metals	1–10	200
Chlorinated cresol	up to 3	190
Alkylolamide derivatives of fatty acids	1–10	180
Glycol ethers	1–10	180
Chlorinated paraffins (C_9 to C_{11})	10–100	130
Fatty alcohols	0.1–1	110
Tertiary alkylolamine	0.1–1	85

* total amount 790 tonnes

Source: Wetterling (1984)

Table 3.9: ***Main components found in hydraulic oils in an industrial survey in Sweden***

Component	Content in a 'typical' hydraulic oil (%)	Volume containing the component (m^3)*
Basic oil	10–100	1,120
Zinc alkyldithiophosphate	0.1–1	800
Silicone oil	0–0.1	660
Alkyl succinate	0–0.1	520
Poly(methyl methacrylate)	0.1–1	670
2,6-Di-tertiary-butyl-4-methylphenol	0.1–1	210
Aryl phosphates except *ortho*-cresyl phosphate	0.1–1	190
Alkylolaminobenzotriazole	0–0.1	190
Triphenyl phosphothionate	0–0.1	190
High-molecular-weight alcohols	0–0.1	190

* total amount not given

Source: Wetterling (1984)

Table 3.10: ***Main components found in rolling oils in an industrial survey in Sweden***

Component	Content in a 'typical' rolling oil (%)	Volume containing the component (m^3)*
Basic oil	10–100	680
Lauric acid	1–10	550
Paraffin fractions	10–100	290
Saponified alkylolamines of distilled animal fatty acids	10–100	70
Mixture of alkylolamines	0.1–1	70
Corrosion inhibitors based on organic esters	1–10	50
2,6-Di-tertiary-butylphenol	0.1–1	50

* total amount not given

Source: Wetterling (1984)

results were subsequently obtained in other studies. DMSO extracts of a pooled sample of 15 commercially available IOW-40 gasoline-engine oils and a pooled sample of used oil (from the 15 component oils) were tested for mutagenicity in *S. typhimurium*. The extract from the used sample only was mutagenic in strains TA 1537, TA 1538, TA 95 and TA 100 in the presence and in the absence of S9; the extract of unused oil showed no mutagenic activity (Schreiner and Mackerer, 1982). Wang *et al.* (1978) reported that an unused oil was not mutagenic but that used oil (obtained from four different cars) was mutagenic to bacteria. Peake and Parker (1980) also reported that used and, to some extent, unused samples of oil were mutagenic.

3.4.2 DNA adducts

The DNA-binding potential of complex mixtures of chemicals that have carcinogenic activity is amenable to study by the highly sensitive ^{31}P post-labelling technique. The method is particularly sensitive when applied to the detection of aromatic DNA adducts such as those formed by PAHs. Aromatic hydrocarbon adducts were observed in DNA isolated from the skin of mice tested with a petrol-engine lubricating oil (Schoket *et al.*, 1989). However, it is of interest that significant amounts of adducts were not observed in mice treated similarly with a diesel-engine lubricating oil.

3.5 Fate of used lubricating oils in marine ecosystems

The environmental fate of used oils has not been evaluated to any extent, but general studies on the fate of various aliphatic and aromatic hydrocarbons, such as those found in petroleum mixtures, and of heavy metals are relevant (e.g. NRC, 1985). Some special interest may be accorded to contaminated sediments, especially any sediments heavily contaminated with spilled oil, where the presence of relatively high levels of metals (such as lead) and various additives may influence the rate of biotransformation of individual compounds.

3.6 Biological effects

3.6.1 Toxic effects

The effects of waste oil on the survival and reproduction of the American flagfish have been studied in detail (Hedtke and Puglisi, 1980). Egg production was impaired by exposure to 3380 $\mu\ell/\ell$ of the water-soluble fraction (WSF). The 30-day LC_{50} for larvae exposed as embryos was greater than 8100 $\mu\ell/\ell$ and that for larvae unexposed as embryos was 755 $\mu\ell/\ell$. The maximum acceptable concentration of toxicant for the water-soluble fraction of used crankcase oil was estimated to fall between 325 and 930 $\mu\ell/\ell$, approx. 0.1%.

Water extracts of a No. 2 fuel oil and a used crankcase oil were examined for their effects on algal communities in experiments lasting several weeks under nearly natural conditions (Bott and Rogenmuser, 1978). Exposure to the extract from used crankcase oil depressed chlorophyll concentrations (biomass), but microscopic observations and pigment ratios indicated that changes in dominant algal types were less dramatic than those exposed to water extracts of No. 2 fuel oil.

Bate and Crafford (1985) studied photosynthetic rates in five phytoplankton species treated with water-soluble extracts of used lubricating oil. Evolution of oxygen and assimilation of carbon were inhibited by the relatively high concentration of aromatics determined in reaction vessels.

Acute toxicity problems should be negligible, given that inputs of used engine oil into the marine environment will principally be from sources such as urban runoff and sewage, and volumes and concentrations presumably will be low per source per unit time.

3.6.2 Sublethal effects

3.6.2.1 Polycyclic aromatic hydrocarbons (PAHs)

The following four sections present critical data for linking, to the extent feasible, concentrations of PAHs in sediment with their toxicological effects.

Field observations have been made of tumours in demersal fish in PAH-contaminated areas (Table 3.11).

Guideline values for PAH in dredging materials destined for ocean disposal have been determined, using several frameworks (e.g. U.S. EPA, 1984; Lang and Chapman, 1985; Tetra Tech., 1986; Chapman *et al.*, 1986; Neff *et al.* ,1987; Battelle, 1988; Chapman *et al.*, 1987a,b; Chapman, 1988; Chapman, 1989) (see Table 3.12). In a summary evaluation of the available sediment-quality frameworks, the field sediment bioassay, the screening level concentration, the sediment quality trend, the apparent effects threshold and the spiked sediment bioassay have been rated as being the most effective for present use in determining sediment quality criteria.

From an examination of information on the biological effects of PAH bound to sediment, Anderson and Gossett (1986) suggested that threshold levels of PAH contamination might be between 5 μg/g dry weight and approx. 200 to 500 μg/g total organic carbon.

Table 3.11: ***Per cent occurrence of liver lesions and neoplasms found in demersal fish in two locations in western North America contaminated with polycyclic aromatic hydrocarbons (PAHs)***

A FIELD TUMOURS/PAHs, VANCOUVER (CANADA)

Observation Site	HPAH*(μg/g)	Liver lesions (%)
Vancouver harbour (outer)	1.33	13.5
Vancouver harbour (centre)	1.86	8.3
Port Moody	2.95–3.71	30
Iono	7.7–17.01	58–75

B FIELD TUMOURS/PAHs, PUGET SOUND (U.S.A)

Observation Site	Total AH(μg/g)	Neoplasms (%)
Eagle Harbor	76	24
Duwamish Waterway	8	18
Everett Harbor	8	9
Makelete	30	5
Hylebos Waterway	13	5
Denny Way CSO	4	5
Case Inlet	1.5	2
Sinclar Inlet	3.0	0
Port Madison	1.0	2

* HPAH = high-molecular-weight polycyclic aromatic hydrocarbons

Table 3.12: ***Screening level values for PAHs, determined using several frameworks***

Framework	Screening level (ppm)
Field sediment bioassay	2.0
Sediment quality trend	3.8
Screening level concentration	7.6
Apparent effects threshold (AET)	9.3
Sediment quality objective	16 (Benthic AET) 18 (Amphipod AET)

Dose–response relationships have been studied in flounder exposed to used oil for approximately 3 months (Fisheries and Oceans, Canada, unpubl. data). The indices investigated were biologically meaningful and included studies on levels of energy reserves in muscle and liver, relationships between organ- and body weight, general condition indices, ion balance, blood parameters, detoxification enzymes and histopathology of liver and gills. With the exception of detoxification enzymes, the exposure did not affect any of the indices.

Evidence links environmental cancers in bottom-dwelling organisms to concentrations of PAHs ranging from approx. 2 to 10 mg kg^{-1} in some localities. In Vancouver Harbour, where 5 to 75% frequency of pre-neoplastic and neoplastic lesions occurs in English sole, a concentration range for total PAH (TPAH) of 1.4 to 36.7 mg kg^{-1} and for HPAH of 1.4 to 32 mg kg^{-1} exists (Goyette and Boyd, 1989). In the Port Moody area of inner Vancouver Harbour, where there are similar concentrations of PAHs (HPAH 2.97 to 31.97 mg kg^{-1}, TPAH 4.4 to 36.7 mg kg^{-1}), the prevalence of lesions rises to 35 to 75%.

To conclude, given the data available, it is suggested that sediment levels of PAH in the range 3 to 5 ppm are of importance in producing adverse biological effects in fish, namely flatfish, which exist in intimate contact with sediments. (Note: 12 to 16 specific parent hydrocarbons are used as markers of total PAH, the complex mixture being understood to contain hundreds of compounds, including nitro-aromatics, azarenes, etc.). It is of interest that a value of 3 to 5 ppm generally represents a concentration approximately 10 times the background, or more, for PAHs from combustion sources. This is an important number to try to derive as accurately as possible, as it becomes an estimate of the LOEC (lowest observable effect concentration) for PAHs in sediments.

3.6.2.2 Lead

The effects of lead on marine biota have been reviewed by GESAMP (1985). Most of the acute toxicity experiments with marine organisms and inorganic lead indicate that effects are seen only after exposure to high concentrations (GESAMP, 1985; Hodson, 1986). Given the nature and volumes of inputs and types of exposure, it is unlikely that lead from used engine oil will dissolve in water in sufficient concentrations to pose a significant threat to marine life. Of more interest would be coastal sediments subjected to low-level chronic inputs from urban-associated sewers and run-off. In this regard it is worth noting that the lead content of dredged material from harbours, channels and estuaries has a reported range of 10 to 1450 $\mu g\ g^{-1}$. Even here, however, inorganic lead may be 'neutralized' through complexation with iron and manganese oxides and organic matter, diminishing toxicity (Campbell and Tessier, 1986).

Are chronic effects due to lead likely? Chapman (1986) studied broad-scale comparative data for sediment chemistry, sediment bioassays and histopathology of bottom-dwelling fish to derive quantitative site-specific sediment criteria for three representative chemical contaminants in Puget Sound, Washington. The criteria, in terms of concentrations at or below which biological effects were shown to be minimal, were 50 ppm for lead and 3.8 ppm for combustion-derived polyaromatic hydrocarbons.

To conclude, given that the average concentration of lead in crankcase oil is approximately 300 to 600 ppm, and that high dilution rates and complexing can be expected in many environments, it is difficult to suggest that lead from crankcase oil is a widespread marine pollutant. Any concern should be more or less confined to sediments in highly contaminated harbours.

3.6.2.3 Additives

Engine oil contains a number of additives, a typical formulation containing 1% zinc dialkyl dithiophosphate (a corrosion inhibitor), 4% barium sulphonate (a detergent), 4% poly(methyl methacrylate) (a multi-functional additive) and 5% polyisobutylene (a viscosity enhancer) (see Table 3.3 and Weinstein, 1974). Such compounds have a low toxicity potential in mammals. Studies with bird eggs also indicate that virgin engine oil, unlike used engine oil, has a relatively low potential for embryotoxicity (Hoffmann *et al.*, 1982). Accordingly, additives present in used engine oils should present little environmental concern. However, more specific information would be useful to verify this conclusion.

3.6.2.4 Dioxins and furans

The compound 2,3,7,8-tetrachlorodibenzodioxin (TCDD) and, to a lesser extent, other dioxins and furans are extremely toxic. The 80-day lethal dose for TCDD ranged from 2 to 23 micrograms per kilogram of body weight for a number of fish species (Kleeman *et al.*, 1988). Effects on growth, survival and behaviour have been observed in fingerling rainbow trout in the picogram per litre range (Mehrle *et al.*, 1988). The limited data suggest that concentrations of dioxins and furans in used oil are relatively low, in the range of picograms per gram. The International Joint Commission sediment quality objective for 2,3,7,8-TCDD (or its equivalents in toxicity) is 10 parts per trillion (Canada, 1990). To conclude, it has recently been established that there are trace levels of chlorinated dibenzodioxins and dibenzofurans in used engine oil. Given that the concentrations of dioxins in used oil are in the parts per trillion range (Table 3.5), it is expected that concentrations of used oil in sediments in the parts per million range would have to be reached before dioxins become an important concern. As in other instances, any concerns should be more or less confined to sediments in highly contaminated harbours or inlets.

3.6.2.5 Industrial oil additives

Given the dilution volumes in various oils and the low inputs of such oils, most classes of these compounds would have a low potential for acute and sub-acute toxicity. In this regard it is worth noting that occupational health guidelines have been set for most of the compounds of interest. However, more data on the marine toxicity potential of selected additives, such as chlorinated paraffins, would be useful.

3.6.3 Conclusions

The acute lethal toxicity potential of used engine oils and various industrial oils in the marine environment is negligible. With respect to sublethal effects, the polycyclic aromatic hydrocarbon contents and the dioxin and furan contents of used engine oil are of interest. There are also gaps in our knowledge of the sublethal toxicity potential of selected additives found in industrial oils. The principal concern for both used engine oils and industrial oils would centre on any concentrated or 'hot spot' sources of contamination connected with specific industries and with urban and industrial harbours or inlets.

3.7 Effects on human health

3.7.1 Polycyclic aromatic hydrocarbons

The carcinogenicity of various PAHs has generally been demonstrated by their ability to act as complete carcinogens in the development of cancers in rodent skin tests. Benzo[*a*]pyrene (B[*a*]P) is the only carcinogenic PAH for which the Environmental Protection Agency (EPA) has published an acceptable concentration based on carcinogenicity. However, the relative carcinogenic potency of various PAHs relative to that of B[*a*]P has been calculated as a means for proposing specific acceptable concentration levels in drinking water for each of the specific PAHs (Rugen *et al.*, 1989) (see Table 3.13).

Table 3.13: ***Proposed acceptable concentrations for specific PAHs in drinking water***

PAH	AET* (μg/litre)
Benzo[*a*]pyrene	0.028
Dibenzanthracene	0.047
Benzo[*j*]fluoranthene	0.37
Benzo[*b*]fluoranthene	1.4
Indenopyrene	4.7
Benzanthracene	6.2

* AET = apparent effects threshold

Source: Rugen *et al.*, (1989)

Some PAHs are regulated with respect to their presence in food. Tolerable levels of B[*a*]P of 1 $\mu g\ kg^{-1}$ and of total PAHs of 100 $\mu g\ kg^{-1}$ wet weight in edible fish tissue have been suggested (Uthe, 1979). The variety of factors influencing bioavailability and rates of uptake and depuration of PAHs makes it exceedingly difficult to link PAH concentration in sediments to body burdens in edible species. However, it has generally been established that the turnover rate of hydrocarbons in higher aquatic organisms such as fish is fairly rapid. Also, analysis of PAHs in tissues generally indicates that levels should be quite low in most commonly consumed fish products.

To conclude, it seems that a slight risk for human carcinogenesis could be assumed through continuous consumption of certain fish species from areas having sediments contaminated with highly elevated levels of PAHs. Also, much of the PAH contamination in sediments in such areas (e.g. harbours, estuaries, confined channels) originates from urban run-off, discharge sources of used engine oil and petroleum combustion by-products, and refineries. Individual experiments would have to be carried out with individual marine species to try to link concentrations of PAHs in sediments to tissue levels in edible products.

3.7.2 Lead

One of the principal metals of interest in used engine oil is lead, which originates from the decomposition of tetraethyl-lead. This is a gasoline additive which is used as an octane booster and is still in use in a number of countries. Lead is highly toxic, especially to the nervous system (Royal Society of Canada, 1986). Its ratings and exposure limits are as follows:

CERCLA – Health = 3

CFPA – Health = 3

OSHA Exposure limit: 50 μg/m^3 8hr TWA

An exposure limit of 50 μg/m^3 translates into a dose of approximately 500 μg per 8-hour day (i.e. 10 μg/kg of body weight for a 50 kg person).

The FAO/WHO recommendation for lead intake for adults is 7 μg per kg of body weight per day. Magos (1989) gave values up to 95 mg/kg for mussels near an industrial discharge but stated that most values are below 3 mg/kg and around 0.014 mg/kg when 'ultraclean' conditions of sampling and analysis are used. He further indicated that the lead content of vertebrate fish is an order of magnitude less than that of shellfish. Later publications indicate lead contamination of shellfish at 2 mg/kg or less and of flatfish from 0.2 mg/kg or less.

To assess possible cancer risk from lead in seafood, GESAMP (1991) considered a 60 kg person consuming 150 g/day of shellfish containing 5 mg of lead per kg. This would constitute an intake of lead of 12.5 μg per kg of body weight per day, which is substantially lower than the no-effect level for kidney cancer in the rat of 3.2 mg of lead per kg of body weight per day. Since the rat renal cancer appears to be mediated through massive accumulation of lead in the kidney, GESAMP considered that the human intake of lead in seafood would not constitute a significant cancer risk. However, there is a risk for other toxic effects since the estimated intake of 12.5 μg per kg of body weight per day exceeds the FAO/WHO guideline of 7 μg per kg of body weight per day.

Given OSHA exposure limits and FAO/WHO recommendations for lead intake, sources of lead from used engine oil may be of importance for the quality of edible seafood products, especially if fish are taken in confined harbours near sewer outfalls, urban stormwater discharges, or other major sources.

3.7.3 Corrosion inhibitors

With respect to additives in engine oil (see Table 3.3), attention is often drawn to the presence of zinc dithiophosphate corrosion inhibitors, which are commonly present at 1% by volume. A blend of zinc dialkyl dithiophosphate lubricant additives showed no evidence of genotoxic activity in bacterial mutation assays or cell transformation assays (Brooks *et al.*, 1983). CERCLA and CFPA have not produced a rating for health hazard, but the exposure limit set by OSHA and ACGIH for mineral-oil mists is 5 mg/m^3. Some appreciation of the overall toxicity of such inhibitors can be attained through comparison with lead, which has exposure limits 100-fold lower.

To conclude, no information is available on the concentration of these compounds in used engine oil; they should be largely destroyed upon combustion. These compounds would also be unstable in the environment. If trace amounts are retained in used engine oil (note that only 1% is in virgin oil) and should trace amounts be found in 'edible' fish taken near discharge areas, it seems difficult to invoke a human health concern, given that the OSHA exposure limit is 5 mg/m^3.

3.8 Effects on man's use of the sea

Since used engine oils are enriched in PAHs and have been shown to be carcinogenic, questions can be asked about the potential for contamination of seafood by a 'known' carcinogen. In this regard it is worth noting that the possibility for significant levels of hydrocarbons from crankcase oil being found in fish is unlikely, with the exception of fish taken from waters having highly contaminated sediments, such as in urbanized/industrialized harbours. Overall, the risk of contamination of seafood by crankcase oil is expected to be low or negligible. Similarly, given the low inputs and the expected low tainting potential of crankcase oil, the possibility for tainting also should be low or negligible.

Are there negative impacts associated with the release of lubricating oils at sea? It is commonly believed that bilge waters, which are often released illegally at sea, are responsible for many seabird kills off the east coast of Canada. It is also reasonable to suggest that much of the particulate oil, i.e. tar balls, found on shorelines in some regions originates from bilge water. There, through impacts on wildlife and amenity shorelines, lubricating oils have an impact on man's use of the sea.

3.9 Summary, conclusions and recommendations

3.9.1 Summary and conclusions

Crankcase oils are important contributors to point sources of combustion-generated PAHs and lead, as well as trace levels of other contaminants such as chlorinated dibenzodioxins.

