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Oil and Dispersants in Canadian Seas— Research Appraisal and Recommendations

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OIL AND DISPERSANTS IN CANADIAN SEAS - RESEARCH APPRAISAL AND RECOMMENDATIONS

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ABSTRACT

This report evaluates knowledge of the fate and effects of oil spilled at sea and the implications of using dispersants, with special reference to Canadian marine environments. Almost 600 references from the scientific literature are utilized. Twelve chapters by individual scientists give perspectives on the Canadian oil industry; fate and behaviour of oil in the sea; microorganisms and degradation of oil; analytical chemistry; and effects of oil, dispersants, and chemically-dispersed oil on phytoplankton, macrophytes, zooplankton, fish, benthic and intertidal organisms, birds, marine mammals, and communities and ecosystems. Recommendations are given for further research that is required and strategies for minimizing effects of spills, again with emphasis on Canadian waters.

RÉSUMÉ

Ce rapport évalue nos connaissances actuelles sur le devenir du pétrole et ses effets en cas de déversement en mer, et les conséquences de l'emploi de dispersants dans le milieu marin au Canada. Plus de 600 travaux scientifiques ont été consultés. Le présent rapport comporte douze chapitres qui ont été rédigés par des spécialistes dans les domaines de: l'industrie pétrolière canadienne; le devenir et le comportement du pétrole déversé en mer; les micro-organismes et la dégradation du pétrole; les méthodes d'analyse; les effets du pétrole, des dispersants et du pétrole dispersé chimiquement sur le phytoplancton, les macrophytes, le zooplancton, les poissons, les organismes et animaux benthiques et intertidaux, les oiseaux, les mammifères marins, les communautés et les écosystèmes. Il comporte certaines recommandations en vue de recherches futures indispensables et donne des conseils sur la façon de minimiser les effets de déversements de pétrole dans le milieu marin canadien.

FOREWORD

This report appraises: (1) the fate and effects of petroleum spilled in Canadian marine environments; and (2) the implications of using dispersants on spills. The review was initiated with the purpose of identifying both knowledge and gaps in understanding problems of oil pollution in northern waters. In particular, the report is intended as a useful background on research-priorities for dispersants, and on policy for their use. With these objectives in mind, each author assessed the scientific knowledge in his field, available up to 1979. Each chapter includes recommendations within the author's field of research. The general recommendations at the beginning attempt to present a concensus, although some items did not receive unanimous support from the authors.

Two points of interest arose during the editorial process. Firstly, all of the authors had difficulty in doing a thorough section on dispersants and on chemically dispersed oil. When pressed for more coverage or for recommendations, most authors complied but added an explanation such as "...in my field, relatively little is known about dispersants." From this it would seem clear that there is a general information-gap on dispersants.

Secondly, many recommendations in the chapters emphasize the need for more work on the fate and effects of oil in the Arctic. Uncertainties about oil effects are often related to lack of knowledge of the "natural" functioning of marine ecosystems, and there is general agreement that this is especially the case in the north. One might add an implicit recommendation to this report: that Canada should strengthen and not reduce or weaken its excellent capabilities for long-term studies of marine environments. We should be employing those capabilities much more strongly, to gain a solid understanding of how marine systems work, especially in regions of hydrocarbon exploration and development. We cannot protect specific marine ecosystems, nor choose the least damaging options in case of accidents, if we do not have a good understanding of how they function.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

GENERAL RECOMMENDATIONS

ITEMS MOST FREQUENTLY CITED

(1) Better use of Canadian and foreign spills as research opportunities. Behaviour of oil in recent spills (IXTOC, in Gulf of Mexico; KURDISTAN, off Nova Scotia) shows that we are still in a poor position for prediction. Following up spills-of-opportunity yields invaluable information on spill behaviour and countermeasures. There should be well-organized but flexible programs, pre-funded and ready to go into action. Follow-up studies should continue over a long period of time.

(2) Experimental oil spills. These are needed to fill existing gaps in knowledge, if such information cannot be gathered from actual spills, or if laboratory work requires large-scale confirmation. Although we do not advocate liberal use of experimental oil spills, some such spills (1-15 m^3) are essential for an understanding of spill behaviour and effects under field conditions.

TOPICS NEEDING RESEARCH

It is not surprising that most of the chapters recommend "more research" on the topic that is the author's speciality. Each reviewer could scarcely do otherwise -- he was asked to put together an overall view of a subject, but was acutely aware of the missing pieces in the puzzle. To re-list all of those items here would serve little purpose, and the reader is referred to individual chapters. Included below, however, are some topics that received particular emphasis. (Eds.)

Living organisms

(3) Activity of oil-degrading bacteria in cold waters.

(4) Effects of oil and dispersed oil on biota which inhabit vulnerable locations. Experiments testing various countermeasures in such places. Locations would include estuaries, lagoons, salt marshes, and under the ice in the Arctic; in some of these places, physical cleanup techniques might cause greater damage than benefit.

(5) Effects on birds. Some species and populations are particularly vulnerable, sensitive, or both. Subjects include: mortality from oil that stays off-shore;

ingested oil; assessment of minimum amount on feathers that triggers temperature stress; narcosis from fumes; and susceptibility to weathered oil. Some marine mammals may be similarly affected.

(6) Sublethal studies. Research should continue to pass from the initial phase of tests for lethality to studies of growth, reproduction, and behaviour. Whole-ecosystem responses are equally important.

Physicochemical Factors

(7) Behaviour of deep-sea blowouts. Knowledge is minimal. Without this, prediction of fate and effects is severely hampered.

(8) Interaction of oil with ice. Here also, there is overall inadequacy of knowledge, particularly for assessing fate and effects in the Arctic.

Dispersed Oil

(9) The fate of dispersed oil. Transportation into bottom sediments; residence time with and without dispersants.

(10) Potential for dispersants to increase or decrease degradation of oil.

(11) Benefits and detriments of dispersant use, for sensitive organisms such as birds and near-surface zooplankton.

(12) Effects on shorelines. There is considerable uncertainty on this topic. Dispersed oil could de-stablize some beaches or be more harmful to biota; consolidated oil could persist and re-pollute in the Arctic.

STRATEGIES TO MINIMIZE EFFECTS OF SPILLS

(13) Mechanical cleanup of oil at sea remains the least-damaging option, but is seldom feasible. If oil is likely to come ashore, use or non-use of dispersants must consider the trade-offs in any given situation. Obviously, any such balanced consideration will be hindered by the gaps in knowledge listed above, and in the individual chapters.

(14) Maximum physical protection is desirable for salt marshes and muddy shores. There seems to be a major dilemma, whether it is beneficial or detrimental to use

dispersants or physical cleanup in such low-energy habitats. Until such questions are answered by research, no standard remedial strategy is evident; hence the need to prevent oil from reaching such locations.

(15) Protection of birds. Even without further research it is clear that oil can be catastrophic for sea birds. Accordingly there is an overriding priority to prevent oil from reaching areas where birds congregate.

(16) Protection of fish spawning-grounds. Fish in young stages of growth must be assumed to have high vulnerability and sensitivity to dispersed oil. In areas where they are concentrated, the use of dispersant requires special consideration and a background of detailed knowledge is necessary.

1 INTRODUCTION

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1.1 Oil - Its History and Characteristics

Petroleum (crude oil and natural gas) originated from organic matter of both plants and animals which accumulated in fine-grained, oxygen-deficient sediments. These sediments, which built up the floors of prehistoric oceans, became compressed during numerous glacial intrusions and were eventually transformed into shale, limestone and sandstone; collectively forming sedimentary rock. As the geological features of the earth took form, these layers were buried deeper within the crust. It is generally believed that through the action of bacteria, heat and pressure, petroleum was formed within these rocks. Overlaying impervious rocks retained petroleum within the crust, except when geological faults allowed migration to the surface. Early civilizations used oil from such natural seeps for waterproofing, lubrication and as a source of heat. In the last 125 years, however, man has taken an active interest in searching for, and using oil in quantity.

From its early use, oil and its various refined products have emerged as a principal energy-source for heating, light and transportation, as well as a prime feedstock for the petrochemical and plastics industries. In 1978, worldwide consumption of oil amounted to 3 076 million tonnes per year, while Canadian consumption was 87 million tonnes per year (BP, 1978). Although upwardly-spiralling costs and a dwindling supply necessitates the increasing use of alternative energy sources, the fact remains that much of the world's economy and lifestyle is based on oil and, as such, it will remain a major energy source for many years to come.

Crude oil itself (that coming from underground formations) is seldom used in its original form, although it is often transported great distances around the world on land or water. Crude oil can contain tens of thousands of different compounds, principally hydrocarbons, with appreciable amounts of combined sulphur, nitrogen, oxygen (S,N,O) and some heavy metals, such as vanadium, nickel, arsenic and lead (V, Ni, As, Pb). Typical chemical composition of a crude oil is shown in Table 1.1.

TABLE 1.1 CHEMICAL COMPOSITION OF A CRUDE OIL

	% Weight
Carbon	84 - 87
Hydrogen	11 - 14
Sulphur	trace to 3
Nitrogen	trace to 1
Oxygen	trace to 2
Water	trace to 1
Heavy Metals	trace to 0.1

All crude oils contain three general classes of hydrocarbons. Paraffin hydrocarbons, such as methane, propane and butane, are straight-chain, saturated hydrocarbons, with valences filled by links to other carbon or hydrogen atoms. Napthenes or cyclo-paraffins, such as cyclopentane and cyclohexane, are hydrocarbons in which the carbon atoms form a ring and are fully saturated. The ring may contain various numbers of carbon atoms; those most frequently found in petroleum contain 5, 6 or 7.

Aromatic hydrocarbons form the third class, and examples are benzene and toluene. These are also ringed hydrocarbons in which each carbon atom is linked to one neighbouring carbon atom by two chemical bonds, thus giving the molecule the appearance of being unsaturated. One type of aromatic hydrocarbon which occurs in many crude oils is the naphthalene type in which aromatic rings are linked together through two common carbon atoms.

Crude oils are characterized and typed, not only by their hydrocarbon composition, but also by their specific gravity, and the amount and chemical nature of the sulphur content. Every single crude oil is a highly individualistic, unique combination of compounds that can differ between geographic formations, and even within the same formation at varying depths. Once the crude oil has been removed from the formation, it is transported to a refinery for breakdown into specific products. This process involves distillation, thermal or catalytic cracking, and subsequent reforming and blending to arrive at a wide range of petroleum products or feedstock. These products, in turn, are often transported over land and water to terminals for distribution and marketing.

The most common types of petroleum products which are likely to be released into the environment, besides crude oil itself, are Bunker 'C' (No. 6 fuel oil), diesel (No. 2

fuel oil) and light products, such as kerosenes and gasolines. Bunker 'C' is the heaviest distillate fraction, with a specific gravity near 1.00. Chemically the majority of its compounds are in the C_{30} range or higher. Diesel is a middle distillate fraction, with specific gravity from 0.825 to 0.850 and composed almost entirely of hydrocarbons in the C_{12} - C_{25} range. Kerosene contains hydrocarbons in the C_{10} - C_{12} range and has a specific gravity of about 0.800; gasoline hydrocarbons are in the C_5 - C_{10} range with a specific gravity of approximately 0.700. All refined products contain proportions of paraffins, naphthenes and aromatics; some of virgin origin, and some arising from cracking within the refinery process. It is apparent that crude oils and their refined products vary widely because of their chemical and physical properties which, in turn, can greatly influence the fate and effects of oil released into the environment.

1.2 Worldwide and Canadian Inputs of Oil in the Environment

Worldwide input of petroleum in the marine environment is estimated to be about 6 million tonnes annually (Wilson and Hunt, 1975). About 35% of this input is attributable to marine transportation; other sources include: river runoff (26%); natural seeps (10%); atmospheric input (10%); nonrefinery industrial wastes (5%); urban runoff (5%); municipal wastes (5%); coastal refineries (3%); and offshore production (1%). The largest single source of oil entering the environment--marine transportation--can, in turn, be broken into causes in order of decreasing contribution: ballast water and tank washing release; bilge water release; dry docking activities; tanker accidents; and terminal operations.

Tanker accidents, often given a high level of publicity, account for only about 3% of all petroleum released into the environment. A more recent estimate of total oil entering the marine environment indicates some reduction in this figure to about 5 million tonnes, because of reduced discharges from tanker operations, resulting from improved technology such as load-on-top techniques (LOT) and changed legislation (Cowell, 1978). Tanker spills, however, increased in magnitude in 1978 and 1979. Other recent events which change the estimates for 1979 include an offshore oil blowout in the Bay of Campeche, Mexico, which released an estimated 0.4 million tonnes in the first four months, and discovery of a large oil-rich layer of water at a depth of 200 metres, containing an estimated 1 million tonnes of oil. This apparently originated from a natural seep off Venezuela (Harvey et al., 1979).

In Canada, oil spill statistics have been compiled for a number of years by the Environmental Emergency Branch of the Environmental Protection Service (EPS) in

Ottawa. These data were based on volunteered information retrieved via the National Analysis of Trends in Emergency System (NATES). It is estimated that NATES includes about 60% of Canadian spills of all types and sizes. In 1978, over 1500 spills were reported, representing about 20 000 tonnes (Beach, 1979). A significant proportion of these came from motor vehicle spills and production spills originating on land, although it would be expected that some proportion would eventually enter waterbodies, either through surface runoff, or into the water table. Canada's largest marine spills are documented in Chapter 3.

In the coming years, a number of events on the international and national energy scenes will have further potential for oil spills affecting Canadian waters and coastlines. Increased oil tanker traffic from Alaska to the mainland west coast of the U.S.A., as well as increased tanker and other maritime traffic in Canada's arctic seas, will create greater possibilities of spills in those areas. Further, the trend in Canada as elsewhere around the world, is towards offshore exploration and production of oil and gas. With this goes the possibility, however remote, of a blowout and sustained release of oil for some period of time. Oil spill statistics are changing even at the marketing level. As a result of consumers' increasing preference for "home oil changes", used crankcase oil is increasingly finding its way into local sewer systems and municipal landfill sites, thus contributing to urban and river runoff.

On the positive side, any future reduction in offshore imports by tankers, and corresponding increase in transportation by pipeline within the country, should lessen the overall potential for spills in Canada, since pipelines are generally considered to be one of the safest means of transporting oil. Canadian refineries are required to meet an oil and grease limit in their effluent, which from 1972 to 1977 resulted in a 38% reduction in total oil discharge (EPS, 1979). By 1980, percentage reduction should be greater still, as all Canadian refineries complete new treatment systems. Further, overall energy conservation and stabilization or reduction in consumption, along with higher prices, will act to reduce the frequency of oil spills. Finally, cleanup costs associated with spills have greatly escalated in the past few years, adding more economic incentive to prevent spills.

1.3 Research and Development in Canada

Canada is faced with some difficult and unique problems regarding oil spills, which revolve essentially around three geographic and physical features of the country:

1) Canada has within its boundary large marine and freshwater resources to protect for commercial, biological, recreational and aesthetic reasons;

2) Canadian waters are typically cold and often ice-covered for portions of the year; and

3) much of the marine environment and coastline is remote and often inaccessible.

While all of these features should in theory spur research concerning fate and effects of oil under conditions typical of Canadian situations; in reality this has not been the case. Only limited field studies of oil spills have been done in the past on controlled or opportunistic spills, and although much has been gleaned from the data acquired, especially those on chronic fate and effects of oil from the ARROW spill of 1970 (see Chapter 3); many unknowns still exist. Arctic field research in particular, is very limited. Interpretation of effects on arctic species are often derived from studies conducted in temperature regions.

Laboratory research has added valuable data on simplistic cause-effect relationships, and in modelling the fate of oil under varying conditions. Such data, however, are limited in their application to field conditions, creating a need for both lab and field work. That such information or data-base on oil spills is required is evident, for three reasons.

1) Assessment from an environmental standpoint of projects or developments at the planning and design stage is now looked on as fairly standard practice. In the case of undertakings involving petroleum, it is usually necessary to consider the environmental implications of an oil spill. Thus it is critical to have an accurate and reliable data-base from which predictive judgements can be made.

2) During an actual spill, decisions must often be made quickly to counteract the spill, using the knowledge available at the time. Many factors determine the extent and type of countermeasures, including the physical resources available, the weather and sea state, safety, and environmental concerns. Knowledge of biological conditions in the spill area, environmental effects as predicted from previous research, and probable behaviour of that particular spill will form the basis for deciding on environmental priorities.

   One of the more sensitive areas of oil spill countermeasures involves the use of oil spill dispersants. Such dispersants, composed of a surfactant dissolved in a solvent, act to break oil into smaller particles, thereby facilitating dispersal into the water column and reducing hydrocarbon concentrations at

the surface, through a lowering of oil-water interfacial tension. Their use is subject to close scrutiny in Canada and most other countries, although it is generally recognized that dispersants can play a countermeasure role in some situations. The extent of that role, however, will depend ultimately on the environmental trade-offs involved in a particular spill. Further chapters will highlight the data-base on dispersants.

3) Post-spill field assessments are critical if researchers are to take full advantage of opportunistic spills. Such assessments add much "hard" information compared to other approaches. Some attempts have been made to further develop and standardize post-spill assessment techniques and methodologies for sample collection, analysis and interpretation. As biological data are used to a greater extent in the courts of law to substantiate damage claims and form the basis for liability suits, it is necessary to have recognized methods, approved by the scientific community, for assessing the effects of oil on the environment.

In the following chapters, the present state of knowledge on oil spills with particular reference to Canada, from which deficiencies in the data-base will be highlighted and decisions on future research needs can be made, is discussed in some detail.

2 FATE AND BEHAVIOUR OF OIL SPILLS

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The physical, chemical and biological processes which occur when oil is spilled at sea, and the identification of processes which are inadequately understood, are described in this chapter. An inventory and overview of the processes, stressing the relative importance of each process at each stage of the spill history, is presented in the first part of the chapter. Each process is examined in detail and gaps in knowledge are identified. Finally, recommendations for research are presented, which if carried out, would elucidate the process rates and mechanisms, and ultimately lead to an adequate understanding of the fate and behaviour of oil spills.

Throughout this review emphasis is placed on spill behaviour under conditions encountered in Canadian waters. Although in many cases the voluminous literature on behaviour of spills in other, usually warmer waters can be extrapolated to Canadian conditions, there are areas of particular Canadian interest, especially interactions with ice in its many forms.

Comprehensive reviews of oil spill processes have been published previously by the National Academy of Sciences (Wilson and Hunt, 1975; Clark and MacLeod, 1977; Karrick, 1977; and McAuliffe, 1977). Only selected statements are referenced here. Detailed documentation of the general statements may be obtained from one of the reviews mentioned above, or from the biennial EPA/API/USCG Spill Prevention and Control Conference Proceedings (e.g. API, 1977).

2.1 Natural Processes that Follow an Oil Spill

A pictorial inventory of the significant oil spill processes on the open ocean, at shorelines, and when interacting with ice is depicted in Figure 2.1. This figure forms the basis of the subsequent detailed discussion. The relative importance of these processes varies with weather, sea conditions (particularly sea state or roughness), wind, temperature and with the nature of the spilled oil. Therefore, it is impossible to describe a "typical" spill. It is important to gain some appreciation of the relative significance of

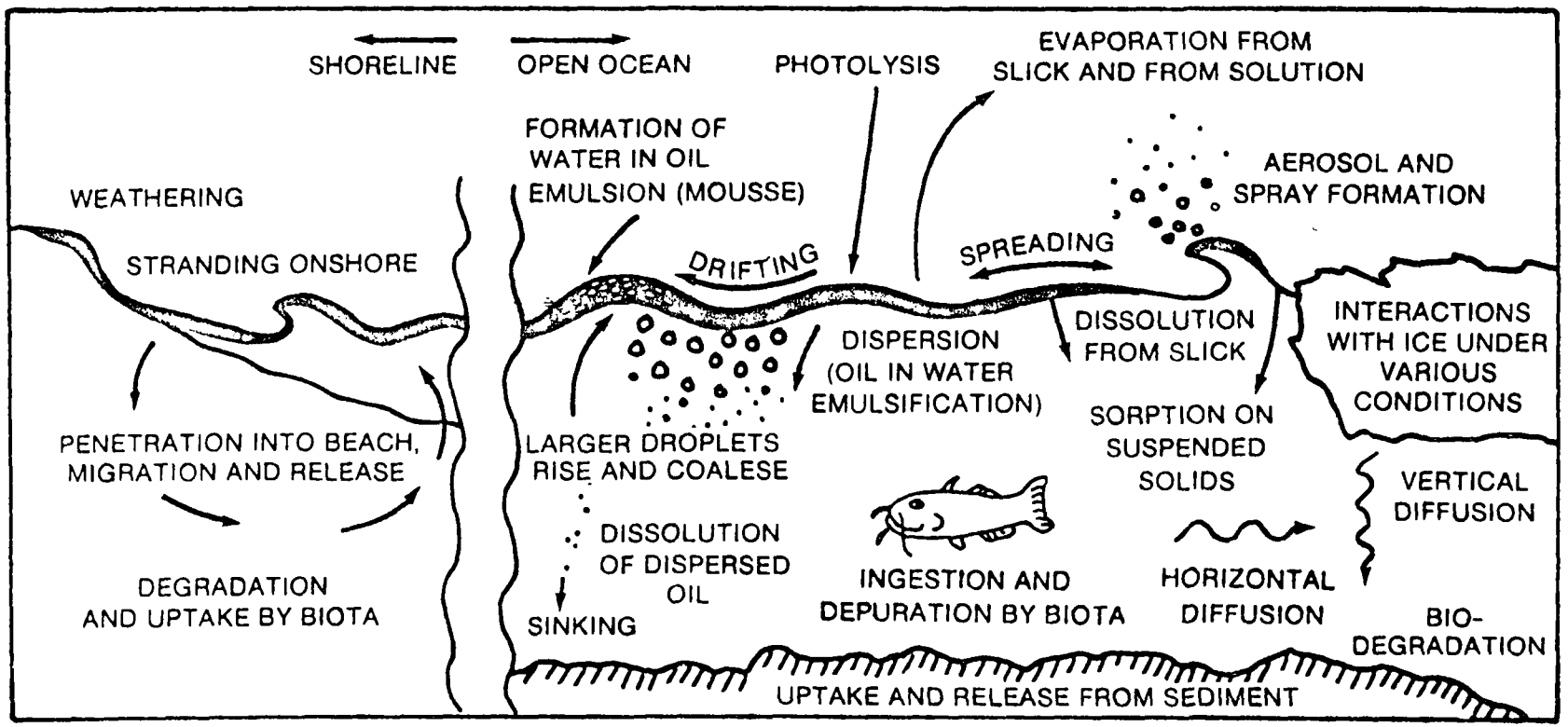

FIGURE 2.1 OIL SPILL PROCESSES

these processes, however, particularly as their roles change during the mass history. A semi-quantitative pictorial mass balance of a spill, in which 100 volumes of crude oil are spilled on the sea surface at time zero is found in Figure 2.2. As time progresses, the oil becomes distributed among atmosphere, water surface, water column and sediment, and becomes converted into chemical forms which differ significantly from the original oil. Examples are photolysis or enzymatic oxidation to alcohols or CO_2. Such "converted", non-hydrocarbon oil is shown as empty or unshaded boxes in Figure 2.2, whereas the hydrocarbon oil is shown as shaded. The times are shown on a logarithmic scale. It must be emphasized that the quantities are only illustrative and would vary considerably from spill to spill. In some cases the values are quite speculative, especially those at 100 days or longer.

A general history of an oil spill could be summarized as follows. During the first day the principal processes are evaporation and dispersion of oil particles into the water column. Some dissolution and atmospheric photolysis may occur but this affects a relatively small fraction of the spill. Evaporation proceeds until 25% of the spill may have evaporated, after two to five days. Subsequent photolytic oxidation in the atmosphere is probably fairly rapid. As the spill spreads and thins, an increasing fraction of the oil is dispersed into the water column, and in many cases the surface slick may disappear. It is suspected, however, that a considerable fraction of the oil remains on the surface, eventually becoming tar lumps which may be stranded on beaches. Biodegradation of dissolved and dispersed oil probably becomes significant after three days and eventually emerges as the most important oil removal process during the first year. Small and unknown amounts of oil sink to the bottom or are ingested by animals of various trophic levels.

An important implication is that the ultimate fate of a specific hydrocarbon depends on its physical and chemical properties. Volatile hydrocarbons of boiling points less than 200°C undergo evaporation and photolysis. Dissolution may be significant for the more soluble hydrocarbons, such as the aromatics. The most significant dissolved hydrocarbons from a toxic viewpoint may be the less volatile aromatics such as naphthalenes, since the single-ring compounds are predominantly lost by evaporation. Biodegradation is likely to be the fastest for normal alkanes and may be negligible for certain highly fused aromatic or multi-ring compounds. Conversion from hydrocarbon to another chemical form does not necessarily imply elimination or even mitigation of the toxic problem. Some oxidation products such as phenols may be more toxic than the parent hydrocarbon.

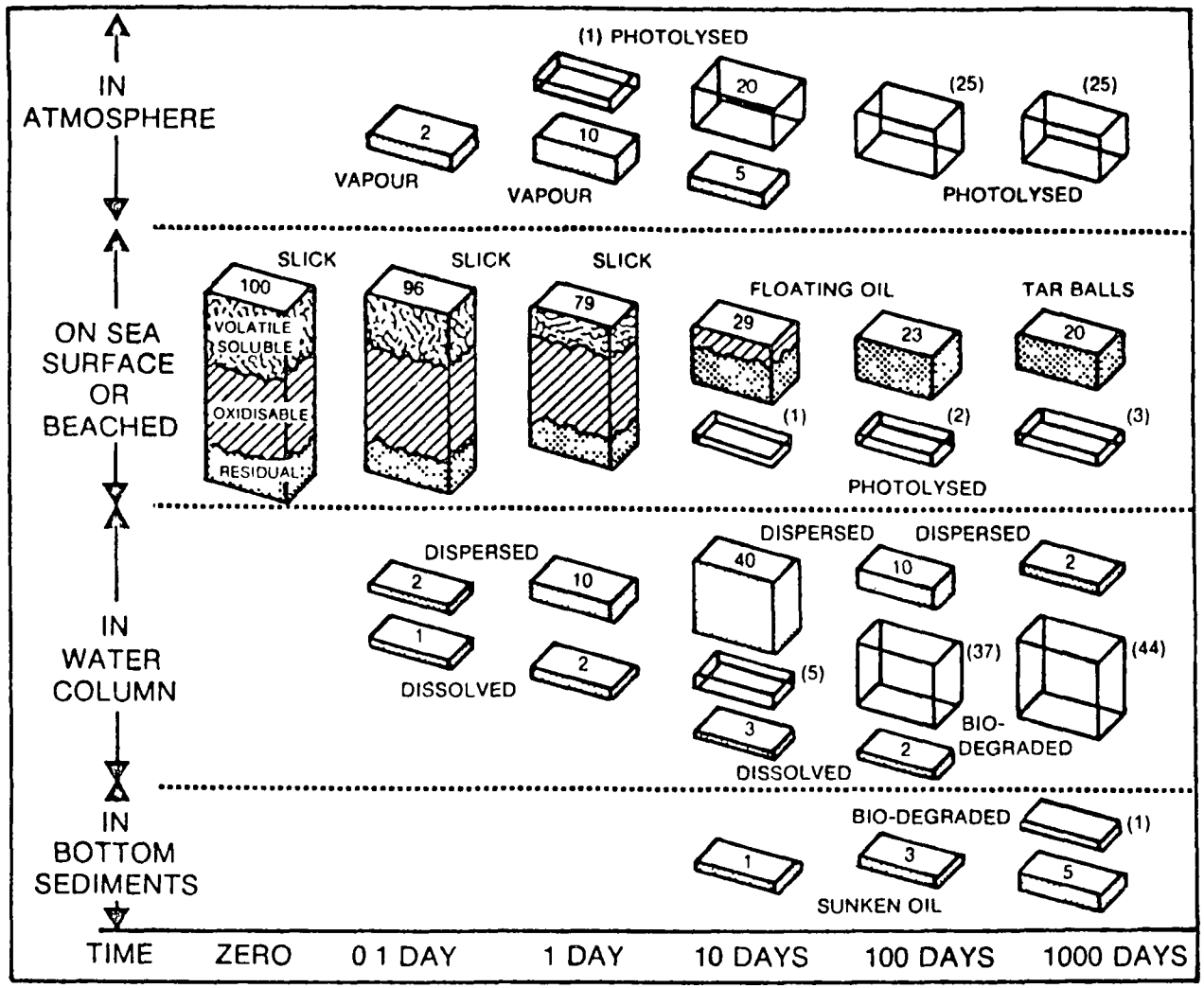

FIGURE 2.2 SPECULATIVE MASS BALANCE; illustrating the distribution and conversion of an initial 100 volumes of oil at various times after spilling. Empty unshaded boxes represent oil converted to another chemical form. (Based on a similar diagram by J.N. Butler, Harvard University).

Ultimately, the oil residue remaining in and on the water differs considerably in chemical nature from the spilled oil. This has important implications for identifying the source of the oils, for long-term toxicity studies, and for monitoring programs. In these cases, it is essential to have a quantitative understanding of the chemical and physical changes undergone by the spill.

Spill behaviour is also dependent upon the nature of the spilled oil. Crude oils vary considerably in density, viscosity, volatility, composition (including sulphur, nitrogen, oxygen and metal contents, as well as hydrocarbon classes), interfacial properties and in susceptibility to stable water-in-oil emulsion formation. In submarine blow-outs, the volume of natural gas may be one hundred times that of the oil, and this may alter the nature of the oil/water interaction. The commercial petroleum-derived products range from heavy fuel oils through lighter grades such as kerosene, diesel fuel and gasoline, and even to highly volatile liquid petroleum and natural gas cargoes. Obviously, a characterization of the oil's significant physical and chemical properties is essential in any attempt to predict its fate and impact.

2.1.1 Pre-slick Behaviour. An often neglected aspect of spill behaviour, but one of considerable relevance to exploration in the Canadian Arctic, is the mechanism by which the oil and gas is introduced to the water surface. Most large marine accidents, as distinct from deliberate discharges, have been from tankers which have collided or grounded and in which oil is steadily released over a period of days from ruptured storage compartments at or below water surface. Quite different behaviour occurs when oil is released from above surface, for example from malfunctions of drilling or production platforms, as occurred in the Ekofisk incident. The oil may spray from the platform, undergoing considerable evaporation before it falls on the surface. Alternately, the oil may be released at the sea bottom, either through or around the well casing, or even at some distance from the well because of transport by a geological fault. Such oil will contact the water column more intimately during its rise, possibly resulting in high dissolution and dispersion rates of those volatile hydrocarbons which would normally evaporate prior to dissolution. An area of particular concern that is not well documented, is behaviour in very deep water such as 300 metre depths which occur in the Davis Strait or Lancaster Sound regions. At these great depths and resulting pressures, methane may form stable, solid hydrates. During the long, slow rise, the oil droplets may be subjected to significant dissolution, degassing and disintegration, and there is a possibility that a large fraction of the finely-dispersed oil will never reach the surface. Oil which does

surface, may be insufficient in concentration to form a continuous slick, due to horizontal dispersion of the rising plume. Horizontal currents will tend to separate the rising oil and gas plumes and the surfacing location may be quite distant from the drilling location. This topic has been reviewed recently by Milne and Smiley (1978) and is of critical importance in assembling a meaningful environmental impact statement for deep drilling operations.

The "Ixtoc I" oil well in the Bay of Campeche, Mexico, which blew out on June 3, 1979, discharging a reported 4 800 m^3 per day, has provided interesting and unexpected insights into full scale blowout behaviour (Ross et al., 1979). The oil and gas burned at the sea surface in a fire about 50 m in diameter and 7 m high, with surprisingly little smoke. The oil became emulsified with water by approximately 70%. The most probable mechanism is that the burning oil-gas froth at the surface is subjected to high turbulence promoting emulsion formation as the burned oil emerges from the fire. Emulsion formation in the well bore or water column may also occur but the loss of volatiles from the oil indicates exposure to the flame evaporation prior to emulsion formation. Perhaps the most significant implication is that the incident has demonstrated our present inability to predict the behaviour of oil releases of this type.

2.1.2 Spreading. The studies by Hoult (1972), Fay (1971) and Blokker (1964), have led to an understanding and a predictive capability which is probably adequate for most purposes. The roles of gravitational, inertial, viscous and surface forces are reasonably well understood and empirical correlations adequately fit actual observations. Less satisfactory is the ability to understand and predict the tendency for the oil slicks to form patches of both thick and thin slicks. This has been described by Jeffrey (1973) and more recently by J.B.F. (1976). This heterogeneous surface distribution of oil is important in spill modelling, since 90% of the oil may form thick patches which occupy only 10% of the area, and the amounts of oil present in the thin 90% area may be insufficient to form concentrations in the water that are of toxicological significance. This complex phenomenon may result in part from changes in interfacial forces during weathering and spreading, and is not amenable to simple laboratory investigation. Further full-scale work in this area is required. Unfortunately, the few reliable aerial observations of oil spill spreading tend to be from experimental spills which are often atypically small.

2.1.3 Drifting. The movement of the oil slick relative to a water surface-drifting is clearly of great importance in modelling an oil spill trajectory, either for impact

assessment or on-scene countermeasures. Surface slicks have been observed to drift at a velocity of 3 to 4% of wind speed. The exact percentage is a matter of some controversy in oil spill modelling circles but is probably of little significance, because wind speeds cannot be predicted, or in some cases even measured, with corresponding accuracy. More important, and still unresolved, is the controversy over the role of the Coriolis forces in causing a wind-driven slick to angle to the wind direction (to the right in the northern hemisphere). Addition of wind and current vectors is relatively straightforward, but there is evidence that this simple process may be inadequate for accurate predictive purposes. Usually the major inadequacy is the unreliable data for currents and wind, rather than of the slick reaction to these effects.

Careful observation of experimental slicks could resolve these difficulties. This issue has been reviewed in some detail by Stoltzenbach et al. (1977) and Rath and Francis (1977).

A related problem is that of Langmuir circulations which may cause oil drifting into windrows. The significance and prevalence of these circulations is not well understood.

2.1.4 Evaporation of Oil from Slicks. Evaporation is probably the best understood of all oil processes, since it is amenable to laboratory simulation and experimentation. Several approaches have been taken by different workers, notably those of Kreider (1971), Butler (1976) and Mackay and Leinonen (1977). The evaporation rate per unit area depends on the oil vapour pressure, which is in turn a function of temperature and composition; and a kinetic or transport term which is best expressed as a mass transfer coefficient, dependent primarily on the level of atmospheric turbulence above the spill, as controlled by wind speed. Evaporation rate is also dependent to a lesser extent on fetch, surface roughness and the gas phase molecular diffusivity of the evaporating hydrocarbon. The preferential loss of volatiles causes an enhancement in concentration of the non-volatiles, and thus an increasing oil density, viscosity and surface tension. An often unappreciated point is that the rate of change of composition depends not only on the evaporation rate but also on the slick thickness, thick slicks undergoing slower compositional changes because of the greater evaporation loss necessary to accomplish a given concentration change. Any studies of oil properties such as toxicity, in which evaporation is a variable, should express extent of evaporation as the fraction of the original mass which has evaporated.

The most satisfactory approach to prediction of evaporation is probably to obtain actual evaporation data for the oil in question from pans (outdoors or in a wind tunnel) under defined conditions of temperature and wind speed. Extrapolation can then be made to marine conditions. An alternative approach is to simulate an oil from a small number of components (possibly ten) and predict the evaporative behaviour by solving the batch distillation equations numerically. Chromatographic analysis of the oil can also be used to assist the assembly of a simulated composition.