There is sufficient evidence for the carcinogenicity in test organisms of combustion sources of PAHs, including those found in crankcase oil.

Crankcase oils are expected to have negligible acute toxic effects in the marine environment. Sediments contaminated with high levels of crankcase oils are expected to be chronically toxic to selected marine species, especially those associated with sediment.

There is some evidence that combustion-generated sources of PAHs in sediment in the range 3 to 5 ppm range can produce adverse effects, including carcinogenesis, in some species. This concentration range represents approximately 10 times the background level for combustion sources.

There is insufficient evidence that current inputs of lead into the marine environment from crankcase oils are of toxicological importance to benthic species. Concerns about toxic effects should be restricted to levels of contamination greater than 50 ppm.

The concentrations of PAHs expected to be found in frequently consumed fish species taken from areas having high levels of contamination of the sediment by combustion/crankcase-oil sources of hydrocarbons may have a slight risk for human carcinogenesis.

The risk of either chemical contamination or the tainting of seafood by crankcase oil is expected to be low or negligible.

With respect to the presence of highly toxic chlorinated dibenzodioxins in used oil, preliminary evidence indicates that concentrations of crankcase oil in sediments in the parts per million range will be required before these compounds become of toxicological importance.

With respect to both environmental and human health, any concerns should be confined principally to areas such as urbanized/industrialized harbours.

Bilge waters containing used crankcase oil and other lubricating oils are probably responsible for many seabird kills off the east coast of Canada.

Little information is available on the inputs into the marine environment of grinding, circulation, hydraulic and rolling oils. With respect to environmental problems, it is expected that both inputs and toxicity potential are low and that the risks to marine species should be small or negligible. This conclusion requires verification.

3.9.2 Recommendations

Chronic toxicity studies are needed to define dose - response relationships for benthic species exposed to sediments contaminated with crankcase oil.

More information is needed on production volumes and quantities of oils other than used crankcase oils (hydraulic oils, rolling oils, cutting oils, and others) entering the marine environment.

More information is needed on the role of bilge discharges in the formation of persistent residues such as beach tar.

More information is needed on the concentrations of chlorinated dibenzodioxins in crankcase oils.

More information is needed on the sublethal aquatic toxicity potential of selected additives found in used and new lubricating oils, and in industrial oils.

More information is needed on the risks to human health of lead-contaminated seafoods taken near areas exposed to discharges of used engine oils in countries still using leaded fuels.

Chapter 4 Use of dispersants and other control agents in oil spill response

4.1 Introduction

4.1.1 Types and uses of spill control agents

A number of types of chemical agents have been proposed or used for control of oil spills. Of these, chemical dispersants – mixtures of solvents and surface-active agents which reduce oil/water interfacial tension and hence stabilize small oil droplets dispersed in the water column – have received the most attention, and are considered here in detail (Section 4.1.2).

Other spill control agents that depend on chemical interaction with the oil, the water or both have been reviewed (Fingas, 1989e; Fingas *et al.*, 1990; Fingas *et al.*, 1991a; Merlin, 1989):

- Emulsion breakers and preventers (4.2.2) – sometimes called 'demoussifiers'.
- Recovery aids – polyisobutylene-based additives (e.g. 'Elastol') (4.2.3) – that convert oil into a viscoelastic substance which is more easily collected than oil.
- Gelling agents – these change oil to solid or semi-solid form.
- Surface washing agents (4.2.4) – surfactants have been used to remove oil from roads and parking lots: these agents may have value for cleaning oiled structures such as piers and ship hulls.
- Herding agents (4.2.5) – surface-active agents which can temporarily reduce the air–water interfacial tension and hence reduce the spreading pressure of slicks.
- Sinking agents (4.2.6) – chalk and related oleophilic mineral powders that were used in the 1960s.
- Biodegradation agents (4.2.7) – these may include enzymes, nutrients or bacterial cultures.

4.1.2 Role of dispersants in spill control

4.1.2.1 Major issues

A study by the U.S. National Research Council (NRC, 1989) attempted to answer the questions:

> Do dispersants do any good?
>
> > Can they help remove oil from water?
> > Can they reduce environmental impact?
>
> Do dispersants do any harm?

Are currently used dispersants more or less toxic than oil?
Is chemically dispersed oil more or less toxic than physically dispersed oil?

Does dispersed oil cause more or less harm than untreated oil?

This chapter considers the above questions in more detail, and updates the existing comprehensive literature reviews (Koops, 1988; NRC, 1989; Neff, 1990).

4.1.2.2 Do dispersants do any good?

In a few carefully planned, monitored, and documented field tests (McAuliffe *et al.*, 1980; McAuliffe *et al.*, 1981; Hurford, 1982) as well as in laboratory tests (Mackay *et al.*, 1984), some dispersants have been shown to be effective on some oils – that is, they have removed a major part of the oil from the water surface.

On the other hand, over 100 experimental spills involving dispersants were recently reviewed (Fingas, 1988; Nichols and Parker, 1985) and the effectiveness of dispersants in the field was deduced to be questionable. Low effectiveness may have been due to the use of inadequate application techniques, such as poor targeting and distribution of aerial sprays, as well as the possibility that the oils were too viscous to be dispersable, that the dispersant formulation was inappropriate, that surfactant was lost to the water column (Fingas, 1988; Chau and McKay, 1988), or that the results were inconclusive because of inconsistencies of observation.

Observations of effectiveness at accidental spills were generally inconclusive (Nichols and Parker, 1985). Some very large spills, such as the *Amoco Cadiz* accident and the IXTOC blowout, were treated with dispersants. Although accounts of the logistics and technique of application have been published (e.g. Lindblom and Cashion, 1983), effectiveness generally has not been documented either qualitatively or quantitatively. Recent attempts to use remote sensing techniques (Goodman and Fingas, 1988; Payne *et al.*, 1991) were encouraging, but the quantitative documentation of spill dispersal is far from routine at present. Until such observational techniques are available, improvement in application techniques seems unlikely.

Knowledge of how dispersants work is largely based on empirical tests, using proprietary formulations (see 4.2.1). For the most effective research on toxicity, surfactant properties, and biodegradation, the full composition and the chemical structures of component materials should be known.

Techniques for applying dispersants from boats (Onstad and Lindblom, 1989) and aircraft have improved with experience, but are still far from routinely optimal. One of the difficulties with application of dispersants is that spraying devices produce a constant rate of application, whereas slicks are highly non-uniform. The dispersant/oil ratio is therefore too low on the thick parts of the slick and too high on the sheen (NRC, 1989). A critical factor in the strategy of application of dispersants is that the viscosity of oil increases rapidly with weathering (Daling, 1988) and at lower temperatures. Since viscous oil is more difficult to disperse, response within a few hours is essential for achieving high effectiveness (Cormack *et al.*, 1986/87). In addition, areas of oil slicks tend to expand linearly with time, and current shear may later increase the area of a slick even more rapidly (Elliott *et al.*, 1986; Onstad and Lindblom, 1989). Thus rapid response – within a matter of hours – is critical to the successful treatment of oil spills with dispersant.

The NRC Committee (NRC, 1989) recommended that dispersants be considered as a potential first response option to oil spills, along with other response options. Implementation of this recommendation must consider logistical requirements, contingency planning, performance and availability of equipment and of dispersants, appropriate regulations and training of personnel.

Dispersants may be most useful in responding rapidly to small spills where they occur routinely, such as in a harbour or at an offshore installation.

4.1.2.3 Do dispersants do any harm?

Concern that chemical dispersants could be extremely toxic to marine life, as the 1960s formulations were, has led to considerable caution in authorizing their use at spill sites. However, laboratory studies of dispersants currently in use have shown that their acute lethal toxicities are usually lower than those of crude oils and refined oil products (Wells and Harris, 1980; Wells, 1984; also see 4.3.1).

A wide range of lethal and sublethal effects of dispersed oil have been observed in the laboratory (NRC, 1989). In general, these effects occur at higher concentrations of dispersed oil than those expected in the water column during treatment of an oil spill at sea (1 to 10 ppm). The toxicity of dispersed oil is primarily due to toxic components of the oil, and hence chemically dispersed oil shows essentially the same acute toxicity as mechanically dispersed oil at the same concentration (also see 4.3.2).

The immediate ecological impact of dispersed oil varies with conditions, but is generally less than that of untreated oil. In open waters, organisms residing on the surface will be less affected by dispersed oil than by an oil slick, but organisms in the water column, particularly in the upper few metres, will experience greater exposure to oil components if the oil is dispersed. If the water is well-mixed, the dispersant will be rapidly diluted and toxic effects will be decreased. In shallow habitats, with poor water circulation, however, planktonic and benthic organisms will be more immediately affected by dispersed oil.

In the longer term, dispersed oil is also much less harmful than untreated oil. For example, untreated oil slicks and evaporation residues are a persistent threat to birds, mammals and intertidal communities, whereas dispersed oil is retained less by surfaces and sediments and hence tends to have less long-term exposure and toxicity. If oil is dispersed before reaching a mangrove habitat, the long-term exposure and effects are less and the habitat recovers faster.

Some significant studies on which the above conclusions are based include Sergy (1987); Gilfillan *et al.* (1985); Getter *et al.* (1985); Ballou *et al.* (1987, 1989); and Knap *et al.* (1985). A full review of mesoscale and field studies, with bibliography, is given in NRC (1989).

It should also be noted that the use of dispersants to reduce adhesion of oil to surfaces can also have the detrimental side-effect of reducing a skimmer's recovery efficiency for treated but undispersed oil (R. Percy, pers. comm.).

4.1.3 Role of other spill control agents

Because of the shortage of research information and rare anecdotal experience, the other agents (see 4.1.1) must be considered to be in a more primitive stage of development compared to chemical dispersants. Some questions are obvious, for example:

- Are emulsion breakers and preventers – 'demoussifiers' – useful control agents? These can improve efficiency of mechanical clean-up or chemical dispersion. Some are effective but not available commercially (Fingas *et al.*, 1990) (see 4.2.2).

- Are recovery aids – polyisobutylene formulations such as 'Elastol' – useful? They have proved effective in small-scale field tests, described in 4.2.3 and 4.4.3. They have considerable promise for improving the efficiency of skimmers.

- Are gelling agents useful? Relatively large amounts of such agents are required, but they can reduce the loss of volatiles, and hence diminish fire hazard in enclosed spaces (see 4.2.3).

- Is there a role for sinking agents? These are not presently used because of ineffectiveness, possible harm to benthos, and resurfacing of oil (see 4.2.6).

- Can biodegradation agents be an important tool for cleaning up a spill? Some of these have shown good performance in the laboratory but irreproducible performance in the field – often indistinguishable from controls. Here major factors are the difficulty in keeping the nutrients with the bacterial culture and preventing indigenous populations of yeasts, fungi, and bacteria from outcompeting the desirable hydrocarbon degraders (see 4.2.7).

Most of the described agents have been proposed on the basis of chemical intuition or small-scale laboratory tests. All agents have had at least a few field tests for effectiveness, although the tests are not always completely described in the literature, and the results of those tests are only rarely presented in quantitative terms (see 4.4.3). Biological impact has only been assessed in qualitative terms.

4.1.4 Testing and regulation of control agents – international perspective

Because of the toxic effects of early chemical dispersants and detergents, associated particularly with the *Torrey Canyon* disaster of 1967, efforts to develop less toxic dispersant formulations were vigorously pursued in the 1970s and 1980s by a number of manufacturers.

Although the precise formulations still remain confidential, the toxicity of these has been tested by standard methods established in each country. The most frequently tested combinations are dispersant, oil, and dispersed oil. Most tests use seawater, and lethality is the usual toxicity response. Typical species are the brine shrimp *Artemia*, the brown shrimp (*Crangon crangon*), the rainbow trout (*Oncorhynchus mykiss;* formerly *Salmo gairdneri*), and the mummichog (*Fundulus heteroclitus*). Although these are not always ecologically relevant, they are easy to culture and yield reproducible test results. In addition, each country usually incorporates indigenous species into standard toxicity methods. For example, the Japanese Government sets toxicity standards for dispersants not only on the basis of fish (i.e. 24-h LC_{50} more than 3000 ppm to the killifish *Orizyas latipes*) but also on the diatom *Skeletonema costatum* (H. Tokuda, pers. comm., 1991).

Species indigenous to the Gulf of Mexico have been the subject of toxicity studies (Shuba and Heikamp, 1989). Tropical species (Thorhaug *et al.*, 1989a, 1989b, 1991) are particularly important. A survey of such toxicity tests was given in NRC (1989) and Duke and Petrazzuolo (1989).

An important recent advance is the measurement of the actual concentration of dispersant, so that accurate exposure data can be obtained now (Scelfo and Tjeerdema, 1991). Such analyses permit precise toxicity tests, using spiked exposures in continuous flow systems (Singer *et al.*, 1991).

A list of those commercial formulations which have passed tests set by the U.S. Environmental Protection Agency (NRC, 1989), Environment Canada (NRC, 1989; Fingas, pers. comm., 1990), the U.K. Ministry of Agriculture, Fisheries and Food (Blackman, pers. comm., 1990), and the French Government (R. Kantin, pers. comm., 1991) will be found in the Appendix to this report (Table 4.1).

The United Kingdom had licensed 118 products, the United States had registered 29, Canada had registered 9 and France had approved 7 products by 1990. There is very little overlap. No product is registered in all four countries. Indeed, only one product, called Corexit 9527 in the United States and Canada and Corexit 9517 in the United Kingdom, is registered in three countries. Four of the seven products approved in France are licensed in the United Kingdom, but none of these is registered in the United States or Canada. Part of this lack of overlap results from similar or identical formulations being marketed under different names or code numbers in different places. It may also be due to the different requirements for approval in different countries.

Regardless of the large number of trade names, only a few dispersant formulations are widely available in quantity, so that they would be useful at a real spill. Corexit 9527 and BP 1100X are ubiquitous, and a correspondingly large data base exists on their effectiveness and toxicity.

4.2 Composition, chemical and physical properties

4.2.1 Dispersants

Knowledge of how dispersants work is not as fundamental as it could be, being based on empirical tests using proprietary formulations. Typical active ingredients are sorbitan monooleate, ethoxylated sorbitan monooleate, polyethylene glycol monooleate and sodium diethylhexyl sulfosuccinate (NRC, 1989).

The general mechanism by which such surfactant chemicals disperse oil into the water column is qualitatively understood, and quantitative models are being developed to predict some aspects of this process (NRC, 1989; Fingas, 1991b). However, a rigorous research programme to understand the physical and chemical phenomena by which dispersant components, especially the surfactants, interact with oil to produce dispersions has been hampered by the restrictions of proprietary knowledge. A recent review of mechanisms of action and laboratory tests is now available (Clayton *et al.*, 1992).

Additional reviews of dispersant types and application techniques were published by Turner (1986) and Fingas (1989 b, c, d, e). Formulations based on microemulsion technology,to produce more effective dispersants, have been proposed (Canevari *et al.*, 1989). Recent studies of dispersion of oil (Belk *et al.*, 1989; Delvigne, 1989) and resurfacing of droplets used a dynamic turbidimeter (Pelletier and Brochu, 1989); quantitative agreement was obtained with a model devised by Mackay *et al.* (1984). Fingas *et al.* (1989a,b,c) have made extensive comparisons of various laboratory tests using a number of oils and dispersants.

They concluded that the most important factor influencing effectiveness is the energy input in the experimental apparatus; for that reason, correlation between the results of various methods is difficult to achieve. Use of dispersants on land-based oil spills is reviewed by Paddock (1989).

On the basis of dispersant composition alone, it is not possible to predict the reduction in oil impact – this depends on many other factors. For example, the evaporation of volatile hydrocarbons from slicks of crude oil results in rapidly increasing viscosity and a corresponding decrease in effectiveness of the dispersant (Cormack *et al.*, 1986/87; NRC 1989). Complete loss of C_1 to C_{10} aliphatic, cycloalkane, and aromatic hydrocarbons from field slicks occurred in less than 2 hours. Loss of aromatic volatiles also reduces the potential for acute toxicity (McAuliffe, 1989a; NRC, 1985; Payne and Phillips, 1985; Payne and McNabb, 1984).

4.2.2 Demoussifiers

Surface-active agents with the proper hydrophilic–lipophilic balance (HLB = 12 to 19) can diminish or prevent the formation of water-in-oil emulsions (mousse), and thereby greatly enhance clean-up capability. They are used in tanks or during pumping to break emulsions (R. Kantin, pers. comm., 1991). The disadvantage is that surfactants with a HLB in this range are more soluble in water than in oil, and will be rapidly diluted in open water (Fingas, 1989d, Fingas *et al.*, 1990). Two products being developed commercially, Exxon Breaxit and Shell LA 1834, were compared with sodium dioctyl sulfosuccinate (Ross, 1986). Only the Shell product prevented formation of an emulsion over a wide range of oils and conditions. Environment Canada has formulated an effective demulsifier (Brand M) (Bobra *et al.*, 1988a,b; Fingas and Tennyson, 1988).

4.2.3 Recovery enhancers

A formulation containing polyisobutylene can enhance the viscoelastic properties of oil and improve the performance of oil skimmers (Waters *et al.*, 1989; Bobra *et al.*, 1988a; Bobra *et al.*, 1987b; Brown *et al.*, 1985; Gershey and Batstone, 1988). A proprietary material of this type, known as 'Elastol', has been tested extensively in the laboratory and at tank scale by Environment Canada (Fingas, 1989d; Bobra, 1987a,b; Bobra *et al.*, 1988a; Fingas and Tennyson, 1988; Laun and Hingmann, 1988; Bobra *et al.*, 1987a; Bobra *et al.*, 1988b). A wide variety of crude oils displayed increased viscoelasticity when treated with doses of 600 to 6,000 ppm of Elastol, some within 15 minutes of application. More viscous oils attained a higher degree of elasticity. Some samples, after 30 days, were as elastic as rubber bands.

Elastol also reduces the spreading of a slick but does not prevent the formation of mousse. Fingas (1989d) proposed that a combination of demoussifier and Elastol could enhance recovery as well as diminish the formation of an emulsion. Most significantly, Elastol reduces the natural dispersion of oil into water by as much as 3 orders of magnitude.

It appears that Elastol and related products are most useful as a way of improving the efficiency of skimmers (Brown and Goodman, 1989). Elastol was briefly tested at an experimental spill off Newfoundland in 1987 (Tennyson and Whittaker, 1988, 1989) (see 4.4.3). Additional studies were also conducted off Nova Scotia in 1987 (R. Percy, pers. comm.). Elastol appears to have considerable promise, especially for recovering small spills before they reach a shoreline.

Environment Canada tested three types of gelling agents, consisting of polymerization catalysts and cross-linking agents (Fingas, 1989d; Fingas *et al.*, 1990). These were:

- A deodorized kerosene with cross-linking agent, produced by British Petroleum;
- A Japanese product, consisting of an amine which forms a polymer;
- Liquefied carbon dioxide with an activating agent, developed by Bannister of the University of Lowell (as cited by Fingas, 1989d).

All agents solidified oil in the laboratory. The BP agent worked best and was tested on a larger scale by the Canadian Coast Guard and oil industry. However, the amount of gelling agent that was required to solidify the oil was up to 40% of its volume, twice the laboratory requirement. In addition, two other problems are noted with gelling agents. First, they react with the first oil they encounter, which generally results in the oil not becoming entirely solidified. Secondly, the cross-linking agents that are used quite often react with other materials, such as the components of booms. Hence gelling agents are rarely considered for spill response by Environment Canada (Fingas, 1989d; Fingas, pers. comm., 1991).