In most cases, the calculations contain the implicit assumption that the oil slick is well mixed vertically, i.e., the time taken for a compound to diffuse to the surface is small compared to the evaporation time. This is undoubtedly not true for thick, viscous slicks, especially those subject to viscosity increase by formation of water-in-oil emulsions. There has been no clear characterization of the conditions in which diffusion is significant within the slick.

Although the available predictive techniques enable evaporation rates and the resultant effects on oil composition to be calculated with an accuracy adequate for most purposes of evironmental assessment, it would be desirable to assemble a standard, generally-accepted approach for evaporation calculations, which would permit the calculation of behaviours of a range of crude oil and petroleum products.

It is believed that evaporation does not occur under ice, so that some components that would normally evaporate would achieve higher concentrations in the water columns under ice.

2.1.5 Evaporation of Oil from Water. It is well established that volatile hydrophobic organics such as hydrocarbons have relatively short residence time in surface waters because of their highly non-ideal (positive) Raoult's Law deviation. These rates can be predicted, and half-lives are typically one day for a surface layer of water ten metres deep (Mackay and Leinonen, 1975). Thus, water just below the surface, contaminated by exposure to a thick slick, may lose the volatile soluble materials rapidly on subsequent exposure to the atmosphere with the slick absent. Measurements reported by McAuliffe (1977) support the view that the combination of evaporation from the slick and from the water column results in the incorporation of relatively small lasting quantities of volatile hydrocarbons into the water column. Present understanding of this process is probably adequate, except in cases such as deep blowouts when the overall evaporation rate is controlled by the rate at which the hydrocarbons diffuse upwards through stratified layers of water.

This process is, of course, absent under ice cover. It is possible that the full mitigating significance of evaporation will not become apparent until comparable data for concentrations are obtained for conditions in which ice is absent, and present.

2.1.6 Water-in-Oil Emulsions (Chocolate Mousse). Some oils, when exposed to turbulent sea-surface conditions, tend to accumulate dispersed water droplets with diameters ranging from 5 to 20 μm. These droplets are sufficiently small that their settling velocity in the oil is negligible, especially if the oil viscosity is high. They are thus permanently retained in the slick. Chemical evidence indicates that oils contain variable amounts of unidentified compounds, or groups of compounds, which stabilize these emulsions, retarding coalescence. The emulsions may contain high proportions of water, (75%), and have viscosities several orders of magnitude greater than the parent oil. This effect is critically important for spill countermeasures, and has been described in a series of papers by MacKay and Oren (1975), MacKay et al. (1973) and Oren and MacKay (1976, 1977).

The general picture which emerges is that the slick is subject to two competitive dispersion processes - formation of water-in-oil, and oil-in-water emulsions. Which process dominates is dependent on the viscosity, thickness and nature of the oil. Although one can speculate with fair accuracy that light oils tend to form oil-in-water emulsions, and heavy oils tend to form water-in-oil emulsions, there is at present no reliable method of predicting which process will dominate for any given oil. Such a predictive capability would be very valuable, especially for the many crude oils which are in intermediate categories. Simple laboratory tests would be invaluable. Further research on the kinetics and mechanism of emulsion formation and identification of compounds responsible for their stability is also desirable.

2.1.7 Dispersion. It is surprising that we are so pitifully ignorant about the dispersion process since it is probably the most important single oil spill process governing the amount of oil in the water column. Comprehensive reviews have been compiled by Stoltzenbach et al. (1977) and Raj (1977) but the nature of the mechanism and the rates remain speculative. It appears that an oil slick subject to natural turbulence of the sea surface tends to break up into small droplets, some of which have a sufficiently small rising velocity that they are semi-permanently incorporated into the water column where they later dissolve and are degraded. The larger drops with higher rising velocities presumably tend to surface and recoalesce with the slick. The mechanisms of formation

of these droplets is far from clear. Raj (1977) has suggested that the dominant mechanism is wave-breaking or white-capping in which the water from a breaking wave plunges onto the oil slick, driving it under the surface as droplets. Presumably, the thinner the slick, the more frequently wave-breaking occurs because of the damping effect of a thick oil slick, and the more likely is the formation of small droplets which become permanently dispersed. It is possible that other mechanisms are operational when oil is dispersed under calmer conditions with no breaking waves, but this remains a matter of some controversy. Other mechanisms could include rainfalls, slick stretching-compression leading to droplet separation, or Langmuir circulations in which slicks may be carried into the water column in down-welling regions.

The principal resistive effect to dispersion is the water-oil interfacial tension which is typically 20 to 30 dynes/cm, enough to require a significant input of energy for the formation of a surface area of small droplets. The issue is not so much the availability of the total amount of energy, since waves contain very large amounts of energy, but rather the availability of the energy in sufficient concentration to permit the new surface to be formed in a small volume. Oil spill dispersants reduce the oil-water interfacial tension and thus facilitate and accelerate the natural dispersion process.

An interesting but probably unimportant process is the formation of near neutrally buoyant water-in-oil-in-water particles, consisting of large (several mm) water spheres surrounded by a thin oil film. These may form and drift for some time under the slick.

The present lack of understanding of the dispersion mechanism, and our inability to predict rates of dispersion of oil slicks is an important gap in knowledge. Meaningful assessments of the impact of oil spills on aquatic biota can only be accomplished if there is a knowledge of the concentration and state of dispersion of the oil in the water under various conditions. This knowledge is lacking, partly because detailed observations and measurements of conditions under actual oil slicks are rare. Laboratory simulation of open seas, particularly under wave-breaking conditions, is very difficult, and exact simulation is probably impossible. This process clearly merits considerable research, both in laboratory and at sea, for the above reasons, and also because it is suspected that the major toxic effect of oil may be from the dissolved oil, and the main dissolution mechanism may be from previously dispersed oil rather than from the slick itself. Oil that sinks may be mostly dispersed oil, which could be the source of long-term benthic contamination problems.

2.1.8 Dissolution. It is believed that dissolved hydrocarbon concentrations encountered under an oil slick, although usually considerably lower than those of dispersed hydrocarbons, may be more toxicologically significant. The relative toxic contributions arising from each form are not clear, and the issue is complicated by the different chemical natures of the hydrocarbons present in each form. The dissolved hydrocarbons are predominantly aromatic in nature, whereas the dispersed hydrocarbons are probably deficient in aromatics. In addition, it is likely that the mechanisms of toxicity are quite different and vary considerably from species to species. With organisms of the same size as the oil particles, it seems unlikely that interaction will be significant, especially if the organism can take evasive action. On the other hand, if the oil particles are of the same size as the usual food source, the organism may accidentally ingest large quantities of oil, or particles may coat and block respiring surfaces. Dissolved oil would probably act by diffusing into vital fluids and organs, thus giving a different type of toxic effect. The separation of the dispersed and dissolved toxic effects as a function of organism type is clearly a matter of considerable importance, particularly if chemical dispersion is considered as a countermeasure.

The rate of the dissolution process which controls the concentration depends on two groups of factors - a thermodynamic or equilibrium group largely consisting of solubility or partition data, and a kinetic group consisting of a combination of a mass transfer coefficient and interfacial area.

The equilibrium information required is essentially the solubility of the oil, which is the sum of the solubilities of its components. Adequate information is available on the solubility of pure hydrocarbons in fresh salt water. Less clear is the solubilization of mixtures of hydrocarbons, in which it appears that simply reducing the component solubility in linear proportion to the mole fractions, will underestimate the solubility (Mackay and Leinonen, 1975). The reasons for this are not clear and require elucidation.

As a crude oil slick weathers and loses its volatile components, its solubility decreases from approximately 30 to 5 mg/litre. The dissolved hydrocarbons are predominantly aromatics, especially benzene and toluene which may constitute half of the total amount of soluble hydrocarbons (Mackay and Shiu, 1975).

The kinetic terms depend on the fluid mechanical regime existing at the oil-water interface. Since oil is viscous, the level of turbulence beneath the slick is usually low, and the mass transfer coefficients are believed to be of the order of 1 cm/h

compared to 20 cm/h at the air-water interface. This effect markedly reduces the rate of dissolution and acts as a buffer between the slick and the water column. A significant route for dissolution may be dispersion of oil followed by dissolution. Mackay and Leinonen (1977) have suggested that small oil particles reach a state of dissolution equilibrium very quickly, so that all reasonably soluble hydrocarbons dissolve. Fortunately, these form a relatively small fraction of the total mass of oil (a few percent); thus dissolved concentrations must be lower than dispersed concentrations by at least a factor of ten and probably of one hundred.

Mathematical expression of dissolution rates from slicks is quite straightforward, but the rate from dispersed oil is very difficult to describe because much of that oil is only temporarily dispersed and coalesces later with the slick. Until there is a clearer quantitative picture of the dispersion regime existing under the slick, it is impossible to predict dissolution rates reliably. It does seem likely that the 10 to 30 cm of water immediately below the slick could contain high concentrations of dissolved hydrocarbons, but concentrations would fall off rapidly at greater depths. Unfortunately, it is very difficult to sample this region reliably, and most experimental work has concentrated on deeper waters, where contamination during sampling is less likely.

2.1.9 Sinking or Sedimentation. This process is poorly understood and deserves more attention because it is becoming increasingly accepted that much of the long-term impact of oil spills is associated with incorporation of oil into marine sediments and benthic organisms, many of which are of economic value (Vandermeulen et al., 1977). Most oils are less dense than water and even after evaporation, it is only under exceptional conditions that the oil density will exceed that of water (Morris et al., 1976). The implication is that sinking will occur only by association of the oil particle with a denser material such as inorganic sediment or organic detritus; from oil presence in fecal matter or, if near neutrally buoyant particulate oil with a slow-rising velocity, is subject to eddy diffusion of sufficient velocity that some of the oil is conveyed to the bottom where it associates irreversibly with sediment. This latter mechanism is most applicable in near-shore turbulent waters. In areas such as the Mackenzie Delta with high sediment loads there may be a significant tendency for sedimentation by association with suspended solids.

No predictive procedures are available for estimating sedimentation rates, which is an obvious area of inadequacy because of the possible economic and ecological significance of this pathway.

The fate of the oil when sedimented is also poorly understood. The physical, chemical and biological release and conversion rates and their mechanisms merit closer study, especially in sediments which support populations which are of economic or ecological significance.

2.1.10 Tar Ball Formation. The residual oil on the surface tends to form tar balls which vary considerably in size and which often have living organic matter on their surface. Presumably, most of these tar balls are ultimately stranded on shore. Some doubts exists about the fraction of the oil which ultimately becomes tar lumps, about their residence time on the water surface, and on their biological significance. This phenomenon has been reviewed in a series of papers by Butler (1975).

2.1.11 Photolysis. The dominant degradation process of hydrocarbons in the atmosphere is photolysis. Photolytic processes are significant at the sea surface, and possibly in solution in near-surface waters. This process can be very important in that the chemically-altered hydrocarbon may be more toxic and soluble than its parent, and the oxidized form may be subject to faster biodegradation, (Burwood and Speers, 1974 and Larson et al., 1977). A knowledge of the role of photolysis in modifying oil behaviour is clearly of considerable importance and more research is required in this field. Gesser (1977) has proposed that photosensitizers may have a role to play as a countermeasure agent by enhancing oil photolysis rates, at least on shore, but the full implications of such an approach are not yet fully assessed.

2.1.12 Aerosol Formation. Under rough sea conditions with high winds, substantial quantities of oil may be conveyed into the atmosphere as aerosol sprays, and may be transported some distance and even onto land. This phenomenon was reported at the recent AMOCO CADIZ spill in France, and although an obvious source of annoyance to those affected, it is probably not of sufficient significance to merit much attention.

2.1.13 Horizontal and Vertical Diffusion. Dissolved or near-neutrally-buoyant dispersed oil is subject to transport in the water column by advecting currents which can be measured using experimental drifting devices, and by random eddy diffusion. The eddy diffusivities are non-isotropic, the horizontal component generally being an order of

magnitude greater than the vertical, and their values are poorly understood (Csanady 1973). Both are important as processes which dilute the oil concentration under the slick and expose distant water volumes to oil contamination. Dye tracer experiments with aerial observation can yield considerable information about currents and horizontal diffusion, but vertical diffusion is unfortunately less well characterized, although it is more important in some respects. It is essential to develop a capability of predicting horizontal and vertical diffusion fields in order that adequate water column models can be assembled in which oil concentrations can be calculated. Of particular concern is the presence of stratified regions of different temperatures or salinities, since these can act as diffusion floors or barriers. A simple experimental system for obtaining diffusivity information is badly needed.

2.2 Biodegradation and Other Biological Conversion Processes

A description of biodegradation is beyond the scope of this chapter, and it is sufficient to state here that the dissolved and dispersed hydrocarbons are converted by micro-organisms into oxidized products at rates which are poorly understood, and which depend on the nature and concentration of the oil, the availability of oxygen and nutrients, temperature and the nature and number of available micro-organisms. Although some half-life estimates are available from laboratory experiments using pure cultures and pure hydrocarbons, it is a matter of some conjecture and controversy at present how and if these rates can be extrapolated to actual marine conditions. This doubt also applies to oil conversion, ingestion or absorption by biota of all levels. It is evident that this area merits further examination, and it is treated in greater depth in Chapter 4.

2.3 Interactions with Ice

Interaction with ice is obviously of considerable Canadian concern, especially in arctic waters which may be subject to ice of various ages and thicknesses for the greater part of the year. The most authoritative and useful work has dealt with the interaction of oil with first-year ice by Norcor (1975) in the Beaufort Sea, and the area has been recently reviewed by Lewis (1976) and Mackay and Paterson (1979).

Any attempt to understand oil behaviour must be predicated on a full understanding of the ice behaviour, which is unfortunately complex and variable in time and location, and in many respects inadequately understood. The incorporation of oil into

growing first-year ice and its subsequent release in the spring has been well documented. The interfacial non-wetting behaviour of oil droplets under ice is adequately understood, but the nature of the interactions between oil, gas and ice are less certain. A matter of some concern and importance is the behaviour of oil under multi-year ice, since if oil is trapped in this ice for some years it could be carried considerable distances, across international boundaries, and into economically important fishing grounds. Another area of interest is the behaviour of oil in ice-infested waters, as occurs off the northeast coast. The continuing movement and grinding of ice floes separated by oil-covered channels could cause the oil to emulsify or spread onto the ice surface, possibly enhancing melting by albedo reduction. Probably only large-scale spills could elucidate such phenomena.

In summary, the entire subject area of oil, gas, and ice interaction is one which merits particular Canadian attention.

2.4 Shoreline Processes

When wind or currents drive oil to shore, the subsequent behaviour may be critically important for economic, ecological, and aesthetic reasons. It is probable that shorelines, including salt marshes, represent the most vulnerable areas for oil contamination. Most Canadian experience has been derived from studies of the ARROW tanker incident, notably those of Vandermeulen et al. (1976, 1977). The interactions of oil and shoreline have been reviewed in a number of publications by Owens (1977, 1978).

Oil stranded on rocky coastlines tends to degrade over a period of months or years under high-energy conditions. More significant is the stranding of oil on beaches or salt marshes in which there is a possibility that some of the oil will become incorporated in sediments and will be released slowly over periods of years. The severity and implications of this process depend on factors such as the type of oil, the energy state of the beach and the rate of biodegradation and dissolution of the oil in the sediment. The dynamics and biological effects of oil migration and release are poorly understood. Some controversy surrounds the issue of whether or not dispersants increase or decrease oil damage in such cases. Progress towards elucidating this issue can only be made by simultaneous consideration of a complex assembly of information about shoreline processes, oil/mineral surface interactions, oil diffusion and migration processes, and companion biological studies. Although this is a formidable task, it is likely that little real progress can be made in shoreline protection and restoration technology until there is a better understanding of these processes.

2.5 Modified Behaviour After Control Operations

The processes described in the previous section were largely those which occur if the oil is allowed to spread, weather and degrade naturally. In many cases, of course, efforts are made to recover, contain or disperse the oil, and this may substantially alter its behaviour. Four techniques are considered here: dispersion, herding, sinking, and burning.

2.5.1 Dispersion. A number of chemical formulations are available commercially which when added to an oil slick, increase the rate of dispersion, resulting in elimination of the surface slick and formation of a relatively high concentration of oil particles in the underlying water column. These products contain surface-active ingredients which reduce the oil-water interfacial tension, thus reducing the energy barrier for formation of the large interfacial area associated with dispersion. The products vary considerably in effectiveness and toxicity, the newer products generally being more effective and less toxic. Of particular interest are the concentrates, or "no mix" products which are very effective even when applied at ratios of 1 volume of dispersant to 30 volumes of oil.

Most regulatory agencies establish approved lists by subjecting the products to tests for effectiveness and toxicity. Unfortunately, no meaningful standard test for either property is available or universally recognized.

Application of dispersants can be from a boat; usually by some spraying system, from shore; either on approaching oil slicks, or on oil which has already beached, or from the air using techniques developed for pesticide application to crops or forests. The effectiveness of the dispersant depends on a number of factors, including the natures of the oil and dispersant, their volumetric ratio, the oil temperature, the water salinity, the method of application, and the prevailing turbulence level at the sea surface. No mechanism has yet emerged by which the amount of oil dispersed under given application conditions can be predicted.

The principal alleged benefits of dispersion are that it prevents fouling of birds and of shorelines. The obvious disadvantage is that organisms in the water column become exposed to higher concentrations of oil. There may also be an increase in benthic exposures as a result of greater sedimentation. Another controversial area is that of the relative impacts of dispersed and undispersed oil on shorelines. Available experimental data suggests that although dispersion reduces adhesion of oil to rocks and sand, it may facilitate penetration of small oil particles into porous sand or sediments. The decision on

whether or not to disperse, therefore, involves a set of trade-offs between environmental impacts which are difficult to assess individually, and very difficult to compare, with the inevitable result that controversy prevails. Given more experimental data on bird mortality, water column effects (especially sublethal), oil concentrations in water, and the actual effectiveness of dispersants under various conditions, it should be possible to devise protocols to assist decision making.

This entire subject area has been the subject of a recent assessment by Koons (1979) from which it was concluded that more information is needed about effectiveness (especially on water-in-oil emulsions and at low temperatures with ice present), on the water column concentrations, on shoreline effects and on aerial application techniques.

2.5.2 Herding. Herding agents, which modify the spreading characteristics of the oil, have been used in countermeasures, although their applicability may be limited to reasonably calm waters such as ports or harbours.

2.5.3 Sinking. Sinking agents have been suggested and used in a number of cases, but because of the slow degradation of sedimented oil, it is generally accepted that their use is undesirable.

2.5.4 Burning. Attempts to burn spills at sea have usually been unsuccessful because of the difficulty of bringing the oil to the high temperature necessary to initiate and sustain combustion. The one area in which burning appears to be feasible is on ice when the oil gathers in relatively thick pools. Low temperatures also favour the retention of volatile components which would otherwise evaporate quickly, leaving the oil more difficult to ignite. Atmospheric pollution arising from the smoke is only a serious problem locally. Questions remain about the fraction of the oil which can be burned, especially when water-in-oil emulsions are present, and about the toxicity of the residue relative to the original oil. Despite these doubts, burning is generally regarded as having a mitigating effect except on some shorelines or marshes where burning has been observed to cause an enhanced and prolonged herbicidal effect. An advantageous feature of burning is that it seems likely that incendiary devices could be developed for aerial application in remote regions such as the Arctic. Experience at the "Ixtoc I" blowout (Ross et al., 1979) suggests that burning may be the best approach for treating blowouts, especially if fireproof booms can be developed to contain the oil longer at the fire.

2.6 Research Recommendations

Subjective assessment of the present state of understanding of oil spill processes has led to the following six suggested study needs, presented in decreasing order of perceived importance.

1) **Deep Sea Blowouts.** There is presently an inadequate understanding of deep sea oil and gas blowout behaviour in terms of the momentum, heat, and mass transfer processes leading to dispersion and dissolution of the rising oil. Also of importance is hydrate formation from gas. Lack of knowledge of these processes precludes meaningful assessment of the impact of deep blowouts. These could be very significant events because of the delays and difficulties which would be encountered in drilling relief wells and because they have the potential to incorporate large quantities of oil into the water column.

2) **Oil/Ice Interaction.** There is an inadequate understanding of oil behaviour in the presence of ice, in heavily ice-infested waters; under multi-year ice; and under first-year ice with gas present. This is of importance in areas such as the east coast, Beaufort Sea and the Arctic Archipelago.

3) **Natural and Chemical Dispersion.** Our present inability to predict or understand the natural dispersion rates of oil from surface slicks into the water column precludes both meaningful estimation of oil slick duration on the surface and accurate prediction of the exposure of near-surface aquatic biota to dissolved and dispersed oil. Since chemical dispersion is one of the few potentially mitigating actions which can be taken, it is obvious that considerable effort should be devoted to establishing and comparing the behaviour and effects, with and without chemical dispersion.

4) **Shorelines.** Since oil can result in considerable and poorly understood economic, ecological, and aesthetic damage to shorelines it is clear that greater effort should be devoted to understanding oil shoreline processes, especially with a view to devising strategies for shoreline protection and restoration.

5) **Diffusion.** If the ability to predict slick dissolution and dispersion rates improves, it will become essential to seek a corresponding improvement in understanding rates of horizontal and vertical diffusion, since these diffusion

rates largely control the decrease in oil concentration and the volumes of water contaminated by oil at various levels. Ultimately, for toxicity assessment purposes it would be desirable to estimate the volumes of water which experience a stated oil concentration for a stated period of time. Diffusion parameters, in combination with oil input rates, largely control the magnitude of these volumes and thus the overall toxic effect.

6) **Sinking and Sedimentation.** These processes, which are very poorly understood at present, merit greater study because they convey oil to a compartment of the environment where they may have profound long-lasting economic and ecological effects. Of particular importance is the development of a capability to predict sedimentation rates in estuarine waters of economic importance.

Another group of processes, listed below, is judged to be of "second order" importance. Although our present understanding of them is inadequate, there exists some capability of predicting environmental impact.

7) **Photolysis.** A fuller understanding of the significance of photolytic processes would be valuable in that these processes might make a relatively large contribution to the overall toxicity and to the biodegradability of oil.

8) **Dissolution.** Since dissolved oil is possibly more toxic at the same concentration than dispersed oil, it is desirable to develop a better understanding of the rates of dissolution by obtaining data on dispersed oil areas, mass transfer coefficients and on the partition of soluble hydrocarbons between oil slicks and water.

9) **Burning.** Burning is an attractive countermeasure since it could be deployed from the air in remote regions. The procedure is not likely to succeed on open cold water, but could work for pools of oil on ice, or oil in leads where spreading is reduced. Obvious developments in technology are needed, as well as assessment of environmental consequences.

10) **Aspects of Oil Behaviour.** Oil behaviour is reasonably predictable for most purposes, but is not adequately understood in three respects. The factors influencing the formation of stable water-in-oil emulsions are not yet fully characterized, and it would be invaluable from a countermeasures viewpoint if

such formation could be better predicted. The reasons for the spreading behaviour of oil into thick and thin patches (and even "pancakes") are unknown and brings significant uncertainty into oil spill trajectory and impact models. Although evaporation is well understood for low viscosity oils, there is less certainty about evaporation from thick viscous oils. Slow diffusion of volatiles through the oil layer would retard evaporation, resulting in enhanced dissolution of these toxic compounds.

11) **Oil Spill Modelling.** A final problem is the present incapability of grasping the relative importance of the many and complex interacting physical, chemical and biological processes which simultaneously control the fate of spilled oil. This inadequacy is typical of environmental science in that it is exceedingly difficult for one individual to assimilate, comprehend and weigh the many processes which occur, and identify the most important interactions. Until this is accomplished, research into oil spill behaviour will tend to remain a collection of individual, disconnected and often irrelevant and poorly conceived research projects. It is increasingly accepted that progress towards understanding complex systems is best made by an iterative modelling approach in which attempts are made to quantify all the processes (however crudely) and gain a feeling for the response of the system to the many inputs. Obviously, computational techniques have a role to play, but computers bring the danger that the model may become excessively complex. The principal advantage of oil spill modelling may be that it forces the modeller to think comprehensively and quantitatively and disciplines him to detect gaps in understanding. Although several attempts have been made to assemble comprehensive oil spill models, none, as yet, have proved adequate. This subject, however, has been recently reviewed by Mackay and Paterson (1978). Perhaps the ultimate aim of research into oil spill fate and behaviour can be expressed in terms of the development of a capability to predict the behaviour of large, controlled experimental spills with reasonable accuracy. That capability does not now exist. To achieve it will require continued research in the laboratory and field into component processes and into the integration of these processes by modelling techniques. Ultimately, the aim must be to validate such models by large experimental spills.

2.7 Summary

The eleven years following the TORREY CANYON incident have seen a marked increase in our understanding of the fate and behaviour of oil spills. The dominant processes have been identified, their relative importance appreciated, and in many cases, adequate mathematical descriptions are available. The remaining problems tend to be those which are not amenable to simple laboratory experimentation and those which are characteristic of severe environments, such as the Arctic, for which we have relatively little experience, yet in which there is hope that substantial petroleum reserves may be exploitable. Considerable progress can be made in the near future by carefully conceived and executed experimental programs. These should attempt to elucidate the dominant processes and to integrate the process rates into an overall model of the physicochemical behaviour of oil spills, whether untreated or subjected to various countermeasures.

Specifically, and in approximate descending order of priority, it is believed that research is urgently needed concerning the following topics: deep sea blowout behaviour; interactions between oil, gas and sea ice of various types; natural and chemically induced dispersions; behaviour of oil at shorelines and in sediments; diffusion of dissolved and dispersed oil in the water column; and sinking and sedimentation processes. It is also desirable to obtain more information about photolysis, dissolution, water-in-oil emulsions, spreading, evaporation, and burning, and to attempt to assemble quantitative expressions for these processes into oil spill models. It is clear that progress can best be made by a combination of studies at various levels, including the laboratory, outdoor tanks and sea-bags, experimental spills on the open ocean and at shorelines, and by exploiting accidental spills, wherever possible, especially those which occur in cold climates.

3 OIL SPILLS: WHAT HAVE WE LEARNED?

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Of the hundreds of oil spills occurring annually in Canadian marine waters (run-off, industrial waste and accidents, ship bilge-washings, etc.) four spills have been the site of research studies - the 1970 ARROW spill, the 1973 Alert Bay spill, the 1974 GOLDEN ROBIN spill and the recent 1979 KURDISTAN spill (see Table 3.1). Of these, the ARROW has received the most attention, both immediately during the spill days as well as in follow-up studies (see addendum on ARROW literature).

TABLE 3.1 CANADA'S OIL SPILLS OF SCIENTIFIC INTEREST

Spill*	Location	Amount of oil spilled (tonnes)	Research projects generated
1970 ARROW	East Coast	9 550	20 - 25
1973 Alert Bay	West Coast	180	2
1974 GOLDEN ROBIN	East Coast	160	2
1979 KURDISTAN	East Coast	6 350	18**

* All spills involved Bunker "C" fuel oil
** Preliminary studies presented at a KURDISTAN Scientific Studies workshop, Bedford Institute of Oceanography, 1979.

Most of Canada's oil spill and oil pollution research, however, does not originate at oil spills, but is instead initiated in the laboratory, segregated from real spills and the surrounding environment. In Canada, less than 25% of research publications for the period 1965 to 1978 were directly spill-related, and the remaining 75% were strictly laboratory studies (Fate and Effects of Oil Working Group, 1977). In terms of financial investment, the figure is even less. This contrast between laboratory and spill studies is even more marked for such countermeasures as field testing of dispersants. With few exceptions, all dispersant studies to date have been carried out under laboratory conditions (Doe et al., 1978).

This absence or lack of on-scene spill studies is surprising, for ultimately the oil spill is the real concern, the final site where all knowledge and study must be focussed. As well, it is the only place where investigators can observe new aspects of spills - for if there is one real lesson learned so far, it is that no two spills are alike. This is evident from the summaries which follow, concerning findings from Canadian oil spills.

3.1 Canada's Oil Spills

3.1.1 The ARROW Spill. With the ARROW in 1970, Canada entered the modern age of tanker spills. Its sinking and the sudden release of nearly 11 400 cubic metres of Bunker "C" fuel oil into Chedabucto Bay waters (Anon., 1970) brought home the two corollaries of oceanic oil spills: (1) that any shore available to tanker traffic is also available to tanker spills; and (2) that a large spill, no matter how infrequent or minimal in relation to the total list of annual world oil spillage, can cause extensive damage within a limited area, with further long-term unknown consequences.

Most of the work done on the ARROW during the early 1970's took place in nearby laboratories on Canada's east coast - at the Bedford Institute of Oceanography, the Halifax Fisheries Laboratory, the Nova Scotia Institute of Technology, at the St. Andrews Biological Station, and the University of Saint John in New Brunswick. In keeping with crisis-research, the initial emphasis was primarily on documenting spill impact on biota, coupled with trajectory work and studies of hydrocarbon distribution in the water column. Most of this effort was of the spur-of-the-moment variety and did not continue beyond the initial flurry of activity. In 1973, however, there began a renewed interest in the long-term consequences of such a major spill and research emphasis changed to include investigations into community disruption and the accommodation of oil and hydrocarbons in the ecosystem. This work is largely the effort of a single laboratory, but it is hoped that eventually there will emerge an understanding of the recovery processes of oiled marine environments, together with a knowledge of the various factors that affect biological and ecological recovery (microbial utilization of hydrocarbons, hydrocarbon metabolism, physiological stress, etc.).

While this work is still continuing, and while the answers are not all in, some general principles have emerged. The work of Neu and others (Bedford Inst. Oceanography) firmly demonstrates the strong influence of surface winds and currents on slick movement. Also, it was learned that spilled oil was not restricted to the surface layers of the water column, but could be detected in varying concentrations several

metres below the surface. Most of this spilled oil in the water column was found to be in micro-particulate form, with a large fraction in the form of minute droplets or particles less than a millimetre in diameter. It was shown that such micro-particulate oil became readily available for ingestion by marine zooplankton. As well, it was demonstrated that such particulate oil could become dispersed over large areas, with ARROW Bunker "C" traces detected in Atlantic waters over 320 km distance from the tanker wreck.

Although the water column took the initial brunt of the spill, it also "self-cleaned" quite rapidly, largely by dilution and sedimentation. After a few months, no hydrocarbons could be detected in the waters of Chedabucto Bay. However, the underlying bottom and shoreline sediments were found to be the long-term reservoirs or "sinks" for spilled oil. Studies in such sink areas between 1973 and 1976 showed that stranded shoreline oil did not remain immobile, but slowly and continuously leached into the shore sediments as well as back into the intertidal waters. Thus, there was a potential for chronic re-oiling of the intertidal and subtidal areas near the oiled shores, as well as the biota associated with these areas. The most vulnerable of these biota appeared to be the burrowing and rooted organisms, clams and seagrasses, for example, which are immobile or are restricted in their movements and are, therefore, continuously exposed to low levels of such re-entering petroleum hydrocarbons. Recent studies have shown that where such stranded oil still remains, some of these organisms have suffered altered metabolism as well as abnormal population structure and recruitment. Clams are unable to rid their tissues of ingested oil, apparently because they lack the enzyme mechanism that would normally handle such foreign compounds - the aryl hydrocarbon hydroxylase system.

One remarkable feature of the ARROW spill was the rate of self-cleaning of oiled shorelines by wave erosion and other natural action. This was shown to be directly related to the energy of the oiled environment, with rapid self-cleaning in high-energy shoreline areas versus slow to imperceptible self-cleaning in low-energy areas such as muddy shallow lagoons and embayments.

Seen in retrospect, although the initial impact of the ARROW spill seemed horrendous in 1970, the overall long-term consequences appear minimal. There remains no demonstrable damage to the ecosystem or to the fishery, except in such isolated "hot-spots" as Janvrin Lagoon and Black Duck Cove. Self-cleaning progressed rapidly, with over 50% of the visible stranded oil removed by natural means within two to three years after the spill. It should be noted, however, that it is still possible to find stranded

ARROW Bunker "C" oil on Chedabucto Bay shorelines. Also a recent survey showed that sediment samples from over 250 stations all contained traces of petroleum hydrocarbons, although these could not be traced to the ARROW spill.

3.1.2 The Alert Bay Spill. This incident involved only about 180 tonnes of heavy Bunker "C" fuel oil. Again, research interest came from nearby laboratories - the Ocean Chemistry Laboratory at Victoria and the University of British Columbia at Vancouver. It seems ironic, however, that despite the loudly voiced concerns over west coast tanker traffic, only two spill studies have emerged from this west coast spill.

As in the ARROW spill, damage to the intertidal biota was considerable, but recovery was judged well underway, one year following the spill. Recovery coincided with the self-cleaning of the oiled shores, with evaporation and dissolution presumed to play large parts in this -- more so in summer than in winter. Surprisingly, four-year old oil samples still retained some large molecular-weight hydrocarbons, identified tentatively as pentacyclic triterpanes. This observation suggested that, even under relatively severe weathering conditions, portions of the hydrocarbon spectrum remain remarkably resistant to degradation, and remain in the environment much longer than hitherto expected.

3.1.3 The GOLDEN ROBIN Spill. This, Canada's only salt marsh spill, involved approximately 160 cubic metres of Bunker "C" fuel oil spilled into Chaleur Bay, an arm of the St. Lawrence separating Quebec from New Brunswick. In the course of the spill, the small Miguasha salt marsh on the Quebec side was heavily oiled. The spill generated very little scientific interest, despite the fact that the salt marsh could not be cleaned, and was thoughtfully left as a scientific reserve for future study. The net result to date has been two reports - one a summary of after-the-fact cleanup tests using burning, sod-cutters and other techniques (Cejka, 1975), and the other a short assessment (Vandermeulen and Ross, 1977).

Surprisingly, in view of the heavy initial oiling, after three years the forepart of the marsh including the primary tidal channel was largely clean of hydrocarbons. Only the back part of the marsh and its secondary tidal channels remained oiled and permeated with hydrocarbons derived from Bunker "C". Revegetation of the oiled back-areas was slow and incomplete, even four years after the spill. Penetration of spilled oil into marsh sediments was minimal, except where heavy machinery had been tried in cleanup. However, considerable degradation of such buried oil had occurred, particularly of the aliphatic fraction. Later microbial work suggested that this degradation resulted from hydrocarbon-utilizing bacteria within the marsh sediments.

In relative comparison to the impact of the ARROW on Chedabucto Bay, the oiling impact on the Miguasha salt marsh was much greater, even though a smaller amount of oil was involved. The oiled marsh areas remain oiled to the date of writing, with very slow recovery of the marsh vegetation. It is likely that any oiling of a salt marsh, anywhere in Canada, will have serious, long-term consequences. Salt marshes probably represent some of the most vulnerable and sensitive shoreline areas of the marine environment.

3.1.4 The KURDISTAN Spill. The breakup and subsequent spill of about 6 350 tonnes of Bunker "C" oil into the cold waters of the Cabot Strait separating Cape Breton from Newfoundland provided a real opportunity to examine the interaction of oil with ice in the field. This was of particular interest in view of Canada's involvement in oil exploration in the Arctic, an area dominated by ice. Research interests were primarily physicochemical, including work on oil erosion, effects of oil on shoreline ice melting, oil-in-ice movement, and other aspects of oil in ice. Personnel involved included staff from the Bedford Institute of Oceanography, Canada's Centre for Remote Sensing, the Environmental Protection Service and the Memorial University of Newfoundland, as well as from a number of private firms in the Maritime region.

Although the spill occurred under somewhat similar circumstances to those of the ARROW, the results were remarkably different. Both spills occurred in winter weather, with winter storms and the presence of ice. The ARROW accident, however, occurred in a large embayment with somewhat predictable surface currents, while the KURDISTAN break up occurred in open ice-covered ocean with little knowledge of surface movements. As well, the oil (Bunker "C" in both cases) behaved differently. In the case of the ARROW, the oil erupted from the vessel in liquid form, and came ashore in masses of chocolate mousse. In the case of the KURDISTAN, the oil remained at sea for a much longer period, and finally reached the shore not as mousse but largely as particles ranging in size from several metres across to less than a millimetre in diameter.

Also, much of the spilled oil did not float on the surface but appeared to float submerged, a metre or more below the surface. This created considerable difficulties in slick monitoring, detecting and tracking, and caused much fouling of fishing gear.

While it is still early to assess the ecological consequences of the KURDISTAN break up, it would appear that the impact on fisheries is less than initially feared. Evidence to date regarding both invertebrate and vertebrate fauna suggests that the spill

had relatively little impact. However, many marine bird mortalities occurred over a large area. Some mortalities among marine mammals have also been attributed to oiling.

3.2 Dispersant Use

Of the spills described only two have in fact been sites of some experimental dispersant use - the ARROW and the GOLDEN ROBIN. During the ARROW operation a number of commercially-available dispersants were tested on an organized basis for effectiveness and toxicology, although these were not employed because of their potential hazard to marine life. The lessons learned following wholesale dispersal of oil spilled from the TORREY CANYON in 1967 remained vivid in memory, and are still the basis of Canada's negative stand toward dispersant treatment of spills. The tests carried out during the ARROW exercise included studies of dispersing capability, and toxicity to Atlantic salmon (Salmo salar), winter flounder (Pseudopleuronectes americanus), and American lobster (Table 3.2).

TABLE 3.2 CHEMICAL OIL DISPERSANTS TESTED DURING THE "ARROW" OPERATION (modified from Anon., 1970).

Dispersant	Effectiveness on Bunker "C"***	Effectiveness on emulsion***	Cleaning Effectiveness*	Toxicity**
Ashland Ridzlick	0	0	-	
BP1100	e	e	-	B-C
BP1100B (hybrid)				B
BP1002				C
Colloid '88	0	0	-	C
Corexit			++(21°C)	
Corexit 7664				A-B
Corexit 8666	0	0	++(5°C)	A
Dispersol SD	0	0	+(5°C),++(21°C)	C
Ezit	e	e	-	
Gulf Agent 1009				C
Petrolad 1-10			++(21°C)	
Polycomplex A-11	0	e	-(21°C)	

* (-) no effect; (+) some effect; (++) effective in cleaning rope. Tests were carried out at two temperatures in some cases.
** Toxicity was evaluated non-toxic (A) to highly toxic (C), with (B) intermediate.
*** (0) Not effective; (e) effective.

While not used in combatting slicks at sea, a limited dispersant trial with BP1100B was carried out to determine its usefulness in cleanup of oil that had come ashore. The site (Rabbit Island in Inhabitants Bay) had been examined subtidally for biota prior to the cleaning tests. Dispersant was applied manually to the oiled rocky shoreline, and after a contact time of 50 minutes, was hosed off into the sea with a high-pressure portable pump.

It was concluded that shoreline cleaning with BP1100B was effective in removing Bunker "C", at least on the surface. The method was judged less effective in cleaning oil on the undersides of rocks and in boulder interstices. Little could be concluded regarding hazard to the biota, since the area was so heavily oiled that no distinction could be drawn between oiled and dispersed plots. However, a cursory visit six years after the spill showed no obvious difference in revegetation from that observed in oiled-only areas (Vandermeulen, unpublished data).

In the case of the GOLDEN ROBIN, four dispersants were tested for effectiveness in cleaning oil from a salt marsh, one year after the spill (Table 3.3). As well, they were tested for their effect on vegetation and benthic organisms, and for their penetration into marsh sediments. The effects on vegetation and benthic infauna were dramatic; within three weeks all marsh vegetation in the test plots had died, with only a few stunted shoots remaining in the plot treated with Sugee No. 2. Two years later, however, the test plots were indistinguishable from the control plots (oil only), with complete recovery of marsh vegetation.

TABLE 3.3 EFFECTIVENESS OF DISPERSANTS IN "GOLDEN ROBIN" TESTS

Dispersant	Oil cleaning effectiveness*
BP1100X	++
Corexit 8666	+
Oilsperse 43	++
Sugee No. 2	-

* products were judged as to their effectiveness in cleaning oiled marsh vegetation. Data provided by C.W. Ross, EPS Ottawa.
(-) no effect; (+) some effect; (++) more effective than others.

The effect on the marsh infauna was highly variable. While there were no immediately observable effects with Sugee No. 2 or Corexit 8666, both BP1100BX and

Oilsperse 43 caused immediate mortalities among polychaetes and clams. There were no observable differences attributable to dispersant use, however, two years later.

While it had been expected that dispersant use might enhance oil penetration into marsh sediments, this was not the case in the samples examined. Chemical analysis of cores taken from the various test plots showed no significant enhancement of oil concentrations below 7.5 cm after dispersant application (C.W. Ross, EPS, pers. comm.).

3.3 Comments

It is probably safe to say that of the world's spills, the 1970 ARROW spill was scientifically one of the most studied and best understood, until the mammoth effort now in progress around the 1978 AMOCO CADIZ spill. This was, of course, because it occurred on the back "door-step" of the Halifax-Dartmouth oceanographic community.

This points out the common denominator that runs throughout the history of spills as research opportunities. The fact that the ARROW and the KURDISTAN received the scientific attention they did is due solely to their proximity to a diverse scientific community with an established oceanographic capability. The work on the Alert Bay spill in B.C., however small, was due solely to the strong interest of the marine chemistry group in nearby Victoria. On the other hand, the GOLDEN ROBIN spill is Canada's missed opportunity to study salt marsh oiling, due largely to the absence of a nearby scientific community and because its "scientific reserve" status was not publicized. The one small study there was carried out "on the cheap", peripheral to other work on oiled sediments.

An obvious conclusion is that since there is no guarantee that future spills will occur near large established marine laboratories, older spills within Canada should be revisited, or special arrangements should be made to visit and examine relevant spills elsewhere.

3.3.1 Foreign Spills. There are two irrefutable arguments for studying real spills, whether Canadian or foreign. One -- each spill is different and holds different information; and two -- the real spill is the ultimate test for laboratory-conceived hypotheses.

That each spill differs from all others is now almost an axiom of oil pollution, recognized by both technologist and scientist. Each spill may differ not only in type of oil, but also in environmental impact and recovery. Furthermore, with each spill there are new facets, new "wrinkles" hitherto unexpected in either kind or degree. An outstanding example was the notion commonly held until 1978, that hydrocarbon concen-

trations under a spill would be high in the upper 5 or 10 metres of the water column, but would drop off rapidly below that depth. The AMOCO CADIZ supertanker spill forever dispelled that belief when it was demonstrated that lethal concentrations of hydrocarbons were found uniformly throughout the water column under certain conditions (Marchand, 1978).

On-site observations made at the AMOCO CADIZ spill also provided invaluable information on oiling effects in tidal rivers and estuaries similar to Atlantic Canada's Bay of Fundy system, on cleanup effects on a heavily oiled salt marsh (Long and Vandermeulen, 1979), and on metabolic repercussions in oiled birds and fish from oiled sea water (Vandermeulen et al., 1978a). This information can be directly applied to our own maritime situation.

Ultimately, of course, the spill is the final testing site for hypotheses formed in the laboratory, from specific controlled experiments. It is also a place where one can formulate new questions, reinforce earlier hypotheses, or encounter unexpected characteristics of transport processes of oil and degradation mechanisms. As recently as 1978, it was thought that on fine-grained sand beaches penetration depths would be minimal and that stranded oil would be available for abrasion and dispersion from swash (Owens, 1978). Studies at the AMOCO CADIZ site by Canadian scientists, however, have added new insights into entrapment of stranded oil into sandy sediments - with potentially far-reaching implications for water table and groundwater contamination (Vandermeulen et al., 1978a, 1978b, Long et al., in prep.)

3.3.2 The METULA Spill. While Canada has not experienced a supertanker spill to date, we do have in the METULA spill of 1974 a good example of what might happen if such an incident were to occur off our east coast. The METULA spill involved some 46 000 tonnes of crude oil and occurred in an environment very similar to our Atlantic/Maritime marine environment with shorelines similar, if not identical, to those found in northern Nova Scotia and Newfoundland.

What sets this spill apart from all the other major spills is that it involved a large amount of crude oil, in a cold climate, and no effort was made to clean it up - thus providing an ideal opportunity to examine in detail the long-term effect and changes of a massive spill with "removal of spilled oil solely by in situ physicochemical and biological physicochemical mechanisms" (Colwell et al., 1978). The spill was visited by several scientists from the USA and some from Europe during the initial spill days. A lesser follow-up visit was carried out a few years later, but to date no Canadian team has visited

the spill site, despite the advantages this would have for our ability to predict the long-term effects of a similar VLCC (very large crude carrier) spill on Canada's east coast.

3.3.3 The AMOCO CADIZ Spill. The AMOCO CADIZ supertanker breakup involved about 200 000 tonnes of light crude oil, and occurred in a marine environment very similar to that of eastern Canada, particularly Nova Scotia and the approaches to the Bay of Fundy. In the course of the spill, over 320 km of north Brittany coastline was oiled to a greater or lesser extent, including a salt marsh, sandy beaches, and river mudflats and estuaries. Because of the similarity to our own eastern coastline, a team of scientists from the Bedford Institute of Oceanography visited the spill area, and carried out a thorough survey of the oil behaviour and impact (Vandermeulen et al., 1978b). In addition, follow-up studies were initiated in particular problem areas similar to those in eastern Canada.

Probably the most outstanding features of this giant spill were the following: the game of chance played by winds and weather which resulted in repeated re-oiling of already oiled shorelines; the effectiveness of the manual cleanup program; the unexpected mortality of offshore bottom organisms; and the vulnerability of some low-energy shoreline systems.

The north Brittany coastline and its offshore current patterns are probably among the most studied in the world, but this did not prevent the continuous re-oiling by daily arrival of new slicks during the weeks following the tanker break-up. Slick movement was extensive, and slicks remained in the area for a much longer duration than had been expected. Cleanup of this spill, if it had been left to nature's own devices, as by wave action and erosion, would have left a layer of oil along most of the coastline for decades. Fortunately, the massive manual cleanup saved the shoreline and the habitat of the coastal marine organisms. Except for the manual effort, the coastline would have been ruined for years to come, pointing out the necessity for man's intervention in cleanup. Nature by itself would have been ineffectual and slow. Nevertheless, the spill had major impacts on intertidal and subtidal invertebrates and kelp beds, causing high mortalities and alterations in structure and dynamics of the shoreline fauna and flora. Surprisingly high mortalities were found in benthic populations of sea urchins, shellfish and bottom crustaceans (amphipods) previously thought to be protected from oil slick toxicity by the overlying deep water column. The cause of their mortalities has not been worked out, but it is clear that oil slicks do not remain simply on the water surface, but that highly toxic components can dissolve into the water column many metres below the

surface slicks. This was known since the ARROW, but the extent of potential toxicity of such dissolved hydrocarbons was not demonstrated until the AMOCO CADIZ spill.

Of particular interest to fisheries was the loss of a year-class in groundfish, attributed to the spill. Offshore fish stocks appeared not to be affected, although individual mortalities occurred in many species. Bird kill was high, particularly among the diving species which would have come in direct contact with oil slicks. A particular problem was the threatened elimination of some nearby nesting colonies, which had experienced high mortalities during the TORREY CANYON spill of 1967, and which were experiencing a return to normal colony size (see Chapter 6).

Long-term impact of the spill is, however, associated primarily with the low-energy areas of the shoreline, the marshes, mudflats and sandy beaches. The vulnerability of salt marsh and muddy lagoons was known from other spills, but this was the first spill where estuarine tidal rivers were oiled. Their vulnerability is of particular interest to eastern Canada because of the tidal nature of the Bay of Fundy and its river system. In France, the AMOCO CADIZ slicks penetrated deep into the upper reaches of the large tidal rivers, oiling the vegetated edges of the river mudflats, and it is expected that stranded oil will remain a factor of pollution for many years in those places. Of particular concern were the economically important oyster farms of the region and ecologically important clam beds of the mudflats, all of which were oiled. Rate of recovery of the oiled rivers and sediments is unknown.

Sandy beaches are also potential long-term sinks of spilled oil slicks. Apparently slicks that were buried within beaches during the spill did not all get washed out by subsequent winter storms, as had been expected. Instead, to this date, layers of oil remain buried deep within many of the Brittany beaches. Whether these are to be viewed as long-term contamination sites is unknown. Some degradation by bacteria does occur in such buried oil, but the rates of degradation are not known. There does exist the potential for groundwater contamination under the dunes.

Dispersants did not play much of a demonstrable role in spill impact. Dispersants were used offshore, largely in the treatment of slicks beyond a certain depth of water. Whether such dispersed slicks were the cause of the observed mortality of offshore benthic organisms is not known, and no evidence exists to support this supposition one way or the other. Dispersants in very small amounts were used to clean some isolated stretches of shoreline, but again any environmental impact data are not available. It would definitely have been useful to make observations on cleaning effectiveness,

oil/dispersant interaction, possible enhanced penetration of oil/dispersant into porous shoreline sediments, etc. However, while the opportunity existed to do these studies or make these observations, researchers were not there to do them. That was unfortunate, especially since dispersants may well be the only contingency alternative in many environments, such as our own arctic regions.

3.3.4 Microbiology - an Obvious Research Gap. During the initial "exposed" phase of an oil spill, the spilled hydrocarbons can be eroded and handled by a variety of processes such as evaporation, dissolution, metabolism, and photolysis. In the following long-term "buried" phase, microbial degradation appears to be the only natural process attacking these chemical pollutants. Yet the process of microbial utilization of petroleum hydrocarbons, and the various factors that regulate or control this utilization, are poorly understood. It is known that all environments contain elements of hydrocarbon-utilizing bacterial populations, and that nitrogen and phosphates can significantly affect microbial degradation of hydrocarbons. Little is known, however, of the rates of degradation of the various hydrocarbons that make up oil, of the population induction processes, of the effects of light, oxygen, temperature, sedimentation, oil particulate size, and a range of other factors. One obvious gap in the literature to date is that of microbiological studies in northern marine waters and sediments. With Canada's "northern interests" it would seem that any studies of oil pollution should include a strong effort on studies of oil degradation, but this is not the case. Up to 1978 there are fewer than half a dozen studies of microbial activity in Canadian marine sediments and waters (Cundell and Traxler, 1973; Mulkins-Phillips and Stewart, 1973, 1974c, 1974b; Bunch and Harland, 1976; Stewart and Marks, 1978). Only one study applies to the Canadian northern marine environment (Bunch and Harland, 1976). Perhaps another two to three are in press.

In view of this dismal state of research it seems ironic that in fact the only real spill-related microbial study, under pseudo-Canadian conditions, was conducted at the site of the METULA spill, because it provided, "a unique opportunity to study a massive spill in a cold region on a long-term basis" (Colwell et al., 1978). Yet no Canadian scientists have visited that site.

3.4 Progress Made

Although Canada's spill research effort has been small, relative to that in the USA and the rest of the world (Table 1), our contribution to understanding spill impact in northern temperate waters is well recognized. This is in part due to the research efforts

of the various federal and private laboratories on the east and west coasts, together with the considerable input from industry through such organizations as PACE (Petroleum Association for Conservation of the Canadian Environment). A further factor has been that the research effort has been fairly sharply limited to problems in the temperate environment, focussing on oil spill factors relevant to Canadian marine waters. Finally, where possible, results and conclusions from basic research studies have been related to field problems (e.g. Fisheries Research Board, 1978).

This is not to say that the problem of oil spills in our temperate and arctic marine waters is solved. It is probably safe to say that with regard to a temperate marine spill, we stand better prepared now than in 1970. The recent KURDISTAN spill (1979) was met with less panic than the ARROW disaster (1970), simply because we had learned to be less pessimistic about its overall impact on offshore fisheries. Instead, contingency plans and countermeasures pressed into action during the KURDISTAN operation focused heavily on such onshore problems as sandy shorelines and low-energy marsh and estuarine regions, the demonstrated onshore "sinks" for spilled oil. However, this 1979 spill also demonstrated our inability to deal with a spill at sea, both in monitoring and predicting slick movement and its containment and cleanup. Despite the fact that our four example spills have all occurred in Canadian temperate waters and have all involved the same oil type, to date we cannot predict or compute a "budget" for such a spill, i.e. how much oil went where and how and when (drifted out to sea, evaporated into the atmosphere, stranded onshore, sank to the bottom, dissolved into sea water, was taken up by organisms). Even less is known of the ultimate fate of spilled oil, other than for some general principles of hydrocarbon metabolism and transfer of hydrocarbons into the marine foodchain. For example, nothing is known of the mechanism of oil's toxicity to many marine organisms, except other than 10 to 100 mg/L seems to be the limit for survival.

The ecological recovery of an oiled marine ecosystem has been observed and monitored for a few spills, most notably the ARROW, and in the USA the 1969 FLORIDA spill off Massachusetts (Fisheries Research Board, 1978). Recovery does occur and appears to happen surprisingly quickly, with estimates ranging from four (Cretney et al., 1978) to ten or fifteen years (Mann and Clark, 1978; Vandermeulen, 1978a, 1978b). These estimates appear to be supported by observations from other spills such as the AMOCO CADIZ.

Intertidal communities are generally the most vulnerable to damage during oil spills. Damage can be severe, and in the case of the AMOCO CADIZ, many parts of the Brittany shoreline experienced near-total mortality of intertidal fauna and flora. Fortunately most intertidal organisms can recolonize by introduction of larval forms from other non-oiled areas. This is a slow process because larval setting for many species involves chemical cues from the intertidal substrates. Oil will disturb this resettling behaviour by interfering with the chemical cueing. Invasion of killed-off areas by opportunistic species also contributes to recolonization.

The use of first-generation, highly toxic dispersants during the TORREY CANYON disaster resulted in massive destruction of shoreline intertidal organisms, both plant and animal. Recovery to pre-spill population levels is still underway today (Southward and Southward, 1978). It is difficult to assess the potential effect of the modern second generation dispersants. More information is needed on the dispersing behaviour of these modern dispersants in the field, especially on the three-dimensional dispersion-dilution of oil in open water. Theoretical analyses suggest a significant dilution in the open ocean, but actual field data do not exist and are very much needed. More information is also needed on the interaction of modern dispersants with the intertidal zone.

As for the Canadian Arctic, we have no data, no knowledge, no experience, and no sound guesses to estimate impact of a spill in those ice-dominated waters. Furthermore, to extrapolate from our temperate-water spills, each differing markedly from one another, to the northern spill is at best educated guess-work. The KURDISTAN spill, which occurred in ice, although in temperate waters, did point out one major problem in the event of an arctic spill - that of detecting and monitoring slick movement in ice-infested waters.

Progress in countermeasure development has been varied. Detecting and monitoring offshore oil slicks is still a major problem, although there has been some qualified success with remote sensing techniques in locating oil on or in ice. Less successful have been similar efforts in locating oil on or in water. So far, actually droppings buoys or other marking devices into the slicks has brought the best results in obtaining trajectory data.

Mechanical containment and cleanup devices have so far been only found effective in inland spills and in the calmest of offshore waters, and have no effect whatever in the presence of ice. Any progress that has been made in the area of shoreline

cleanup has been largely in learning which techniques to avoid, such as large-scale removal of shore sediments, and in learning to use manual cleanup techniques wherever possible. Some studies have been carried out on the use of chemicals to protect beaches from oiling, but to date these have been strictly laboratory studies without actual field/spill experience.

The chemical treatment of oil, dispersing it into the water column before arrival onshore, is at the moment the only alternative to mechanical attempts at controlling offshore oil pollution. This is an unhappy alternative at best, in that it runs counter to the philosophy of conservation -- i.e. to separate the marine foodchain from the pollutant. New chemical dispersants, reputedly with no harmful side-effects, have been developed. Since this approach appears to be the only real alternative to ineffectual mechanical means, and since it is widely practised in other parts of the oceans such as the recent Gulf of Mexico blow-out, research on the topic should be encouraged. This is necessary for the development of a better understanding of the effects of chemically dispersed oil on the marine environment, and of chemical dispersants that are compatible with marine foodchain processes in their chemical composition and in their effect on the dispersed oil.

3.5 Recommendations

1) In Canada not enough use has been made of either Canadian or foreign spills as opportunities to study spill behaviour and assess countermeasures. Opportunities must be made for studies at spill sites, both during the initial phase and in the long-term. Of particular interest here is the METULA VLCC spill (crude oil) which was left uncleaned along shorelines similar to those of northern Nova Scotia or Newfoundland.

2) There must be strong encouragement for follow-up studies of spills to assess their long-term impact on the environment, as well as the long-term fate or distribution of petroleum hydrocarbons in the marine environment.

3) There must be special encouragement for studies of oil-utilizing bacteria and their role in its degradation under various Canadian marine conditions.

4) There must be strong research emphasis on effects and countermeasures in oiled low-energy environments such as lagoons, estuaries and salt marshes.

3.6 Addendum on Spill Literature Not Cited in this Chapter

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4 MICROORGANISMS AND THE DEGRADATION OF OIL UNDER NORTHERN MARINE CONDITIONS

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Bacteria and fungi are unique biological organisms in that they are capable of utilizing petroleum hydrocarbons and/or crude oil as a food source. During this process, some hydrocarbons are converted to carbon dioxide and cell material, while others are partially oxidized and/or left untouched as a residue. This phenomenon has been the basis of industrial processes for the production of single-cell protein from non-protein-containing petroleum hydrocarbons. It is also the basis for the projected use of such organisms in the cleanup of oil spilled in the environment (Vandermeulen, 1978b; Atlas, 1977; Bartha and Atlas, 1977; Colwell and Walker, 1977; Karrick, 1977). The role of petroleum-degrading microorganisms in the biogenesis and deterioration of oil deposits has also been the subject of recent investigations (Jobson et al., 1978; Milner et al., 1977).

In order for microorganisms to be effective in removing oil spilled in the environment, those present need to have the genetic ability to grow on petroleum hydrocarbons. This ability to grow is readily lost in some bacteria (Gram negative cells) but not in others (Gram positive cells) if oil or compounds present in oil are not in the environment. This ability is affected by environmental conditions such as temperature, salinity, pH, oxygen and nutritional factors; in particular, nitrogen and phosphate must be present in the range which permits the growth of petroleum hydrocarbon-degrading microorganisms. The chemical composition of oil also has an effect on the biodegradative pattern observed. The relationship of these factors to the microbial degradation of oil under northern marine conditions is discussed in this chapter.

4.1 Oil Composition and Biodegradation

Oil can be fractionated by chromatography (Jobson et al., 1972) into four major components: asphaltenes (complex polycyclic ring systems); saturates (paraffinic components; e.g. n-alkanes, isoprenoids, cycloalkanes); aromatics (mono-, di-, tri-, tetra- and penta-ring systems); and a polar fraction (consisting of nitrogen-, sulfur- and oxygen-containing compounds). The physical and chemical properties of oils vary depending on

the proportions of these fractions present. The most toxic components of oil are found in the low molecular weight components (e.g. mono-aromatics such as toluene or short chain n-alkanes such as pentane and hexane). These components are quite volatile and are readily lost by evaporation. For example, approximately one-third of the weight of Prudhoe Bay crude oil may be lost via evaporation under ambient conditions. The most readily biodegradable compounds present in oil are found in the saturate and aromatic fractions (Jobson et al., 1972, Walker et al., 1976). Even if these components are present, their utilization will be determined by the chemical composition of the rest of the oil (Westlake et al., 1976).

Even if an oil is biodegradable, no single or mixed oil-degrading bacterial culture is capable of completely utilizing all of the compounds present in the whole crude oil. Oil subjected to microbial degradation has an altered paraffinic and aromatic content and the residue is enriched in asphaltenes and the polar, nitrogen-, sulphur- and oxygen-containing fractions (no evidence of biodegradation of these has been obtained to date) (Jobson et al., 1972; Walker et al., 1976). Such residual oils have a reduced toxicity level, however, as the result of microbial activity and the evaporation of low molecular weight components.

4.2 Distribution of Oil-degrading Microorganisms

The microbial flora of a marine or terrestrial environment not only varies from location to location but also at a given site with time. The types of microorganisms found depends on the nutrients which are present, and on the existing physicochemical parameters. The flora of a polluted site is quite different from that found in a pristine environment. For example, if oil is present, there is a greater incidence of petroleum-degrading bacteria and fungi and a faster rate of removal of freshly added oil than in areas where oil is not present. Studies during the last two decades indicate that petroleum-degrading bacteria and fungi are ubiquitously distributed throughout the marine world (and terrestrial) ecosystems (Mulkins-Phillips and Stewart, 1974c; Roubal and Atlas, 1978). This is due in part to spent industrial and automotive lubricants which are inadvertently introduced to the marine environment and in part to existence of natural oil seeps as at Norman Wells, NWT and Cape Simpson, Alaska (Grossling, 1976). The natural addition of petroleum precursors and possible inducers of oil-degrading capability via plant and animal debris also contributes to the ubiquitous distribution of oil-degrading capability amongst marine microorganisms.

Information concerning the incidence of oil-degrading microorganisms has been obtained indirectly using growth (increase in cell number or mass) on a pure aliphatic hydrocarbon such as tetradecane or dodecane as an index of ability to grow on a whole crude oil. Data have been obtained recently indicating that for fungi, at least, the ability to grow on such compounds is not a good index of capability of growth on a whole crude oil (Davies and Westlake, 1979). More meaningful information has been obtained by using a "synthetic" crude (i.e. a mixture of hydrocarbons representing those found in oil) (Mulkins-Phillips and Stewart, 1974c; Walker and Colwell, 1974), or a whole crude "spiked" with specifically labelled hydrocarbons (Roubal and Atlas, 1978). The use of synthetic or whole crudes can yield information on the rate of loss of individual or groups of compounds by coupling changes in biomass with changes in the chemical composition of the oil. Chemical analyses can be accomplished by chromatography (Jobson et al., 1972) or chromatography and mass spectrometry (Walker et al., 1976). Such information is required to form a data-base for predicting how different oils will be utilized by microorganisms. These latter techniques, in particular those utilizing whole crudes, can also be used to measure the potential effect of the toxicity of oil composition on microbial activity. The oil used in such studies should be representative of those produced near and/or to be shipped through the area being investigated, as the chemical composition of an oil determines in part its biodegradability characteristics (Westlake et al., 1974).

Microbial modification of oil is not restricted to the earth's surface. It has been implicated in the biogenesis of the Athabasca bitumen sands (Rubenstein et al., 1977) and is projected as being active in altering the chemical character of oil presently being produced (Anonymous, 1972a). It has been observed in the oil producing industry that one readily noticeable change in oil produced from reservoirs where microbial action is taking place is an increase in the hydrogen sulfide content of the oil.

4.3 Oil Biodegradation in Northern Marine Waters

Very little information is available on the distribution, and factors affecting the activity, of oil-degrading microorganisms in Canadian marine waters. Some information is available on the fate of oil spilled in 1973 between the northern end of Vancouver Island and the British Columbia mainland (Cretney et al., 1978). Baseline data are being obtained on microbial oil-degrading activities in the northern Puget Sound and the southern shores of the Strait of Juan de Fuca (north-western Washington State) (Westlake

et al., 1978). As a result of the development of Prudhoe Bay oil fields, extensive studies are being carried out on the distribution and activity of oil-degrading microorganisms in the Gulf of Alaska (Atlas et al., 1978) and in the Beaufort Sea (Roubal and Atlas, 1978). Little recent information is available, other than the studies of Bunch (1974) and Bunch and Harland (1976), on such activities in adjacent Canadian waters where drilling is now in progress; similarly, there is a paucity of information on the situation in the waters of the Canadian high Arctic. Studies are underway in eastern Canadian waters (e.g. Davis Straits via Imperial Oil and Federal Government activities) prior to major oil explorations in that area. Such information will be useful in establishing baseline patterns but it is doubtful if enough information will be obtained to be useful in evaluating the potential use of microorganisms in degrading oil spilled in northern Canadian marine environments.

A recent symposium was very useful in that it collated existing data on this subject (Fisheries Research Board, 1978). A summary review of information presented indicates that the activity of oil-degrading microorganisms under northern marine environments will be severely limited in its contribution to the removal of oil spilled under these "severe" environmental conditions (Vandermeulen, 1978). The information presented suggests that it would be unrewarding simply to carry out studies on the distribution and activities of oil-degrading microbes per se in this geographical area. Their presence and activity depend on the degree of pollution of the system with oil hydrocarbons and their activity depends on the prevailing nutrient and physical status of this environment. Activity is also related to the mechanical energy levels present in the various parts of an environmental system. Therefore, such investigations must be interdisciplinary in nature; chemical, physical and microbiological data must be obtained in an integrated program to fully evaluate the ability of oil-degrading microorganisms to function in northern marine systems. It also is necessary that "baseline" data (e.g. Griffiths et al., 1978) be obtained now, before industrial activities result in extensive contamination of these areas with petroleum hydrocarbons. The availability of such information will make it possible to project the effectiveness, which would appear to be minimal, of oil-degrading microorganisms in removing oil spilled under northern Canadian marine conditions. Such data would be useful in assessing the ecological impact of an oil spill.

4.4 Factors Including Dispersants that Affect Microbial Utilization of Oil in the Marine Environment

Oil entering the marine environment can be removed from the water column by evaporation, sedimentation into either subtidal or intertidal materials, or biodegradation. Only the oil components lost by evaporation (i.e. the low molecular weight, volatile components) are not available for biodegradation. Unless environmental conditions are suitable for growth, however, no biodegradation will be observed even if the oil spilled is biodegradable. In a marine environment, parameters like pH and salinity are in ranges which will permit the growth of oil-degrading bacteria and fungi; sufficient oxygen for growth, however, will be present only in the water column and in the intertidal areas. Oil incorporated into anaerobic (oxygen-free) sub-tidal sediments will not undergo biodegradation, as the initial attack on hydrocarbon molecules by microorganisms requires oxygen.

Nutritional factors (in particular the nitrogen and phosphate content) in natural environmental situations are critical in determining the rate of oil removal from both marine (Atlas and Bartha, 1972) and terrestrial (Jobson et al., 1974) systems. It is suggested from data (Mulkins-Phillips and Stewart, 1974b) that in open oceans in the temperate to polar zones, phosphate is limiting, whereas in intertidal areas the environment appears to be deficient in nitrogen (Westlake et al., 1978). Altering these parameters in the marine ecosystem is very difficult because of the water-soluble nature of the potential sources of nitrogen and phosphate. Some success has been reported using an oleophilic source of these nutrients to accelerate the role of biodegradation of an experimental spill in a marine system (Olivieri et al., 1976).

Under northern marine environmental conditions, even if the oil spilled is biodegradable and sufficient oxygen, nitrogen and phosphate are present, the rate of oil degradation will be limited by the prevailing cold temperatures (Atlas, 1975). Recent data indicate that biodegradation takes place in ice-free conditions and that little if any degradation can be expected under ice (Atlas et al., 1978). Even when open water is present, the rate of biodegradation is slow, not only being limited by temperature but also by the poor nutrient status of the environment.

The use of dispersants (i.e. chemicals which increase the contact surface area between oil and water) is being considered as a method for treating oil spilled in northern marine environments. The effect of such compounds on the microbial degradation of oil has not been extensively investigated except for studies by Mulkins-Phillips and Stewart

(1974a). This is in spite of the fact that many but not all microorganisms produce bioemulsifiers when growing on hydrocarbons (Zajic and Panchaz, 1976). The use of dispersants on oil spills should result in a more rapid dissolution of the low molecular weight toxic components of oil (Lupton and Marshall, 1979). Therefore, not only must the toxicity of the dispersant be considered, but also its effects on the toxicity of oil. As oils vary in their chemical composition and physical properties, the potential interaction of dispersants with different oils must be investigated in order to determine whether or not marine biological systems are affected by the addition of dispersants. Assuming that only biodegradable dispersants are used, the effect of the addition of more biodegradable carbon (i.e. the dispersant) on the carbon/nitrogen ratio of the environment, which already has an imbalance in this parameter, must be considered. This point is particularly important if nitrogen and phosphate amendments are to be added to an oil spill to accelerate biodegradation processes.

The physical character of the oil also has an effect on its biodegradability. Tar balls, although containing readily biodegradable compounds, are resistant to microbial attack. Some oils which have been subjected to microbial attack (e.g. removal of n-alkanes, equivalent to clathration) have a lowered pour point; that is, they remain liquid and retain their flow characteristics at low temperatures (Crawford et al., 1977).

The disappearance of oil from a marine environment depends on many factors --the volume and chemical-physical properties of the oil spilled and the amount of available energy in the system, which can be biological, chemical, mechanical or thermal. Owens (1978) concludes that mechanical processes such as wind, waves, tides and ice are the most important of these energy systems and that the residence time of oil decreases as the mechanical energy level increases. The effect of ice formation is to decrease the effectiveness of these processes in removing oil. Mechanical processes are also important to microbial activities in oil removal: they aid in the dispersion of oil; re-aerate water columns; resuspend oil present in sub-tidal and intertidal sediments; and provide a continuous input of microorganisms and fresh nutrients. All these processes interact in controlling the effectiveness of microorganisms in removing oil from a marine environment.

4.5 Summary

The interactions of the various physical and chemical parameters which control the microbiological degradation of oil under environmental conditions are

summarized in this chapter. The effectiveness of utilizing microbiological degradation as an aid in cleaning oil spilled in northern marine systems cannot be fully evaluated at present. Information is required on the distribution and activity of oil-degrading microorganisms and on the status of the controlling physicochemical parameters in northern marine ecosystems. Until such data are available, the potential role of oil-degrading microorganisms in protecting this northern environment can only be based on hypotheses and speculations.

4.6 Recommendations

Very little information is available on the distribution and factors controlling the activity of oil-degrading microorganisms in northern Canadian waters. Research directed at obtaining this information should have a high priority and should be part of an inter-disciplinary program directed to obtain data as to how this environment would respond to an oil spill. Such information would be of value in evolving effective containment and cleanup programs.

The effect of dispersants on the microbial oil-degrading process must be investigated. Such studies must include research on the toxicity of oil (and the oil plus dispersant) and its effect on the carbon/nitrogen ratio of the already stressed environment.

The long-term effects of oil incorporated into sediments must be investigated. Such oil will be released slowly into the water column and thus contribute to the "chronic toxicity" of oil spilled in a marine system. In addition, this oil is subject to microbial attack (via alkyl and aryl hydroxylases) under growth-rate-limiting conditions. The products of such growth include, in particular, oxidized hydrocarbon molecules which are not only much more reactive but also potentially more toxic in the biological food chain.

As the alkyl and aryl hydroxylase enzymes found in oil-degrading microorganisms are also found in shellfish and higher biological forms, the effects of dispersants on the toxicity of oil to higher life forms must be investigated. This is particularly important in areas where such life forms constitute a major food supply.

5 THE EFFECTS OF PETROLEUM HYDROCARBONS ON PHYTOPLANKTON AND MACROPHYTES

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5.1 Phytoplankton

The effects of petroleum hydrocarbons on phytoplankton have been extensively reviewed by Corner (1978); Vandermeulen and Ahern (1976) and Johnson (1977). Galtsoff et al. (1935) were amongst the first to report the adverse effects of oil on phytoplankton when they noted that a heavy layer of Lake Pelto crude oil inhibited the growth of the diatom Nitzschia closterium after one week. These authors also found that the Water Soluble Fraction (WSF) of this oil was inhibitory at high concentrations.

These and many subsequent studies, primarily using axenic algal cultures and either oil emulsions or aqueous extracts of varying (and often unknown) concentrations, have amply demonstrated the inhibitory effects of petroleum hydrocarbons on both marine phytoplankton (Mironov and Lanskaya, 1969; Mommaerts-Billiet, 1973; and Pulich et al., 1974), and freshwater species (Kauss and Hutchinson, 1975; Soto et al. 1975a; 1975b). In general, the patterns of effects are similar, being an extension of the lag phase in population growth, and a depression of the exponential phase. In most cases, however, normal growth was resumed unless the test medium was heavily contaminated.