However, in Japan, gelling agents are approved by the Government because they repress volatilization of light fuel oils, and thereby reduce the risk of fire and explosion when recovery is done in enclosed places (MDPC, Tokyo, pers. comm., 1991).

Tests at CEDRE in France (Merlin, 1989) of the BP product RIGIDOIL and of another called NORSOREX revealed that higher doses than the manufacturers' recommendation had to be used, but that solvents such as benzene, xylene and cyclohexane and monomers such as vinyl acetate and methyl methacrylate could be gelled as well as oil products.

4.2.4 Shoreline washing agents

Surfactant formulations with a high hydrophilic–lipophilic balance (HLB) are used to remove oil from roads and parking lots. They may be useful to clean oil contamination from ships, concrete piers, and other surfaces, but tests by Environment Canada have shown many to be no more effective than water (Fingas, 1989d; Fingas, pers. comm.).

The Exxon product Corexit 9580 (Fiocco *et al.*, 1991) was developed specifically to reduce the adherence of oil to shoreline surfaces, and was tested in the field at Prince William Sound, Alaska, in 1989–90. Quantitative results are available and show that this agent ranks high in a laboratory surface washing test; it has low toxicity compared to other agents (Fingas, pers. comm., 1991).

Cleaning agents have also been formulated specifically for removing oil from birds (see 4.3.3).

4.2.5 Herders

When a surfactant is added to water near an oil slick, the rapid decrease in surface tension of water causes the slick to shrink away from the point where the surfactant was added, and hence to decrease the spreading pressure of the oil. Shell Oil Herder (long-chain alcohols) was given much attention about 20 years ago (Garrett, 1969; Barger, 1973) as a way of collecting oil into a smaller area prior to mechanical removal. It was also proposed for use on beaches to diminish adherence of oil (Nightingale and Nichols, 1973). Some field tests (Nagy, cited by Fingas, 1989d) showed, in contrast to the earlier work, that utility of oil herders was limited to calm waters, and that they are used rarely (Fingas, 1989d).

Three 'collectors' are licensed in the United Kingdom (see Table 4.1), e.g. Corexit OC5, Finarep and Shell Oil Herder. Limitations noted by The Shell Oil Company (J.P. Fraser, pers. comm.) include the need for oil to be in the correct viscosity range (i.e. not sheen or weathered oil), recognition that the collected slick will move with the wind, interference from snowfall, and relatively short duration of the effect.

4.2.6 Sinking agents

Chalk, lime and oleophilic materials denser than water were used at one time to sink oil slicks (Brown, 1971; Dick and Feldman, 1975), but are no longer recommended or permitted. As the oil descends, part of it is released from the sinking agent and resurfaces. Subsurface life is exposed to higher concentrations of oil, without the potential for dilution offered by dispersants. Biodegradation rates in the benthos tend to be slower, especially under anoxic conditions. Most importantly, suffocation of benthic organisms by the sinking agent and greatly increased exposure of bottom-dwelling organisms to oil are considered highly undesirable. No sinking agents are commercially available, and they are generally prohibited by environmental regulations in Canada, the U.S., and other countries (Fingas, 1989d). Because of general dumping regulations, none is licensed for use in the United Kingdom (Blackman, pers. comm.).

4.2.7 Biodegradation enhancers

The enhancers include nutrients, enzymes, and bacterial cultures, some with special genetic modification. They are often called 'bioremediation agents'. Laboratory tests show increased degradation rates. These agents have effectively degraded oil in impoundments and sewage-treatment facilities. They have low effectiveness on open water, because of rapid dilution of both the bacterial culture and the nutrient stock (NRC, 1985, 1989; Fingas *et al.*, 1990). A recent review concluded that there is insufficient evidence of enhanced biodegradation upon addition of microbes to oil, whether at sea or stranded (Owen, 1991).

Microbial degradation occurs in aerobic soils and surficial sediments, and can be enhanced by tilling, but tends to be limited to the straight-chain aliphatic and the simpler aromatic components of the oil (NRC, 1985) and is extremely slow on barren terrain. During the Baffin Island Oil Spill Study, oiled supralittoral sediments were treated with fertilizer (Owens, 1984). These showed no increased degradation through five years of monitoring. A test of one product on a spill in British Columbia showed no increased degradation on oiled rocks treated with a fertilizer (Roberts, 1974). However, tests on Arctic shorelines in Norway showed increased biodegradation (Sendstad *et al.*, 1984) and favourable results have been reported for a product which uses a surfactant to suspend fertilizer and make it more available to the oil (Ladousse *et al.*, 1987). Experiments on the Brittany coast demonstrated that more than 80% of n-alkanes, independent of pollution level, were removed from oiled intertidal sediments after 16 months. The limiting factor appeared to be oxygen, not the concentration of nutrient (Bodennec *et al.*, 1987).

Laboratory studies to simulate tidal movement on a beach revealed that isobutyraldehyde diurea briquettes, which produced a slow continuous release of nutrients, would be most suitable for field application (Safferman, 1991).

The development of the oleophilic fertilizer Inipol EAP 22, laboratory studies, and some successful field tests of this bioremediation agent have been reviewed by its developers (Ladousse and Tramier, 1991). In addition, new laboratory studies compared Inipol EAP 22 with a water-soluble nitrogen/phosphorus formulation recommended by OECD. Cumulative oxygen uptake, microbial growth, and analysis of hydrocarbons by gas chromatography/mass spectrometry showed that, after six weeks of incubation at 15 °C, almost all of the alkanes of an Alaskan weathered crude oil had been utilized, and polycyclic aromatic constituents had been significantly degraded. Without the nutrient additives, degradation did not occur (Tabak *et al.*, 1991).

Laboratory tests of 10 different (anonymous) biodegradation-enhancing products revealed two products which were significantly different from inorganic nutrients and caused 94–95% removal of alkanes in 11 days. The decision was made to test only these two products in the field at Prince William Sound, Alaska (Venosa *et al.*, 1991).

At Prince William Sound, Alaska, a co-operative effort of Exxon, the USEPA, and others compared the effects of Inipol EAP 22, a slow-release nitrogen/phosphorus formulation (Customblen 28-8-0), and water-soluble nitrogen and phosphorus during 1989–90 on oil spilled by the *Exxon Valdez*. In both laboratory and field tests, numbers of hydrocarbon-degrading micro-organisms and changes in residual oil showed the efficacy of these bioremediation techniques (Chianelli *et al.*, 1991).

Preliminary results from another study in Prince William Sound, in which Inipol EAP 22, isobutylidene diurea, and granular nitrate/phosphate fertilizer were compared, suggested that all treatments resulted in extensive biodegradation. However, it was noted that natural biodegradation at the control sites also occurred at a 'surprisingly rapid rate' (Glaser *et al.*, 1991).

Waxy crude oil (Terra Nova) spilled on a sand beach in Nova Scotia was degraded by the indigenous biota in a few days if there was less than 0.3% oil in the sediment, but degradation took as long as 6 months for 3% oil. Similar concentrations of oil were resistant to biodegradation in the saltmarsh, where the rate is limited by availability of oxygen. Nutrient enrichment increased the degradation rate, especially at higher concentrations, so long as the oil did not penetrate below the aerobic zone (Lee and Levy, 1991).

The *Mega Borg* spill in the Gulf of Mexico, in June 1990, was treated with 100 pounds of bacterial formulation developed by Alpha Environmental in Austin, Texas. Unfortunately, the results were ambiguous due to disruption of the test area during the first 24 hours (OSIR, 1990a).

Dispersants, since they increase the surface area of oil droplets, might be expected to influence biodegradation. Some laboratory studies and all mesocosm studies have shown that the rate of biodegradation of dispersed oil is equal to or greater than that of undispersed oil (NRC, 1989).

4.2.8 Hot water washing

Steam cleaning, sandblasting, and washing with hot water to remove oil from piers, vessels, and rocks has been common since the early days of oil spills (Nelson-Smith, 1972; Cormack, 1983). The advantages are not only aesthetic, but can help diminish harm to birds and mammals which use the intertidal and supratidal zones. The disadvantages are primarily in the harm done to the community of algae and invertebrates (Broman *et al.*, 1983). The CONCAWE (1981) field guide covers the matter succinctly: "The techniques of hydraulic cleaning and sand blasting, including steam cleaning, and high and low pressure hydraulic cleaning, can be used to disperse oil from rock surfaces. Care must be taken because intertidal flora and fauna could be damaged by these techniques."

The 1989 spill from the *Exxon Valdez* accident in Prince William Sound oiled hundreds of kilometres of shoreline and hence was an occasion for a variety of techniques for shoreline treatment and a serious damage-assessment programme. Contamination by hydrocarbons caused major adverse impacts to the intertidal biota, but treatment with high-pressure hot water often caused more serious impacts than the oil. The treatment with hot water removed oil from the upper and mid-intertidal zone, where its effects were restricted to relatively tolerant organisms such as barnacles, mussels, and rockweed. The intent was to collect the oil offshore as it was removed, but when this was not effective, the oil was transported into the lower intertidal and shallow subtidal zones, where it affected relatively more sensitive and productive biota such as hardshelled clams and crustaceans (Houghton *et al.*, 1991).

4.2.9 Burning

Burning of oil slicks, while not a chemical treatment in the sense of the others discussed here, is an important option because it leaves relatively little residue to contaminate the sea. Sorbents to act as a wick, collecting oil in sufficient thickness to permit it to burn, and pyrotechnic materials, to assist ignition and flame propagation, are limited by the large amount of material needed to improve efficiency of combustion. Hence current experiments have concentrated on containing the oil by a fireproof barrier and igniting it before most of the volatile components have evaporated.

Combustion experiments on n-decane, toluene, and Alberta Sweet crude oil were used to estimate the energy transfer required for burning of a slick (Evans *et al.*, 1988). Outdoor burning tests of an oil slick contained by a prototype high-pressure waterjet barrier (Comfort and Punt, 1989) showed that the barrier reduced the opacity of the smoke but also reduced the burn efficiency, due to formation of an emulsion.

Burning was tested at the *Exxon Valdez* spill (Skinner and Reilly, 1989; Allen, 1991). On the evening of the second day, approximately 40 hours after the spill, the weather was calm and 12,000–15,000 U.S. gallons of crude oil were successfully collected with a fireproof boom and burned, reducing it to an easily collected toffee-like residue with a small fraction of its original volume.

Residents of Tatitlek, several miles from the burn site, reported irritated eyes and throats, and were frightened because they had not been informed of the test (Davidson, 1990). The Alaska Department of Environmental Conservation would have permitted further burning as long as residents were notified and communities were not harmed, but, by the evening of the third day, conditions were no longer favourable, and no further tests were conducted.

Since 1989, burning *in situ* has gained much attention as an alternative response technique, especially in ice fields, remote areas, or the open sea. The main technical problem remains the sustaining of an efficient burn; the main drawback is the combustion by-products, which may appear to be threatening. However, when the long-term environmental effects of the untreated oil are compared with the effects of combustion products, burning may turn out to be a favourable choice. To make this comparison, considerable research is needed on the chemical composition and toxicity of the emissions from combustion of crude oil *in situ* (Jensen, 1990; Jensen and Tibeau, 1991; MSRC, 1991).

4.3 Toxicology

4.3.1 Dispersants

In general, laboratory studies of dispersants currently in use have shown that their acute lethal toxicities are variable, but generally relatively low compared to that of petroleum. Data from over 100 studies are summarized in Table 4.2, in which the number of studies reporting a toxicity threshold in a particular concentration range is given for three widely used dispersants (Corexit 7664, Corexit 9527, and BP 1100 X) as well as similar studies of the water-soluble fractions of crude oil or oil–water dispersions. Note, for example, that of the 32 studies on Corexit 7664, seven gave toxicity thresholds greater than 10^4 ppm, seventeen in the range 10^3 to 10^4 ppm, and none in the range below 100 ppm. In contrast, in only one study of petroleum was the threshold above 100 ppm, and 29 of the 33 fell in the range where the threshold was less than 10 ppm. Thus, in a majority of the tests, Corexit 7664 was found to be about 1000 times less toxic than petroleum (NRC 1989, pp. 96–123; Wells and Harris, 1980; Wells, 1984). Laboratory studies on dispersants have continued, using both standard species and local indigenous species as potential organisms for regulatory testing.

For example, recent studies (Singer *et al.*, 1990, 1991) focussed on the sensitive early life stages of four typical Californian species: the kelp *Macrocystis pyrifera*, red abalone (*Haliotis rufescens*), a mysid (*Holmesimysis costata*) and the top smelt (*Atherinops affinis*). Corexit 9527 at 2.4 ppm for 48 h significantly reduced the growth of kelp gametes. The values of LC_{50} for the animals ranged from 1.6 ppm (abalone embryos) to 40 ppm (top smelt larvae). Among common test organisms, only sea-urchin gametes are more sensitive (0.003–0.05 ppm) than those of red abalone (Hagström and Lönning, 1977).

Unlike hydrophobic hydrocarbons, dispersants are accumulated in marine organisms only to a limited extent because some components are readily metabolized (Payne, 1982) and elimination is rapid (Lee, 1989). Many sublethal responses to exposure to dispersants have been measured, but generally at concentrations higher than predicted for the environment (NRC, 1989).

Direct application of dispersant to birds and mammals (or their habitats) is almost certainly harmful, because dispersants destroy the water repellency and the insulating capacity of fur or feathers (Lambert and Peakall, 1981; Peakall *et al.*, 1987; Hubbs Marine Institute, 1986; Payne, 1982) and some components are readily metabolized. Dispersants have been used to clean oiled sea otters. However, virtually nothing is known about the effects of dispersed oil, as compared with untreated oil, on marine mammals. Dispersants may render the oil less adherent, but may also facilitate the loss of natural oils and decrease insulating properties.

4.3.2 Dispersed oils

A wide range of acute and chronic sublethal effects of water-borne dispersed oils have been observed in the laboratory (NRC, 1989). These effects occur in most cases at concentrations comparable to or higher than those expected in the water column during treatment of an oil spill at sea (1 to 10 ppm), but seldom at concentrations less than those found several hours after treatment (less than 1 ppm). The times of exposure in the laboratory (24 to 96 hours) are much longer than predicted exposures during dispersal of a slick (1 to 3 hours), and the effects would be expected to be correspondingly less in the field.

Laboratory bioassays have shown that acute toxicity of dispersed oil generally does not reside in the dispersant, but in the more toxic fractions of the oil (Wells and Harris, 1980; Wells, 1984; Bobra *et al.*, 1984; NRC, 1989). Chemically dispersed and mechanically dispersed untreated oil, at the same concentration in water, show the same acute toxicity. This conclusion is obscured in the literature by a large number of studies which quote total oil per unit volume of the experimental system (including the slick on the surface), rather than the actual concentration of hydrocarbons to which organisms are exposed. This conclusion also applies to specific formulations available in the 1970s and 1980s – second- and third-generation dispersants – especially the Exxon Corexit series.

Table 4.2: ***Acute toxicity thresholds reported for some common dispersants and compared to petroleum***

		Threshold concentrations (ppm)					
		$>10^4$ (less toxic)	10^3 to 10^4	10^2 to 10^3	10 to 100	1 to 10	<1 (more toxic)
Dispersant	Total[a]	Number of studies with threshold in range noted above					
Corexit 7664[b]	32	7	17	8	0	0	0
BP 1100X[b]	26	4	17	5	0	0	0
Corexit 9527[b]	25	0	1	6	10	5	3
(Petroleum[c])	33	0	1	0	3	15	14

Note: a Number of data sets reported to 1986.

b Source: NRC (1989), p. 114.

c Source: NRC (1985) and Capuzzo (1987). 48 to 720 h LC_{50} for a variety of marine zooplankton exposed to water-soluble fraction of crude oil or oil–water dispersion.

Studies on the persistence of hydrocarbon fractions in a range of habitats, with and without dispersants, show that reduction of chronic exposure is the key to reducing biological damage (NRC, 1989).

Complex interactions occur in tropical habitats such as coral reefs (Knap *et al.*, 1985; NRC, 1989) and seagrass beds (Thorhaug *et al.*, 1989a, 1989b and 1991). Although low concentrations of dispersed oil have little effect (see 4.4.2), dispersal of a slick directly over a reef could produce concentrations that are acutely toxic. Hence, dispersal away from the reef is recommended.

A hazard assessment of chemically dispersed oil spills to seabirds combined exposure analysis with toxicology on such materials (Peakall *et al.*, 1987) for the first time. Toxicity of oil dispersed with Corexit 9527 is similar to that of oil alone. The effect of two feeding regimes, pursuit diving and surface diving, was considered. Calculations indicated that the amount of oil likely to be taken up by a bird while moving through the water column is small. The major oiling of birds occurs at the surface, and will occur so long as there is a slick. Hence dispersants must be highly effective to significantly reduce exposure of birds to oil.

4.3.3 Other agents

Four cleaning agents marketed in Norway and Switzerland were tested for their effectiveness in rehabilitating oiled birds on domestic ducks and common eiders (Jenssen and Ekker, 1989). By using more efficient detergents, the cleaning time was reduced by approximately 50%, and the insulation of plumage was restored. However, water-repellence was not re-established until the plumage was dry. Cleaning oiled birds in cold water resulted in hypothermia.

The surface-active agent "Elastosol" (the same as the additive Elastol) with oil was tested on seagrasses, corals, mangroves, and fish and found to be of low toxicity (Thorhaug *et al.*, 1989b).

4.4 Mesocosm and field studies on dispersants

4.4.1 Physical and chemical experiments

As noted in 4.1.2, chemical dispersal of oil can be effective in the laboratory (Mackay *et al.*, 1984), but it is much less effective at sea. The NRC (1989) report concluded that, while elaborate field experiments have shown that up to 80% of an oil slick could be removed from the surface, and that dispersants had beneficial effects in diminishing the adherence of oil to surfaces, these conclusions were based on only a few studies. Hence, controversy over how effective dispersants are in removing oil from the water surface has continued.

In addition to the chemical interaction of dispersant and oil, microscopic mixing processes occur as dispersant lands on oil and penetrates it while subject to turbulence originating in the air and water. Additional factors include evaporation, emulsification, and spreading of the oil into patches of varying thickness (Mackay and Chau, 1986; Chau and Mackay, 1988).

The effect of dispersants on the retention of oil by sediments has received only a little attention (NRC, 1989). One recent field study of the effects of agents on the behaviour and retention of spilled crude oil in a simulated streambed channel was conducted in south-central Alaska with dispersants OFC D-609 and Corexit 9550 (Clayton *et al.*, 1989). The development and testing of Corexit 9580, an agent specifically designed to reduce adhesion of oil to shoreline surfaces, was described by Fiocco *et al.* (1991).

Gas chromatography with mass-spectrometric detection was used to compare distributions of hydrocarbons in surficial sediments near the site of the Pac Baroness spill, off California, 1988, with the composition of a sample of the source oil (Hyland, *et al.*, 1989; Payne *et al.*, 1991). Sediment from the vicinity of the wreck contained elevated levels of petroleum components that clearly originated from the oil on board the sunken vessel. Community structure of benthic infauna was compared with that at control sites. Distinct biological effects were found in the immediate surrounding area – reduction in number of species, in number of individuals, and in abundances of several component species. The initial levels of contamination and associated environmental effects are unique for the extreme water depth (430 m). Although some dispersant was used on the *Pac Baroness* spill and remote-sensing methods were tested for their ability to detect dispersal of the oil slick (Onstad and McCloskey, 1989; Payne *et al.*, 1991), it is unlikely that any of the observed benthic effects can be attributed to the use of a dispersant.