Other work, notably by Russian authors on Black Sea phytoplankton, indicated that the sensitivities of various species differ considerably (Mironov, 1968; 1972). It was also shown that the effects varied with oil concentration. Mironov and Lanskaya (1966) found that a low concentration of oil (expressed as 0.001 mL/L) inhibited cell division of Melosira moniliformis, but stimulated that of Ditylum brightwellii. In addition, it was found that 1.0 mL/L oil caused a 100% reduction in Ditylum cell numbers over a period 24 hours, although ten times that concentration (10 mL/L) produced no measurable effect on Melosira over a period of three days.

Additional evidence of varying degrees of sensitivity to oil by phytoplankton species is provided by Pulich et al. (1974). These authors investigated the effects of two crude oils, and their WSF, No. 2 fuel oil, and various distillates, on the growth of six

species of phytoplankton. It was found that one species, Chlorella vulgaris var. autotrophica, was inhibited by the water-soluble components of the low B.P. fractions, which had no effect on Thalassiosira pseudonana and Agmenellum quadruplicatum, but these latter two species were more sensitive to the water-soluble components of the high B.P. fractions. A range of sensitivities to the water-soluble components of No. 2 fuel oil was also noted.

Evidence that petroleum hydrocarbons can stimulate photosynthesis in certain phytoplankters has been provided by Dunstan et al. (1975) who measured the growth of four marine algae exposed to volatile aromatics in the concentration range 0.1-100 mg/L. The growth rate of Dunaliella tertiolecta was stimulated, and there were variable responses for other species.

The enhancement of phytoplankton photosynthesis at low (ppb) hydrocarbon levels has also been demonstrated by Gordon and Prouse (1972). Studying the effects of one crude and two fuel oils on natural phytoplankton from Bedford Basin, these authors found that all three oils inhibited photosynthesis when present in concentrations of 50-300 μg/L, yet stimulation was observed at a concentration of 50 μg/L. Parsons et al. (1976) also found that hydrocarbons in low concentrations (5 μg/L) enhanced photosynthesis by a natural phytoplankton "population" dominated by Nitzschia sp. A "population" dominated by Skeletonema costatum, however, reacted differently. This "population" showed the greatest enhancement by aromatics at 50 μg/L concentration, by n-alkanes at 100 μg/L concentration, but n-alkenes depressed photosynthesis at all concentrations (5-500 μg/L).

It should be noted that in both the studies just referred to, natural phytoplankton "populations" were used; in addition, the actual hydrocarbon concentrations in the medium were measured and the concentrations used were similar to those normally encountered in the field. Gordon and Prouse (1972) also found that large evaporative losses of hydrocarbons could be expected to occur during the course of an experiment (90% over two weeks in their case). A similar effect was reported for naphthalene (a volatile oil component) by Vandermeulen and Ahern (1976) who suggested that such changes during the course of an experiment will affect the results, and probably account for the observed initial inhibitory activity and subsequent recovery.

At this point it should be noted that much of the earlier work was carried out without knowing the initial concentrations of WSF in test media, these being prepared by various agitation methods and subsequent filtration, although in some cases oil emulsions were used directly. Concentrations resulting from these methods, although not actually

known, are suspected to be in the high ppm range and are, therefore, greater than can be expected in the open ocean. Such levels may be reached after an actual oil spill, but then only for short periods and within a relatively restricted area. Grahl-Nielsen et al. (1978) measured 200-300 μg/L of total hydrocarbon in the water column following a spill of 2000 tons of Iranian crude near Karmoy Island. The concentration was down to background levels a month later. A Finasol dispersant was used on part of this oil, which produced a measured hydrocarbon concentration of 1000 μg/L (= 1 ppm) in the water column immediately after the spill. This hydrocarbon was in trace quantities three months later. Aromatics from the oil were present at concentrations of 2 μg/L initially, decreasing to 0.6 μg/L for undispersed oil, and 12 μg/L decreasing to 0.2 for the dispersed oil.

The difficulty in extrapolating early effects-data to actual field situations is, therefore, readily apparent. Prouse et al. (1976) found that both crude oil and No. 2 fuel oil, when added after the lag phase, in concentrations similar to those in the oil-contaminated waters of Bedford Basin (19 - 787 ppb), had no significant effect on cell division by Dunaliella tertiolecta and a Fragilaria sp. over a period of twenty-four days.

There is evidence that the effects of petroleum hydrocarbons on phytoplankton may vary seasonally. Thus, Gordon and Prouse (1972) found more marked effects in spring than in fall, and Fontaine et al. (1975) found that the effects of Kuwait crude WSF in the English Channel were more pronounced in summer than in spring. The effects of water temperature also vary markedly with species where they have been noted, but there is as yet no discernible consistent pattern of response.

The physiological condition of phytoplanktonic algae may be a factor contributing to the variability in response to hydrocarbons. Stoll and Guillard (1974) have shown that batch-cultured marine diatoms deficient in phosphorus were more susceptible to naphthalene (reduction of growth rate) than those not so stressed i.e. with high cell-phosphorus.

Controlled ecosystem experiments, which represent a step closer to field situations than is possible in laboratory experiments, show basically similar patterns of responses to those outlined above.

In one such experiment (Lacaze, 1974) a suspension of Kuwait crude oil produced a decrease in primary production, the rate of decrease diminishing with the loss of volatile aromatics. A more extensive experiment of this type (Lee et al., 1977) using the WSF of Number two fuel oil at an initial concentration of 40 ppb, caused a decrease in the abundance of diatoms with a commensurate increase in the numbers of micro-

flagellates. Although a similar change occurred in the control, it was to a lesser extent, and the diatoms of the oil enclosure did not recover at all, as they did in the control.

Apart from some of the studies previously mentioned (Gordon and Prouse, 1972; Prouse et al., 1976, Parsons et al., 1976; and Lee et al., 1977), little work has been done on the effects of oil on marine phytoplankton from Canadian waters, and none at all on arctic marine assemblages. Some information exists on the effects of oil on Canadian arctic freshwater phytoplankton. Dickman (1971) measured a tenfold decrease in the primary production of phytoplankton from an arctic pond (which was dominated by flagellates) as a result of administering aged Norman Wells crude oil. Snow and Scott (1975) reported an increase in the abundance of blue-green algae, primarily a non-heterocystous Oscillatoria sp., in an arctic lake upon which Norman Wells crude oil had been spilt.

Shiels et al. (1973) have studied the effects of Prudhoe Bay crude oil on Alaskan marine phytoplankton and macroalgae in the Port Valdez area, and found similar patterns of responses to those outlined above, i.e. enhancement at low hydrocarbon levels and inhibition at higher levels with species-specific variability.

Recently, there has been renewed interest in arctic under-ice biota. The subject has been reviewed by Horner (1976), and although ecological significance of these communities has yet to be definitively assessed, it is usually accepted that they are of considerable importance. They are, moreover, in a highly vulnerable position with respect to oil contamination from an underwater blowout, and nothing is known of the effects of oil on epontic algae.

5.2 Macrophytes

The damaging effects of oil on macrophytes are as variable as those for phytoplankton, although the "sample size" of experiments is less. The subject has been reviewed by Johnson (1977). The large kelp Macrocystis was not adversely affected by oil from the wreck of the TAMPICO MARU, but in fact was found to have increased in abundance following the spill. This was possibly a result of decreased pressure of grazing by urchins, which were killed off by the spill (North et al., 1965). Freshwater phytoplankters have been seen to bloom following an experimental spill of Prudhoe Bay oil on an Alaskan tundra pond for similar reasons, i.e. reduction in grazing pressure. In this case the herbivorous planktonic crustacea were killed off by the oil (Miller et al., 1978).

The disappearance of Zostera, (eel-grass) in certain areas has, however, been attributed to oil pollution (Anonymous, 1953). Thin films (0.1-0.0001 mm) of several crude

oils have been found to adversely affect Fucus vesiculosus, Laminaria digitata, Porphyra umbilicalis and Enteromorpha sp. by reducing CO_2-exchange, thereby lowering gaseous diffusion rates and exerting a toxic effect on photosynthesis. Shiels et al. (1973) found a range of species-specific responses of marine macroalgae to Prudhoe Bay crude oil. These responses included enhancement, inhibition, and in some cases, no effects were observed.

Nothing is known of the effects of oil on macroalgae in Canadian arctic or sub-arctic waters.

5.3 Mechanisms of Phytotoxicity

Strangely enough, relatively little work has actually been carried out on this subject, which has been reviewed by O'Brien and Dixon (1976). From studies on terrestrial plants, Van Overbeek and Blondeau (1954) suggest that hydrocarbon molecules disrupt the plasma membrane by displacing natural lipids, thereby affecting semi-permeability. Baker (1970) proposes a similar disruptive mechanism for organelles such as mitochondria. This could then cause inhibition of the TCA cycle and oxidative phosphorylation, as noted by Vandermeulen and Ahern (1976) while studying the effects of naphthalene on Monochrysis lutheri.

Currier (1951) indicated that physical factors were important in considering phytotoxicity and found that the adverse effects of aromatics in aqueous solution were inversely related to their solubility. Kauss et al. (1973) also found that the toxicity of aromatics to freshwater Chlorella increased along the series benzene, toluene, xylene and naphthalene, with water solubility decreasing in reverse order.

Polynuclear aromatic hydrocarbons (PNAH) have been found to stimulate growth in red algal sporelings, (Boney and Corner, 1962; Boney, 1974). These authors also found that carcinogens found in fossil fuel produced the same effect. It is possible, although never demonstrated, that crude oil could contain auxins or auxin-like substances which may account for some of the observed stimulation.

An interesting observation, and a significant one, if it is of widespread occurrence, concerns the effect of naphthalene on the freshwater alga Chlamydomonas angulosa (Soto et al., 1975b). The results of this study suggest that naphthalene (and, therefore, possibly other oil fractions) can affect the intracellular proportions and interconversion of metabolic substrates such as protein and lipid. The effects did, however, appear to be reversible. Such an effect could have significant implications with respect to primary and secondary production and also microbial decomposition. The effects of whole crude oil on multicellular Black Sea algae were investigated by Davavin

et al. (1975) who found that it inhibited biosynthesis and modified the polymerization of DNA and RNA.

5.4 The Effects of Chemically-dispersed Oil on Phytoplankton and Macrophytes

There is very little information documented concerning the effects of chemically dispersed oil on phytoplankton. Studies that have been carried out have largely been of the bioassay type (e.g. Strand et al., 1971); which have dealt primarily with relative toxicities rather than specific ones for either whole oil or its fractions or aqueous extracts.

The main problem attending this work is a lack of information concerning initial concentrations and subsequent changes during the course of the experiment. It has been reported that crude oils dispersed by Corexit 7664 are more toxic to phytoplankton than oils alone. The dispersant toxicity itself was found to be minimal, but No. 2 fuel oil became more toxic when dispersed (Batelle, 1973).

Mommaerts-Billiet (1973) found that Finasol with an aromatic carrier lengthened the lag-phase of the nanoplankter Platymonas tetrathele to a greater extent than did a water-solution Finasol. Diminished growth rates were also noted at high concentrations. The dispersant mixtures were as toxic as the dispersant itself (at its concentration in the mixtures), the toxicities were, however, less than for oil alone. The older types of dispersant have been found to be generally quite toxic to most forms of marine life. Boney (1968) found that five such detergents were quite toxic to intertidal algae, the reproductive stages being particularly sensitive, although again there was a range of sensitivity with two species, (Polysiphonia lanosa and Porphyra umbilicalis) having an unexpectedly high tolerance. In another study, a marine lichen was also found to be similarly sensitive.

A recent study in Canadian marine waters (Deception Bay, Newfoundland) using natural phytoplankton, a Venezuelan crude oil and one of the more recent "no-mix" dispersants (Corexit 9527), has provided useful insight into how dispersant effects may be predicted (Trudel, 1979). At concentrations likely to be encountered at spill sites, the dispersant did not affect the phytotoxicity of the dispersed oil, and carbon-fixation was inhibited by 10% by an oil-in-seawater concentration of 100 ppb. A dose-response curve was generated which, in conjunction with a horizontal turbulent diffusion model for any given location, could be used to predict the short-term effects of dispersed oil on phytoplankton. Scott et al. (1979) studied the effects of Norman Wells crude oil and the dispersant Corexit 9527 in a controlled freshwater ecosystem experiment. They found

that there was a greater decrease in phytoplankton biomass as a result of dispersing the oil compared to the effects of the oil alone, at least in the initial stages. The dispersed oil did, however, produce a luxuriant periphytic growth on the sides of the ponds.

5.5 Conclusions

A range of phytoplankton responses exists with species-specific toxicities to both oil fractions and whole oils, depending on how they are introduced. A range of responses is also apparent within natural phytoplankton assemblages, with such factors as water temperature and physiological conditions contributing to the variability.

Low concentrations of hydrocarbon appear to stimulate phytoplankton activity, and higher levels depress it. This generalization applies equally to freshwater and marine species.

It would seem that photosynthesis is a sensitive parameter which is depressed by hydrocarbons in the ppb range, as is algal growth. Both conditions are readily reversible at this level of contamination and usually of short duration. This is significant in terms of present background levels of hydrocarbons and those resulting from an actual spill in the open ocean. Here, ppm levels would likely produce an acute effect on some phytoplankters but would not ordinarily be expected to persist or to drastically alter the overall abundance of phytoplankton in a given open-ocean area. There are, however, other areas (e.g. in coastal embayments) where such effects may be significant in a chronic sense or produce ecological shifts at ice-edge interfaces and under the ice itself.

The effects of oil on marine macro-algae follow a similar pattern to the effects on phytoplankton, although less work has been carried out on the subject, and none at all in Canadian waters.

If the phytotoxicity of crude oil or its components is mediated via cell membrane disruption, or if cellular metabolic substrates are being changed, then chemical dispersants could affect such a mode of action. Nothing is known concerning such a comparative evaluation for either unicellular or macro-algae.

The use of chemical dispersants will accelerate the introduction of oil into the water column and the mixture may be more toxic than oil alone. There are, however, indications that the newer types of dispersant are less toxic than oil alone, as are the mixtures they produce. Far too little work, however, has been done in a comparative or even an absolute sense to be able to reach any meaningful conclusions regarding the effects of dispersed oil on marine plants under all conditions in which dispersants might be used.

5.6 Summary and Recommendations

There is a severe lack of information regarding the effects of oil on phytoplankton in Canadian arctic and subarctic waters. There is an even more profound ignorance of the effects of chemically-dispersed oil in the same waters. There is no information at all concerning the effects of either oil or chemically dispersed oil on marine macrophytes in Canadian waters.

This lack of knowledge is commensurate with a general low level of information with respect to arctic marine ecology and the understanding of biological processes involving the lower trophic levels in northern waters.

For impact assessment purposes in Canada, it is usually assumed that the effects of petroleum hydrocarbons on phytoplankton will be ephemeral, as the communities are often dense and ubiquitous. In general, this may be a reasonable assumption, at least for oceanic conditions, but there are situations, e.g. nearshore areas and embayments, ice-edges and under the ice itself, where such effects could be chronically disruptive to ecosystems. Dispersants may ameliorate or exacerbate the effects of oil in such locations.

There is clearly a need for research concerning the effects of both oil and chemically-dispersed oil on arctic and subarctic marine phytoplankton and macrophytes. Such work should include effects on individual species, associations and mechanisms of phytotoxicity, primarily in a comparative sense to evaluate any differences with respect to oil alone or dispersed oil.

It is recommended that any such studies should be accompanied by comprehensive work on chemical fate and that an interdisciplinary approach be used to maximize the data return and further the understanding of trophic level inter-relationships, accumulations and transfers. Such work should also be carried out during a minimum time-span of five years and it would probably be enhanced by using a combination of field spills, controlled ecosystem experiments and laboratory studies. Specific recommendations are as follows:

(1) There is very little predictive ability stemming from previous studies which could be used to estimate the anticipated effects of oil or dispersed oil on phytoplankton. Dose-response curves for oil concentration and phytotoxicity should be generated for arctic and sub-arctic phytoplankton assemblages and combined with horizontal turbulent diffusion models to predict effects of real spills.

(2) Although the actual ecological significance of epontic phytoplanktonic communities has yet to be firmly established, it is generally agreed that they may be very important in certain circumstances. The effects of fresh oil, emulsified oil, and chemically dispersed oil on these communities should be investigated.

(3) The effects of oil and chemically dispersed oil on arctic and subarctic sublittoral macroalgae are unknown. As these communities are significant in terms of nearshore faunal associations and shallow-water production, more work is required to assess the effects of petroleum hydrocarbons on these plants.

(4) The phytotoxic effects of petroleum hydrocarbons differ in severity with respect to different phytoplankters and even to the same phytoplankter at different times of the year. Further studies of the range of effects of both oil and chemically dispersed oil are required for characteristic phytoplankton associations (or populations) in different water masses at different seasons.

(5) Petroleum hydrocarbons have been shown to affect the inter-conversion of biochemical cell constituents. Although such effects are apparently reversible, it is necessary to determine the degree of reversibility, the threshold concentration for irreversibility, the extent (if any) of modification as a result of oil being in a chemically dispersed form, and the ecological consequences of such effects.

(6) Little is known of the actual mechanisms of oil phytotoxicity, although there appear to be several. Further studies are required on how phytotoxicity is affected by chemical dispersion of oil, or by differing sizes of oil droplets.

6 ZOOPLANKTON

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This chapter evaluates and summarizes the state of knowledge on the effects of spilled oil and chemically dispersed oil on zooplankton living in Canadian marine waters. Attempts are made to outline critical areas of ignorance. This review is based largely on references cited by the "Fate and Effects of Oil Working Group" (1977) and Doe et al. (1978), updated by more recent information. Earlier reviews of the effects of oil on zooplankton, covering worldwide literature, have been provided by Kühnhold (1977) and Corner (1978).

Responses of coastal or neritic zooplankton to floating and dispersed petroleum oil have been studied by numerous investigators in recent years. Zooplankters, as floating or weakly swimming organisms, are very important secondary producers in marine ecosystems. Planktonic production ultimately supplies energy for littoral, sublittoral and benthic communities. Zooplankters are planktonic for their entire existence or for only specific stages (early, reproductive, non-parasitic) of their life cycle. Their abundance, species types and distributions vary dramatically with the seasons, current patterns, availability of nutrients, water temperature and salinity, geographic location, time of day, and many other factors. As individuals, most zooplankters studied to date are very sensitive to dispersed and dissolved petroleum. This sensitivity must be assessed within the context of the natural variability of their populations, however, and consequent variation in vulnerability, in any assessment of the impact of oil on zooplankters (Rice et al., 1979).

Surface spills of oil undergo many physicochemical changes while spreading, such as evaporation, dispersion, dissolution, photo-oxidation and microbial degradation (see Chapter 2). In all cases, organisms at the sea surface or in the upper metres of the water column would be exposed to particulate oil and its dissolved fractions for many hours or days. Concentrations of total petroleum hydrocarbons under surface slicks have recently been reported to range from 0.001 to 28 mg/L (Wilson and Hunt, 1975; McAuliffe, 1977). Much effort is being directed to qualify and quantify hydrocarbons over time

periods following different spill conditions. The uniqueness of each spill makes it difficult to generalize on concentration, composition and duration of the oil in the water (see Chapter 3). The application of dispersants to oil slicks may alter some characteristics of the hydrocarbons in the water and, especially with effective dispersants, produce oil dispersions with smaller and more evenly distributed oil particles. Threshold effect concentrations, described in the following sections, must be reliably linked to data on the fate of spilled and dispersed oil in the water column.

6.1 The Effect of Oil on Zooplankton

The effects of oil on zooplankton have been studied with protozoa, coelenterates, ctenophores, polychaetes, molluscs, crustaceans (barnacles, copepods, amphipods, mysids, shrimp, lobsters, crabs), echinoderms, urochordates, teleosts and mixed species (see Table 6.1). Important members of the zooplankton that have not been studied in oil exposures are some protozoa (such as foraminiferans and radiolarians), coelenterates (siphonophores), molluscan pteropods, various crustacea (cladocerans, ostracods, cumaceans, isopods, and euphausiids), larvaceans, and chaetognaths. Very few arctic zooplankters have been studied in oil experiments. One-third of the studies report results in terms of nominal (added) oil concentrations, while the other two-thirds of the studies report results in terms of initial measured concentrations of hydrocarbons in the test-solutions. Most studies lack many details of the composition and concentration/time relationships of the prepared oil dispersions, and none attempt constant concentration, flow-through conditions. This situation makes meaningful comparative toxicology difficult (also see Craddock, 1977 and Rice et al., 1977 concerning this problem). Between 80% and 90% of the studies were conducted in the laboratory, and most of these concerned single species.

Very little is known about the interaction of petroleum oils and marine protozoa. Reported studies (Elmhirst, 1922; Spooner, 1968; Andrews and Floodgate, 1974) show that marine ciliates and amoebae are apparently unaffected by "oily water". Ciliates ingest globules of crude oil and oil residues along with organic particles and bacteria, but flagellates do not.

Medusae of the arctic coelenterate, Halitholus, were not killed by nominal concentrations of 10-200 mg/L of four crude oils dispersed in seawater (Percy and Mullin, 1975). In contrast, the marine ctenophore Pleurobrachia was quite sensitive (1-day LC_{50}=0.59 mg/L) to water extracts of fuel oil. Pleurobrachia absorbs naphthalenes from

TABLE 6.1 SUMMARY OF RESPONSES MEASURED IN ZOOPLANKTON EXPOSED TO OILS, DISPERSANTS AND MIXTURES.

	Ciliates	Amoebae	Coelenterates	Ctenophores	Polychaetes	Molluscs	Cirripeds	Copepods	Amphipods	Mysids	Shrimp	Lobsters	Crabs	Echinoderms	Urochordates	Fish eggs/lar.	Mixed spp.	Mixed spp. in field
Lethality	1	1	5	1	5	5	1	5	1	1	5	3	3	1	1	5		1
Behaviour							1	3		1	1	1	1			1		1
Feeding	1					1	1	4				1				1		1
Uptake, dep.				1				1			1		1				1	1
Development					2	1						1	1			4		1
Growth						1			1			1	1			1		
Physiology											1		1			4		
Reproduction								1	1				2	3		3		
Diversity, SC.*																	1	4

Legend: 1 - OIL; 2 - DISP. ONLY; 3 - OIL, DISP.;
4 - OIL, O/D MIX.; 5 - OIL, DISP., O/D MIX.;
*SC - Standing crop measurements.

solution and depurates them, but is not able to biodegrade any oil hydrocarbons (Lee, 1975; Lee and Anderson, 1977; Lee and Takahasi, 1977).

Even though polychaetes are very important components of the benthos, information on the sensitivity of their seasonal planktonic stages to oil is minimal (Table 6.1). Eggs and larvae seem relatively resistant to spills, and experimental exposures to fuel oils and kerosene (Wilson, 1968b; George, 1970; Chia, 1973). Although data do not exist for comparative toxicity at well defined oil concentrations for the planktonic stages of polychaetes, Chia (1973) suggested that survival may be related to egg and larval size.

Oil exposures with molluscan eggs and larvae (Woelke, 1972; Chia, 1973; Renzoni, 1973; LeGore, 1974; Renzoni, 1975; Umezawa et al., 1976; Byrne and Calder, 1977; Le Roux, 1977), particularly oysters, mussels and clams, showed that dispersed crude oil and water soluble fractions (WSF's) of crude oil had strong effects on fertilization, but usually only affected embryonic development and larval survival at nominal concentrations greater than 10 000 mg/L nominal. Water-soluble fractions of various oils killed clam embryos between 0.23 and 12 mg/L (2-day LC_{50}'s - concentration at which 50% mortality occurs) and clam larvae between 0.05 and 2.1 mg/L (10-day LC_{50}'s), (Byrne and Calder, 1977). Cyclic aromatics and heterocyclic compounds were usually considered to cause the toxicity. Ingestion of oil droplets proved fatal to oyster and mussel larvae (Umezawa et al., 1976), whereas pure hydrocarbons stimulated the growth of mussel larvae at 1-100 mg/L (Le Roux, 1977). Threshold concentrations for the embryos and larvae of very few species have been derived, even though littoral and sublittoral molluscs are ecologically and commercially important in Canadian waters.

Barnacle larvae are immobilized at nominal concentrations of 25-50 mg/L, killed rapidly at much higher nominal concentrations (5 000 mg/L), but are able to recover from one-hour exposures to nominal concentrations lower than 100 mg/L (Parker et al., 1971; Woodin et al., 1972; Chia, 1973; Morton and Wu, 1977). Threshold concentrations at which narcosis and death occur are unknown. Larvae ingest oil and eliminate oiled faeces when exposed to 2-10 mg/L (measured) suspensions of crude oil. Barnacle larvae successfully settled in oiled areas in Puget Sound, Washington, within 6 months of a spill (Woodin et al., 1972), but the impact of slowly released oil from oiled shorelines on resettlement has not been quantitatively studied.

The response of planktonic copepods to oil contamination has been well studied, for adults (Mironov, 1968, 1969b; Spooner, 1969; Conover, 1971; Parker et al.,

1971; Lee, 1975; Percy and Mullin, 1975; Corner et al., 1976; Berdugo et al., 1977; Harris et al., 1977; Lee and Anderson, 1977; Lee and Takahashi, 1977; Lee et al., 1977; Vandermeulen and Hemsworth, 1977; Mackie et al., 1978a; Ott et al., 1978; Sekerah and Foy, 1978; Spooner and Corkett, 1979). The WSF's of oils paralyse copepods at concentrations as low as 0.2-0.5 mg/L, but recovery is possible from 15-min exposures to several mg/L. Levels between 0.05-100 mg/L of dispersed oils or their components are lethal to adult and copepodite stages, the threshold level varying with the species, type of oil and length of exposure. Dispersed light fuel oils, with LC_{50}'s between 1 and 3 mg/L, appear to be more toxic than dispersed crudes. Fully-developed eggs containing nauplii were killed over several days by 0.08 mg/L alkylated naphthalenes. Methylated aromatics are more toxic to copepods.

Sublethal studies on copepods have been extensive, especially for metabolism. Copepods ingest various sizes of oil particles from oil dispersions, and such particles pass through their guts and form part of the faeces. Feeding rates can be slowed by exposure to dispersed crude oil at 1-2 mg/L (nominal) or increased when algae are immobilized by naphthalene. The uptake of specific aromatic hydrocarbons from the water into the tissues has been demonstrated in numerous experiments; with naphthalene, such uptake can occur from concentrations as low as 0.0002 mg/L and is more from the diet than from solution. Once taken up, naphthalene and its water soluble metabolites reach internal equilibrium concentrations within 8 days, at levels of 40 and 175 μg/g in tissue, but depurate rapidly to less than 5% of equilibrium concentrations when animals are returned to clean seawater. Lipid content may be a major factor determining the retention time of hydrocarbons. In addition, small copepods accumulate more naphthalene per unit of body weight than do large copepods.

Only two studies have been conducted with planktonic stages of amphipods, both with juvenile Gammarus oceanicus (Lindén, 1976 a, b). Larvae were much more sensitive than adults to physically dispersed crude and fuel oils, and more sensitive to light fuel oil (2-day LC_{50}=approx. 0.3 mg/L) than to crude oil (2-day LC_{50}=approx. 0.8 mg/L) and No. 4 fuel (2-day LC_{50}=approx. 6.2 mg/L). Larval growth rates were significantly lowered by a 60-day exposure to 0.3-0.4 mg/L of weathered crude oil dispersion, and brood sizes were reduced when egg-bearing females were exposed for 20-23 days to 0.3-0.4 mg/L of the same oil. Benthic amphipods may contribute larvae to the plankton, or periodically become planktonic themselves, so this group may be adversely affected by both dispersed and sedimented oils -- this requires more study.

Juveniles of benthic mysids, newly released from their brood pouches, are in the plankton or hyperbenthos for short periods of the year. Juvenile stages of Mysis stenolepis are very sensitive to dispersed Venezuelan crude (Wells, unpubl. data), being incapacitated by 3 h in 5.3 mg/L and by 6 h in 1.7 mg/L, and having a 4-day LC_{50} of 0.05-0.17 mg/L (average initial measured concentration). Mysids are very abundant in the summer in shallow sublittoral waters and are also hyperbenthic in the centre of some coastal bays; more work is required to assess their vulnerability to dispersed and sedimented oils.

A large number of studies have dealt with the effect of oil exposure on planktonic decapods. Five studies with larval and adult shrimp, Pandalus spp. and Eualus spp., and the WSF's of various oils and pure hydrocarbons show that the 4-day LC_{50}'s range from 0.5 to 7.9 mg/L, larvae and adults showing equal sensitivity (Bean et al., 1974; Vanderhorst et al., 1976; Broderson et al., 1977; Mecklenburg et al., 1977; Sanborn and Malins, 1977). Shrimp undergo narcosis (possibly reversible) prior to complete immobilization and death. Molting increases the sensitivity of Pandalus larvae to WSF's of oil (Mecklenburg et al., 1977). Larvae of Pandalus platyceros were killed by 0.008-0.012 mg/L naphthalene in 1-1.5 days, and at lower concentrations took up and accumulated naphthalene, metabolized it, and discharged approximately 80% of it when returned to clean water after brief exposures; in contrast, metabolites were retained for a surprisingly long time (Sandborn and Malins, 1977). The sensitivity to, and accumulation of, petroleum hydrocarabons by shrimp should be investigated further due to their commercial importance.

Studies with lobster larvae (Wells, 1972, 1976; Wells and Sprague, 1976; Forns, 1977; Capuzzo and Lancaster, 1980) and two dispersed crude oils showed that sensitivity varied with stage of development and molting cycle. The 4-day LC_{50}'s were between 1 and 4 mg/L. The 30-day LC_{50} and threshold concentration for slowed rate of development were both approximately 0.14 mg/L. Larvae exposed to dispersed crude oil often turned red-yellow, feeding rates were lowered over a 24 hour period at 0.19 mg/L, and small numbers of rare, intermediate third and fourth stage larvae developed. An increased demand on protein catabolism may be the result of oil exposures during larval development. The survival and development of larvae from oil-exposed eggs, and the bioenergetics of oil-exposed larval populations should be given further consideration, in order to assess the potential harm from inshore oil spills to the valuable lobster fisheries of the Atlantic coast.

Laboratory studies on the response of brachyuran crab larvae to oil are numerous (Lichatowich et al., 1971; Vaughan, 1973; Rice et al., 1976a; Bigford, 1977; Brodersen et al., 1977; Caldwell et al., 1977; Donahue et al., 1977; Mecklenburg et al., 1977; Sanborn and Malins, 1977; Winters et al., 1977; Christiansen and Stormer, 1978; Laughlin et al., 1978; Wells, unpubl. data). In most cases, 4-day LC_{50}'s for various oils were below 5 mg/L, with fuel oil dispersions showing greater acute toxicity than crude oil dispersions. Early larval stages were most sensitive. Many factors, especially type of oil dispersion and the molt cycle, influenced larval sensitivity. Oil dispersions caused crab larvae to undergo a time/concentration-dependent paralysis. Threshold concentrations for paralysis were well below the 4-day LC_{50}'s. Such narcosis, however, may be reversible. Larvae of Cancer did not avoid swimming into surface slicks of crude oil (Rice et al., 1976) and responses to gravity were depressed, then enhanced, as development progressed (Bigford, 1977). A single study with Cancer larvae showed that an 18-24 h exposure to 0.008-0.012 mg/L of naphthalene caused uptake and narcosis, but larvae readily depurated naphthalene when returned to clean seawater (Sanborn and Malins, 1977). Several studies have demonstrated slower rates of development at concentrations between 0.3 and 1.5 mg/L, with growth inhibited in some cases. Molting of oil-exposed larvae was delayed, inhibited at 0.6 mg/L, or less successful after a 24 h exposure to 1.1-1.9 mg/L WSF crude. No studies with brachyuran larvae developing from oil-exposed eggs have been reported. Larvae from commercially important species like the Tanner and Snow crabs have not been studied in hydrocarbon experiments, neither has the success of settling on oiled sediments been appraised for the megalopas of various species.

Despite the ecological importance of echinoderms, (starfish, sea urchins, etc.), and the great diversity of species on the southern B.C. coast, only six studies report toxicity of oil to their eggs and larvae (Allen, 1971; Chia, 1973; Lonning and Hagström, 1975a, b; Lonning, 1977b; Falk-Peterson, 1979). No threshold concentrations have been derived. The fertilization process appeared to be less sensitive to dispersed oil than the early cleavage stages of eggs (Allen, 1971; Lonning, 1977b). Urchin embryos were strongly affected during differentiation (Falk-Peterson, 1979). Larvae of several species of starfish showed widely varying sensitivities to WSF's of fuel oil (Chia, 1973). Detailed oil tests with sea urchin eggs and larvae should be pursued further, considering their common use as experimental material and the importance and often dominance of the adults among the inshore benthos.

The sole urochordate (Boltenia) tested in the laboratory was relatively sensitive to WSF's of No. 2 fuel oil (Chia, 1973), although threshold concentrations were not established.

Studies on the effects of oil or its constituents on marine fish eggs and larvae have been primarily with herring (Clupea spp.) and cod (Gadus morhua), exposed to various crudes, No. 2 and 6 fuels, and benzene (James, 1926; Kühnhold, 1969, 1970, 1972a, b, 1974; Hakkila and Niemi, 1973; Struhsaker et al., 1974; Lindén, 1975, 1976c, 1978; Rice et al., 1975, 1976a; Eldridge et al., 1977; Longwell, 1977; Lonning, 1977a; Struhsaker, 1977; Carls, 1978).

Fish eggs, with 4-day LC_{50}'s of 1-10 mg/L to various oils, are less sensitive than fish larvae and become more resistant to oil dispersions as embryonic development progresses beyond gastrulation. The WSF's of floating oils have killed eggs in laboratory and field exposures. Survival of Pacific herring eggs was reduced after spawning females were exposed to 0.8 mg/L of benzene for several weeks (Struhsaker, 1977). Pacific herring eggs may be very vulnerable to effects of oil spills as they are deposited in intertidal zones, in contrast to the bottom spawning of Atlantic and Baltic herring. Oil exposure during embryogenesis has its primary lethal and sublethal effects in the high production of larvae that die soon after hatching, morphologically deformed larvae and larvae with abnormal flexures of the tail. Such effects, observed after continuous exposure to 10-15 mg/L crude and fuel oils and 35-45 mg/L benzene, depend on the stage of the egg at the beginning of exposure. Embryos also grow more slowly and experience changes in heart activity when exposed to oil dispersions. The time of hatching of herring eggs was delayed after exposure to 3-6 mg/L of No. 1 fuel; the success at hatching of oil-exposed herring and cod eggs declined significantly, relative to concentration and time of exposure of eggs, with no hatching of herring eggs at 10.6 mg/L of No. 1 fuel. The effect on egg survival and development of hydrocarbon accumulation in maturing fish gonads requires further study (Kühnhold,1977).

Fish larvae are sensitive to dispersed oils and their components, with 4-day LC_{50}'s of 0.18 to 0.36 mg/L No. 2 fuel for cod and mackerel larvae, 3-12 mg/L crude and fuel oils for herring larvae, and 20-25 mg/L benzene for herring larvae. Acute toxicity appears to diminish with age of dispersion and lower water temperatures. Mortality of larvae is a less sensitive stress response than aberrant swimming behaviour, narcosis and tissue injuries. Neither herring nor cod larvae actively avoid experimental surface slicks of crude oil, but repeatedly enter them. Herring larvae narcotized by benzene may

recover in clean water. Larvae continually exposed to dispersions of crude oil show tissue damage to the primordial fin and other larval integuments, reduced body size (at concentrations as low as 5-10 mg/L benzene), reduced feeding in the post-yolk sac stage, and altered respiration rates. Cod larvae became less resistant to oil dispersions with the onset of feeding following absorption of the yolk sac. The high sensitivity of certain fish larvae to oil dispersions is well known and should be studied further with laboratory and field populations of other species.