4.4.2 Biological experiments

Numerous laboratory and field experiments were reviewed by NRC (1989). Chemically dispersed oil in open water conditions contains concentrations of dissolved hydrocarbons which can be orders of magnitude lower than the lethal toxicity levels for a wide range of organisms (NRC, 1985, 1989; McAuliffe, 1989b).

The "Tropical oil pollution investigations in coastal systems" (TROPICS) project (Getter *et al.*, 1985; Ballou *et al.*, 1987, Ballou *et al.*, 1989) was a long-term multidisciplinary field experiment, concerned with effects of untreated and chemically dispersed Prudhoe Bay crude oil on mangroves, seagrasses and corals in Panama. Its purpose was to evaluate whether chemical dispersants can reduce the environmental impact of oil spills in tropical waters; because there are so few such studies, it has been frequently cited.

Dispersion of crude oil has prevented mortality in mangrove trees and preserved the community; undispersed oil kills the trees and destroys the habitat (also see section 2.6.2). Survival, abundance and growth of the dominant species were correlated with the extent of contamination. Untreated oil had severe long-term effects on mangrove communities, but minor effects on seagrasses, corals and their associated organisms. Chemically dispersed oil caused declines in the abundance of corals, sea urchins and other reef organisms, reduced the growth rate in one species of coral, and had minor or no effects on seagrasses and mangroves (Ballou *et al.*, 1989).

Dispersion of crude oil has diminished its long-term effects on subtidal organisms in the Arctic (Sergy, 1987).

Recovery of a Nova Scotian saltmarsh during two growing seasons, following experimental spills of crude oil and the dispersant Corexit 9527, was reported by Crowell and Lane (1988). The creek edge zone (dominated by tall *Spartina alterniflora*) showed little effect, but the midmarsh zone (dominated by dwarf *S. alterniflora*) was severely impacted and displayed relatively little recovery over two growing seasons.

Studies on corals from Bermuda (Knap *et al.*, 1985; Wyers *et al.*, 1986) and elsewhere have already been reviewed (NRC, 1989). When corals were exposed to oil and dispersed oil under field conditions, exposure to hydrocarbons was greater in dispersant-treated plots than in untreated oiled plots. However, no effects were observed on growth of corals exposed either to oil or to dispersed oil for 24 hours and measured one year after the exposure. Knap *et al.*, (1985) concluded that "in the long term, *Diploria strigosa* appears relatively tolerant to brief exposures to crude oil chemically dispersed in the water column". Corals exposed for 5 days to oil or dispersed oil showed reduced growth in comparison to the controls. Exposure to dispersed oil also appeared to delay recovery of corals under stress by low temperatures (NRC, 1989).

As with other organisms and habitats, the primary factor controlling effects is exposure to the water-accommodated fraction of the oil. When toxicities are based on such analytical measurements, there are no major differences between physically and chemically dispersed oil. However, these experiments were limited to only one species of coral, and other reef organisms, such as crustaceans, echinoderms, and other invertebrates, are known for their sensitivity to both chemically and physically dispersed oil. Therefore protection of the entire reef community, perhaps by dispersal of the oil offshore, is a priority.

In a recent work (LeGore, *et al.*, 1989), portions of a coral reef in the Arabian/Persian Gulf were exposed to oil (Arabian Light crude), dispersant (Corexit 9527), and oil–dispersant mixtures (LeGore *et al.*, 1989). Growth rate of corals was measured for one year, using Alizarin Red stain. Growth appeared unaffected by exposure to the toxicants under test conditions. Some species of *Acropora* exposed to the dispersed oil for 5 days exhibited delayed, but minor, effects, apparent only during the relatively cold winter season.

In contrast to the more cautious NRC (1989) recommendation – avoiding dispersant use in "shallow water with poor circulation" – McAuliffe (1989b) argues that dispersal of oil in shallow near-shore waters can in many cases be less harmful than permitting the oil to come ashore.

Several experimental oil spills, designed to support research on spill response, have been performed in recent years in Canada, Great Britain and Norway, among others (NRC, 1989). However, since the API-sponsored dispersant study at Searsport, Maine, carried out in 1981, attempts to obtain permits to perform experimental spills of significant size in U.S. territorial waters have met with little success. However, collaborative projects with other countries should be encouraged.

4.5 Effects on human health of use of dispersants

Direct exposure of work crews and bystanders to dispersant spray could be harmful, but such potential effects are covered by product safety data for each formulation.

Use of dispersants might affect human health in a number of indirect ways. Most obvious is the increased acute exposure of subsurface and benthic organisms and fish to the toxic components of dispersed oil, such as polycyclic aromatic hydrocarbons, and the short-term transfer of these, through consumption, to people, with unknown consequences.

However, the quantities of PAHs found in seafoods are for the most part equal to or less than the levels reported in other food sources (NRC, 1985; see section 3.7.1). The major exceptions to this are seafoods harvested in the vicinity of municipal outfalls, creosoted pilings, or local sources of petroleum hydrocarbons. There is no experimental evidence to suggest that chemical dispersal of oil either increases or decreases contamination of marine organisms (also see 4.6.2 below).

Another important potential hazard of oil and petroleum products to humans is fire and explosion. Because chemically dispersed oil is in fine droplets in the water column, mass transport through the water to the vapour phase might be expected to be more difficult, evaporation might be slowed, and fire hazard would be less. On the other hand, because of the larger surface area presented by small droplets, the mass-transport rate and evaporation rate might increase.

Some experimental evidence on this point is provided by an investigation of the use of dispersant to aid flushing of fuel spilled into sewers (Fingas *et al.*, 1989f). These results supported the second hypothesis. Dispersant increased the volatilization rate and hence the amount of vapour; therefore dispersants apparently do not act to diminish explosion hazard.

As mentioned above (section 4.2.3), gelling agents are used to reduce the volatility of light fuel oils and thereby diminish fire hazards (MDPC, Tokyo, pers. comm.).

4.6 Effects on man's use of the sea

4.6.1 Fishing gear

No reported studies on dispersed oil contacting fishing gear have been found. However, it seems reasonable that, since dispersed oil is less adherent to surfaces (NRC, 1989), fouling of fishing gear would be mitigated by application of dispersants to an oil slick. Dispersant formulations are sometimes used to clean oiled nets.

4.6.2 Fish tainting

There is no published experimental evidence on the effect of dispersants on tainting in fish, but, for the same amount of hydrocarbon in the water, dispersants do not alter uptake or toxicity (NRC, 1989), and hence tainting is not likely to be affected. Absorption through the gut of fish is small; most absorption in fish is through the gills and tends to follow an equilibrium partitioning model. Wilder (1970) compared the tainting of lobsters painted with crude oil and with crude oil-dispersant (an early Corexit formulation), and found no difference.

4.6.3 Aquaculture

Fouling of nets and floats is an important impact of oil spills on aquaculture facilities, and dispersing the oil would be expected to reduce that impact (cf. 4.6.1).

A spill of light crude at Milford Haven, Wales, in 1989 moved up the estuary and contaminated cages at a trout farm. The owners were advised not to clean the cages *in situ*, but to take them ashore, clean them with a proprietary dispersant/degreaser, and prevent the wash fluids from re-entering the farm waters, where they might be retained in the bottom silts (Blackman, pers. comm.).

Studies on salmon (NRC, 1989) showed no significant difference in survival or return to their home pond of fish exposed either to untreated oil (0.5 mm slick) or to chemically dispersed oil (105 ppm).

When the *Exxon Valdez* spill first occurred, considerable effort was made to protect fish hatcheries in Prince William Sound, particularly Sawmill Bay, where 150 million salmon fry were scheduled to be released (Bayliss *et al.*, 1991; Skinner and Reilly, 1989; Davidson, 1990). Since the water near the grounding site was of the order of 30 m deep, dispersal of the oil, and its dilution to non-toxic concentrations, might have been important elements in protection of the fish hatcheries. However, protests against chemical dispersants from fishermen's representatives (Davidson, 1990) resulted in reliance on local mechanical containment, which appears to have been successful (Noerager and Goodman, 1991; Ciancaglini, 1991).

4.6.4 Beaches and other public amenities

Dispersal of an oil slick offshore can reduce the eventual adherence of the oil to beach sand, piers, and boats, and thus mitigate the impact. Application of dispersants to stranded oil tends to make the oil penetrate more deeply into the sediments and thus worsens the impact (NRC, 1989).

4.6.5 Wildlife sanctuaries and marine parks

As noted in Section 4.3.1, direct application of dispersants to birds or marine mammals is hazardous because it can destroy the water repellency of their plummage or fur. Therefore application of dispersants by aerial spraying should not be done near known nesting, breeding or haul-out areas.

As noted in sections 4.3.2 and 4.4.2, the short-term impact of an oil spill on a coral reef area can be increased if the oil is dispersed at high concentrations on the reef, and hence dispersal away from the reef was recommended. The impact on mangroves is definitely reduced by dispersal of oil; dispersal may make the difference between loss of the mangrove community and its survival (NRC, 1989).

4.6.6 Water intakes – public and industrial

In some regions of the world – such as Bermuda, several Caribbean islands, and the Middle East – desalination plants provide an important source of drinking water. Oil, even when naturally dispersed, can enter the intake of such a plant and contaminate an entire drinking water supply with hydrocarbons (Kruth *et al.*, 1987). Cooling-water intakes for power plants are similarly vulnerable.

4.6.7 Other economic considerations

The NRC (1989) report notes, without evidence, that there is considerable economic incentive in coastal recreational areas to protect beaches from spills or to clean them up quickly. Clean-up of contaminated boats, sea walls, and harbour equipment can be expensive. In a marina where boat owners pride themselves on the appearance of their craft, pressure for clean-up is likely to be even more intense than in an industrial harbour.

Costs of mechanical clean-up of oil (spill sizes of 10,000 to 100,000 bbl) have, in the past, ranged from $10 per bbl to $5,000 per bbl, with an average of $600 (White and Nichols, 1983; Lasday, 1989; Moeller *et al.*, 1987). Operation of aircraft and vessels at sea and shoreline clean-up are the most expensive components. When dispersant has been effective, total costs have ranged from $15 per bbl to $65 per bbl (Lasday, 1989); however, when dispersants were used on spills of heavy fuel oil they were not effective, and total costs were $460 to $680 per bbl (Moeller *et al.*, 1987).

The 240,000 bbl *Exxon Valdez* spill (Skinner and Reilly, 1989) cost vastly more than those in the past. Exxon paid $235 million in claims without protest immediately after the spill (OSIR (Oct. 4, 1990) 1990b) and spent approximately $2 billion on clean-up in 1989 and $200 million in 1990 (OSIR Sept. 20, 1990) 1990b). The State of Alaska made $21 million in grants during 1989 (OSIR (Nov. 9, 1989) 1990b). Exxon settled with the United States and Alaska for $1.125 billion (OSIR (October 10, 1991)). The total of these items, $3.56 billion, yields an estimated clean-up cost of $15,000 per bbl!

4.7 Conclusions

Most of the research to date (Nov. 1991) on spill control agents has been concentrated on chemical dispersants. Very little research, particularly field tests, has been published yet on any other agents, including solidifiers and biodegradation enhancers.

Dispersants, properly applied, can help remove oil from the water surface and dilute it to non-toxic concentrations. This reduces the impact of oil on surface wildlife and the risk of contamination of the shoreline. More valuable, but less well-known, is that the application of dispersants to oil before it strands on a shoreline can reduce the adhesion of oil to structures, sediments and organisms, and can reduce the environmental impact, particularly to mangrove habitats.

Recovery enhancers (i.e. elasticizer additives) may improve the efficiency of mechanical clean-up, particularly for small spills. Emulsion breakers (i.e. demoussifiers) also show promise.

Chemical dispersant formulations currently in use have an acute toxicity less than that of many crude and refined oils. The toxicity of chemically dispersed oil is no greater than that of mechanically dispersed oil at the same concentrations.

Application of dispersant or hot water to oil that is stranded on structures or rocky shores can re-mobilize the oil, but the dispersed oil may be transported to the sublittoral zone. Application of dispersant to oil stranded on a sandy beach tends to increase its penetration into the sediment.

Dispersal of oil in shallow water with poor circulation increases the exposure of benthic and subsurface organisms, and can intensify acute toxic effects at or near the point of application, yet it can reduce the chronic effects, due to decreased residence time.

Elasticizer additives may improve the efficiency of mechanical clean-up, particularly for small spills. Gelling agents are useful for reducing fire hazard in enclosed spaces, by reducing the loss of volatiles.

4.8 Recommendations

Laboratory and field studies should be conducted to elucidate quantitatively the roles of adhesion and absorption in the environmental impact of oil and dispersed oil.

Additional investigations on the toxic effects of both untreated oil and dispersed oil on surface-dwelling organisms that could be affected by oil slicks are desirable.

Long-term studies are needed of the recovery of selected ecosystems where oil and dispersed oil has impacted. These would be particularly useful if carried out at sites where the effects of oil and dispersed oil have already been studied on a shorter time-scale. As restoration projects are attempted in seagrass, mangrove and other habitats, they should include a long-term study of how thoroughly the habitat has been restored. Internationally organized laboratory and field studies should continue, to document the long-term effects of dispersed oils on shallow-water marine communities, at all latitudes.

Laboratory studies should be conducted to determine the effect of chemically dispersed oil, under exposure conditions comparable to those expected in the field, on the water-repellency of fur and feathers and on the filtration capacity of whale baleen.

Research is required on the mechanics of the resurfacing and spreading of dispersed oil to guide improvement in strategies for the application of dispersants.

Changes are made in dispersant formulations but are not often made known outside the manufacturing company; such changes decrease the value of research using proprietary products, and should be made explicit by the manufacturer.

Research is needed on additives which improve the efficiency of mechanical clean-up.

Internationally organized experimental spills are needed for a number of research objectives, such as:

- to improve remote sensing of movement of slicks, of the thickness of a slick on water, and of oil on shorelines;
- to find techniques for applying dispersants and other treatment agents to the thickest part of the slick in the most effective form (optimum droplet size and concentration);
- to obtain quantitative field data on the adherence of dispersed oil to surfaces and the resulting long-term persistence and ecological effects of the oil;
- to obtain quantitative field data on the effectiveness (fraction of slick dispersed and time to resurfacing of the dispersed oil) of different dispersants under different environmental conditions with different types and degrees of weathering of oil;
- to assess the ecological effects and effectiveness of bioremediation, chemical washing, and other methods of treating the shoreline; and
- to evaluate adequately both the technology for burning *in situ* and the chemistry of combustion emissions from small and mesoscale field trials. These should be performed in a variety of ocean environments with different types of oil and degrees of weathering. The studies should focus on the efficiency and completeness of burning, the chemistry and environmental fate of combustion products of the burn, and biological effects on local organisms.

Chapter 5 Wastes from offshore petroleum operations

5.1 Introduction

This chapter focuses on the fates and effects of wastes associated with offshore oil and gas exploration and production. Waste substances are discharged routinely during normal oilfield practices and form a part of the waste stream entering the marine environment. The past fifteen years, since publication of GESAMP (1977), have seen many advances in understanding the impacts from such discharges, as well as the development of new technologies to minimize the input.

Information and data on these issues are available mainly from the North Sea and from Canadian and United States exploration and production areas only.

This chapter addresses a number of questions of environmental relevance, such as:

> What quantity of waste substances is introduced to the marine environment during exploration and production, on both a local and a regional basis?
>
> What is the relative importance of discharges from the oil and gas industry in relation to the many other anthropogenic inputs into the marine environment?
>
> To what degree do the effects of exploration and production differ in spatial and temporal dimensions?
>
> How persistent are the effects; when does recovery occur?
>
> Are there any particularly sensitive marine environments which require special consideration, and how good is the database for these?

5.2 Sources and types of waste discharges

Exploration involves the drilling of wells to determine the nature of potential hydrocarbon reservoirs. These operations are of short duration at a given site, lasting only weeks to a few months, and usually involve only one well. The wells tend to be drilled in a vertical orientation and with water-based drilling muds, although oil-based drilling muds are being used with increasing frequency for exploration drilling. Discharges are composed mostly of drilling fluids and drill cuttings.

Development drilling follows the drilling of wildcat or exploratory wells, and may continue into the production phase of operations when the commercial reservoir is being exploited. These operations usually involve a large number of wells, many of which are deviated or step-out wells drilled with oil-based drilling mud, and are typically conducted from a fixed platform. There is, however, a trend in many of the offshore development areas to use many single vertical wells and sub-sea completion to develop a field. Discharges include drilling fluids, drill cuttings, and well-treatment fluids.

Table 5.1: ***Typical quantities of wastes discharged during offshore oil and gas exploration and production activities***

	Approx. amounts (tonnes)
Exploration sites (ranges for a single well):	
Drilling mud – periodically	15 to 30
– bulk at end	150 to 400
Cuttings (dry mass)	200 to 1,000
Base oil on cuttings	30 to 120 (a)
Production site (multiple wells):	
Drilling mud	45,000 (b)
Cuttings	50,000 (b)
Production water	1,500/day (c)

(a) Actual loss to environment may be higher (Chenard *et al.*, 1989)

(b) Estimate based on 50 wells drilled from a single offshore production platform, drilled over 4 to 20 years (Neff *et al.*, 1987)

(c) From a single platform (Menzie, 1982)

Production activities begin as each well is completed during the development phase. The production phase involves active recovery of hydrocarbons from producing formations. Development and production activities may occur simultaneously until all wells are completed or reworked. Waste streams of production water are the largest discharges during production operations. The bulk volumes of typical discharges from offshore oil and gas activities are shown in Table 5.1. Major discharges, in terms of quantity, are predominantly formation water, derived from the petroleum reservoir, as well as drilling fluids and cuttings, ballast water and storage displacement water. Minor discharges usually include produced sand, deck drainage, well-completion and workover fluids, cement residues, blowout-preventer (BOP) fluid, sanitary and domestic wastes, gas and oil processing wastes, slop oil, cooling water, desalination brine, and test water from the fire-control system. Atmospheric emissions and inputs from flaring are largely unquantified.

Drilling fluids are those materials used to maintain hydrostatic pressure control in the well, lubricate the drill bit, remove drill cuttings from the well, and stabilize the walls of the well during drilling. Once formulated and in use, the drilling fluid is usually referred to as a drilling mud. Drill cuttings are the solids resulting from drilling into sub-surface formations, and are brought to the surface of the well in the drilling-fluid system. Drilling fluids and cuttings are processed through a solids-control system and, as needed, a supplementary cuttings-treatment process. Drilling fluids and any cleaning fluids used to clean cuttings are largely recycled, while cuttings are disposed of overboard or, in circumstances where drilling occurs in particularly sensitive areas, may be transported to either an offshore disposal site or to shore for further treatment and disposal. Spent water-based drilling muds are usually dumped overboard at the end of drilling the well, while oil-based muds are usually recycled and reprocessed.

An issue surrounding the discharge of drilling fluids is the use of drilling-fluid lubricants, which are used to combat occasional problems of differential sticking and increased torque during drilling, especially in overpressured formations or when drilling deviated wells. These lubricants are typically hydrocarbon-based, and may be added as a 'slug' or 'pill' (i.e. a single bulk volume introduced to the circulating muds which remains segregated in the system, at least initially) or be an initial component of the drilling-fluid mixture, in particular of water-based drilling fluids. Relatively large volumes of the hydrocarbon lubricant can be discharged if the lubricant pill is not recovered or when the water-based drilling mud is dumped at the end of the drilling period. An investigation of the situation in the Canadian offshore showed that, for exploration wells, diesel pill/lubricant volumes ranged from approximately 1 to 100 m^3 (Engelhardt, 1990, pers. comm.).