Mixed zooplankton species have been exposed to water extracts of No. 2 fuel (0.010-0.040 mg/L) in CEPEX enclosures (Lee and Takahasi, 1977; Lee et al., 1978), and individually in the laboratory for studies of hydrocarbon uptake, metabolism, storage and depuration (Lee, 1975). Planktonic crustacea (amphipods, copepods, euphausiids, crab zoea) exposed to a variety of labelled hydrocarbons, took them up from the water and metabolized them to various hydroxylated intermediates, whereas no metabolism was observed in ctenophores and jellyfish (Lee, 1975). During one season, there were no significant differences in the species and standing crop of the zooplankton in the CEPEX oil and control enclosures, but in the following year in a similar experiment, the ciliate and rotiferan populations were dominant in the oil-treated enclosures and fed on microflagellates. These studies and others (Davies et al., 1979; Heinle et al., 1977; Vargo, 1980) point out the different capabilities within the zooplankton for accommodating to the presence of oil hydrocarbons and the variability in responses that might be expected among field populations and communities when exposed continuously to low levels of oil-derived hydrocarbons.

Field observations on zooplankton have been made at the spill sites of the TORREY CANYON (O'Sullivan and Richardson, 1967; Smith, 1968; Spooner, 1969; Clark and Finley, 1977), ARROW (Conover, 1971), Marsh Point Refinery (Woodin et al., 1972), ARGO MERCHANT (Clark and Finley, 1977; Longwell, 1977; Brown and Cooper, 1978; Polak et al., 1978), BRAVO (various authors, 1977), TSESIS (Lindén et al., 1979), and AMOCO CADIZ (Hendrikson et al., 1978; Mackie et al., 1978a; Samain et al., 1978; Spooner, 1978). Observations are presently being made on the Scotian Shelf off Nova Scotia in association with the KURDISTAN spill (R. O'Boyle, 1979). There is usually little detected damage or significant prolonged change to plankton populations in the open areas near the spills, and, except at the TORREY CANYON where first generation dispersants were used, some resettlement of oiled shorelines occurs within months of severe oiling. Individual organisms at spills have been affected through direct mortality (fish eggs,

copepods, mixed plankton), adherence of oil (fish eggs, feeding appendages of copepods and amphipods), uptake and retention of aromatics, and abnormal development (fish eggs). Copepods ingest and defecate oil particles without apparent ill effects (Conover, 1971; Lindén et al., 1979). Other more subtle effects on individual organisms, suggested from the laboratory studies, may have gone unnoticed. Observations on zooplankton at spill sites are relatively rare and seldom quantified; this situation should certainly be remedied if the information derived in the laboratory is to be interpreted within the field context. It is obviously very difficult to design sampling programs and techniques at spill sites that take into account the natural variability (seasonal, regional, annual) of zooplankton populations. However, one quantitative approach would be to measure levels of cycloalkanes and aromatics in plankton from such areas, since these compounds are normally not present, although other possible sources of aromatics and their natural production should not be disregarded (Corner and Harris, 1976). Microscopic and histopathological examinations of the same specimens should also be performed.

6.2 The Effects of Dispersants and Chemically Dispersed Oil on Zooplankton

6.2.1 Dispersants. In current literature, numerous laboratory studies on aquatic toxicity of dispersants are reported, many of these being lethal tests. Toxicity depends on the chemical composition of dispersants (type and aromatic content of solvent, molecular structure of surfactant), the condition of dispersants in water (chemical stability, concentration and duration, temperature, hardness, salinity and oxygen content of water), and various characteristics of the exposed organisms (species, age, stage of development, health, and previous exposure and acclimation to surfactant) (Wells, unpubl. ms.). It is unlikely that large numbers or many species of zooplankton would be exposed to dispersants alone during the control and cleanup of a spill. However, studies have been conducted with zooplankton to ensure the development of non-persistent and effective agents of low toxicity, and to understand the toxicities of chemically dispersed oils.

Laboratory studies with dispersants or their surfactants and zooplankton have been conducted with coelenterates (Latiff, 1969), polychaete larvae (Latiff, 1969; Bellan et al., 1971; Äkesson, 1975), molluscan larvae (Hidu, 1965; Tracey et al., 1969; Renzoni, 1973), copepods (Smith, 1968; Foy, 1979), decapod larvae (Portmann and Connor, 1968; Latiff, 1969; Czyzewska, 1976; Doe and Wells, 1978), echinoid gametes, embryos and larvae (Lonning and Hagström, 1975 a, b, 1976; Hagström and Lonning, 1977), and

ichthyoplankton (Smith, 1968; Wilson, 1972, 1974, 1976, 1977; Lindén, 1974). A more recent study tested dispersants with a variety of marine eggs and larvae (Lonning and Falk-Peterson, 1978). These studies tested early and later ("first and second generation") dispersants, and anionic and nonionic surfactants. Briefly, these studies show a reduction in the acute toxicity of many second generation dispersants (2-day and 4-day LC_{50}'s are greater than 100 mg/L), compared to the early dispersants. Toxicity varies, however, with phylogeny, life history, and physiology of the particular species. The very small data base and varied experimental methods, which exclude measurements of the surfactants and dispersants in solution, preclude many generalizations. Toxicities vary even with newer dispersants such as Corexit 7664, for which larval Crangon had an incipient lethal level (ILL) of 1.6 mg/L while Pleurobrachia had an ILL of 670 mg/L, or Corexit 9527 with its very high acute toxicity to sea urchin spermatozoa and much lower toxicity to copepods. Consequently it may be quite incorrect to conclude that the newer dispersants are non-toxic. It appears, however, that they are often much less toxic to zooplankton than is physically-dispersed oil.

Crustaceans as a group are particularly susceptible to petroleum-based dispersants. The fertilization process of sea urchins and the early development of fish are easily affected by dispersants (Lonning and Falk-Peterson, 1978). Newly fertilized fish eggs and recently hatched fish larvae are more sensitive to dispersants than developing fish embryos. There may also be differences in sensitivity due to size of organisms, season, onset of feeding in fish larvae, and nutritive condition. Dispersants act physically on the respiratory surfaces or organs, and reversibly, depending upon exposure time, on the nervous systems of aquatic organisms. The smaller zooplankters such as copepods have large surface/volume ratios and high metabolic rates which may make them more vulnerable to dispersant contact, uptake and internal toxic action.

The continuation of comparative toxicology of the newer dispersants for marine eggs and larvae, as in the work of Lonning and Falk-Peterson (1978), would do much to define the hazards of the new formulations.

6.2.2 Chemically Dispersed Oil. The aquatic toxicity of dispersant-oil mixtures is influenced by both the dispersant (chemical composition and toxicity, ratio of dispersant to oil, effectiveness at dispersal) and by the dispersed oil (volume dispersed, stability of dispersions, physical and chemical properties, physical and chemical toxicity of the oil).

Laboratory studies with chemically dispersed oil and zooplankton have been conducted with coelenterates (Latiff, 1969), polychaete larvae (Latiff, 1969; Äkesson, 1975), oyster larvae (Renzoni, 1973), copepods (Spooner and Corkett, 1974; Sekerah and Foy, 1978), decapod larvae (Latiff, 1969) and ichthyoplankton (Kühnhold, 1972b; Lindén, 1975, 1976c). The number of studies conducted with Canadian zooplankters is very small (Table 6.1); in only one case (Sekerah and Foy, 1978) is the assessment based on measured hydrocarbons, and most studies are on lethal, not sublethal, responses.

Collectively, however, these studies show: (a) the apparent greater toxicity of dispersant-oil mixtures (in various ratios) compared to the dispersant; (b) the relatively high concentrations of crude oil and dispersant required to affect fecal production in copepods (oil 10 mg/L: dispersant 2 mg/L nominal); (c) the high sensitivity of shrimp larvae to a 4:1 mixture of Corexit 7664 and Iraqian crude oil (ILL=0.36 mg/L); and (d) the similarity in responses of fish embryos and larvae to chemically dispersed oil and oil alone. Crustaceans are more sensitive to chemically dispersed oil than bivalve molluscs and fish. The respiratory organs and nervous systems of aquatic organisms have been identified as major sites for the toxic action of oil-dispersant mixtures. Zooplankters paralysed or disoriented due to contact with dispersant-oil mixtures may recover if exposure times and uptake of hydrocarbons are not too great. The data suggest that "no-observed-effect concentrations" (N.O.E.C., Maki, 1979) for indefinite time periods for larval polychaetes, larval decapods and newly hatched fish larvae may be much lower than 0.5 mg/L of measured hydrocarbons, when oil is chemically dispersed. The sensitivity of these zooplankters must be confirmed experimentally, in the laboratory and in CEPEX type enclosures, and the implications of using dispersants considered accordingly.

6.3 Summary

The previous sections, summarized in Table 6.1, demonstrate that a considerable number of laboratory studies have been conducted, and observations made, on the toxicity of oils, dispersants and chemically dispersed oils to marine zooplankton found in Canadian waters. Most work has dealt with oil only. Collectively, these studies show the moderately to highly acute toxicity of naturally dispersed oil to various groups of zooplankton (Table 6.2). Most of the 4-day LC_{50}'s, based on measured concentrations, range from 0.1 to 12 mg/L; these values are very close to predicted values of 0.1 to 10 mg/L of soluble hydrocarbons for larvae, eggs and pelagic crustacea (Moore and Dwyer, 1974). Based upon the available lethal data (Table 6.2), there is no marked difference in sensitivity between the planktonic ctenophores, molluscs, crustacea and teleosts.

Numerous adverse sublethal effects have been observed among oil-exposed zooplankton (Table 6.1), at concentrations often well below 1 mg/L (total measured hydrocarbons) for exposures varying from several days to weeks. Many important groups of organisms, however, have not been adequately studied or studied at all. This fact, together with the variation in exposure conditions and in tested life stages, precludes a meaningful generalized summary on oil effects on zooplankton. There is, in addition, a paucity of interpretable information on the acute and chronic toxicities of chemically dispersed oils to key members of the temperate and arctic zooplankton. Consequently, not even a general relationship is known, between threshold effect concentrations for key species, and concentrations measured under chemically dispersed spills in Canadian waters.

TABLE 6.2 SUMMARY OF MEDIAN LETHAL CONCENTRATIONS OF PETROLEUM OILS AND ZOOPLANKTON FOUND IN CANADIAN MARINE WATERS. All concentrations are in mg/L, measured in the water.

Groups of Zooplankton	Type of Petroleum Oil ((No. of days) LC_{50}'s)		
	Crude Oils	No. 2 Fuel Oils	No. 4 Fuel Oils
Ctenophores		(1 d) 0.59	
Molluscs (embryos)	← (2 d) 0.23-12	→	
(larvae)	← (10 d) 0.05-2.1	→	
Crustacea			
Copepods (larvae and adults)	← 0.05-100	→	
(adults)		(4 d) 1-3	
Amphipods (larvae)	(2 d) 0.8	(2 d) 0.3	(2 d) ~6.2
Mysids (juveniles)	(4 d) 0.05-0.17		
Decapods			
shrimp (larvae and adults)	← (4 d) 0.5-7.9	→	
lobsters (larvae)	(4 d) 1-4		
	(30 d) 0.14		
crabs (larvae)	← (4 d) <5	→	
Teleosts (eggs)	← (4 d) 1-10	→	
		(4 d) 0.18-0.36	
(larvae)	← (4 d) 3-12	→	

The applications of dispersants to spilled oil over several days, weeks or months, depending on the type of spill, could increase both the initial concentrations of the dispersed oil and duration of exposure to it, as well as changing its composition in the water. The high sensitivities of certain species, especially during fertilization, early embryonic development, hatching and larval phases, suggests that damage occurs to the zooplankton during oil spills. Indeed, some damage has been observed at spills. The extent and significance of such damage to populations and communities of zooplankton depends very much on the location, size, extent and duration of the particular spill. Blowouts in the Arctic or off eastern Canada could conceivably continue for months or years, and large spills in coastal sounds, inlets and bays could contaminate the water column for many weeks during crucial spring and summer periods of productivity. In such cases, the susceptibility of local populations of zooplankton to significant lethal and sublethal damage would probably be high, and might rank closely with the known level of immediate effects imparted by oil spills to birds and intertidal organisms. In contrast to birds, however, populations of zooplankton and intertidal organisms could recover fairly rapidly due to gradual recruitment from other areas.

Since damage, or lack of it, to zooplankton in the field is very difficult to quantify and interpret, a more concerted toxicological effort on key species, especially arctic ones, is warranted and should be given a high priority. This may be, in the short term, the only way dispersants of lowest toxicity to marine zooplankton may be chosen, and the only way available to quantitatively assess the acute and chronic consequences to zooplankton of dispersant use on oil spills in Canadian marine waters.

6.4 Recommendations

It is very important that quantitative observations and analyses of representative zooplankters, especially species in the neuston, be made at accidental and experimental spill sites to test laboratory conclusions on sensitivities and overall impact, and to suggest realistic laboratory testing protocols. Such observations and analyses might include: external microscopic examinations, histological examinations of respiratory surfaces and tissues, analyses of tissue for specific aromatics, in situ bioassays and exposure-recovery tests. Descriptions of abundance and distribution at the spill sites should be made but interpreted cautiously. Experimental spills with unique communities of zooplankton, such as under-ice and ice-edge communities, must be conducted.

Bioassays should be conducted to simulate real exposure conditions at spill sites. Exposures of at least one dominant zooplankter to chemically dispersed oils should be performed with both constant concentrations (continuous-flow) and declining concentrations (continuous-flow). In declining concentration tests, single and multiple exposures could be used, for chemically dispersed fresh and weathered oils. Levels of hydrocarbons in tissues, behaviour of organisms, and histological, developmental and physiological responses should be measured as exposures progress.

Selected marine zooplankton (dominant species at various developmental stages) from both temperate and arctic waters should be incorporated into acute screening and experimental bioassays testing dispersants, alone and with oils. Bioaccumulation potential, tissue levels of contaminants, mortalities, and selected behavioural, histological, developmental, and physiological responses should be measured in such bioassays.

Such toxicological work with zooplankton and chemically dispersed oils should include comprehensive descriptions of the composition of all materials and their histories of storage. Standardization of both oils and dispersants and their major components is recommended for such work. Studies should include oils, dispersants and their combinations in realistic but varied ratios. Studies should also include detailed quantification, in a time series, using gas chromatographic and/or spectroscopic techniques, of concentration and composition of major constituents, and analysis of particle size distributions over time.

There is a continuing need for research concerning: (a) the effects of non-ionic surfactants on selected zooplankton; (b) the avoidance behaviour and paralysis/recovery of key species exposed to dispersed oil and selected component hydrocarbons; (c) the effects on chemoreception; (d) the effects on mechanics and success of suspension feeding in key zooplankters; and (e) the bioaccumulation, toxic mechanisms and metabolism of oil, chemically dispersed oil, and its major aromatic components. The contributions to acute and chronic toxicity of particulate oil and selected dissolved hydrocarbons, with and without dispersants, should be evaluated using some of the above response criteria and at least one key organism.

The implications of the chemical dispersal of oil on plankton feeding and production require more consideration -- possible disruptions to ecological processes important to the zooplankton, such as primary productivity and food transfer to micro-and mega-zooplankton, should be hypothesized and studied. Open tanks and CEPEX bags seem

ideal for such studies, especially when coupled with controlled laboratory experiments. In addition, the implications of reduced diversity, abundance and biomass of key zooplankters to populations of their predators (fish, birds and cetaceans) should be considered.

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7 EFFECTS OF OIL HYDROCARBONS AND DISPERSANTS ON FISH

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7.1 Toxicity of Oil

Petroleum is widely believed to be poisonous to fish, and indeed this can be proven under laboratory conditions; but there is little evidence that intoxication occurs upon brief exposure to the levels of 0.2-2.0 mg/L found in the vicinity of real-world oil spills (McAuliffe, 1977). Much of the older (and some of the more recent) toxicity research has been inconsistent in methodology; the most serious difficulty has been the failure to measure actual oil concentrations in the water column or test environment (Rice et al., 1977). Oils from different sources vary in toxicity, probably as a function of the content of low-molecular weight aromatic hydrocarbons of one or two rings (Anderson et al., 1974). For testing, it is wise to choose oils that are similar to the ones of direct concern in the environment studied, e.g. Prudhoe Bay crude in marine British Columbia, and Venezuelan crude in eastern waters.

Recent work of Rice et al. (1976) approached proper technique, in that oil concentrations were measured in parallel with toxicities, using fish species and oils relevant to the area under study (northern Pacific coast). Solutions of the "water-soluble fraction" (WSF) of oils were made by slow stirring of oil and water; oil concentration was then determined before dilution to test strength. The Cook Inlet crude oil had 96-hour LC_{50}'s of 1.3 to 2.9 mg/L for four species of fish; those for a lighter (No. 2) fuel oil ranged from 0.8 to 2.9 mg/L. The 24-hour LC_{50}'s were not significantly higher; most damage was immediate. Since the exposures were static and aerated, it is likely that the low-molecular weight aromatics were driven from solution within the first day. Work by Morrow et al. (1975) using pure monocyclic aromatic hydrocarbons, however, supports the immediate-or-not-at-all manifestation of lethal intoxication. DeVries (1976) produced data on different species supporting the above results.

Measurements made on three other species by Anderson et al. (1974) revealed that toxicity is more a function of the oil tested than of the species employed, and the

critical parameter may be the solubility of the oil (see Table 7.1). Earlier works, in which actual oil concentrations were not monitored (e.g. Hakkila and Niemi, 1973; Morrow, 1974; Rice, 1973) give misleading high estimates of toxic concentrations, in the tens and hundreds of parts per million. Oils appear to be less toxic in seawater than in freshwater (Anderson and Anderson, 1976); whether this is due to different solubilities or to changes in ion permeability of gills is not yet resolved, however. Of the various life stages of fish,

TABLE 7.1 ACUTE TOXICITY OF SEVERAL OILS TO MARINE FISH (expressed in terms of median lethal concentrations of added and dissolved oil).

Oil	LC_{50} (Range in mg/L or μL/L) Oil Added	Oil Dissolved (WSF)
S. Louisiana crude	3700 - 80000	5.5 - 19.8
Kuwait crude	9400 - >80000	6.6 - 10.4
No. 2 fuel	33 - 260	3.9 - 6.9
Bunker	Too high to measure	1.9 - 3.9

(Data abstracted from Anderson et al., 1974)

larvae appear to be most sensitive, especially near the time of yolk sac absorption, when mortalities are naturally high (Rice et al., 1975; Struhsaker, 1977). Eggs are more resistant than adult fish (Rice et al., 1975).

"Sublethal effects" represent a complex and confusing field of research, in part because the ecological significance of many sublethal responses are difficult to substantiate. Among the responses studied have been avoidance (of WSFs), "coughing" (gill purging), metabolic rates, activity, reproduction, and growth (Patten, 1977). In our own laboratory, exposure of cunners to 0.3 to 0.8 mg/L crude oil (measured) for an entire season caused cessation of feeding and eventual death from starvation. The gonads of the exposed females failed to mature, and their livers failed to enlarge normally during maturation. Other work has detected effects on eye lens size (and possible interference with vision) (Hawkes, 1977), spleen size, and blood chloride levels (Payne et al., 1978b).

7.2 Accumulation and Tainting

Aside from toxic reactions of the target species, effects of oil on higher predators and human consumers of fish have been postulated. Oils contain polycyclic

hydrocarbons, and certain polycyclic hydrocarbons have been implicated in carcinogenesis; therefore, the search for relationships between oil pollution and carcinogenesis in fish has been solidly supported and vigorously pursued (Dunn and Stich, 1975, 1976). The sensitive Ames test for mutagenicity and potential carcinogenicity, however, gave negative responses for all crude and refined oils tested. Used crankcase oil and "synthetic" crudes give strong positive reactions; these do not seem to be associated with polycyclic hydrocarbons but rather with more polar compounds (Payne et al., 1978a; J.F. Payne and A. Rahimtula, unpublished data).

The alkane fractions of petroleum are readily taken up by fish. Uptake is highly selective and the resulting alkane carbon number distributions reflect the species and tissue examined rather than the composition of the applied oil (Blackman and Mackie, 1973; Corner, 1975; Giam et al., 1976; Hardy et al., 1974; Mackie et al., 1978c; Varansi and Malins, 1977). Alkanes, although extensively studied in water, sediment, and organisms, do not appear to be the constituents of toxicological or organoleptic (i.e. commercial) interest.

Aromatic hydrocarbons are even more vigorously absorbed by fish (Neff et al., 1976; Varansi and Malins, 1977), and are substantially more toxic than alkanes. The rate of uptake increases with the number of fused aromatic rings (Roubal et al., 1977) and the extent of alkyl substitution (Roubal et al., 1978). Petroleum-derived aromatic hydrocarbons are for the most part highly alkylated - as opposed to pyrogenic aromatics.

The mechanisms of toxicity are not well understood. There is reason to suspect that aromatic hydrocarbons accumulate in structural lipids and disturb the permeability of membranes (Payne et al., 1978b; McKeown and March, 1978), as well as the functioning of enzymes that depend on membrane integrity for their activity, notably nerve membrane ion pumps (Dixit and Anderson, 1977; Stegeman and Sabo, 1976; Varansi and Malins, 1977). The abysmal lack of fundamental research into membrane structure and function is responsible for this inability to document the mechanism of oil effects.

Tainting of fish by petroleum hydrocarbons has been frequently recorded, but the petroleum components responsible for tainting have not been identified. Connell et al. (1975) have implicated alkanes (a "kerosene-like" mixture of alkanes); Ogata and Miyake (1975) methylated benzenes; and Brandal et al. (1976) naphthalenes; none of these studies excluded other categories of compounds. Brandal et al. (loc. cit.) produced reliable concentration data demonstrating that 40-50 μg/L hydrocarbons in the water resulted in tainting of salmon in four days; saithe was not tainted, although its flesh

contained measurable amounts of hydrocarbons. Despite closures of fisheries after some oil spills, cases of reported tainting that are known to the author were not substantiated in controlled tests with taste panels.

7.3 Metabolism of Oil

The aromatic constituents of oil are readily oxidized by the mixed-function oxygenase enzyme complex found in liver and some other organs. The resulting, more polar compounds (epoxides, phenols, vic- and trans- dihydrodiols) may be condensed with water-soluble carriers such as glucuronic acid to yield hydrophilic conjugates that can be excreted in the bile or urine. Roubal et al. (1977) demonstrated the formation of at least six metabolites of naphthalene in salmon.

Petroleum causes induction (increase) of oxygenase activity in every fish species so far examined (Burns, 1976; Gruger et al., 1977; Kurelec et al., 1977; Payne, 1976, 1977; Payne and Penrose, 1975; Stegeman and Sabo, 1976). The induction phenomenon has been proposed as a monitor for petroleum contamination (Payne, 1976; Payne and Penrose, 1975). The metabolism of aromatics has been thoroughly reviewed (e.g. Corner, 1975, Varanasi and Malins, 1977), but there is only limited evidence to support the metabolism of alkanes by fish (Whittle et al., 1977).

7.4 The Effects of Oil Dispersant Use

7.4.1 The Toxicity of Dispersants. The toxicities of surface-active agents are not directly related to their effectiveness; toxicity is primarily a function of the chemical class of detergent (Abel, 1972). As a result, it has been possible to formulate dispersants with extremely low acute toxicities, i.e. LC_{50}'s greater than 10 000 mg/L (Canevari, 1973; Doe and Harris, 1976; Perkins et al., 1973; Swedmark et al., 1973; Wells and Doe, 1976; Wells and Keizer, 1975).

Sublethal effects have been observed at much lower concentrations, but the significance of these is very much open to question. Such effects concerned ontogeny (Lindén, 1975; Wilson, 1976), fertilization (Lonning and Hagström, 1976), and bradycardia (Kiceniuk et al., 1978), for example.

7.4.2 The Toxicity of Dispersant-Oil Mixtures. It is practical to consider dispersants only as mixtures with oil, because of stringent regulations on dispersant use in Canada (Anonymous, 1973; Ross, 1975) as well as low toxicities. Without question, the toxicity of applied oil is increased by dispersants (Anonymous, 1973a; Lindén, 1975, 1976; Swedmark

et al., 1973), but this appears to be due solely to the increased solubilization of oil by dispersants. B.K. Trudel (pers. comm.) demonstrated no effect of dispersants on the inhibition of photosynthesis by oil when actual dissolved oil concentrations were measured. W.R. Penrose (unpublished) measured C_{14}-fluorene uptake by fish in the presence and absence of dispersant; when fluorene levels were less than the solubility of the hydrocarbon, the dispersant had no influence on uptake rates. Wells and Harris (1980) tested 1:1 mixtures of Corexit 9527 and No. 2 fuel oil against rainbow trout and threespine sticklebacks, and found an additive effect, supporting the hypothesis that oil is the primary cause of lethality to fish when mixed with an effective, low-toxicity dispersant.

At sublethal concentrations, oil-dispersant mixtures can affect swimming activity (positively or negatively) and equilibrium (Swedmark et al., 1973). Hydrocarbon-based dispersants such as BP1100X also elicited avoidance behaviour (loc. cit.).

In laboratory-scale experiments, an equal weight of dispersant caused the level of "accommodated" (filterable) oil to increase from 50 to 1000 ppm (W.R. Penrose, L.L. Dawe and M.R. Sandeman, unpublished). Aside from the potential of lethal intoxication, the greater likelihood of tainting by brief exposures must be considered. In this context, the effect of dispersants on the uptake of various classes of hydrocarbon has not been investigated.

7.5 Summary and Recommendations

7.5.1 Acute Toxicity. Although acutely lethal levels of oil are of the same order of magnitude as the highest levels measured in uncontrolled spill situations, there are few records of significant fish kills caused by oil spills. This is probably because concentrations decrease drastically with distance, depth and time. Avoidance behaviour by fish may not occur and is unlikely to be responsible for the absence of kills.

Toxicity of an oil can probably be predicted from the content of mono- and bicyclic aromatic hydrocarbons, although this has not been investigated in a systematic way.

Chemically dispersed oil is no more specifically toxic than undispersed oil; its higher apparent toxicity is due to the increased rate and extent of solubilization caused by dispersants.

Fish larvae are more sensitive to oil than eggs or adults, and might be seriously at risk near a spill if conditions trap them in a highly-concentrated area near the oil. The use of dispersants in such situations would be inadvisable, and pre-application sampling for ichthyoplankton should be implemented, a) where larval concentrations are suspected; b) when a more valuable resource is not at risk; and c) when such sampling will not delay dispersal until weathering of the oil has made it impossible.

7.5.2 Sublethal Toxicity. Long exposure of fish to intermediate levels of dissolved oil can cause behavioural changes, including inhibition of feeding. Exposure times in the order of months are unlikely with most commercial species of fish, which are mostly migratory and only temporarily become resident during spawning. Areas of known spawning activity should not be subjected to chemical dispersal operations until more is known about effects on spawning behaviour.

8 BENTHIC AND INTERTIDAL ORGANISMS

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Much research has been carried out during the past decade in an attempt to resolve problems related to oil spills. Some conclusions reached thus far concerning the effects of petroleum and dispersants on benthic organisms, and evaluation of the adequacy of the available information are reviewed on this chapter. Important aspects of the problem about which the information is deficient, speculative or contradictory are identified and briefly discussed.

8.1 The Biological Effects of Petroleum Hydrocarbons

8.1.1 Habitat Vulnerability and Immediate Impacts. Observations of many large accidental oil spills have provided a comprehensive picture of the immediate impacts that may occur in particular habitats. Attempts have been made to rank different types of coastal environments according to vulnerability (Gundlach and Hayes, 1978), considered to be primarily a function of the general geomorphology. Concise lists have appeared summarizing some of the more general, obvious nearshore impacts associated with specific oil spills (Wilson and Hunt, 1975; van Gelder-Ottway and Knight, 1976). Reported impacts range all the way from little or no biological damage to extensive habitat damage and massive mortalities.

Laboratory studies have unambiguously demonstrated the lethal and sublethal toxicity of many petroleum products and dispersant formulations to an array of marine organisms. Although the potential for damage is great, the expression of this potential in an actual spill situation is modulated by a range of physical, chemical, and biological factors (Percy and Mullin, 1975; Straughan, 1972). The impact is a function not only of the nature and degree of biological alteration, but also the magnitude of the area affected. Failure to consider geographic scale underlies much of the confusion concerning the seriousness of oil spills.

One of the important variables governing oil impact is the nature of the habitat into which the oil intrudes. Oil does not spread uniformly in the marine

environment, but tends to accumulate in specific habitats. The intertidal zone and adjacent shallow subtidal areas are particularly vulnerable to oil accumulation and also to long persistence of oil. These facts, coupled with the visibility, ready access and ease of survey of the littoral zone have resulted in the accumulation of large amounts of information, ranging from rigorously quantitative to purely anecdotal. From this, generalizations with varying degrees of validity have been derived.

Oil represents both a physical and a chemical hazard, and intertidal species are especially vulnerable to the physical effects. Most research has focussed on the chemical toxicity of dissolved or finely dispersed oil, and what little is known about physical effects has largely been derived from field observations. Sessile species such as barnacles may be smothered by heavier oils (Straughan, 1972), while mobile animals such as amphipods may be immobilized and cemented to the substratum or trapped in surface slicks in rock pools (Ottway, 1971). Heavily oiled sea weeds and sessile animals may be torn from the substratum by wave action (Cowell et al., 1972). These are extreme cases resulting from particularly heavy contamination. Little is known about physical effects of light to moderate oiling or about the ability of organisms to recover.

Many intertidal species are relatively resistant to oil. Some are capable of producing copious quantities of mucous which prevents oil adhering to them. Other species, such as bivalve molluscs, are able to isolate themselves for variable periods from the external environment and may in this way survive temporary heavy oiling. Further study of these and other survival strategies would enhance our understanding of biological impacts of spilled oil.

8.1.2 The Effects on Benthic Flora. While laboratory studies have been widely employed in evaluating lethal and sublethal effects of petroleum on benthic animals, information about oil effects on benthic plants has been largely derived from field studies. These have covered habitats ranging from high-energy rocky shores to low-energy mud flats and salt marshes, and it is clear that magnitude and duration of impact vary according to the nature of the intertidal zone. In general, though, plants growing in the intertidal zone experience severe exposure during a spill.

Intertidal flora of exposed shores in Canadian waters is dominated by various species of bladder wracks (fucales). Both laboratory tests and field observations suggest that these are resistant to moderate levels of petroleum (Ganning and Billing, 1974; Ravanko, 1972; Notini, 1978), particularly in high energy situations where exposure is brief. This tolerance may be partially attributable to a mucilaginous coating to which oil

does not readily adhere (Nelson-Smith, 1972b). If oiling is particularly heavy or prolonged, however, extensive damage to populations may occur (Green et al., 1974; Thomas, 1978). Other macroalgal species appear to be more sensitive, being particularly susceptible to pigment bleaching and loss of turgor (Clark et al., 1973; Nelson-Smith, 1968b). Re-establishment of floral communities is usually rapid, particularly if oil is removed quickly by wave action, or if intertidal herbivores have been decimated by the oil (North et al., 1964).

Attached macroalgae have no intimate trophic relationship with the substrate and this tends to minimize their exposure to hydrocarbons accumulated in the substrate (Vandermeulen and Gordon, 1976).

Much attention has been paid to the effects of oil on salt marshes, not only because of their particular ecological significance, but also because such areas are characterized by low wave-energy and a finely divided, porous substratum, factors conducive to the persistence of hydrocarbons. Plants inhabiting salt marshes vary in their sensitivity to oil (Cowell et al., 1972). Annuals are generally more sensitive than perennials, which have extensive underground storage structures from which new growth can arise (Baker and Crapp, 1974; Hampson and Moul, 1978). The principal effects of the oil are destruction of foliage, impairment of root function, inhibition of stolon development and production of new roots. Unlike macroalgae, marine cryptogams have an intimate trophic relationship with the substratum; high levels of oil in the substrate usually result in high levels in the plants (Vandermeulen and Gordon, 1976). The physiological effects of petroleum upon marsh plants have been reviewed by Baker (1971b). There have been indications that both the magnitude of impact and the recovery rate vary according to the season of oiling (Baker, 1971e).

Baker (1970a, 1971a, 1973) concluded that moderate single-pollution incidents caused minor, short-term changes in temperate salt marsh vegetation, with few, if any, lasting effects. In contrast, successive or continuous low-level pollution by petroleum caused severe damage to the vegetation, resulting in erosion of the substratum. Often, an oil spill can give rise to repetitive applications of oil to a given area. Also, significant quantities of oil may become trapped in a marsh substratum, and subsequent gradual discharge may inhibit recolonization of the area (Hampson and Moul, 1978).

Lighter oil fractions appear to be particularly toxic, killing not only growing shoots but also the roots of some species (Baker, 1971a). Although weathered crude oil is generally less toxic to marsh plants than fresh oil under laboratory conditions (Baker,

1971a), in one field test, weathered oil had as great an impact on a marsh community as did fresh oil. This unanticipated result was attributed to the fact that more of the viscous weathered oil was trapped by the plants and incorporated into sediments, leading to chronic exposure at higher concentrations (Bender et al., 1977).

8.1.3 Uptake and Metabolism. Much attention has been devoted to the rate of penetration of petroleum hydrocarbons into marine organisms, and their subsequent fate. The studies can be grouped in several categories: uptake and depuration; metabolism and detoxification; effects of the hydrocarbons and metabolites on metabolic processes; and the potential food chain transfer of biologically resistant components. Marine benthic organisms have figured prominently in most of these studies.

Marine organisms absorb many petroleum hydrocarbons into their tissues rapidly. The extensive literature dealing with the uptake and depuration of hydrocarbons has recently been reviewed (Lee, 1977; Varanasi and Malins, 1977) for both laboratory exposures and animals collected in contaminated areas. Organisms accumulate hydrocarbons both by absorption from seawater and by ingestion with food. However, petroleum hydrocarbons bound to sediments are not readily absorbed by benthic detritus feeders (Anderson et al., 1977; Rossi, 1977; Roesijadi et al., 1978). There is evidence that the level accumulated depends to some degree on the lipid content of the animal (Stegeman and Teal, 1973). The hydrocarbon content of the tissues during exposure to oil represents the resultant of dynamic uptake and depuration processes (Lee, 1977). Most organisms eliminate (or depurate) hydrocarbons rapidly following transfer to clean seawater. Lee (1977) found that half-lives of several hydrocarbons in tissues of bivalves ranged from 2 to 7 days. Such initial rapid discharge of the bulk of foreign hydrocarbons appears to be characteristic of many species of marine benthic organisms, although a significant residue persists for extended periods (Clark and Finley, 1975; Stegeman, 1974). A characteristic two-phase loss curve is indicative of rapidly exchanging and stable hydrocarbon compartments within the organism (Stegeman and Teal, 1973). The rapidly-exchanging compartment contains cyclic saturated aromatic hydrocarbons (Ehrhardt and Heinemann, 1975; Neff et al., 1976). The precise location in the organism and the long-term physiological consequences of these biologically resistant hydrocarbons are at present a matter of conjecture.

Available information about biotransformations in tissues has been concisely reviewed (Malins, 1977; Varansi and Malins, 1977). This is a particularly active area of research and few firm generalizations can be drawn at this time. The principal areas of

investigation include: elucidation of the nature of enzyme systems responsible for transforming various classes of hydrocarbons into less toxic or more readily excretable compounds; determination of the occurrence of specific detoxification mechanisms among different taxonomic groups; determination of the types of hydrocarbon metabolites arising from the various biotransformation pathways; and examination of effects of various hydrocarbons and metabolites on a variety of cellular metabolic processes that underlie observed physiological effects.