Well-treatment fluids are used in stimulating a hydrocarbon-bearing formation, in reworking a well to increase or restore productivity, and in completing a well for oil and gas production.

Production water is usually brought up from the hydrocarbon reservoir during the production of oil and gas. The proportion of water to petroleum will vary with the particular formation, and typically increases with the production life of the field so that water may become the predominant fluid. Production water includes brine, brought up from the hydrocarbon-bearing strata along with produced oil and gas, as well as formation water, injection water, and any chemicals circulated downhole or added during the process of oil/water separation. The global offshore input of hydrocarbons from discharges of production water was estimated to be between 7,500 and 11,500 tonnes per year (NRC, 1985); this estimate has since been revised to 47,000 tonnes per year (see Section 2.3.2, 1990 estimates). Davies *et al.* (1989) present figures showing that about 10% of the oil discharged by United Kingdom offshore petroleum exploration and production comes from production water, but this proportion is expected to rise steadily as fields come to the end of their workable life and controls on discharging of oil-based muds become stricter. Latest PARCOM (1991) statistics indicate that about 20% of oil discharged from North Sea petroleum operations in 1989 came from production water.

Produced sand consists of the accumulated formation sands that are generated during production and the slurried particles used in hydraulic fracturing. Such sand is coated with formation hydrocarbons.

Oil/water separators are the usual method for treatment of produced water, produced sand, completion fluids and workover fluids, storage-displacement water, ballast water, deck drainage and bilge water. Discharge from the oil/water separator is usually overboard, but might also be piped to an offshore outfall or injected into the formation.

Desalination waste, cooling water, and domestic liquid wastes are commonly discharged untreated.

Sanitary wastes originate from toilets and domestic wastes originate from sinks, showers, laundries, and galleys located on drilling and production facilities. Sanitary wastes often undergo chlorination before discharge to the sea.

Atmospheric emissions originate from flaring of hydrocarbons and from exhausts from generating plant and machinery. Combustible wastes are at times burned on board the drilling unit, when they are not shipped to shore. There has been little investigation of this type of waste, although fallout from flaring was considered an issue at a Beaufort Sea production test well in 1988 (Canada Oil and Gas Lands Administration, unpublished data). In this instance, a heavy oily residue was deposited on the ice surrounding the test site which, upon analysis, was determined to be similar to the produced crude oil, consisting of higher-molecular-weight fractions of the crude oil. Fallout slicks from offshore flaring are considered to be regular features of well-testing at North Sea installations, but these are intermittent and usually of short duration. However, inputs from flaring are not well quantified at present, and there are unpublished reports that they contribute large quantities of hydrocarbons, in particular PAHs, to the marine environment. Claims have been made that up to 30% of hydrocarbons flared during well testing may escape combustion and end up in the sea (Kingston, 1991). Recent data from the Valhall field indicated that, during one day of well testing, the incidental loss to the sea was over 350 metric tons (Reiersen, 1991, personal communication). Treatment, in these instances, may be limited to improving the efficiency of combustion systems.

Pipeline discharges occur when produced oil and gas is piped to shore for further processing. The discharges consist of chemically treated water, cleaning agents such as methanol, and gel 'pigs' to separate or drive transported fluids. Such discharges are also associated with the construction, hydrostatic testing, commissioning and maintenance of the pipelines. Although the volumes in the North Sea may be very large (e.g. 300,000 m^3 of treated water), such discharges are infrequent and of short duration (hours to days). Chemically treated or 'inhibited' water typically contains a biocide, an amine corrosion inhibitor, and bisulphite salts to scavenge free oxygen. The chemicals typically used in the North Sea, for example, are of low acute toxicity and high degradability.

5.3 Regulatory controls

Regulatory controls governing the discharges from offshore oil and gas activities vary among the jurisdictions and change over time as new information on the effects of discharges is assessed. An overview of permitted offshore discharges is summarized in Table 5.2 (Neff *et al.*, 1987). Discharge guidelines in the United States and Canada reflect these elements. A protocol for the protection of the Mediterranean Sea is also under preparation which includes control of discharges from exploration and production operations (UNEP, 1991). However, in many regions of the world the materials used offshore are discharged into the sea without control regulations either at the national or the international level.

In the case of the North Sea, discharge regulations vary between national sectors, but all are designed to meet the requirements of the 1974 Paris Convention on the Prevention of Marine Pollution from Land-based Sources. Oil in water discharges must meet a 40 ppm standard, while residual petroleum-derived oil on cuttings from the use of oil-based drilling muds must meet an oil on dry solids standard of 100 g/kg before discharge. Further, it is intended that, by 1994, all polluting discharges of oil-based muds on cuttings from exploration and appraisal wells will cease, and a date for their cessation from development wells will have been set. Recent developments of the technique for disposal of cuttings by reinjecting a slurry of the ground-up material into a geological formation, which has been used successfully in Alaskan waters and the Gulf of Mexico, may be a practical way to achieve zero discharge of oil from this source. The use of diesel-based muds is banned in the North Sea. There are as yet no Paris Commission (PARCOM) standards for chemical discharges, but a Harmonized Scheme for Testing and Evaluation is being developed, from which each national authority will set its regulatory controls. This will seek to eliminate the discharge of materials in Part I of Annex A to the Paris Convention (organohalogens, mercury and cadmium and their compounds, persistent synthetic materials, persistent petroleum

Table 5.2: ***Major permitted discharges and potential impact-causing agents associated with offshore oil and gas exploration and production***

Drill cuttings – 1100 tonnes/exploration well, less for development well

Drilling fluids – 900 tonnes/exploration well, 25% less for development well

Cooling water, deck drainage, ballast water – may be treated in an oil/water separator

Domestic sewage – primary activated sludge treatment

Sacrificial anodes, corrosion, antifouling paints – may release small amounts of several metals (Al, Cu, Hg, In, Sn, Zn)

Production water – treated in oil/water separator to reduce total hydrocarbons to mean of 48 ppm, daily maximum 72 ppm

Source: Neff *et al.*, (1987)

compounds, and substances which cause taint), to reduce inputs of materials in Part II (organic compounds of phosphorus, silicon and tin, non-persistent petroleum compounds, arsenic, chromium, copper, lead, nickel, zinc and their compounds), and to forestall or eliminate discharge of substances in Part III (radioactive substances). The Commission aims to base controls on lethal/sublethal tests in four trophic compartments, as well as on biodegradability and bioaccumulation potential. It is the current position of PARCOM (circa 1991) that all materials used offshore require controls.

5.4 Chemical composition of exploration and production wastes

From the perspective of environmental hazards, the concern should be less over the origin of the discharge than over its chemical nature, amount and biological availability. There are relatively few discharges which can be considered significant in size or potential toxicity.

5.4.1 Drilling fluids

Drilling fluids are discharged in exploration, development and production drilling, and may involve water-based or oil-based drilling muds, or both. The choice of potential constituents is enormous and encompasses over a thousand different products on the drilling-fluid market. The significant components, from the perspective of problems associated with discharge, are fewer, although still numerous.

Typical compositions of water-based mud have been described by regulatory agencies (e.g. U.S. EPA Generic Drilling Fluid), by individual investigators trying to achieve some standard testing approach, and by petroleum industry associations. The United Kingdom Offshore Operators Association (UKOOA), has provided data on a typical water-based mud composition such as that used in the North Sea and in other offshore areas (UKOOA, 1990, pers. comm.; also see Table 5.3).

Minor constituents of water-based drilling muds include inorganic salts, surfactants and detergents, corrosion inhibitors, lubricants (diesel and mineral oils as spotting agents or pills, and as general lubricants in the form of an oil-in-water emulsion), biocides and a variety of specialty additives for unique drilling problems.

Table 5.3: ***Base mud composition for a water-based drilling mud, showing components common to nearly all muds***

Component of mud	Amount (pounds per barrel*)
Bentonite	0 to 50
Barite	0 to 500
Caustic soda	0 to 5 (can be substituted by caustic potash)
Soda ash	0 to 3 (can be substituted for sodium bicarbonate)
Sodium bicarbonate	0 to 3 (as soda ash)
Seawater	Any proportion
Fresh water	Any proportion – normally in prehydrated bentonite
Drill solids	0 to 100

* one pound per barrel = 2.851 g ℓ^{-1}

Source: U.K. Offshore Operators Association, 1990., pers. comm.

A more detailed description of the additives in water-based muds is given in Table 5.4. Formulations of drilling fluids are evolving all the time in response to new technical developments and needs. For instance, the continuing concern about the use of oil-based drilling muds in the North Sea has led to advances in water-based mud formulations to try to match the mineral-oil-based drilling muds in performance, such as the development of new lubricants and shale-stabilizing agents.

Relatively few substances form the major components of oil-based drilling muds, although the number of minor components which may be used is very large. Typical compositions, showing the major components, are shown in Table 5.5.

There was a shift during the 1980s away from the use of diesel oil as the oil phase in an oil-based drilling mud towards 'non-toxic' or 'low-toxicity' mineral oils, basically paraffin oils. No diesel-oil-based mud has been used in the North Sea, for instance, since I985. Efforts to replace the current low-toxicity mineral-oil muds with newer formulations based on 'non-mineral oil' liquid phases in the drilling mud continue. Details of these compositions are not yet released, but they are derived from animal, vegetable or synthetic organic products (Blackman, 1990, pers. comm.).

Attention has been paid to the discharge of heavy metals along with drilling muds and cuttings. Mercury, chromium, zinc, cadmium, copper, lead and nickel can come from components of drilling fluids, including the weighting agents (e.g. barite) and residual pipe-dope and threading compounds. The drill cuttings themselves can be contributors to the discharge of heavy metals. The issue is well reviewed in Thomas *et al.* (1984) and Neff *et al.* (1987). Formation water is usually low in heavy metals in comparison to drilling discharges.

5.4.2 Production water

The composition of production water includes dissolved salts, dissolved and colloidal hydrocarbons, dissolved organic compounds, trace metals, chemical additives used during

Table 5.4: ***General water-based mud types, denoting additives that mud types may contain***

	FLUID LOSS ADDITIVES AND VISCOSIFIERS							DISPERSANTS/THINNERS				SHALE INHIBITORS		ELECTROLYTE pH ADJUSTMENT					SPECIALITY PRODUCTS			
GENERIC MUD TYPE	OMC[1]	PAC[2]	Starch	Poly-acrylate	High temp Polymer	Xanthan gum	Guar gum	Ligno-sulfonate	Lignite	Low mol. wt. p. acrylate	Methylated tannin	PHPA[3]	Gilsonite	Potassium Chloride	Sodium Chloride	Gypsum $CaSO_4$	Caustic Potash	Lime $Ca(OH)_2$	Biocide	Oxygen Scavenger	Corrosion Inhibitor	Lubricant
Minimum concentration ppt	0.25	0.25	1	0.25	0.25	0.1	0.25	0.1	0.1	0.1	0.25	0.1	1	5	0	2	0	0.1	0.1	0.1	0	1
Maximum concentration ppt	8	6	12	4	10	4	4	15	15	1(?)	4	3	12	90	108	8	5	20	2	1	10	20
BASE MUD													X						X	X	X	X
BASE/POLYMER FL	X	X	X	X									X						X	X	X	X
BASE/POLYMER VIS	X	X	X	X		X	X						X						X	X	X	X
BASE/HIGH TEMP POLYMER	X	X		X	X				X	X	X		X						X	X	X	X
BASE/POLYMER INHIB	X	X	X	X	X	X						X	X						X	X	X	X
BASE/ELECTROLYTE INHIB	X	X	X	X	X	X						X	X	X	X	X	X	X	X	X	X	X
BASE/DISPERSED								X	X	X	X		X						X	X	X	X
BASE/DISPERSED/POLYMER	X	X	X	X	X	X		X	X	X	X		X						X	X	X	X
BASE/DISPERSED INHIB	X	X	X	X	X	X		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
BASE/SALT SATURATED		X	X		X	X		X	X	X	X	X	X		X					X	X	X

[1] OMC = oxymethylcellulose

[2] PAC = polyanionic cellulose

[3] PHPA = partially hydrolysed polyacrylamide

Source: United Kingdom Offshore Operators Association (UKOOA) 1990

Table 5.5: ***Composition of oil-based drilling muds***

Component of mud	(a)	(b)
Mud weight	1.2 g/cm^3	
Low-aromatic oil (paraffin)	30% (b)	31.3
Water	29%	
Barite	27%	60.8
Sodium chloride	12%	
Calcium chloride		
Lime	2%	0.2
Clay (organophilic clay)		
Emulsifier (fatty acid amide)		2.2
Dispersant and oil wetting agent (modified imidazoline)		1.8
High-temperature stabilizer (Gilsonite/asphaltene)	3%	
Dispersant (calcium sulphonate)		
Emulsifier component (calcium oxide)		
Viscosifier		0.2

(a) Quantity by volume. Source: Chromalloy (1982), in Thomas *et al.* (1984).

(b) Quantity in percent by volume. Source: Davies and Kingston, in press.

petroleum production processes, and suspended solids. The formation-water component of production water is, in effect, a brine which derives its salinity predominantly from the major ions also found in seawater (e.g. sodium, calcium, magnesium, potassium, chloride, sulfate). The concentration of dissolved salts ranges from less than 3 g/ℓ to about 300 g/ℓ, although most formation waters are considered of marine origin and are greater in salinity than seawater (Collins, 1975). Sulfur levels can also be quite high. Neff *et al.* (1987) determined that the metals barium, beryllium, cadmium, chromium, copper, iron, lead, nickel, silver and zinc can be present at substantially higher concentrations than in seawater. The usual environmental concern, however, revolves around the total quantities of petroleum-derived hydrocarbons and related organic compounds released to the sea, and the aromatic components in particular. Somerville *et al.* (1987) report that formation water from North Sea reservoirs contains about 0.1% non-hydrocarbon organic matter, predominantly salts of the lower-molecular-weight fatty acids. It also contains 20 to 40 ppm dissolved hydrocarbons, mainly benzene, toluene and C_3-alkyl benzenes.

Formation water also contains small amounts of radionuclides, particularly radium-226 and -228, as well as their radiodecay daughters. Radionuclides in formation water precipitate when they come into contact with sulphates in sea water and form a radioactive scale. The formation of scale can concentrate the radioactivity until it reaches a level when it needs to be disposed of as a radioactive waste. Although the levels of radioactivity are low, the introduction of radioactive substances and wastes into the sea is addressed by international conventions (e.g. London Dumping Convention 1972) and is receiving continued attention as a regulatory issue in many countries.

Oil/water separation systems act to remove particulate or dispersed oil, but are not effective in removal of dissolved petroleum hydrocarbons and related organic compounds. The amount dissolved depends on the fractional composition of the petroleum and is inversely related to the molecular-weight distribution of the hydrocarbon fractions. Analyses by Middleditch (1981), Sauer (1981), and Jackson *et al.* (1981) show a range of concentrations for hydrocarbons in production-water effluents from less than 20 to over 50 ppm, with a high degree of variability in relation to both source and method of analysis. Data from the North Sea show similar concentrations (Somerville *et al.*, 1987).

Once oily water from various sources has gone through the oil/water separator, the so-called produced water effluent derives its chemical composition not just from formation water (although this is the major waste stream) but also from other inputs such as deck drainage, ballast water and displacement water. These inputs contribute a variety of other organic and inorganic contaminants, although they tend to be minor in their overall contribution to the waste discharge.

5.4.3 Sanitary wastes

There has been some concern about the practice of treating sanitary wastes with free chlorine, and the interaction of discharged residual free chlorine with hydrocarbons and other organic components in the waste stream, potentially forming organochlorine compounds. However, under usual discharge conditions, even in the photic zone and at the sea surface, such interactions are very unlikely to produce high concentrations of compounds more complex than mono- and di-substituted aromatics such as the chlorophenols. The risk is of possible tainting of sessile or resident organisms in the water column in the immediate path of the discharge, rather than a health risk to the eventual consumer from complex organohalogens. For this reason, chlorination is probably best avoided at installations very close to shallow beds of commercially harvested invertebrates or close to ground fisheries, and alternative treatment methods should be used. Potent mutagenic compounds are known to be produced in trace amounts during chlorination of sewage (Payne *et al.*, 1980) but the fate and significance of these in marine ecosystems has yet to be determined.

5.4.4 Surfactants

Apart from the use of ferro-chrome, chrome, sodium and calcium lignosulphonates, sulphonated lignites, sulpho-methylated tannins and sodium asphalt sulphonates as components in drilling muds, surfactants are widely used in other mud additives, cuttings cleaners, degreasers, corrosion inhibitors and descalers. In May 1990 there were at least 91 products, from 27 suppliers, on the lists of the U.K. Notification Scheme for the Selection of Chemicals for Use Offshore which contained surfactants as primary or secondary components. Using the toxicity classification of Column B of the IMO Hazard Evaluation Assessment (GESAMP, 1989), 84% of products listed under the U.K. scheme fall into the less toxic categories 0 to 2. (Based on 96-hour LC_{50} determinations, 0 represents acute lethal toxicity at greater than 1000 mg/ℓ, 1 at 100 to 1000 mg/ℓ, and 2 at 10 to 100 mg/ℓ.)

5.4.5 Biocides

There are special concerns about the use of biocides in offshore activities. There were 117 products, supplied by 37 companies, listed as biocides in the U.K. Notification Scheme for the Selection of Offshore Chemicals in April 1990 and therefore available for use by the offshore oil and gas industry. However, the number of different compounds used was much smaller (49), although some compositions are known only in generic terms, such as aliphatic dialdehydes, quaternary ammonium salts, oxyalkylated phenols, fatty diamines or isothiazolines. By far the most numerous, and the largest by amounts used after sodium hypochlorite, are the formalin-releasers and glutaraldehyde. These form part or all of at least 31 products. A biguanidine salt is also widely used, and a variety of quaternary ammonium salts is also very popular. Thiazolines and their derivatives are less widely used. The use of carbamates or thiocarbamates is strongly discouraged. The use of pentachlorophenates and dichlorophenols has been banned. Using the aquatic toxicity classification of the IMO Hazard Evaluation Assessment (GESAMP, 1989), two-thirds of the biocides listed in the United Kingdom fall into the 'less toxic' categories of 0 to 2.

The concern about biocides is equal in the Canadian and the United States jurisdictions, with similarly restrictive regulations being in place or under consideration. Aldehydes and quaternary amines are in common use and many chlorinated hydrocarbons are prohibited.

5.4.6 Chemicals for enhanced recovery of oil

This is an area which, to date, has seen little application offshore. This situation may change as more oil fields reach the end of their normal production life. Enhanced oil recovery treatment has been carried out with propane and CO_2, as well as by polymer flooding, using latex polymer. In neither instance is this likely to pose a chemical hazard in marine waters.

5.5 Environmental effects

5.5.1 Drilling discharges

The various organic and inorganic, water-soluble and insoluble, volatile and non-volatile components of drilling-waste discharges have seen much evaluation in recent years for short-term and long-term toxicities (Boesch and Rabalais, 1987). A recent detailed review of the issue of drilling wastes, of both water- and oil-based drilling muds, has been published as the proceedings of the 1988 International Conference on Drilling Wastes (Engelhardt *et al.*, 1989). The following discussion presents the main concerns about the environmental effects of drilling discharges from exploration and production. It should also be noted that ecological concerns about oil in drilling discharges/wastes, and recent developments in the use of reinjection as a means of disposal of cuttings, are leading to rapid changes in regulatory strategies in the North Sea oil fields (Kingston, 1991, pers. comm.).