8.1.4 Physiological Effects. Biological systems consist of different levels of organization ranging from subcellular to supra-specific, and oil effects may be expressed at several levels. There exists a complex hierarchy of causes and effects, commencing with subtle changes at subcellular levels, resulting in physiological dysfunctions that may culminate in significant alterations in either the structure or dynamics of an ecosystem. It is primarily these latter, large-scale manifestations that are of particular concern in evaluating the effects of oil spills. It is obvious that such changes reflect a summation of short- and long-term effects upon individual organisms. In order to understand ecological impacts of spilled oil, it is necessary to consider not only lethal toxicity, but also the many subtle sublethal effects, that in themselves may appear to have minimal significance.

8.1.5 Lethal Effects. Many short-term lethal toxicity tests have been carried out on benthic species, using many different types and fractions of crude oil. The available data has been concisely tabulated for taxonomic groups by Craddock (1977). An early generalization from such data is that much of the immediate toxicity is attributable to low-boiling aromatics (Ottway, 1971) and thus refined products are generally more toxic than crude oils and lighter crudes tend to be more toxic than heavier crudes.

Generalizations based on taxonomy have been less successful. Moore and Dwyer (1974) summarized toxic concentrations for eight groups of organisms. Flora and finfish were most resistant to oil, while benthic crustaceans and larval stages in general were most sensitive. The authors conceded that it was difficult to justify the groupings in view of the wide variability and uncertain significance of available data. Rice et al. (1976a) attempted a similar correlation for subarctic marine organisms. Finfish were most sensitive while holothurians and molluscs were most resistant. Crabs and shrimps were considered more sensitive than amphipods, isopods, mysids and barnacles. These authors also stated that predictions would not be reliable because of variability within

each group. Attempting to rigorously correlate lethal petroleum concentration and taxonomic position is not a particularly fruitful line of investigation.

Other attempts at formulating generalizations have focussed on global and local habitats and upon life history stages. It has been suggested that arctic and subarctic species may be more sensitive to petroleum than warm water species (Rice et al., 1977). This may be due to the fact that the hydrocarbons persist longer in colder water, resulting in increased exposure, rather than to any intrinsic differences in sensitivity. Rice et al. (1976b) concluded that subtidal invertebrates were generally more sensitive to petroleum than intertidal ones. In view of the variety of adaptations employed by intertidal species to cope with a naturally stressful habitat (Newell, 1970), this could well be a valid generalization. Another generalization that appears to be broadly applicable is that larval stages are more sensitive to petroleum than adults (Broderson et al., 1977; Lindén, 1976a; Moore et al., 1973), with a few significant exceptions (Rossi and Anderson, 1976). This particular aspect has been discussed in detail by Rice et al. (1977).

Tests for acute lethality are properly used for initial, rapid evaluations of toxicity questions, and they are not easily extended to predictions of ecological consequences of oil spills (Craddock, 1977). As in other kinds of pollution, the major ecological changes are likely to arise from biological dysfunctions occurring at sublethal concentrations.

8.1.6 Sublethal Effects. Crude oil and its derivatives influence a wide range of biochemical, physiological and behavioural processes in benthic organisms, and a prodigious amount of data supports the current view that sublethal effects are a threat to marine populations. Observed effects on various physiological processes have been tabulated by Wilson and Hunt (1975), and according to taxonomic groups by Johnson (1977).

Most biological processes are altered by oil exposure, provided the concentration is high enough, or the duration long enough. It is of little significance merely to demonstrate a biological response to oil exposure, however, and some important questions must be asked. Firstly, which responses are induced by oil concentrations that may occur widely in the habitat during an oil spill? Secondly, which of the observed effects are likely to have direct, ecologically significant consequences? Effects associated with an affirmative answer to the second question can be ones considered "critical", while those of direct consequence only to the individual organism can be considered subcritical effects.

8.1.7 Subcritical Effects. Respiratory metabolism has been widely used as a sensitive indicator of changes in physiological state during exposure to environmental stress. Results of studies dealing with effects of petroleum on metabolic rate suggest an underlying complexity in the response that defies generalization at present (Percy, 1977). This is hardly surprising in view of the broad range of potentially toxic compounds in crude oil and the array of metabolic components available to interact with them. Petroleum products have been shown to both stimulate (Gilfillan, 1973; Hargrave and Newcombe, 1973) and depress (Avolizi and Nuwayhid, 1974; Major, 1977; Percy, 1977) the metabolic rate of benthic invertebrates. Often, both responses can be induced in the same species by different concentrations of the same oil. It is probable that several biological and physical factors play a role determining both the direction and magnitude of the metabolic response. Although the ultimate consequences of modifications in metabolic rate are often uncertain, there can be little doubt that if the hydrocarbon stress is sufficiently great or prolonged, then critical physiological effects will ensue.

Studies on the effects of petroleum on photosynthesis have mostly involved phytoplankters. The few studies on benthic macrophytes have been reviewed by Johnson (1977). Effects vary from pronounced inhibition of photosynthesis to marked stimulation, depending upon the oil, the concentration, the duration of exposure and the species. Although alteration in photosynthesis occurs at concentrations that may occur in the immediate vicinity of an oil spill, it is difficult to evaluate the overall ecological significance in view of the conflicting data.

Small quantities of carcinogenic compounds are present in crude oils (Blumer, 1971). There is evidence that such compounds are responsible for inducing neoplastic growth and lesions in marine benthic organisms. Crabs (Albeaux-Fernet and Laur, 1970), bivalves (Yevich and Barszcz, 1976), and bryozoans (Powell et al., 1970), have all been reported to exhibit abnormal tissue growth when collected from areas severely contaminated by petroleum. Lesions and neoplastic growth occurred in several different tissues. In most cases, however, the evidence for a cause and effect relationship has been largely circumstantial. Attempts at inducing neoplastic growth by exposing organisms to petroleum products in the laboratory have been unsuccessful (Stainken, 1976; Yevich and Barszcz, 1977). Not enough information is available to properly assess the ecological consequences of these histological changes. However, indications are that the effects could be severe, particularly if gills and reproductive tissues were involved.

Neuromuscular effects have been noted in many benthic species following exposure to petroleum products. Frequently, this took the form of pronounced narcosis characterized by a reduction in muscular activity (Corner et al., 1968; Dicks, 1973; Sanborn and Malins, 1977; Stainken, 1976) or ciliary activity (Chipman and Galtsoff, 1949). Locomotory activity of crustaceans may be severely reduced during oil exposure (Percy and Mullin, 1975; Swedmark et al., 1971) or in contrast, hyperactivity may occur (Bean et al., 1974; Hargrave and Newcombe, 1973; Karinen and Rice, 1974); perhaps representing an escape response. Some benthic crustaceans exhibit loss of equilibrium, reflected in erratic swimming or crawling (Lindén, 1976a). Serious ecological consequences could ensue for species in which pursuit of prey or escape from predators was severely impaired.

Some of the neuromuscular effects may reflect alterations in structure and function of cellular membranes. Potential interactions between hydrocarbons and cell membranes have been discussed by Van Overbeek and Blondeau (1954) and Goldacre (1968). Regulation of osmotic and ionic balance of body fluids is dependent upon the integrity of biological membranes, but few such studies have been made for oil and benthic species. Studies of osmoregulation of shrimp and oysters showed significant but apparently transitory changes (Anderson and Anderson, 1976).

Chemoreceptor function is another membrane-related process that may be affected by petroleum hydrocarbons. Some behavioural disturbances that are outlined below may have their origin in impaired chemosensory structures. At present, the evidence is largely circumstantial for damage to chemoreceptors by petroleum (Atema et al., 1973; Kittredge et al., 1974).

8.1.8 Critical Effects. Growth may prove a useful indicator of pollution stress in benthic organisms. Disturbance of this process would seem to entail clear ecological consequences and probably reflects the cumulative impact of interacting physiological, biochemical or behavioral dysfunctions. The effects of petroleum on growth have been examined in a variety of benthic polychaetes, molluscs and crustaceans.

Growth of both larvae and juveniles of the polychaete Neanthes arenaceodentata, was markedly reduced during exposure to petroleum hydrocarbons (Rossi and Anderson, 1978). Phenol also inhibited the growth of larval polychaetes (Äkesson, 1975). Studies at spill sites to date, however, have failed to demonstrate significant effects on polychaete growth (George, 1970, 1971; Mohammad, 1974). Growth of bivalve molluscs may be impaired by heavy oiling (Dow, 1975; Thomas, 1978). Carbon flux is markedly reduced in clams in an area contaminated by fuel oil (Gilfillan et al., 1976).

This implies that less carbon is available for maintenance, growth, and reproduction. A similar reduction in carbon flux occurred in mussels exposed to crude oil in the laboratory (Gilfillan, 1975). Other species of bivalves appear to be more resistant. Growth of mussels was not altered following the Santa Barbara spill (Harger and Straughan, 1972); while mussels and abalones from the vicinity of a natural oil seep grew at rates comparable to those from unoiled areas (Straughan, 1976). Oyster growth was not affected by acute exposure to dispersed oil (Anderson, 1975), nor by chronic exposure under an oil slick (Mackin and Hopkins, 1961). Larval growth and development of oysters, however, may be impaired (Benijts and Versichele, 1975; Renzoni, 1973, 1975).

Benthic crustaceans vary in the degree to which their growth is impaired by exposure to petroleum in the laboratory. Chronic exposure to No. 2 fuel oil significantly reduced growth of the grass shrimp (Anderson, 1975; Tatem, 1977). Exposure to hydrocarbons also reduced growth of amphipods (Lindén 1976a), mud crabs (Laughlin et al., 1978) and barnacles (Corner et al., 1968). Some crustaceans are resistant to hydrocarbons and growth is unaffected, except at concentrations approaching the chronically lethal level (Caldwell et al., 1977; Cox and Anderson, 1973; Milovidova, 1974; Percy, 1978).

Growth and the molt cycle are closely associated processes in crustaceans and environmental stress affecting one can be expected to cause a corresponding change in the other. Lockwood (1967) and others have suggested that increased sensitivity to environmental stress during molting may be a general phenomenon among crustaceans. Several studies have demonstrated that benthic crustaceans are more sensitive to petroleum during molting than during the intermolt period (Karinen and Rice, 1974; Mecklenburg et al., 1977; Wells and Sprague, 1976). This could have serious consequences for species that migrate into shallow coastal waters to molt and reproduce (Karinen and Rice, 1974). Mecklenberg et al., (1977) speculate that the increased sensitivity is attributable to an increased permeability of the exoskeleton during molting which facilitates penetration of toxic compounds into the tissues. Other studies have demonstrated that sublethal exposure of larval stages of some benthic crustaceans can impair the rate of development by delaying, and in some cases completely inhibiting, the molting process (Caldwell et al., 1977; Katz, 1973; Wells 1972). The molting of several other species appears to be largely unaffected, or perhaps even slightly stimulated by exposure to petroleum (Mecklenburg et al., 1977; Neff et al., 1976; Percy, 1978).

Interference with reproductive processes of a species may clearly result in changes in population structure and community dynamics. Crude oil and a number of its fractions have been shown to affect most of the distinct phases of reproduction of several benthic organisms, the most sensitive phase varying with species. Atema et al. (1973) and others have suggested that low levels of petroleum hydrocarbons may impair mating in some marine organisms by interfering with chemotactic responses. Takahashi and Kittredge (1973) found that petroleum in extremely low concentrations abolishes the pheromone-induced mating stance of crabs. Oil exposure also inhibits the characteristic precopula stage of the amphipod Gammarus oceanicus (Lindén, 1976a).

In the case of organisms that release gametes into the water, petroleum hydrocarbons may interfere with fertilization and subsequent development of the egg (Nicol et al., 1977). Liberated spermatozoa of the rockweed, Fucus edentatus (Steele, 1977) and of several bivalves (Renzoni, 1973) are particularly sensitive to petroleum. In sea urchins, the fertilization process itself appears to be unaffected by the presence of oil (Allen, 1971; Lonning and Hagström, 1975a).

The embryonic differentiation of many species is susceptible to disruption by petroleum hydrocarbons. Cleavage in sea urchins is severely inhibited by a variety of petroleum products, with some of the heavier fractions being more toxic than lighter refined fractions (loc. cit.). In contrast, later embryonic-stage bivalves show little if any effect (Renzoni, 1973), although petroleum inhibits fertilization.

Significant reductions in fecundity occur in crabs (Tatem, 1977), polychaetes (Äkesson, 1975; Carr and Reish, 1977), and amphipods (Lindén, 1976a) exposed to hydrocarbons.

Reproductive disturbance in the field has been rarely demonstrated. Mussels contaminated during the West Falmouth oil spill were apparently sterilized (Blumer et al., 1970). Polychaetes suffered no detectable reproductive impairment (George, 1970), nor did sessile barnacles or limpets following the Santa Barbara spill, although the breeding rates of stalked barnacles and mussels from lower intertidal areas were reduced (Straughan, 1971). Reproduction appeared to be normal for molluscs and barnacles near natural oil seeps (Straughan, 1977). An unexpected increase in reproductive activity of meiofaunal copepods occurred in experimental beach plots treated with chronic low levels of crude oil (Feder et al., 1976). The reason for this increase was not established.

Disruption of normal behaviour patterns may be critical; erratic locomotion and lethargy from neuromuscular narcosis have already been mentioned. More complex

behaviour patterns, mediated by chemical messengers (pheromones) in the water also appear sensitive. Petroleum may remove the messenger compound from the water phase (Blumer et al., 1973), mimic or mask the messenger compound (Atema et al., 1973), or damage the chemoreceptor tissues themselves (Atema, 1977).

Few examples of behavioural disturbance have been demonstrated experimentally; those involving reproduction have already been discussed. The majority of examples involve interference with the ability to detect and respond to normal food by crustaceans (Atema, 1977; Atema and Stein, 1974; Blumer et al., 1973; Takahashi and Kittredge, 1973), echinoderms (Crapp, 1971a; Whittle and Blumer, 1970), and gastropod molluscs (Brown et al., 1974a; Eisler, 1975; Jacobson and Boylan, 1973). Laboratory testing leaves some uncertainty about the occurrence and significance of effects on reproduction and feeding under field conditions. Suggestive, but far from conclusive, are field observations of possible attraction of lobsters to spilled oil (Blumer, 1970) and the continuation of breeding coloration and postures in male fiddler crabs beyond the normal season (Wilson and Hunt, 1975). Other behavioural effects involving repulsion from oil-tainted sediments have also been reported both in the laboratory (Percy, 1977) and in the field (Atlas et al., 1978). These animal/sediment behavioural interactions need to be more fully investigated because of their potentially important influence on benthic recolonization following an oil spill.

8.2 The Biological Effects of Dispersants and Chemically Dispersed Oil

The highly toxic dispersants of the late 1960's were soon superceded by less toxic mixtures, and much of the information concerning biological effects is based on dispersants that are no longer considered suitable for field use (Corner et al., 1968; Perkins et al., 1973). Generalizations are difficult to make because a wide array of crude oil and dispersant combinations have been tested. It is clear that as dispersants become less toxic, primary consideration must again be given to adverse biological effects of oil itself. The critical problem is that chemically dispersed oil penetrates in greater quantities into a wider variety of habitats, and appears to be far more toxic than physically dispersed oil (Ganning and Billing, 1974; Griffith, 1972; Mills and Culley, 1972). This is generally attributed to the fact that soluble toxic compounds dissolve more rapidly, and finely dispersed oil interacts more intimately with organisms, resulting in longer exposure, because of increased stability.

It is generally assumed that chemical dispersion of spilled oil sets in motion a continuing, irreversible dilution process that effectively eliminates the likelihood of

significant chronic exposure of marine organisms. Although it is obvious that chemical dispersion of oil slicks increases the concentration in the water column and decreases the amount of oil reaching intertidal habitats, the potential effects on transport of oil to subtidal benthos is largely a matter of conjecture. Interacting physical and chemical factors could increase the concentration of dispersed petroleum transported to the substratum. The interaction of dispersants and dispersant/oil mixtures with different types of benthic substrates are poorly understood. Little is known about the action of dispersants in facilitating oil entry into the substratum or about effects upon persistence in the sediment. Dispersants absorbed on sediment particles may result in toxic effects on meiofauna and epifauna (Bleakley and Boaden, 1974; Wilson, 1968a). Bleakley and Boaden suggest that the recovery of meiofauna may be inhibited by the persistence of dispersant in the sediment. This aspect, although beyond the scope of this chapter, is an important element in the information required to make intelligent judgements about dispersant use.

8.2.1 Lethal Effects. A great deal of unpublished lethality data has accumulated, much of it for benthic species. Such screening for lethal toxicity is an essential first step in evaluation of new dispersants, but the following review will concentrate for the most part on the more relevant information for mixtures of dispersant with oil. Similarly, from the point of view of decision-making in relation to oil spills, there is a relatively low priority for such queries as the precise manner in which dispersants kill marine organisms, the uptake of components of the dispersants by marine organisms, and their bioaccumulation, metabolism, biotransformation and depuration.

In the majority of lethal toxicity studies, complete dispersant formulations have been tested. Kaim-Malka (1972) carried out tests on a variety of benthic crustaceans, however, using different classes of compounds present in dispersants, and was able to rank these according to levels of toxicity. This more analytical and comparative approach to toxicity testing might yield results having some predictive value as well as providing some insights into the nature of the biological effects.

Although there is ample evidence that the newer dispersants are essentially non-toxic, it must be emphasized that this rating is based solely on the results of short-term lethal bioassays (Canevari, 1971; McManus and Connell, 1972; Perkins et al., 1973; Sprague and Carson, 1970). Studies on sublethal or chronic effects of dispersants are few compared to the broad array of such studies carried out with petroleum, but it appears that dispersants may affect some of the same physiological processes discussed for oil.

8.2.2 Sublethal Effects. Lack of information concerning sublethal effects of dispersants and oil/dispersant mixtures on benthic organisms precludes any broad generalizations. Clearly, the deleterious effects summarized below are not common to all dispersants and the relevance of many physiological effects to field situations remains to be demonstrated.

Many dispersants have a rapid narcotic effect on marine organisms, usually reflected in decreased locomotory activity and general insensitivity to stimuli (Arthur, 1968; Hargrave and Newcombe, 1973; McManus and Connell, 1972). This may involve an impairment of the shell-closing ability of bivalves (Simpson, 1968; Swedmark, 1974) or the adhesive function of the foot in gastropods (Crapp, 1971a; Perkins, 1968). In some species an initial increase in locomotory activity, probably an escape response, precedes narcosis (Czyzewska, 1976; Sullivan, 1971; Swedmark et al., 1971). Extreme loss of equilibrium may occur in some mobile species (Mills and Culley, 1972). It is likely that many of these neuromuscular effects are attributable to disturbances in the structure and function of biological membranes (Goldacre, 1968; Hagström and Lonning, 1977).

Many dispersants seem to depress the respiration of marine benthic invertebrates (Avolizi and Nuwayhid, 1974; Hargrave and Newcombe, 1973; Percy, 1977). Corresponding reductions in rate have been reported for certain processes of intermediary metabolism (Chaplin, 1971). Exposure to oil/dispersant mixtures appears to cause more variable effects, presumably because of differences in the oils. Respiratory and photosynthetic metabolism of benthic macrophytes may be impaired by dispersants (Brown, 1972; Ganning and Billing, 1974; Lacaze, 1972-73), although in the latter study two of three dispersants, (Sefoil and Corexit 7664), had no effect on photosynthesis. In some plants, the effect of dispersants on primary production is exacerbated by increased "leakiness" of cell membranes, resulting in loss of photosynthetic products. Dispersants have not been implicated in the induction of neoplastic growth, but there is evidence that they may cause severe tissue damage, involving necrosis (Perkins, 1968), edema (Braaten et al., 1972), and disruption of cell membranes (Goldacre, 1968; Hagström and Lonning, 1977).

Examples of behavioural responses that have been shown to be influenced by dispersants are virtually non-existent. The few studies that have been done suggest the potential for a range of effects almost as extensive as that for crude oil. Both dispersant and oil/dispersant mixtures reduced the feeding activity of polychaetes in a field test (Levell, 1976), and burrowing activity of bivalves may also be impaired (Swedmark et al.,

1971). Both of these examples may, in fact, represent narcotic effects. Synthetic, non-ionic surfactants cause an escape response in molluscs, similar to that elicited by the steroid glycosides produced by predatory starfish. Prolonged exposure to low concentrations of surfactant, however, appears to fatigue molluscan chemoreceptors and they become more susceptible to attack (Mackie, 1970). There was some evidence that this occurred following the TORREY CANYON spill, according to the same author.

Reproduction of benthic organisms may be particularly sensitive to dispersants, although nothing is known about effects on initial reproductive behaviour. Successful fertilization of eggs is reduced, with little indication of the precise cause (Boney, 1970; Granmo, 1972; Granmo and Jørgenson, 1975; Lonning and Hagström, 1976; Renzoni, 1973). A partial explanation for gametes released into the water may be reduced motility or viability of sperm (Boney, 1970). Some dispersants, such as Corexit 8666, may retard the rate of fertilization without altering the final number of embryos produced (Lonning and Hagström, 1975a). The effects of oil/dispersant mixtures are in some instances more severe than effects of either substances alone (Lonning and Hagström, 1976). The fecundity of predatory gastropods can be severely reduced if either they or their prey species are exposed to dispersants, (Eisler, 1973). Detergents have been shown to prolong the maturation of polychaete eggs (Bellan et al., 1972). In one of the few pertinent field observations, it was found that the reproduction of polychaetes in areas contaminated by fuel oil was not detectably affected. In contrast, in nearby areas of shoreline treated with dispersant, surviving animals were sterilized and produced no gametes during the year that they were studied (George, 1970). This small amount of available evidence suggests that effects on reproduction are of potential ecological significance and warrant further investigation.

Information on growth is equally sparse. The more toxic first-generation dispersants affected growth of gastropods (Bryan, 1969; Perkins, 1970) and bivalve larvae (Hidu, 1965; Simpson, 1968). Limited information about some of the newer dispersants indicates minimal effects on growth of molluscs (Perkins et al., 1973) and benthic algae (Tokuda, 1977); except perhaps at very high concentrations.

8.3 Information Gaps

The foregoing clearly reveals that a great deal of information is available about the effects of oil upon marine benthic organisms, but coherent patterns are lacking. Most of the sublethal effects isolated are from laboratory studies, and their ecological relevance must be clearly established. Until this is convincingly done, the rationale for

engaging in more detailed laboratory studies will remain open to serious question. Laboratory experiments, no matter how carefully designed and executed, are generally inadequate as representations of processes occurring during an actual oil spill. Laboratory conditions are inherently stressful to marine organisms and this may exaggerate the biological effects of particular exposure conditions. Also, during laboratory exposures, organisms are prevented from actively avoiding high concentrations of oil as they may do in a field situation. Furthermore, natural weathering and dispersion processes are virtually impossible to duplicate routinely in the laboratory. The greatest difficulty is that exposure levels in a field situation vary continuously and erratically with both space and time. Thus, exposure levels in a spill situation are scarcely predictable, and indeed have seldom been adequately documented in such an occurrence. While constant level experiments in the laboratory might permit reasonable predictions of effects under fluctuating concentrations, the lack of predictability in the field makes such translation from laboratory to nature virtually impossible for pollution.

Sufficient information is now available concerning the general nature of many of the sublethal effects to permit the design of experiments suitable for examining their occurrence during accidental or experimental oil spills. Considerable discrimination is required in the selection of sublethal effects for further study -- priority should be given to physiological effects having direct and readily apparent ecological consequences such as impairment of growth, reproduction or behaviour. In particular, to understand recolonization and recovery processes, information is needed on effects of chronic exposure to contaminated sediment, especially information on behavioural responses of benthic species.

Sparse information on the effects of dispersants or oil/dispersant mixtures, compared to that for petroleum alone, makes it difficult to predict environmental consequences of using dispersants. Many new dispersants are considered non-toxic on the basis of acute lethality tests, but usually there is little information about possible sublethal effects. It would appear highly desirable to investigate the sublethal effects of dispersants and oil/dispersant mixtures.

In comparison with the intertidal zone, the subtidal habitat has been virtually ignored during impact studies of major oil spills. Despite the general assumption of lesser damage, observations from a few spills have indicated considerable impact on sublittoral benthics.

After the DONA MARIKA spill, large numbers of narcotized and dead animals were observed in subtidal areas (Baker, 1976a) and significant population changes in subtidal benthic species have been reported in the vicinity of other major oil spills (Cabioch et al., 1978). It is probable that many of the sublethal effects commonly occur among species inhabiting shallow sublittoral areas. Greater attention should be paid to documenting both short- and long-term biological changes in subtidal benthic habitats under field conditions. Such studies should be coordinated with investigations of processes influencing accumulation and residence times of petroleum hydrocarbons in subtidal sediments. There is also some uncertainty whether dispersants affect penetration of oil into substrates, and subsequent residence times.

The meiofauna of both intertidal and subtidal areas have been consistently neglected in investigations of accidental spills and in laboratory studies of biological effects. This is a serious knowledge gap in view of the tendency of oil to accumulate and persist for extended periods in the sediment. Feder et al. (1976) found that three species of meiobenthic copepods increased in both abundance and reproductive activity following oiling of beach plots, a result that has yet to be satisfactorily explained.

The composition, distribution and ecological significance of the meiofauna have been comprehensively reviewed by McIntyre (1969). This category of fauna includes both a permanent component (nematodes, copepods etc.) and a temporary component consisting of larval stages of many macrobenthic species. Thus destruction of meiofaunal elements could have both trophic and reproductive consequences for the benthic community.

In contrast to the situation for benthic animals, where there is a need for confirmation in the field of the many biological effects demonstrated in the laboratory, the opposite appears to be true in the case of benthic macrophytes. There is a need for studies to be carried out under controlled conditions in order to define the effects of petroleum and dispersants more precisely. This is true for both intertidal and subtidal seaweeds. Much of the available physiological and biochemical information is based on studies on phytotoxic oils and crop plants (Baker, 1971b).

Our knowledge of acute and chronic effects of petroleum upon salt marsh plants is more extensive, thanks largely to the field and laboratory studies carried out by the Orielton Research Unit in Great Britain. The widespread acceptance of the general principle that more damage may be done to contaminated salt marshes by attempting to clean them, than by permitting natural recovery, appears to preclude the need for

detailed studies on the effects of dispersants on marsh plants. The same reticence in the use of dispersants is not always apparent when rocky shores are heavily oiled. Therefore, the physiological effects on rockweeds and kelps of acute exposure to some of the more recent dispersants must be examined more rigorously.

Few laboratory studies and even fewer field studies have been carried out on the effects of oil on benthic organisms in the Arctic. Most of the previous comments concerning major data gaps are equally applicable to Arctic marine ecosystems. Many of the generalizations derived from work conducted in temperate seas will be applicable in arctic waters, with a few important exceptions. Reference has already been made to the difficult extrapolation from laboratory to the field. The problem is even more acute in polar regions, where the divergence between laboratory and habitat conditions is likely to be even more pronounced. Of even greater import is the fact that knowledge of the structure and dynamics of polar marine communities lags far behind that of other areas. Predicting ecological consequences of a particular effect on a given species is accordingly more difficult. The only remedy for this is more incisive studying of how arctic ecosystems function, rather than the limited inventories that are usual in northern environmental studies.

The epontic or under ice community of spring-time arctic sea ice may in some respects be considered an inverted benthos. Although it has been speculated that the impact of oil on this community would be severe, there is as yet little concrete evidence to support this view. Furthermore, the precise significance of this epontic assemblage in the overall dynamics of the Arctic marine ecosystem is still largely a matter of conjecture. It is unlikely that such a complex system can be duplicated satisfactorily in the laboratory; thus information about effects of oil can best be obtained from studies in the field.

Difficult logistics and adverse working conditions, coupled with the expected intense cleanup efforts, make it unlikely that accidental oil spills in arctic waters will provide a suitable opportunity for carrying out major studies of oil effects in the field. A potentially more fruitful approach (scientifically, if not politically) involves carrying out a well-planned multidisciplinary investigation of moderately-sized experimental spills at carefully selected sites in the Arctic.

8.4 Recommendations

Flexible, well-organized, contingency research programs should be formulated to test specific hypotheses on the impact of accidentally spilled oil on benthic

communities. Only in this way will it be possible to make maximum use of the scientific opportunities provided by oil spills.

In studies of accidental spills, more attention should be paid to short- and long-term effects on benthic species inhabiting subtidal areas. Petroleum and dispersant effects on the meiofauna in both intertidal and subtidal benthic habitats must be studied; both accidental and experimental oil spills could be effectively utilized.

Field studies are required to examine the role of dispersants in facilitating the transport of oil into the substrate, as well as their effects on the residence time of oil. Efforts should be made to substantiate the occurrence and relative significance under field conditions of potentially important sublethal effects that have thus far only been demonstrated in the laboratory.

The newer "non-toxic" dispersants that have been approved for use should be examined for adverse sublethal effects that may result from acute exposure to dispersant and oil/dispersant mixtures. In studies of sublethal effects of petroleum and dispersants, priority should be given to ecologically critical effects, namely those involving growth, reproduction or behaviour.

The behavioural responses of benthic infauna and epifauna to oil-and dispersant-contaminated sediments should be examined more closely in order to facilitate understanding of benthic recolonization processes.

Experimental spills are required to study the effects of spilled oil on the "epontic" or under-ice community that is a characteristic feature in the Arctic and subarctic areas.

Experimental spills are required to determine; a) the residence time of crude oil in intertidal and subtidal sediments in arctic areas, both in the presence and absence of dispersants, and b) the short- and long-term effects of oil and oil/dispersant mixtures on intertidal and subtidal benthic organisms.

9 BIRDS, OIL AND THE CANADIAN ENVIRONMENT

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Birds are the animals most at risk from oil spills. The first major kill of seabirds following an oil spill occurred as long ago as 1907. The schooner THOMAS W. LAWSON, the supertanker of its day, went aground on the Scilly Isles in the western English Channel, spilling 1 400 tonnes of oil. The seabird colonies in that area have never fully recovered. They and other Channel colonies were dealt a further blow 60 years later after the wreck of the tanker TORREY CANYON, when 84% of the Atlantic Puffins (Fratercula arctica) on Sept Iles in Brittany, died, and again in 1978 with the wreck of the AMOCO CADIZ. The first comparable Canadian incident was the wreck of the tanker ARROW, which occurred in Chedabucto Bay, Nova Scotia, in 1970. The seabird mortality caused by this, however, will probably be surpassed by that from the break-up of the KURDISTAN off Cape Breton in 1979. The English Channel experience is a portent of what can be expected in Canada from the inevitable spills which accompany Alaska tanker traffic along the West Coast, offshore oil exploitation in Arctic and Atlantic waters, and the opening of the Arctic to shipping (see reviews by Bourne, 1976; Holmes and Cronshaw, 1977; and the background bibliography of Vermeer and Vermeer, 1974).

Major incidents like these are the ones which get publicized, but in fact, oil pollution is chronic and there is a constant dribble of small spills. In the last six months of 1971, 28 offshore oil slicks, mostly of unknown origin, were reported off eastern Canada (Brown, 1973). These were not major spills, but then the size of a spill is no indication of the number of birds it may kill. The ARROW spilled 9 000 tonnes of Bunker 'C' and killed at least 7 100 birds; but a mere 27 tonnes or less leaked from the barge IRVING WHALE at the same time and killed at least 5 500 birds along the south coast of Newfoundland (Brown et al., 1973).

Oil-induced mortality of birds in Canadian waters is a serious problem of unknown dimensions. For several reasons, all mortality figures are gross underestimates. Many slicks, for instance, never reach land (20 of the 28 mentioned above did not do so), and in such cases one can only compare the slick's track with what is known of seabird distributions and guess at possible effects (Brown, 1973). The situation is only a little

better when dead, oiled birds are washed ashore. Here one can count corpses per kilometre, extrapolate to the length of oiled beach, and come up with some kind of estimate, but it will be a very incomplete one. Bird corpses sink, and perhaps only 20% of them ever come to land (Hope-Jones et al., 1970); the percentage must be smaller for eastern Canadian waters, where the prevailing winds tend to carry the corpses out into the Atlantic. Moreover, the species which do come ashore are not necessarily a representative sample of those oiled at sea (Powers and Rumage, 1978). Estimates are, in any case, biased towards the more easily patrolled sand and gravel beaches, as opposed to rocky shores. Finally, corpses may be hidden under cover or by snow, be indistinguishable from lumps of tar, or they may be removed by scavenging animals (Brown et al., 1973).

Canada borders on three oceans and the Great lakes, and there are vulnerable concentrations of aquatic birds in all of them. The seabird colonies, where the birds are most heavily concentrated, are in the Gulf of St. Lawrence, east Newfoundland, south-east Labrador, Hudson Strait, south east Baffin Island, north Baffin Bay, Lancaster Sound, and the Langara, Queen Charlotte and Scott Islands areas of British Columbia.

Concentrations of non-breeding seabirds are found in many of these areas, as well as in the Bay of Fundy; on the Newfoundland fishing banks; along the coasts of central Labrador and west Vancouver Island; and in Lakes Erie and St. Clair. More specific examples might include the spring and fall staging area for migrating Greater Snow Geese (Chen hyperborea), at Cap Tourmente in the St. Lawrence estuary, the swimming migration routes of Common and Thick-billed Murres (Uria lomvia) with their chicks from Lancaster Sound to Southwest Greenland and from Newfoundland and Hudson Strait to Labrador, and the concentrations of Red Phalaropes (Phalaropus fulicarius), and other seabirds in late summer along the offshore 'front' of the Labrador Current (based on Brown et al., 1975; and Vermeer and Vermeer, 1975).

The species most likely to be oiled are those which spend much time on the water, especially if they are divers and sit low in the water. In Canada those most at risk are alcids such as murres, puffins, and dovekies; diving ducks (e.g. eiders), loons, grebes, coots, cormorants, fulmars and shearwaters (Brown et al., 1973; Vermeer and Vermeer, 1975). Black-legged kittiwakes (Rissa tridactyla), pelagic gulls, and phalaropes, the only swimming shorebirds, would also be vulnerable. By contrast, the larger gulls spend much of their time on shore, and this reduces their chances of coming into contact with oil; the danger to most shorebirds would be indirect, through the damage which oil does to their feeding habitat.

9.1 The Effects of Oil on Birds

The initial effect of oil on a bird is to cause matting of the feathers and derangement of the feather barbules (Hartung, 1967), which in turn leads to the breakdown of waterproofing and insulation. The feathers of a light to moderately oiled Mallard (Anas platyrhynchos), absorb enough water to add 7-10% to the body weight (Holmes and Cronshaw, 1977). Flight, therefore, becomes more energy-consuming, and less efficient if the flight feathers are contaminated; swimming and diving are also hindered. This decreased mobility, makes the birds less able to collect the food needed to meet their increased energy requirements. An increasing spiral of debilitation begins which usually ends with the bird's death.

The breakdown of insulation brings cold air and water directly into contact with the skin. The heat loss of heavily oiled Mallard and Scaup (Aythya marila, Aythya affinis), may increase, respectively, to 1.7 and 2 times the normal figure; to meet this, basal heat production in both species increases by over 30% (McEwan and Koelink, 1973). As an indication of the severity of the breakdown, a heavily oiled Mallard may be under the same temperature stress at + 15°C as an unoiled bird is at -26°C, and from that point on, its survival is measured by the size of its energy reserves (Hartung, 1967). Oiled birds mobilise their fat first and then their muscular energy reserves, after which they die (Croxall, 1976). Autopsies show abnormal conditions of the lungs (haemorrhage, pneumonia), adrenals (cortical hyperplasia), pancreas (acinar atrophy), nasal salt gland (hypertrophy), gasterointestinal tract (swollen, hyperaemic areas; oily coating on the walls), kidneys (congestion; toxic nephrosis) and liver (fatty degeneration) (Austin-Smith, 1968; Croxall, 1976; Hartung and Hunt, 1966; Miller et al., 1978a, b; Powers and Rimage, 1978). White blood corpuscle numbers are reduced, increasing the chances of infection; this presumably explains why many oiled birds suffer from aspergillosis, a fungal disease of the lungs not directly related to the effects of oils.

There is still no evidence of the amount of oil required on the feathers to break down waterproofing and insulation. The often-quoted claim that 'a small spot on the belly is often sufficient to kill the murre' (Tuck, p. 192, 1961) requires confirmation. A lightly-oiled bird has a good chance of preening the oil off its feathers; Birkhead et al., (1973) found that oiled Common Murres (Uria aalge), Razorbills (Alca torda), and Great Black-backed Gulls (Larus marinus) at a Welsh colony cleaned themselves in about two weeks. Under the colder conditions of the Canadian environment it is likely that thermoregulation would break down long before this, especially if the bird was unable to

rest on land; but this creates another problem. Preening involves passing the feathers through the bill, and some oil will inevitably be swallowed; a mallard, relatively lightly oiled with 6 g of oil, ingested 2 g within 3 days (Hartung, 1965).

It has generally been assumed that swallowing oil gives rise to the gross abnormalities revealed by the autopsies, but this is by no means certain. It has been difficult to induce these conditions consistently by oral dosing. Thus Miller et al., (1978b) gave their young Herring Gulls (Larus argentatus) a single dose of only 0.2 mL of crude oil and found at autopsy 9 days later, significant hypertrophy of the nasal gland, liver, and in some cases, adrenals, as well as changes in intestinal tissue morphology. In contrast, Holmes and Cronshaw (1977) found no gross abnormalities in adult mallards which had been fed crude or No. 2 fuel oil in 90 consecutive daily doses of 5 mL (in one case, 10 mL). There was some adrenal hypertrophy but the lungs, liver and intestine all appeared healthy; there were only minor changes in intestinal morphology, and, in life, the ducks had maintained and even increased their body weight. It is possible that birds of different species and ages may vary in their susceptibility to ingested oil, just as species vary in ability to respond to rehabilitation and in reactions to temperature stress (Drinkwater et al., 1971; McEwan and Koelink, 1973). Holmes and Cronshaw suggest that the gross abnormalities are the terminal results of the birds' failure to cope with sudden environmental stress. Ingestion of oil apparently causes only minor physiological stress (of which adrenal hypertrophy is a symptom), but this makes the birds less able to cope with future stresses. Other experiments show that mallard will survive well on daily doses of crude oil, but such birds die off very rapidly when subjected to an abrupt drop in air temperature or an increase in the salinity of their drinking water.

Even quite small doses of oil can lead to physiological stressing - such as single doses of 0.5 mL or less in domesticated mallard and in young wild Herring Gulls and Black Guillemots (Cepphus grylle), and adult Leach's Storm-petrels (Oceanodroma leucorhoa), (Butler et al., 1979; Crocker et al., 1974, 1975; Miller et al., 1978a, b). These inhibit the transfer of water and sodium ions across the intestinal mucosa, and the extrarenal excretion of sodium ions through the nasal gland, putting the bird into a state of osmotic imbalance which eventually results in dehydration; the enlargement of the nasal gland is a partial counteraction to this. Weathered crude oil appears to be a more effective inhibitor than unweathered oil, and oil particles formed after the application of dispersants are also effective. Paradoxically, McEwan (1978) was unable to demonstrate enlargement of the nasal gland in orally dosed Glaucous-winged Gulls (Larus hyperboreus).

This, however, may be an artifact created by an overly-short interval between dosing and autopsying his birds, compared to that used by Miller et al., (1978b) in their experiments with the closely-related Herring Gull.

There are conflicting claims about whether or not oil ingestion inhibits nutrient transfer across the intestinal wall. Holmes and Cronshaw (1977) were unable to demonstrate this in mallard, nor could Gorman and Simms (1978) in young Herring Gulls from Scotland. On the other hand, Miller et al. (1978a, b) claim that nutrient transfer was inhibited by oil ingested by young Herring Gulls from New England and, presumably as a consequence of this, the birds' growth rates were less than those of controls. Gorman and Simms suggest that this cessation of growth was a natural function of age and not the result of the ingested oil. However, the reduction of growth in young Black Guillemots dosed with oil (Miller et al., 1978a) is not subject to this criticism. Clearly, further research is needed.

Another possible effect of oil needs to be explored. Crude oils with a high aromatic content have a narcotic effect on marine life (Southward, 1978). It is possible that the inhalation or ingestion of these fractions could act as a partial anaesthetic and hinder the birds' attempts to escape from the oil.

Finally, oil can have indirect effects which, in the long run, may be just as serious as those which have already been described. Mallard orally dosed with 2 g of lubricating oil stopped laying completely for two weeks (Hartung, 1965). Japanese Quail (Corturnix corturnix japonicus) orally dosed with Bunker 'C' laid fewer eggs than did controls during the four days following dosing, and the hatching success ('hatchability') of those which were laid was only about half the normal rate (Grau et al., 1977). Yolks of eggs laid during the first 24 hours after dosing were abnormal in structure and staining properties. Two crude oils and No. 2 fuel oil also affected yolk structure in quail, chickens and Canada Geese (Branta canadensis).

Oil on the surface of the eggs reduces hatchability in mallard, Common Eiders (Somateria mollissima); Louisiana Herons (Hydranassa tricolor); Laughing Gulls (Larus atricilla); and Sandwich Terns (Thalasseus sandvicensis) (Albers, 1977; Coon et al., 1979; Hartung, 1965; Szaro and Albers, 1977; White et al., 1979); the embryos die 2-3 days after the oil is applied. It takes as little as 0.005 mL of mineral oil, covering only 5% of the total surface, to cause a significant decline in the hatchability of mallard eggs. Under natural conditions, such small quanities could easily be transferred to the eggs from the feathers of the incubating parent; a wild, oiled Great Black-backed Gull managed to clean

itself, but the eggs it was incubating failed to hatch (Birkhead et al., 1973) and, in an experiment, mallard eggs died when the sitting female was smeared with 5 mL of mineral oil (Hartung, 1965).

The claim that oral doses of crude oil reduce the growth rates of young Herring Gulls and Black Guillemots has already been discussed (Miller et al., 1978a, b). The dosed guillemots remained significantly lighter than their controls for as long as 20 days after their single 0.2 mL doses. In nature, this amount of oil might well be present on a single contaminated fish. The result in this case was to leave the birds 20% underweight by the time of the normal fledging date.

Taken together, the three factors discussed above could have serious effects on the bird's breeding success. Many seabirds lay only a single egg; they will often replace it if it is lost, but will continue to incubate if the embryo dies in the shell. The consequence is a wasted breeding season. Moreover, the relative shortness of the Canadian summer, especially in the Arctic, means that the correct timing of breeding is crucial. Oil-induced delays in ovulation or growth rate could mean that the chick will leave the nest either late or underweight, and its chances of survival are reduced in either case. Loss of chicks is not too serious in a species like the mallard whose large clutch compensates for a naturally high mortality. But for species like murres with a low natural mortality, loss of chicks and wasted breeding seasons are serious matters. As it is, their populations are already declining in the face of other man-induced increases in mortality (Gaston and Nettleship, 1978).

9.2 Countermeasures

In the event of a spill, countermeasures such as chemical dispersants could be dangerous to seabirds, though there is at present no evidence of this from field studies (Bourne, 1976). Oral doses of the dispersant Ara-Chem did not inhibit the transfer of water or sodium ions in mallard ducklings (Crocker et al., 1975), but the experimental birds subsequently appeared weaker and less active than did the controls. Further research is needed. Dispersed oil particles did inhibit transfer, so dispersal in itself does not necessarily solve the problem. Moreover, an incompletely dispersed film of oil and dispersant would probably present much the same hazard as an unreduced oil slick (Croxall, 1976).

There has been some controversy about whether or not birds are positively attracted to oil slicks, perhaps mistaking them for calm areas such as convergence fronts where food is plentiful. Bourne (1968, 1976) has reviewed the evidence and concludes

that, if anything, birds avoid slicks; there is no indication that birds have ever been attracted to a major oil spill. They may, however, be attracted to minor ones; I have seen Northern Fulmars (Fulmarus glacialis) attracted to and sitting in a minor bilge leak from a ship off Labrador. But whether or not the attraction is positive, it should in theory, as Bourne (1976) suggests, be possible to discourage birds from visiting areas in which there are oil slicks. Ducks and shorebirds might be kept away from inshore areas by firing star- or cracker-shells. This would, however, be difficult out at sea. Of the three basic principles of bird dispersion - deterrence, counter-attraction and habitat modification (Brown, 1974) - the last is impracticable in a marine environment. Seabirds are usually unresponsive to deterrents; roosting gulls may initially disperse in response to an Av-Alarm acoustic system, but quickly habituate to it (Brown, unpublished); at sea, the system will disperse Red Phalaropes, but not Greater Shearwaters (Puffinus gravis). Attracting birds to baited areas away from oil spills would work only with such scavengers as gulls, fulmars and shearwaters, and would probably need to be done on a massive scale, perhaps involving a whole fishing fleet, if it is to be effective.

Unlike most marine organisms, oiled seabirds can be cleaned; rehabilitation techniques are described by Anon. (1972b), Naviaux (1972) and Smith (1975). However, such operations are long and costly; the oiled seabirds must be taken to a central cleaning station and then maintained there for several weeks after cleaning while they convalesce. (A Canadian Wildlife Service possession-permit is mandatory for this). Rehabilitation centres require much volunteer help, and this will only be available near large cities.

Surprisingly, a bird's chances of recovery are not necessarily related to the degree of oiling (Drinkwater et al., 1971; Holmes and Cronshaw, 1977). Ruddy Ducks (Oxyura jamaicensis) and grebes have the lowest chance, and mallard and canvasbacks (Aythya valisineria), the highest; mallard oiled in San Francisco bay in 1973 had a recovery rate of over 70%. But in most cases -especially in remote coastal areas - by the time an oiled bird is found and is weak enough to be caught, it is too far gone to be rehabilitated; humane despatch is the kindest treatment. Even under the most favourable circumstances, rehabilitation is basically a sop to conscience rather than a panacea -a last resort when all other countermeasures have failed.

9.3 Summary

Although the wrecks of the ARROW in 1970 and the KURDISTAN in 1979 have been the only major oil spills in Canadian waters so far, such incidents are bound to be repeated, especially along the Alaska tanker route by the West Coast, and as con-

sequences of the exploitation of offshore oil in Atlantic Canada and the increase in shipping in the Arctic. Pollution by minor spills is chronic and largely unnoticed, yet these are probably just as hazardous as the few well-publicized incidents. Diving birds such as the alcids, murres, puffins, dovekies diving ducks, eiders, loons, grebes, coots, cormorants and also fulmars, shearwaters and phalaropes are the most vulnerable species. The most vulnerable areas are in the waters adjacent to breeding colonies and feeding areas offshore when birds are locally concentrated, in the Pacific, Atlantic and Arctic, and areas which support a large waterfowl population, such as Lakes Erie and St. Clair, and Cap Tourmente in the St. Lawrence estuary.

Birds are most vulnerable to oil. Its immediate effect on them is to break down the feather structure which provides waterproofing and insulation. Temperature stress, and the direct and indirect effects of oil ingestion, then follow and are usually fatal. Oil may also act indirectly by affecting the laying rate and hatchability of eggs and the growth rate of chicks - sublethal effects which in the long-term would reduce the chances of survival of both individual birds and breeding populations.

Oiled birds can be rehabilitated, but only with difficulty and expense; humane despatch is usually the kindest treatment. Rehabilitation should be thought of only as a last resort, to be used only when all other countermeasures fail.

9.4 Recommendations

The following topics need further investigation:

a) methods for estimating bird mortality caused by oil spills which do not come ashore;

b) the nature of the pathological effects of oil ingestion, and their short- and long-term influences on the mortality of oiled birds;

c) the minimal amount of oil on a bird's feathers needed to trigger temperature stress;

d) the possible role of narcosis following exposure to high aromatic oil fractions in hindering birds from escaping a slick; and

e) the possible toxic effects of chemical dispersants on birds.

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10 THE EFFECTS OF OIL ON MARINE MAMMALS

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Oil pollution incidents involving marine mammals are few, and the published records are scant. Most observations are unquantified and sketchy accounts of oiled mammals, from pollution of unknown sources. Obituary reports which implicate oil exist for California sea lions (Zalophus californianus) and northern elephant seals (Mirounga angustirostris) on San Miguel Island, California (Nelson-Smith, 1970); harp seals (Pagophilus groenlandicus) in the Gulf of St. Lawrence (Warner, 1969); unidentified seals in Chedabucto Bay, Nova Scotia (Anon., 1970, Vol. 2, p.46-47); and grey seals (Halichoerus grypus) along the coast of Wales (Davis and Anderson, 1976; Nature in Wales, 1970). Seldom, however, is the supportive evidence adequate to unequivocably link any deaths with the presence of oil. There are also casual sightings of oil-fouled seals in the Canadian Arctic (Müller-Willie, 1974); the Gulf of Alaska (Morris, 1970; Hess and Trobaugh, 1970); the Antarctic (Lillie, 1954); the English Channel area (Spooner, 1967), the southern Irish Sea (Davis, 1949; Davis and Anderson, 1976); and Dutch coastal waters (Van Haaften, 1973).

Recently, oiling experiments using living sea mammals or their fresh pelts reveal problems of irritation, thermoregulation and metabolism after contact with and ingestion of oil. Damage by oiling of pinnipeds (earless seals) has been investigated by Kooyman et al. (1976, 1977); Øritsland (1975); Smith and Geraci (1975); Geraci and Smith (1976); Englehardt et al. (1977) and Davis and Anderson (1976). Similar studies have been attempted on sea otters (Enhydra lutris) (Williams, 1978) and muskrats (Ondatra zibethica) (McEwan et al., 1974).

In the following discussion, a distinction is drawn between sensitive and vulnerable. A sea mammal is sensitive to oil contact and ingestion if, for any morphological or physiological reason, it is easily harmed by or intolerant of the pollutant. Examples of sensitive species are the sea otter, wholly insulated by a rather delicate fur coat, and the ringed seal (Phoca hispida), when seasonally stressed by a month-long moult. At a population level, some marine mammals are vulnerable to oil spills since their life

histories (specialized foods habits, colonial breeding behaviour, preferred travel routes and traditional haunts) are likely to ensure contact with accidental and chronic oil pollution. White whales (Delphinapterus leucas) which congregate and probably calve in a few selected Arctic embayments, or polar bears (Ursus maritimus) which retire to popular late summer retreats to await freeze-up, fall into this vulnerable category.

With a meagre knowledge of the physical susceptibility and behavioural responses to oil pollution in whales, seals, polar bears and other sea mammals, we must recognize those habits and habitats which are essential to their survival and propagation. In the event of a major oil spill such as an offshore drilling blowout or tanker grounding, protection of critical feeding and breeding sites, if known, must be attempted in order to ensure the eventual recovery of a population suffering natural or man-caused mortality. For example, there is little value in the ambitious and expensive rehabilitation (capture, cleaning and release) of oiled seals and polar bears if persistent or irreparable damage occurs in such key habitats (Stirling et al., 1976).

10.1 The Morphological Effects of Oil Contact

10.1.1 External Openings and Appendages. Heavy fouling by oil can stick flippers to the body and plug, or at least irritate, body openings of some marine mammals. Warner (1969) reported that harp seals in the Gulf of St. Lawrence, completely covered with a viscous, tar-like oil, had difficulty swimming, and probably died of exhaustion. On San Miguel Island, near the site of the Santa Barbara Channel spill, the San Diego Union (Anon., 1969) reported that elephant seal pups were encrusted with a coating of oil, sand, pebbles and sticks; this caused them difficulties in opening their eyes. At the same time, Newsweek magazine reported the stranding of a dolphin, with an oil-clogged blowhole and lung haemorrhage (Geraci and Smith, 1977). In Chedabucto Bay, Nova Scotia, a small number of seals may have died of suffocation when their nose and mouth openings were plugged with Bunker "C" fuel oil by the ARROW grounding (Anon., 1970). Davis and Anderson (1976) presumed that two grey seal pups, encased in oil, were unable to swim, and subsequently drowned when washed off an oil-polluted beach of Skomer Island, West Wales. Other oiled pups had difficulty in shedding their natal fur which was bound together by the thick, tarry oil.

Geraci and Smith (1976) determined experimentally that fresh, Norman Wells crude oil of relatively low viscosity and high volatility caused no mechanical damage to ringed seals during short exposures. In fact, when the oiled seals were released into clean water, their hair coats showed scarcely any visible evidence of oil immersion after 4 days.

However, these seals did suffer severe but transient eye irritation. Within minutes of immersion in a holding tank, covered with a 1-cm thick layer of oil, the seals showed signs of blinking, squinting, excessive lacrimation, severe conjunctivitis (inflammation of the mucous membrane connecting the inner eyelid and eyeball) and swollen nictitating membranes. In one case, corneal erosions and ulcers were evident after the 24-hour exposure period. This damage was due, in part, to the evaporation of the oil's pungent, volatile fractions. The seals' eye irritations generally disappeared within 20 hours of removal from oil-covered waters. These researchers, and others (Nelson-Smith, 1970), stress that longer exposures and prolonged contact with volatile oil could cause permanent eye disorders, and even blindness. Whales, porpoises and dolphins could be as sensitive as seals (Geraci and Smith, 1977).

Oil-fouling from a floating slick may interfere with the baleen feeding apparatus of whales. Right whales (Family Balaenidae), sometimes skim the surface waters for planktonic food, with their straining baleen plates partially exposed (Watkins and Schevill, 1976).

10.1.2 Insulation. In simplest terms, the acute damage of direct oil fouling of sea mammals depends on their means of unregulated insulation, whether fur, fur and blubber, or blubber alone. Kooyman et al. (1976) categorized seals, sea lions, walruses (Odobenus rosmarus) and sea otters into three major groups based on thermal conductance (heat flow per unit area) of their blubber-free pelts. However, all sea mammals, including polar bears and cetaceans, fall into one of these categories. 'Bare-skinned' whales, dolphins, porpoises and walruses are probably the least sensitive to oil contact, in terms of thermoregulation. Their primary barrier to heat-loss is a thick skin and/or a layer of subcutaneous fat or blubber. The thermal conductance of flensed blubber is similar to that of asbestos (Scholander et al., 1950a), although blood circulation through living blubber reduces this insulative value (Hart and Irving, 1959). Due to complete or near-nakedness of cetaceans and walruses, oil cannot damage their body insulation. It is unknown whether oil fouling affects their regulated thermoregulatory mechanisms, such as peripheral blood circulation and superficial tissue cooling.

In contrast, sea otters and Alaska fur seals (Callorhinus ursinus) rely primarily, if not wholly, on a well-groomed, mostly waterproof fur coat which traps an insulative layer of warmed, stagnant air against their skin - similar to the SCUBA diver's dry suit (Morrison et al., 1974). Unfortunately, oil can easily matt, clump or disarrange this fur, resulting in loss of waterproofing and buoyancy, and causing chilling, hypothermia,

exhaustion and death (Kenyon, 1975; Kooyman et al., 1977; Williams, 1978). The oiled pelt of a sea-otter pup or a juvenile fur seal is twice as conductive to heat flow as that of unoiled pelts (Kooyman et al., 1977). Experimental oiling of live muskrats - whose fur may be somewhat comparable to that of sea otters - showed that thermal conductance of fur increased by 122% when heavily coated with crude oil. McEwan et al. (1974) found that oiled muskrats remained out of water for up to one month, during which period they preened excessively. They concluded that "it is doubtful that muskrats exposed to moderate quantities of oil could meet their high energy requirements in view of their dependence on water, both for feeding activities and a place for refuge". This conclusion probably applies to sea otters as well.

Polar bears, phocid (earless) seals, sea lions and all hair-bearing sea mammals keep warm both by body coverings (guard hairs and/or woolly underfur) and subcutaneous blubber (Bryden, 1964; Irving and Hart, 1957; Scholander et al., 1950; Frisch et al., 1974). Their sensitivity to direct oiling is highly variable, depending on the fur's significance to total unregulated insulation. Usually, the fur's insulative value is relatively small for animals wetted to the skin, but this differs greatly between species, or changes with age, general health and season (Kooyman et al., 1976, 1977; Geraci and Smith, 1976; Hart and Irving, 1957; Grisch et al., 1974). The insulative value of fur is determined by the thermal conductance of the stagnant medium - either water or air - between the hairs, not the properties of individual hair. One centimetre of trapped water provides about the same insulation as 2 to 3 cm of blubber (Frisch et al., 1974). For example, polar bears with long winter fur and 3 cm of underlying blubber gain about 11% of their total unregulated insulation in water from the fur's entrapped layer of warmed water of up to 15 mm thick (Frisch et al., 1974). In comparison, the shorter fur of the harp seal, possessing the same amount of fat, maintains a 2 mm stagnant-water layer which contributes only 2% insulation. It is not surprising that a mild oiling of adult seal or sea lion pelts does not significantly alter their thermal conductance during water immersion (Kooyman et al., 1977).

Fur assumes greater insulative value in air, especially for seals and polar bears exposed to Canadian Arctic winds and sub-zero temperatures. In turn, the risk of oil contamination may increase for some species. Unwetted fur acts as a wind barrier and provides a thin blanket of still air (Hart and Irving, 1959). This additional insulation assumes significance, for example, during ringed seals' spring moult and obligatory haulout (Geraci and Smith, 1976; Øritsland, 1975). Fresh, low-viscosity oil, such as Norman Wells

crude, does not disrupt the hair's structure in short-haired pinnipeds such as the ringed seal, nor does it significantly alter its insulating values at varying wind speeds (Øritsland, 1975). A heavy crude or weathered Bunker "C" oil may be more damaging (Geraci and Smith, 1976). Any coating of a dark oil does, however, increase radiation transmittance of light-coloured pelage and, ultimately, this can affect solar heating of the skin (Øritsland, 1975). The biological and ecological significance to hauled-out seals is unknown.

Newborns of some phocids, such as the harp and ringed seal, are temporarily covered with very little blubber and thick, white lanugo - an excellent fur protection against skin cooling by wind, until sufficient blubber grows and homeothermy stabilizes in the first weeks of life (Øritsland and Ronald, 1973). Oil fouling of these sensitive 'white coats' through pollution of their undersnow birth lairs, or by direct contact with their contaminated mothers, could cause chilling and hypothermia. Harp seal pups aged 2 to 4 weeks, possess lanugo but also 2 to 5 cm of blubber - enough by itself to insulate against heat loss when totally coated with Norman Wells crude oil (Geraci and Smith, 1976).

10.2 The Physiological Effects of Oil Contact and Ingestion

10.2.1 Metabolism and Body Temperature. Oil-fouling can cause an elevated metabolic rate for aquatic mammals which rely wholly on fur as insulation. Oiled muskrats exhibited metabolic rates of 20% above normal, three days after contact (McEwan et al., 1974). A light oiling of fur seals (60-100 mL of crude oil over 30-40% of the pelage) caused a compensatory 50% increase in heat production (Kooyman et al., 1976). The investigators concluded that "the added burden of oil ... makes it questionable that oiled (fur) seals could sustain themselves long if they remained in cold water. In due course, they would probably experience exhaustion, hypothermia and death". Post mortems of oiled sea otters also list hypothermia as a possible cause of death (Kenyon, 1975). How long an oiled sea mammal can sustain its normal body core temperature by increased metabolic heat production depends on the extent of fouling, exposure to cold air and water, and the animal's general fitness. When naturally stressed, for example, by poor feeding conditions, annual hair moult, or heavy parasite infection, death can be rapidly triggered by oil pollution (Geraci and Smith, 1976; Kenyon, 1975; Williams, 1978). The metabolism of ringed and grey seals and probably other sea mammals insulated primarily by blubber, appears relatively unaffected by direct oil contact, at least in the short-term.

Oiled marine mammals sometimes lose weight because of increased metabolism, and sometimes cessation of feeding occurs. Heavily-oiled muskrats lost 11% of body

weight within 3 days of an experimental immersion in crude oil, and up to one-quarter body-weight in 3 weeks (McEwan et al., 1974). Peak weights of accidentally-oiled grey seal pups were significantly lower than those of unoiled pups. Average growth rates (1.03 kg/day) were also less by about 28 percent (Davis and Anderson, 1976), although these findings may, in part, reflect the disturbance caused by veterinarians and scientists. Smaller pups often have poorer chance of survival.

10.2.2 Uptake and Excretion Pathways. Sea mammals can accidentally inhale volatile oil fractions, and ingest oil when grooming, suckling or eating. Brief contact of ringed seals with floating crude oil causes rapid oil absorption and accumulation in body fluids and tissues. Some oil is initially swallowed by the seals in their thrashing and churning struggles to escape oiling; however, the main uptake pathways are probably through the skin or respiratory surfaces, or both (Smith and Geraci, 1975). Inhalation of volatile, toxic benzene fractions occurs when the oil slick is fresh and unweathered (Geraci and Smith 1976; Engelhardt et al., 1977). Measurable levels of oil metabolites were found in the blubber, brain, muscle, kidney and liver of ringed seals immersed in oil-covered waters for 24 hours. The highest levels were evident in the urine and bile (39 and 58 μg/g, respectively, after 2 days' oiling), suggesting that the kidney and liver are the principle sites of oil detoxification and excretion (Englehardt et al., 1977). Some oiled seals had mild kidney lesions, probably related to "an unsuccessful attempt to concentrate and/or excrete the oil or its metabolites via the urinary system" (Smith and Geraci, 1975). Longer exposures to oil would probably increase tissue accumulations, particularly the blubber (Kooyman et al., 1976). It is not known at what concentration detoxification by the liver or excretion by the kidney might fail.

Ringed seals that were experimentally fed oil-contaminated fish are acutely stressed. Ingested benzene and napthalene are quickly absorbed into the blood through the gut (Englehardt, 1978). However, Geraci and Smith (1976) concluded that these adult ringed seals were not irreversibly harmed by ingesting 5 mL/day of Norman Wells crude for 5 days; this was also true for harp seal pups which were fed even higher doses of up to 75 mL. Although these amounts of oil probably represent the upper limit of what a seal might ingest from live, oil-tainted prey, there was only transient release of liver enzyme into the plasma. This was considered negligible damage but, nonetheless, an indication of liver-poisoning substance in the body fluids (Geraci and Smith, 1976).

10.3 Behavioural Responses to Oil Pollution

Migrating grey whales probably detected and avoided surface slicks of oil offshore of the Santa Barbara Channel blowout (Butler et al., 1974). It remains speculative whether or not other species of whales, seals, sea lions and other sea mammals recognize oil slicks as a potential threat and immediately swim or dive away from contaminated waters. Japanese poachers have used gasoline and kerosene to repel otters from rocky shores into the sea; these petroleum products are repugnant to the otters' keen sense of smell (Barabash-Nikiforov et al., 1947). In contrast, Williams (1978) observed that captive sea otters did not avoid oil-covered waters, even after repeated exposures, or when given the choice of clean water; these findings may reflect the experimental stress of captivity and confinement.

Davis and Anderson (1976) surmised that grey seals contacted floating oil at sea off southwest Wales, or encountered thick accumulations of oil in their coastal breeding caves and on nearby beaches. Pups become oiled directly from stranded oil, and indirectly through physical contact with their mothers. The cows could locate their pups, whether oiled or un-oiled, by smell. However, oil ingestion during suckling, and cessation of nursing, are potential risks if cow seals are oil-fouled (Geraci and Smith, 1976). Female ringed seals may abandon helpless, oiled pups or risk their death by removing them from contaminated birth lairs (Geraci and Smith, 1976).

Schweinsburg et al. (1977) speculate that polar bears, annually deprived of seal prey during the arctic summer, could scavenge oiled seabird carcasses washed up on beaches, with unknown consequences.

Oil slicks in offshore leads of Arctic pack ice may delay or prevent bowhead and white whale migrations in the southern Beaufort Sea. Entrapment in growing sea ice or ultimately arrival at calving locales in the Mackenzie estuary could result in death and poor calf survival, respectively (Fraker et al., 1978).

10.4 The Effects of Chemical Dispersants and Dispersed Oil

Chemical dispersants serve as 'shampoo' detergents, sometimes used experimentally to remove crude oil from sea mammal pelts. Unfortunately, such cleaning attempts seldom restore the oiled pelt to its original condition. Although detergents such as Polycomplex A-11 (also a commercial oil dispersant) remove crude oil without permanent damage to the fur of sea otters, natural skin oils are also removed and the fur's water repellency is lost (Williams, 1978). Kooyman et al., (1976) conclude that any agent

(including chemical dispersants) which increases the wetability of the fur of, for example, sea otters and fur seals, will increase the thermal conductance of the pelt. Unless grooming quickly repairs this damage, cold water leaking through the fur and against the skin can cause fatal chilling. Excessive grooming can also scratch away large amounts of underfur, a further complication in restoring body insulation (McEwan et al., 1974).

Based on such scanty information, oil dispersant chemicals are themselves a physical threat to some fur-insulated sea mammals. Nonetheless, dispersion of large oil slicks is probably a useful countermeasure tool, assuming that both the floating oil and the applied chemical are effectively diffused into the water column. The risks of direct fouling and of inhalation toxicity when swimming at the sea surface would be reduced, especially in cold icy situations where natural weathering and evaporation of oil slicks is slow.

10.5 Problems of Oil-related Research on Sea Mammals

Oil-related research using live sea mammals often requires difficult capture logistics and expensive holding facilities. Public endearment of many species usually labels oiling experiments as inhumane and unnecessary. Some animals such as sea otters are rare or endangered. Baleen whales and other large cetaceans are probably too large for captivity experiments. Researchers who manage to conduct tests on live mammals are often hampered by biased results, in part a function of captivity stresses and small sample sizes (Geraci and Smith, 1976; McEwan et al., 1974). Nonetheless, it is argued that laboratory tests using pieces of oiled fur pelts cannot reveal the adaptive responses of living animals. For example, an oil-fouled pinniped may haul-out and groom, roll in the snow, shiver and elevate its body metabolism, or shift its peripheral blood circulation to compensate for chilling, and so on. Whether or not such responses are successful depends on the species characteristics, the individual's general health, age or sex, nature of the oil, length of exposure and season of the year - to name but a few factors.

Almost every person - scientist, politician and general public alike, agrees that research effort and funds should be expended immediately following major oil spills in Canada's marine waters. Careful behavioural observations of oiled mammals and thorough post-mortems of dead mammals provide useful information. Such 'after the event' studies can lead to controversial interpretations, for example, the Santa Barbara spill debate on sea lion and seal deaths by Nelson-Smith (1970), Brownell and LeBoeuf (1971), and LeBeouf (1971), but more often generate better impact assessments and pose more precise

questions for further study. Post-spill studies of oiled grey seals in west Wales waters illustrate such benefits (Davis and Anderson, 1976; Cowell, 1979). Sadly, in the past, most spill-of-opportunity investigations are slow to respond, poorly organized and under-funded.

A general plea for continued research on sea mammal population dynamics, (reproduction and feeding biology) is appropriate at this point. Oil may act like a trigger for some pinnipeds which are already weakened by harsh vagaries of nature (heavy ice, poor food supply, parasitism or normal life functions). Without such background understanding, critical places and periods of animals' life cycles remain uncertain; likewise, the seriousness of local or widespread oil pollution defies speculation. As aforementioned, moulting ringed seals in expected weakened physiological state may rapidly succumb to oil slick exposure, albeit brief (Geraci and Smith, 1976). Pregnant, nursing, and mating grey seals driven by group behaviour to pre-selected beaches, may not avoid shore-stranded oil (Cowell, 1979).

Studies of population dynamics also aid in separating naturally induced changes from those of man-caused accidents. In the absence of such monitoring studies, marine industrial activities such as offshore oil and gas development may be unfairly blamed for changes in numbers, distribution and productivity that may be occurring because of natural factors (Stirling et al., 1976).

Obviously, a seal is not always the same seal, nor is oil always the same when addressing the effects of oil spills on sea mammals. We will always be left to best guesses and extrapolation, using limited experimental data on unrelated species (for example, muskrats and even seabirds) and post-spill observations from marine regions outside Canada.

10.6 Recommended Research

For any future laboratory/field experiments and post spill studies, research priorities should reflect the oil sensitivities of the individual animal and, more importantly, the species' vulnerability at the population level. Sea mammals which rely on unregulated insulation (hair/fur and blubber, hair/fur alone) are probably very sensitive to oil fouling, whether swimming or at rest. If large numbers of such mammals congregate to feed or breed in shallow, coastal waters and shorelines where oil also accumulates and persists, the oil threat is worsened. Ringed seals (particularly the pups), polar bears, northern fur seals, and sea otters fall into these categories. With this in mind, the following research is judged as important:

1. Effects of different oils (crude, bunker, refined), weathered and fresh, on thermal conductance of pelts in air and water. Seasonal and age differences in pelage under various ambient air/water temperatures should be tested. Species commonly found in Canada's coastal waters should be chosen.
2. Effects of dispersant/oil mixtures and chemical dispersant alone on cetaceans such as beluga (adhersion to skin), and pinnipeds and polar bears (disruption of body insulation, loss of natural hair waxes and oils).
3. Chronic effects of crude oil on target organs (kidney, liver) and external openings, particularly eyes, of pinnipeds exposed to prolonged oil contact. Naturally-stressed animals (moulting, nursing, starving) should be considered as test animals.

10.7 Summary and Conclusions

Sea mammals may or may not avoid a floating oil slick or oil-stranded beach, depending on the spill's timing and extent. Even if they do recognize oil as a threat, avoidance by swimming and diving is not always possible. Behavioural stimuli (nursing of pups, mating) may overwhelm avoidance reactions.

Contact fouling by heavy or weathered oil can cause sticking of appendages and plugged body openings of pinnipeds. Soiling and evaporation by light crude also irritates eyes, nostrils and other mucous membranes of seals.

Oil fouling of seals, otters and other fur/hair insulated mammals can cause chilling and hypothermia, loss of buoyancy, elevated metabolism, slowed growth rates, cessation of feeding and associated weight losses, increased solar heating of skin, and death.

Pinnipeds can accidentally ingest oil when grooming, suckling or eating. Uptake of toxic hydrocarbon fractions into the tissues, blood and other body fluids is rapid, and constitutes an acute but probably reversible stress. Since the liver and kidney are probably the principle sites of detoxification and excretion, prolonged exposure to oil would cause more serious pathological damage, such as lesions.

Chemical dispersants are damaging wetting-agents which remove natural skin oils and destroy the fur's water repellency. This is particularly dangerous to sea mammals insulated and/or buoyed to a large degree by their body covering (polar bears, sea otters, fur seals). However, assuming chemical dispersants are thoroughly dissipated into the

water, along with the target oil slick, this countermeasure tool can reduce the risk of acute oil fouling and toxic fume inhalation.

All research opportunities involving oiled sea mammals in the event of oil-tanker and subsea blowout accidents must be thoroughly investigated, with adequate funding, particularly in light of inherent difficulties in oil experimentation using live sea mammals.

11 COMMUNITIES AND ECOSYSTEMS

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This chapter will review work on the effects of oil and dispersants on natural communities and their non-living surroundings. Other chapters cover work on specific groups of organisms.

11.1 The Effects of Oil

Much of the literature arising from projects specifically designed to describe the effects of oil on marine communities and ecosystems is recent. This is partly because most such studies are long-term and also because suitable techniques are new and controversial (Mann and Clark, 1978). Useful information has also accumulated incidentally during other studies; few of them are Canadian but results from spills in arctic and temperate areas are considered to be pertinent.