Acute toxicity tests have been carried out on many drilling mud formulations, usually according to some 96-hour LC_{50} protocol. A summary of acute marine toxicity data for selected drilling muds is presented in Figure 5.1 (Thomas *et al.*, 1984). Similar reports exist for phytoplankton (Østgaard and Jensen, 1985). It is evident that, while the toxicity is species-specific, some generalities can be made. For instance, values of 96-hour LC_{50} for the majority of formulations are in an approximate range of 1 to 10%. The range of LC_{50} values over species is usually less than 100-fold for a particular mud system. Because the usual standard tests have been made with laboratory species, suitable for toxicity screening purposes, new trophic-level test data are needed, using species from the field. Typical clay–

chrome lignosulphonate muds are only slightly toxic (LC_{50} values of 0.1 to 1%) to practically non-toxic (LC_{50} greater than 1%) for most organisms, using the acute toxicity standards of IMO (GESAMP, 1989). Oil-based drilling muds are not dissimilar from water-based muds except the diesel-oil-based muds, which show a toxicity 3 to 260 times greater than the paraffinic, low-toxicity, mineral-oil-based drilling muds. It is generally accepted that it is the emulsifiers and surfactants used in oil-based mud formulations which make the greatest contribution to acute toxicity (e.g. Østgaard and Jensen, 1985).

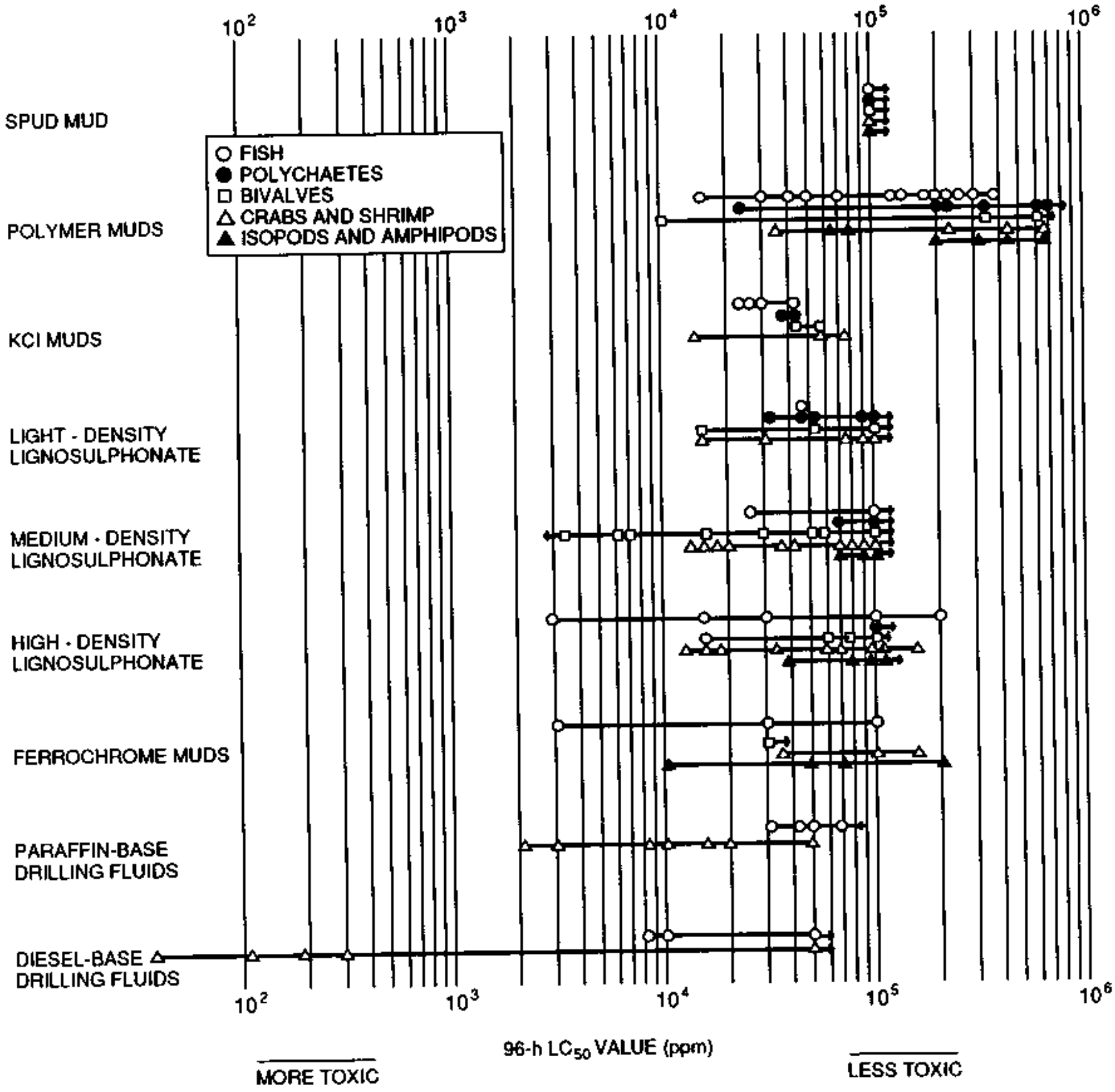
The fate and bioavailability of heavy metals from drilling muds and cuttings has seen much attention. Barium, chromium, lead, mercury, zinc and cadmium are found in various drilling muds, especially in weighting agents. In exploratory drilling, these metals generally are restricted to an area less than one hundred metres from the drilling site. On a basis of mass balance, the retention of metals in sediment was found to be low, suggesting active redistribution; only barium was found to be present in significant quantities (Boothe and Presley, 1989; Bothner *et al.*, 1985). The energy regime of the discharge site influences the retention of metals from drilling wastes, as demonstrated for disposal of cuttings from exploration wells at three low-energy Arctic sites (Snyder-Conn *et al.*, 1990).

Much of the information on fate and effects for drilling discharges from production comes from the North Sea, which can conveniently be sub-divided into two parts. The waters of the more shallow (less than 50 m) southern North Sea are well mixed almost all the year round but the deeper northern North Sea (100 to 200 m) is strongly stratified in the summer. The flushing time of the whole North Sea is of the order of one year, but flushing is generally faster in the south (0.3 year) and slower in the deeper northern waters. Oil fields are concentrated in the north; gas fields are in the south (Davies and Kingston, in press). Around some multi-well sites in the North Sea, elevated concentrations of heavy metals in sediment have been reported out to 1,000 m, but the elevations do not always correlate with elevated barium levels, suggesting that they are derived from sources other than the barite weighting agent (Blackman, 1991). Most commonly, heavy metals in drilling muds are present as sulfides, which have been found to be of low bioavailability and toxicity in laboratory evaluations.

The methods available for determining the spatial distribution of discharged drilling wastes have been limited. Although barite is frequently used to determine the extent of deposition of solids around a drilling site, a useful method for lignosulphonate muds has been described only recently (Sauer *et al.*, 1989). When oil-based drilling muds are used, measurement of hydrocarbons in sediment is a good method for fingerprinting the contamination source and is quantitative (Erickson *et al.*, 1989; Yunker and Drinnan, 1987), at least when single wells were drilled or only one mud type was used.

The discharge of diesel oil, when used as a drilling-fluid lubricant in circumstances of differential sticking or increased torque, continues to receive attention in Canada and the United States. Recent studies have shown that most of the diesel oil goes into the water column upon discharge, rather than into the sediment, and dissipates rapidly (Boehm *et al.*, 1989). Regulatory questions remain about residual toxicity of the mud after attempted removal of the diesel pill from the mud system and about an acceptable level of diesel in mud for bulk discharge of a diesel-lubricant-contaminated water-based drilling mud.

Figure 5.1 ***Lethal toxicity ranges of generic types of drilling mud with major groups of marine fauna***



Source: Thomas *et al.*, (1984)

Field studies demonstrate a relationship between the amounts of oil-based drilling cuttings accumulated at production sites and the degree of change in biota in the receiving area. Oil-based drilling muds are implicated as primary causative agents. The following major changes have been identified (Addy *et al.*, 1984; Davies *et al.*, 1984; Dicks *et al.*, 1987; Drangsholt *et al.*, 1988; Gray *et al.*, 1990; Reiersen *et al.*, 1989; Somerville *et al.*, 1987; Vogt *et al.*, 1988):

- bioaccumulation of hydrocarbons in fish and invertebrate tissues;
- physiological changes in fish, including induction of detoxifying enzymes;
- smothering of benthos by physical covering as well as reduction of oxygen levels from organic loading and from induction of sulphur-reducing bacteria; and

- community changes in benthos.

Examples of two effects are given in Figures 5.2a and 5.2b. However, field observations have not shown that the use of 'low-toxicity' mineral-oil-based drilling muds gives a marked improvement in the impact of the discharge of cuttings (Kingston, 1987; Reiersen *et al.*, 1989).

Questions also continue on the relative environmental advantages of oil-based versus water-based drilling muds. The concerns are raised mainly in production scenarios (Davies *et al.*, 1989; Reiersen *et al.*, 1989). Experimental studies suggest that recovery rates may be lower when oil-based muds are used as compared to water-based muds, but these studies used high loading levels of contaminants (Bakke *et al.*, 1989b; Dow *et al.*, 1990), comparable only to those in the immediate vicinity of drilling sites.

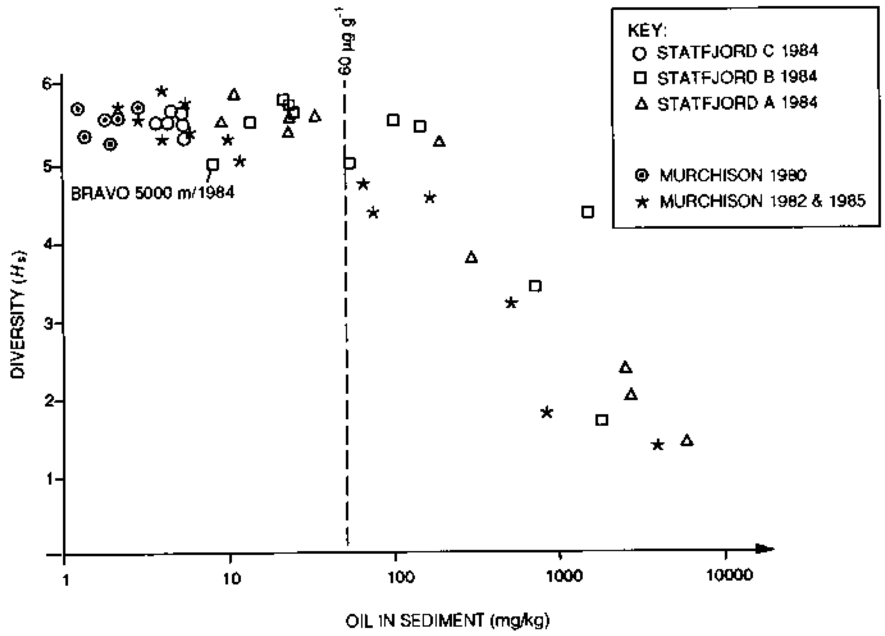
There is no doubt that the extent and degree of benthic damage from the discharge of water-based muds and cuttings is much lower in oil development and production drilling than when oil-based muds are used. The Paris Commission is currently seeking to define 'oil-contaminated cuttings'; that is, to determine the level of contamination by mineral oil below which the environmental effects are no more damaging than those from the discharge of typical cuttings from drilling with water-based muds.

Recent surveys around offshore platforms in the Norwegian, Netherlands and United Kingdom sectors of the North Sea are providing evidence of biological changes at very low elevations of sedimentary concentrations of petroleum hydrocarbons (two to three times background values) (Reiersen *et al.*, 1989; Gray *et al.*, 1990). Gray *et al.* (1990) have shown that there are subtle effects on the benthic community as far away as 3,000 m from a major petroleum installation (Figure 5.3). Similar effects are reported for other platforms in the Norwegian sector of the North Sea (Gray, 1991, pers. comm.). These complex changes in structure of the benthic community have been determined using newly applied multivariate statistical techniques (Warwick and Clarke, 1991). As might be expected, there is a strong inverse relationship between diversity (H_s) and concentration of oil in the sediments. Figure 5.2a shows this relationship for two North Sea oil fields. Reiersen *et al.* (1989) state that reductions in diversity begin at sediment hydrocarbon concentrations between 10 and 100 ppm, suggesting that reductions in diversity could begin at oil concentrations as low as 25 ppm. Figure 5.2a suggests a level of approximately 60 ppm. However, new evidence suggests that some of the more sensitive species might be affected at sediment oil concentrations as low as 10 ppm (Figure 5.2b).

By comparison, there is evidence that the levels of hydrocarbons in sediments between five and fifteen kilometres from production platforms in the densely exploited East Shetland Basin of the North Sea are showing significant increases over pre-operational levels (information from the Scottish Office, Agriculture and Fisheries Department, and other unpublished sources). There has also been considerable drilling of single wells over the whole area. However, gas-chromatographic evidence shows these long-chain hydrocarbons to have come from sources other than or additional to oil-based drilling muds. Shipping discharges, production water, and flaring inputs are implicated (Kingston, 1991; Davies and Kingston, in press).

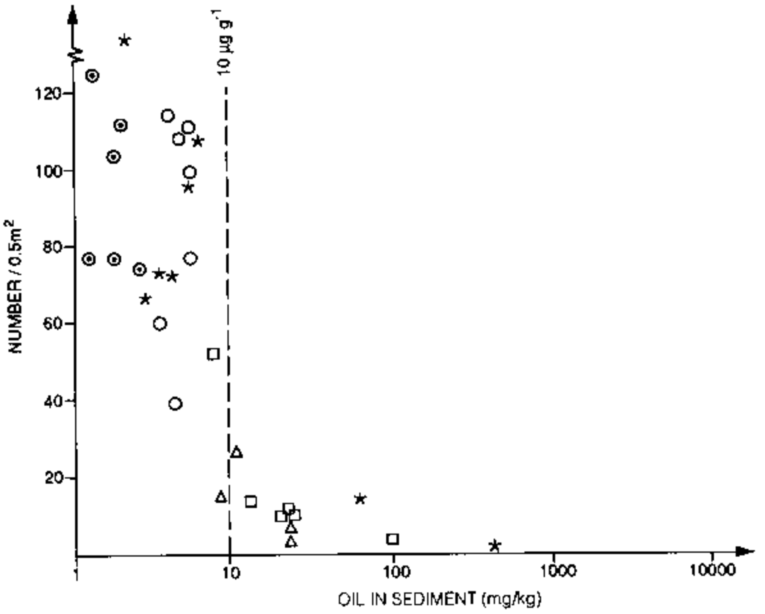
There is increasingly better segregation of the effects of development or production activities and those of exploration drilling. The difference between the two activities can be attributed

Figure 5.2a: ***Relationship between diversity (H_s) and sediment oil concentrations at the Norwegian Statfjord field and the United Kingdom Murchison Field***



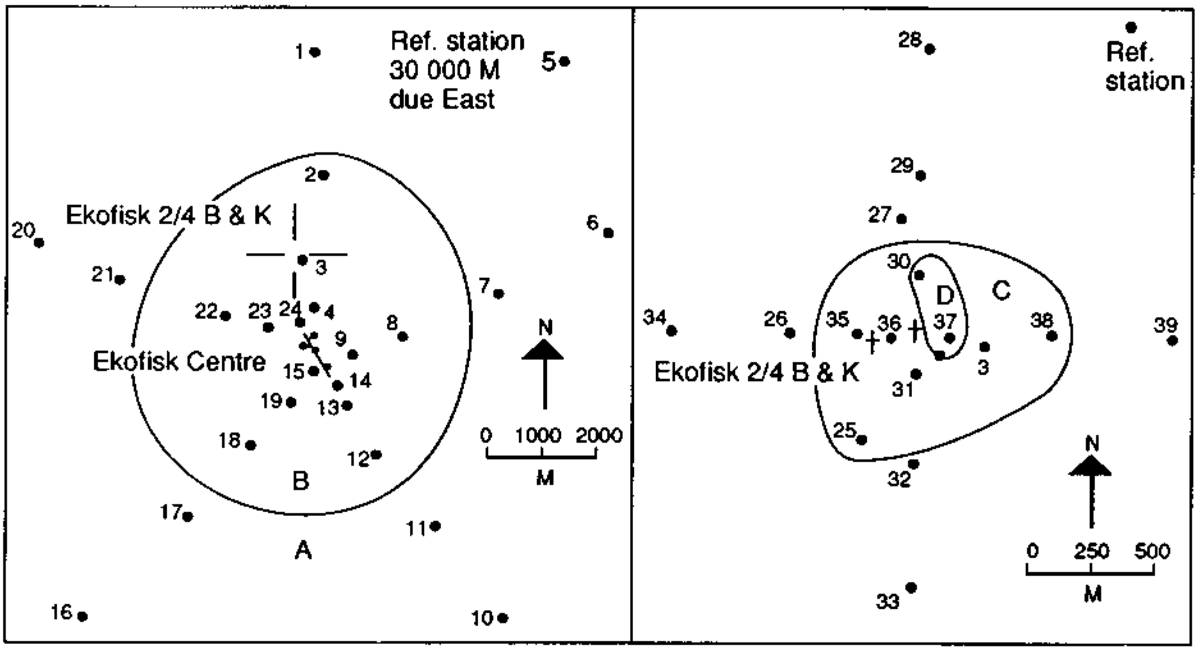
Sources: Matheson *et al.*, (1986); Mair *et al.* (1987)

Figure 5.2b: ***Relationship between abundance of*** **Aonides paucibranchiata** ***(a "sensitive" benthic species) and sediment oil concentrations at selected North Sea platforms***



Source: Davies and Kingston, in press

Figure 5.3: ***Effects on biota around the Ekofisk production installation, assessed by multivariate analysis: Group A, area of low barium, low total hydrocarbon concentration (THC), low percentage of discharged mud; Group B, area of high barium, low THC, low percentage mud; Group C, area of high barium, low THC, medium percentage mud; Group D, area of high barium, high THC, high percentage mud***



Source: (Gray *et al.*, 1990)

to the difference in the number of wells drilled at a multi-well production site versus the single-well exploration site. Until recently, however, the paucity of environmental data at exploration sites has forced a tacit application to the exploration scenario of information from, for instance, North Sea production installations where, in many instances, water-, diesel-oil- and mineral-oil-based drilling muds were used at one site. It appears that, in the case of single-well sites, contamination along the axis of the prevailing current extends for one quarter or less the distance found for development/production sites (Davies *et al.*, 1989; Reiersen *et al.*, 1989; Yunker and Drinnan 1987; Erickson *et al.*, 1989; Jenkins *et al.*, 1989). The zone of biological effects is also less in the case of single wells, generally within 250 to 500 metres of the drilling site. A summary of North Sea data on contamination from oil-based drilling muds is presented in Table 5.6. Local contamination and biological effects from exploratory wells can be expected to last for much shorter times, perhaps not beyond one season of winter storms, especially in shallow waters.

Mair *et al.* (1987) and Davies *et al.* (1989) have also evaluated their data sets for indications of recovery. It appears that even heavily contaminated production areas may show a decrease in the extent of effects once drilling ceases, so that, after one to two years, the effects zones become smaller, with enhanced physical and biological degradation of contaminants. Grahl-Nielsen *et al.* (1989) reported degradation of oil on cuttings discharged from an exploratory well drilled with diesel-oil-based mud, in which case an apparent threshold for the onset of degradation was 1,000 µg/g. Also, colonization of the most affected area by opportunistic benthic species can occur within a few months (Kingston, 1987; Gray *et al.*, 1990).