Fortunately, much of the material on the effects of oil on communities and ecosystems has been summarized in reviews. These cover various aspects such as shores (Addy et al., 1976; Baker, 1971c, 1976a, c; Crapp, 1971b; Nelson-Smith, 1968a, 1972; Owens, 1977; Thomas, 1973); salt marshes (Baker, 1971a, 1971b, 1971f, 1976a, b); algae (Vandermeulen and Ahern, 1976); plant physiology (Baker, 1971b); animal behaviour (Dicks, 1976); general (Butler et al., 1974; Michael, 1977; Kerr, 1977); and specific spills (Clark et al., 1973, 1978; Duerden, 1975; Leppäkoski, 1973; Michael et al., 1975; Thomas, 1973; Nicol, 1976; Sanders, 1978; Southward and Southward, 1978).

The magnitude and persistence of ecological effects on shoreline ecosystems depends on the amount of oil retained in the habitat. Disappearance rates vary with the type of oil, being generally rapid for volatile fractions, intermediate for crude oils and slow for residuals (Addy et al., 1976; Cretney et al., 1978; Keiser et al., 1978; Thomas, 1973, 1977). The effect is greatly modified by climate, however, being slow in colder areas and negligible under ice. A further important factor is the exposure to sea and wind of the spill site or contaminated shoreline, since exposed locations favour rapid weathering (Mackie et al., 1978b; Owens, 1977a, 1978; Thomas, 1973, 1977). Rates of

disappearance of oil mixed with sediment vary with sediment type, oxygenation and exposure conditions (Hampson and Moul, 1978; Owens, 1978; Teal et al., 1978; Thomas, 1973). Anaerobic sediments retard biodegradation processes.

Despite their critical importance to oiled ecosystem recovery, quantitative measurements of oil remaining at contaminated sites are rare (Clark et al., 1978; Colwell et al., 1978; Hampson and Moul, 1978; Thomas 1977). Small quantities of residual oils or heavy fractions of crude oils, however, will remain in temperate intertidal and benthic environments for many years (Colwell et al., 1978; Hampson and Moul, 1978; Keiser et al., 1978; Southward and Southward, 1978; Thomas, 1977; Vandermeulen and Gordon, 1976). Even relatively light fractions will remain indefinitely in anaerobic sediments (Hampson and Moul, 1978; Teal et al., 1978; Thomas, 1977).

11.1.1 Open Sea. The initial ecological effects of an oil spill in the open sea depend on many factors. All or much of a large spill may disappear, particularly if oil or water temperatures are high (Mackie et al., 1978b). Ecological effects have not been investigated in situ in the open sea but experimental work suggests that planktonic ecosystems may be affected. Phytoplankton vary in their responses to oil depending on the species, and the type and concentration of oil (Mironov, 1967; Nuzzi, 1973; Shiels et al., 1973; Vandermeulen and Ahern, 1976). Inevitably, there are changes in species composition and abundance patterns, an unusually extreme example being the promotion of single-species blooms (Nicol, 1976). Many species show increased photosynthesis at very low concentrations in the laboratory (Gordon and Prouse, 1972; Shiels et al., 1973; Vandermeulen and Ahern, 1976). At higher oil concentrations there is retardation of photosynthesis, growth, and reproduction (Mironov, 1970; Shiels et al., 1973; Vandermeulen and Ahern, 1976).

Similar general results have been found with zooplankton communities. Many crustaceans show alteration of the moult cycle as well as reproductive patterns and growth characteristics, in oil-polluted waters (Butler et al., 1974; Corner and Harris, 1976; Percy and Mullin, 1975; Wells, 1972, 1976; Whittle and Mackie, 1976). It is known that oil particles become incorporated in the food of filtering species. While much is egested or excreted, part may pass through the food web, although the ecological effects of this are unknown and may not be significant (Butler et al., 1974; Conover, 1971). The effects of oil in nature are difficult to evaluate with all plankton communities because of

the rapidly changing composition of the oil with age. The relevance of laboratory work to field conditions remains unknown because of this, and the lack of field study.

Few data are available on the effects of oil on fish communities. Limited mortalities are frequently recorded at spills, particulary at spills of lighter oils (Butler et al., 1974; Gooding, 1971; Mironov, 1970; Thomas, 1973), and some fish may avoid contaminated areas. Evidence suggests that in sufficient concentrations, oil affects the development of fish eggs, resulting in reduced hatch and abnormal larvae (Mironov, 1967, 1969a, 1970). Circumstantial evidence suggest that species composition and diversity of the stock may change in an oil spill area (Nicol, 1976).

11.1.2 Benthic Communities. Some of the oil in the water column is inevitably transferred to the benthic system, both mechanically and in food webs. Studies on subtidal benthic communities in oil spill areas have documented the incorporation of oil into sediments and demonstrated broad ecological effects (Hampson and Moul, 1978; Leppäkoski and Lindstrom, 1978; Michael et al., 1975; Sanders, 1978, Sanders et al., 1972). Extensive early mortalities have been observed with light oil, and in all situations, long-term effects involving changes in diversity and variability of oiled communities have occurred. Oiled sites have shown increases in opportunistic species as compared to clean locations. These studies show a slow return to normal conditions over a period of several years following a spill (Leppäkoski and Lindstrom, 1978; Michael et al., 1975; Sanders, 1978).

11.1.3 Shoreline Biota. Whereas there is little evidence that oil at sea has catastrophic effects on ecosystems, shores are often devastated. Effects vary with the type and quantity of oil and with its degree of weathering. Large quantities of any oil released close to shore will have severe effects. Light oils and fractions cause immediate heavy mortalities, (Addy et al., 1976; Crapp, 1971b; Hampson and Moul, 1978); however, these weather rapidly and residues are much less toxic, at least on a short-term basis. Where either weathered crude or fresh residual oils, such as Bunker "C", go ashore in quantity, smothering may cause extensive mortalities (Baker, 1976b; Crapp, 1971b; Nelson-Smith, 1972a; Smith, 1968; Thomas, 1973). Heavy oil adhering to intertidal algae causes tearing away during wave action (Crapp, 1971b; Ganning and Billing, 1974; Nelson-Smith, 1972a; Thomas, 1973). These early and obvious effects decline rapidly, although re-oiling or remobilisation of stranded oil causes local re-occurrences. In salt marshes, initial oiling may kill annuals and aerial portions of perennials (Addy et al., 1976; Baker, 1971b, 1976b;

Crapp, 1971b; Nelson-Smith, 1972a; Thomas, 1973). On muddy shores, oil concentrates in burrow mouths of buried fauna. These may die, or evacuate the burrow, to succumb on the surface or be eaten by predators (Nelson-Smith, 1972a; Thomas, 1973).

Following these early changes, shore ecosystems show, over a period of several years, other effects resulting from the toxicity of remaining oil, alteration of the environment, or ecological imbalances caused by initial or later effects (Clark et al., 1973; Notini and Hagström, 1974; Southward and Southward, 1978; Thomas, 1973). Since there are still demonstrable effects from the TORREY CANYON spill in 1967 and the ARROW disaster in 1970, these alterations may be of extended duration.

The effect of oil on intertidal algal communities has received particular attention. A wide range of effects have been recorded, although in general, the shore algae are quite resistant to oil pollution. In the worst cases, usually involving light oils, extensive mortalities have occurred, while in other cases, a wide variety of algae has become bleached and lost fronds. Interference with normal photosynthesis, growth and reproduction has been demonstrated in many cases of moderate oiling, whereas in very light oiling there have been records of enhancement of growth (Addy et al., 1976; Baker, 1976b; Boney and Corner, 1959; Boney, 1974; Clark et al., 1973; Ganning and Billing, 1974; Leppäkoski, 1973; Mironov and Tsymbal 1975; Nelson-Smith, 1968a; Steele, 1977). Where community changes have been followed for long periods, it has been found that the high intertidal species are hardest hit and sometimes eradicated. The upper limits of the zones occupied by upper-shore algae are lowered, narrowing the total zone occupied, and normal distribution is not re-established until the oil disappears (Thomas, 1973, 1977). This field evidence, along with experimental results, suggests that algae are unable to settle and survive in the presence of oil (Mironov and Tsymbal, 1975; Thomas 1973). Lichens in the splash zone are reportedly resistant to oil but show reduced photosynthesis in severe cases (Brown, 1972).

Recorded effects on intertidal animals are just as varied as those on plants. Severe oil pollution often causes either extensive mortality or narcosis so that animals lose adhesion, to be carried away or consumed by predators (Addy et al., 1976; Baker, 1976; Crapp, 1971b; Nelson-Smith, 1972a; Notini and Hagström, 1974). In other cases, relatively little effect on most faunal species has been observed even with heavy oiling (Baker, 1976b; Clark et al., 1973; Crapp, 1971b; Thomas, 1973). It is curious that barnacles are badly affected in some cases and apparently totally unaffected in others.

Chronic oiling or re-oiling produces more severe effects than a single spill and most of the fauna is eliminated (Addy et al., 1976; Baker, 1976; Nelson-Smith, 1972a).

Evidence is accumulating that disturbances to intertidal communities cause ecological imbalances and subsequent cyclical phenomena that may take years to subside (Addy et al., 1976; Baker, 1976b; Clark et al., 1978; Hampson and Moul, 1978; Nelson-Smith, 1972a; Southward and Southward, 1978; Straughan, 1975; Thomas, 1978). Typically, oiling or oil removal has serious effects on communities of herbivores, and their disappearance promotes unusually heavy algal growths, followed by abundant herbivores, etc. The net results are relatively large community differences between oiled and unoiled systems, many years after initial pollution (Southward and Southward, 1978; Thomas, 1978).

In salt marshes, too, effects following the initial oiling mortalities may persist for many years. Partial mortalities of dominant grasses continue (Thomas, 1973, 1977), but with declining oil, grasses return to vigorous growth (Addy et al., 1976; Baker, 1971a, 1971d, 1976; Nelson-Smith, 1972; Thomas, 1973, 1977). However, with successive spillages, or in chronic cases, mortality is often complete (Addy et al., 1976; Baker, 1976b; Hampson and Moul, 1978; Thomas, 1973). In such cases, disappearance of grasses may cause accelerated erosion and habitat degradation (Hampson and Moul, 1978).

On sheltered mud or sand flats below marshes, communities of infauna may also show continued slow mortalities while oil remains (Thomas, 1973, 1977), and evidence is accumulating that normal growth processes in molluscs may be upset (Gilfillan and Vandermeulen, 1978; Thomas, 1978).

11.2 Dispersants and Dispersed Oil

Evidence available to date suggests that offshore slicks and spills cause less extensive ecological damage than those in confined waters or those impinging on shorelines. Unfortunately it is not yet clear whether this is a valid conclusion or one biased by lack of critical observations on the effects of oil in the open sea. The offshore use of dispersants, however, does aid the process of dilution of oil into a large volume of water, which lessens the total effect at sea and reduces the chances of oil reaching shores or protected bays and lagoons.

In contrast to this situation, the use of dispersants for the cleanup of shorelines or very sheltered and shallow bodies of water such as lagoons, generally results in more extensive ecological disturbance than the oil alone.

If, as described above, the effects of oil on communities and ecosystems are complex and often conflicting, the situation with regard to dispersants is even more confusing. With them, we face an array of products of widely varying toxicity, and an even wider gulf between laboratory and natural situations. Toxicity tests of dispersants without oil can guide the selection of appropriate ones, but such tests are not applicable to the field because there, the dispersant is always in combination with oil. Even laboratory assays with emulsified oils are difficult to apply because they are generally at constant concentration, whereas concentrations in the field vary widely. As is the case with oil, long-term studies are few and far between. Nevertheless, the body of available literature does contain valuable observations and data.

The behaviour of dispersants or emulsified oil at sea naturally involves the entire depth to which surface water mixes. As a result, emulsifiers and emulsified oil affect larger volumes of water than oil alone, but at much lower concentrations. Emulsification may also result in an increased transfer of oil to the sea bed (Nelson-Smith, 1970). These consequences may alter the main site affected by the oil and spread the effect over a much larger area. Ecological consequences may thereby be reduced or go unnoticed.

11.2.1 Open Sea. In an open sea situation, dispersants and dispersed oil are present in the plankton community. Results and observations on plankton vary; observations showing extensive mortalities are rare but moderately toxic effects seem general. Dispersants at concentrations expected in surface waters are toxic to general plankton and larvae (Anon., MS 1974; Shelton, 1971; Smith, 1968) and their emulsifying action on oils increases the uptake of oil in food chains (Anon., MS 1974). Very low concentrations have negligible effects and low concentrations with added nutrients may enhance growth and reproduction of phytoplankton and bacteria (Gatellier et al., 1973).

The effects of dispersants on fish in nature are not well known but several studies have shown that emulsified oil harms gill tissues and their functioning (Culbertson and Scott, 1968; Mironov, 1970). In open waters, fish may avoid waters containing emulsifiers and oils, but in some shallow-water ecosystems, fish inhabiting crevices etc. may be killed (Nelson-Smith, 1968a).

11.2.2 Shoreline Biota. As with straight oil pollution, it is on the shore that the greatest impact of detergents and emulsified oil is seen. The reasons are several; at sea these materials dilute or disperse rapidly, while on shore they are essentially undiluted

and may pool in depressions and crevices. The intertidal zone is regularly exposed by tides and thus amenable to direct study; overdoses or accidental dispersant spills on shores impinge directly on ecosystems.

As with oil, effects vary with shore communities involved. Observations show varied effects on dominant rocky-shore algae. The species most common in temperate waters, Ascophyllum nodosum, Fucus vesiculosus and F. spiralis seem resistant to dispersants (Crapp, 1969; Nelson-Smith, 1968b). Others among the brown algae (e.g. F. serratus) and red and green algae, are very susceptible to damage and die at high concentrations (Cullinane et al., 1975; Gatellier et al., 1973; Hackett and Wait, 1969; Nelson-Smith, 1968b; Spooner, 1967). Intertidal lichens, notably resistant to oil, are very seriously affected by dispersants (Brown, 1971; Lacaze, 1972-73; Ranwell, 1968; Spooner, 1967). Laboratory experiments show that intertidal algae are ten times more sensitive to dispersants than to oil, in terms of respiratory effects (Ganning and Billing, 1974).

Accounts of the effects of dispersants on hard-shore animal communities show very similar results. Most of the common browsing and filter-feeding molluscs are very susceptible to dispersants, being either killed or narcotized so that they become susceptible to predation or wave action (Addy et al., 1976; Anon., MS 1974; Baker, 1976a, b; Bellamy et al., 1967; Cowell, 1971; Crapp, 1969; 1971b; Cullinane et al., 1975; Hackett and Wait, 1969; Leppäkoski, 1973; Nelson-Smith, 1968b; Spooner, 1967, 1971). Other invertebrates such as crustacea show similar effects (Nelson-Smith, 1968a). Damage is reduced if dispersants are greatly diluted but in this state they are ineffective for shore cleaning (Baker, 1971a). Inevitably, these devastating effects on intertidal herbivore communities have large ecological effects. Algae return quickly to treated areas and grow rapidly in the absence of grazing (Crapp, 1969; Nelson-Smith, 1968a, 1968b; Smith, 1968; Southward and Southward, 1978). Subsequently, grazers return in unusually high numbers and cyclic imbalances set in, taking many years to die down (Southward and Southward, 1978).

Dispersants are often spilled on terrestrial plant communities on cliffs and along shorelines. There, all species die, seeds are killed and the ready penetration of detergent into soils ensures long-term effects (Frost, 1974; Spray et al., 1974).

In salt marshes, concentrated dispersants cause virtually complete mortalities of natural communities (Baker, 1971a, 1976a, b; Cowell, 1971). Additionally, dispersant treatment results in greater penetration of oils which have long-term toxic effects and remain almost unchanged for years in anaerobic sediments (Baker, 1976a, b).

11.3 Conclusions Concerning Dispersant Use

It is evident that we know little about the effects of oil slicks, naturally or artificially emulsified oil, or dispersants in the open sea. This is mainly because the study of the open sea pelagic ecosystem in situ, is very difficult and expensive, and laboratory experiments under constant conditions can never duplicate and only broadly approximate the real situation. Nevertheless, oils, dispersants and combinations of the two, have been shown to cause adverse effects on many pelagic organisms, except when exceedingly diluted. A further involvement of oil droplets is their incorporation into food chains, where their effects are largely unknown. Since many decisions on oil spill cleanup methods include an assumption that oil at sea is relatively harmless, more emphasis should be placed on determining the effects of oils and dispersants at low concentrations in the open sea. This is especially evident now that long-term effects on intertidal and shallow water communities are being demonstrated many years after a spill, when oil remains only in exceedingly small amounts.

At sea, oil tends to disappear rapidly, but if it comes ashore it will concentrate there through the mechanical action of waves. Even though weathering may reduce volume and short-term toxicity, residues are likely to remain for years, except for spills of very light fractions. Dispersants or emulsifiers applied to shores will reach biota in a concentrated state since they must be virtually undiluted to effect useful cleaning. It is not surprising then, that the effects of a spill alone, or combined with cleanup attempts, are usually catastrophic to shore communities. Any large spill coming ashore will result in immediate heavy mortalities caused by toxicity, smothering or mechanical effects. Until recently, few really long-term studies of affected communities have been carried out. Those that have been published, however, show broad and long-term ecological effects on a wide variety of animals and plants. Changes in community structure have occurred in all cases studied, covering a wide variety of locations, oils and climates. For example, molluscan growth patterns change and seaweeds may not settle and grow normally for years. The reasons for these long-term effects remain unknown and almost unstudied, but laboratory experiments strongly suggest that basic metabolic processes are affected even at very low concentrations. These aspects clearly need more study.

There has been much criticism of both laboratory and field study methods and the difficulty of applying laboratory results to nature is widely acknowledged. Pollution

situations, however, rarely offer the conditions required for closely controlled experiments. It seems preferable to gain as much information as possible in as practical a way as possible; rather than reduce our efforts because methods are poor. The literature clearly shows that much of our useful data concerning the effects of oil and dispersants on marine communities and ecosystems, has come from careful ecological observation rather than from controlled experiments.

At present, the attitude toward funding long-term studies is very negative; this must change if we are to gain sound understanding on which to base oil spill cleanup technology. Much could be gained, too, from the careful before-and-after study of deliberate, controlled spills.

11.4 Recommendations

At present, ecologists seem to be in substantial agreement about the best course of action to be taken following a spill. This is based on the following general conclusions: 1) oil, emulsified oil, or dispersant, causes less ecological damage in an open-sea situation than on shores or in shallow lagoons; 2) oil dispersed in the open sea by mechanical or chemical means dissipates rapidly, thereby reducing its potential for ecological harm; 3) on shorelines, oil seems less harmful than dispersant, especially in sedimentary locations; and 4) on shores, mechanical cleanup has generally been less damaging than cleanup with dispersants (Anon., MS 1974; Baker, 1976b; Crapp, 1969; Gatellier et al., 1973; Leppäkoski, 1973; Nelson-Smith, 1968a, 1970; Thomas, 1973, 1977). It would, therefore, be logical that every attempt should be made to stop oil reaching shores, and that if mechanical methods such as booms are ineffective, dispersants should be used. If oil reaches shore, it would seem best to leave it for natural weathering if possible. In any case, it could be hazardous to use dispersants in salt marshes or on muddy shores. In such locations it could increase toxic effects and facilitate penetration of sediments where weathering and natural degradation would be exceedingly slow (Baker, 1971a, 1976a, b; Cowell, 1971). In oiled marshes, if cleanup must be carried out, the cutting and burning of oiled vegetation may be less harmful. On rocky shores, the quickest recovery occurs if oil is left alone, except for very thick deposits which can be mechanically removed. If social pressures dictate cleaning, mechanical methods are considered less harmful than dispersants, although these chemical aids may be used very carefully provided they are of low toxicity (Anon., MS 1974; Baker, 1976b; Cowell, 1971; Leppäkoski, 1973).

11.5 Summary and Recommendations for Study

More attention to the ecological effects of oils and dispersants in the open sea is needed. On shorelines, ecologists must concentrate on long-term follow-up of the effects on organisms and communities. An effort should be made to make laboratory studies more applicable to natural systems. Carefully controlled experimental oil spills under a wide variety of conditions would aid both the study of effects and cleanup techniques.

11.6 Action

Every effort should be made to contain oil spilled at sea by mechanical means. If oil on the open sea cannot be contained it could be treated with dispersants to aid dilution and to avoid its being driven ashore. Oil on shorelines should be removed mechanically if it is thick or on recreational shores, or left to weather naturally if it is thin. It seems generally undesirable to use detergents for cleaning shores.

12 ANALYTICAL CHEMISTRY

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Petroleum is a complex mixture of hydrocarbons representing several classes of compounds, the most important of these being alkanes, cycloalkanes, and aromatics (Gruse and Stevens, 1960). These classes are not sharply divided, as the aromatic compounds often contain alkane substituents and many of the ring structures are mixed aromatics and cycloalkanes. In addition, petroleum contains small quantities of compounds with hetero-atoms; oxygen, sulphur, nitrogen, phosphorus and also trace amounts of metals; vanadium, nickel which may significantly affect the analytical procedures, as well as the refining processes and the various uses of petroleum products.

No single compound that is unique to petroleum is present in sufficient quantity to act as a "tag" or marker for petroleum for monitoring purposes.

Analysis of such mixtures is always a difficult task, and the petroleum industry carries on a continuous search for new methods of physical testing and chemical analysis. The analysis of petroleum hydrocarbons in environmental samples (water, sediment, soil, biological tissue) often presents additional problems: low oil concentrations; interference from biological compounds; and changes of oil composition produced by environmental exposure. The most important of the latter changes is the evaporative loss of the more volatile petroleum components during exposure, sampling and sample preparation, and analysis.

Petroleum analysis in environmental samples has received much attention during the last ten years. The initial emphasis, and probably the greatest effort, was directed to the development of "fingerprinting" methods for the identification of oil spill

sources. To date, in spite of all the techniques investigated, no one technique has been accepted as a standard method (GESAMP, 1976). The present trend is toward multi-parameter analysis, utilizing two or more independent techniques such as gas chromatography with flame ionization and flame photometric detectors, mass spectrometry, infrared, ultraviolet and fluorescence spectra, column chromatography and metal analyses. Reviews on this subject have been published by Gruenfeld (1973) and Bentz (1976).

In oil spill studies, a large number of samples are analyzed for the presence and concentration of petroleum hydrocarbons; this necessitates simple and rapid techniques. The most common procedure is spectrophotometry of water, sediment or tissue extracts in solvents such as hexane, cyclohexane or carbon tetrachloride. Gordon and Keizer (1974a) are among the workers who have used fluorescence spectrometry; others have based their oil analyses on infrared absorbances (Brown et al., 1974).

In the last few years an increasing emphasis has been put on the development of analytical methods used in the studies of specific pathways, biotransformation and bioaccumulation processes of petroleum hydrocarbons in various marine, freshwater and terrestrial ecosystems. The techniques used in these instances are usually more complex and time-consuming than those employed in general oil spill surveys (Youngblood et al., 1971; Zitko and Carson, 1970; Wong et al., 1976). A common goal of such pathway studies is the identificaiton and determination of hydrocarbon classes which may be responsible for specific effects on the ecosystem, or which may be consumed or produced by chemical and biological transformations.

The remainder of this review is a brief description of present practices of analysis for petroleum and dispersants in environmental samples, particularly for oil spill monitoring and in fate and effect studies.

12.1 Sampling and Pretreatment

Oil source identification is usually based on the analysis of bulk oil samples skimmed off the water surface or scraped off contaminated shore materials. Sampling problems have been discussed by Gordon and Keizer (1974b), and recommended procedures for the collection, identification, and handling of such samples have been reviewed by Lieberman (1973).

In oil spill monitoring and in fate and effect studies, samples of water, sediment and biological material are collected by the same methods which are used in the

sampling of other environemntal contaminants. The problem of analyzing low concentrations of oil in environmental samples is compounded by the fact that most analytical methods are sensitive only to specific compounds or compound classes, which are present in the sample in much lower concentrations than that of the total oil. This requires a larger sample than might be indicated by the concentration of the oil. As an example, the determination of ppb concentrations of oil with a sensitive method, such as fluorescence spectrometry, requires about a one litre water sample or a 50 to 100 g sample of sediment or biological material. Gas chromatographic analysis for specific compounds might require 20 to 100 times more in a sample.

Prior to the extraction of water samples, a special dilemma may be posed by the need to pre-filter the water. Some of the studies included in this survey have reported filtration or centrifuging of the water samples prior to extraction (Wong et al., 1976); some investigators extracted unfiltered water samples and reported the results as "dissolved and dispersed oil" (Levy and Walton, 1973). Some uncertainty may be present here: while suspended organic and inorganic matter may interfere with the analysis of unfiltered samples, filtration may also create problems by removing adsorbed or colloidally-dispersed hydrocarbons. The resolution of this problem, especially at very low hydrocarbon concentrations, may require the analysis of extracts from both filtered and unfiltered water samples.

12.2 Solvent Extraction

With a few exceptions (direct GC injection of bulk oil samples, purging of water samples for dissolved volatile hydrocarbons), most presently employed methods of analysis rely on the concentration and transfer of the petroleum hydrocarbons from the environmental sample to a selected solvent. The solvent is chosen for its effectiveness in hydrocarbon recovery from the sample, for ease of its separation from the sample, and for its compatibility with the analytical method used. As an example, benzene is an effective solvent, but it interferes with UV and fluorescence detection methods. One way of circumventing this problem is to use an effective extracting solvent, such as benzene or methylene chloride, followed by the evaporation of the solvent, and to take up the extract in hexane or cyclohexane (Gordon and Keizer, 1974a).

12.3 Analysis of "Total Oil"

The most commonly used methods employ infrared or fluorescence spectrometry on the hydrocarbon extracts from environmental samples (Brown et al., 1974; Gordon and Keizer, 1974a). These methods are calibrated against a reference oil (crude oil or a petroleum product) which is suspected or is known to be the source of the oil in the environmental samples. This produces comparable results as long as the environmental sample has the same composition as the reference oil. Because of their different sensitivities to aromatic and non-aromatic petroleum components, these methods may consistently under-report or over-report total oil concentrations where the oil composition in the environmental sample is different from that of the reference oil. In spite of this uncertainty, the relative simplicity of total oil analyses makes them the choice methods in oil spill monitoring that involves large numbers of samples.

12.4 Compound Class Analysis

The known biases of some analytical techniques have been used successfully in studies seeking certain types of information. While the GC technique will "see" only those petroleum components volatile enough to pass through the chromatographic column, it has been widely used to demonstrate the disappearance of normal paraffins during bacterial degradation (e.g. Farrington, 1976). Infrared spectra are quite sensitive to the appearance of carbonyl compounds in aging oil samples, while UV and fluorescence methods are very useful in detecting and determining aromatic and polyaromatic petroleum components in biological tissue (Zitko, 1975).

One form of class analysis consists of synchronous scanning of both excitation and emission wavelengths in fluorescent spectroscopy, with a wave length difference of about 30 nm (Wakeham, 1977). The emission peak heights at 280, 320, 360 and 400-480 nm are a measure of the relative amounts of 1-, 2-, 3-, and higher-ring aromatic hydrocarbons. The spectra may thus indicate changes in the composition of the aromatic fraction of the oil produced by evaporation or biodegradation processes. To use this technique, full understanding of the theoretical background is essential.

An increasing number of studies (Warner, 1976; Zitko, 1975; Paradis and Ackman, 1975; Nagy et al., in prep.) have reported the use of column chromatography for the separation of alkanes, aromatic and polar compounds in environmental petroleum

samples. This technique is more time-consuming than total oil analysis, but it gives more information on how various types of oil components behave in the environment.

Column chromatography is also useful for dealing with extracts of biological samples, to remove bio-organic materials in the extracts before analysis of hydrocarbons. As an example, Youngblood and co-workers (1971) have used column chromatography to separate lipids from hydrocarbons in extracts of marine benthic algae. The column chromatographic technique is, indeed, the most commonly used tool in the analysis of petroleum hydrocarbons in the presence of bioorganic materials, involving the separation, identification and determination of all hydrocarbon classes in the extracts of both contaminated and uncontaminated biological samples (Youngblood et al., 1971; Youngblood and Blumer, 1973; Zitko, 1975; Warner, 1976).

The column separation technique commonly employs polar stationary phases such as silica gel, alumina, or a combination of the two. The hydrocarbon extract is placed on the column with a minimum amount of solvent and eluted with solvents of increasing polarity (e.g. hexane < benzene < methanol). The first solvent is chosen to elute mainly alkanes and cycloalkanes, the second eluent removes mainly aromatic hydrocarbons, while the last eluate contains polar compounds, some polyaromatics, aromatic-naphthenic rings and heterocyclic petroleum components. The reported procedures vary considerably in the selection of column sizes, column material, solvents and solvent volumes, producing somewhat different separations. Nevertheless, the approach has considerable merit, as it produces far more information than total oil analysis.

The separated compound classes are usually subjected to additional analyses to detect changes of composition within the classes. A variety of analytical techniques have been used for this purpose including gas chromatography with flame ionization and flame photometric detectors (Warner, 1976), GC/MS techniques (Youngblood and Blumer, 1973), spectroscopic methods such as IR, UV and fluorescence (Zitko, 1975), a combination of GC, UV and IR techniques (Nagy et al., in prep.), and thin layer chromatography (Paradis and Ackman, 1975). In some studies, derivation of specific hydrocarbon classes was reported (Youngblood et al., 1971).

Wong and co-workers (1976) reported the use of high pressure liquid chromatography (HPLC), with UV and fluorescence detectors, in the analysis of polyaromatic hydrocarbons in seawater, sediment, and biological tissue. This technique appears very

promising and may yet rival gas chromatography in the analysis of complex hydrocarbon mixtures (Veenig, 1975; Thruston, 1978).

12.5 Volatile Petroleum Components

The analysis of volatile petroleum hydrocarbons in water is employed to detect submarine seeps of oil or natural gas, or the presence of crude oil, light petroleum products, or natural gas components in groundwater. Very sensitive methods have been developed (e.g. Mackay et al., 1975) based on the vapor-liquid equilibration technique originated by McAuliffe (1969). Other methods are based on purging water samples with helium and analyzing the purged volatile hydrocarbons by gas chromatography (Lu and Polak, 1976).

12.6 Analysis of Oil Spill Dispersants

Very little work has been published in this area, presumably for the following reasons: a) the development of dispersants with very high effectiveness-toxicity quotients has proceeded to the point where toxicity (and therefore analysis) is of secondary interest to cleanup operations; b) the composition of dispersant mixtures is known, but is proprietary information, and researchers may find it unsatisfying to conduct structural analysis that is effectively redundant; and c) like oil, dispersants are complex mixtures requiring functional group analysis rather than species analysis.

For research purposes, particularly in the areas of biodegradation, effectiveness, and toxic interactions with oil, analytical procedures are essential, and so is knowledge of dispersant structure. Some work on structure and analysis has been done in one of our laboratories by one of us (W.R.P.), with the assistance of M.R. Sandeman and L.L. Dawe. In the following section, items that are stated as fact, but unreferenced, belong to this body of unpublished work. The techniques were adapted from the chemistry of nonionic surfactants, particularly from the texts of Rosen and Goldsmith (1972) and Schick (1966).

In this research, oil spill dispersants were found to be nonionic surfactants, usually dissolved in a suitable solvent. Most of the popular dispersants had a hydrocarbon-based solvent; some used water or alcohol (e.g. Corexit 7664), and a currently widely used dispersant, Corexit 9527, utilizes a glycol.

12.6.1 Chemical Manipulation. Most dispersant surfactants were extractable into organic solvents. For particularly hydrophilic surfactants, however, convenient solvents

such as methylene chloride had insufficiently large distribution coefficients. N-butanol was chosen, therefore, as a universal extraction solvent; two extractions with 0.25 and 0.05 volumes were suitable for freshwater and salt water. Evaporation of butanol was hastened by addition of water (1:1) and removal of the azeotrope. A final evaporation from benzene served to dry the sample for analysis.

Since this work was done, Jones and Nickless (1978) have proposed the use of hydrophobic resins (XAD-4) for removal of nonionic surfactants from large volumes of water. This method merits investigation.

Chromatography for preparative or cleanup purposes was straightforward. The sample, in methylene chloride (or a less polar solvent), was added to a column of silica gel in methylene chloride. Washing the column with methylene chloride removed the solvent. The surfactant was eluted with 10% (v/v) methanol in methylene chloride. This method served for all analytical purposes, but for preparative separations was unsuitable for water-, alcohol-, or glycol-based dispersants.

12.6.2 Qualitative Analysis. Structural analysis of the separated surfactants was based on the methods outlined in Rosen and Goldsmith (1972). BP1002 in all its versions was basically a polyethoxylated para-alkylphenol. Corexit 9527 was a mixture of surfactants of unknown structural classes. All other nontoxic dispersants tested were of one structural class, the 'polyethoxylated polyhydric alcohol stearic acid esters'. Classification was straightforward and based on IR spectroscopy and spot tests as described in the Rosen and Goldsmith text (1972).

Fingerprinting of dispersants for regulatory purposes may be a more practical proposition than fingerprinting of petroleum. Although the nature of the surfactant chemistry made hundreds of isomers and homologs possible, silica gel chromatography tended to separate on the basis of the number of ethoxylate groups per molecule (Burger, 1963). Thin-layer chromatograms (silica, water-saturated ethyl acetate-1% acetic acid, visualized with iodine vapour) showed patterns of 5-15 zones that were distinct for each dispersant tested. The use of programmed multiple development TLC (Jupille and Perry, 1976) gave finer resolution of zones in co-chromatography of samples and standards; a very simple apparatus was constructed in our laboratory for this purpose.

12.6.3 Quantitative Analysis. All approved dispersants contained esterified stearic acid. Dried samples were transesterified with methanolic HCl (Anonymous, 1973) to methyl stearate which could be determined with precision by gas chromatography. The

method failed for trace analysis, due to the high ambient content of stearic acid (0.1 to 10 mg/L) in seawater.

Many dispersants (not Corexit 9527) contain the polyethoxylate functional group. Tobin et al. (1976) developed an earlier technique of heating surfactants with 40% dry hydrogen bromide in acetic acid. The product, 1,2-dibromoethane, was detectable with high precision by gas chromatography. We found that for conventional low-toxicity dispersants, the sensitivity of analysis in seawater extended to less than 1 mg/L.

A combination of all the techniques outlined in the section above, permitted the complete characterization of a typical dispersant, Corexit 8666.

12.7 Summary

For both oil and dispersants, the need for multi-parameter analysis is recognized for identification of sources (forensic work) and also for studies of behaviour and effects in marine and freshwater environments. In the latter area, the most promising development for analysis of oil is the use of column chromatographic techniques for the separation and identification of compound classes of petroleum hydrocarbons.

12.8 Recommendations

Sampling procedures still leave much to be desired, particularly at low hydrocarbon levels. The hydrophobic nature of glass and particularly plastics make the development of strictly laid-down and validated procedures essential. The entire question of filtering versus not filtering samples needs to be rigorously addressed.

Further development of high pressure liquid chromatography should be encouraged. Besides, including desirable features of both gas chromatography and optical methods, the technique is also adaptable to automation, and appropriate instruments are already available.

Programmed multiple development TLC of Corexit 9527 indicated at least three series of surfactant types. Because no polyethoxylate was present, analysis of stearic acid content was the only available approach. Other functional groups should be investigated for the trace analysis of this popular 'no-mix' dispersant.

Manufacturers of dispersants should make available to research and operational workers the identities of one or more practical functional groups, or an analytical technique valid to 0.5 mg/L. In doing this, they would not necessarily compromise the

properietary knowledge of their formulations. Fingerprinting of dispersants should be tested under field conditions.

It is obvious that there is a diversity of specialized chemical techniques for assessing oil. To obtain maximum results from any investigation of oil in the environment, full communication and co-operation between disciplines is essential at all stages, from planning to publication.

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