Table 5.6: ***Area of seabed around North Sea drilling sites affected by oil-based drilling muds (OBM)***

Sector	**Well sites examined** (Number of sites for U.K. area only)	**Average size/shape of zone**
United Kingdom (a)		
Major biological effects	40 development 380 single	500 m radius 250 m radius
Subtle biological changes	40 development 380 single	2,000 x 1,000 m ellipse 1,000 x 500 m ellipse
OBM hydrocarbons present	40 development 380 single	4,000 x 8,000 m ellipse 1,000 x 2,000 m ellipse
Norway (b)		
Major biological effects	development single	1,000 m radius 500 m radius
Minor	development single	3 to 5,000 m radius 1,000 m radius
Hydrocarbons present	development single	5,000 x 10,000 to 12,000 m ellipse 2,000 x 4,000 to 6,000 m ellipse

Sources: (a) Davies *et al.*, (1989); (b) Gray, 1991, personal communication, citing Norwegian State Pollution Control Authority annual reports for 1989 – 1991

In the context of relative environmental risk, it is important to compare the size of zones of influence attributable to activities of the petroleum industry to the extent of disturbance from other marine activities. The combined area of gross biological effects due to petroleum production in the United Kingdom sector of the North Sea, for instance, comprises about 106 km^2 or 0.04% of the United Kingdom offshore jurisdiction (Davies *et al.*, 1989). By comparison, the area of reduced benthic diversity at a single North Sea fly-ash dumping ground was 43 km^2 (Bamber, 1984). As an additional comparison, the area swept by fishing trawls in the Irish Sea in 1978 has been calculated to be approximately 2.5 times the area of its seabed (Brander, 1980). The disturbance of the seabed that is caused by normal fishing practices, such as beam trawling, is described by De Groot (1984) and Redant (1987). The results of ongoing studies in Canada and the Netherlands may further quantify the gross effects of such human activities on the sea.

Further, from Davies *et al.* (1989), the area in which subtle biological effects can be detected is about 400 km^2 or 0.13% of the total United Kingdom sector of the North Sea. If the term 'effects' is defined to include the outer area in which hydrocarbon contamination from oil-based muds can be measured, but without accompanying biological effects, then the total area is approximately 1602 km^2 or 0.55% of the area of the United Kingdom sector of the North Sea. However, the recent evidence for extensive elevations of 'background' hydrocarbon levels in the East Shetland Basin means that, in this area, overall contamination has increased.

Studies in the Norwegian sector of the North Sea show that severe biological effects cover an area of 250 km^2, subtle biological effects about 1,000 km^2, and the full extent of contamination by hydrocarbons (defined as a doubling of background THC levels) probably 3,000 km^2 (Gray, 1991, pers. comm., citing Reiersen, Norwegian State Pollution Control Authority). However, such areas of biological and chemical changes have not been shown to be persistent (Bakke *et al.* 1989a; Davies *et al.*, 1989).

5.5.2 Production water

Compared to the massive information base which exists for drilling discharges, environmental data on production water are very limited. Proceedings of the 1992 International Produced Water Symposium should augment this information (Ray and Engelhardt, in preparation) as well as consideration of the November 1991 Proceedings of the International Conference on Health, Safety and Environment in Oil and Gas Exploration and Development at the Hague (Society of Petroleum Engineers). In general, produced water is considered as being non-hazardous (96-hour LC_{50} values range from 0.1% to greater than 1%), using the GESAMP standards for toxicity. A recent example for the North Sea is given for the copepod *Acartia tonsa* (Girling and Streatfield, 1988). Zooplankton appear to be the most vulnerable group to produced water, the phytoplankton and fish larvae (herring and cod) being more robust to any direct effect (Gamble *et al.*, 1987). However, teratogenic changes were noted experimentally in the embryos of the silverside (*Menidia beryllina*) at high exposure (10 to20% of produced water, for one week) (Middaugh *et al.*, 1988).

Toxicological and ecological effects of production water have been reviewed in detail by Middleditch (1984), Neff *et al.* (1987) and Somerville *et al.* (1987). Their conclusions, which address concerns raised in both U.S. and North Sea jurisdictions, can be summarized as follows:

- the concentrations of toxic chemicals in most production waters are well below individual species' 96-hour LC_{50} levels, indicating that there should be no acute toxicity beyond the immediate vicinity of the discharge;
- the measured toxicity in production water is probably due to the presence of biocides;
- dispersion models show that dilution from the discharge point occurs rapidly to some 1,000-fold dilution within 50 m of discharge, lending support to the assumption that sublethal effects are unlikely beyond this range;
- there is no evidence of the accumulation of hydrocarbons from production water in sediments around existing production sites;
- experimental field studies have demonstrated accumulation of hydrocarbons from production water in marine organisms;
- few laboratory studies have been carried out on the sublethal or chronic effects of production water on marine organisms; and
- there is, however, the possibility of ecological effects of the discharge of production water on benthic communities for production sites under special circumstances of enhanced environmental vulnerability, such as shallow coastal or estuarine waters.

Concerns about production water exist because large amounts of hydrocarbons and other toxic materials are released to the marine environment over the production life of an oil field. This evokes questions about long-term accumulations of contaminants in the sea and gradual ecological change of exposed marine systems.

5.6 Effects on human health

This review is not concerned with the effects of drilling and production chemicals on rig personnel, but only with effects that might arise following discharge into the marine environment. There is no reasonable expectation that people working in the offshore industry or enjoying recreational amenities at sea are likely to be exposed to discharged chemicals in the vicinity of exploratory drilling or production facilities.

The preceding sections suggest that the range of chemicals disposed in the offshore does not occur at concentrations which would pose any significant risk to human health from ingestion of seafood. Regulatory controls which limit such discharges are in place in North America and Europe. For example, implementation of the requirements of the Paris Convention for Annex A, Part 1 materials should prevent such chemical discharges to the North Sea.

Some fish caught close to oil and gas production installations in the North Sea have been shown to contain elevated levels of petrogenic hydrocarbons in fish tissues, especially liver tissue. In some instances, this contamination has originated from drilling wastes (Drangsholt *et al.*, 1988; McGill *et al.*, 1987; Parker *et al.*, 1990;, Sjogren *et al.*, 1989). In all cases, the concentrations have been low and cannot be considered to indicate any significant health risk to a human consumer of fish muscle tissue. A different aspect of contamination of fish with hydrocarbons, but not related to human health concerns, is the matter of tainting of fish flesh, as discussed in Section 5.7.

5.7 Effects on fisheries

5.7.1 Tainting by drilling muds, cuttings, and production water

Of all the compounds used in drilling fluids and muds referred to in section 5.4, only the mineral-oil components of oil-based muds are liable to taint fish, using the accepted definition of taint (see Chapter 2). The compounds of interest might be the base oils themselves or oils used as solvents/carriers of other components such as emulsifiers. Though cuttings are washed before disposal, they still retain adsorbed oil (Davies *et al.*, 1984), and it is possible that fish, particularly bottom-living fish, could be tainted by discharged cuttings. It has been shown (Howgate *et al.*, 1977) that flatfish and crustaceans that were kept on sand that had been experimentally contaminated with crude oil became tainted very quickly, but the experimental conditions of that trial might well not represent conditions prevailing in the heap of cuttings beneath a platform. A study commissioned by Maersk Olie og Gas A/S (COWIconsult, 1986) showed that, in tank experiments, plaice exposed to sediment containing a number of oil-based muds were tainted to different extents.

McGill *et al.* (1987) caught dabs (*Limanda limanda*) at 550 to 860 m and at 1000 to 1870 m from the Beatrice oil platform in the northern North Sea. Samples were evaluated for taint by panels of 8 or 9 experienced assessors. The authors used a criterion of at least half the assessors detecting taint for defining a sample as tainted. By this criterion no samples were tainted, although taint was detected by at least one assessor in about half of the samples. Chemical analysis showed the presence of petrogenic hydrocarbons in samples from the 550 to 860 m zone (samples from the 1000 to 1870 m zone were not analysed). The level of contamination was not related to the presence or absence of taint.

Parker *et al.* (1990) described a similar, but more extensive, survey of fish caught near gas fields in the southern North Sea. Dabs, plaice (*Pleuronectes platessa*), and sole (*Solea solea*) were caught at distances of 200 and 500 metres from three platforms and at a reference site about 25 km upstream of the cluster of platforms. Drilling had ceased at the sites 2 to 18 years before the survey. Using the criterion already described, of half the panel members detecting taint, 9 out of 36 plaice, 1 out of 38 dabs, and 0 out of 10 soles were classified as tainted. The intensity of tainting seemed to be related to the drilling history (type of base oil and time elapsed since drilling) of the platforms, but the conclusions were complicated by differences in relative proportions of species caught at the different sites and the hint that plaice from a site were more tainted than the other species. Chemical analysis showed the presence of petrogenic hydrocarbons in fish from the platform sites but not in fish from the reference site. Again, there was no association between contamination by oil and taint. In cases where fish were classed as tainted, the intensity of taint was rated at no more than slight, and, bearing in mind that the evaluations were carried out by trained assessors under conditions designed to facilitate detection of taint, the authors did not expect that this intensity would be noticed by the typical consumer following typical culinary practices.

Maersk Olie og Gas A/S commissioned a study to determine if operations associated with drilling of wells would taint fish (COWIconsult, 1986). Plaice, dab and cod (*Gadus morhua*) were caught at distances up to 45 km from four wells in the Danish sector of the southern North Sea while they were being drilled or immediately after completion of drilling and from four reference sites away from drilling activities. The fish were evaluated for taints by two experienced assessors who differentiated between oily and non-oily taints. It was found that up to 60% of the plaice from the batches caught at the various locations off the drilling sites were affected by oily taints, but none of the dabs or cod were tainted. On average over the four sites, 26% of the plaice caught within 5 km of the wells were tainted and less than 10% at 10 to 45 km.

Saithe caught off an oil production platform in the U.K. sector of the North Sea (Picken, 1989) and cod caught off a platform in the Norwegian sector (Rasmussen *et al.*, 1992) were found not to be tainted.

The results from the surveys of fish caught near platforms illustrate the problem of evaluating data on tainting of fish caught in the wild due to the variability in 'natural' flavours (section 2.2.8) and the difficulty of unambiguously attributing taint to oil-related activities. In surveys involving flatfish, members of the sensory panels reported that the taints in fish from the platform sites were not always "oily" – indeed, the assessors in the Maersk study specifically differentiated between "oily" and "non-oily" taints – and it was found that some fish from the reference sites also were classed as tainted. It appears that plaice from the southern North Sea at least have a background incidence of unusual flavours which makes it difficult to attribute any perceived taint unequivocally to the effects of drilling activities.

Davies *et al.* (1989) present figures showing that about 10% of the oil discharged by the U.K. offshore oil industry comes from production water. This could possibly be a source of tainting compounds since it contains 20 to 40 mg/ℓ of dissolved hydrocarbons, mainly benzene, toluene and C_3-alkyl-benzenes. If the reported concentrations of individual components found in water from the Brent field are typical (Somerville *et al.*, 1987), then the benzene and alkyl-benzenes are present at about 5- to 10-fold their sensory threshold concentrations in water (see 2.4.2) (Fazzalari, 1978). Additionally, Ernst *et al.*, (1987) have shown that water-soluble fractions of crude oils can taint down to concentrations of dissolved hydrocarbons of around 0.1 mg/ℓ. It is likely that undiluted produced water could pose a risk of inducing taint in fish exposed to it. Estimates of dispersion of discharged water (Somerville *et al.*, 1987) showed that the plume of production water discharged from a platform is diluted at least 1000-fold within 1000 m of the discharge point and possibly within 100 m. This dilution would bring the concentration of dissolved hydrocarbons down to well below that which could induce taint and reduce the risk of tainting in fish caught by commercial fishing to an insignificant level.

Somerville *et al.* (1987) reported that formation water from North Sea oil reservoirs also contains about 0.1% of non-hydrocarbon organic matter, predominantly salts of lower-molecular-weight fatty acids. Though some lower fatty acids have strong odours, the concentrations of individual acids were below their sensory detection thresholds even before any dilution on discharge. This component of production water would not be expected to taint fish.

Davies *et al.* (1989), in a summary and review of environmental survey data from around platforms in the U.K. sector of the North Sea, discussed taint as an effect and referred to reports (McGill *et al.*, 1987; Parker *et al.*, 1990) discussed above. They also presented data from a survey of round fish caught in or near the East Shetland basin in which none of the fish were found to be tainted. McIntosh *et al.* (1990), in a paper to ICES, reported that none of 149 cod, 16 plaice and 22 dabs caught in 37 ICES squares in the northern and central areas of the North Sea were tainted. Of these squares, 14 contained installations for oil or gas production and a further 11 were associated with exploration activity.

5.8 Conclusions

The impacts of operational discharges of wastes from oil and gas exploration and production activities are upon the marine environment circumscribed, and smaller than those from other human marine activities (e.g. fishing, dredging).

Data from both the North Sea and the Gulf of Mexico show that biological changes have occurred in benthic communities as far as 5 km from production sites, mainly attributable to the discharge of drilling wastes, including cuttings.

Major biological changes around production sites are reported to extend to maxima of 500 to 1,000 metres from source, and hydrocarbon contamination to maxima of 8,000 to 12,000 metres.

There is no evidence that discharges of production water, in the absence of other wastes, affect benthos. Their chemical composition, and the dilution regimes around offshore installations, suggest that such effects could only be significant in shallow inshore areas.

The effects of drilling discharges from single-well exploration and multi-well development and production activities are similar qualitatively, but differ greatly in magnitude, spatial extent and predicted recovery rates.

Recovery of impacted sites begins soon after cessation of drilling, as shown for a number of sites in the North Sea.

Given their typical chemical composition and the amounts discharged, there is no reason to expect any human health hazard from the discharge of chemical wastes from offshore exploration and production.

The discharge of oil-based drilling muds and of cuttings from exploratory drilling has the potential to taint flatfish, but it is expected that any effect would be limited to the drilling period or a year thereafter.

A small proportion of flatfish caught in the vicinity of some North Sea production installations that had previously used oil-based mud were found to be tainted. Although the discharge of production water from platforms has the potential to taint fish on the basis of initial concentration, dilution of the discharge plume within 1,000 m of the discharge site renders the risk negligible.

5.9 Recommendations

Information on impacts, additional to existing offshore North Sea and North American data, should be obtained from a larger variety of environments and latitudes in more vulnerable localities, such as shallow or enclosed waters and the Arctic.

Monitoring of chemical and biological effects of production sites should continue, in order to strengthen the data base for assessing long-term ecological change in the peripheral zones of effects, to better differentiate the effects of water-based from oil-based drilling muds and of mineral-oil-based from non-mineral-oil-based muds, and to evaluate recovery of the impact zone, leading to an enhanced scientific basis for regulatory management decisions.

The nature and scale of the impacts from flaring need to be established.

Because the results of only a few studies are available, there should be further scientific surveys of benthic resource species, e.g. flatfish and shellfish, in the vicinity of drilling installations to assess the risk of tainting.

Regulations for the control of discharges of wastes and other matter from offshore platforms and installations have to be established on the national, regional and global levels.

Appendix

Table 4.1: ***Licensed, registered, or approved oil spill response products***

Product name	Manufacturer	Type	Country
ABR Bi-Chem	Sybron Chem, Salem, VA	B/O	US
AE Biosea Process	Alpha Environmental, Austin, TX	B/O	US
Agma DR 379	Agma PLC	CON	UK*
Agma OSD 540	Agma PLC	HC	UK
Agma OSD 559 (= EP559)	Agma PLC	CON	UK
Agma superconc 379 (= DR91)	Agma PLC	CON	UK
Ameroid OSD/LT	Drew Ameroid UK Ltd	HC	UK
Applied 8-42	Applied Chemicals Ltd.	HC	UK
Aquarite AWX	Albright & Wilson Ltd	HC	UK
Ardrox SR 61	Ardrox Ltd	HC	UK
Arpal OSD 95SC	RP Adam Ltd	CON	UK*
Arrow Emulsol Conc Type A	Arrow Chems Group Ltd	CON	UK
Arrow Emulsol Conc Type B	Arrow Chems Group Ltd	CON	UK
Arrow Emulsol Superconc LE 2	Arrow Chems Group Ltd	CON	UK* (LE3)
Atlan'tol 3211/E (EC.OATALN'TOL?)	Atlan'tol Laboratory	CON	UK
Atlan'tol AT7-floating	Atlan'tol Laboratory	HC	UK
Atlas Colrelx OSD	Atlas Prod & Serv Ltd	HC	UK
Atpet 787	ICI Specialty Chemicals	CON	UK
Bactozyme	International Enzymes, Las Vegas, NV	BIO	US
Bioreico R93	Societé Reico	CON	FR
Bio Solve	Metra Chem, Shrewsbury, MA	W	US
Bioversal	Bio Versal USA, Inc., Mt. Prospect, IL	W	US
Bio-zyme	High-Line Chemicals, Saskatoon, Saskatchewan, Canada	BIO	US
BMD SM 53	Smyth-Morris Chems Ltd	HC	UK
BP 1100 X	BP Detergents Ltd, Scotland	HC	(US)
BP oil solidifier	BP Chemicals Ltd	SOLIDIFIER	UK
CD 202	ICI plc (Paints Division)	CON	(UK*)
Centisolve 010	Century Oils Ltd	CON	(UK*)
Centisolve 011	Century Oils Ltd	CON	UK*
Cleansea III	Gamlen Chem Co UK Ltd	CON	UK*
CN-110	Chemex Inc., Lafayette, LA	?	US
Cold Clean 500	Essex Fire & Safety, Houston, TX	W	US
Compound W-1911	Petrolite Ltd	CON	UK
Compound W-1986	Petrolite Ltd	CON	UK
Compound W-2096	Petrolite Ltd	CON	UK*
Conco Dispersant K	Continental Chem, Clinton, NJ	CON	US
Corexit 7664	Exxon Chemical, Houston, TX	W	US
Corexit 8667	Exxon Chemical, Houston, TX	HC	US, UK
Corexit 9123	Exxon Chemical, Houston, TX	CON	UK*
Corexit 9130	Exxon Chemical, Houston, TX	CON	UK
Corexit 9517 (= 9527)	Exxon Chemical, Houston, TX	CON	UK*
Corexit 9527	Exxon Chemical, Houston, TX	CON	US, CAN, (UK*)
Corexit 9550	Exxon Chemical, Houston, TX	HC	US, CAN
Corexit 9580	Exxon Chemical, Houston, TX	SHORELINE CLEANER	US, CAN
Corexit 9600	Exxon Chemical, Houston, TX	CON	UK
Corexit CRX-8	Exxon/Esso Chemical		CAN
Corexit OC5	Essochem Performance Chems Ltd	COLLECTOR	UK*, US
Custombien	Sierra Chem. Co., Milpitas, CA	BIO	US

*Table 4.1: **Licensed, registered, or approved oil spill response products (continued)***

Product name	Manufacturer	Type	Country
Dasic Slickgone LT2	Dasic Internat, Romsey, U.K.	HC	UK* (LT4)
Dasic Slickgone LT2 (= LT = LT2?)	Dasic Internat, Romsey, U.K.		CAN
Dasic Slickgone LTSW	Dasic Internat, Romsey, U.K.	CON	UK* (LTS also)
Dasic Slickgone NS	Dasic Internat, Romsey, U.K.	SOLV	(US), UK*
Dasic Slickgone SC 100	Dasic Internat, Romsey, U.K.	CON	UK*
De-solv-it	Orange-Sol, Inc., Gilbert, AZ	?	US
Destroil	Anti-Pollution Chemicals Ltd	CON	UK
Destroyl	Spectrum Maintenance Services	HC	UK
Dispersant 11	Dubois Chem, Cincinnati, OH	CON	US
Dispolene 34S	SEPPIC	CON	UK*
Dispolene 36S	SEPPIC	CON	FR, (UK*)
Dispolene 38S	SEPPIC	CON	UK*
Drew Dispersant LT (= OSD/LT)	Drew Chem Co, Boonton, NJ	CON	CAN
Ebbclean	Bestobell Paints & Chems Ltd	HC	UK
EC.O ATALN'TOL AT7 (Atlan'tol?)	ASPRA Inc, Seattle, WA	W	US
EDF Emulsa Fire	SynTech Products Int., Toledo, OH	W	US
EEC Biological Media	Environmental Engineering Consultants, Stillwater, OK	BIO	US
Elastol	General Technology, Manassas, VA	VISCOELASTIC	US, CAN
Emkem Spillwash LT	Emkem International Ltd	HC	UK* (Super Con LE3)
Emulso A-1984	Toho Chemical Industry Ltd	CON	UK*
Emulso E-309	Toho Chemical Industry Ltd	HC	UK
Emulsol LW	Arrow Chem Group Ltd	HC	UK
Enersperse 1037	BP Oil Ltd. Detergents Division	CON	(UK*)
Enersperse 1100 (= BP 1100X)	BP Detergents, W. Lothian, Scotland	HC	UK, US
Enersperse 1100 X	BP/PetroCan Chem		CAN
Enersperse 1495	Youngs Detergents Ltd	CON	UK*
Enersperse 1583	Youngs Detergents Ltd	CON	UK*
Enersperse 1990	Youngs Detergents Ltd	HC	UK
Enersperse 700	BP Detergents, W. Lothian, Scotland	SOLV	US, CAN
Ergospill 1502	Energeco S.A.	CON	UK
Finarep	Petrofina (UK) Ltd	COLLECTOR	UK*
Finasol OSR-121	Petrofina (UK) Ltd	HC	UK*
Finasol OSR-2	Petrofina (UK) Ltd	HC	UK
Finasol OSR-3	Petrofina (UK) Ltd	HC	UK
Finasol OSR-4	Petrofina (UK) Ltd	HC	UK
Finasol OSR-51	Petrofina (UK) Ltd	CON	UK*
Finasol OSR-52	Petrofina (UK) Ltd	CON	UK, FR
Finasol OSR-7	Amer Petrofina, Dallas, TX	W/CON	US, UK
Fleetex 83/1 (= Quell Oil)	Isaac Bentley & Co Ltd	CON	UK
Fleetex BD 3	Isaac Bentley & Co Ltd	HC	UK
Formula 98	Malone Chem., Linden, NJ	W	US
Gamlen Oil Dispersant	Gamlen Chem Co (UK) Ltd	CON	UK
Gamlen Oil Dispersant LT	Gamlen Chem Co (UK) Ltd	CON	UK
Gamlen Oil Dispersant OD4000 (PE998)	Societé Gamlen	CON	FR
Gamlen OSR 2000	Gamlen Chem Co (UK) Ltd	HC	UK, CAN
Gamlen OSR 4000	Sybron Chimie France S.A.	HC	UK*
Gamlen OSR LT 126	Gamlen Chem Co (UK) Ltd	HC	UK
Gold Crew	Ara Chem, San Diego, CA	W/CON	US
Grancontrol O	C & A Products, Elmwood Pk., NJ	W	US
Greensafe S	Kayclean (UK) Ltd	HC	UK
Greensafe W	Kayclean (UK) Ltd	CON	UK
HA 1232	Atlas Chem. Ind. (UK) Ltd.	CON	(UK*)
Hydrobac	Polybac Corp., Allentown, PA	BIO	US
Inipol EAP 22	Elf Aquitaine	BIO	US
Inipol IP 80	Elf Aquitaine GRL	CON	UK*, FR
Inipol IP 90	Elf Aquitaine GRL	CON	UK*, FR, US

Table 4.1: ***Licensed, registered, or approved oil spill response products (continued)***

Product name	Manufacturer	Type	Country
Jansolv-60	Sunshine Tech, W. Hartford, CT	W/SOLV	US
Lankromul OSD	Lankro (Diamond Shamrock)	HC	UK
Liquid Oil Bond-200	Toho Titanium Co., Tokyo, Japan	GEL AGENT	US
LTOD	Anti-Pollution Chemicals Ltd.	CON	(UK*)
Magna MEP 554	Baker Oil Treating/Magnachem Ltd	CON	UK
Magna ML 897	Baker Oil Treating/Magnachem Ltd	CON	UK
Magnotox	Magnus Maritec, Palisades Pk., NJ	W/CON	US
Mare Clean 505	Mitsubishi Intern, New York, NY	SOLV	US
Micropro Now Bac	Environmental Remediation, Inc., Baton Rouge, LA	BIO	US
Micropro D	Environmental Remediation, Inc., Baton Rouge, LA	BIO	US
Micropro Super Cee	Environmental Remediation, Inc., Baton Rouge, LA	BIO	US
MC #1 Dispersant	Safeworld Products, Brentwood, TN	W	US
Munox 101	Microlife Technics, Sarasota, FL	BIO	US
Munox 201	Microlife Technics, Sarasota, FL	BIO	US
Munox 501	Microlife Technics, Sarasota, FL	BIO	US
Nalfleet 9-010	Nalfleet Marine Chemicals	CON	UK
Nalfleet Maxi-Clean 2	Nalfleet Marine Chemicals	HC	UK
NEOS AB 3000	NEOS Co, Kobe, Japan	HC	US, UK
NK-3	GFC Chemical, Lafayette, LA	W	US
Nokomis 3C 4-F (Slik-a-way)	Groundwater Tech/oil Recovery Sys	CON	UK
No-scum	Natural Hydrocarbon Elimination Co., Houston, TX	BIO	US
Norsorex	Custom Environmental	SOLIDIFIER	CAN
O.M.I. Type One Dispersant	O.M.I. Ltd	HC	UK*
O.M.I. Type Three Dispersant	O.M.I. Ltd	CON	UK*
Oclansorb	Walker Air Cond (UK) Ltd	ADSORBANT	UK
OFC D-609	Chem Link Petroleum, Oklahoma, OK	CON	US
Oil Bond-100	CdF Chimie S.A., Paris	PLASTICIZER	US
Oil Herder	ASt, Inc., Long Beach, CA	COLLECTOR	US
Oil Spill Disp./NF (new formula)	Chemo Hellas Ltd	HC	UK
Oil Spill Elastol	General Technology, Manassas, VA	VISCOELASTIC	US, CAN
Oilex 3225 Oil Spill Dispersant	Kjemi-Service A/S	HC	UK
Oilsperse 43	Diachem Industries		CAN
Omni-Clean	Delta-Omega Tech., Lafayette, LA	W	US
OSD 1B	Chemie Appliquee Marin Industrie	CON	UK
OSD/LT (new formulation)	Drew Chem, Boonton, JN	CON	US, CAN
Petro-Green ADP-7	Petro-Green, Dallas, TX		US
Petrobac	International Biochemicals (UK) Ltd; Polybac Corp., Allentown, PA	BIO	UK, US
Petrobac 8	International Biochemicals Ltd		UK
Petrocon Oil Spill Eliminator IV	Petrocon Marine Chemical Corp	HC	UK
Petrodeg-100	Bioteknika International Inc. Arlington, VA	BIO	US
Petrodeg-200	Bioteknika International Inc. Arlington, VA	BIO	US
Petrolock	Custom Environmental	SOLIDIFIER	CAN
Petromend MP-900-W	Petromend, Dallas, TX	W/CON	US
Petrotite M.M.E.	Heath Consultants Inc., Stoughton, MA	W	US
Phenobac	Polybac Corp., Allentown, PA	BIO	US
Phirex	Environmental Security, Inc., Gloucester, MA	ORG	US
Premier 99	Gold Coast Chemical Corp, Hollywood, FL	SA	US
Proform-Pollution Control Agent	Proform Products, Palo Alto, CA	W/CON	US
Quell Oil Cl	Lankro (Diamond Shamrock)	CON	UK
Rawflex	Custom Environmental	SOLIDIFIER	CAN
Re-entry KNI	Envirosolv, Inc., Jacksonville, FL	?	US

Table 4.1: ***Licensed, registered, or approved oil spill response products (continued)***

Product name	Manufacturer	Type	Country
Remospill 1	Performance Chemicals Ltd	HC	UK
Rigidoil	BP Chemicals Ltd	SOLIDIFIER	UK
Rochem Oil Spill Remover (WSA)	Rochem Chemicals (Belgium) Ltd	HC	UK
Ruffnek cleaning agent	Malter International, Gretna, LA		US
Sana oil disperser	Petrofina (UK) Ltd.	CON	(UK*)
Scavenger Slick Dispersant	Edgar Vaughan & Co Ltd	CON	UK
SDS-300	Services Marketing Group, Houston, TX	HC	US
Seacare OSD Conc. 2021	Perolin Marine	HC	UK
Seacard OSD Conc. 2021X	Perolin Co Ltd	HC	UK*
Seacare OSD Conc. 2023	Perolin Marine	CON	UK*
Seacare OSD conc. 2023X	Perolin Co Ltd	CON	UK*
Seacle L-500	Dai-Ichi Kogyo Seiyaku Co Ltd	HC	UK
Seaclean	MTM Specialist Products Ltd	CON	UK
Sea-Jell	Ajinomoto Co. Inc., Tokyo, Japan	GEL	US
Servo CD 2000	Servo Chemische Fabriek BV	HC	UK
Servo CD 2009	Servo Chemische Fabriek BV	CON	UK*
Shell Demulsifier LA 1843	Shell Chemicals (UK) Ltd	DEMULSIFIER	UK*, CAN
Shell Dispersant Concentrate	Shell Chemicals (UK) Ltd	CON	UK
Shell Dispersant HEC	Shell Chemicals (UK) Ltd	CON	(UK*)
Shell Dispersant ND	Shell Chemicals (UK) Ltd	HC	UK*
Shell Dispersant VDC	Shell Chemicals (UK) Ltd	CON	UK*
Shell Oil Herder	Shell Chemicals (UK) Ltd	COLLECTOR	UK*, US
Simple Green	Sunshine Makers Inc., Huntingdon Harbour, CA	W	US
Silk-A-Way	MI-DEE Prod, Pleasanton, CA	W	US
Slickgone LT	Dasic Internat, Romsey, U.K.	CON	CAN
Slickgone NS	Dasic Internat, Romsey, U.K.	CON	US
Slicktreat 1200	IDF Production Chemicals Ltd	HC	UK*
Slicktreat 1400	IDF Production Chemicals Ltd	CON	UK*
Slicktreat 1600	IDF Production Chemicals Ltd	CON	UK*
Slix-Treat	Hydrokem I/S	CON	UK
Spillaway	Forward Chemicals Ltd	CON	UK
Super all #38	Tavelle Corp., Hollywood, FL	CLEANING AGENT	US
Superdispersant 25	Noble Consultancy Service	CON	UK
Surflo OW1	Exxon Chemical Energy Chemicals	CON	UK
Surflo RD2284	Exxon Chemical Energy Chemicals	CON	UK
Techmar 125 Spillclean	Techmar Chemical Co Ltd	HC	UK
Techsol Superconcentrate	Techsol Manufacturing Ltd	CON	UK*
Teklene TC 48	Teckem Ltd	HC	UK
Toho Cactus Clean LA-500	Toho Titanium Co Ltd	CON	UK*
Topsall No.30 cleaning agent	Sutton North, Mandeville, LA		US
Toxigon 2000	Formula IV Corporation, Scottsdale, AZ	?	US
Tretolite 2922	Petrolite Ltd	CON	UK
Tros Seaclean	TR Oil Services Ltd	CON	UK
Type L, DBC plus	Flow Laboratories Inc., McLean, VA	BIO	US
Type R-5, DBC plus	Flow Laboratories Inc., McLean, VA	BIO	US
Unisperse M 74	Universal Matthey Products	EMULSION BREAKER	(UK*)
Water Witch Slickleen Concentrate	Liverpool Water Witch	CON	UK
Welchem Wellaid 3300	Amoco Chemicals UK Ltd	CON	UK
Welchem Wellaid 3315	Amoco Chemicals UK Ltd	CON	UK*
Wellaid 3316	Welchem, Inc., Houston, TX	?	US
WMI-2000	Waste Microbes Inc., Houston, TX	BIO	US
Woodace Briquettes	Vigoro Industries Inc., Fairview Heights, iL	BIO	US
X-3125 Oil Spill Dispersant	MW Webber & Co Ltd	HC	UK

Notes:
BIO = biological additive
CON = concentrate
HC = hydrocarbon base
ORG SA = organic surfactant
SOLV = other solvent base
W = water base

Canadian listings are from the Environmental Protection Service, March 1991 (products)

UK listings are from a May 1990 printout of approved oil treatment products, Food and Environment Protection. Act of 1985 (RAA Blackman, 1990, pers. comm.; 124 products in all). Products withdrawn or expired were omitted from this list. Items noted with an asterisk (*) were listed as "qualified products" by the Warren Spring Laboratory, Feb. 1989. Items on this list but not on the May 1990 MAFF list are in brackets.

US listings are based on the product schedule of the EPA National Contingency Plan, Sept. 1990 (73 products). Brackets indicate the product was included in the 1987 list but not in the 1990 list.

French listings are from R. Kantin, CEDRE, pers. comm.

Part III – Bibliography

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Acronyms

ACGIH	American Conference Government Industrial Hygienists
ACOPS	Advisory Committee on Pollution of the Sea
AET	Apparent Effects Threshold
AH	Aromatic Hydrocarbons
API	American Petroleum Institute
B(a)P	Benz[*a*]pyrene
BIOS	Baffin Island Oilspill Study
BOP	Blow-out preventer
CARIPOL	Caribbean Pollution Monitoring Programme
CEDRE	Centre de Documentation de Recherche et d'Experimentations
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act (USA)
CFPA	Canadian Fire Protection Association
DFO	Department of Fisheries and Oceans (Canada)
DMSO	Dimethyl sulphoxide
DNA	Deoxyribonucleic acid
E & P	Exploration and Production
ECETOC	European Chemical Industries Environmental and Toxicological Centre
EHS	Evaluation of the Hazards of Harmful Substances Carried by Ships
EPA	Environmental Protection Agency (U.S.A.)
FAO	Food and Agriculture Organization of the United Nations
GC/MS	Gas chromatography/mass spectrometry
GESAMP	Group of Experts on Scientific Aspects of Marine Pollution
GLC	Gas–liquid chromatography
HLB	Hydrophilic–lipophilic balance
HPAH	High-molecular-weight polycyclic aromatic hydrocarbon
HPLC	High-performance liquid chromatography
IARC	International Agency for Research on Cancer
ICES	International Commission for the Exploration of the Sea
IGOSS	Integrated Global Ocean Station System
IMO	International Maritime Organization
IOC	Intergovernmental Oceanographic Commission

ISO	International Standards Organization
LMW	Low molecular weight
MARPOL	International Convention on the Prevention of Pollution from Ships, 1973 as modified by the Protocol 1978 relating thereto (MARPOL 73/78)
MARPOLMON	Marine Pollution Monitoring Programme
MDPC	Maritime Disaster Prevention Centre
MERL	Marine Environmental Research Laboratory (Rhode Island)
NAS	National Academy of Sciences (USA)
NATO	North Atlantic Treaty Organization
NFPA	National Fire Protection Association
NOAA	National Oceanographic and Atmospheric Administration
NRC	National Research Council
OBM	Oil-based drilling mud
OECD	Organization for Economic Co-operation and Development
OSHA	Occupational Safety and Health Administration (USA)
OSIR	Oil Spill Intelligence Report
PAH	Polynuclear aromatic hydrocarbon
PARCOM	Paris Commission
QSAR	Quantitative structure–activity relationship
SFT	Norwegian State Pollution Control Authority
SIM	Selective ion monitoring
TCDD	Tetrachlorodibenzodioxine
THC	Total hydrocarbons
TPAH	Total polycyclic aromatic hydrocarbons
UKOOA	United Kingdom Offshore Operators Association
UNEP	United Nations Environment Programme
UNESCO	United Nations Educational, Scientific and Cultural Organization
USCG	United States Coast Guard
USGS	United States Geological Survey
WHO	World Health Organization

Units and conversion table

APPROXIMATE CONVERSION FACTORS

	Crude oil*	To					
		Tonnes	(long) Tons	Barrels	Gallons (imperial)	Gallons (US)	Tonnes/ year
		MULTIPLY BY					
From	Tonnes (metric)	1	0.984	7.33	256	308	-
	(long) Tons	1.016	1	7.45	261	313	-
	Barrels	0.136	0.134	1	35	42	-
	Gallons (imperial)	0.00391	0.00383	0.0286	1	1.201	-
	Gallons (US)	0.00325	0.00319	0.0238	0.833	1	-
	Barrels/day	-	-	-	-	-	49.8

* Based on average (Arabian Light) 33.5°API gravity

UNITS

1 metric tonne = 2,205 lbs
1 long ton = 2,240 lbs
1 short ton = 2,000 lbs
1 kilolitre (kl) = 6.29 bbls

PREFIXES

mega	M	10^6	centi	c	10^{-2}
kilo	k	10^3	milli	m	10^{-3}
hecto	h	10^2	micro	μ	10^{-6}
deca	da	10	nano	n	10^{-9}
deci	d	10^{-1}	pico	p	10^{-12}

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Rep. & Stud. No.	Title	Date
1	Report of the Seventh Session	1975
2	Review of Harmful Substances	1976
3	Scientific Criteria for the Selection of Sites for Dumping of Wastes into the Sea	1975
4	Report of the Eighth Session	1976
5	Principles for Developing Coastal Water Quality Criteria	1976
6	Impact of Oil on the Marine Environment	1977
7	Scientific Aspects of Pollution Arising from the Exploration and Exploitation of the Sea-bed	1977
8	Report of the Ninth Session	1977
9	Report of the Tenth Session	1978
10	Report of the Eleventh Session	1980
11	Marine Pollution Implications of Coastal Area Development	1980
12	Monitoring Biological Variables Related to Marine Pollution	1980
13	Interchange of Pollutants between the Atmosphere and the Oceans	1980
14	Report of the Twelfth Session	1981
15	The Review of the Health of the Oceans	1982
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17	The Evaluation of the Hazards of Harmful Substances Carried by Ships	1982
18	Report of the Thirteenth Session	1983
19	An Oceanographic Model for the Dispersion of Wastes Disposed of in the Deep Sea	1983
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21	Report of the Fourteenth Session	1984
22	Review of Potentially Harmful Substances. Cadmium, Lead and Tin	1985
23	Interchange of Pollutants Between the Atmosphere and the Oceans (second report)	1985
24	Thermal Discharges in the Marine Environment	1984
25	Report of the Fifteenth Session	1985
26	Atmospheric Transport of Contaminants into the Mediterranean Region	1985

Rep. & Stud. No.	Title	Date
27	Report of the Sixteenth Session	1986
28	Review of Potentially Harmful Substances. Arsenic, Mercury and Selenium	1986
29	Review of Potentially Harmful Substances. Organosilicon Compounds (Silanes and Siloxanes)	1986
30	Environmental Capacity: An Approach to Marine Pollution Prevention	1986
31	Report of the Seventeenth Session	1987
32	Land–Sea Boundary Flux of Contaminants: Contributions from Rivers	1987
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